

Additions and Corrections

Stereochemical Studies on Protonated Bridgehead Amines. ¹H NMR Determination of Cis and Trans B-C Ring-Fused Structures for Salts of Hexahydropyrrolo[2,1-a]isoquinolines and Related C Ring Homologues. Capture of Unstable Ring-Fused Structures in the Solid State [*J. Am. Chem. Soc.* 1989, 111, 2487-2496]. BRUCE E. MARYANOFF,* DAVID F. MCCOMSEY, RUTH R. INNERS, MARTIN S. MUTTER, GARY P. WOODEN, STEPHEN L. MAYO, and R. A. OLOFSON

Page 2491: For improved clarity, the last sentence in column 1 should be modified to read as follows (new words italicized): One might suppose that **3b**-HBr adopts the cis B conformation to avoid an adverse 1,3 syn-axial interaction between the 6-phenyl and NH groups *in the trans form*, although a potentially unfavorable syn-axial interaction between the C3 methylene and H5 is offered in trade (*also to avoid a severe 1,3 syn-axial interaction between the 6-phenyl and C3 methylene in the cis A form*).

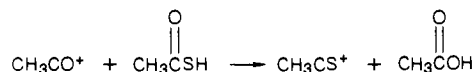
Page 2492, column 1: The value 10.02 in the equation is not correct; it should read 10.32.

Page 2494, column 1: Note—The precise nature of the minor cis species of **20**-HCl is not established. Since a cis A form with a chair piperidinol would have a very bad 1,3 syn-axial interaction, a twist piperidinol may be prevalent.

Fragmentation and Structure of C₂H₃S⁺ Ions [*J. Am. Chem. Soc.* 1989, 111, 859-865]. R. G. COOKS,* MD. A. MABUD, S. R. HORNING, X.-Y. JIANG, CRISTINA PARADISI, and PIETRO TRALDI

Page 860, Figure 1: The first energy barrier starting from the left should be labeled as a → e.

Page 860, eq 1: The carbonyl oxygens are missing in the two neutrals:



Page 861, left side, next to last line: The carbonyl oxygen is missing in CH₃C(=O)SCH₃.

Page 864, footnote 48: C₂H₃S⁺⁺ needs be replaced by C₂H₂S⁺⁺.

Page 864, footnote 53: In the second line "activation" needs be replaced by "isomerization".

Insertions of Electrophiles into Metal-Carbon Bonds: Formation of New Carbon-Nitrogen Linkages Mediated by the (η⁵-Cyclopentadienyl)dinitrosylchromium Group [*J. Am. Chem. Soc.* 1989, 111, 2097-2104]. PETER LEGZDINS,* GEORGE B. RICHTER-ADDO, BEREND WASSINK, FREDERICK W. B. EINSTEIN, RICHARD H. JONES, and ANTHONY C. WILLIS

On p 2103 of this article, we state that the reduction potential of NO⁺ in CH₂Cl₂ has been estimated as being in the range -0.22 to -0.11 V. So that there is no confusion on this point, we would now simply like to add that this estimate is undoubtedly too low, a point clearly made by the original estimators in their paper (ref 34).

A New Method for the Estimation of Partition Coefficient [*J. Am. Chem. Soc.* 1989, 111, 3783-3786]. NICHOLAS BODOR,* ZOLTAN GABANYI, and CHU-KUOK WONG

Page 3786: In eq 10, the second term should be + 6.106 × 10⁻²S instead of - 6.106 × 10⁻²S.

A Kinetic Study of Sulfide Oxidation by Sodium Hypochlorite Using Phase-Transfer Catalysis [*J. Am. Chem. Soc.* 1989, 111, 3958-3961]. JAMES H. RAMSDEN, RUSSELL S. DRAGO,* and RICHARD RILEY

Page 3958: The error limits were left off the rates in Table I. The values are 89 ± 11; 22 ± 4; 29 ± 5.

Page 3959: In Table II columns of data were transposed; the correct table is given in its entirety here.

Table II. Initial Rates of *n*-Butyl Sulfoxide Formation with PTC

expt	amounts of reactants, ^a mmol				initial rate × 10 ⁵ , M s ⁻¹
	Bu ₂ S ^b	OCl ^{-c}	PTC	TPPMnCl	
4	1.45	2.9	0	0	0.40 ^d ± 0.06
5	1.45	2.9	0.62	0	1.7 ± 0.3
6	1.45	2.9	0.62	0.0060	11 ± 2

Computer Software Reviews

Ball & Stick. Version 2.2r4. Copyright 1988,89 by Norbert Müller and Alexander Falk: Altenbergerstrasse 69 A-4040 Linz, Austria. List price US\$299.00.

Ball & Stick is a molecular graphics utility for the Apple Macintosh 512KE, Plus, SE, II, and IIx computers. The program reads and interprets files containing information on atomic coordinates and bonding, creating various three-dimensional representations of the molecular structure from this information.

The program requires a minimum of 512K RAM + 128K ROM and an external double-sided 800K disk drive or a hard drive and supports the MC68020 and MC68881 processors or later versions. The program is shipped on a single 3.5-in double-sided double-density disk and is not copy protected, allowing for personal backup copies only. Color graphics for color monitors and printers are also supported. This version can handle up to 8000 atoms, depending on system configuration, while a higher version specifically for the Mac II series (Ball & Stick II 2.2 list price \$359.00) can process up to 32 000 atoms. Currently, the program is distributed directly by the authors.

Ball & Stick allows for input from a standard TEXT file. Although the program does not include an editor to create and modify these files, any text-processing program can be used to accomplish this. The program supports three input formats: Moldat format, Internal Coordinates, and Crystallography. A description of each is contained in the manual. The Moldat format is also used by some other Macintosh chemistry programs such as MacModel and MacMolMec. It is important to note that although the program supports an atomic labels and coordinates only format called "Crystallography", this version does not accept crystallographic unit cell dimensions, fractional coordinates, symmetry operations, or thermal ellipsoid parameters. Cartesian coordinates in angstroms are used in all three input formats.

A variety of molecular representations is available through this program, including wireframe, stickball, simple space filling, and space filling models. The program offers three types of perspective: pseudo, which produces wedged bonds only; partial, which puts only bonds in perspective; and full, which puts both atoms and bonds in perspective. The user can also set the relative viewing distance to customize the effect of the

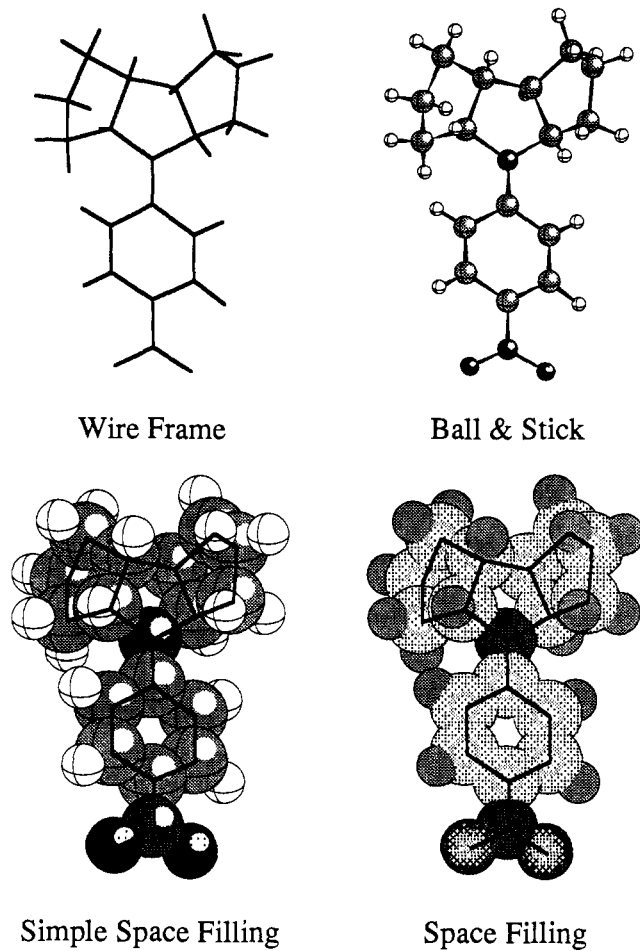


Figure 1.

perspective. An option for no perspective is also available. In addition, fully customized stereo pairs are attainable for each of the models, with a red/green stereo option for the wireframe model. The program also includes a "mirror image" function for creating an enantiomeric structure. All of the models are generated by using an object-oriented format, giving the maximum printout resolution available on the printer used. The images can be copied to the clipboard for use in other applications or saved as standard PICT files compatible with most object-oriented graphics programs. Figure 1 illustrates the four representations available, pasted into and printed from MacDraw II with a LaserWriter. The latter program also supports plotting in color and both printing and plotting outputs were impressive. The different graphic representations maintained excellent resolution and clarity regardless of the scale used for printing. Direct output from Ball & Stick to the LaserWriter is of slightly higher quality.

Of the four models offered, the wireframe is by far the fastest and least memory-consuming to generate. The stickball, simple space filling, and space filling models take progressively more time and memory to generate and print, but these demands are very reasonable for the results given. The stickball and simple space filling diagrams each offer two general types of atom representation, with radius and color specific to each element. The appearance of the atoms, the radii and colors assigned to each element, and the appearance of the bondsticks can be fully customized by the user. The simple space filling model stamps the atoms on the screen from back to front, saving time and memory through neglect of sphere-sphere boundary calculations. If such detail is required, a second, more detailed, type of space filling model is also available. An overlay skeleton is available for both space filling models, which superimposes a wireframe model (without hydrogens) over the existing space filling model. If requested, atom labels are placed inside the respective atoms, replacing the depth shading or highlighting effect that is present without the labels. It is unfortunate that this version regenerates the entire picture after each modification, taking several minutes each time for larger molecules. This effect can be practically avoided, however, by working initially with the wireframe model, which takes very little time to generate, and then switching to a more complicated model after making necessary adjustments.

Ball & Stick provides a user dialog method for non-real-time rotation

around an axis or through an Euler rotation. It also provides for atomic plane alignment and axis alignment. Plane alignment is accomplished through selecting three atoms with the mouse and choosing the appropriate option from the menu. Bond rotations can also be achieved through mouse atom selection. In addition, the INFO window offers several other possibilities for molecular modification. With the INFO window open, the user selects the atoms with the mouse that he/she wishes to study. The INFO window then displays the atom types and coordinates, bond lengths, bond angles, and dihedral angles for each group of up to four atoms selected. These parameters can then be easily altered to modify the original model, which can then be saved on disk.

Although the program offers no real-time rotation or animation routines, a Hypercard stack titled MovieMaker is included with Ball & Stick, which can use a series of PICT files generated by the Rotation Animation or Batch Processing options as frames in an animated sequence. The Rotation Animation option uses the current model and user-specified rotation instructions to generate the series of PICTURE files, while Batch Processing uses a series of input files (of the formats mentioned above) to generate the "movie". Animated sequences can thus be generated either from a user-controlled rotation operation or from a series of input data files, which could include the output files of other molecular modeling programs.

The Ball & Stick manual is very well written and easy to comprehend yet generally thorough and technical in its descriptions of the program's functions and limitations. A new user should be able to perform simple tasks immediately and access the program's full potential within minutes of reading the comprehensive manual.

Sophisticated, yet user friendly and straightforward, Ball & Stick is a graphics package useful for both scientific and academic applications. With strong attention to detail through user control and customization, this package provides a rich variety of possibilities for molecular structure representation, including publication quality printouts of the generated models.

John P. Feagins, *The University of Texas at Austin*

EQCAL. BIOSOFT: P.O. Box 580, Milltown, New Jersey 08850. List Price \$199.00.

EQCAL is described as a "program for calculating equilibrium composition of free ions in buffer solutions". It is written in Turbo Pascal for the IBM PC, XT, AT, and compatible computers. This program requires 256 K of memory and utilizes color graphics if available. A math coprocessor will speed up execution but is not necessary.

This is a single purpose program that will calculate the equilibrium concentrations in complex systems. Up to 8 components and 34 species (combinations of components) can be handled by this program. To illustrate, H^+ and PO_4^{3-} are considered components while HPO_4^{2-} , $H_2PO_4^-$, and H_3PO_4 are considered species in the phosphoric acid system. Components and species are entered into the program in tabular form with a matrix defining stoichiometric relationships. Analytical concentrations are entered for components only. Species are defined by the reaction

COMPONENTS \Rightarrow SPECIES

and equilibrium constants are entered for all species as the overall formation constants. Data entry is made as easy as it can be for complex chemical systems. When executed, the program assumes pH to be constant and calculates the equilibrium concentrations of all other components and species by using a free energy minimization method.

The prospective user must be cautioned that this is a highly specialized program. The author developed the program for complex systems such as buffered mixtures of EGTA, Ca^{2+} , and ATP. It will not calculate the pH of solutions since pH must be entered and it is assumed to be a fixed value. The user cannot enter concentrations of species but must convert them to component concentrations first. These last two restrictions greatly limit the generality of the program, but other readily available programs already perform these functions.

The program also has some quirks that the user will usually discover quickly. First is the necessity of using overall formation constants for all equilibria. For example, the familiar pK_a values of phosphoric acid of 2.15, 7.20, and 12.35 become 21.70, 19.55, and 12.35, respectively, as $\log K_f$ values. Second, the matrix used to define the system must be started in the first available column or some very interesting and unusual results are obtained. Third, the program will continually warn the user that data may be lost if files are not saved to disk, even immediately after saving a file. Last, if a row of the entry table is omitted the program will still calculate a concentration for the phantom entry.

The instruction manual is sufficient although it must be read carefully. In one instance, however, the manual alludes to the fact that ionic strength and activities are important in equilibrium calculations and that this program somehow includes these considerations. A number of calculations were performed on the phosphoric acid system with various

analytical concentrations of phosphate at constant pH. The relative concentrations for all components and species were the same, indicating that no ionic strength effect was incorporated.

As indicated earlier, this program is highly specialized and will be of use to those who are deeply involved in systems that can be defined as the author does. The prospective user should be aware that it is by no means a general equilibrium program.

Nell Jaspersen, *St. John's University*

Desktop Molecular Modeller. Oxford Electronic Publishing: Oxford University Press, Walton Street, Oxford. £300 (\$595.00); 50% academic discount. Site Licence £950, for an unlimited number of copies.

DTMM is a molecular modelling program that can be used for computer graphic display, building from simple fragments or molecules and manipulation of molecular structures. DTMM is written in Pascal by Dr. M. James C. Crabbe, Reader in Microbiology at the University of Reading, and Dr. John R. Appleyard of Polyhedron Software Ltd. The essential hardware requirements are an IBM PC, XT, AT or PS/2 microcomputer, or fully compatible PC, DOS 2.0 or above, 512K RAM and a graphics adapter, including CGA, EGA, VGA or Hercules Graphics card. Optional hardware includes a Microsoft Mouse and a maths coprocessor (8087, 80287, or 80387). The reviewer used a ENSONTECH XT (without a maths coprocessor) and a ENSONTECH 286 AT (with a 80287 maths coprocessor), both with EGA screens and both with keyboard control. 16 Memorex 286 AT's (without maths coprocessors) and 11 Sperry 286 AT's (with maths coprocessors), the former with VGA screens and the latter with EGA screens, were used to run the program for undergraduate teaching. No IBM compatibility problems were experienced with any of these microcomputers.

Once set up the DTMM program is loaded from its own directory or hard disk by typing DTMM; a logo and software agreement screen are followed by a *menu bar* with the following options:

FILE STYLE VIEW CALC EDIT UTIL

Each command may be accessed by the first letter of each command or by movement of the highlighted box with the horizontal cursor arrow keys, → and ←, followed by pressing the return key. This results in the appearance of a drop-down MENU, under the appropriate command option, with 6–10 items. Each item on the drop-down menu can be accessed by pressing the appropriate number, by using the cursor keys, or by using a mouse. As access by letter or number is simple and fast, this method was preferred by the reviewer. All menu items have a simple help facility available on the F1 function key.

The FILE menu allows access to both the molecule and the fragment data files, which are organic or biochemical in type. Alternative data files may be built from scratch by using a screen editor, such as XED, by saving a molecular constructed on the screen (the SAVE MOLECULE option on the FILE menu) or by porting a data file from a mainframe package, such as CHEM-X, or from the Cambridge Crystallographic Data Base. Molecules containing up to 1500 atoms and bonds may be viewed and up to 1800 atoms and bonds may be displayed if the system has a maths coprocessor fitted. The STYLE menu offers six alternative display modes, from stick, color stick, green/red stereographic stick, fast fill, to space fill and ball and stick. Conversion between these display options is remarkably fast, except for the space fill option, and is helped by the programs double-buffering capability. All the solid displays, including the outline and shade options, can be enhanced by a simple but effective highlight toggle (H). The color option involves shades of grey on a monochrome display screen; it is limited to four colors on CGA screens, and allows a choice of up to 16 colors on an EGA or VGA screen. In EGA, the stick and color stick displays are extremely fast and clear, while the range of colors in fast fill and ball and stick is sufficiently fast and clear that the additional expense of a VGA screen is hardly justified. For reasonably sized molecules, greater than 30 atoms, the speed of the space fill option is sufficiently slow to justify the use of a maths coprocessor, the presence of which noticeably increases the speed of all the display options. The appearance of the stick and the ball and stick displays can be enhanced by line thickening (T) and perspective (P) toggle options. All the display styles can involve an atom-labeling option (I), except for the hydrogen atoms, with a level of clarity that would do credit to some mainframe graphics packages. While all these toggle options improve the quality of the displays, they noticeably slow down the screen refresh times. All displays, excluding the space fill option, involve a rotate option, via the cursor arrow keys, a translate option, via

the l, r, u, d, b, and f keys, and a zoom and pan capability on the Home and End keys. All of these options are best carried out in a stick mode of display, to optimize a view, before a color fill display is used. The F2 key offers a convenient toggle between the stick and the ball and stick display option.

By a combination of the menu options of the VIEW, CALC, and EDIT commands, the atoms in a molecule may be changed to create different molecules, e.g., CH₄ to SiF₄ or [SO₄]²⁻. Equally, two molecules or fragments may be joined to form a larger molecule, e.g., two CH₃ fragments to form C₂H₆. A major feature in the latter is an approximate energy minimization facility, which is reasonably fast for small molecules, but can be time consuming for ring containing molecules, without a maths coprocessor. However, a major teaching attraction of the energy-minimization process is that the change in geometry between each cycle is displayed on the screen, with the appropriate energy changes displayed in a window. This facility goes a long way toward removing the "black-box" aspect of the energy-minimization process, especially for undergraduate users. DTMM has "DTMMshow" facility for producing a slide-show of a sequence of captured displays and should be invaluable in a lecture environment. Slide files produced using DTMMshow are in an extended .PCX format and the first image in a slide file may be imported into suitable programs, such as PC Paintbrush, Word Perfect 5, or Ventura Publisher, for incorporation into other documents. However, the present reviewer was unable to check this facility.

The DTMM package is accompanied by a 97-page ring-bound manual, which contains five excellent introductory tutorials on the use of DTMM. These are essential reading, especially for the energy-minimization procedure. The manual contains the details of the setup procedure and for customization of the program to the users requirements. The provision of an index to the manual would considerably enhance its usefulness.

At its face value DTMM represents one of the best and least expensive molecular modelling software programs currently available. The range and quality of the display options are excellent and good enough for photographic reproduction or for slide preparation. The availability of the energy-minimization procedure takes the program clearly beyond the capability of any ball and stick molecular modelling kit in the laboratory. For the first time, this package makes available an IBM based molecular modelling capability to non-crystallographers, which at EGA resolution in color can now compete on equal, or better, terms with any programs currently available on the Apple Mackintosh microcomputer, in this price bracket. For this reason alone it should succeed. However, it has an additional feature, namely, it is the most user friendly menu driven operating system that this reviewer has seen to date. This means that in educational circles, it has an enormous potential as an interactive molecular modelling package, that even First Year students can use, without any previous microcomputer experience. It can be used as a simple introduction to display the shapes of Inorganic and Organic molecules, effectively in three dimensions. In Inorganic Chemistry teaching it can be used as backup to sections on Valence State Electron Pair Repulsion Theory and to the teaching of Crystal Chemistry courses on ionic and covalent lattices. Such courses could be introduced by a DTMMshow slide sequence, followed by exercises in which the student is asked to reproduce a selection of the displays, directly from data file or by building from the molecule or fragment library. At a slightly more advanced level, courses on space group symmetry can be introduced, using dummy atoms to display a unit cell and equivalent position data to display the full contents of a unit cell. For recording student progress, the final displays produced can be captured by a screen dump to a inexpensive IBM Graphics Printer (DOS <3.0) or in shades of grey (DOS 4.0).

Put together DTMM represents a major breakthrough in the 3D color display of the shape of simple Inorganic and Organic molecules, at a price within the reach of both school and University teaching programs, a use that will only be limited by the imagination of the instructor and may well awaken an interest in the shape of chemical molecules at a first year university level. In terms of Computer Aided Teaching, the DTMM program is even more important, as it involves an interactive program that students can use independently, to explore the shape of molecules, to build simple molecules, to calculate their bond lengths and bond angles, and to show how their shape influences their total energies. These are options that are in the highest traditions of Computer Aided Learning.

Brian Hathaway, *University College Cork*