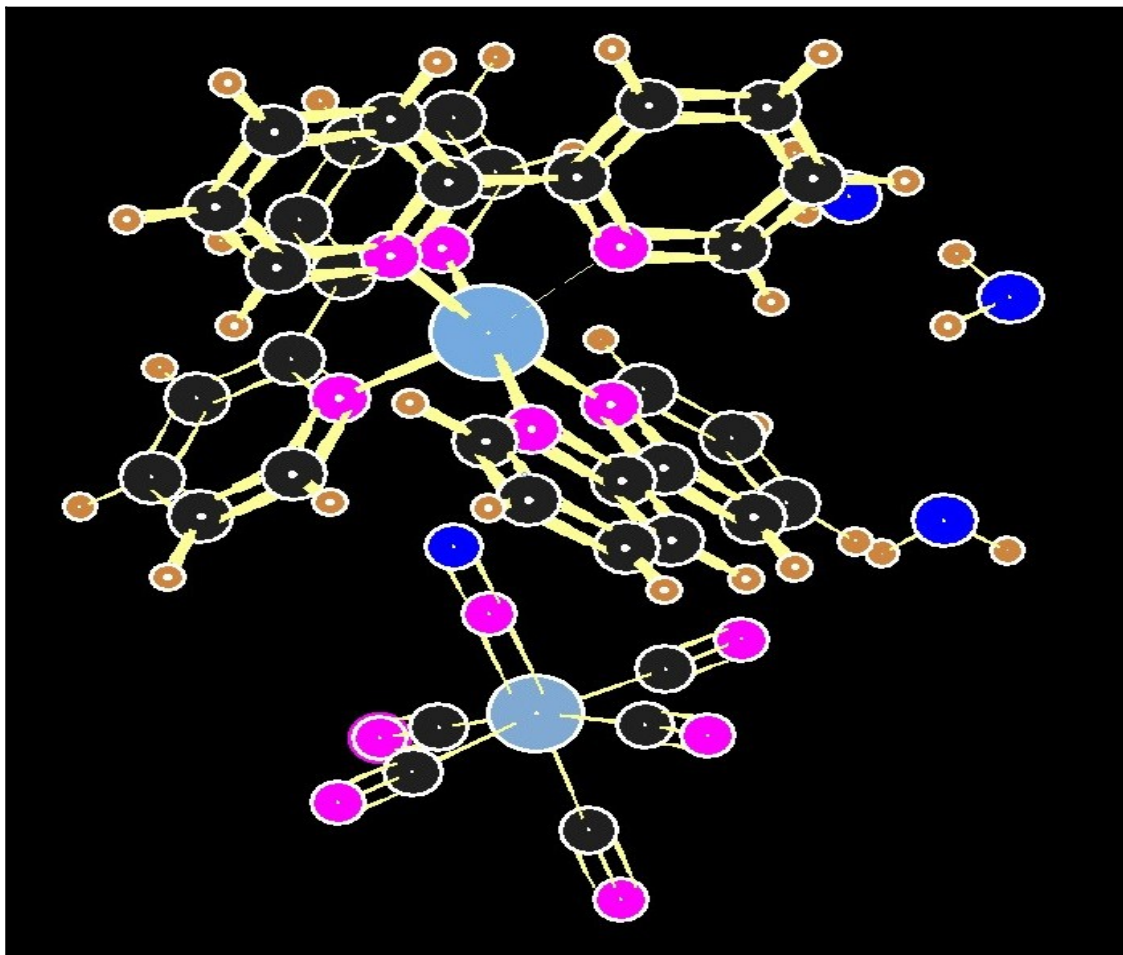# StruMM3D*

{Str3Di32 Molecular Structural Analytics and the QVBMM Force Field}

An Intelligent, 3-Dimensional, Molecular Mechanics, Molecular Modeling Programme, for Chemists and Crystallographers.

Version 10.0.0.X, September 2024

Copyright – Vernon G. S. Box, Ph.D.

MAIL INQUIRIES TO:
Exorga, Inc.
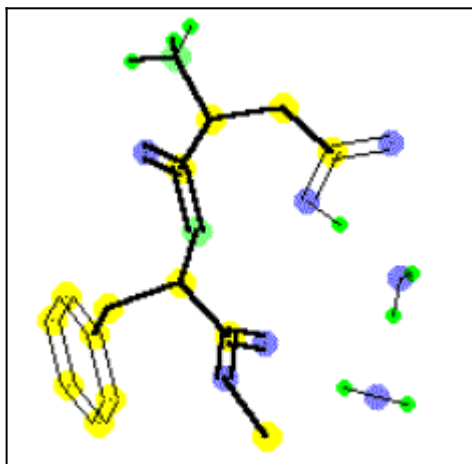**P. O. Box 56**
Colonia, NJ 07067

E-MAIL INTERNET: software_support@exorga.com
INTERNET WEBSITE: http://www.exorga.com
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* For all versions of Microsoft's Windows OS

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StruMM3D

1.0 Introduction

StruMM3D is a full-featured molecular modeling programme, written for execution in the Microsoft WINDOWS ® OS (environment). It has precise molecule drawing and sophisticated structure analytical capabilities. StruMM3D facilitates the reviewing of the structures of organic and covalent molecules whose atomic coordinate data have been obtained from diffraction (neutron, electron, X-ray crystallographic) studies. StruMM3D executes the very modern, high level, Quantized Valence Bonds Molecular Mechanics, (QVBMM) Force Field. This force field is based on an enhanced (by Vernon G. S. Box) version of the Gillespie–Nyholm Valence Shell Electron Pair Repulsion (VSEPR) theory, and the fundamental principles of Valence Bond (VB) theory.

StruMM3D was conceived, coded and developed by Vernon G. S. Box. All of the software coding and algorithms were developed and implemented only by him. There are no other contributors to the project, and no proprietary software/code from any other programme has been incorporated into StruMM3D. Whenever possible StruMM3D uses the operating systems features, and open source programs for some support functions, like graphics conversions.

StruMM3D is an intelligent programme that reviews all of the features of the molecular model upon its loading into memory. The displayed structure shows colour coded evaluations of bond type, bond length and bond order, occurrence of van der Waals interactions, and other stereo-electronic features, all without the intervention of the user. All hydrogen bonds possible, between hydrogen and any source of electron density, are identified by the program and automatically used in assessments of the molecular energetics and structural features. All π-electron delocalization features are automatically assessed by the programme during the loading of the molecular model, and the programme assesses both aromatic and non-aromatic delocalization features. Indeed, for molecules and molecular models which have all of the atoms fully valence satisfied, StruMM3D calculates the stereo-electronic energy before the molecular model is displayed.

Thus StruMM3D will learn and know more about the stereo-electronic/strain properties of the newly loaded molecular model (molecule) in the brief interval of loading the molecular model into memory, than its user. All the user needs to do is to solicit any required information using StruMM3D's menus.

StruMM3D enables you to create, examine, modify and manipulate molecular models of covalently bonded molecules, including complex metal complexes like the metallocenes. The structure energies of these molecular models can be minimized. StruMM3D also enables you to perform the structure energy minimizations of molecules in batch mode. Thus, you can create or modify the structures of several molecular models using StruMM3D, and then use one the supplied utility programs to minimize

the energies of all of these structures, while you are engaged in some other activity.

By using the utility programme Str3DiUtils, coordinate data from many other molecular modeling programmes can be imported, displayed, and examined by StruMM3D.

Eventually, the number of structures, and their data files, that you regularly view using StruMM3D will become too large for you to manage/manipulate easily, and so StruMM3D has been outfitted with a MOLECULE LOG that is activated whenever you wish to store the coordinates of a new, or modified, molecular model in a storage file. This log contains the file names and the functional group features of molecular models that are present on your storage drive, so making it very easy for you to review or to retrieve the structural data files you wish. The features of this log will be described below.

StruMM3D and its supporting programmes are copyrighted and all rights to the programmes are reserved. The programmes may not be reverse engineered, or altered in any way, except with the explicit knowledge and consent of the author (Vernon G. S. Box). Users must obtain a licence to use the software. The code will remain the intellectual property of the author.

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1.1 Hardware Requirements for Executing StruMM3D

There are no special requirements for executing StruMM3D on any Windows compatible computer. StruMM3D, like all Windows programs, requires any one of the Microsoft Windows operating systems (95/98/ME/NT/2000/XP/Vista/Windows 7/8x/10/11); a two, or three, button mouse/trackball, a VGA, or better, display. An internet browser, and WORDPAD, or NOTEPAD, will also be used. These applications are normal parts of the Microsoft Windows operating systems.

Monitor, Video Card, Mouse/Trackball - Any modern video card will perform adequately, as also will any modern monitor. The main programme window will always open in the top left corner of your screen. Any standard two, or three button mouse, or trackball, will do.

Storage/Thumb Drives - While StruMM3D is small enough to enable it to be executed from thumb drive, or a high density floppy storage drive, (since it does not access the drive frequently), a hard-storage drive will be best. The important files, MSVBVM50.DLL, MSVBVM60.DLL and OLEAUT32.DLL, must be present in C:\WINDOWS\SYSTEM if you are using WINDOWS 95/98/ME, or C:\WINNT\SYSTEM32 if you are using WINDOWS NT/2000/XP/Vista/Windows 7/8x/10/11. These files can also be present in the directory/folder \STR3DI. These files are normally supplied by MicroSoft with all normal installations of its operating systems.

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1.2 Installing and Setting Up StruMM3D

There are two possible installation programmes that can be used - StruMM3D_Setup_Files.Exe, or Str3DiSrc.Exe. These are self-unzipping archives. These programmes can be are supplied on a CD, by e-mail, or you can downloaded from the WWW.EXORGA.COM website. Each of these supplied programmes have a complete set of StruMM3D's programmes and many sample, template, structure data files, and the information files/manuals that will assist you to use the programme properly. Read the information at WWW.EXORGA.COM/EXSITE/htm for details.

The StruMM3D programme should not normally be installed into the computer's drive C:, without special instructions, but it can be installed into a sub-directory, sub-folder, on any drive. For computers

that have several drives, it is best to initially install StruMM3D in its own sub-directory on whatever drive you select.

Using Str3DiSrc.Exe

If you have downloaded this file, then simply copy it into the root folder, the root directory, of whichever drive, let's say drive X:, or X:\MyChemistry, you wish to use, right_click on it, and select "Run as Administrator". Instruct the "extraction" to deposit the files in this folder indicated, which will create X:\Str3Di, or X:\MyChemistry\Str3Di.

The newly created directory/folder will contain all of the files you need.

For the first running of the programme, just go to the folder X:\Str3Di, or X:\MyChemistry\Str3Di, now go to the \Str3DI directory, open the file STR3DIDRIVE.DAT in WORDPAD, or NOTEPAD, and in the third line change the letter C: to X:, if you had created X:\Str3Di, or X:\MyChemistry, if you had created X:\MyChemistry\Str3Di, save the file.

NOTE the COLON after the drive letter- X:. The colon is important!

Then, click on StruMM3D in the folder \Str3Di, to launch the programme. Once the programme is running, create a shortcut to it on your desktop by selecting the "HELP" option from the main menu, then "create shortcut".

It is important to remember that many structure/template files are included so that you can begin to look at structures almost immediately, and to explore the usage of the programme.

Using StruMM3D_Setup_Files.Exe

If you downloaded this file from www.Exorga.com/Exsite/htm, then locate your Downloads folder, where the file would have been saved. If not, it would be best to create a folder X:\TEMP, on any drive, if your system does not already have this sub-directory, and save the StruMM3D_Setup_Files.Exe file into it.

Once StruMM3D_Setup_Files.Exe is in X:\temp, then navigate to X:\temp, click on it, and direct that all the files be extracted into this directory (X:\temp), by accepting the defaults. If the file was saved in the Downloads folder, then go to that site and do as instructed above.

Open a command prompt window (admin), by right_clicking on the START button. Now navigate to the folder X:\temp, or wherever Downloads is, to find the file StruMM3D_Setup_Files.Exe. Downloads is usually at C:\Users\User_name\Downloads, or C:\Users\Your_Name\AppData\Local\Downloads.

Then enter the text "Install X:" - to create the installation in X:\Str3Di, or "Install X: \MyChemistry", to create the installation in X:\MyChemistry\Str3Di, where X: is the target drive, and \MyChemistry the target folder, onto which you wish to install StruMM3D.

NOTE the spaces and the COLON after the drive letter- X: If you omit the target drive letter, X:, or D:, or whatever, then the files will be installed onto drive C: or some sub-folder thereof.

Read and follow the instructions displayed on the screen during the installation and the installation will be uneventful. Once the programme has been installed, go to the directory X:\Str3Di, or X:\MyChemistry\Str3Di, and click on StruMM3D.

Uninstalling StruMM3D

The installation does not write data into the computer's Registry and so to uninstall, simply delete the directory \Str3Di and all of the files therein.

Shortcuts to StruMM3D

"Shortcuts" are useful for accessing programs, rather than having to click on the file name while running Windows Explorer. You can place a shortcut to StruMM3D onto your desktop, while StruMM3D is running, by selection the option - HELP/CREATE SHORTCUT. StruMM3D will create two shortcuts, StruMM3D and StruMM3DX. You can also make a "shortcut" for StruMM3D by right-clicking on that programme file, in the \Str3Di folder, and dragging it onto the desktop. Following the instructions to Place/copy this "shortcut" onto your desktop.

An Important Note!

If the Downloads folder is not on the same drive as the system temp, system temporary folder, there will be issues. Normally, for most Windows installations, both folders are on drive C:.

Current Users of StruMM3D

Current Users of StruMM3D who just wish to update their installations with the latest features and files should download the file StruMM3DUpd.Exe and copy this file into their \Str3Di folder. This is a self-unzipping archive and simply clicking on it will trigger the process. It is obviously important that you instruct the unzipping to place the files into the \Str3Di folder if asked and that you replace the present files with the newer ones, over-write the old files,

The Windows User Access Control (UAC) Issue

Microsoft, in its zeal to protect users from them selves and from externally acquired malware, has enforced the User Access Control (UAC) functionality in Windows 10. Whenever one wants to run/execute a program/app that can change any data/in Windows, a warning screen opens and asks the user if he/she is sensible enough to proceed.

This happens even with some Microsoft programs, and especially if one wants to use the command prompt to do things.

During the StruMM3D installation using StruMM3D_Setup_Files.Exe, an entry is made into the Task Scheduler that allows StruMM3D to be run/executed in an unhindered fashion if it is launched using the file StruMM3DX.Bat, located in the Str3Di folder.

The batch program assocstr.bat enables one to associate all of the common Str3Di file types with StruMM3D.Exe, so that clicking on a Str3Di file will not trigger Big Brother to come asking if you know what you're doing. The program assocstrx.bat also enables one to associate all of the common Str3Di file types with StruMM3DX.Bat, so that clicking on a Str3Di file will not trigger Big Brother to come asking if you know what you're doing. Only perform ONE of these associations.

It will always be best to use StruMM3DX.Bat to load and run StruMM3DX.Exe since StruMM3DX.Bat enables the automatic updating of StruMM3D.Exe

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2.0 StruMM3D's Commands

StruMM3D was designed to be very user-friendly and highly interactive, so that its major features can be accessed without the need for extensive training. All of the commands used by StruMM3D are displayed in the programme's main menu and its sub-menus, see the image of the running program below, and in the windows that appear when some tasks are initiated.

StruMM3D always supplies suitable prompts, and even suggests the format and values for the data required to be entered. When just starting to use StruMM3D it is best to enable the programme to help you along with informational prompts. The default starting mode for new users is indeed with this feature activated. It is wise to leave this feature activated until you are quite comfortable with StruMM3D, and then you can turn it off.

StruMM3D is almost crash-proof during normal usage. However, StruMM3D can be bombed by the intentional introduction of bad data into some critical routines and so care should still be exercised. However, StruMM3D, like all complex computer programs, is likely to have imperfections and so your comments on its ease of use, the presence of bugs and, most importantly, improvements you would like to see, are still avidly sought. StruMM3D is reviewed and upgraded regularly because it is used in an organic chemical research environment. Register users of StruMM3D will obtain free lifetime upgrades.

Some of the data required by StruMM3D must be entered by using the keyboard, while other data can be rapidly entered using the mouse. Thus, StruMM3D allows data entry by either object, or both. Please note that atomic symbols are case sensitive. For example: for bromine - BR and br are incorrect; Br is correct, but if you insist, StruMM3D will "auto-correct" these for you. Whenever bond lengths must be entered, you must pay attention to the values you use, or the results will be unpredictable.

Simply put, you need to remember your chemistry if you wish to use StruMM3D without having major problems.

Users that have not done at least one semester of organic chemistry will have problems because they must have some familiarity with normal bond length data and dihedral angle data even though StruMM3D will often prompt the user for bond length and dihedral angle data and show the suggested values.

It is very important that you recognize that in StruMM3D instructions to "click" the mouse means a left-click. Otherwise right-click are frequently used, and double-left-clicking is reserved for one unique

operation.

An image of the screen while running StruMM3D is shown below. The background image (the wall paper) will obviously vary from computer to computer depending on the user's fancy. StruMM3D will use the lower part of the screen to display information, or to prompt you for data, whenever necessary.

The StruMM3D Working Screen
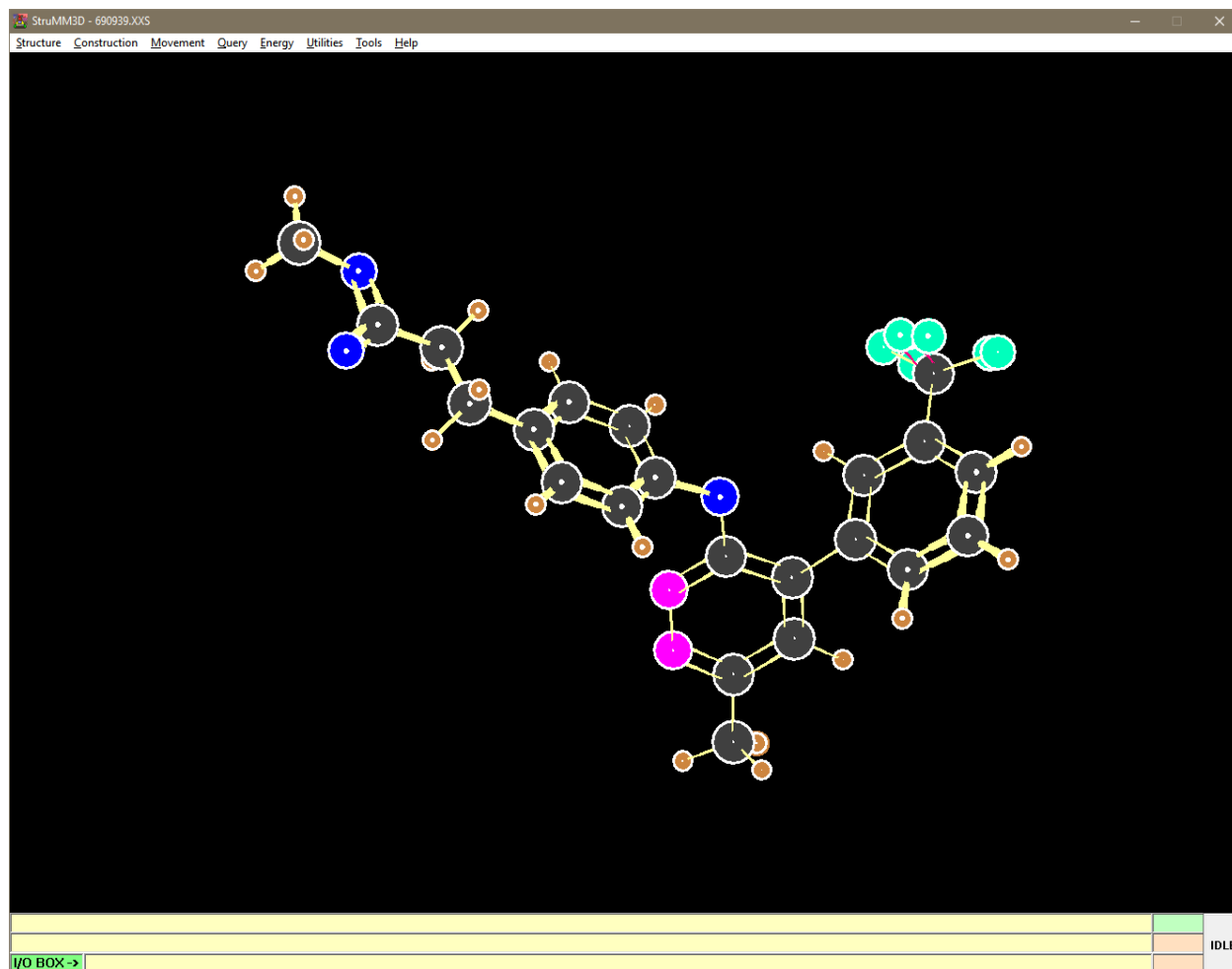
Whenever StruMM3D needs input from you it will display a prompt, or a hint, asking that you to provide it. The prompts and hints are always displayed in the horizontal labels that run all the way across the screen below the picture display window. There are two of these labels and below these is a text box, the data I/O BOX, into which you can type information. At the bottom right there is a stack of small, shorter, labels, for StruMM3D suggested values or answers, adjacent to the prompt labels and the data I/O BOX.

StruMM3D will usually display possible answers, or values, in the small rightmost labels, or suggested values boxes. The topmost of these suggested values boxes is special, and is coloured a very pale green.

If you are prompted for data and values appear in the suggest data box, and if you simply click on OK, the value in the topmost, green, suggest data box will be automatically used. If the data or value that you wish to use is in another suggested value box, then click on that box, and then click OK. If the data, or value, you wish to use is not displayed in any of the suggest data boxes, and StruMM3D thinks you can provide alternate data (and will indicate this by changing the colour of the Data I/O BOX to the pale green, and too the colour of the adjacent label to its left), you will then be allowed to type the

desired information into the Data I/O BOX.

If you are working with imported coordinate data from a CIF or PDB file, for example, then after the structure is loaded you might wish to look at the original data, CIF/PDB etc, file to view some item of the details. By clicking the label captioned "I/O BOX", the original data file will be opened by NotePad and the text displayed. Remember to close it when you are done.

Whenever StruMM3D wishes to simply alert you to some event, or give you information to which no inputted response is required, the topmost, pale green suggested value box will become red, with the word INFO in it.

There are eight main items in the main menu, and each item's "drop down" menu (a sub-menu) will display the sub-items listed. These groups are related by their function. For example, the menu item that control all translation/rotational exercises to be accomplished on the molecular model will be found in the MOVEMENT group of the main menu. The commands, along with their functions, are described below.

Occasionally the main menu items/commands/routines might not produce the desired function (maybe because you have been clicking too many buttons and left too many routines incomplete). Just use the menu commands STRUCTURE/REVIEW STRUCTURE DATA to clear the commands stack and things should return to normal. If this doesn't help, then try using STRUCTURE/CLEAR MEMORY, or at worst, save your data/structure, close the programme, and restart.

STRUMM3D'S MAIN MENU'S COMMANDS

STRUCTURE
Load a Structure - recall the coordinate data for a molecule from a storage file and show the molecule
Open Molecule Log - view the molecule log using NotePad, or search for, and load, a molecule using StruMM3D
Save a Structure - write the coordinate data of a molecule to a storage file, with the same file name
Save As - write the coordinate data of a molecule in memory to storage, with another file name, and its description
Alter Structure Display Mode - change the structure display characteristics, to/from Covalent Radius/Display Modes and colour depth
Review Structure Data - review the coordinate/structure data for the molecule(s) in memory, and clear the command stack
Clear the Memory - clear all tasks and incomplete molecules from the memory. For recoveries, the molecular model is saved and reloaded.
Erase a Molecule - erase a molecule, prompted for which molecule if two are displayed
Delete a data file - erase a coordinate data file from the hard storage drive
Move a data file - move the data from one location/folder/sub-directory to another
Protect a data file - make a data file read-only, so that it cannot be erased, or over-written, accidentally
Exit - end programme, saving the current programme environmental settings

CONSTRUCTION
Create/Modify a Molecule - draw a new molecule, or modify an existing structure
Add Atoms/H/lp/le - add hydrogens, and/or lone pairs, and/or lone electrons, or any other atom to a molecular skeleton
Erase Atoms - erase any atom
Change a Bond Length - change the length and, if desired, the type of any bond, or create a new bond
Change an Atom Type - change any atom's type and automatically adjust the existing bond lengths
Change Metal/loid Atom Oxidation Number

Link Template Structures - form a bond between any two structures onscreen with full control of bond length and stereo-chemistry.

Make One Logical Structure - link several structures into one molecule or logical structure (e.g. a unit cell)

Fragment a Structure - chop a molecule into two parts along a desired cleavage plane, or using selected atoms

Enantiomerize - reflect a molecule about the Z-axis and so create its enantiomer

Re-Number a Structure - re-number the carbon skeleton of the molecule

Change Structure Size - make a molecule larger/smaller, like zooming in/out, for a better perspective

MOVEMENT

Move/Query Molecule - translate or rotate one, or both, of the molecules that are onscreen, and examine their structural features

Position an Atom - move a molecule to place a selected atom at a reference point on the screen

Orient a Structure - orient any pair of atoms along the X-axis with one selected atom at a reference point

Dock two Structures - bring two independent molecules close enough together for them to influence each other stereo-electronically, if they are linked into one logical structure.

Adjust the docking distance (what we like to call the "van der Waals buffer zone") between the docked sites

Rotate/Examine a Bond/Dihedral Angle - rotate and adjust bond angles and dihedral angles creating new conformers, (also interchange Z- and E-alkenes)

Auto-Rotate - continuously rotate a molecule for display

QUERY

Molecular Geometry - measure geometrical parameters of the molecular model – also available in the - "MOVEMENT/MOVE/QUERY MOLECULE - feature

Delocalization - search for and display delocalized $\pi-$systems and aromatic rings

Sub-Structure - search for functional groups, or any linear/branched 3 or 4 atom structural unit

Lone Pair Interactions - identify and quantify lone pair interactions

Steric/Electronic Interactions - identify and quantify steric, dipolar and torsional interactions

Missing Bonds - identify the instances when structures simulated from x-ray coordinate data have missing bonds because of atom coordinate data errors

An Atom's Coordinates - identify any atom and its bonding partners

An Atom's Status - identify and change, if desired, any atom's $\pi-$status

Relocate an Atom/Molecule - Relocate a molecule, based on relocating a selected atom

Molecular Formula - display the molecular formulae of the molecules in memory

Molecular Weight - calculates the molecular weight of the molecular model, and gives the %age atomic composition data.

Molar enthalpy of Formation - Calculate the enthalpy of formation for molecules composed of C, H, O. The routine is being constructed.

Molecular Volume - get the smallest, sphere or cube, in which the molecule can tumble freely

File/Structure Name - display the file name. or structure name, if they are the same

ENERGY (These routines use the QVBMM force field.)

Calculate Molecule Energy - estimate/calculate a molecule's energy

Minimize Molecule Energy - minimize a molecule's energy

Minimize Dihedral Energies - minimize the energies of all of the dihedral atoms (angles) stored in the Dihedral Angle Array

Minimize Atom Energy - Auto - minimize an atom's energy under StruMM3D's control

Minimize Atom Energy - Manual - minimize an atom's energy interactively (user controlled)

Select Dihedrals for Minimization - measure dihedral angles and store their atom numbers in the Dihedral Angle Array. These dihedrals can be energy minimized

UTILITIES

Program Parameters - adjust StruMM3D's "environmental" settings (see below)
Toggle Layer View - use to view the structures of large molecules, by looking at "slices" of the entity
Enter X-Ray Data - enter data from x-ray crystallographic structural determination into StruMM3D
Write XYZ File - use the data of a molecule in memory to create a simple XYZ format file
View the Structure Data Log - for the molecule currently in memory, to access structural data
Print Molecular Coordinate Data - print the coordinate and bonding data of the molecules onscreen
Copy Image to Clipboard - copy the images of the molecules onscreen to the clipboard and to JPG or BMP files
Print Molecular Graphics - how to paste the clipboard captured image into any graphics-capable programme
View Dihedral Array - review the dihedral angle data currently in memory
Flush Dihedral Array - remove all dihedral angle data currently stored in memory
Load Terminal Dihedrals - put dihedral angles for one or two atom side chains into the dihedral array
View Command Array - normally used only for diagnostics, review "open/running" routines via their "command" codes.

TOOLS

Calculator - a versatile calculator that evaluates mathematical string expressions, and can memorize them for future use.
Access the Internet - will open your default web browser to enable you to browse for information

HELP

Help - Opens this document that can then be read (use "wrap to window" option), or printed
Update StruMM3D - go to the WWW.EXORGA.COM website to look for new versions of StruMM3D
Upgrade StruMM3D - allows you to convert the limited version to the 20,000 atom version if you have the software key that can be obtained from Exorga, Inc.
About StruMM3D - Copyright, Authorship and Version information.
Create Shortcut – place an icon for StruMM3D on the desktop
Associate StruMM3D – set up the association of StruMM3D with files that have extensions of its native format

KEYBOARD-ENTERED COMMANDS

Occasionally StruMM3D will ask you to enter data into the I/O BOX, which is the lowest information bar on the screen, and the cursor will blink there. The I/O BOX can also be used as another way of adjusting StruMM3D's environmental parameters, which are described below.

StruMM3D will ask that you enter data like atomic symbols, bond lengths, bond angles, etc, when it needs these. Then, you simply enter the requested data.

If you wish to adjust the StruMM3D programme environment or the values of some of the programme's parameters, then you wait until StruMM3D is idle, the displayed command button tells you so, then click the mouse pointer in either edge/end of the I/O BOX (the lowest screen info bar), and the tilde (~) will appear. You may then enter "~ command X", or "~ command", (without the quotation marks) where command is the parameter you wish to change, and X is any additional data like a parameter value. Then hit the ENTER key. Note that the "~" part of the command is obligatory.

Thus, "~ L" will toggle the bond line setting and "~ P" will toggle the audio setting. Some of the environmental commands will carry additional data that must also be entered. There are also several non-environmental commands that can be entered using "plain English" terms instead of single letters. These will be described in the section on the Environmental Controls.

REMEMBER

All of StruMM3D's commands can be accessed by clicking on the menu items, and then the suitable sub-item, or by pressing the "ALT" key followed by the key corresponding to the underlined "hot" letters in the menu and sub-menu items' names.

The names of these commands should be almost self-explanatory, but the commands will be discussed below. You should remember that StruMM3D will always provide enough information for you to use its features and this extensive "user prompting" should allow you to accomplish almost any task that you can reasonably think of, if you have a clear idea of what it is you wish to do. You will occasionally see a red label entitled INFO close to the {OK} button at the bottom right of the screen. This label tells you that the text shown at the bottom of the screen is for information only, and that you should click on {OK} to continue.

StruMM3D was originally designed as a tool for organic chemists, crystallographers, and all students of organic chemistry. Recently, the programme has been enhanced to embrace metals, their salts and their complexes. The features of this molecular modeling programme might not be easily understood by someone without a minimal background in organic chemistry. This computerized tool will greatly facilitate your understanding of molecular structure and stereo-electronic interactions, but you must THINK LIKE A CHEMIST while using this programme.

StruMM3D is designed to enable the user to initiate and execute almost any operation that has ever been done in molecular modeling, and some that cannot be done by other programmes, but sometimes one must use a sequence of logical steps/commands to achieve the goal.

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2.1 Environment Controls (Toggles) and Screen Modes

StruMM3D's operating environment, the way structures are drawn, the positions of the supporting windows, etc, can be adjusted to suit your tastes by the clicking on "UTILITIES" in the main menu and then "PROGRAM PARAMETERS". The new window that is displayed lists all of the current parameters, including the environment controls in individual boxes. The default setting of these "environment" controls is shown by a string of letters in the form:

$$S \ L \ C \ h \ M \ n \ T \ Q \ W \ v \ d \ z \ P$$

These controls are "toggles". Clicking them once turns on or off various features and clicking them again restores the previous state.

c - toggle the colour style of the structure atoms, in the default mode bonds are dominant, atoms in the other. When atoms are bold solid spheres, their peripheral (outer layer) colour shows the atom's charge.
d - toggle a thorough analysis for bonds that might be affected by x-ray coordinate data errors, especially coordinate errors involving $\pi-$atoms.
h - toggle the hiding of selected atoms onto the structure
l - toggle the selection of a line pattern for drawing 3D structures
m - toggle the displaying of information/prompts, for new users. More Help. Whenever you are experienced enough you can turn this feature off, if you wish. n - toggle the numbering the atoms of the structure
p - toggle the sound effects embedded in StruMM3D.
q - toggle the start up, or load, mode from simply displaying to quantitative (measuring mode –

molecular measurements)

s - toggle the auto-size feature that fits the molecular model's size to the current window

t - toggle the automatic creation of a temporary file of the molecule(s) in memory, TempDataBkup.sxs, if a structural change occurs. Prompts file name change. A valuable recovery routine

v - toggle the Covalent Radius Mode display, drawing the covalent radii about the atoms. Covalent Radius Mode is similar to using van der Waals structures

w - toggle the writing the atomic symbols onto the structure

z - toggle displaying of partial charges on atoms when so requested

If a feature has been enabled, the letter for that feature appears in the UPPER CASE. In the example shown, the writing of the symbol for all hydrogens -h, numbering the atoms -n, showing measuring menu only on start up -q, and showing covalent radii -v are disabled; while track mol. data/temporary file writing -T, writing of atomic symbols -W and displaying additional help (More_Help) -M, are enabled. Note the upper/lower cases of the letters.

A slider control enables the adjustment of the size of the StruMM3D display window. The slider pointer settings roughly correspond to video adapter settings as follows – VGA - 1, 2; SVGA - 3, 4; higher resolutions 6 to 12. The maximum setting of the slider is 12, and generates the largest working screen. After the slider is set a label captioned N-i or N-o indicates the positions at which StruMM3D's supporting windows will be displayed. For example, if the label shows 2-i then all of the supporting windows will be displayed within the frame of the StruMM3D's parent window. 2-o will place the supporting windows outside of the parent window. You might wish to use a larger window and moving the slider pointer to the right will increase the windows size, while moving it to the left will decrease the window size. As we change the slider pointer position, the number N changes, larger number – larger screen, and the number in the window position toggle changes too. Setting this environmental toggle to 6 (by moving the slider pointer to 6) will enlarge the working screen area. 6-i and 6-o will place the supporting windows inside and outside of StruMM3D's parent window, respectively, so providing you with an uninterrupted view of the molecular model display window. For higher resolution displays use the larger slider settings to get larger screens.

The toggled {d}, or {D}, or {#} control allows you to enable StruMM3D to compensate for experimental errors that were realized during the X-ray crystallographic determination of the structure of a molecule that has π–bonds. If the control is in the {# }state, then StruMM3D does everything automatically and any user input experimental error is usually ignored.

If these experimental errors inadvertently make some π–bonds too long, then StruMM3D might not detect delocalization involving these bonds in the π–system. When {d} is toggled, and becomes the upper case letter {D} (- sLchMnTpWvDzP -), or {D} is toggled, and becomes the character {#} (- sLchMnTpWv#zP -) in the environmental command string, then StruMM3D re-examines the lengths of single bonds that are flanked by π–bonds to check if these bonds' lengths are close to the range of lengths of delocalized π–bonds.

If the lengths of these "borderline" single bonds are within the range of the x-ray crystallographic experimental error, then StruMM3D will show these bonds as delocalized π–bonds. The size of the X-ray crystallographic experimental error in determining the atomic coordinates is reflected by the errors in the resulting bond lengths, and can be as high as 2.2% for large biopolymers, but is usually less than 1.5% for small molecules. We recommend a setting of 1.5% for routine use.

The "environment" includes the very important upper bond length range parameter. You are only allowed to change the range for single bond lengths and StruMM3D derives the other bond length ranges therefrom. The single bond length range should be set to less than 2.00%, unless you wish to perform some specific molecular modeling experiments that will not be meaningful under normal

circumstances. See the discussion on Str3data.Dat below. The recommended value for this setting is 1.00%

Another way of adjusting StruMM3D's environmental parameters is to wait until StruMM3D is idle, the displayed command button tells you so, then click the mouse pointer into a corner of the I/O BOX (the lowest info bar), which should then clear and display the tilde ~ . You may then enter "~X", (without the quotes) where X is the parameter you wish to toggle/adjust, and then hit the ENTER key. Note that the "~" part of the command is obligatory. Thus, "~L" will toggle the bond line setting. You can enter several commands in one line, each separated by a tilde, like ~L ~M ~ C. If you add a trailing tilde the current setting of some other variables is displayed after all your settings have been done, like ~L ~M ~ C ~. Spaces are not important.

When entering environmental commands at the keyboard there are sometimes "plain English" alternatives to the single letters. There are presented (in quotation marks) below, but remember that the quotation marks are NOT used in the keyboard commands.

Many of these online commands are toggles, when they just switch a feature from one form/type/style, to another, and otherwise they effect the changing of the sizes of some parameters. If the command requires an added parameter/value, then ensure that you leave a space between the command and the parameter, and between the parameters, if needed (like ~ tidy 1 ~ xu 1).

Adjust bad bonds - "adjbnd N". A toggle if integer N is not specified. N = 1 for auto-adjust. N = 0 do nothing.
Adjust bond range threshold – "brt" by up to +/- 0.05 units
Adjust atom display radius- "dr f" Or "disprad f" (float f = -0.267 to +0.1)
Adjust molecule size - "size" Or "s" or "s N" (N is an integer)
Adjust upper bond range limit - "bndrx F" (float F = 0.0 to 0.015, the default is 0, F > 0.015 will give unusual results)
Adjust van der Waals buffer zone - "vdwb F" or "vdwbuffer F" (float F = 0.324 to 1.500)
Adjust transitional single electron bond upper bond order - "tsbo F" (float F = 0.01 to 0.499)
Adjust metallic TBO status - "tbom F" (float F = 1 to 6)
Atom Color Style - "atomcolor" Or "color" Or "c"
Automatically refresh the covalent data file – "refrcv N". If N = 0 the cancel and do nothing
Auto Zoom - "zoom"
Bond line style - "bondline" Or "bond" Or "l"
Charge display - "charge" Or "z"
Delete unbonded atoms - "unbonded" Or "xu" Or "xu N". N = 1 turns it on, N = 0 turns it off.
Delete too closely bonded atoms - "tooclose" Or "xc" Or "xc N". N = 1 turns it on, N = 0 turns it off.
Delocalization - "delocal" Or "deloc" Or "d"
Hide/show atoms - "hide" Or "h" OR "h Cl Br N P"
Image format - "img n" or "imgformat n". if n = 0 then images saved as JPG else as BMP
JPG quality - "jpgqual n", where 25 < n > -25
Load the query screen, for molecular measurements and information, after a structure is loaded - "query" Or "q". Keep Q enabled.
Make JPG or BMP file automatically - "jpgbmp N". N = 1 turns it on, N = 0 turns it off.
Minimization Calculation Mode - "mcm N" (interger N = 0 to 2, the default is 0, 1 sets the most thorough minimum search)
Minimization Energy Limit - "mel N" (interger N = 1 to 4, the default is 2, 4 sets the most thorough minimum search)
Minimize very long range Interactions - "mvlri N" (integer N = 0 or 1, the default is 0, 1 might give unusual results)
Mouse gesture to rotate molecule - "mg" Or "musg" Or "musgesture"
Numbering of skeleton - "numbers" Or "number" Or "n"

Oxidation Number Auto-adjustment - "ox F". float F = 0 turns this feature off, F > 1 restores the default value.
Program sounds/audio - "phon" Or "audio" Or "p" Or "sound"
Show Covalent Radii Display - "CRDM" Or "v"
Show hints/prompts on what next to do - "hint"
Show minimization of dihedrals rotations - "smdr"
Show more in context help - "morehelp" Or "moreinfo" Or "m"
Show preview of mol. energy before energy minimization - "mep" or "info"
Show van der Waals Interactions - "showvdwi" or "vdwi"
Tidy up the file system - "tidy 1". "tidy 4" will really deep clean the folder and convert all BMP files to JPG if the file converter is present.

StruMM3D accesses the internet, the World Wide Web, to check if your program needs to be updated (and to download the update if needed), and to access the help files. If you have difficulty getting into the internet, or don't want StruMM3D to access the internet, you can disable this feature by adding "~ nowww 0" (without the quotation marks) as the last line in the file StruMM3DConLine.Dat, which is in the \Str3Di folder.

The "adjbnd" switch (auto-adjust bad bonds)is extremely powerful and must be set knowingly. If the value is 1 then all bonds with out-of-range lengths are automatically adjusted by StruMM3D. This could be a problem when trying to set up a transition state model. For normal viewing and manipulation of models use "adjbnd 0" (auto-adjust off) to enable the detection of bond length errors in the molecular model, and to set up transition states. Use "adjbnd 1" (auto-adjust on) when dealing with molecular models containing multiple bond length errors, as we see in the placements of hydrogens in many X-Ray structures, or when quickly setting up transition states without the need to follow the changing bonding processes. Play with this setting to find out when to use it, but first save the model to storage for possible retrieval, remembering that the changes to the molecule in memory are sometimes not easily reversed.

The "unbonded", or "u", toggle switches StruMM3D between allowing unbonded (single) atoms in logical structures, or not. This is done to facilitate the reviewing of x-ray coordinate data, but StruMM3D does not perform energy calculations on logical structures that have unbonded atoms. Another way to handle badly placed atoms is to use the STRUCTURE/REVIEW STRUCTURE DATA routine from the main menu. The too closely bonded atoms – "too close" Or "xc" switch will also facilitate the viewing of x-ray coordinate data. Normally StruMM3D will delete atoms that are much too closely positioned, but when this feature is turned off, especially for x-ray structures, StruMM3D will tolerate it.

The "size" toggle does not need to have a suggested size with it. StruMM3D will automatically present you with a size adjusting routine.

The "environmental status" and the current scale sizes of the molecules in memory are always captured at the end of a session, or if StruMM3D's memory is cleared. These values are restored at the beginning of the next session, or on resumption, after clearing the memory.

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3.0 StruMM3D'S Important Features
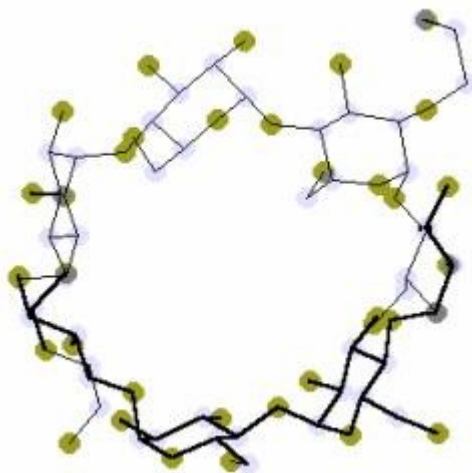
When just starting to use StruMM3D it is best to enable the programme to help you along with informational prompts. The More_Info/More_Help/M toggle must be activated, and be upper case. The default starting mode for new users is indeed with this feature activated. It is wise to leave this feature activated until you are quite comfortable with StruMM3D, and then you can turn it off.

If StruMM3D is idle, the displayed command button tells you so, and you move the mouse over the graphics screen, then StruMM3D will inform you by posting a message in the I/O BOX (the lowest bar on the screen). When you are executing some routines, if you move the mouse over the graphics screen, StruMM3D will also use this I/O BOX to prompt you as to the kinds of activities you may engage in. StruMM3D will also need you to enter data into the I/O BOX, from time to time, and then you will see the cursor blinking in the I/O BOX. To clear the I/O BOX, in order to enter data, just move the mouse pointer into it. If you clear the I/O BOX, and then move the mouse pointer back over the graphics screen, the advisory message will reappear.

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3.0.0 Structures Carry Colour-Coded Information

StruMM3D's molecular models show all bonds onscreen consistent with their bond lengths and bond orders. Thus all double bonds (bond order 1.5 to 2.5) appear as double lines and triple bonds (bond order 2.5 to 3.5) as triple lines.

Single bonds (bond order 0.5 to 1.5) appear as one solid line. Single bonds whose bond orders are greater than 0.95 appear as yellow lines. Single bonds whose bond orders are less than 0.95 and greater than 0.5 appear as pale green lines Transition-state-like single bonds, which are usually one electron bonds and are partially formed single bonds, have bond orders less than 0.5, and appear as one broken/dashed line. Green transition state bonds represent forming bonds and red bonds represent breaking bonds.

Double bonds are normally yellow parallel lines. Brown double bonds are borderline between single and double. StruMM3D sees these as bonds that have bond orders less than 1.5, but close to 1.5, and whose lengths are, within the range of experimental error of the diffraction experiment, sufficient to enable them to be classified as double bonds. This bond classification assessment by StruMM3D can be enabled, or disabled, by the user.

When all of the valencies of the atoms in a molecule have been satisfied, a fully elaborated molecular model, StruMM3D will assign partial charges to atoms as directed by the QVBMM force field. The type of charge on an atom is shown by the colour of the halo around that atom. For example, 1-fluoropentane, below, shows yellow halos for negatively charged items (atoms and lone pairs), and green halos for positively charged atoms.
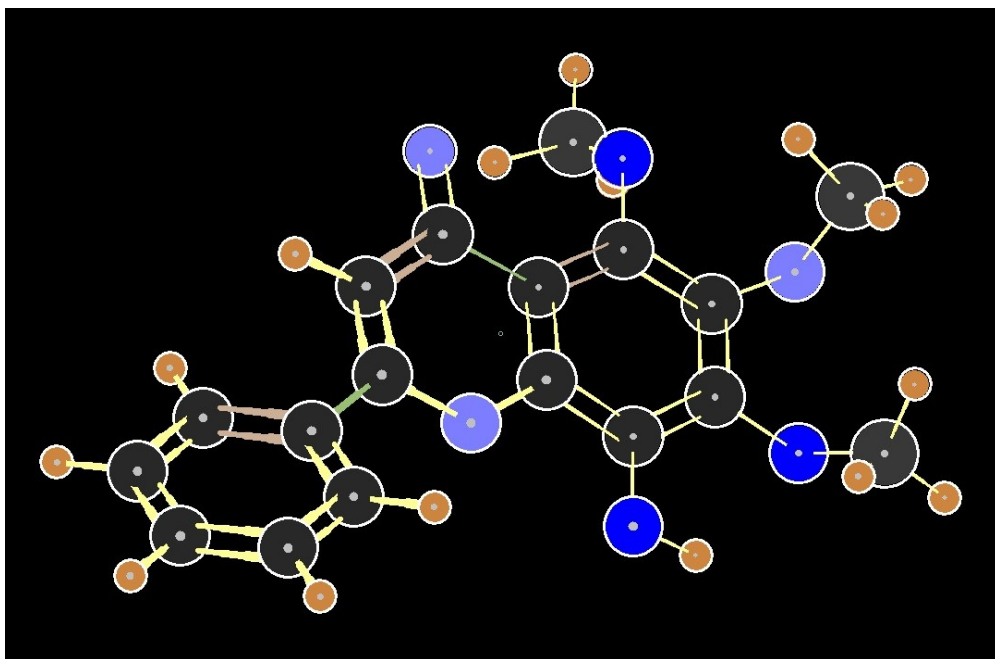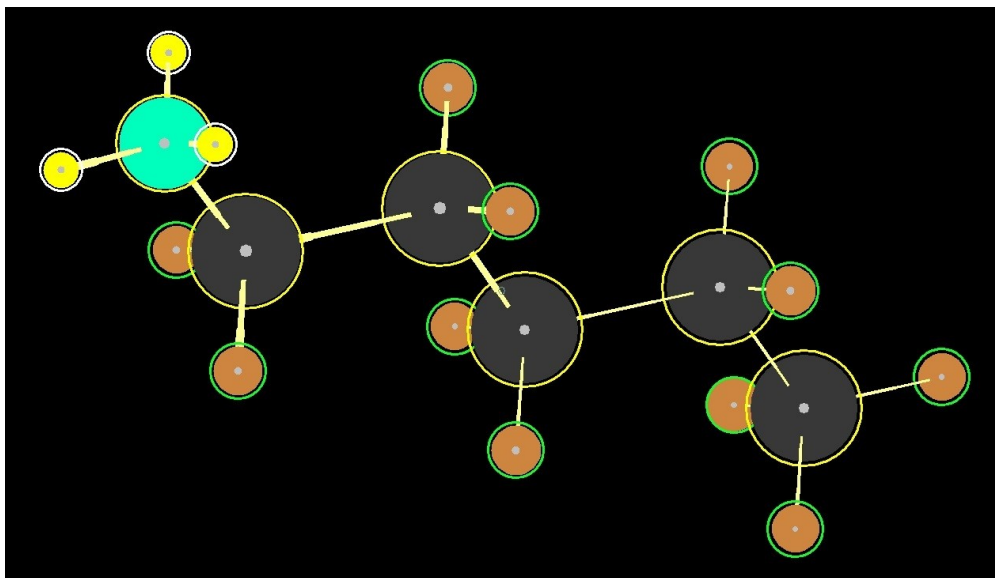
The chromene structure, above, shows some borderline double bonds and enables the user to assign a confidence factor to the diffraction experiment since one of these borderline double bonds is in an aromatic phenyl group and all of these bond lengths ought to be similar. Notice that the long single bonds are associated with the long double bonds.

Sometimes StruMM3D draws attention to unusual bonding patterns by an atom, or to unusual hybridization types. The chromene has 6 oxygen atoms. Three are a bold blue and have normal tetrahedral geometries, with their lone pairs in sp3 orbitals. Three oxygens are pale blue in colour. One is the π-atom of a carbonyl group and the geometries of the other two oxygens have been assessed as them having their electron pairs in non-delocalized σ- and π-orbitals.

The occurrence of non-delocalized σ- and π-orbitals, or sp3, lone pairs on oxygen is being disputed by theoreticians, because some theoreticians have taken an "all or none" position. However, the diffraction data of oxygen containing molecules unequivocal show that both can, and do, exist even in the same molecule.
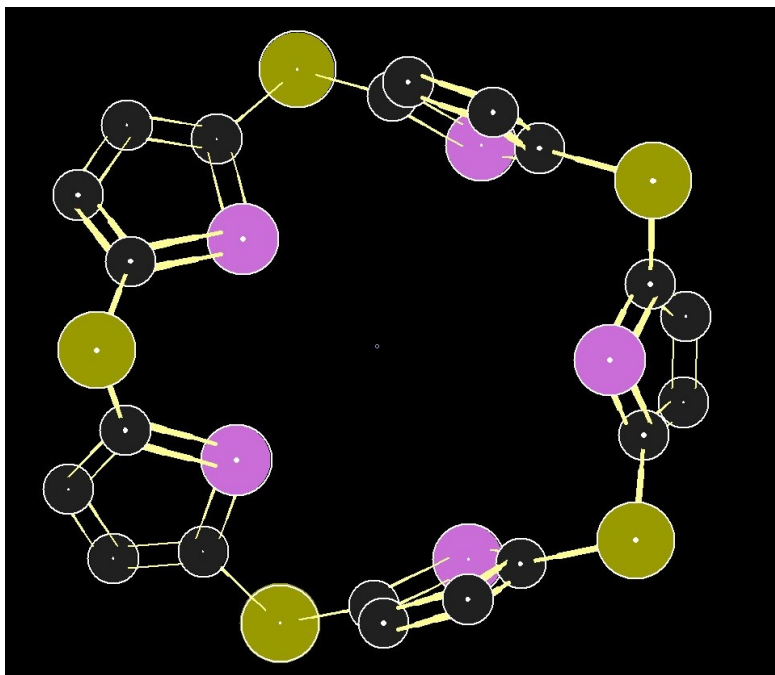
Sulfur atoms that use only their s-, p- and their derived hybrid orbitals are normally yellow, but the sulfur in thiophene, that uses d-orbitals in its bonding, is violet.

StruMM3D enables a user to look at the molecular model and to rapidly, at a glance, assess some of the key features of the molecule, before starting to manually measure the structural features that might be involved in interesting stereo-electronic intrigue. As with the chromene structure the association of long bonds with short bonds suggest that some atoms are slightly mis-sited, and one can then manually measure the various lengths to support, or negate, this notion.

In order to convey a sense of three-dimensionality to the StruMM3D molecular models, notice that the bonds are slightly wedge shaped, with the thicker end of the wedged bond, and hence that associated atom, closer to the viewer. Thicker wedges have been tried but seem to show less desirable characteristics when viewing the structures of large molecules.

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3.0.1 Structure data files

A structure data file should not contain blank lines. Not at the top, end, or within the body of the file. These files must have a name AND extension, and can be stored in any directory. However, some directories are automatically searched by StruMM3D and these are preferred. All coordinate data are stored in files in X-ray unit cell scaled sizes.

Structure data files all end with the letters "xs", and those that bear the extensions ".dxs", ".sxs", ".xxs", ".xlc" and ".xcc" will be saved, and if needed, retrieved and processed by StruMM3D automatically (without you instructing StruMM3D about the location or the appropriate directory). StruMM3D will ensure that these files are stored in their default directories. You must know the location (drive and directory, or path specification) of data files that have other types of extensions. When you attempt to

"load" a file, StruMM3D always enables a directory to enable you to search the drives for the files you need to process.

The convention for the use of file extensions is based on the following rules:

- X-ray coordinate data files, from the experimental diffraction methods, have extensions that start with "x", like xxs
  Files generated/modified/minimized by StruMM3D should have extensions that begin with "s", like sxs
  You should use the additional letters "xs" to complete the extensions of file names of molecules produced/modified, or will be used, by StruMM3D, e.g., glucose.sxs, or glucose.xxs.

A molecule that was drawn or modified by StruMM3D should be saved in a file with the extension ".sxs". This allows the data to be automatically saved and retrieved from the sub-directory x: \Str3Di\data. Other extensions can be used, like ".sun", to enable the file to be automatically retrieved from x:\Str3Di\data by virtue of the "s" at the beginning of the extension, but this is not recommended.

If X-ray coordinate data is processed by StruMM3D, the selected file name will automatically be given extensions ".xcc", for the raw crystal data, and ".xxs" for the orthogonalized coordinate data. StruMM3D regards ".xcc" files as storage files and uses ".xxs" files as normal structure data files. StruMM3D will open both .sxs and .xcc files. After clicking on the menu commands to import and process x-ray data, you can import stored ".xcc" files and StruMM3D will automatically use them to generate the corresponding ".xxs" files. A molecule whose orthogonalized coordinate data originated from an X-ray crystallographic study, but was assembled by a text editor, should also be given an extension ".xxs". These extensions will enable StruMM3D to save and automatically retrieve these files from the sub-directory x:\Str3Di\xray.

A utility provided, TIDYSTR.BAT, will hunt through the sub-directories of \Str3Di and will place these specially designated structure data files in their correct sub-directories. StruMM3D runs this batch file occasionally, automatically. You can manually do so too, if desire, either by double clicking on its name while in using the WINDOWS Explorer, or by going to the MSDOS shell, then to \Str3Di, and then typing - "TIDYSTR path-to-Str3Di-Folder YEA YEA YEA YEA" at the RUN, MSDOS or COMMAND prompt. When run from within, or initiated by, StruMM3D, a wider range of housekeeping chores are performed.

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3.0.2 Load a Structure - Importing a Structure From The Storage Drive

There are basically two easy ways to load a structure's data file into StruMM3D.

1. *Run/execute the program StruMM3D and use the menu command STRUCTURE - LOAD A STRUCTURE*

As stated above, structure data files that bear the extensions ".sxs", and ".xxs", will be retrieved and processed by StruMM3D automatically. Structure data files from other molecular modeling programs should be stored in the directory \str3di\imports.

The LOAD A STRUCTURE menu option, calls an information screen that reminds you of the location of the various data files and the identity of the storage drive that is active (in use). The LOAD A STRUCTURE window also shows you a list of the last 6 structure files that you worked with. This window prompts you for the name of the required data file, or you can use the directory/file displays to

locate the file, or you can click on the file in the "recently used" list (if it is there). Just follow the prompts. Some menu items can to be double clicked to speed things up. You'll learn which by trial.

2. *Open Windows Explorer and navigate to the folder that has the structure data file, or better yet, to a folder named \Str3Di\Graphics.*

If the Windows Explorer view options are set to "details", then you'll see the file name. If you had associated the StruMM3D file extensions with StruMM3D, then when you left click on the file's name the modeling exercise begins immediately.

If the Windows Explorer view options are set to view the "thumbnails" (small graphics associated with a file), then all the graphics that StruMM3D had generated from viewing structures in the past will be on display. Then, you can right click on the desired one, select "open with" from the menu, and select StruMM3D. The modeling exercise begins immediately.

As of version 8.2.0.10, the StruMM3D the graphics options are completely available.

If the {Q} environmental flag has been activated, then the MOVEMENT window is automatically launched, since this window is focal to the measurement of the geometric parameters of a molecular model. Menus that are not "measurement" functions are disabled in this mode. Simply exit the MOVEMENT window to revert to the general functionality of the programme.

If the data file has one of the extensions given above, then you simply give the brief name of the file, filename.ext - without drive/path specification, and the data is retrieved and the structure displayed. If the file is stored in \Str3Di\DATA, then you can supply only the name - without the extension .sxs - and the data is retrieved and the structure displayed. If the file's extension is not known to StruMM3D, then you should supply the full path name, that includes the drive name and the source directory - drive\directory\filename.ext, or you can navigate to the file using the directory/file displays. If you have a data file in a directory that StruMM3D does not know about, then you should also enter the whole file name, with the drive and path - a:\molecules\glucsa.sxs.

The OPEN MOLECULE LOG command also allows you to examine the catalogue of previously saved molecules, to enable you to find a target structure. The SEARCH THE MOLECULE LOG allows you to find desired structures, saves them to the folder \Str3Di\Searches and then you may use these files as you wish.

Occasionally, when you import a structure from a CIF file the resulting coordinate data file name will be different from the file you selected. The CCDC gives x-ray crystal structure determinations code names, like BELLUZ, and these code name are easier to use when retrieving data from the Internet. But sometimes the CCDC gives the downloadable coordinate data file a numerical name, like 1234567.cif, while embedding the CSD code within the text in that data file. StruMM3D will retrieve the CSD code and name the output file, generated by Str3DiFileConv, with this code. You can use the search option for CIF and PDB files to locate your target molecule by looking back at the original CIF or PDB files.

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3.0.3 Saving a Structure To The Storage Drive

If you wish to save the coordinate data of a structure onscreen to the storage drive, then use either SAVE STRUCTURE, or SAVE AS from the main menu.

If you select SAVE STRUCTURE then StruMM3D will simply overwrite the coordinate data already stored on the hard drive, and you will not be prompted for any other information.

If you select SAVE AS, then StruMM3D will display the same information screen discussed above for LOAD, and the full file name currently in use, and will then prompt for a name. If you simply press ENTER, then StruMM3D warns about overwriting the data file on storage and, if you insist, it does so. If you gave a new file name then the current data is saved under that new file name, and the file name in memory is updated. If you wish to save the data to another directory, then give the entire path name. For example, by entering b:\sugar\galact.sxs you will save the data in directory b:\sugar. StruMM3D always checks the file name to ensure that it meets MSDOS's standards. Once you have decided on the file name and have pressed ENTER, StruMM3D will ask you for a brief description of the molecule. The file name, and the description, will be written into the MOLECULE LOG, a database of the file names, description and dates of all molecules modified or created by StruMM3D.

StruMM3D keeps an eye on the atomic composition and stereochemistry of the molecule in memory and might ask you to rename the molecular model if you have made changes to it. This is a very useful for keeping track of structures. There is a main menu option for searching the MOLECULE LOG.

If data from files with non-StruMM3D extensions, like ".mmx", ".mm2" or ".inp", are in memory and you command an auto-save, SAVE STRUCTURE, then these data are saved into their parent directories, for example \Str3Di\mmx, with the extensions ".sxs". For example, if you had data for butane.mmx in memory and you commanded SAVE STRUCTURE, then a new file - butane.sxs - is generated in the directory \Str3Di\mmx and will be in native StruMM3D format. The ".mmx" and ".mm2" files cannot be overwritten by either command SAVE STRUCTURE, or SAVE AS. Data with non-StruMM3D file names are automatically backed up into \Str3Di\Data.

You can also refresh the data file on storage (if they have extensions ".sxs" or ".xxs"), with modified data in memory, and preserve the old file name. Suppose you have rotated a molecule into a view that you prefer and you wish to retrieve this "view" henceforth, then select SAVE STRUCTURE from the FILE menu, and the data file on storage will be updated without questions. The data in memory will be saved with the same, current, file name.

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3.0.4 Auto-Capturing of New Coordinate Data

TempDataBkup.SXS and FileName_Temp.SXS - The Safety Nets

Few things are worse than losing a structure after you have spent several minutes modifying it, or drawing it! The way to hedge against this unhappy event is to manually save the data frequently, File/Save. If the program is instructed to automatically save the structure's coordinates each time it has been modified, StruMM3D will save the current file data into \Str3Di\Data\TempDataBkup.sxs.

The environmental command/setting {t} can be toggled, as described above, to enable the writing of a data file "TempDataBkup.sxs" into the directory \Str3Di\DATA if the atomic composition of your molecular model has been changed. This mode is active when the environment string displayed at the main menu has the letter {T} capitalized, as shown.

If there is a structure change, the current TempDateBkup.sxs is moved to \Str3Di\Temp\TempDataBkup.sxs and the current (modified) data backed up into \Str3Di\Data\TempDataBkup.sxs. So you can get back your pre-mod data from the backup in \Str3Di\Temp. Another modification will move the data as above.

If you have modified the data from \Str3di\Data\ABCDE.sxs and you wish to save it back to the same folder, StruMM3D will rename it to ABCDE_temp.sxs and save it in folder \Str3Di\Temp to prevent you from overwriting the current data. You can continue to work on the structure, now named ABCDE_temp.sxs.

Remember, if you are working on a molecule whose data was stored in FileName.SXS, then StruMM3D will write interim data to the \Str3Di\Temp folder with the file name FileName_Temp.SXS and you can continue to work on the molecule under that name, so preserving the original data until you finally decide to discard it.

The following events trigger the process of capturing the structure coordinates of the model:

a second structure is imported to place two structures onscreen, the coordinates of both are captured one of two structures onscreen is deleted, the coordinates of the remaining structure is captured atoms or lone pairs are added/deleted to/from a structure, the coordinates of the new structure is captured.

Every effort has been made to prevent StruMM3D from "crashing", whether because of the use of erroneous structure data, or user indiscretions. However, if StruMM3D has been "pushed" into a crash, StruMM3D will try to intercept this event and will save the coordinates of the current structure(s) into the file \Str3Di\Data\Temp\FileNameERROR.SXS.

These FileNameERROR.SXS structures can be reloaded/recalled in the usual way, even if they contain structure errors. By selecting the option FILE/REVIEW STRUCTURE DATA, you can remove the structural errors from the current molecules.

Thus, if you have toggled the {T} option, the modified current structure data can normally be retrieved from either TempDataBkup.sxs and/or FileNameERROR.sxs.

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3.1 Bond Type – Bond Length Relationships. The Automatic Detection of π–Atoms

The Bond State - Vernon G. S. Box (ResearchGate, May 2024)

The function linking bond length to bond type, the bond state, for a given pair of atoms, is shown below in Table 1 for a small number of common bonds. Similar data can be generated for any pair of atoms engaged in a covalent bond up to quintuply bonded pairs.

$BL = BL_0 * BTLC\text{^}n$

Where, for a given pair of atoms, BL is the length of the observed single bond. BL_0 is the length of the simplest covalent single bond as would be predicted by adding the covalent radii of the bonded elements. The best atomic covalent radii to use are those derived from length of the single bond between each element and an alkane carbon, as in the methylated CH3-X molecule, since the methyl group offers very little to pertub the orbitals of atom X. The BTLC (Bond Type Length Constant) is a constant of value 0.965450369, and n is the bond state quantum number, an integer from -6 to +14, including zero.

The step wise discontinuity imposed on the data by the mathematical relationship, the demand for integer values of n, reveals the reality of the quantization of the data produced and hence the reality of the quantization of bond lengths and bond types

The bond type/length relationship, shown in Table 1, has been incorporated into StruMM3D's structure analysis and recognition algorithms. This relationship makes it possible for StruMM3D to accurately predict the bond length between any pair of atoms, for any type of bond, and so is the most powerful structural analysis algorithm ever introduced into molecular modeling.

Table 1
Bond State - Bond Type Correlated to Bond Length (Angstrom unit)

n	C-C $1.532 * BTLC^n$	C-N $1.48 * BTLC^n$	C-O $1.40 * BTLC^n$	Comment
	Single	**Bonds**		
-6	1.89182	1.82760	1.72881	
-5	1.82646	1.76446	1.66908	Longest?
-4	1.76335	1.70350	1.61142	non-classical
-3	1.70243	1.64464	1.55574	B.O. ≈ 0.5
-2	1.64361	1.58782	1.50199	
-1	1.58682	1.53296	1.45010	
0	1.53200	1.48000	1.40000	Simplest
1	1.47907	1.42887	1.35163	Dienoid
2	1.42700	1.37950	1.30493	Shortest
	Double	**Bonds**		
2	1.42700	1.37950	1.30493	Longest
3	1.3786	1.33184	1.25985	Delocalized
4	1.33100	1.28582	1.21632	Simplest
5	1.28500	1.24140	1.17430	Shortest
	Triple	**Bonds**		
5	1.28500	1.24140	1.17430	Longest
6	1.24060	1.19851	1.13373	Delocalized
7	1.19976	1.15710	1.09456	Simplest
8	1.15637	1.11712	1.05674	Shortest

(For all integral values of n, from -6 to +8. Dienoid refers to undelocalised unsaturated, for example 1,3-butadiene or propenal. B.O. is bond order, Box's BTLC (Bond Type Length Constant) is 0.965450369.)

StruMM3D uses the geometrical features of the molecule(s) in memory to determine the presence of π–atoms, delocalized π–systems, and aromatic rings in their structure(s). The π–atoms present in a displayed molecule are shown by double/triple bonds.

StruMM3D uses the structural features of the molecular model to automatically detect the presence of carbocations, carbanions, singlet carbenes, alkynes, vinyl anions and cations, ketenes and their nitrogen analogues. You will have to create the molecule with the correct structural features, which are quite intuitive. For example carbanions must be tetrahedral and have a lone pair of electrons, while carbocations must be flat π–atoms with a "missing" valency (popularly, but foolishly, known as an "empty" orbital, since it is the presence of electron density that defines the reality of an orbital).

If there are coordinate errors in your data and these cause some bonds to be longer than they ought to be, then StruMM3D might not correctly detect the bonded atoms as being π–bonded. In this case, you

should use the environmental toggle command {d} to enable StruMM3D to make allowance for the data error, and then most, if not all, of the $\pi-$bonds will be correctly identified.

The menu command DELOCALIZATION instructs StruMM3D to search the molecular model for delocalized and aromatic $\pi-$systems, and to highlight the aromatic $\pi-$systems. Whenever there is delocalization in a $\pi-$system, StruMM3D shows double bonds between the atoms that comprise the $\pi-$system. These are not meant to represent "cumulated" double bonds like those found in allenes, and indeed the geometry (flat and non-linear) will verify this. Use the toggle {d} to ensure that bonds are drawn as single, double, or triple (π-atoms not circled) and then you should see aromatic systems as cyclic units with double bonds between all adjacent atoms. If a double bond is missing from the ring, then you know there might be a data error and DELOCALIZATION will not "find" that aromatic ring. You should then toggle {d} to see if the missing double bond is restored and, if it is, then DELOCALIZATION will find the aromatic system.

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3.2 Identifying Atoms in Structures Using the Mouse or the Keyboard

StruMM3D allows you to label atoms of structures with either their appropriate atomic symbols or with numbers (that have been determined by the programme's ranking of the atoms by their valence states). These numbers can be entered into the programme, at the keyboard, whenever StruMM3D prompts you to identify particular atoms. However, we often do not "clutter" the images onscreen with these numbers and then the mouse is invaluable in making these selections.

Normally, whenever StruMM3D prompts you to select/identify an atom, you can left-click the atom with the mouse and then confirm the selection by left-clicking the {OK} button. You can also simply right-click the atom and the selection is made and confirmed simultaneously. You should left-click on an atom if you are not sure that it is the desired atom, before confirming you selection by left-clicking on the {OK} button. However, if you are sure of the selection, then simply right-click the atom.

The only exception to this is when you are identifying atoms in order to measure some geometrical feature of the molecule. You would have first selected "QUERY" from the main menu, then "MOLECULAR GEOMETRY" from the sub-menu, and then StruMM3D tells you to click on the atoms involved. At this point you must left-click on each atom and, after you have made your final selection, you then left-click the {OK} button, or right-click a blank part of the screen (far from the structure).

You must not double-click an atom during the use of the "MOLECULAR GEOMETRY" routine since that might trigger unexpected events

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3.3 Measurements of Molecular Parameters - QUERY

Selecting "QUERY" from the main menu allows you to measure every important structural parameters of the molecule in memory. These include interatomic distances, bond lengths, bond angles, dihedral angles, and very approximate NMR spin-spin splitting (coupling constants) for vicinal protons whose dihedral angle has been measured. Atoms involved in steric interactions, and lone pairs involved on through-space n-n, n-s, n-p interactions can be located, and the sizes of these interactions measured. Pyramidalization of sp2 atoms and a host of other interesting molecular features can be observed and measured by using these commands imaginatively.

The sub-items in the "QUERY" menu are self explanatorily named, and are easily used, because

StruMM3D prompts you for the data it needs.

Querying n-n or steric interactions allows you to append the data onto a "LOG" file. Thus, the data for glucose.sxs can be saved in glucose.log, if you so desire. StruMM3D supplies suitable prompts to enable you to activate the feature to store the data. Querying dihedral angle data automatically stores the dihedral atoms in the DIHEDRAL ANGLE ARRAY, which can be used during structure energy minimization to handle dihedral angles.

If you selected "MOLECULAR GEOMETRY" from the QUERY sub-menu, or MOVE/QUERY MOLECULE from the MOVEMENT menu, the MOVEMENTS window, further described in the next section, will be opened and its QUERY button will be activated with the colour green or red.

The main menu option - MOVEMENT/MOVE/QUERY MOLECULE - is the normal way to access the geometry measuring mode of the programme. You can also reorient (turn/move) the molecule, while in this mode, to better expose the molecular features that you wish to measure.

Clicking on the QUERY button in the MOVEMENT window will toggle it between GREEN and RED. When this button is RED, the potential energy associated with the bond length, bond angle, or dihedral angle, will be displayed along with the measured quantity. In this mode, the items in StruMM3D's main menu will not be available to you. When this button is green, the measured quantity will be displayed, but not always with the associated potential energy, and StruMM3D's main menu will be totally accessible.

In order for the QUERY button to be toggled into its RED mode, the molecular model MUST be fully elaborated with all atoms displaying their full valencies (no missing atoms or lone pairs). It is only then that the potential energy of the selected structural feature can be determined.

If the QUERY button is GREEN, then the CONSTRUCTION menu is available and you can alter some of the molecular features. If your actions result in a molecular model that is not fully elaborated, then you will not be able to toggle the QUERY button back into its RED mode. It is not advisable to change atom types, by using the CONSTRUCTION menu, while the MOVEMENT window is open. This can cause undesired results and crash the programme. If the QUERY button is in the RED mode, the CONSTRUCTION menu is NOT available, and to access it you must toggle the QUERY button into the GREEN mode.

StruMM3D will normally open the Movements window in the correct mode, with the QUERY button RED if the molecular model is fully elaborated, or GREEN if it is not.

You will "single-left-click", on each of the atoms involved in the selected structural feature, after selecting each atom the relevant quantity associated with the set of atoms will be displayed. Thus, clicking on two atoms automatically shows the distance, three atoms shows- the bond angle, and four atoms shows- the dihedral angle. At the end of the atom selection process, after the data has been displayed, click on the {OK} button to clear the display and get ready for another measurement. Again, clicking on two atoms gives the distance between them, clicking on three atoms gives the angle at the second atom, clicking on four atoms gives the dihedral angle. You must not "double-click" an atom during the use of this routine.

REMEMBER, that if you wish to get potential energy data, the QUERY button must be in its RED state, and all of the atoms involved in the selected structural feature must be in the same molecule and, if necessary, be contiguous, otherwise you will be shown the measured quantity without the associated potential energy. If you wish to measure features that involve non-contiguous atoms in two different molecular models then the QUERY button must be toggled to its GREEN state.

Always click {OK} to end and clear the measuring routine.

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3.4 Molecular Manipulations

StruMM3D possesses the full range of translation/rotation (Movement - MOVE/QUERY MOLECULE), enantiomerization (Construction - Enantiomerize), molecule fragmentation (Construction - Divide Structure), template and fragment linking to make more complex units or unit cells (Construction - link Structures), and other capabilities needed by any molecular modeler. Rotations and translations are always fastest when you are moving only the molecular framework, without atomic symbols or numbering displayed.

Some of these operations require no input from the user after they have been activated from the main menu (e.g. enantiomerize and link Structures), the other operations will call up their own special windows and provide a generous amounts of prompting to assist the user to complete these tasks.

The MOVEMENTS window - for translating or rotating a molecule - has the following features:

- The size of the motion can either be selected from boxes in the window, or a "custom" quantity can be entered into a text box that is provided
  Clicking on the directional icon translates or rotates the chosen structure in the logical direction suggested by the icon.
  Access is provided to the "MOLECULAR GEOMETRY" routine by clicking on the {QUERY} (measure) box.
  Clicking on "Pivot Atom" and then on any atom selects that atom as the reference atom. If you click away from the molecule (no atom) the center of mass of the molecule(s) is selected.
  The pivotal atom in the molecule chosen can be "jumped" to a precisely selected site by using the {JUMP} command in the window. This is very valuable for the creation of new molecules from templates, as will be described below.
  The {StepWise} button - that signals Non-continuous motion - changes into a {Continuous} button - that signals Continuous motion - when you click on it. Then, just holding down the left mouse button when the pointer is on any of the direction buttons will cause continuous motion until you let go of the mouse button.
  When the routine is set for continuous motion, clicking the vertical {Paused} button changes it to a {Moving} button and starts continuous motion.
  If the {Motion} button is clicked, it will toggle the mode of motion between continuous and stepwise, along with a colour change for the appropriately affected buttons.
  The blank rectangle sited below the "compass rose" is actually a gesture box. If you click and drag the mouse pointer in this box, then the molecule will be rotated, or translated, in the appropriate direction, consistent with your gesture.
  The {Motion}, {Step wise} or {Continuous} buttons, and the {Paused} or {Moving} buttons are toggles. Clicking a particular button changes the button from one state to the other, the {Motion} button is the "master" toggle.

The ROTATE BOND window - for changing a molecule's conformation - has the following features

- The energy of the molecule can be monitored continuously. This is very computational intensive and can be slow if you are not using a modern computer.
  The conformer onscreen can be minimized without leaving the window.
  The conformer onscreen can be saved, with the same or any other file name desired.
  The bond rotations can be done automatically, if you set the dihedral/distance required, or

manually, with continuous energy updates.

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3.5 Calculated Elaboration of Molecular Skeletons

Using the options in the CONSTRUCTION sub-menu

StruMM3D will elaborate valence-incomplete atoms into their full structure by adding other atoms, lone pairs, or hydrogens to them. The main menu option is ADD ATOMS/H/LP.

The locations of the added atoms are calculated using the geometry of the molecule at the target atom and so the positions of the added atoms are determined by the hybridization status of the atom that is being elaborated. StruMM3D will elaborate valence-incomplete atoms in any one of two modes - StruMM, and MMX or OTHER (like that used for PCModel, MMX or MM2/3/4).

StruMM3D's native elaboration mode is "STRUMM" and all heteroatoms, including the halogens, are given their appropriate number of lone pairs. MMX or OTHER assumes that oxygen and nitrogen flanked by $\pi-$bonds must have delocalized lone pairs (not a valid assumption) and does not put lone pairs on the other heteroatoms. MMX or OTHER, like STRUMM, puts two lone pairs on oxygen and one on nitrogen, but, unlike STRUMM, does not put lone pairs on halogens.

StruMM3D will prompt you for the atoms on which to perform structure elaborations. The options are "ALL", "NONE", or "SELECT". StruMM3D will automatically elaborate all of the atoms in a molecule, with hydrogens and lone pairs of electrons, if one selects "ALL". There is no further user input until the routine is done.

If an individual atom is to elaborated, then use the option "SELECT". This is an extremely powerful and useful routine. StruMM3D will ask you to select the atom to be elaborated, and eventually to select the types of new atoms to add, when it has decided where to place these new atoms. By using this routine carefully, you can create quite complex molecules, and with direct control of any stereo-chemistry. This routine is a natural compliment to the CHANGE ATOM routine which will enable you to replace any atom in an existing structure with another, with complete control of stereo-chemistry, and complete control of bond lengths to the new atom.

Elaborating an atom is the method of choice for adding a new atom to an existing atom that is already joined to at least one other atom.

StruMM3D will not attempt to elaborate metal/metalloid atoms. You have to add substituents to these atoms manually by using the CREATE/MODIFY a MOLECULE routine from the main menu.

Artificial atoms - see section 4.2.1 below - will only be given lone pairs by the elaboration routine, but you can change these to hydrogens, or whatever you wish, by using the CHANGE ATOM routine.

Occasionally one encounters sp3 atoms that support bond angles that are greater than 118 degrees. Very often these sp3 atoms are incorrectly located in the parent molecule (a coordinate error). The ADD ATOMS/H/LP routine will ignore these atoms, but will flag and report them, so allowing you to treat them as you wish. The positions of these atoms can be adjusted using the routine to minimize the energy of an atom (Energy - Minimize Atom Energy), until they support bond angles less than 118 degrees. Then, the ADD ATOMS/H/LP routine will handle these atoms normally. You can also elaborate these atoms manually by using the CREATE/MODIFY a MOLECULE routine. The Energy - Minimize Atom Energy routine will be discussed below.

StruMM3D is designed to ensure that the sizes of lone pairs borne by heteroatoms are related to the covalent radii of these heteroatoms. Therefore, it might be necessary for you to replace the lone pairs that are currently parts of your existing structure data files. If the lone pairs are missing when you call a structure onscreen, select ADD ATOMS/H/LP, instruct StruMM3D to elaborate "all' the atoms, and StruMM3D will replace the missing lone pairs or hydrogens.

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3.5.1 Adding/Deleting Individual Atoms

If the X-ray data of a molecule has badly placed hydrogens, use the ERASE ATOM routine to delete all of the hydrogens, then use ADD ATOMS/H/LP to replace them. If only a few hydrogens are badly positioned then delete these atoms individually using ERASE ATOM and use ADD ATOMS/H/LP to replace them.

When elaborating the atoms of a structure, try to ensure that the molecule is not in an unreasonable conformation that would force the new atoms, hydrogens, or lone pairs, to coincide or overlap. StruMM3D will not allow overlapping atoms in the same structure, and it deletes the lower priority, or higher structure number, atom automatically. Multivalent atoms always have higher priorities than those that support fewer valencies.

If you simply delete an atom then StruMM3D will add hydrogens and/or lone pairs to the remaining atom, appropriately, if you so desire.

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3.5.2 Establishing Stereo-chemistry. Using the Routine ADD ATOMS/H/LP

If you instruct the routine to elaborate an existing individual atom that you "SELECT" (this is as opposed to asking StruMM3D to elaborate "ALL" of the atoms), StruMM3D will place a circular cursor where it intends to place the new atom and then prompt you for the type of atom to add. In this way you can control the orientation of newly added atoms, e.g. axial and equatorial, and so add different types of new atoms to the central atom with controlled stereo-chemistry. StruMM3D also prompts you for bond type (single/double/triple, as 1. 2, or 3) when needed.

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3.5.3 Changing The Type, or Covalent Radius, of an Atom. Using Routine CHANGE ATOM

If you are using a molecule as a template structure and wish to change one atom to another, for example to change a particular hydrogen to a fluorine atom, enter select the main menu option CHANGE ATOM, and StruMM3D will prompt you for the atom's number and the other needed data. Changing an atom automatically adjusts the new bond length to the appropriate mean value. StruMM3D will also add hydrogens and/or lone pairs to the new atom, appropriately.

It is hardly likely that you'll ever need to change an atom's covalent radius, especially if your molecular models use the atoms in the first three rows of the periodic table. However, in another scenario, most likely if you are working with transition metal complexes, you might wish to examine the effect of changing the covalent radius of the metal atom/ion. The main menu option QUERY/AN ATOM'S STATUS will enable you to examine the basic attributes currently being used for that atom, and also to change the atom's/ion's covalent radius. This is a very powerful routine and must be used cautiously. If

the atom's/ion's covalent radius is reduced too much, then bonding to its erstwhile partners will cease and StruMM3D might erase the atom/ion.

StruMM3D has been empowered to automatically adjust the covalent radii of transition metal complexes that have more than 7 ligands. Interesting molecules, like the metallocenes, in which the metal atom is coordinated to ten, or more, centers are automatically processed and the information entered into the molecule's log file.

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3.6 Adjusting, Scaling Up/Down, Molecular Size

StruMM3D will adjust the size of the molecule onscreen through any range of sizes. The routine CHANGE STRUCTURE SIZE will prompt you to vary the size of the model by using the "larger" or "smaller" buttons. Clicking on the {OK} button, or carriage return, ends the routine. This scaling algorithm enables you to "zoom in/out" to get a closer "look" at a part of a molecule. Interesting geometric features, like puckering at $\pi-$atoms, can then be closely observed.

The AUTOSIZE feature allows StruMM3D to rapidly "fit" the molecular model to the size of the screen. This is especially valuable when a large molecule is brought onscreen. It's also visually exciting.

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3.7 Versatile Molecular Drawing Capabilities

StruMM3D's and StruMM3D's drawing routines have been extensively reworked to enable users to continuously retain contact with the three dimensionality of the drawing process. These revisions have greatly simplified the drawing process. StruMM3D's "draw" window has been carefully designed to ensure that "ease-of use" has been retained in StruMM3D.

StruMM3D's CONSTRUCTION window enables you to add new atoms onto an existing structure accurately, with any bond type/length, and to draw structures with any feature and any atom type. The window always displays appropriate bond lengths and angles for use in the drawing process. The drawing process should be carefully planned before being executed to ensure speed and success. The discussion and examples given below will illustrate the need for, and efficacy of, engaging in this time/energy saving planning process.

Using the drawing routine will require you to click {OK} in the drawing routine window, or the main window, as is appropriate. Just be patient and watch for the visual prompts.

StruMM3D can minimize the energy of the structure in memory, so correcting structural inaccuracies. Thus, if the model constructed is not as refined as one would wish, the geometry of this model can be corrected by using the MINIMIZE MOLECULE ENERGY routine. Carefully drawn models will require less time for their structure energy minimization, regardless of the programme used. Thus, the precision drawing capability of StruMM3D is distinctly advantageous.

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3.8 Structure Energy Minimizations In StruMM3D

During a structure energy minimization exercise StruMM3D's molecular mechanics module (Quantized Valence Bonds Molecular Mechanics - QVBMM) sequentially vibrates each atom in the molecule,

through varying amplitudes, until the atom's most energetically stable position is found. This process is repeated for each atom, and/or lone pair, until the lowest energy structure of the molecule is realized. The minimum energy structure obtained will usually be at the "bottom" of the nearest local energy minimum "well", but you must remember that this might not be the most stable structure for that molecule, the global minimum.

If acyclic dihedrals in the molecule are not adjusted, see below, then the QVBMM module will usually approach the nearest local minimum to within 0.2 kcal/mole for acyclic molecules and cyclic molecules that do not have large pendant acyclic moieties. These energies are within the thermal vibrational energies of a molecule at room temperature, and so the structures provided by StruMM3D will usually be almost identical to the structures at their "true" local minima. By selecting the options that enable the energies of the adjustable dihedrals angles in the molecule to be explored during the minimization process, the approach to the nearest local minimum will be within 0.05 kcal/mole.

StruMM3D provides three levels of structure energy minimization – "Normal", "Anneal", and "Special".

The "Special" minimization mode is the most rigorous because it perturbs every dihedral in the molecular model in order to help the model settle into its minimum energy structure. This manipulation is especially valuable when minimizing the energies of molecular models that have π−bonds that might be non-planar or have distorted angles. The "Special" minimization mode will generate the best minima, but it is also the slowest mode since it does a much more extensive searching for the structure's minimum energy.

For more rapid, and only slightly less reliable, minimizations, use the "Normal" mode, which will usually approach the nearest local minimum to within 0.02 kcal/mole for most flexible molecules, and within 0.01 kcal/mole for the more rigid molecules.

The "Anneal" mode simulates the heating of the molecule to a very high temperature (the bonds are made less rigid) and then its cooling to room temperature under the conditions of the "Normal" mode's constraints. The "Anneal" mode does not always provide the best minimum energy structures, but is very useful for structures that have become trapped in high energied local minima. It is often very advantageous, especially if the molecular model is reluctant to come to rapidly to a minimum energy, to follow a minimization in the "Anneal" mode with one in the "Special" mode.

We have encountered molecules whose structure energies actually rise when they are subjected to the "Special" minimization mode. These molecules usually benefit from structure energy minimization using the "Normal" mode. This fact emphasizes the need to perform batch minimizations on duplicated files - saved in another directory other than the normal working directory - so that if the structure energy minimization process fails, you can always go back to the original structure file.

IMPORTANT NOTE - Except for special circumstances, like when working with a very crude initial molecular model, or when working with large delocalized entities like DNA/RNA, ensure that StruMM3D environment's delocalization flag is turned off before you begin to do a normal, routine structure energy minimization. However, if StruMM3D environment's delocalization flag is turned on there ought not to be a problem with the quality of the minimization process, or the resulting structure.

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3.8.1 Minimize Molecule Energy - For Molecules or Individual Atoms, Automated

Introduction

Energy minimization routines are found under the ENERGY menu. The structure must have no more than 1024 atoms and lone pairs.

Minimum Search Protocols

StruMM3D now has two routines for executing the actual process of structure energy minimization. One process will move a selected atom in an established pattern, looking for the position in which that atom is at its lowest energy, and repeat this for each and every atom in the molecule. The other routine moves a selected atom, looking for the position of that atom at which the molecule is at its lowest energy, again for each and every atom in the molecule.

The routine that constantly monitors the molecular energy requires much more effort, and many more calculations than the routine that monitors the atomic energies. Thus the molecular energy monitoring routine takes a bit longer than the other, but gives a much better energy minimum. Obviously small molecules can be expeditiously minimized using the molecular energy monitoring routine, while large molecules will require special strategies, but still longer times, to enable StruMM3D to use the atomic energy monitoring routine.

StruMM3D now automatically selects an appropriate routine, based on the size of the molecule being manipulated. This environmental MCM (minimization calculation mode) parameter is set from the I/O BOX, when the programme is "idle", by clicking in the I/O BOX and entering (without the quotes) "~MCM n" where n is 0, 1, or 2. The setting 0 allows StruMM3D to auto-select the Minimization Calculation Mode, setting 1 forces the programme to use only the most rigorous, but slower, molecular energy monitoring mode, and setting 2 forces the programme to use the faster, but less rigorous, atomic energy monitoring mode.

Minimum Energy Limit

When most of us think about the minimum energy structure of a molecule, we think about the zero point energy structure. In reality, no molecule ever exists in this static structure, but exists in some higher energied vibrational state. The minimum energy a molecule can attain will be some vibrationally excited state, determined by the environmental energy (light, collisions) available to influence the molecular energy. So searching for the zero point energy structure is usually almost pointless, but it does yield a limiting perspective for the shape and energy of the molecular potential energy surface.

StruMM3D is set up to search for as low an energy structure as you wish, even though it might take quite some time to get there, or you can limit the thoroughness of the search and end up with some vibrationally excited mode structure. You can adjust the thoroughness with which StruMM3D will search for the zero point energy structure by using the I/O BOX.

When the programme is "idle", click the mouse pointer in the I/O BOX, (the lowest info bar, which should then clear), and enter (without the quotes) "~MEL n", where n is an integer between 1 and 4. The setting 1 gives the least thorough search, and the setting 4 gives the most thorough search.

If you think carefully about the details of getting to the zero point energy structure, without resorting to using template structures and substructures, you will realize that it will require a lot of searching of the bowl-shaped energy "well", because many conformations of a molecule can have a given value.

Obviously then, the most thorough search will take the longest time, and the least thorough search the shortest time. In any event, you can follow the way the energy of the structure is changing during the energy minimization process, and terminate the process whenever you desire.

Minimization Move/Rotate Value

During a structure energy minimization the programme twirls the molecule through space to break up environmental symmetries. This is not a useless action, and is a bit too complicated to discuss here, but it is necessary.

Some More Details

If a structure is not, or could not be, created as carefully as was desired, then StruMM3D's structure energy minimization routine, called by MINIMIZE MOLECULE ENERGY, will correct the structural flaws.

If MINIMIZE ATOM ENERGY - AUTO is called, then StruMM3D prompts you to select the atom, and then that atom is automatically moved to its most stable site in the appropriate molecule.

The routine MINIMIZE MOLECULE ENERGY first ensures that all of the atoms have been elaborated to their full valencies and then proceeds with the task. The native elaboration mode is "STRUMM", rather than "MMX" or "OTHER", and all heteroatoms are given their appropriate number of lone pairs. If the molecule has been elaborated in "MMX" or "OTHER" mode prior to calling MINIMIZE MOLECULE ENERGY, then StruMM3D will normally add any other lone pairs or hydrogens needed to complete the elaboration to "STRUMM" mode and then proceed to minimize the energy of that entity. However, if a molecule has been elaborated in "MMX" or "OTHER" mode, then it is sometimes best to simply erase all of the lone pairs (ERASE ATOMS) and then to give the command MINIMIZE MOLECULE ENERGY. The molecule is automatically elaborated in "STRUMM" mode before the minimization routine begins.

Unlike most other molecular modeling programs, StruMM3D will minimize the structure of any one of two molecules that are in memory. StruMM3D asks the user to identify the molecule to be processed.

If you wish to check the energy of a molecule, without doing a minimization, then use the command CALCULATE MOLECULE ENERGY. If there are two molecules, you will be prompted to select the molecule and the energy of the appropriate molecule (with its current bond lengths and angle) will be calculated and displayed.

The routine MINIMIZE MOLECULE ENERGY always pauses, very fleetingly, at the end of each minimization cycle, to allow you to terminate the operation. The end of a cycle is signaled by the updating of the energy of the model. Clicking on the red Stop button in the pop-up windows that displays the current energy distribution and values during the execution of the energy minimization routine will terminate the procedure, display the current status, and then return you to the main menu. Thus, you can "trap" any conformation of the molecule being processed, for further examination.

The structure energy minimization routine MINIMIZE MOLECULE ENERGY is sensitive to local minima. The minimization routine normally does not use an overt dihedral angle driver, so that the conformational features of the nearest local minimum will usually be obtained. Selected dihedrals can, however, be driven to their minima, as will be described below.

In going to the nearest local minimum, large conformational changes will occur rapidly in a model whose energy was initially very high. As the energy decreases and conformational changes proceed more slowly, then each conformation available can easily be trapped and examined. This enables the user to change a low energied conformation of a molecule to another one of similar energy, and to observe the way this new conformation would "relax" by changing its bond lengths and angles. Most molecular modeling programmes do not allow us to study the features of relaxed conformations that are not at local minima, nor do they allow us to examine those conformations that are close to "local maxima".

The minimization routine does not always generate the global minimum energy conformation of a molecule unless the current conformation is within the vicinity of this global minimum. However, minimum energy structures are more easily generated than their relaxed "higher energy" counterparts. Intelligent manual manipulation of a given structure can usually place that structure in the vicinity of the global minimum, or maximum, so allowing StruMM3D to complete the required task.

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3.8.1.1 Minimize Dihedral Energies - Automated

Molecules with 1-atom or 2-atom side-chains - like amino groups, methyl groups, ethyl groups, are regarded as molecules that possess "terminal" dihedral angles. For example, methylcyclopentane will have one terminal dihedral angle composed of the H-C-C-C atoms of the methyl group's hydrogen, its carbon, the ring atom to which the methyl group is attached and an adjacent ring atom. Ethylcyclopentane will have two "terminal" dihedral angles, one involving the C-C bond in the ethyl group and the other the C-C bond between the ethyl group and the ring.

StruMM3D will automatically identify these terminal dihedral angles and store the atom number data in the DIHEDRAL ANGLE ARRAY. StruMM3D will minimize the energies of these dihedral angles, if you so desire, when the structure energy of the molecule is minimized.

The DIHEDRAL ANGLE ARRAY is also used to store the numbers of atoms whose dihedral angles have been queried by the QUERY - MOLECULAR GEOMETRY routine, or which were identified during a dihedral search when using the QUERY - SUB-STRUCTURE routine. Remember that the powerful QUERY - SUB-STRUCTURE routine will allow you to identify and store the dihedral angle atoms of any sub-structural entity that you wish. Thus, if the molecular model is a highly folded linear alkane, and you use the QUERY - SUB-STRUCTURE routine to search for the C-C-C-C entity, then ALL of the carbon-based dihedral angles in that alkane will be identified, and the atom numbers stored in the DIHEDRAL ANGLE ARRAY, if you so desire.

These dihedral angles will have their energies minimized, if you so desire, during a normal MINIMIZE MOLECULE ENERGY request. If you invoke the MINIMIZE DIHEDRAL ENERGIES routine then only the dihedral angles will have their energies minimized, not the entire molecule. Thus, this routine will convert a folded linear alkane into the anti-anti-anti-etc conformation if all of the dihedrals in that alkane were stored in the DIHEDRAL ANGLE ARRAY.

Note that the energy of the alkane molecule would NOT be the minimum energy because StruMM3D would not yet have relaxed all the bond lengths and angles in the molecule. However, once the MINIMIZE MOLECULE ENERGY routine is used, then the alkane will be in its most stable conformation, possibly the global minimum.

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3.8.1.2 More ways to Minimize Dihedral Angles - ROTATE a BOND

The ROTATE a BOND routine enables you to rotate bonds and to create new conformations is described below in section 6.0.0. One of the features of that routine is a "button" on the routine's menu that allows you to completely explore the dihedral energy of the bond you are examining, by performing a complete rotation about that bond. This routine gives you –

- The option to store the torsional rotation angle vs energy data in a .log file, so that you can graph it later, or otherwise examine it

The ability to perform the rotation with whatever angular increment you desire (for example, a 10 degrees unit of rotation will obviously create a less detailed energy map than a 2 degree unit of rotation)

The ability to automatically move the dihedral into the most stable position discovered during the energy mapping.

You must be aware that the energy of the molecular model will not be at its minimum, even when the dihedral has been set to its minimum, because all of the other structural features of the molecular model were static during that energy mapping, and other bonds/angles/dihedrals that were affected by the repositioning of the rotated atoms did not have a chance to move to their minimum energy positions. However, the newly, partly energy minimized structure will be at lower energy than the original, and this will be demonstrated by the molecule's energy in the window. The displayed molecular energy will not be the truly minimized energy, but that of the conformation with its current bond lengths and angles.

The ROTATE a BOND routine also allows us to rotate any bond in a molecule in a highly controlled fashion. While "manually" or "automatically" rotating a bond in a molecule, the energy of each new arrangement can be monitored in the context of its current, unminimized, bond lengths and angles. Thus, the ROTATE a BOND routine can be use to rotate bonds into their lowest energy conformations, so that subsequent structure energy minimization leads to the global minimum.

During the use of the ROTATE a BOND routine, the MINIMIZE MOLECULE ENERGY routine can be summoned to immediately minimize the energy of each new conformation and, if desired, the new conformation/structure can be saved for later examination. The relevant commands appear in the window of ROTATE a BOND to signal their availability.

The minimization of the conformational energy associated with a given dihedral quartet can be done automatically by selecting the "automatic" rotation command and then selecting MOVE, without specifying a desired dihedral angle of distance. This process can be performed for each dihedral angle in the molecule.

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3.8.1.3 Searching for Global Minima

If the minimization routine, MINIMIZE MOLECULE ENERGY, is called after the user has measured some of the dihedral angles in molecule A, then the molecule's energy is minimized in concert with the driving of the selected dihedrals to their minima. You can invoke the SELECT DIHEDRALS FOR MINIMIZATION routine, then select the desired dihedrals in molecule A by measuring them, and then call the minimization routine. The routine alternates between minimizing the structure energy of the molecule by moving each atom to its most stable position, and rotating each dihedral to its minimum energy. In this way, the molecule is driven to the nearest local minimum energy conformation that is influenced by the selected dihedrals.

If all of the available dihedral angles in a simple molecule have been identified, either by using the – QUERY/MOLECULAR GEOMETRY or the QUERY/SUB-STRUCTURE routines - then the molecule can first be placed in its lowest dihedral energy state by invoking the MINIMIZE DIHEDRAL ENERGIES routine. At this point, invoking the MINIMIZE MOLECULE ENERGY routine can generate the global minimum. Cycling between these two routine can bring the molecule to its global minimum if one cycle doesn't.

3.8.2 Minimize Atom Energy - Manually - For Individual Atoms, Manually

Occasionally, particularly when reviewing X-ray crystallographic coordinate data, one has a molecule in which one atom is incorrectly positioned. The MINIMIZE ATOM ENERGY routine will enable you to adjust the atom's position in the structure in an interactive way. During the use of MINIMIZE ATOM ENERGY, the displayed data includes the lengths of bonds to the target atom, bond angles at that atom, and bond angles including that atom. The "energy" of the atom at its current position in the molecule is also shown. By moving the atom to minimize this energy, one can place the atom in its best, most stable, location. However, you can also place the atom in some other, arbitrarily chosen, position, but you must remember to watch the "bond energies" as you do so. Bond energies greater than 50 kcal/mole should be regarded as warning flags for possible structural disasters.

While MINIMIZE ATOM ENERGY - MANUAL is completely interactive, guided by measured bond length/angle parameters and controlled by the user's manipulation of the X, Y and Z motions (using the x, y and z keys) and the unit of motion, MINIMIZE MOLECULE ENERGY - AUTO is an automated routine that is completely controlled by StruMM3D and can only relocate any atom to its most stable position.

3.8.3 Structure Energy Minimization of Heteroatom-Containing Molecules

The location of a molecule's hydrogens by X-ray crystallography is usually highly unreliable, and the location of lone pairs is impossible. The ADD ATOMS/H/LP, MINIMIZE ATOM ENERGY and MINIMIZE MOLECULE ENERGY routines are therefore very useful in the examination of X-ray crystallographic data of molecules that have heteroatoms.

In some of my research, I explore the interactions of lone pairs of electrons of the oxygen atoms of monosaccharides. The X-ray crystallographic data of a sugar provide the molecule's C and O molecular framework and I use ADD ATOMS/H/LP to add hydrogens and lone pairs to that skeleton. If a bond angle at any atom is unusually large, then the lone pairs and/or hydrogens added by ADD ATOMS/H/LP are placed in unusual positions and these need to be adjusted to more realistic, lower energied, sites. Obviously, I do not wish to adjust the positions of all of the other atoms in that sugar's skeleton, since their positions were determined by an experimental method, but the lone pairs can, and should, be relocated.

The routines MINIMIZE ATOM ENERGY and MINIMIZE MOLECULE ENERGY are ideal for this task. Lone pair interactions are highly dependent on the medium's polarity. They are most exaggerated in non-polar, non-hydrogen bonding solvents and can be quite small in polar, hydrogen bonding solvents that preferentially interact with these high electron density sites. An important example of this solvent dependence is the anomeric effect shown by monosaccharides, like glucose. The α–anomers of simple sugars are usually more stable than their β–anomers in the non-polar media. However, in water, the α–anomer of glucose is less stable than the β–anomer. Most chemistry is performed in organic media (low polarity) and so the MINIMIZE MOLECULE ENERGY routine is designed to consider lone pair repulsions when it processes molecules that contain heteroatoms.

StruMM3D always treats torsional interactions of bonding and non-bonding electron pairs in the sequence of importance: n-n >> n-s > σ–s. This priority sequence, lone pair - lone pair repulsions greater than lone pair -bond pair repulsions than bond pair - bond pair repulsions, is well known from VSEPR theory and has truly stood the test of time. Interactions involving π–bonds are assumed to be

slightly larger in magnitude to those involving σ–bonds.

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3.8.4 Structure Energy Minimization of Heteroaromatic Molecules

Cyclic conjugated heterocyclic molecules will be aromatic if they have only nitrogen or sulfur as the heteroatoms, do not contain carbonyl groups in their rings (like the pyridones and other lactams), and obey Huckel's Rules. Whenever there is an oxygen atom in the ring the molecule will not usually be aromatic, with the exception of the unstable pyrylium salts. You must remember to consult your chemistry texts since some molecules that possess the features that would allow you to predict that they are aromatic, are in fact not aromatic. Remember that 9-hydroxyanthracene does not exist, instead the molecule is anthrone, a ketone.

Fusion of a heteroaromatic ring to a benzenoid nucleus greatly reduces the aromaticity of the heterocyclic moiety, and heterocycles that are weakly aromatic when isolated (unfused single rings) become non-aromatic upon fusion to benzenes. When drawing heterocyclic systems that can be aromatic, it is best to assume that they are aromatic when isolated and not aromatic when fused to a more strongly aromatic carbocyclic systems, pyridines and thiophenes.

The minimization routine will optimize the structure of any ring system that you created to be an aromatic entity, even if it is not supposed to be aromatic. This is a valuable feature, as it will allow you to create and minimize both the structures of 1,3,5-cyclohexatriene and benzene and then compare their features. You can also perform this exercise for other aromatic and non-aromatic pairs of molecules.

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3.9 Comparing Two Molecules For Identity

The first, and obvious step is to compare their molecular formulas by using the command QUERY/MOLECULAR FORMULA. If you wish to verify that two molecules (A and B) are identical, then simply overlap them in space, exactly, or as best as you can, by using the ORIENT STRUCTURE routine, along with the rotation/translation features in MOVEMENT. Remember that until you command StruMM3D to link these molecules they will remain separate entities so that you can move them around individually, as you wish. After you have properly overlapped the two structures, again check their molecular formulas by using the command QUERY / MOLECULAR FORMULA, and then command StruMM3D to link them using LINK STRUCTURES.

The presence of two atoms within one covalent radius of each other will cause one of these atoms (that with lower priority or higher structure number) to be deleted. Thus, the structure that remains will be structure A, and any atoms of structure B that were not identical, or close, to the position of an atom of structure A. You can now recall the original structure A, that you should have saved, and visually compare the molecules onscreen, looking for additional atoms in the "modified" structure A. The QUERY/MOLECULAR FORMULA routine will show the molecular formula of each molecule present onscreen and this will enable you to decide if the "modified" structure A had "gained" any atoms from structure B, i.e., those that did not overlap with the atoms of structure A.

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3.10 Searching a Large Molecule For a Functional Group or Sub-Structural Unit

When you are reviewing the structure of a large, complex biopolymer, like a DNA/RNA fragment or a protein/polypeptide, you often will want to locate and scrutinize specific parts of the molecule. For example, if you want to look at the conformational features of methionine residues in a protein that has 1000 amino-acid residues it would be time-consuming, and sometimes confusing, to manually search the mass of atoms for these methionine units.

The SUB-STRUCTURE routine - find a sub-structural motif - prompts you to specify a 2, 3 or 4 atom unit to search for, by asking for the types of atoms and their π–statuses (single, double or triple bonded). You enter the data, as prompted, in the sequence in which the atoms are attached to each. After you specify the types of the 4 atoms, you are asked if the fourth atom is attached to atom number 3 (linearly attached) or if it forms a branch and is attached to atom number 2. Having decided, then the search begins.

Each occurrence of the sought substructure results in StruMM3D moving the molecule to put the unit in the center of the screen, and highlighting the unit by circling the atoms involved. At that time, you are also given access to the MOVEMENT routine so that you can manually reorient the molecule to examine the substructure carefully. The search can be continued. Each "hit" is highlighted, as above, until no other units are found, or you instruct StruMM3D to quit.

This is a very powerful routine since it does greatly simplify the process of examining large molecules. The limitation of the substructure to 4 atoms is not to be seen as a disadvantage, because you only need select 4 atoms to specify/identify any functional group you can think of. Indeed, this search can distinguish between a secondary alcohol and a phenol, and an aldehyde and a ketone, etc.

The data generated by the search can be stored in a .log file for that molecule. The instructions that appear in the information screen will prompt you to decide whether to store the generated data, or not. Most importantly, any dihedral angle searches, if successful, can be stored in the DIHEDRAL ANGLE ARRAY, which can be used during structure energy minimization to handle dihedral angles.

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3.11 Preparation of Templates, Cutting Fragments from Molecules

Often one wishes to cut out a section of a molecule that is regularly studied so that the moiety can be used as a template, or one might wish simply to separate two individual molecules that are grouped as one structural until (they might be in the same unit cell). There are two routines that facilitate this process, DIVIDE STRUCTURE, that allows you to fragment a molecule, and ERASE ATOM.

Except during the loading of the coordinate data for a new molecule, StruMM3D does not allow the presence of unlinked single atoms, these are automatically deleted. This very valuable feature prevents lots of atomic debris from accumulating within and around models, and can be used to great advantage. Suppose there is a molecule that has a sequence of 6 atoms linked, 1-2-3-4-5-6, and the command ERASE ATOM is called to delete atom 5 (you select ERASE ATOM and then StruMM3D prompts for the atom to delete). Upon deleting atom number 5, the atom number 6 would be an isolated atom and StruMM3D will automatically delete it also. Thus, if the carbon of a methyl group is deleted, then all of the hydrogens vanish.

Fragmenting (DIVIDE STRUCTURE) a molecule is a highly prompted process that will only be allowed if there is one structural unit onscreen. Upon calling the routine, you have the option of rotating or translating the molecule so that the piece to be removed is clearly visible or distinguishable from the rest. When the molecule is in the desired orientation, StruMM3D prompts you to select one of the two main options for accomplishing the fragmentation process.

You can either –

- cleave (divide) the molecule along a vertical plane (following the Y-axis) that you select, or select each of the contiguous atoms of a part of the molecule that you wish to excise.

To cleave (divide) the molecule along a selected vertical plane, you move the mouse pointer to a position at which the vertical, cleavage plane should be established (transects the molecule in the desired fashion) and then left-click that point. The routine then effects the cleavage, the atoms on the right of the screen are placed in a new structure B and those on the left remain in structure A.

The option to select comes with two modes. You can –

- either manually select each of the contiguous atoms of a part of the molecule that you wish to excise by clicking on each of these atoms in turn, and when you have selected all atoms then click on the OK label,
  or, if there are discrete parts to your molecular model (for example if you are working on a dimer, or an oligomer) you can ask StruMM3D to automatically select all of the atoms in one "unit", and then click on any atom in that "unit".

The selected atoms become the new structure B. The new structure B is not junk and can be manipulated in any way desired. If no atoms have been deleted and the fragments have not been moved, the LINK STRUCTURES routine will recombine these two fragments into the former whole.

You are also offered the option of displaying one, or both, of the two fragments in Covalent Radius Mode. This option can be very useful for visualization if one fragment is embedded within the other.

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3.12 StruMM3D Uses XYZ Files for Exporting Coordinate Data

Since XYZ structure files are very small and widely used, StruMM3D will write a XYZ file for a logical structure in memory for ease of distributing StruMM3D models to other programs. StruMM3D will no longer write either a MM2, or a MMX file for a logical structure in memory, however, StruMM3D will continue to read MM2 and MMX files, among many other popular formats.

Before creating the corresponding XYZ structure data file, it is important to elaborate the molecule, ADD ATOMS/H/LP, to its full valence state using the appropriate mode, OTHER, by using the WRITE XYZ FILE routine. If the wrong mode of elaboration is used, then the programme that will subsequently import/handle these files (MMX, MM2, PCModel, or whatever) will either give error messages, or will handle the structures incorrectly. Store all ".mmx", ".mm2", and ".inp" files in folder \Str3Di\MMX.

Although XYS files can conveniently be created by StruMM3D in order to allow you to move the data to another molecular modeling programme, remember that StruMM3D will also read most, if not all, files generated by any other molecular modeling programme available, and display the structure of the molecule. This makes a valuable link between StruMM3D and other molecular modeling programs.

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3.13 Reviewing Diffraction-Generated Atomic Coordinate Data

The commonly used, experimental diffraction (x-ray, neutron, electron) studies provide our most reliable insights into molecular structure. These data are specially handled by StruMM3D in order to

preserve the authenticity of the experimental data. StruMM3D needs only the X, Y, and Z coordinate data, and element type for each atom in any molecule in order to successfully reconstruct all of the features of that molecule. These data can be manually entered into StruMM3D, in any random sequence of atoms, by using the ENTER X-RAY DATA routine, as will be described below.

The data can be entered in any sequence of atoms, regardless of their connectivity, since StruMM3D independently determines the connectivity during the process of loading a structure's data. Users of other molecular modeling programmes will immediately recognize the inherent advantages in this VERY valuable routine, since complex connectivity lists are required by most other programs, and an error in the connectivity list renders the data useless. These other programmes also require their users to enter bond types, along with their connectivity lists, while StruMM3D automatically determines bond types from the coordinate data, so saving the user lots of trouble.

StruMM3D often simplifies the structure review process of newly loaded x-ray coordinate data in order to show exactly what the crystallographer's data contains, errors and all, but this is sometimes a problem.

Often X-ray crystallographic data show other molecules in the unit cell, like solvent, in addition to the molecule being studied. StruMM3D will handle all of the coordinates given for such a "structure" as one logical unit, and all the entities in that logical structure will be manipulated as a unit. The current logo molecule from the crystallographic study of aspartame shows this feature. You can make each sub-unit independent by using the fragment command, DIVIDE STRUCTURE.

When importing diffraction-generated coordinate data, StruMM3D will, by default, show all of the atoms in a unit cell, even if some of these atoms are unbonded (not connected to any others). StruMM3D will not perform structure energy minimizations on logical structures that have unbonded atoms. StruMM3D will also, by default, show all atoms even if they are unrealistically close to others.

While both of these scenarios point to obviously structurally incorrect representations, we have felt it important to enable the user to "see" what is in the imported data, and then to provide the user with methods to correct these problems. You can remove/delete these unbonded atoms, and the atoms that are obviously incorrectly placed (too close), by using the main menu item STRUCTURE/REVIEW STRUCTURE DATA.

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3.13.1 Entering Coordinate Data at the Keyboard

After you have selected ENTER X-RAY DATA at the main menu, you will be prompted to supply the file's name and data on the unit cell axes and angles, and the coordinates and type of each atom. You do not specify the file name's extension. Two data files will be generated. One data file will have an extension ".xcc" and will contain the unit cell parameters and the fractional coordinates, while the other file will have extension ".xxs" and will contain the orthogonalized coordinates used by StruMM3D (an example is shown below). No blank line should be present in these data files, at the beginning, middle or end, as they generate errors.

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3.13.2 Using Coordinate Data From an ASCII Text File, XCC and XCX files

XCC and XCX files are simple text files (ASCII file format) that contain the non-orthogonalized (non-perpendicular unit cell axes), or fractional coordinate data of a molecule. These data can be modified

into the form shown below for use by StruMM3D. The data must be kept in plain text, ACSII format.

XCC Files

.An example, shown below, is for a spirohemithioketal molecule. The text in brackets are comments for your guidance here and are not added to the actual files.

20.158, 37.0.075, 13.523, "Filename" (the unit cell axes lengths and file's name)
89.2, 90.6, 90, "+" (angles between the axes: a, b, c and a place holder "+")
.02688, .00803, .3096, "S" (fractional coordinates X, Y, Z, respectively, and atom type)
-.037, .07312, .3408, "O"
.1273, .08629, .525, "O"
-.0822, .07467, .1358, "O"
.003, .06971, .0273, "O"
-.0479, .0666, .4443, "C"
.0066, .0841, .5067, "C"
.073, .0687, .4749, "C"
.082, .0743, .3647, "C"
.0241, .05935, .3042, "C"
-.0405, 0, .224, "C"
-.0255, .0153, .1222, "C"
-.0195, .0574, .1223, "C"
.0298, .0725, .1972, "C"
-.1103, .0817, .0416, "C"
-.0537, .0792, -.0296, "C"

This file must be given a name with an extension of XCC, for example: spirso1.xcc. These XCC files are used to store raw X-ray coordinate data. These files are native to StruMM3D which recognizes them and will automatically use them to generate XXS files if they are used in a structure importation process. They can be "loaded" to display a structure. They are created when you enter X-RAY DATA manually, at the main menu, or are created by Str3DiFileConv.

XCX Files

Occasionally we'll need to retrieve diffraction data from the older literature. This data was usually presented in tables (atom type X Y Z etc) but the coordinates were all multiplied by 1000 or 10000 to convert them to integers. It is often possible to copy the table section into the clipboard and to paste it into a text editor like Notepad.

For example, the diffraction data for ethylmagnesium bromide dietherate is shown below.

Br 1413(2) -0212(3) 2113(2) 67(1) 106(3) 94(2) -5(3) 19(1) 9(4)
Mg 2762(4) 0185(8) 0962(5) 61(4) 82(7) 81(5) 5(7) 9(4) 9(9)
O(1) 2247(14) 1824(14) 0023(15) 71(12) 67(15) 126(20) -23(13) 38(14) 21(18)
O(2) 2453(12) -1195(14) -0374(14) 58(11) 84(15) 102(16) 8(13) 6(12) -16(17)
C(1) 4410(12) 0261(24) 1726(15) 34(9) 98(21) 80(15) -25(21) 5(11) -4(27)
C(2) 4759(19) -0529(27) 2797(23) 110(20) 146(37) 151(28) 15(28) 18(20) -75(32)
C(3) 1147(13) 2258(26) -0480(18) 28(12) 175(34) 62(16) 32(22) 32(15) 21(32)
C(4) 0930(21) 3284(24) 0313(24) 115(23) 92(26) 163(29) 34(25) 87(25) -33(29)
C(5) 2989(28) 2665(29) -0336(31) 85(26) 143(35) 110(38) 3(31) - 19(31) 6(33)
C(6) 3342(21) 2163(31) - 1388(36) 87(21) 165(37) 262(46) 33(27) 100(30) -32(41)
C(7) 1414(14) -1473(22) -1071(21) 36(13) 113(28) 127(25) 9(18) 57(17) -43(28)
C(8) 1303(20) -0886(28) -2335(22) 99(19) 173(37) 144(27) -4(29) 53(19) -31(32)

C(9) 3224(22) -2111(27) -0550(30) 61(19) 104(29) 146(39) 11(24) 22(28) 46(34)
C(10) 3239(25) -3286(27) 0312(26) 133(29) 154(36) 138(32) 25(30) -49(29) 16(34)

Neither StruMM3D nor Str3DiFileConv will use coordinate data in this form since the unit cell parameters are missing, and so we need to provide some more information, the coordinate multiplier, the lengths of the axes and the angle between the axes, to enable this data to be usable by StruMM3D, and Str3DiFileConv, which is its default file importer. Adding the information, as shown below, by inserting two lines at the top containing the crystal data, will generate a file, which we must give a file extension of XCX. Note that the coordinate multiplier must be enclosed within quotation marks, like the file name, to allow it to be recognized.

13.18, 10.27, 11.42, "EtMgBr" (the unit cell axes lengths and file's name)
90, 103.3, 90, "0.0001" (angles between the axes: a, b, c and the coordinate multiplier)
Br 1413(2) -0212(3) 2113(2) 67(1) 106(3) 94(2) -5(3) 19(1) 9(4)
Mg 2762(4) 0185(8) 0962(5) 61(4) 82(7) 81(5) 5(7) 9(4) 9(9)
O(1) 2247(14) 1824(14) 0023(15) 71(12) 67(15) 126(20) -23(13) 38(14) 21(18)
O(2) 2453(12) -1195(14) -0374(14) 58(11) 84(15) 102(16) 8(13) 6(12) -16(17)
C(1) 4410(12) 0261(24) 1726(15) 34(9) 98(21) 80(15) -25(21) 5(11) -4(27)
C(2) 4759(19) -0529(27) 2797(23) 110(20) 146(37) 151(28) 15(28) 18(20) -75(32)
C(3) 1147(13) 2258(26) -0480(18) 28(12) 175(34) 62(16) 32(22) 32(15) 21(32)
C(4) 0930(21) 3284(24) 0313(24) 115(23) 92(26) 163(29) 34(25) 87(25) -33(29)
C(5) 2989(28) 2665(29) -0336(31) 85(26) 143(35) 110(38) 3(31) - 19(31) 6(33)
C(6) 3342(21) 2163(31) - 1388(36) 87(21) 165(37) 262(46) 33(27) 100(30) -32(41)
C(7) 1414(14) -1473(22) -1071(21) 36(13) 113(28) 127(25) 9(18) 57(17) -43(28)
C(8) 1303(20) -0886(28) -2335(22) 99(19) 173(37) 144(27) -4(29) 53(19) -31(32)
C(9) 3224(22) -2111(27) -0550(30) 61(19) 104(29) 146(39) 11(24) 22(28) 46(34)
C(10) 3239(25) -3286(27) 0312(26) 133(29) 154(36) 138(32) 25(30) -49(29) 16(34)
END

The text in brackets at the end of the first 2 lines are there for information/instruction only and MUST not be put into a working XCX file. Any other details may be added here, like symmetry operators, the journal and author information, and these will be ignored by StruMM3D. ****

This file will be named EtMgBr.XCX.

StruMM3D, and Str3DiFileConv, will recognize the XCX files, will automatically take care of the bracketed numbers and other baggage, and will convert this file into an xcc file format, above, which is native to StruMM3D.

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3.13.3 Using Orthogonalized Data From an ASCII Text File

XXS and SXS Files, StruMM3D's Native Data Files

Text files that contain the orthogonalized (perpendicular cell axes) and actual (not fractional) coordinate data of a molecule can be prepared in the form shown below for direct use by StruMM3D. This is the format in which StruMM3D generates structure coordinate data.

Any word processor can be used to create these files outside of StruMM3D, but the data must be kept in an ACSII format. An example is shown below. The data sequence is X, Y, Z coordinates, "atom", 1.

It is worth remembering that PDB files are presented as orthogonalized atomic coordinate data.

.0000011, 5.000001, 90.00001, "C", 1
.9497223, 4.504333, 88.89368, "C", 1
2.396851, 4.504333, 89.42039, "C", 1
2.499374, 3.571915, 90.64172, "C", 1
1.549652, 4.067581, 91.74805, "C", 1
.1025238, 4.067581, 91.22134, "C", 1

These data files should be given the extension ".xxs" or ".sxs".

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3.14 Viewing large, Complex, Molecules

Occasionally you wish might to examine the interior portions of large complex molecules, especially molecules like the DNA polymers that are "layered" in structure (the layers being the base pairs). Simply turning the molecule back and forth might not allow you to "see" interesting internal structural features. The UTILITIES / TOGGLE LAYER VIEW routine enables you to look at "slices" of the molecule through the YZ plane. While you are in the MOVEMENT / MOVE / QUERY MOLECULE routine, you can orient a suitable axis of the molecule along the Z-Axis, and then "step" through the internal features of the molecule by moving the molecule along the Z-Axis.

Remember that the Z-Axis has a value of zero on the surface of the screen, and the value increase as you go into the screen, so that negative values are in front, and positive values are to the rear, of the screen.

You can adjust the "thickness" of the viewed layer by adjusting the integer in the yellow text box at the bottom right of the UTILITIES/PROGRAM PARAMETERS window. This parameter is a multiplier that will be used with StruMM3D's current default length of the C-C bond, and will be used to specify the inter-planar distances. In our experience, a value of -3 provides a "thickness" equivalent to almost exactly two base pairs in a DNA helical stack. So this value allows you to view two base pair units, or one base pair unit, as you wish. Making this value large will increase the "thickness" of the "slice". The value must be negative.

Another way to focus on an atom's immediate environment is to use the FOCUS button in the MOVEMENT window. This toggle is located at the bottom of the MOVEMENT window and is a pale red color when the window is just launched, indicating that the feature is inactive, and the structural drawing will be normal. Clicking on the FOCUS button with change the color to green, showing that the feature is active. Now, any atom that you select to be the PIVOT atom, by clicking on PIVOT and then the atom, will have all of the distant atoms removed, so showing only the selected pivot atom and its immediate neighbours. Molecular measurements can be done as usual. To turn the feature off, just click on the FOCUS button to toggle it into the pale red, inactive, state, then select any atom to be the pivot atom (or click PIVOT then on a blank screen space to make the pivot be the center of mass of the molecule).

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3.15 Printing Images, Pasting Structures Into Documents - Using the Graphics

The COPY STRUCTURE IMAGE routine will copy the screen's bit-mapped image(s) into the WINDOWS clipboard and this image can then be pasted, from the clipboard, into any graphical

applications. The image can then be captioned, graphically stylized or modified, and then be printed in that context. If there are two molecules onscreen, you will have the option of selecting either, or both, for capture into the clipboard. JPG or BMP files are simultaneously created in the working directory containing the images of the molecules. These files can be used in any graphics application.

These images will be of "publication quality", and will suffice for most purposes of record keeping, for use in classroom, and for other formal and informal presentations. Obviously, the higher the resolution of the screen, the better the image will be. These images are colour coded, not black and white, which does improve their presentation quality, especially when they are projected to screens, or sent to colour printers.

The molecular images in this document were generated as described above.

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3.16 Conserving Available Memory

You can specify the largest molecule that StruMM3D will be required to display. In most molecular modeling programs you can abuse your computer's memory resources by configuring the programme to work with molecules that are much larger than those that you would ever actually examine. Then, you would tie up valuable computer memory resources that would greatly facilitate multitasking operations done by the operating system. The current version of StruMM3D automatically restructures and minimizes the memory usage once a structure has been imported. This frees up memory resources and facilitates multitasking.

Even though you do not need to, it is very easy to manually modify the environmental setting for the largest number of atoms and lone pairs in the molecules to be reviewed by selecting PROGRAM PARAMETERS at the main menu. If there are molecules in memory, then these will be saved before the parameters are adjusted and so no data will be lost during the adjustment.

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3.17 Automatic Structure Rotation

You might wish to continuously rotate the molecular model to view it, or just to be entertained. Select AUTO-ROTATION at the main menu and then choose whether to rotate about the X- or Y-axis. Rotations are fastest when StruMM3D does not have to write in the atomic symbols. You can turn off the symbol writing with and/or before doing "animated rotations".

Pressing a number key during auto-rotation invokes a pause, corresponding to that number of seconds, between the steps. Thus, pressing 5 introduces a 5 second pause between each movement. The AUTO-ROTATION command assumes that rotation will be about atom 1 and so you should place atom 1 in the center of the screen before beginning, by using MOVEMENT with MOVE / QUERY MOLECULE or POSITION, if you so desire.

To terminate the dazzling display click the TERMINATE button, or press any key, or the space bar.

StruMM3D, version 1.6x and newer, can also perform automatic rotations in the MOVEMENT / MOVE / QUERY MOLECULE routine. The windows displayed will now contain a "button" that will toggle molecular movements between continuous and non-continuous. The "buttons" in this window are now completely interactive and you can change motion type and direction "on the fly". When translating a structure there is the danger of moving it off screen, but you can always reverse the motion to bring it

back.

If you have move the molecule off the screen and don't know where it is, then exit from all running routines and double-click anywhere on the screen. The molecule will be re-positioned properly.

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3.18 Undocumented Features

One key directive that has been adhered to in the development of StruMM3D is that it must be extremely modular, in code as well as in function.

The basic commands of StruMM3D enable you to do many other interesting things, especially when used in various sequences and combinations, as was exemplified above. For example, comparing two structures by using the routines LINK STRUCTURES and MOLECULAR FORMULA. StruMM3D will impress by the quantity and quality of the display of scientific data. It is a full-featured molecular modeling programme.

You will be able to accomplish many important molecular modeling tasks not yet mentioned, in addition to those described above. The only tool you will ever need to execute these undocumented features expeditiously is an active mind, since the required programme features/algorithms are present in StruMM3D.

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4.0 StruMM3D's Important Resource/Support Files
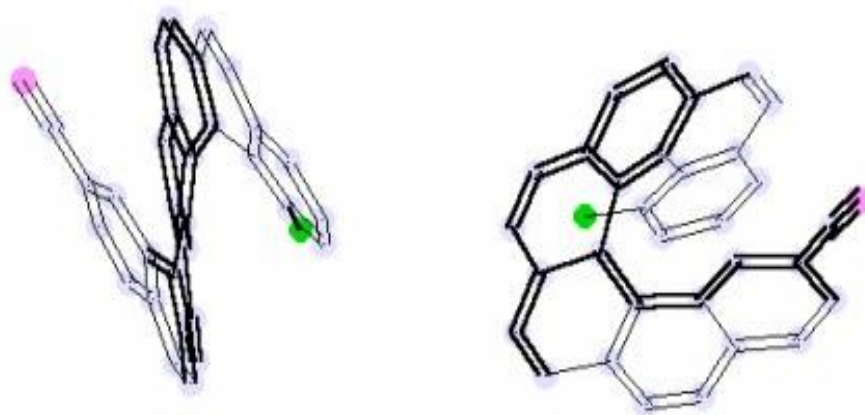
StruMM3D requires complete access to the files Str3disp.Dat and Str3data.Dat. These files must not be write-protected, their file attributes must not be "read-only" or have attribute "+r", but must be "read/write" or have attribute "-r". You can set the file attribute by using the operating system's WINDOWS Explorer.

The EXE files were compiled with Microsoft's Visual Basic 6.00 (Service Pack 3) and so the run-time module MSVBVM60.DLL must be stored in the directory \WINDOWS\SYSTEM, as well as OLEAUT32.DLL.

The files with extension .DAT are very important and they MUST NOT BE MODIFIED other than by the programme, except where stated otherwise.

The STR3DIDRIVE.DAT file, that is stored in C:\ProgramData, in the root directory/folder, must be left unmodified. It is generally of critical importance, but is particularly important when using StruMM3D as a helper with the Internet Explorer web browsers.

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4.1 Str3display.Dat

The first time that you execute StruMM3D, you might be asked about the sizes of the molecules you will work with, and your video system. These data will be stored in the file \Str3Di\Str3display.Dat in an ASCII format. It MUST be present in the directory \Str3Di. If you wish to change any of this information, then use the command PROGRAM PARAMETERS to access the window that contains the important data for "setting up" the programme. The new information you provide will replace that in Str3display.Dat.

Remember that if you update StruMM3D it is always best to delete the old display/environment settings file (str3display.dat) before running the new version of StruMM3D.

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4.2 Str3data.Dat

This file contains the important data on the types of atoms, and their covalent radii, that StruMM3D will recognize. It MUST be present in the directory \Str3Di. The "covalent radius" of the lone pair shown in Str3data.Dat is used by StruMM3D as a reference and must not be altered unless you are extremely

clear about what you are doing.

After many years of empirical observations we established that bond lengths are almost always equal to, or are about 1.00% less than, the sums of the covalent radii of the component atoms in their simplest molecules. The covalent radii for the oxidation states of carbon are derived by halving the distances of the C-C bonds in their simple compounds, alkanes, alkenes, alkynes. Similarly, the covalent radii of oxygen are derived from the C-O bonds of ethers and aldehydes or ketones.

These simple bond lengths are remarkable because they are applicable to a wide variety of molecules. For example, the carbon-carbon single bond length used by StruMM3D (C1C, 1.532 Angstroms), is the value of that bond's length in simple molecules, like ethane, and this bond length corresponds to a bond order of 1. StruMM3D uses an algorithm to predict the entire bond length range of C1C bond lengths found in stable organic molecules, regardless of the structural milieu, or the hybridization of the carbons, and this does apply to transition states (where the bond orders are less than 0.5). This algorithm applies to, and is verifiably true, for all other bond types. Aromatic molecules are no exceptions since they have double bonds, their chemistry is very similar to that of alkenes, and their bond lengths fall within the range of carbon-carbon double bond lengths (C2C, 1.331 Angstroms ± 6.02%).

Although you can add new data to Str3data.Dat, in the displayed format, we strongly recommend that you don't do that before discussing it with us.

If you chose to adjust the data in Str3Data.Dat, be VERY careful. StruMM3D will sometimes ignore a bond between two atoms if the data in Str3data.Dat is badly chosen, or will show a mess. In this event, close StruMM3D, modify Str3data.Dat using any text editor, restart StruMM3D. You can also correct the data, and reset StruMM3D's variables by the command CLEAR MEMORY. The new data will then be available to StruMM3D.

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4.2.1 Creating and Using Artificial Atoms via Str3data.Dat

You can add "artificial atoms" to the Str3data.Dat list and then use these to construct molecules. This is a truly revolutionary feature of the STTR3DI molecular modeler because it allows you do "what if" simulations that are impossible with other molecular modelers.

For example, suppose you wanted to examine an analogue of a pyran, but you wanted to replace the ring oxygen with another atom whose covalent radius and electronegativity were the same as oxygen, but which would bear two hydrogens - without charges on the central atom - instead of two lone pairs. No such atom really exists, but you could introduce a "new" atom "Xo" into Str3data.Dat, in the section where atoms and their covalent radii are listed, but in the range of values 10 to 15.

You will name this "new" atom "Xo". The leading "X" tells StruMM3D that this is an artificial atom and the subsequent letters tell StruMM3D which atom you want the "new" atom to simulate in bonding characteristics. Thus, "Xo" will simulate oxygen, and "Xcl" will simulate chlorine, while "Xn" will simulate nitrogen. To complete your data, you must give this new atom the covalent radius you wish it to have, and the electronegativity (Pauling's). Thus you could give "Xo" the covalent radius of oxygen, or some similar value, and use the current Pauling estimate of the electronegativity of oxygen.

StruMM3D will automatically generate associated important data for this atom like its bond lengths to other atoms and all of the other parameters that you might need.

Str3data.Dat is set up as shown below.

```
50
"C" , .766 , 2.55 , 1
"Si" , 1.08 , 1.90 , 2
"P" , 1.114 , 2.19 , 3
"B" , .786 , 2.04 , 4
"N" , .704 , 3.04 , 5
"O" , .644 , 3.44 , 6
"S" , 1.114 , 2.58 , 7
"Se" , 1.16 , 2.55 , 8
"." , .1 , 0.00 , 9
"Xa" , .766 , 2.55 , 10
"Xc" , .766 , 2.55 , 11
"." , .1 , 0.00 , 12
"." , .1 , 0.00 , 13
```

CAUTION - Do not alter the number at the top, 50 in this example. Only add new atoms in the empty numbered slots, for example, 9 and 12 -13.

Keep these new atoms to a minimum, and re-use the ones that are present by changing their designators and covalent radii. Two artificial atoms are presently embedded in the data, both with the covalent radii of carbon. Xc will simulate carbon, as also will Xa until you change the designation to something else, like Xp (a phosphorous analogue). Xa is, of course a totally new artificial atom and can be given any covalent radius, and electronegativity, you chose.

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4.3 The Molecular Database, Molecule.Log

StruMM3D's Built in Database

Whenever you create a new structure, or modify an existing structure, or simply wish to save the coordinates of an existing structure under a different file name, you will invoke the main menu commands STRUCTURE/SAVE AS. After saving the data, StruMM3D will ask you for a brief description of the structure's features, and the file name, the description and the date will be saved into the text-based file named MOLECULE.LOG.

These files are maintained, and regularly updated, by StruMM3D. Only make changes manually if you absolutely must.

You can browse through MOLECULE.LOG by using the main menu commands STRUCTURE/OPEN MOLECULE LOG, when the default text application, usually NotePad, will launch the molecule.log file. All the data stored in that file will be searchable.

You can also manually use your NotePad application to open molecule.log.

A Visual Database Using StruMM3D's Graphic Files

Another interesting option, especially for users that would prefer a visual method for identifying structural data files, can be realized from the use of the UTILITIES/COPY IMAGE TO CLIPBOARD

menu item. Whenever an onscreen image is copied to the clipboard, apart from being available for pasting into a document/publication, or image processor like Microsoft's Paint, that image is also save to the folder in the JPG or high resolution BMP format.

If you use Windows Explorer to open/view the working folder, the view can be adjusted so that graphics files, like the BMP, or JPG, or GIF, files of the molecules that were copied to the clipboard, are shown by thumbnails (small version of the image). These thumbnails are not only true reproductions of the image, but are also full coloured, large and clear enough to enable you to recognize the molecule that was being modeled.

These thumbnails can essentially form the basis of a visual database to enable you to identify and work on a particular molecule, rather than having to remember which file name corresponds to which molecule. However, these thumbnails are normally opened using some graphical software, like Microsoft's Paint.

Starting with StruMM3D version 8.0.0.14 , if you right click on the thumbnail, then select "Open With" from the menu, you can opt to use StruMM3D to open this file. The first time through you will have to guide the program to the folder bearing StruMM3D (\Str3Di) and then select StruMM3D. Be careful not to opt to use StruMM3D as the default to open graphics file. In subsequent runs, the StruMM3D will be available the moment you click on "Open With".

When StruMM3D is used to open a thumbnail in a Str3Di folder, or sub folder, as long as the original structural data file is still in that sub folder, StruMM3D will open the structural data file and start the molecular modeling exercise.

The thumbnail can be a BMP, JPG or GIF file. StruMM3D only saves graphics as JPG or high resolution BMP files. BMP files are large and can eventually take up a considerable amount of hard drive space. You can convert these BMP files to smaller JPG, or GIF files. We recommend JPG files. You can use any third party software to do these graphics format conversions, or if you install ImageMagick's format conversion software, Magick, StruMM3D can do this for you automatically via the cleanup batch program TIDYSTR.

DBOX32, a molecular database manager

DBOX32, a molecular database manager and general purpose database programme, has also been developed for use with StruMM3D. DBOX32 will enable you to create databases that contain text-based information and also have access to StruMM3D and the coordinate structural data for any organic molecule. These databases can contain many records of molecular structural data and their related physical or chemical properties. These databases can easily be assembled and maintained. DBOX32 will only be available to registered users of StruMM3D, and will be supplied with instructions for its use as a molecular database manager.

Users of DBOX32 would have been supplied with a database named STRMOLS. You should rename this database to MOLECULE, by changing the file name using WINDOWS EXPLORER (left click on the file in EXPLORER and use the rename option). You should keep the directory \DBOX on the same drive as that which hosts the directory \Str3Di. This is VERY important.

We can supply users of DBOX32 with a small utility - UPDTMOL - which will extract records from MOLECULE.LOG and add these to the database MOLECULE. When you run UPDTMOL, this programme will create new files in the database MOLECULE, using the information in the MOLECULE.LOG, so that you can run more controlled molecular modeling exercises directly from DBOX32, which will interact directly with StruMM3D.

UPDTMOL is supplied with a data file - UPDTMOL.DAT - which stores data from the database MOLECULE, like the maximum number of records that each sub-file of MOLECULE can hold, and the numbers of the fields that correspond to data STRUCTURE DECSRIPTION, STRUCTURE NAME and STRUCTURE CREATION DATE. This simple file is set up for the database MOLECULE and can be modified if you have modified the database MOLECULE. It is very important to keep the data in UPDTMOL.DAT consistent with that in the database MOLECULE, or you will corrupt the database. UPDTMOL and UPDTMOL.DAT will only work with the DBOX32 database named MOLECULE and MOLECULE.LOG.

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4.4 StrUMM3D's Opening Molecular Display

When StruMM3D is started, it displays a charming visual of a rotating molecule. This molecule can be one drawn and structure energy minimized by StruMM3D. The StruMM3D compatible coordinate data for this "start up" molecular model should be saved to the data file STRLOGO.LXS, which is then stored in the directory \Str3Di. It is important that the molecule's structure be complete (all valencies satisfied) and that the molecule's energy be minimized by StruMM3D.

The start up logo, STRLOGO.LXS, is VERY important in the initial setting up of StruMM3D. It is used to ensure that there are no hardware, specifically CPU generated floating point errors, when StruMM3D is executed. The start up logo will alternate between STRLOGO.LXS and any CIF file that might be present in the folder \Str3Di.

Another way to add a new start-up molecule is to copy any CIF file into the \Str3Di folder. Don't use library files. Check these CIF files before you use them to ensure that they do not have format errors. If there are several CIF files in the \Str3Di folder, then StruMM3D will use the first one that it finds, in an alphabetic file name search. The "molecule of interest" program, in which users can ask that a particular CIF file be used as the start up logo is also ongoing. Just let us know which molecule you want to see when you start StruMM3D.

Small molecules are retrieved and rotated faster than large ones, but the user's "taste" in organic molecules will normally determine what kind of molecules will be used. I like sweet things, so the logo you will first see will be that of aspartame. Change it if you wish to.

StruMM3D will always begin to rotate your selected start up molecular model about the vertical - the Y-axis – but using the keyboard's arrow keys might provide nice surprises.

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4.5 Str3Dmax.Bat and Str3DBatch

StruMM3D can be run from the MSDOS command prompt, or from the START/RUN Windows menu option, to minimize the structure energies of a particular molecular model in a folder, provided that this file has been saved in StruMM3D's native coordinate format. The format for running StruMM3D in batch mode is -

StruMM3D full_path_file name minx arg1 arg2 arg3

arg1 can be
a - for automatic termination after 8 minimization cycles
q - for automatic termination after 4 minimization cycles

t - for automatic termination after 20 minimization cycles

arg2 can be
s - for minimization using the "special" mode, automatically adjusting all dihedral angles
n - for minimization using the "normal" mode, automatically adjusting all terminal dihedral angles
t - for minimization using the "normal" mode without automatically adjusting any terminal dihedral angles

arg3 can be
newlog - to generate a new log file for storing the minimization data
lastlog - to keep on using the last logfile, which can have a user customized name.

STR3DMAX.BAT will run StruMM3D in batch mode to enable you to minimize the energies of ALL, or selected, molecular models in a particular folder. The format for running the batch file is -

STR3DMAX X:\DATA_DIRECTORY file name1 file name2 file name3 etc (up to 8 file names) newlog/lastlog

- where X: is the designation of the drive, on which the data resides, and DATA_DIRECTORY is the full path name to the folder in which the data for the molecular models are stored. The file names can use MSDOS wild card format. Thus a file name of * will have all files processed, a file name of ch* will have files whose names begin with CH processed. Up to 8 separate file name descriptor can be used. The last parameter, newlog or lastlog, does not have to be specified, but the default setting is lastlog. The "lastlog" setting tells STR3DMAX to put the data generated into the last log used.

When you do a batch minimization for the first time StruMM3D begins to generate a file of the logs you use for your batch energy minimizations. This file is named STR3DMINLOG.DAT. StruMM3D will write a log of time, file name, final energy for each minimization done while it is operating in batch mode. The log will be normally be named Str3dMinXXYYZZZZ.log, where XXYYZZZZ is the current date string. It is stored in the \Str3Di directory, and is compatible with all spreadsheets.

STR3DMAX normally puts all of the minimization data into the last log you used. You can use the operating system text processors, WORDPAD or NOTEPAD, to enter a custom log name at the end of the list of logs in STR3DMINLOG.DAT and StruMM3D will put all of the data into that log. When you use the "newlog" parameter in STR3DMAX.BAT, the new log will be named Str3dMinXXYYZZZZ.log, where XXYYZZZZ is the current date string. Or you can just continue to customize your log names.

A copy of STR3DMAX.BAT should have been enclosed with your software. The key line in the batch file is - for %%a in (%strwrkdir%\%1.sxs) do E:\Str3Di\StruMM3D %%a minx a s %3

Use the text editor to change the drive location for the StruMM3D programme (this example assumes that \Str3Di is on drive E:), and to look at the arguments after the word minx. Change the drive designation and these arguments, as listed above, as you need to. DO NOT MAKE ANY OTHER CHANGES IN THIS FILE.

STR3DBATCH is a small programme that will enable you to execute the batch operations described above, without having to tangle with the complexities of the STR3DMAX.BAT batch file. This programme is not only easier to use, but also more versatile in its abilities to select the various modes of minimization for StruMM3D.

Always perform batch minimizations on duplicated files - saved in another directory other than the normal working directory - so that if the structure energy minimization process fails, you can always go back to the original structure file.

4.6 Str3DiFileConv

One great strength of StruMM3D is its ability to recreate a truly three-dimensional molecular structure from coordinate data and atom types, and then to exactly identify and reproduce the key stereo-electronic features of the molecule. The implementation of the unique structure analytical algorithms embedded in StruMM3D requires no participation by the user and, after many years of rigorous testing, can truly be said to be almost perfect. Several scientific publications have been generated by using StruMM3D to re-examine the experimentally derived diffraction coordinate data from many important biomolecules. These studies have invariably drawn attention to previously unnoticed stereo-electronic effects in these bio-molecules.

The major sources of experimentally derived diffraction coordinate data for important bio-molecules are the Cambridge Crystallographic Data Center, (CCDC), the Brookhaven Protein Database (PDB), and the iUCr Structure Reports website. These organizations publish their data in their own, unique and valuable, formats, from which it can sometimes be laborious to extract the needed coordinate data.

Str3DiFileConv will extract the relevant coordinate, and other, data from the CCDC (CIF, CSD) and PDB files and will then generate new structure data files in the StruMM3D native formats. StruMM3D works intimately with Str3DiFileConv.EXE, and if these programs are present together in the \Str3Di directory, then the interaction of these two programs is automatic. Indeed, if you have Str3DiFileConv.EXE, then you can simply associate StruMM3D with the CCDC and PDB files, and opening these files with StruMM3D will automatically display the structures embedded in the data.

Str3DiFileConv will also extract the relevant data from XCX, MM2, MM3, MM4, MMX, INP, XYZ, MOL, MOL2, MDL, MOPAC, and M3D files and generate new files in the StruMM3D native formats. Using Str3DiFileConv, StruMM3D will handle all files imported from, or generated by, other widely used molecular modeling programs. Str3DiFileConv.Dat is EXTREMELY important to the proper running/execution of StruMM3D and Str3DiFileConv, and must never be deleted.

Unfortunately, there are often problems in structure file formats, or file contents, that can/will disrupt Str3DiFileConv's actions kill the file/coordinate importation process. StruMM3D will then alert the user about these file/coordinate importation process problems and allow the user to view and correct these errors in the offending CIF, PDB, or whatever, file, using the computer's text editor.

The functionality of Str3DiFileConv has now been included in one of the Str3Di DLLs, and so , while the actual EXE file is absent from the Str3Di folder, it's capabilities are available to StruMM3D. Str3DiFileConv will skip any line of atom coordinate information if the first (X) coordinate number is an integer, unless the file being processed is an XCX file, above. Also keep an eye out for missing "end of data" markers, and other careless author generated errors which are frequently found in CIF and PDB files.

5.0 Constructing a molecule with StruMM3D - Create/Modify a Molecule
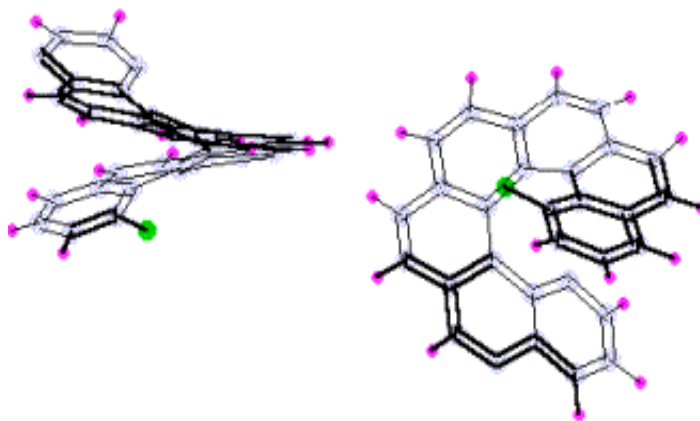
5.0.1 Introduction

Mechanical models are undoubtedly very important learning tools, and are often quite useful as guides to the construction of molecular models, since they present you with a rough view of the final structure. However, mechanical models can limit our understanding of the dynamics, conformational properties, and the reactions of organic molecules. These models are rigid, with fixed bond angles/lengths, and cannot show bond angle/length changes when they are used to construct most molecules. Mechanical models therefore cannot accurately convey the dynamics of creating a strained molecule.

A consideration of the bond angle/length changes that accompany the transformation of one molecule into another often clarifies the features of that reaction that determine its activation energy profile.
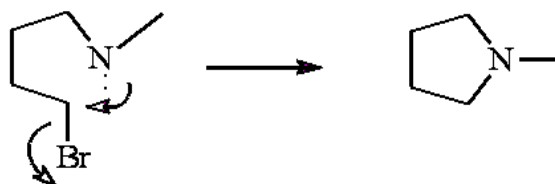
During the conversion of Br-CH2-CH2-CH2-CH2-NH-CH3 into N-methylpyrrolidine, all the bond angles and bond lengths of the starting acyclic molecule are undergoing changes. If pyrrolidine is created using a molecular modeler that requires us to know that the bond angle in a five-membered ring is about 108 degrees (rather than about 111 degrees as found in an acyclic molecule), then we would understand more clearly the subtleties of this seemingly simple chemical transformation. StruMM3D allows us to approach structural organic chemistry from this viewpoint and encourages us to develop a familiarity with bond lengths, angles, the 3-dimensional viewing of organic molecules, and the dynamic processes involved in their transformations.

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5.0.2 Precision in Construction

The construction of a molecule with StruMM3D is greatly simplified if a mechanical model, or a clear three-dimensional sketch, of that molecule is made before attempting to construct it onscreen. Then, the required shape can be viewed at first hand. This in turn gives a good feel for the way the onscreen molecule must be constructed and for the way bond lengths, bond angles and dihedral angles must be

modified.

StruMM3D constructs molecules with full control of their 3 dimensional features and so the molecular models are in the conformations desired. Drawing a 2-dimensional (flat) molecule using StruMM3D is extremely easy. However, drawing a 3-dimensional molecule is a bit more demanding. The extra effort required is however well spent since the desired stereo-chemical features at chiral centers are fully controlled.

The controlled molecular construction offered by StruMM3D is also very advantageous if structure minimizations will be done, since the computation time required to minimize the energy of a complex molecule is dramatically reduced.

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5.1.0 The Coordinate Frame of Reference
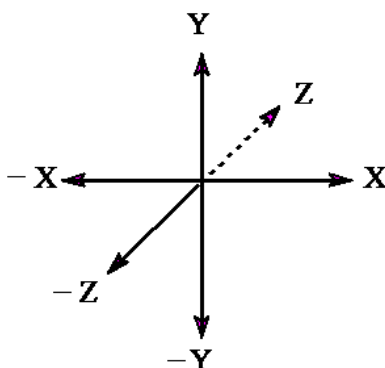
The point 0, 0, 0 is in the center of your screen. The X and Y axes are horizontal and vertical, respectively, in the plane of the screen and the Z coordinate is perpendicular to, into/out of, the screen. Note that Y increases upward and decreases downward. Z = 0 on the surface of the screen and increases inwardly (into the screen). An atom at coordinates 10, 10, 10 is farther away from you (into the screen) than an atom at 10, 10, 1.

StruMM3D allows you to use wedge shaped thinner lines or broken (dashed) lines to portray bonds that are farther away (into the screen) in an attempt to further enhance the 3-dimensionality of the molecular models. The environmental toggle {L} switches the display between these line patterns.

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5.1.1 Drawing Commands and Their Format

The process of constructing a new molecule, or building on an existing one, is very heavily prompted. StruMM3D will suggest, wherever relevant and at every step, the numerical values of bond lengths, bond angles and dihedral angles, and the format for entry of non-numerical data, in order to facilitate the process and to guide the inexperienced user.

When the drawing routine is invoked by selecting the CREATE/MODIFY a MOLECULE routine, StruMM3D displays the DRAW, drawing, window and its menu of drawing commands. You first specify the type of the starting atom, or select an atom from an existing structure to be the starting atom. If you chose a starting atom for which StruMM3D has no data it will not comply. Thereafter, you supply the data needed for the new bond by manipulating the controls of the DRAW window. Then click on {OK} and the new bond will be established.

StruMM3D uses a simple notation for identifying the types and multiplicities of bonds. These are shown below:

C1C - a carbon to carbon single bond
C2C - a carbon to carbon double bond
C3C - a carbon to carbon triple bond
C2#C - a carbon to carbon delocalized, or aromatic, double bond
C3#C - a carbon to carbon delocalized, or aromatic, triple bond
C1Br - a carbon to bromine single bond
C2O - a carbon to oxygen double bond
C2#N - a carbon to nitrogen delocalized, or aromatic, double bond

During the drawing process, the atom types and bond type shown in the DRAW window can be modified by clicking on the control and entering the desired data using the keyboard. When all of the data necessary to draw a new bond is present in the DRAW window, then bond should have a constitution and "type" similar to those shown above. Changing the bond data will prompt StruMM3D to suggest default sizes for bond lengths and bond angles, but these can also be changed, cautiously, before commanding StruMM3D to proceed (clicking OK). If you are in doubt about suitable bond lengths to use, then there is a "FIX" button that will suggest the correct default values.

Remember that the atom in the left hand text box is the host atom (to be explained further below).

If you wish to see the three dimensional profile of the model that is being constructed, but you do not wish to exit the drawing routine and so lose track of where you were, then clicking {VIEW} in the DRAW window instructs StruMM3D to rotate your model, step wise, through 360 degrees, in 15 degree intervals, about the Y-axis (the vertical). Hitting a number key during the rotation introduces a pause between the rotation steps corresponding to that number of seconds. Hitting 5 introduces a 5 second pause. StruMM3D stops the rotations at the precise position from which it started, so that you may resume drawing.

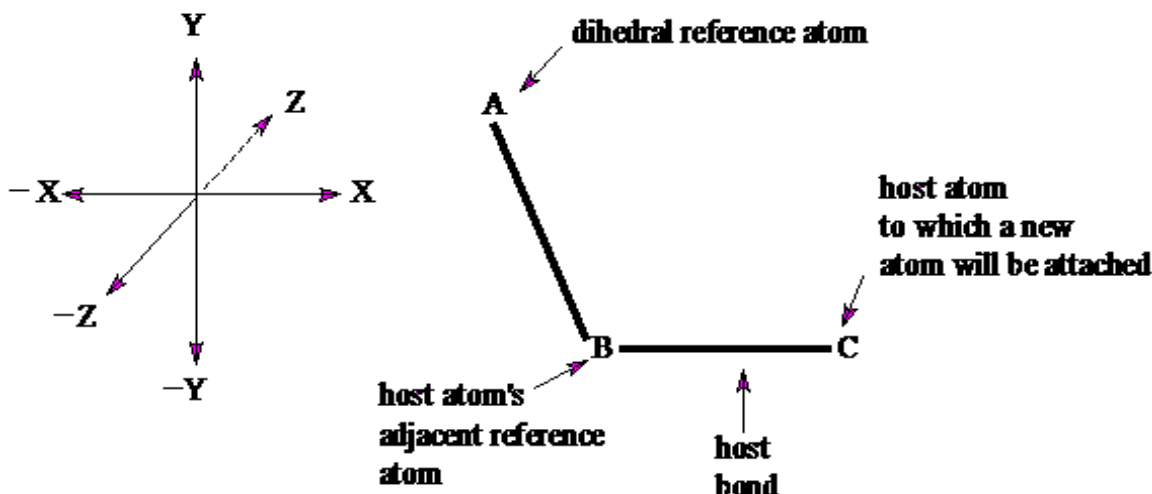[Contents](#)

5.1.2 Positioning New Atoms

When a new structure is being constructed, StruMM3D instructs you to chose the starting atom, and then always places the second atom to be placed to the right of that starting atom. You simply provide the new bond length and atom type in accordance with the prompts.

New bond angles and dihedral angles (to other new atoms) are entered in the frame of reference discussed below. There are three important atoms needed for the correct positioning of a new atom.

a) The "host atom" (to which the new atom will be attached).
b) The host's "adjacent reference atom", that supports the "host bond", and creates the reference for measuring the new bond angle.
c) The "dihedral reference atom", from which the new dihedral angle, to the new atom, can be exactly specified.

StruMM3D requires that you introduce a new atom in the context of an existing "host bond", that will always be oriented horizontally (parallel to the X-axis) with the host atom to the right. The dihedral reference atom will be positioned in the X-Y plane, to the left of the host atom. Dihedral angles are measured with respect to the X-Y plane, also defined by the designated dihedral reference atom, and so with respect to the vertical (Y-axis).

This arrangement of the three key atoms, α–-B--C, is automatically established by the programme, as is shown below. New bond angles are measured with respect to the host bond.

After a new atom is added to the host atom, StruMM3D prompts for the number of the next host atom, adjacent reference atom and dihedral reference atom, and then automatically reorients the molecule's drawing site, as required above.

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5.1.3 Always Draw Three Atoms

The first three atoms of any new structure MUST lie in the same plane and so the DRAW routine is especially set up to facilitate the building of that core. IT IS CRITICALLY IMPORTANT THAT YOU ALWAYS DRAW A NEW STRUCTURE WITH A MINIMUM OF THREE ATOMS. If you wish to draw methane, draw H-C-H as a minimum structure. For ethane and ethene, draw C-C-H, and C=C-H as the minimum structures.

Remember that after you select the starting atom, the next atom will always be positioned to the immediate right of that atom, along the X-axis. Subsequently, atoms are always positioned somewhere to right of the "host" atom, as you decide from bond angle and dihedral angle considerations.

The ADD H/LP routine will not always do a good job if the structure has less than three atoms. This routine needs three atoms to establish the "hybridization" status of the central atom, and hence the appended atoms. Simply adding the third atom during DRAW will prevent lots of problems.

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5.2 Drawing Flat Molecules

Planar molecules and aromatic rings are very easily drawn. The buttons used for one dimensional drawing have one letter and are labeled : a, c, r, i, o. These buttons indicate the position of the new atom with respect to the host atom and its bond (host bond) to the adjacent reference atom.

a - anti-clockwise, greater Y, same Z coordinates.
c - clockwise, smaller Y, same Z coordinates.
r - right, greater X, same Y and Z coordinates.
i - inward, greater Z, same X and Y coordinates.

o - outward, smaller Z, same X and Y coordinates.

If we have a new bond, as below center in the diagram, the host atom, from which the new bond will be drawn, will be on the right, and its adjacent reference atom will be on the left. By selecting the button the new atom will be placed as shown, clockwise on the original bond, and selecting the button would put the new atom in an anti-clockwise position, as in the diagram. The new bond angle is that which you instructed StruMM3D to use.

X = new atom
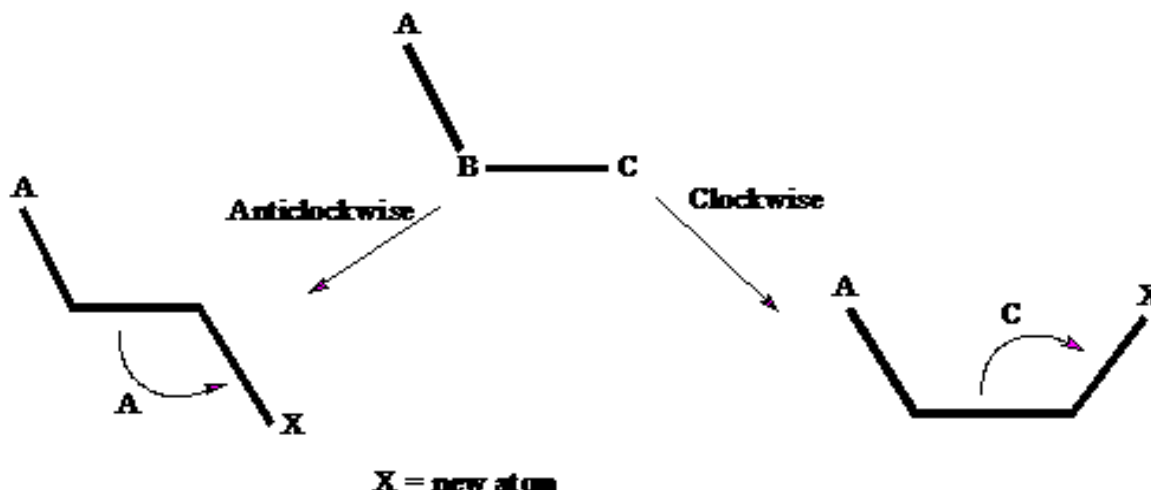
Thus, selecting the buttons c, c, c (or a, a, a), in sequence, and supplying the requested bond angle data, would place atoms in the same plane at positions shown below.
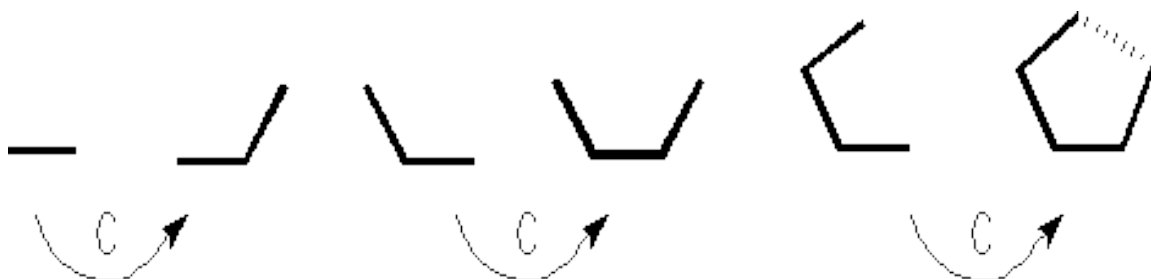
The EXIT button, or a failure to select a host atom, halts the drawing process, reviews the data, and completes all implied bonds. Thus, if the fifth atom is within bonding distance of the first atom, then StruMM3D will make that bond.

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5.3 Drawing Puckered Molecules

Puckered molecules, like cyclohexane, will be almost as easy to draw as flat ones. You should examine a mechanical model to better visualize the target and the dihedral angle relationships in the model, because you will need to know these, bond lengths and bond angles, in order to draw your target with precision. The three dimensional commands all have two letters. These commands (buttons) place the new atom

UI - Upwards and Inwards, using the specified dihedral angle
UO - Upwards and Outwards, using the specified dihedral angle
DO - Downwards and Outwards, using the specified dihedral angle
DI - Downwards and Inwards, using the specified dihedral angle

Inward and outward refer to the dihedral angle to be established with respect to the XY plane, and so the dihedral reference atom. Note that a dihedral angle of 60 degrees, drawn by the command UI, will produce a dihedral angle of 60 degrees, syn, with respect to the dihedral reference atom. However, a dihedral angle of 60 degrees, drawn by the command DI, will produce a dihedral angle of 60 degrees with respect to the X-Y-plane, but now anti to the dihedral reference atom - hence a true dihedral of 120 degrees (180 - 60) with respect to the dihedral reference atom.

The precision and three dimensionality of the drawing routine might cause some of the drawn atoms to seem to be superimposed on the screen during the process of construction (have the same X- and Y- but different Z-coordinates). However, the molecular model can be viewed globally, at any time, by using the hitting the button VIEW}, already discussed above, in order to rotate the model and so reassure you of the true 3-dimensional perspective.

You must remember that StruMM3D will automatically orient the molecule as shown in section 5.1.2, and so the directions in which you project the new atoms might not always be intuitive if you do not have a suitable 3-dimensional perspective. These locations for new atoms are most easily appreciated by paying attention to the 3-dimensionality of the model being constructed, or by viewing a mechanical model of the 3-dimensional molecule.

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5.3.1 Drawing a Cyclohexane

Draw the first C-C bond (C1 to C2) and then by supplying the following drawing commands and responding to the prompts that follow each command, you will complete the cyclohexane:
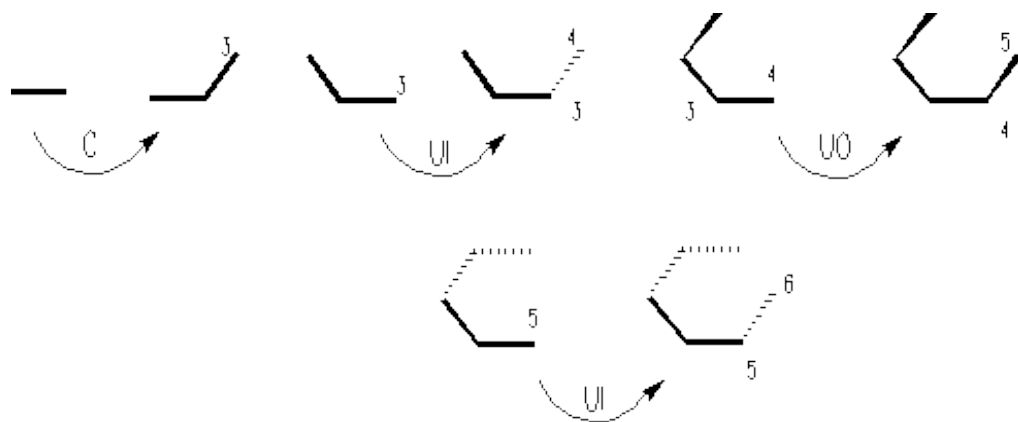
a - to new C-3, now select C-3 as the host atom
ui - to new C-4, now select C-4 as the host atom
uo - since the C-1 - C-2 bond is up and outwards, then the C-4 - C-5 bond must be parallel to the C-1 - C-2 bond and so you select uo to establish the to new C-5, now select C-5 as the host atom
ui - similarly, you would then select ui to establish the new C-6

You should not have to draw from C-6 to C-1 since StruMM3D will sense that these atoms are within bonding distance and automatically links them using a bond type (single, double or triple) that corresponds to that bond length. If StruMM3D does not complete the ring, then you have some bad geometry someplace in the drawing.

Note that StruMM3D allows you to follow the 3-dimensionality of the drawing process by clearly distinguishing between bonds that are in, in front of (heavy solid lines), and behind (dashed lines) the X-Y plane, as is depicted in the diagram. You can also follow the 3-dimensionality of the construction,

at any step, by using the command to twirl the molecule.

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5.3.2 Drawing The Cis- and Trans-Decalins

Draw, or import, a cyclohexane, use ADD ATOMS/H/LP to attach an equatorial carbon at C-5 (the new C-7) and an axial carbon at C-6 (the new C-8), and then resume drawing at C-7. Select C-6 to be the dihedral reference atom, then use the command {UO} or {UI} to create the next new bond parallel to the C-6 - C-8 bond. Next, opt to continue drawing from the new C-9 and complete the ring by creating the new bond parallel to the C-5 - C-6 bond by using the appropriate command, as shown above. The C10 to C-8 bond will be established automatically.
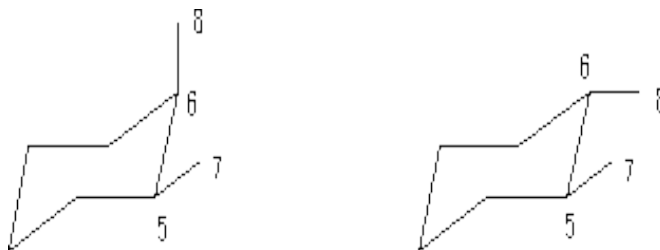
These instructions were formulated by looking at a mechanical model of each molecule and the orientation of the bonds with respect to the frame of reference defined above in section 5.1.2. Planning a construction is always important to the speed and success of the process. After you have become familiar with the view of the graphical interface, the obvious three dimensionality of the model being constructed also allows you to draw molecules spontaneously.

You can also add the hydrogens to the structure and you will see that you can simply replace a hydrogen on each methyl group by a carbon to generate the additional ring. Once the new carbons are in place StruMM3D completes the ring automatically.
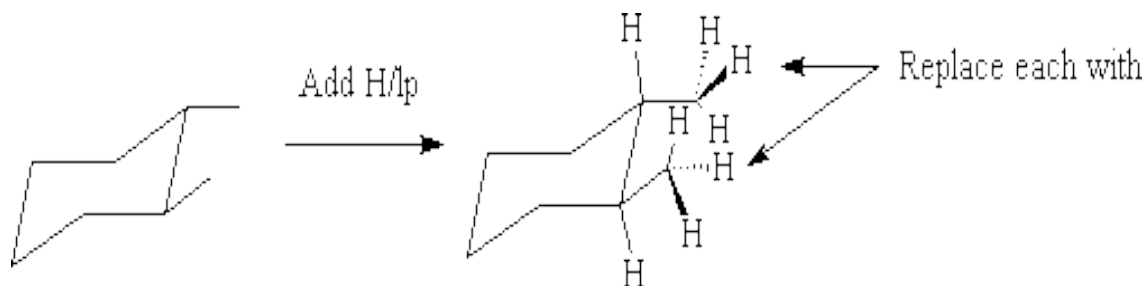
The strategy of replacing hydrogens, or carbons, of existing structures to generate a more complex one is well worth learning and using. These replacements are done with known stereo-chemistry and the resulting models are excellent because StruMM3D adjusts the bond lengths as the atoms are changed.

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5.4.0 Creating Transition States, Modifying Models into Transition States

Unlike other molecular mechanics programmes, StruMM3D will process Transition State models that have both breaking and forming bonds, simultaneously.

The default status of Transition State models of addition reactions is that all Transition State bonds will

be made. The default status of Transition State models of Sn2 reactions is that one bond will be made and the other broken. In Sn2 Transition State models, StruMM3D decides which bond to make, and which to break.

Normally, StruMM3D will correctly set the make/break statuses of the Transition State bonds, based on their bond energies, but StruMM3D will allow you to inspect and modified the Transition State model before any structure energy minimization is performed. Elimination reactions present the greatest challenges, and after these Transition State models are created, StruMM3D will allow you to inspect and modified the Transition State model before any energy determination is made, and before any structure energy minimization is performed.

You can prompt/force StruMM3D to review the bonding in a Transition State model that is fully elaborated with all hydrogens/lone pairs/etc., by using the main menu option ENERGY/CALCULATE MOLECULE ENERGY

You can make or create a Transition State model by either docking the "reactants" and then moving these together, through the van der Waals barrier, until the Transition State bonds have been established, or you can take the "product" and move/lengthen bonds joining the appropriate atom until they have Transition State characteristics.

StruMM3D will show all Transition State bonds as either GREEN or RED dashed lines. The green bonds will be made, and the red bonds will be broken.

Sn2 Reaction   E2 Reaction   Z-Addition Reaction
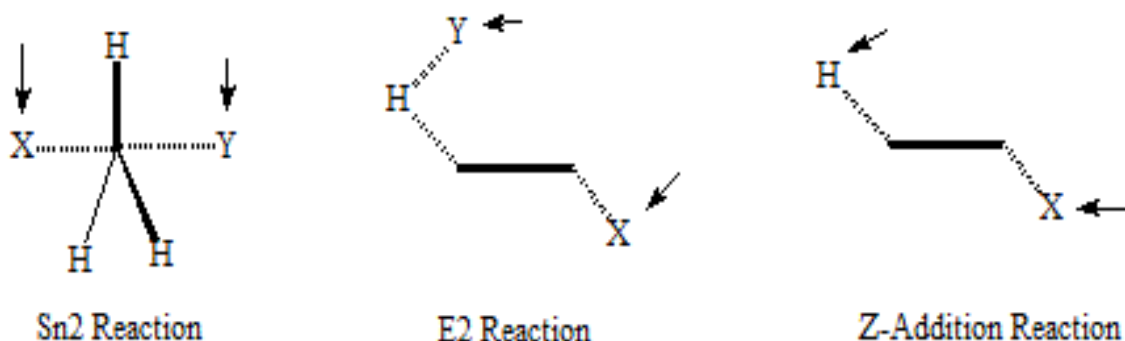
Above you will see some examples of how StruMM3D will depict some common Transition States. Notice that the Transition State bonds will always be dashed and the fully formed bonds will always be solid. If you stretch, in StruMM3D, a bond, you will see that as soon as the bond gets long enough, to a bond order less that 0.5, the depiction will automatically change to that shown below.

Whenever you are prompted to review the make/break characteristics of the Transition State bonds, and wish to make a change, remember to click/select only the outermost atoms, shown by the arrows. If you click/select an inner, or central atom, the results will be highly unpredictable. So, do NOT EVER select the central, or inner, atom.

If you ask StruMM3D to automatically adjust the distance between two atoms, or when you are exploring distance – energy relationships in transition states, it will automatically generate a chart of energy vs distance, as well as offering you the opportunity to save these data for future use.

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5.5.0 Working With Metal Salts and Coordination Complexes

StruMM3D does not know, or ask for, the oxidation state of metal ions in their salts and complexes, and we have tried to enable StruMM3D to automatically determine this, in order to minimize the instances of user-introduced error in the modeling/simulation exercise.

StruMM3D starts all of its molecular modeling exercises using the covalent radii of the atoms involved, since it was developed initially for organic, covalent, molecules. So, initially, when the unit cell of the sodium chloride crystal was modeled, the sodium ion seemed to be "bonded" to its six nearest neighbouring chloride ions by "single" bonds, each of bond order about 0.8. This bond order was indicative of a "normal" covalent single bond, and was much larger than expected for a transition state bond, or a single electron single bond, < 0.5

An empirical study revealed that if the radius of the metal ion, in its salt's unit cell, was adjusted to its proper size, the apparent "total bond order" of the metal ion was almost identical to the metal ion's charge or oxidation state. This finding was surprisingly congruent with Pauling's Rules for crystal structures of metal salts, except that Pauling's electrostatic bond strength is simply Z/CN (charge divided by coordination number) and is oblivious of inter ionic distances. StruMM3D seeks to measure "covalent" bond orders and hence bond strengths. Thus, the convergence of StrMM3D's algorithms and the Pauling Rules augurs well.

The StruMM3D algorithms work very well if the metal salt, or coordination complex, is fully elaborated, all the ligand sites are filled and there are no dangling valencies. In the event that the metal salt, or coordination complex is not fully elaborated, then StruMM3D will attempt to use the available data to predict the full coordination number of the metal ion and so estimate the "bond orders" of the bonds/association, present.

Obviously caution is required if partial structures are being examined.

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6.0.0 Rotating A Bond - Generating New Conformations - ROTATE a BOND

Rotating a bond requires that you identify six important atoms:

1. An atom that will be the stationary reference for measuring distances to a moving reference atom (one of the atoms to be moved).

2. An atom that will be the reference for measuring dihedral angles with the moving reference atom (above), note that the atoms 1 and 2 can be the same atom, or can be different.

3. The atom on the axis of rotation, that will not be attached to the atoms to be rotated.

4. The other atom on the axis of rotation, that will be attached to the atoms to be rotated.

5. The atoms to be moved, and all of the atoms attached to these atoms, that you also wish to be moved. StruMM3D automatically moves hydrogens and lone pairs that are attached to polyvalent atoms. Select tetravalent, skeletal, atoms before selecting other atoms.

6. The atom, among those to be moved, that will be used to monitor distances and dihedral angles with the reference atoms 1, and 2.
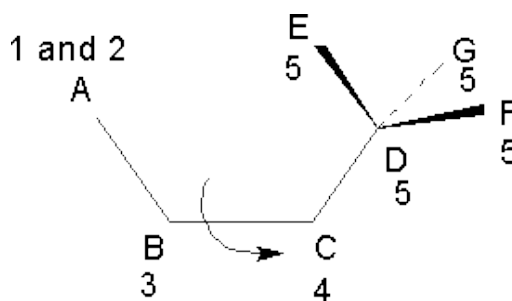
For the system α–B-C-D(EFG), above, if you wish to use atom A as the reference atom for dihedral angle and distance measurements with respect to the movable atom D, and you wish to rotate about the β–C bond, moving atoms C, D, E, F and G, then the numbers indicate the categories of these atoms as above. Any of the atoms D, E, F or G can be selected to be the moving reference atom, but you can see the obvious value of using atom D for the purpose of measuring dihedrals and distances from atom A.

StruMM3D offers you two methods for selecting the atoms to move along with the rotating axis atom -

a manual method - when you click on an atom then click {OK} to confirm (of just right-click on that atom)
an automatic method - when StruMM3D selects all of the atoms sequentially bonded to the rotating axis atom.

It is advantageous to use the manual method for selecting atoms that are in a ring, but the automatic method is the method of choice in acyclic systems. If you are using the manual method when selecting the atoms to move along with the rotating axis atom, try to select those atoms attached to the rotating axis atom last. Start selecting the far atoms and work towards the rotating axis atom.

The atoms are identified by either specifying their numbers at the keyboard, or by clicking on them when prompted, followed by confirming the selection by clicking on {OK} or by right-clicking the atom when prompted.

The ROTATE a BOND window also prompts you for any other required information including:

incremental angle of rotation, (you can enter a number you desire in the text box provided)
direction of rotation + for clockwise and - for anti-clockwise
whether to monitor the energy of the molecule or not
whether to rotate the bond automatically or stepwise (manually).

Having selected/identified the reference atoms, above, and the other parameters, StruMM3D then re-orients the molecule to show the perspective along the rotation axis, and so highlight the projected dihedral angle. Then, clicking {MOVE} instructs StruMM3D to move the desired atoms stepwise (for the manual manual rotation), or automatically, into the desired position.

The data displayed in the ROTATE a BOND window can include the distance between the centers chosen, the dihedral angle and the energy of the conformations you have generated, depending on how you configured the routine. These data is updated for each new conformation. The displayed energy will not be the truly minimized energy, but that of the conformation with its current bond lengths and angles.

The energy of any conformation can be minimized, without leaving the routine, by pressing the {MINIMIZE} button, and the structure data of any conformation can be saved by pressing the {SAVE CONFORMER} button.

The routine will also drive that selected dihedral to its minimum energy conformation if you select automatic rotation, and clear the dihedral angle box of its value (if any). Then, clicking {MOVE} lets StruMM3D seek the nearest local minimum for that dihedral.

Remember that the routine also has the ability of the routine to map dihedral energies and place the dihedral into the minimum energy position. This was discussed in section 3.8.4.

The Dihedral Energy Profile routine will drive the selected dihedral through 360 degrees, at selected angle increments, while measuring the strain energy of each conformation. The data can be stored for future use, or with some external graphing agent. StruMM3D will automatically provide a chart of the measured energy profile in an Energy vs Dihedral Angle plot. If there is a discontinuity in the plot, then the line colour is purple, otherwise it is black.

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6.1.0 Change Bond Angles, Create Cyclopropanes and Cyclobutanes

One of the major, and most frequently met errors, in x-ray diffraction data, is the presence of weird bond angles, especially at heteroatomic sites. We have seen x-ray structures with bond angles of 130 degrees at sp3 oxygen atoms! How does one change/correct these errors?

A simple, but highly precise and controlled, bond angle changing process, for example changing the bond angle at atom 2 in the diagram below, is to use the ROTATE a BOND routine and:

a) identify atom 1 as the reference atom (for distances and dihedral angles),
b) identify atom 2 as the fixed atom of the rotation axis,
c) identify the atom 2 as the other end of the axis,
d) identify the atom 3 as the movable atom, and any other atoms attached to it, but you have to manually select these atoms.

The EXAMINE ANGLES windows will prompt you to alter the bond angle in a stepwise controlled fashion.

This routine helps you to understand how small changes in a given bond angle will affect the overall structure energy.

This very powerful routine can also be used to precisely construct cyclopropanes and cyclobutanes.

For example, if you rotate the central C-C bond of a butane molecule to generate an eclipsed conformation, with the geometry you need in the finished product, then -

replace, use the CHANGE ATOM routine, one of the eclipsed hydrogens with a carbon
delete the other eclipsed hydrogen
change the new bond angle to 60 degrees

StruMM3D should then complete the cyclopropanoid structure.

Similarly, if you -
replace both eclipsed hydrogens with carbons
change the new bond angles to 90 degrees

StruMM3D should then complete the cyclobutanoid structure.

It Is Also Interesting That….

The MINIMIZE ATOM ENERGY - MANUAL routine will also enable you to interactively adjust any set
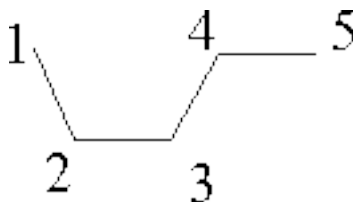
of bond angles and bond lengths, for a chosen atom, with great precision, and to move this atom to the desired position while guided by the data shown onscreen. This is a very powerful routine since you can see the potential energetic consequences of your actions.

Another use of the ROTATE a BOND routine, described below, does not offer the precision or overall control of that one has when using MINIMIZE ATOM ENERGY.

You must identify the 3 atoms that form the angle and one nearby, suitable, atom to participate in a rotation axis. In the example below, the 3 atoms enclosing the angle, and the other nearby atom, are numbered 1 to 4, consecutively. Thus, to change the 1- 2 - 3 bond angle in the system below (and simultaneously the 3 -4 - 5 bond angle) then:

a) identify atom 1 as the reference atom (for distances and dihedral angles),
b) identify atom 2 as the fixed atom of the rotation axis,
c) identify the atom 4 as the other end of the axis,
d) identify the atom 3 as the movable atom, and any other atoms attached to it, but you have to manually select these atoms.

You can also opt to move the atom 5, if you desire to preserve a relationship between this atom and

atom 3.

Thus you will move atom 3, and any other that you selected, about the 2 - 4 axis, relative to atom 1, 2 and 4, and so change both the 1 - 2 - 3 angle, and possibly the 3 - 4 - 5 angle. In this example only the 2 - 3 - 4 angle will remain constant if atom 5 is not moved, but the 3 - 4 - 5 angle can also be kept constant if atom 5 is moved. Notice that no bond lengths are altered.

This process reflects the reality of moving an atom in any rigid molecular framework. When 1 internal atom in any molecule is moved by itself, without changing any bond lengths, at least 2 bond angles that are associated with the moved atom will be changed simultaneously. If only the length of a non-terminal bond is altered, at least 1 bond angle that is associated with the atom moved will also be altered.

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6.2.0 Drawing A Bicyclo[3.2.1]octane - An Exercise in Creativity
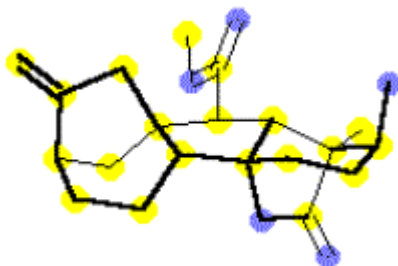
By linking simple units, any complex molecule can be rapidly constructed with a large degree of geometrical precision. This process of linking sub-units to create larger, more complex structures, is in fact, the most powerful method for constructing new molecules. One can also modify an existing structure, or template, in order to achieve the construction of more elaborate molecules. For example, to draw a bicyclo[3.2.1]octane, one could follow either of the two routines outlined below.

1. Draw a cyclohexane and change two cis 1,3-diaxial hydrogens to carbons. Then, -
EITHER Immediately invoke the CHANGE BOND LENGTH routine and instruct StruMM3D to link these two new carbons with a single bond. Upon exiting from this routine, immediately, as instructed, invoke the structure energy minimization process, which will do a preliminary "clean up" of the structure, and then will add hydrogens, and then will complete the process of fixing up the structure.

OR use the ADD ATOMS/H/LP to place hydrogen onto the new methyl groups, then selectively erase the two hydrogens that are closest to the axis of the bond to be established. You can reorient the structure, using the MOVEMENT / TRANSLATE-ROTATE routine, in order to best see these hydrogens. Each of these "methyl" groups will now only have 2 hydrogens and these carbons will be properly valenced when the new bond has been established. Now invoke the CHANGE BOND LENGTH routine and instruct StruMM3D to link these two new carbons with a single bond. Upon exiting from this routine, immediately, as instructed, invoke the structure energy minimization process, which will do a preliminary "clean up" of the structure, and then will complete the process of fixing up the structure.

OR

2. Simply position a two carbon unit (ethane) symmetrically over a cyclohexane that is in the desired boat or chair conformations, and within bonding distances of the appropriate ring carbons. You can use

any two 1,3-diaxial hydrogens as guides to enable you to position the two carbon unit properly. Then invoke the LINK STRUCTURES routine. Hydrogens can then be removed and replaced by using the ADD ATOMS/H/LP routine. Linking will be described more extensively below.

OR

3. Another much more involved method for constructing a bicyclo[3.2.1]octane would involve the folding of a cis-1,3-dimethylcyclohexane, having the methyl groups axial, along the 2 - 4 axis, in order to bring the two methyl groups together within the distance required for a new C - C bond. This process is tedious, and would not be generally applicable, but not without value, since it allows us to appreciate some of the dynamics involved in the intramolecular bonding of atoms.

Thus, one would import a cyclohexane molecule, ensure that it has all of the hydrogens attached, and use the CHANGE ATOM routine to convert two axial (1, 3) hydrogens into carbons. It would now be useful to remove all of the hydrogens to leave the bare skeleton and reduce the visual congestion, by using the ERASE ATOM routine. These hydrogens can be replaced at the end of the exercise by using the ADD HYDROGENS and LONE PAIRS routine.

Now :

- Draw a cis-diaxial 1,3-dimethylcyclohexane, with the methyl carbons attached at atoms 1 and 3, omit or delete all of the hydrogen atoms in order to have a simple structure
  Fold the molecule along the axis of the 2 and 4 carbons, moving carbon 3 and its methyl group, use C-7 (the methyl on C-1) as the reference atom, C-2 and C-4 the axis atoms, and C-3 (with its methyl carbon) the movable atom
  Similarly, and alternatingly, fold the molecule about the 2 - 6 axis, moving C-1 and its methyl carbon, using C-8 (the methyl on C-1) as the reference atom
  Perform each rotation manually, in +/- 5 degree units, until StruMM3D establishes the new bridging bond, and continue to fold the molecule until the desired length of the bridging bond is achieved.

When this routine is used to construct a bicyclo[3.2.1]octane, the resulting structure is similar in its bond angles to the bicyclo[3.2.1]octane moieties found in the X-ray crystallographic structures of the gibbane diterpenoids. This leaves one to wonder if the actual chemical process is also simply mechanical rather than involving the elaborate re-hybridization of atoms etc., as quantum chemistry suggests.

This procedure also shows the multiple consequences of folding a molecule, and the effect of changing the bond angle at an atom on the disposition of the other atoms attached to that atom. Each intervening conformation can be saved in a series of temporary files and then valence elaborated (placing hydrogens on the carbons) in order to fully grasp these bond angle distortion consequences.

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7.0.0 Building Tetrahedral π–Groups - Sulfones, Sulfoxides, Phosphates Etc.

Normally, StruMM3D expects tetrahedral centers to be saturated (non-p) and will not manipulate these further. However, tetrahedral -groups, like phosphates, sulfoxides, sulfones etc., can be constructed by creating the tetrahedral units with their desired elemental compositions and then using the routine CHANGE BOND to adjust the desired bonds, lengths and characters, from single bonds to double bonds.

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7.1.0 Converting Tetrahedral Atoms to π–Centers.

It is now widely recognized that π–carbons are not constrained to support bond angles of 120 degrees. For example, the O-C-C bond angles of acetate and benzoate esters, which are opposite to the carbonyl oxygens, are usually about 109 degrees rather than 120 degrees. It is generally observed that angles in π–groups composed of more than one type of atom are not readily predicted.

The availability of the minimization module encourages us to re-designate a disubstituted center from tetrahedral to trigonal (-) in order to elaborate it as a π–atom, rather than reconstructing the entire unit, particularly since the tetrahedral angle might be similar to the trigonal angle. The CHECK ATOM STATUS routine allows you to do this re-designation. StruMM3D uses the following π–atom and symbolic designations:

Atom π–atom status Symbol

tetrahedral 1 atom type used, e.g. C or Br or H
trigonal (p) 2 # if aromatic or delocalized, else atom type
digonal (p) 3 # if aromatic or delocalized, else atom type

Selecting the CHECK ATOM STATUS routine at the main menu allows you to review and adjust the π–symbolic status of any atom. Simply follow the prompts.

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# 8.0.0 Linking Pre-assembled Templates To Construct a New Molecule

8.1.0 Positioning and Orienting Two Molecules For Linking

StruMM3D will link, using the routine CONSTRUCTION - LINK TEMPLATE STRUCTURES, two molecules that are onscreen by orienting the two molecules so that the centers to become the new bond will be within bonding distance of each other or are overlapped.

This routine can be used most easily and successfully if the atoms that will eventually be linked by a new bond have all of their valencies fully elaborated. In this way, the programme can replace one of the atoms bonded to the proposed bonding center with the template structure, and vice versa. The bond will then be formed precisely, with a known bond angle, and stereo-chemistry.

When the routine is called, and there must be two molecules onscreen, it prompts you to identify, for each molecule, the bond that will be utilized in the linking. For each bond, one atom will be discarded and the other will be bonded.

For example, if you wish to link two cyclohexanes to make an axial-equatorial linked cyclohexylcyclohexane, then one could construct the entire molecule, or link two preformed cyclohexanes together. The fact that a new single bond will be formed will introduce the consideration to the conformational arrangement of one ring to the other. These problems are easily solved by linking two preformed cyclohexanes as is described below.
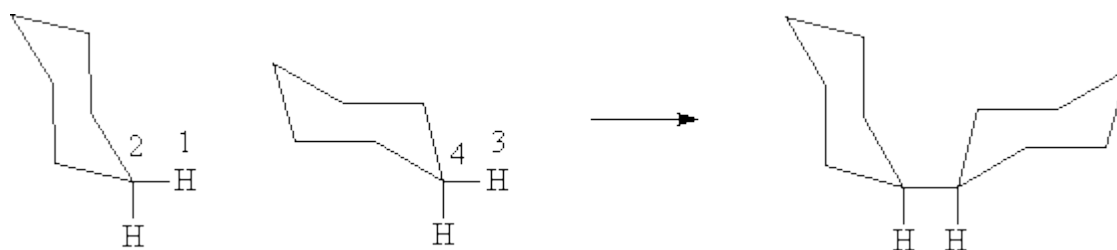
1. Click on CONSTRUCTION/LINK TEMPLATE STRUCTURES

2. When prompted, identify atom 1 as a disposable atom for molecule A, since it will be lost/deleted soon, and atom 2 as the bonding atom.

3. Identify atom 3 as the disposable atom for molecule B, and atom 4 as the bonding atom.

4. The routine now asks what bond type to use, single double or triple (1, 2, or 3) to link the two bonding atoms, and then reorients, and re-positions the structures in preparation for linking.

5. You will now be given the opportunity to rotate/move either, or both, units to suitable dihedral, viewing, or other orientations. If you are planning to generate a double bond, then this is important since you must inspect the new dihedrals to ensure planarity (or nearly so), as this drastically influences the new structure's energy. If you are planning to generate a single or triple bond, you can omit this step.

6. If you opt to rotate one of the units, to ensure that you are rotating about the "soon to be formed" bond, when the MOVEMENTS window is opened, click on PIVOT and click on either atom 2, or atom 4. Then ensure that the movement mode is ROTATE. Now you can do whatever you wish without modifying the new bond length accidentally.

7. Once you either ignore the rotate/move option, or accept it and then close/exit from the

MOVEMENTS window, the linking is performed.

StruMM3D automatically erases all of the overlapped atoms and you are left with a precisely constructed molecule in which no bond angles have been guessed or estimated.

It is useful to use hydrogens on the atoms to be linked, as the disposable atoms, but any atom can be so designated. Using fully elaborated atoms helps in the visual estimation of dihedral angles. After linking these hydrogens, or other disposable atoms, will automatically be discarded.

Remember that overlapping atoms are not normally allowed (except when viewing X-Ray crystallographic structures) and StruMM3D will automatically delete the atom of lower priority.

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8.2.0 Linking Two Molecules

The CHANGE BOND LENGTH and MAKE ONE LOGICAL STRUCTURE Routines

StruMM3D possesses a routine to change bond lengths, that is called by the routine CHANGE BOND LENGTH. This routine is extensively prompted and allows you to change the length of a bond, while repositioning the "movable" atom and its attached atoms.

The command CHANGE BOND LENGTH has two extra features.

If you wish to link two structures, or two atoms, by simply moving one close to the other along the straight line that joins the two atoms to be bonded to each other, then you can tell StruMM3D to change the length of the "bond" between those two atoms, from bond order 0, to whatever you bond you wish. By selecting an appropriate inter-nuclear distance (suitable for a single, double, or triple bond). You must ensure that the resulting bond angle and molecular conformation will be suitable before using CHANGE BOND LENGTH in this fashion.

Thus, you can position the two structures by using the ORIENT STRUCTURE routine, from the MOVEMENT menu, to orient the two molecules properly, as described in section 8.1.0 above, and also using the MOVE/QUERY MOLECULE routine to set any dihedral angles you might wish to. Thereafter, use the MAKE ONE LOGICAL STRUCTURE command to join the two molecules.

If you wish to link two atoms within the same molecule, and their current inter-atomic distance is greater than that of their normal single bond length, then you can tell StruMM3D to change the length of the "bond" between those two atoms, from bond order 0 to whatever you wish (single double triple). Now, when StruMM3D asks for a desired bond length you must enter 0 (zero) and StruMM3D will tell you to go immediately to the structure energy minimization routine to complete the process. The new bond will be established under the guidance of the structure energy minimization routine.

We always fully elaborate the atoms that will be linked, by adding their hydrogens and lone pairs, and then these other atoms provide us with suitable "handles" to guide us in orienting the structures into their best locations and dihedral situations. In the business of forming a new bond intramolecularly, simply delete the two hydrogens (or lone pairs, or other combination) that are closest to the axis of the "new" bond, and so ensure that you will have little difficulty with the structure energy minimization that you will need to perform.

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9.0.0 Docking Two Molecules and Creating Molecular Clusters

Solvation effects and structural dimerization effects are very important features in organic chemistry. Indeed, the energy of solvation can dramatically lower the enthalpy of a molecule in solution, as too can the simple dimerization of a molecule. The dimers of amides and carboxylic acids are cases in point. The differential solvation of the 1,2-dihalocyclohexanes is a topic that has been studied by Box et al., and published in the Journal of Molecular Structure, 2003.

So, every now and then you might wish to look at the energetics, and structural/geometric characteristics, of "dimers". The "dimer" might be composed of two identical molecules or two different molecules, like a solute and a common solvent. The study of these dimers will obviously require us to "dock" two entities, initially, and to examine the stability and structure of the entity. Later, one might add more solvent molecules, or other molecules, to the entity to enlarge it into a formal molecular "cluster" of several molecules. We'll use the term "cluster" to refer to a docked group of two or more molecules.

All molecular clusters are "held" together by favourable dipolar interactions, especially strong hydrogen bonding, and so the first task will be to identify the atomic sites that possess the desired dipolar features. Since StruMM3D uses lone pairs in its calculations and molecular graphics, these entities can also be used directly as docking features. Ideally, when suitable atoms/lone pairs are brought close together, the resulting attractive interactions will stabilize the resulting cluster. These atoms/lone pair sites of dipolar features will be the "docking sites" that will be used in the exercised described below.

In essence, a hydrogen bond will be the result of a through space, dipolar interaction, of a lone pair with a hydrogen of a polarized H-X bond. This must be so simulated. You CANNOT overlap any lone pair, or any atom, in one molecule with any other atom/lone pair, intra-molecularly, or inter-molecularly, since the programme will see this as an error and will delete the overlapping atoms.

The zone between the interacting atoms/lone pairs, will be referred to as the van der Waals buffer (vdWb) zone. While StruMM3D uses 0.75 Angstroms as the default thickness of this buffer zone, based on the x-ray crystallographic studies of strongly hydrogen bonded clusters, like DNA double helices, you can adjust the size/thickness of the vdWb zone between the docked atoms by using the "Adjust van der Waals buffer zone - "vdwb F" or "vdwbuffer F" (F ranges between 0.324 and 1.500)" command-line feature in the I/O BOX. You can change the value of the vdWb zone within the range from 0.324 to 1.5 Angstroms. Make changes with care! 0.324 Angstroms is a very small van der Waals buffer zone, and this value/possibility is retained only for exploratory uses. Values between 0.65 and 1.5 Angstroms should be selected after first examining the x-ray structures of analogous docked systems.

The QVBMM force field, and StruMM3D, uses an extremely punitive energy potential to discourage violations of the van der Waals buffer zone, and while there are no reliable experimental calibrations of these van der Waals buffer zone violations, StruMM3D treats any violation as problematic. This also helps to prevent the inadvertent overlapping of atoms/lone pairs in the docking process and in the structure energy minimization of docked molecules.

At their very simplest, a docking site could be the hydrogen at the end of a highly polarized bond. and the complimentary docking site would be a lone pair. We must remember, for example, that in the ammonium ion, $[NH4]+$, the nitrogen does not carry all of the positive charge. The charge is distributed primarily over the hydrogens and so each hydrogens each carries a significant partial positive charge, making these hydrogens good docking sites. Similarly, an alcohol, or alkoxide, will use a lone pair on the oxygen as its primary docking site for interaction with a partially positively charged, complimentary, docking site in another molecule.

If you think about a simple molecule like water, there is one way to dock two water molecules so that the cluster has one hydrogen bond. There are two ways to dock these molecules so that the cluster has two hydrogen bonds. There is one way to dock two water molecules so that the cluster has three hydrogen bonds. The one hydrogen bond arrangement per pair can lead to a three dimensional cluster of many water molecules, but the two and three hydrogen bond arrangements will lead only to linear cluster of many water molecules. Most simple molecules will have several potentially useful docking sites, and so you are either going to have to decide which of these sites will be most favourable, or you might chose to explore each and every docking site in order to find the best group of docking sites.

StruMM3D has been set up to enable you to select two docking sites in each molecule. Thus, in order to dock two molecules you will select two docking sites in each molecule that have complimentary dipolar features, and are similar distances apart, in each molecule, as is represented figuratively in the diagram below, if red and green are complimentary charges. The docking sites 1 and 2 that you select in one molecule will be docked with the docking site 3 and 4 in the other molecule, respectively. Site 1 will be docked with site 3, and site 2 with site 4.

Let us assume that the more complex structure (on the left) is molecule A, and you have selected the green circle as docking site 1 (atom 1), and the red circle as docking site 2 (atom 2). You would then select the red rectangle in molecule B as the docking site 3 (atom 3), and the green rectangle in molecule B as the docking site 4 (atom 4), so ensuring that the red site 1 docks with the green site 3 and the green site 2 will dock with the red site 4. Normally, these colour matched sites would also correspond to suitably matched dipolar sites.
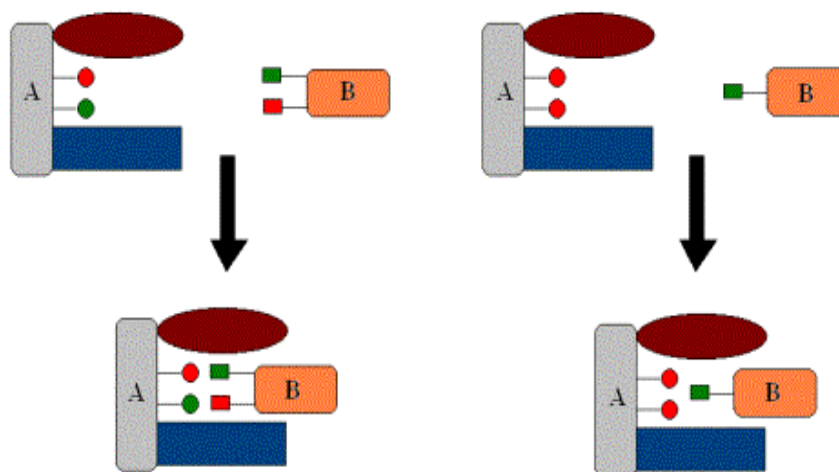
You MUST select TWO docking sites in Molecules A and B, and the same docking sites can be selected twice, giving the situation shown above. StruMM3D will always ask you to identify two sites in each molecule, but just select the same site twice. The docking process is highly visualized and automated, and will proceed, as described, uneventfully, to provide a cluster pair as shown figuratively above, in the diagram. Notice that when one docking site is selected in Molecule B, that this site will be positioned symmetrically with respect to the two docking sites selected in Molecule A.

After you identify the docking sites, and manually orient them to "face" each other, StruMM3D will –

1. properly orient, then bring the molecules together,
2. offer you the ability to adjust the arrangement (by using the MOVE/QUERY MOLECULE routine),
3. then link the pair of molecules into one logical structure.
Thereafter you have the option of minimizing the structure energy of the cluster.

The routine is quite versatile and powerful. For example, you can dock the hydrogen of chloroform with

one suitable lone pair in another molecule, or with two closely sited lone pairs (each on one atom) in a molecule like 1,2-dichlorobenzene. Once again, this routine, in combination with the others available, will enable you to do many explorations, and StruMM3D's limitations will be determined by your imagination.

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10.0.0 The Automatic Detection of Delocalized π− and Aromatic Ring Systems

Very often you will view the structure of an aromatic entity, which was determined by x-ray crystallography, and you will notice that one or two of the ring bonds are single bonds, rather than properly being double bonds, i. e. delocalized. Invariably this will be due to faulty coordinate data for one or more atoms in that aromatic system. In fact, the image above is from the x-ray crystallographic data and you can see that the bond length data for this molecule is extensively incorrect. Note that the axial halogen atom is attached to an atom in a bond that is exactly the length of an isolated double bond!

Occasionally one encounters coordinate data in which there are atom coordinate errors and that bonds that ought to be delocalized are too long to be recognized by StruMM3D as such. For example, the structure onscreen might show a "benzene ring" with one (or more) ring bond as a single bond, instead of all six, because an atom coordinate error would make that bond longer than 1.42 Angstroms. The environmental toggle, {d} to {D}, found in UTILITIES - PROGRAM PARAMETERS, will allow StruMM3D to review the data for the π−atoms and, if a "single" bond in the aromatic system is very close to the range of bond lengths for delocalized bonds, StruMM3D will then show this bond as a double, delocalized, bond.

You should also remember StruMM3D's QUERY / DELOCALIZATION routine enables you to search the molecular model and highlight any aromatic systems it finds. Often, some aromatic systems are not found because of bond length errors, as above, but after the toggle {d} to {D} has been activated, the QUERY / DELOCALIZATION routine will normally find all of the π−systems that should have had the geometries of aromatic π−systems.

The QUERY / DELOCALIZATION routine the toggle {d} to {D} are based on a new appreciation of aromaticity, and the structural features of truly delocalized, aromatic π−systems, as is explained below.

Huckel's rules are probably the best-known empirical criteria for deciding whether a given cyclic conjugated molecule can possibly be aromatic, or not. These rules stated that the entity/moiety must be cyclic and planar; must be composed of π−atoms only, and must possess $4N + 2$ π−electrons. These rules suggested that all molecules that satisfied these criteria should be aromatic, but in reality many such molecules are not aromatic because their π−electrons are not globally delocalized. Indeed, Huckel's rules and Molecular Orbital calculations on conjugated π−systems are valid ONLY IF these conjugated π−systems are truly delocalized.

After StruMM3D was developed, VESCF calculations revealed that bond orders of 1.5 and 2.5 corresponded exactly to the interface of single, double and triple bond lengths. These data, and an extensive analysis of bond length data from the X-ray crystallographic literature confirmed the notion that bond lengths are indeed quantized. Thus, while StruMM3D's automatically detects π−atoms by using bond length data from X-ray crystallography, it also determines the bond order range in which any bond lies (a necessary consequence of the bond length).

A study of bond lengths, bond orders of non-π and π–systems, and the features of typical aromatic molecules like benzene, pyridine etc., has led to the formulation of a new set of rules for the definition of an aromatic system. These new rules are based on the observation that all bonds of a given multiplicity must have lengths within a well-proscribed range.

In other words, bond lengths are quantized, as are all energy dependent entities at the atomic level.

For example, all C=C double bonds must have bond orders greater than 1.5 and less than 2.5, and lengths within the range 1.331 ± 6.02% Angstroms. Similarly single and triple bonds have well proscribed ranges of lengths and bond orders. These new rules can be formulated in terms of bond lengths or bond orders.

Any bond that has a length within the range (about ± 7%) embracing the length of a similar isolated bond in an unperturbed molecule will be identical in type and character to that isolated bond. Single bonds must have bond orders < 1.5. Double bonds or delocalized π–bonds must have bond orders > 1.5 and < 2.5. Triple bond must have bond orders > 2.5.

All aromatic molecules/moieties must therefore be contiguously cyclic, and each ring bond must have a bond order greater than 1.5, or have a bond length within the range of lengths of a true π–bond of that type/constitution. For example, each ring bond in benzene has an order of 1.6667 and a length of 1.39 Angstroms (within the double bond range of 1.331 ± 7.02% Angstroms), but the ring bonds of furan do not satisfy these criteria and so furan is not aromatic. In essence, if lone pairs are considered to be substituents, each atom in an organic aromatic system must support bonds whose total bond order will be greater than 4 (4.3334 for benzene and pyridine), and hence each of these atoms can formally be considered to be pentacoordinated (NOT pentavalent).

Since this new set of rules is based on bond lengths and bond orders, that are determined by the presence/absence of true delocalization, one does not have to assume the number electrons that are delocalized, often a source of uncertainty and an important criterion for Huckel's rules and Molecular orbital calculations. The new rules lead directly to the definition of a delocalized π–system, since each bond in a delocalized π–system must have a bond order and bond length consistent with that of the appropriate type of π–bond and this rigorous, physically measurable definition of delocalization is unambiguously experimentally verifiable.

For a review of the data and concepts that lead to the new definition of aromaticity, read:

The Relationship Between Bond Type, Bond Order and Bond Lengths. A Re-evaluation of The Aromaticity of Some Heterocyclic Molecules, Heterocycles, 1991, 32, 2023-2041.

The significance of the bond lengths and bond orders of conjugated unsaturated organic molecules. The role of hetero-aromaticity in the tertiary structures of DNA; Heterocycles, 1992, 34, 1631-59.

The Molecular Mechanics of Quantized Valence Bonds, J. Mol. Model., 1997, 3, 124.

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11.0.0 A Note on Molecule Size/Volume and van der Waals Radii

It must be obvious that the size of an atom, or simple ion, cannot be changed by the application of heat or any other form of rotational/vibrational energy. However, the size of a covalently bonded molecule will vary depending on its vibrational energy state.

Indeed, there are two important considerations that must be accepted when thinking about the size of a molecule -

- the size at absolute zero, of the zero point energy (ZPE) structure, when there is no conformational movement or change

- the size at normal temperatures, when there is conformational movement or change and the molecule is in some elevated rotational/vibrational state.

The Zero Point Energy Molecular Volume/Size

If we think clearly about the size/volume of a molecule at its zero point energy, and initially, for simplicity, imagine the mechanical/Newtonian structure, rather than the quantum mechanical structure, then we must conclude that the edges of the molecule must be fuzzy.

Even at absolute zero, because electronic motion cannot cease, and this electronic motion must induce a vibrational motion into its bond, bond vibration cannot ever cease. Since the electrons are the "glue" that hold covalently bonded atoms together, and electrons always move, it also follows that every covalent bond must also be vibrating at absolute zero.

We tend to think about bond length as the average distance between any two covalently bonded atoms., the ZPE distance. We don't think about the minimum and maximum lengths due to the bond vibration. However, if you tried to put the hydrogen molecule ion (H_2^+) into a "box" then the box must have dimensions that will accommodate the molecule in its most "expanded" geometry, when the bond lengths would be maximal, or it would not fit.

The Room Temperature Volume/Size

If we raised the temperature of our hydrogen molecule ion (H_2^+), then it would begin to acquire various rotational energy modes and also begin to "wag". Then the box must become even larger and must have dimensions that will accommodate the molecule in its most "expanded" geometry, when the bond lengths would be maximal (in that thermal energy state), and the "increased thickness" due to the wagging motions would be significant.

The Room Temperature Volume/Size of Organic Molecules

From the discussion above, it follows that even methane will require a larger "box" than could be computed based on its geometry and ZPE bond lengths. The introduction of more random motions and geometries into molecules that are conformationally mobile will obviously require corresponding enlargements of the "box".

The higher the temperature of the complex, covalently linked molecule, the bigger the "box" must be.

These are the considerations that make the entire discussion of the size, or volume, of a molecule, a complex one, and also bear directly on the concept of the "van der Waals" radii of atoms and the "van der Waals" sizes of molecules. We know that the van der Waals radii of covalently bonded atoms are

usually held to be larger than their normal atomic, or covalent, radii. The van der Waals radius is estimated for experiments that measure "real", thermally perturbed, size/volume.

StruMM3D uses these concepts when estimating molecular sizes/volumes, and uses the concept that the van der Waals atomic radius is an artifact of the thermally perturbed "real" size/volume of a molecule in which the atoms have their normal covalent radii.

The business of moving our discussion from a Newtonian basis to one based on quantum mechanics (QM) will be fraught with grief because electrons are not particulate entities in QM, their motion cannot be discussed, and neither so can the natures and motions of atomic nuclei. However, the simple logic of the Newtonian concepts discussed above cannot be ignored, and we have the nice situation here in which the experimental proof of our discussion is outside of our capabilities, as is gleefully expressed by the Uncertainty Principle. Worse still, QM allows bonds to be as long as they wish, even to infinity, so how do we measure molecular volume?

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11.1.0 A Note on Heteroatomic Lone Pairs

In VB theory, the traditional view of the nature of the lone pairs on an oxygen atom places them in sp3-like atomic orbitals. This works well for all alcohols and simple ethers. More recently, the Quantum mechanical theoreticians have suggested that these lone pairs of electrons should be distributed between a sp2-like orbital (the σ–pair) and a p-orbital (the π–pair), largely because this facilitated their calculations and approximations. Indeed, in controversial areas of stereo-electronic theory, like the anomeric effect in sugars and acetals, the QM theoreticians have even gone as far as suggesting that both models/concepts are essentially equivalent, and so it does not matter which is used.

VB, and VSEPR, theory would seek to impose great geometric restraints on the shapes of oxygen atoms that bore either the σ–, π–electron pairs, or the two sp3 electron pairs. The two sp3 electron pair model would be required to have a basic tetrahedral structure, while the σ–, π–electron pair model would be required to have a trigonal structure.

On the other hand, the fluidity with which QM theory allows the mixing of all and any orbitals would allow any geometry at any atom, while simply varying s- and p-orbital characteristics (percentages) as is needed. Interestingly, all with scant regard for the principles of energy quantization.

However, from a strictly experimental point of view, one could question the notion that oxygen could adopt either the σ–, π–electron pairs, or the two sp3 electron pairs, model. What experimental evidence do we have?

After reviewing the X-ray crystallographically determined structures of many thousands of organic molecules that contain oxygen atoms, we have concluded that the experimental evidence does support the existence of both structural motifs for oxygen.

The cyclodextrins illustrate the simplest case, and one that is highly convincing because both motifs exist in the same molecule. All of the bonds in a cyclodextrin must be simple single bonds and there is no π–bonding in these molecules. The X-ray data for these molecules clearly show that the alcoholic oxygens, and the ether oxygen atoms that are within the monosaccharide rings have bond angles of about 110 to 113 degrees, are clearly distorted tetrahedral, and must have two sp3 electron pairs On the other hand, the glycosidic oxygens (that bridge the monosaccharides) all have bond angles close to, greater than, 117 degrees, and as much as 120 degrees, and are clearly distorted trigonal sites that must have σ–, π–electron pairs.

On reflection, this is probably why these cyclodextrins are such excellent chelating agents.

Other simple molecules, like aryl methyl ethers, in which the ether linkage is planar with, or orthogonal to, the aromatic ring show the two possible structural motifs even while the bond length data for the ether linkages affirm that only single bonds are present (there is no π–bonding or π–electron delocalization involving the ether oxygen).

The QVBMM force field has been enhanced to embrace these structural features of oxygen, and all other heteroatoms that could present similar structural intrigues. This is the latest enhancement to the VSEPR theoretical model.

StruMM3D now automatically detects oxygen, nitrogen, and sulphur atoms that have σ–, π–electron pairs. These atoms are then shown as having trigonal geometries. The σ–electron pair is obviously within the trigonal plain. The π– electron pair is depicted as having one electron in each lobe of its presumed p-orbital, which is consistent with the normal distribution of electron density in a p-orbital that carries an electron pair.

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FINALLY
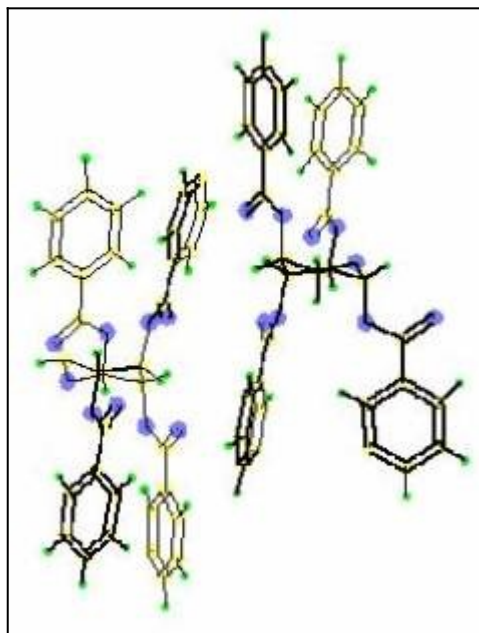
Thank you for using StruMM3D, and let's hope that your molecular modeling will be successful and satisfying.

We shall always welcome reports of bugs, and suggestions for the improvement of the programme.

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