

temperature (ca. 20 °C) for 12 h. IR (CCl<sub>4</sub>):  $\nu$  = 3380–3320 (w), 2940 (w), 1620 (s), 1610 (s), 1520 (m), 1495 (w), 1465 (w), 1400 (w), 1335 (w), 1295 (m), 1270 (m), 1225 (w), 1195 (m), 1180 (m), 1140 (w), 1115 (m), 1050 (w), 920 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.47 (s, 3 H), 3.89 (s, 3 H), 7.01–7.07 (m, 1 H), 7.04 and 8.23 (AA'BB' system, 4 H), 7.45–7.52 (m, 2 H), 8.01 (br s, 1 H). <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>):  $\delta$  = 20.9 (q), 55.4 (q), 114.0 (d), 117.9 (d), 120.4 (s), 123.6 (s), 124.5 (d), 129.5 (d), 134.4 (s), 134.8 (d), 137.6 (s), 145.2 (s), 153.6 (s), 161.0 (s), 173.0 (s).

**3-Hydroxy-5-methoxyflavone (3n).** 218 mg (ca. 100%) was obtained as yellow needles from EtOH, mp 174–176 °C (lit.<sup>27</sup> 172 °C), when a solution of 218 mg (0.843 mmol) of epoxide **2n** in 1.0 mL of chloroform-*d* was left to stand at room temperature (ca. 20 °C) for 24 h. IR (CCl<sub>4</sub>):  $\nu$  = 3350–3290 (w), 2960 (w), 2850 (w), 1630 (s), 1595 (m), 1445 (w), 1420 (w), 1355 (m), 1335 (m), 1275 (m), 1215 (m), 1195 (w), 1175 (w), 1125 (w), 1110 (m), 1105 (w), 1080 (w), 1035 (w), 1010 (w), 945 (w), 710 (m), 695 (m), 665 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.93 (s, 3 H), 6.71 (d, *J* = 9.27 Hz, 1 H), 7.04 (d, *J* = 8.54 Hz, 1 H), 7.39–7.45 (m, 5 H), 8.16 (m, 2 H). <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>):  $\delta$  = 56.3 (q), 104.9 (d), 110.2 (d), 127.3 (d), 128.5 (d), 128.8 (s), 129.8 (s), 130.8 (s), 133.9 (d), 138.5 (s), 142.3 (s), 157.1 (s), 159.4 (s), 172.7 (s).

**3-Hydroxy-2-methoxyflavanones 4b,f from Methanolysis of Epoxides 2.** **3-Hydroxy-2-methoxy-4'-methylflavanone (4b).** A solution of epoxide **2b** (227 mg, 0.900 mmol) in methanol (30 mL) was stirred at 0 °C for 12 h under a N<sub>2</sub> atmosphere. The solvent was evaporated (ca. 20 °C (15 Torr)), and flavanone **4b** (255 mg, ca. 100%) was isolated as a colorless powder, mp 136–156 °C, (from CHCl<sub>3</sub>/petroleum ether). IR (CCl<sub>4</sub>):  $\nu$  = 3640–3600 (w), 3520–3480 (w), 3060 (w), 3020 (w), 2980 (w), 2960 (w), 2850 (w), 1720 (s), 1620 (s), 1595 (m), 1525 (m), 1475 (s), 1315 (m), 1240 (m), 1190 (m), 1145 (m), 1100 (m), 1030 (m), 980 (m), 700 (w), 670 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.36 (s, 3 H), 3.11 (s, 3 H), 3.13 (s, 1 H), 4.28 (d, *J* = 4.48 Hz, 1 H), 7.04–7.11 (m, 1 H), 7.14–7.24 (m, 3 H), 7.51 (d, *J* = 8.37 Hz, 2 H), 7.53–7.60 (m, 1 H), 7.84 (dd, *J*<sub>1</sub> = 7.79 Hz, *J*<sub>2</sub> = 0.68 Hz, 1 H). <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>):  $\delta$  = 21.2 (q), 50.4 (q), 74.9 (d), 106.4 (d), 117.9 (d), 119.2 (s), 122.2 (d), 127.2 (d), 127.3 (d), 129.3 (d), 132.1 (s), 136.5 (d), 139.3 (s), 157.4 (s), 191.7 (s). MS (70 eV): *m/z* (rel. abund.) = 284 (51, M<sup>+</sup>), 252 (100, M<sup>+</sup> – CH<sub>3</sub>O), 237 (18, M<sup>+</sup> – C<sub>3</sub>H<sub>7</sub>O), 224 (17, M<sup>+</sup> – C<sub>3</sub>H<sub>8</sub>O), 223 (27, M<sup>+</sup> – C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>), 164 (29, M<sup>+</sup> – C<sub>9</sub>H<sub>12</sub>), 149 (17, M<sup>+</sup> – C<sub>9</sub>H<sub>11</sub>O), 135 (11, M<sup>+</sup> – C<sub>9</sub>H<sub>9</sub>O<sub>2</sub>), 121 (93, M<sup>+</sup> – C<sub>10</sub>H<sub>11</sub>O<sub>2</sub>), 119 (49, M<sup>+</sup> – C<sub>9</sub>H<sub>9</sub>O<sub>3</sub>), 105 (12, M<sup>+</sup> – C<sub>10</sub>H<sub>11</sub>O<sub>3</sub>), 93 (22, M<sup>+</sup> – C<sub>11</sub>H<sub>13</sub>O<sub>3</sub>), 91 (33, M<sup>+</sup> – C<sub>11</sub>H<sub>13</sub>O<sub>3</sub>), 77 (15, M<sup>+</sup> – C<sub>11</sub>H<sub>11</sub>O<sub>4</sub>). Anal. Calcd for C<sub>17</sub>H<sub>16</sub>O<sub>4</sub> (284.3): C, 71.82; H, 5.67. Found: C, 72.34; H, 5.93.

**3'-Chloro-3-hydroxy-2-methoxyflavanone (4f).** According to the above procedure, a solution of epoxide **2f** (212 mg, 0.78

mmol) in methanol (10 mL) was stirred at ca. 20 °C for 24 h under a N<sub>2</sub> atmosphere. The residue, after evaporation of the solvent (ca. 20 °C (15 Torr)), gave after repeated recrystallizations from CCl<sub>4</sub>/petroleum ether flavanone **4f** (158 mg, ca. 100% at 67% conversion) as colorless needles, mp 138–143 °C. IR (CCl<sub>4</sub>):  $\nu$  = 3640–3620 (w), 3520–3480 (w), 2940 (w), 2860 (w), 1700 (m), 1605 (m), 1580 (w), 1470 (w), 1460 (m), 1420 (w), 1370 (w), 1305 (m), 1140 (m), 1090 (s), 1060 (m), 1025 (m), 1000 (m), 990 (m), 950 (w), 720 (m), 700 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.14 (s, 4 H), 4.28 (d, *J* = 3.92 Hz, 1 H), 7.10–7.20 (m, 2 H), 7.37–7.43 (m, 2 H), 7.49–7.53 (m, 1 H), 7.58–7.65 (m, 1 H), 7.68–7.69 (m, 1 H), 7.88 (dd, *J*<sub>1</sub> = 7.77 Hz, *J*<sub>2</sub> = 1.66 Hz, 1 H). <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>):  $\delta$  = 50.6 (q), 74.6 (d), 105.6 (s), 117.9 (d), 119.0 (s), 122.6 (d), 125.4 (d), 127.4 (d), 127.8 (d), 129.6 (d), 129.9 (d), 134.7 (s), 136.8 (d), 137.4 (s), 157.0 (s), 191.2 (s). MS (70 eV): *m/z* (rel. abund.) = 306 (6, M<sup>+</sup> + 2), 304 (18, M<sup>+</sup>), 274 (6, M<sup>+</sup> – CH<sub>3</sub>O), 273 (21, M<sup>+</sup> – CH<sub>3</sub>O), 272 (55, M<sup>+</sup> – CH<sub>3</sub>O), 243 (15, M<sup>+</sup> – C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>), 209 (12, M<sup>+</sup> – C<sub>6</sub>H<sub>6</sub>O), 184 (11, M<sup>+</sup> – C<sub>4</sub>H<sub>5</sub>ClO<sub>2</sub>), 181 (10, M<sup>+</sup> – C<sub>7</sub>H<sub>7</sub>O<sub>2</sub>), 152 (15, M<sup>+</sup> – C<sub>8</sub>H<sub>8</sub>O<sub>3</sub>), 141 (11, M<sup>+</sup> – C<sub>9</sub>H<sub>4</sub>ClO), 139 (32, M<sup>+</sup> – C<sub>9</sub>H<sub>6</sub>ClO), 121 (100, M<sup>+</sup> – C<sub>9</sub>H<sub>8</sub>ClO<sub>2</sub>), 111 (25, M<sup>+</sup> – C<sub>10</sub>H<sub>6</sub>ClO<sub>2</sub>), 105 (15, M<sup>+</sup> – C<sub>9</sub>H<sub>8</sub>ClO<sub>3</sub>), 93 (12, M<sup>+</sup> – C<sub>10</sub>H<sub>6</sub>ClO<sub>3</sub>), 77 (41, M<sup>+</sup> – C<sub>10</sub>H<sub>8</sub>ClO<sub>4</sub>), 76 (20, M<sup>+</sup> – C<sub>10</sub>H<sub>9</sub>ClO<sub>4</sub>). Anal. Calcd for C<sub>16</sub>H<sub>13</sub>ClO<sub>4</sub> (304.7): C, 63.07; H, 4.30. Found: C, 63.32; H, 4.38.

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**Registry No.** **1a**, 525-82-6; **1b**, 41255-30-5; **1c**, 4143-74-2; **1d**, 19725-49-6; **1e**, 10420-75-4; **1f**, 1849-61-2; **1g**, 29976-75-8; **1h**, 88952-74-3; **1i**, 29976-77-0; **1j**, 60402-30-4; **1k**, 60402-30-4; **1l**, 42079-78-7; **1m**, 26964-24-9; **1n**, 22395-22-8; **2a**, 134051-30-2; **2b**, 134051-31-3; **2c**, 134051-32-4; **2d**, 134051-34-6; **2e**, 134051-33-5; **2f**, 134051-35-7; **2g**, 136764-51-7; **2h**, 136764-52-8; **2i**, 136764-53-9; **2j**, 136764-54-0; **2k**, 136764-55-1; **2l**, 136764-56-2; **2m**, 136764-57-3; **2n**, 136764-58-4; **3b**, 19275-68-4; **3h**, 78396-37-9; **3i**, 6971-17-1; **3n**, 7478-60-6; *cis*-**4b**, 136764-61-9; *trans*-**4b**, 136764-62-0; *cis*-**4f**, 136764-63-1; *trans*-**4f**, 136764-64-2; ClC<sub>6</sub>H<sub>4</sub>-*m*-COCl, 618-46-2; 2-acetyl-4-methylphenol, 1450-72-2; 2-(chlorobenzoylmethylcarbonyl)-4-methylphenol, 136764-60-8; dimethyldioxirane, 74087-85-7; 4-chlorobenzoic acid, 2-acetyl-4-methylphenyl ester, 136764-59-5.

**Supplementary Material Available:** <sup>1</sup>H and <sup>13</sup>C NMR spectra of epoxide **2l** (2 pages). Ordering information is given on any current masthead page.

(27) Looker, J. H.; Hanneman, W. W.; Kagal, S. A.; Dappen, J. I.; Edman, J. R. *J. Heterocycl. Chem.* 1966, 3, 55.

## On the Iconic Nature of Conformational Pictures and Their Recognition

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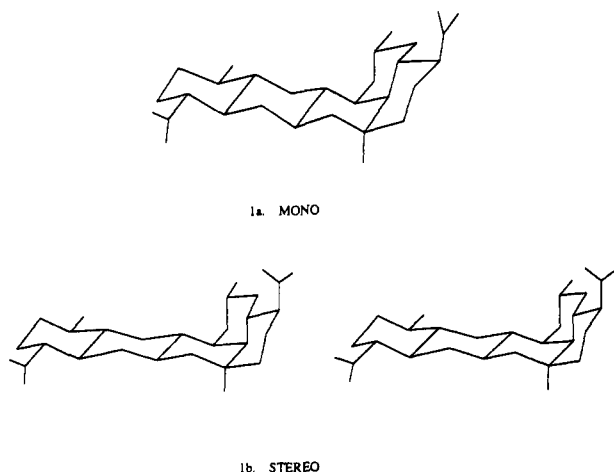
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An algorithm for recognition of hand-drawn conformational pictures is presented in the form of a program "ZED". The problem is defined and discussed in terms of "unprojection", creation of a three-dimensional object from a conformational picture. The behavior of ZED is illustrated with numerous stereoscopic views of the results of unprojection. An unexpected limitation to unprojection is encountered: the fact that conformational pictures are *icons*, not actual projections.

Central to organic chemistry is the problem of *representation* of organic molecules, the relationship between

the molecular objects, and our pictures and models thereof.<sup>1,2</sup> We deal here with the question of machine



**Figure 1.** Monoview and stereoview of unprojection of a typical conformational drawing.

recognition of two-dimensional conformational pictures of three-dimensional organic molecules. The molecules we consider are alicyclic hydrocarbons, but the techniques employed are considered to be applicable to the more general case. We illustrate the problem and our results in Figure 1. In Figure 1a we see a hand-drawn<sup>3</sup> machine-readable conformational figure copied from a recent journal.<sup>4</sup> In Figure 1b we see a stereoview of the same molecule generated by program ZED. For our purposes here we accept a stereoscopic view as being the actual object, the "real thing" as it were. It is this transformation of a conformational picture back into the actual object that we address here.

**Unprojection.** We refer to construction of a three-dimensional object by analysis of its two-dimensional projection as "unprojection". The ability to unproject a chemical drawing seems to be a reasonable operational definition of "recognition".<sup>5</sup> Unprojection of chemical pictures is a necessary prerequisite of numerous chemical activities, the following of which are representative:

1. Conformational diagrams of structures are a universal mode of communication between organic chemists. Recognition of these diagrams is remarkably insensitive to the quality of the drawings employed.

2. Unprojection of conformational pictures is a major difficulty in teaching Organic Chemistry at the University level. Numerous unstated conventions, some of which are noted below, create similar difficulties at the machine level.

3. Unprojection is a nontrivial problem for the following reason: A conformational picture is a projection, not of an object itself, but of the *intellectualization* of an object.<sup>6</sup> This additional translation step generates certain difficulties and ambiguities in the reverse process of unprojection. Conformational pictures may appear to be correct superficially but in fact be syntactic nonsense. Unstated canonical rules for drawing conformational pictures are common (we note some of these below). One is led to the

(1) Robinson, R. *J. Chem. Soc.* 1917, 876.

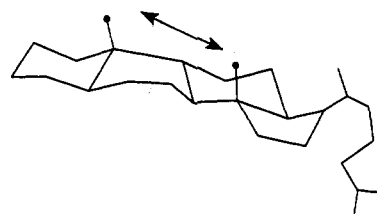
(2) *Representation in Chemistry*; Hoffmann, R., Laszlo, P., Eds.; Diogene: Paris, UNESCO, 1989; Vol. 147, p 24.

(3) Figures drawn with the Chemical Art program WIMP, available from Aldrich Chemical Co.

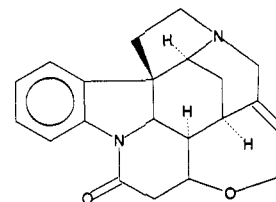
(4) van Aarssen, B. G. K.; Kruk, C.; Hessels, J. K. C.; deLeeuw, J. W. *Tetrahedron Lett.* 1990, 31(32), 4645.

(5) Hoffman, R. *Angew. Chem., Int. Ed. Engl.* 1988, 1593.

(6) A particularly succinct and perceptive analysis of the representation problem and its significance to computer applications in organic chemistry has been given: Suckling, C. J. In *Comprehensive Medicinal Chemistry*; Hansch, C., Sammes, P. G., Taylor, J. B., Ed.; Pergamon: New York, 1990; Vol. 4.



**Figure 2.** What is the distance between these two points?



**Figure 3.** A picture which is *not* a projection.

observation that conformational pictures possess a strongly iconic aspect. We discuss this below. An additional source of difficulty is experimental error, the hand-drawn nature of conformational pictures. Poorly drawn images must be dealt with. In the extreme this renders the problem intractable to algorithmic solutions.

4. Hand-drawn conformational pictures (or other two-dimensional structural diagrams) are the proper way of communicating with computers. The ideal toward which we should strive is one wherein the same chemical picture suffices for interpersonal as well as man-computer discourse. It should *not* be the chemists responsibility to learn a new "notation" when communicating with a machine. A trivial example is illustrated by Figure 2 and the question: "What is the distance between the two indicated angular methyl groups?". Unprojection as described below gives the "natural answer" of 4.0 Å.<sup>7</sup> A less trivial example is that of an "Indole Alkaloid Machine",<sup>8</sup> dealing with the chemistry and synthesis of multicyclic fused ring systems such as vinblastine, strychnine, etc. Communication with this type of program in any mode other than that of conformational pictures is unthinkable.

**Conformational Pictures.** In order to be specific as to the range of chemical diagrams covered here, we make the following reasoned but basically ad hoc divisions:

1. Firstly, we have such things as Sawhorse, Newman, and Haworth projections. Formalisms of this type, while highly useful in the appropriate context, are not considered further.

2. Secondly, we have flat renditions of conformationally rich molecules. The conventional picture of strychnine (Figure 3) is an example, as are the typical flat pictures of steroids, macrolide antibiotics, etc. These flat pictures are not conformational pictures as we use the term here, even though they are, in many cases, also governed by grammatical rules of well formedness. Deduction of their shape, while a fascinating and approachable question, is not considered further.

3. Thirdly, we have pictures considered to be actual projections of molecules. It is the machine recognition or "understanding" of these, illustrated in Figure 1, that is the subject of this paper. In this realm, a conformational picture is actually an attempt to show the shape of the molecule by rendering a projection, rather than dealing in

(7) Measured from Dreiding models, the distance is 4.4 Å. Since we are dealing with *hand-drawn* pictures, we must pick one of the bonds as being accurate. The distance quoted in the text is derived assuming that the C9-C10 distance, 53 pixels in the drawing, corresponds to 1.54 Å.

(8) Whitlock, H., unpublished work.

configurational issues as in the above cases.

**Analysis of Conformational Pictures.** Given a drawing understood to be a "conformational picture" in the above sense, and the idea of unprojection, we phrase the following two-part question:

- (1) What is the three-dimensional object portrayed?
- (2) What are the rules for answering (1),  
i.e. *how do we know?*

Phrasing ones understanding as a computer program is a great aid in achieving concreteness, so our "answer" to these questions is presented as the behavior of a computer program ZED discussed below,<sup>9</sup> when given as input a hand-drawn but machine-readable conformational picture.<sup>10</sup> The computer code comprising this program is presented in the supplementary material together with a brief discussion of its logic.

Input to ZED is a two-dimensional conformational picture: the Z coordinates of all atoms are zero. Its output is the three-dimensional chemical structure,<sup>11</sup> one manifestation of which is a stereoscopic view such as are used here. If unprojection fails, a description of the syntactic difficulties encountered in analysis is produced. Because unprojection is carried out in a chemical context, several constraints must be satisfied in the operation of ZED in order that the analysis produces chemically interesting results. These constraints are as follows:

1. The output should be chemically correct, that is make chemical sense (but see below).
2. Projection of the three-dimensional output onto a surface perpendicular to the axis of viewing should produce *exactly* the input picture. Unprojection is thus a mathematical inverse of the projection operation. Input and output differ *only* in that unprojection assigns a value to the Z coordinate of each atom: the X and Y coordinates are unchanged. Thus a poorly drawn picture must produce a poorly constructed molecule. This is necessary for two closely related reasons: (2a) We are dealing with intellectualizations of molecules and not the molecules themselves. The question is thus "what is the structure that was drawn?" rather than "what is the structure?". (2b) We must never second guess the chemist. He or she is permitted to bend the rules as long as it is clear exactly what is meant. Examples are given below.

It is important to emphasize one point: questions of stability, energy minima, most favored conformations, etc. are *not* the subject of this work.

**Previous Work.** Corey's classic work on machine-assisted organic synthesis<sup>12</sup> details early work on machine input of chemical structures. Use of three-dimensional cues for structure input has been exploited effectively by

Wipke.<sup>13</sup> Unprojection is related to distance geometry<sup>14</sup> in that both are attempts to deduce three-dimensional structures from other data. Otherwise their input data are unrelated. Traditional nonnumeric applications of computers to chemistry focus on connectivity and display issues<sup>15</sup> rather than representation issues such as discussed here.

Unprojection does not deal with questions of connectivity as such. Corey and Feiner<sup>16</sup> have discussed the symbolic evaluation of conformations. Dolata and Carter<sup>17</sup> have described a PROLOG program that deduces acyclic conformations from connectivity data. Deduction of conformations of terpenoids from flat connectivity information and *configurational clues* (see below) has been investigated by De Clercq,<sup>18</sup> as well as Cohen et al.<sup>19</sup>

**Conformational Pictures of Rings.** For our purpose a "conformational picture" is an undirected graph. Its vertices and edges are labeled, but only minimally. Several examples (input files to ZED) are given in the supplementary material. As a file a conformational picture is a very simple object made of three subobjects:

1. The first is a pair of integers: the atom and bond count.
2. Next is a set of atom records. An atom has X, Y, and Z coordinates. All Z coordinates in a picture are zero. Each atom has attached to it several properties, the only one of which is relevant here being *class*. The class of all atoms is initially "Z" (for Zip, nothing). Atoms are separated into two meaningful classes by graph traversal, "R" for R groups, and "G" for rings. Atom records are illustrated by

[0],19.493,00.000,0.0,Z,-,-,C

[1],48.734,15.000,0.0,Z,-,-,C

[2],77.974,12.000,0.0,Z,-,-,C

3. Next is a set of bond records. Each bond record contains: (a) A pair of ordinals specifying the atoms bonded. (b) A bond type (one byte) which may be single, double, triple, or aromatic. These properties are produced by the drawing program employed. (c) Bond "stereochemistry" (not used by ZED) which may be one of the set {Skinny, Wedge, Fat, Dotted, Jagged}. (d) Bond "hide" property. A bond with this property is in front of any intersecting bond. This means that *both* atoms of a hiding bond are in front of *both* atoms of an intersecting bond.

**Bond and Atom Stereochemical Designators.** The conventional graphical devices used to indicate various stereochemical aspects of molecules are divisible into two groups that have fundamentally different meanings and uses.

First we have bond properties in the set {"WEDGE", "JAGGED", "DOTTED", "DOTTEDWEDGE"}. These are configurational cues and are used conventionally to designate configurational information. In particular these properties impose on the atom pair defining the bond an order which references the *plane of the root atom*. This

(9) The program ZED (source and executable) is available as supplementary material and on request from the author. ZED is written in C and C++ (Borland Turbo C++). It runs on an IBM PC or compatible and requires a EGA graphics adaptor. Unprojection of a molecule such as the steroid shown in Figure 1 requires approximately 3 s.

(10) The sequence of operations is (1) Draw a picture in WIMP 2001 to produce a picture as a \*.NFT file. (2) Run program EXX with the \*.NFT file as input. This program strips off various nonchemical things such as rounded rectangles, etc. and produces an ASCII file \*.XXX; This is the passed to ZED. Program EXX is included with ZED.

(11) Program ZED produces the following output: (1) The input \*.XXX file, with substituent classification marks and Z coordinates added, but with X and Y coordinates *unchanged*. (2) An optional Encapsulated PostScript (\*.EPS) picture file of the stereoview. (3) An optional WIMP (\*.NFT) file, also of the stereoview. Figures in this paper were made in this manner. ZED permits rotation of the object after unprojection and will draw a stereoview on the TV set.

(12) (a) Corey, E. J.; Wipke, W. T.; Cramer, R. D. III. *J. Am. Chem. Soc.* 1972, 94, 421. (b) Corey, E. J.; Howe, W. J.; Pensak, D. A. *J. Am. Chem. Soc.* 1972, 96, 7724.

(13) Wipke, W. T.; Dyott, T. M. *J. Am. Chem. Soc.* 1974, 96, 4825-4834.

(14) *Distance Geometry and Conformational Calculations*; Crippen, G. M., Ed.; Research Studies Press, John Wiley & Sons: New York, 1981.

(15) *Computer Aids To Chemistry*; Vernin, G., Chanon, M., Eds. John Wiley: New York, 1986.

(16) (a) Corey, E. J.; Feiner, N. F. *J. Org. Chem.* 1980, 45(5), 757. (b) Corey, E. J.; Feiner, N. F. *J. Org. Chem.* 1980, 45(5), 765.

(17) Dolata, D. P.; Carter, R. E. *J. Chem. Inf. Comput. Sci.* 1987, 27, 36.

(18) De Clercq, P. J. *Tetrahedron* 1984, 40(19), 3717, 3729.

(19) Cohen, N. C.; Colin, P.; Lemoine, G. *Tetrahedron* 1981, 37, 1711.

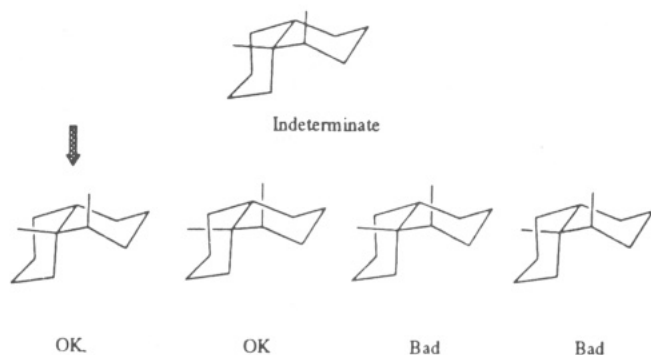


Figure 4. Illustrating the transitive nature of crossed bonds.

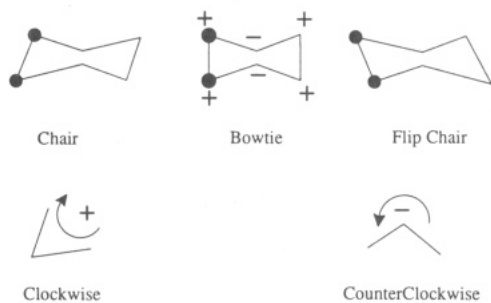


Figure 5. Turn sign conventions for walking a ring.

set of properties finds use primarily in two cases: flat projections as that of strychnine above and in dealing with molecule containing a run of carbons that implicitly defines a reference plane (see below). Configurational designators are *not* normally used in conformational views and thus are ignored by ZED.

Secondly we have those in the set {"HIDE"/"NOHIDE", "SKINNY", "FAT"} that impose a spatial ordering on *bonds*, but not atoms. They comprise spatial cues and tell us something about the bond as a whole: it is normal (SKINNY), "in front" (FAT), or crossing a bond behind it (HIDE). Interestingly none of these three are really necessary. Unprojection gives an enantiomeric pair of 3D objects, one of which may be arbitrarily taken. HIDE and FAT properties merely select one of the enantiomers. This set of properties is used by ZED.

In addition to their role as stereochemical cues the second set offers the opportunity of drawing nonsense structures. This is illustrated in Figure 4. There are  $2^n$  ways we can have  $n$  designators in a conformational projection, but only two of these represent real projections. The others are invalid in that they require that two atoms be mutually in front of or behind one other.<sup>20</sup> This simple parity check is useful in catching this type of optical illusion. Projections such as those in Figure 4 are *very* difficult for people to analyze, because our unstated rules for canonicalization of projections imply that we look *down* on objects. Thus the indicated projection in Figure 4 is what people normally produce by unprojection.

We now consider the process of unprojection. Since the basic process is the same for all rings recognized, we discuss the case of chair cyclohexane as an example in some detail. The first step in unprojection is to classify a ring and the atoms therein in a manner which is characteristic of the ring type (chair, boat, etc.) but which is insensitive to details of the artwork and orientation of the picture.

(20) Because the HIDE property imposes a partial ordering on the bonds (and hence atoms) of a molecule, it is possible to make limited deductions concerning relative depth positioning. It is thus also possible to derive contradictions.

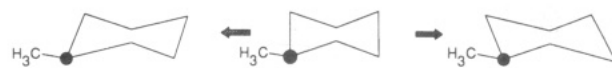


Figure 6. The effect of distortion on the equatorial nature of a cyclohexane substituent.

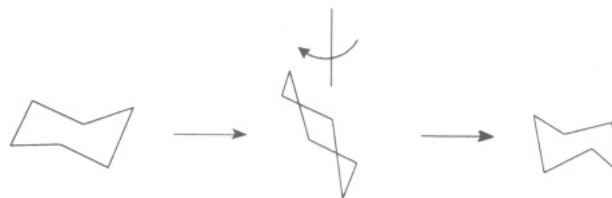


Figure 7. Illustrating the *actual* process of flipping a chair cyclohexane.

If we think of ourselves as standing on a figure, we may walk around the ring in a clockwise manner. At each atom we turn either right or left. Changing the direction of the walk simply reverses the sense of the turn at each atom. Right clockwise and left counterclockwise turns are illustrated in Figure 5. A given atom is characterized as either "plus" or "minus" according to which way we turn when we encounter it in a clockwise walk. This is illustrated in Figure 5 for the chair, bowtie, and flip cyclohexane conformations, each of which has four "plus atoms" and two "minus atoms". The black-dotted atom is a "+" atom in each case.

A complete path around the ring defines a cyclically permutable string (a "sign-string") of plusses and minuses. An atom may be classified according to the traversal sign-string generated when it is the start (the *first* atom encountered) of a clockwise walk. If we specify the starting atom the ring may be uniquely classified in the same manner. In each of the conformational pictures above the black (+) atom is also a "+++" atom. The shaded atom is a "+" and "+-+-" atom. There is another pair of ++++- and +-+-+ atoms at the other end of the ring. All three chair pictures in Figure 5 fall into the same classification: each is a "++-+-" ring. We thus see (or at least assert) that the real difference between chair and flip-chair cyclohexane pictures lies *only* in how the bowtie conformational picture is distorted.

The above classification of atoms is the key to recognition of chairs, flip-chairs, boats of various sorts, and bowtie-chairs. A chair is a six-sided polygon with no bond-crossings and the sign-string ++-+-+. This classification serves us well in recognizing conformational projections. Classification of the picture by sign rather than magnitude of polygon angles permits us to recognize drawings of a wide degree of quality. It is also orientation independent. We must note however that this classification follows from considerations of how chemists perceive conformational pictures and not from any "first principles".

Once a chair is recognized we must classify it as either pure-chair or flip-chair. These are the two limiting deformations of the bowtie form. The distinction between pure- and flip-chair thus is made in the following manner: (1) Both pure- and flip-chairs have the traversal sign-string (clockwise traversal) "++-+-+". We consider the two adjacent plus atoms. (2) If the angle of bending at the first plus atom is greater than at the second, the projection is of a pure-chair. (3) If the angle at the first plus atom is less than at the second, the projection is of a flip-chair.

By this classification three of the six rings in Figure 1 are pure and two are flip. But for classification of substituents it really does not matter if they are the same.

In either case (and for bowtie or square) the axial or equatorial nature of a substituent is independent of this

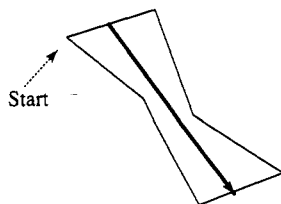


Figure 8. Canonicalization of a ring's sign-string.

classification. This is illustrated in Figure 6.

We note in this regard that the projection of a flipped pure-chair is not that of a flip-chair but a rather unesthetic object as shown in Figure 7.

**Classification of Chair Substituents.** For most (but not all) cyclohexanes a substituent may be viewed as axial or equatorial. Which it is rests on the vector arrangement between the ring and bond vectors. Assuming a "pure-chair" cyclohexane projection this axial-equatorial classification is done in the following manner.

First we define a starting atom of the ring. For a pure- (as compared to "flip") chair this atom is that one which (a) is a  $+++-$  atom (see Figure 3), (b) has a sharper ring traversal angle of turning than the neighboring  $+++-$  atom, and (c) since there are two of these in a chair, is the leftmost one. If the  $X$  distance of this atom is less than the average distance of ring atoms from its centroid then we select on "upness", because the ring is tipped on end. This process defines a starting atom, "Atom0", in the clockwise traversal of the chair ring.

Second, a vector is defined from the midpoint of the Atom0-Atom1 bond and the other end of the ring, the midpoint of the Atom3-Atom4 bond. This is illustrated in Figure 8, which shows the ring vector computed for a chair drawn in the orientation shown.

Third, we compare the bond vector of a substituent with the ring vector to classify a substituent as one of the set {Axial, Equatorial, Unknown}. This is done by the obvious method of labeling bonds perpendicular to the ring vector as axial and those approximately coaxial with it as equatorial. One of course has to check such things as absolute direction of the bond vector and its distance to verify that they are within the range that makes syntactic sense. This is accomplished by a data-driven routine which walks around the ring, checking the substituents at each atom for a fit with a pattern stored in the data section of the program. One may illustrate the process by the following code fragment that classifies substituents on the starting  $+++-$  atom of a chair ring.

case CH0:

```

if (th < 0.0) {
  if ((class == RGP) &&
      ((vth > r130) || (vth < r50))) return(HUH);
  return(AXTYPE);
}
if (th < bend) return(EQTYPE);
return(HUH);

```

Here variables  $th$  and  $vth$  are the turn angles to the substituent and to the ring vector respectively. Variable  $bend$  is the ring traversal angle. Variable  $class$  tells whether the substituent is part of another ring or not. Loosely translated, this code says that if the substituent goes left at an angle between  $-130$  and  $-150^\circ$  it is an axial group (unless its part of another ring when it is axial regardless of the numerical value). If the turn is to the right

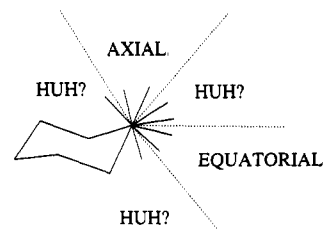


Figure 9. Regions in the plane corresponding to classifiable substituent types.

at any angle it is equatorial. The values returned are in the set {AXTYPE, EQTYPE, or HUH}, "HUH" meaning unknown.

The above process is "data driven" in the following sense. A ring has an associated array of switch variables (e.g. CH0). For a pure-chair it is the array {CH0, CH1, CH2, CH3, CH4, CH5} (integer values all different). For a flip-chair the array is {FL0, ..., FL5}. For a "pure-boat" (see below) the array is {FL0, FL1, FL2, CH3, CH4, CH5}; the left end unprojects to a flip-chair and the right to a pure-chair. At any point in traversal of the ring the effective unprojection is encoded by the array's switch variable, together with the associated switch code. This abstraction could probably be replaced by one which computes the local unprojection directly. This was not done since it would seem to require that all four bonds to carbon be drawn.

The process of classifying substituents is illustrated in Figure 9. Whether a substituent is axial or equatorial depends on whether it lies in a cone relative to the ring vector. How permissive this cone is depends on three things:

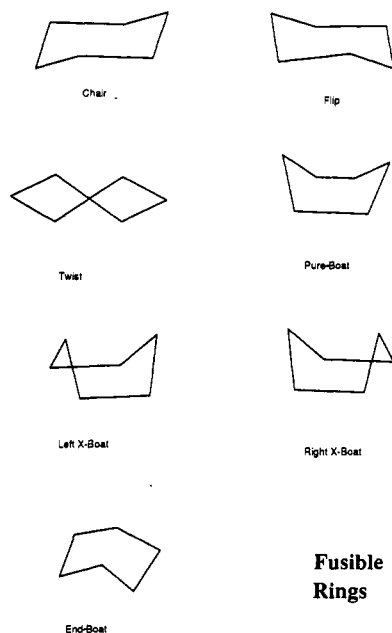
1. It depends on whether the substituent is an "alkyl" group or part of another ring. What is an acceptable C-4 substituent angle of bend (as in Figure 9) for a bicyclo-[2.2.1]- or -[4.1.0]heptane is in the HUH cone and hence unacceptable (i.e. uninterpretable) for an alkylcyclohexane. Similarly, equatorial substituents lying in the bottom or middle HUH cones are bad; they must be moved down from the middle HUH cone, but not too much.

2. It depends where on the ring the substituent is. We remember that we are dealing here still with two-dimensional objects: axial and equatorial cones of acceptance vary with position on the ring. Classification is thus very position dependent.

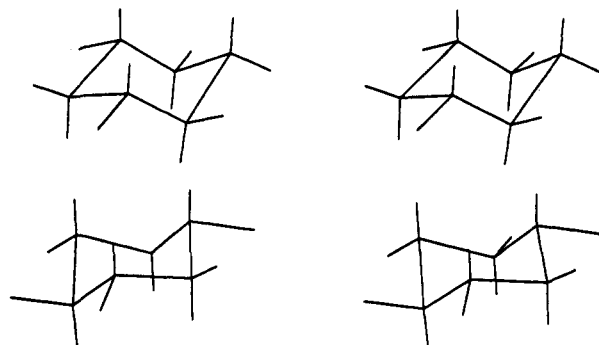
3. The exact size and extent of the cones of acceptance are ultimately a matter of taste. Thus it depends on how demanding we are in accepting a substituent as being axial, equatorial, or unknown ("HUH") (and hence rejected) stereochemistry. Personal preferences and artistic ability are important in defining the acceptance cones. In the limit of requiring perfect projections, HUH cones would expand; at the other limit they would disappear completely. Neither of these extremes is useful.

**Unprojection of Chair Cyclohexanes.** Unprojection is completed by a data-driven assignment of  $Z$  values to the ring and substituent atoms, in that order. A logical "demon"<sup>21</sup> walks around the ring. At any given point, in addition to its history, it is aware of the next ring atom in the walk and any nonring substituents attached to the current atom. The  $Z$  increment associated with the next step in the walk (either out a chain or on the ring) is

(21) Highly recursive structures such as those dealt with in representing chemical structures are conveniently handled with the language C, but only upon addition of suitable control structs such as these ring reader demons. These and other programming aspects of this problem are dealt with in the supplemental material.



**Figure 10.** Rings with recognizable axial and equatorial (fusible) substituents.

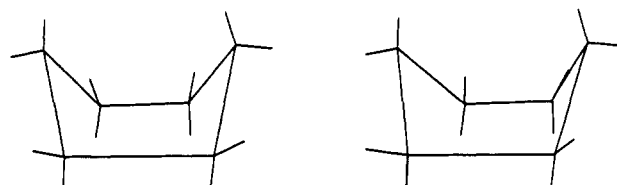


**Figure 11.** Top: stereoview of unprojected hand drawing of a chair cyclohexane. Bottom: stereoview of the object after 3D rotation to show the distortions attending hand drawing.

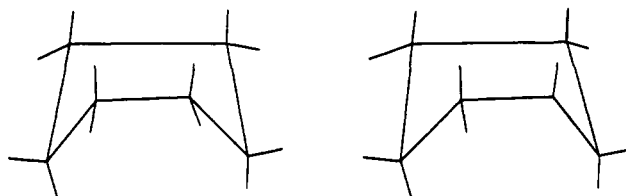
fetched by table lookup on the triple key, for example {pure chair, atom #0, equatorial substituent}. In this case lookup gives relative *Z* values for an equatorial substituent and next ring atom in the walk. This is normalized to the longest bond in the drawing. Thus the entry for the above example is the pair {-1.0, 0.0}. The first (-1.0) says that when atom 0 is arrived at in clockwise ring traversal (from atom 5) its normalized *Z* increment is  $(1.0 \times \text{longest\_bond} \times 0.6)$ , where "longest\_bond" is the longest bond in the molecule and 0.6 is a rough value following from trigonometry of the chair ring. A more exact value is of no advantage. The second entry (0.0) says that an equatorial atom attached here has the same depth as the atom attached to it. Axial substituents need no table entry since their *Z* increment is always zero.

This procedure works well for simple unfused rings. Figure 1 shows the results of unprojection of a modestly elaborate system of fused six-membered rings. The unprojection procedure may be applied with considerable success to the set of "fusible rings", those with recognizable axial and equatorial substituents. As presently implemented the set of fusible rings is made up of pure and flip chairs, pure boats, left and right X-boats, twist-boats, and end-boats as shown in Figure 10.

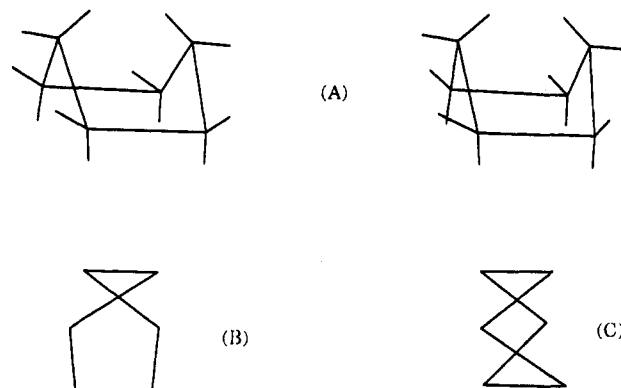
Unprojection of a simple chair gives Figure 11, presented as a stereoview. The top view is the result of the above described unprojection. The bottom view is derived by



**Figure 12.** Stereoview of an unprojected pure-boat drawing.



**Figure 13.** Stereoview of the unprojection of a pure-boat drawing first rotated in the plane.



**Figure 14.** Top (a): stereoview of an unprojection of a "left X-boat" cyclohexane. Bottom (b): generic "X-boat" and "double X-boat" drawings.

spatial rotation of the object about the vertical axis. This rotated view is useful in showing the built-in distortions attending the hand drawing of conformational projections. Application of this procedure to a simple flip-chair gives exactly analogous results and is not pictured.

Figure 12 shows a stereoview arising from unprojection of a "pure-boat", one with no crossing bonds. As noted above the left end of a pure-boat projection is the same as that of a flip-chair, and the right as a pure-chair. In this respect we note that the approach used here is insensitive to planar rotation of the projections. This is illustrated in Figure 13, which pictures the result of first rotating the projection of Figure 12 and then carrying out the unprojection. The same three-dimensional nature is evident. Because of the rule that "the bottom object is in front", this object appears "wrong". This is, as mentioned above, an example of every projection's having two enantiomeric unprojections and arises from the orientation-free approach used by ZED.

Figure 14a shows a stereoview of a "left X-boat", a boat whose projection has a pair of crossed bonds. The analysis of this case is unexceptional in that one may classify and assign *Z* coordinates to ring and substituent atoms in the manner described above; the result is aesthetically acceptable. Not shown is the unprojection of a "left X-boat", which proceeds in a directly analogous manner. Figure 14b illustrates the X-boat theme. Distortion of Figure 14b produces X-boat projections, just as distortion of the bowtie above affords pure- and flip-chairs. Figure 11c illustrates the so-called "double-crossed" projection. This, which is the basis of still another chair projection, is not considered further here.

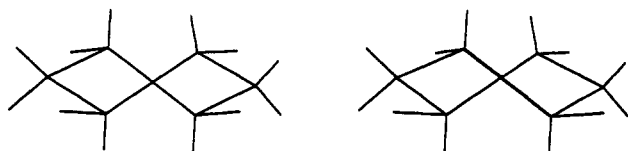


Figure 15. Stereoview of an unprojection of a twist-boat cyclohexane.

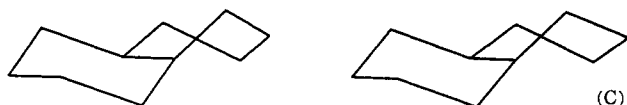


Figure 16. Stereoviews of unprojections of drawings of several fused ring system drawings.

That old favorite, the twist-boat, is, surprisingly, handled smoothly with no conceptual extensions needed. Figure 15 illustrates this ring system with axial and equatorial substituents shown.

Figure 16 shows several unprojections based on these rings. These illustrate (especially 16d!) the power of the very simple procedure employed. Inspection of Figure 16 emphasizes the very important point that the ring categorization scheme discussed above, while orthogonal in a two-dimensional sense, is highly degenerate in a three-dimensional sense. This is apparent in Figure 16d where a variety of boat projections are present, but the simple pure-boat at the top is used.

The case of the end-on projection of a boat (as in bicyclo[2.2.1]heptane, see Figure 17) is, surprisingly, totally different. Figure 17 shows a common projection of camphane, its unprojection, and a rotation of the latter. This is unsatisfactory when judged on chemical criteria. The unprojection has the bond angles, bond lengths, and position of the bridging atom all wrong. This clearly fails our stated criteria of producing on unprojection three-dimensional objects that "make sense". Experimentation with ZED leads us to the following conclusion: the commonly accepted<sup>22</sup> end-on projection of a boat is an icon,



Figure 17. Top: stereoview of unprojected bicyclo[2.2.1]heptane. Bottom: the same unprojection after rotation of the 3D object to expose its features.



Figure 18. Stereoview of the unprojection of a structure (twistane) drawing possessing both end-boat and twist-boat subdrawings.

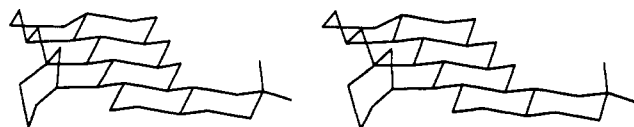
not a projection of a chemical object. We use the work icon in the sense of its being an idealized but perhaps distorted pictorial representation of something. While convenient in an artistic and intellectual sense it is *not* correct. What does this mean in the context of unprojection and the understanding of conformational pictures? Not much, except that analysis of projections containing end-boat parts must be done by keying on less iconic substructures. This is in fact what one does intellectually when dealing with this type of drawing. An example is twistane in Figure 18, whose projection contains both twist- and end-boat parts. The successful unprojection shown arises from pursuing the twist- rather than the end-boat.

**Fused Rings.** Fused decalins and related systems such as that pictured in Figure 1 are unprojected by a context free parse that is equivalent to walking a diamond lattice. Similar use of the diamond lattice has been used as the basis of conformational analysis of medium- and large-sized rings.<sup>23</sup> Central to the unprojection analysis here is the *aggregate ring*. This simple idea is defined (and generated) in the following manner. In the initial walking of the molecule to detect alkyl chains and rings, a list of rings present is made. Any two rings of this list of rings that have a *common* ring atom comprise an aggregate ring. They are added to a list that, in its totality, defines this aggregate ring. An equivalency class is thus defined. Crudely, fused and spiro rings belong to the same aggregate ring, but rings that are simply attached to each other do not. Chemically, a steroidal A-D ring system is one aggregate; a steroid bearing a saponin side chain comprises two. The glycosidic rings of an oligosaccharide (not sharing ring atoms) are all separate.

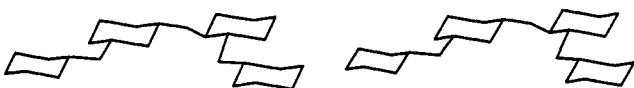
Each structure then has a list of aggregate rings. When walking an initially chosen ring (which is guaranteed to be on exactly one aggregate ring) we assign equatorial or axial nature to substituents when encountered, as discussed above.

(22) E.g.: *The Springer Verlag Molecule Template*; Vogtle, E., Ed.; Verlag Chemie: Weinheim, Germany, 1979.

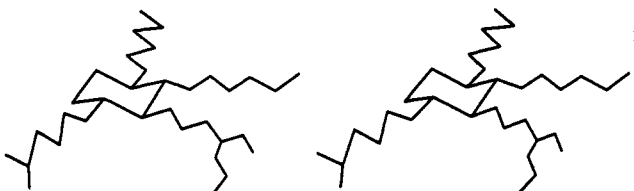
(23) Saunders, M.; Houk, K. N.; Wu, Y.-D.; Still, W. C.; Lipton, M.; Chang, G.; Guida, W. C. *J. Am. Chem. Soc.* 1990, 112, 1419-1427.



**Figure 19.** Stereoview of the unprojection of a molecule having a single aggregate ring. The perspective produced is upside down.



**Figure 20.** Stereoview of the unprojection of a drawing of a system having multiple connected but unfused rings.



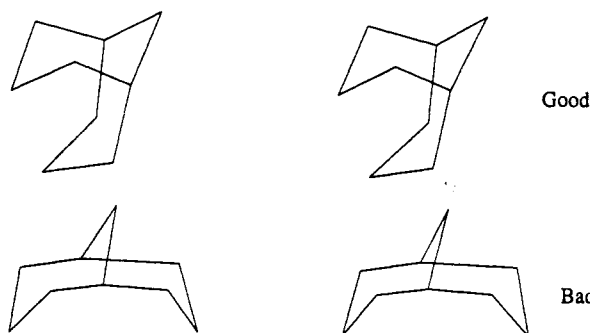
**Figure 21.** Unprojection of a drawing of an appendaged ring, wherein the perspective is retained by the unprojection process.

When an attached atom is part of the current aggregate ring, the ring containing it is walked in a recursive sense. Success is signaled by assigning Z coordinates in a consistent manner; failure is signified by incompatible Z's. Backtracking is of necessity employed, since each ring has two perspectives, above and below. While we present this as an analogy to walking the diamond lattice, it is in fact somewhat more general than this would imply. It works satisfactorily on both chairs, pure-boat, both right and left X-boats, and twist-boats as well. The only requirement is that we assign axial or equatorial labels to each ring substituent. Figure 19 shows a stereoview of a fused ring system unprojected by ZED. It has both chair and boats and an upside down perspective arising from the backtracking analysis.<sup>24</sup>

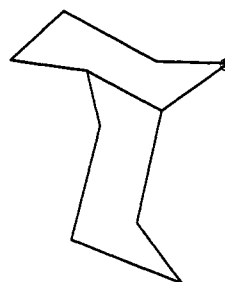
**Sugars.** From the conformational picture point of view this important structural class is unexceptional. Sugars do however illustrate another and different aspect of unprojection, the placing of rings relative to one another. A drawing made up of a series of rings connected in an acyclic context comprises a tree whose nodes are the rings and whose edges are the connecting R chains. The result of unprojection procedure as described so far is each ring's having locally consistent Z coordinates assigned. There is no constraint on one ring vs another, since they belong to separate aggregate rings and are analyzed separately. One ring is chosen arbitrarily and the tree is walked moving the atoms as encountered either in, out, or neither as appropriate. The result is pictured in Figure 20.

In walking the tree above, our demon proceeds along an R chain in a Z direction determined by the branching from the ring. This simple and natural rule permits us to unproject "zigzag" alkyl groups in a wonderfully satisfying and realistic manner! This is illustrated by the unprojected cyclohexane in Figure 21. The stereoview presented here shows how the zigzag alkyl groups are arranged in a manner that is in direct agreement with ones interpretation of the picture.

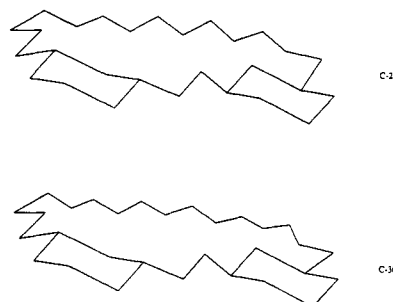
**Iconic Pictures.** Unprojection of the end-on view of bicyclo[2.2.1]heptane discussed above (see Figure 17) illustrates a fundamental limitation of machine recognition



**Figure 22.** Top: stereoview of the unprojection of a syntactically correct drawing of bicyclo[3.3.1]nonane. Bottom: unprojection of a syntactically incorrect but common drawing of this ring system.



**Figure 23.** A commonly encountered but nonsense conformational drawing.



**Figure 24.** Two iconic structural drawings.

of projection formula, one that was not envisaged at the start of this work. Certain of our normal conformational pictures are in fact only idealized representations of the actual projections. While one can attempt systematization of these, we merely note several examples here.

1. The conventional end-on view of bicyclo[2.2.1]heptane is an *icon* as this term is defined earlier. Manual projection of a Fieser<sup>25</sup> or Dreiding<sup>26</sup> model shows this to be the case. No great importance should be attached to this: it merely exhibits the artistic nature of conformational pictures.

2. A related iconic picture that is common is that of bicyclo[3.3.1]nonane (Figure 22). Figure 22a is a "valid" projection (successfully unprojected). Figure 22b is an invalid but frequently encountered iconic picture. We note that ZED, by keying on the X-chair, was able to carry out a complete unprojection as shown. Closely related is the iconic diagram of *cis*-decalin shown in Figure 23. While this fails on grammatical grounds,<sup>27</sup> it is a commonly encountered iconic conformational diagram.<sup>28</sup>

(25) Aldrich Chemical Co., Milwaukee, WI.

(26) Buchi, G., Basle.

(27) Loosely, this diagram is syntactically wrong because the dotted carbon on the top ring, which *must* be equatorial, is (must be) placed incorrectly. It lies in the "HUH" zone as discussed above.

(24) The polycyclic system shown, while successfully unprojected, is near the space limits of the current version of ZED.



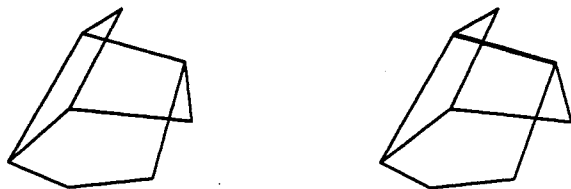


Figure 25. Stereoview of the unprojection of a complicated drawing.

4. Macrocyclic ring projections have their own logic, the basic conformational and pictorial rules for which have been enumerated by Dale.<sup>29</sup> Unprojection of these is not addressed by ZED. The basic rule for construction of these projections seems to be to connect runs of *all-anti*-butane units oriented in various ways. Unprojection will proceed in this way also. The iconic nature of conformational pictures is apparent when we consider the two different molecules shown (monoscopic view) in Figure 24. The bottom picture is derived from the top by simply addition of two carbons to the back *anti*-butane run; otherwise they are identical.

(28) Corey, E. J.; Feiner, N. F. *J. Org. Chem.* 1980, 45, 757-764.

(29) Dale, J. *Acta Chem. Scand.* 1973, 27, 1115-1129, 1130-1148, 1149-1158.

In summary, the curious fact about iconic projections as illustrated above is that, because they are *representations*, the fact that they are not projections at all is immaterial for most purposes. One merely has to learn the rules for interpreting them!

**Conclusions.** Machine recognition of conformational pictures is possible. The problem is complicated by several features, foremost of which is the iconic nature of some structural diagrams. This iconic aspect of structural diagrams and, indeed, structural formula in general, was noted by Sir Robert Robinson as early as 1917.<sup>1</sup> Secondly, it is useful to classify the various graphics objects associated with stereochemical pictures of organic molecules into two groups: those (Wedge, etc.) that impose a spatial ordering on *atoms* and those (Fat bond, etc.) that impose a spatial ordering on *bonds*. These are fundamentally different marks. Thirdly, a simple program (ZED) is described that is remarkably successful in interpreting these pictures. It succeeds in many cases by proceeding in a manner that is, frankly, surprising. Our favorite example of unexpected success is a drawing of bicyclo[3.3.0.0<sup>2,6</sup>]octane, taken from ref 27. Unprojection affords the stereoview as illustrated in Figure 25.

**Supplementary Material Available:** The program ZED (47 pages). Ordering information is given on any current masthead page.

## Electroorganic Reactions. 38. Mechanism of Electrooxidative Cleavage of Lignin Model Dimers

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The mechanisms for oxidative cleavage of several phenolic ethers, models for lignins, have been investigated by a detailed comparison of the result of anodic oxidation at nickel anodes in alkaline electrolyte with that of oxidation in acetonitrile in the presence of a triarylamine redox catalyst. The latter reaction is unambiguously initiated by single-electron transfer (SET), and in this case the major product of cleavage is aldehyde (vanillin or syringaldehyde derivatives). At nickel anodes polymerization is predominant although the aldehydes are formed together with larger amounts of the corresponding carboxylic acids. Combinations of 4-hydroxyl,  $\alpha$ -keto,  $\beta$ -O-aryl, and  $\beta$ -hydroxymethyl functionality are shown to be crucial for the oxidation at nickel; the carboxylic acid formation probably involves a route with initial hydrogen atom abstraction at the surface. Important chemical conversions precede and accompany oxidation in alkaline media, and these are associated with the propensity for polymerization.

Lignins are three-dimensional biopolymers comprised of oxygenated phenylpropane units<sup>1</sup> (Figure 1). Their oxidative degradation to useful low molecular weight aromatic compounds such as vanillin and syringaldehyde has been much studied and is commercially important. Degradation is achieved typically by oxidation with nitro aromatics,<sup>2</sup> air in alkaline solution at high temperatures,<sup>3</sup> electrochemical oxidation,<sup>4</sup> and a combined nitro aromatic/electrochemical oxidation.<sup>5</sup> Fungal degradation of lignin is also oxidative,<sup>6</sup> and one of the relevant enzymes, ligninase, is able to oxidize relatively simple lignin models.<sup>7</sup> The key reaction is cleavage of C $_{\alpha}$ -C $_{\beta}$  bonds (Figure 1), and this reaction may involve electron transfer in at least some of the above-described processes. However, the mechanisms for such oxidative cleavages are poorly understood.

This paper attempts to elucidate the mechanism of electrochemical degradation at nickel anodes in strongly alkaline solution. This process has many of the features of other, commercially used, methods, and the conclusions should have considerable general value. Product profiles

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