

The carborane cage $C_2B_{10}H_{10}$ forms a very regular icosahedron with $C-C = 1.634$ (3) Å; the $B-C$ bonds range from 1.692 (3) to 1.720 (3) Å, $B-B$ bonds from 1.739 (3) to 1.802 (3) Å, both $C-H$ bonds = 0.97 (2) Å and $B-H$ bonds range from 1.06 (2) to 1.12 (2) Å. The $S-C$ bonds in the isopropylidene-dithio ring, 1.859 (2) and 1.867 (2) Å, are slightly longer than the mean distance for a single $C-S$ bond of 1.83 (2) Å (Abrahams, 1956). On the other hand, $S-B$ bonds in the same ring, 1.840 (2) and 1.853 (2) Å, are shorter than the $S-B = 1.92$ (2) Å known for the ligand derivatives of boron compounds (Sands & Zalkin, 1962; Šubrtová, 1971).

C(3) has a tetrahedral configuration with an average $C-C = 1.519$ (3) Å and an average value of six angles of 109.4 (1)°. $C-H$ distances in the methyl groups range from 0.92 (2) to 1.07 (2) Å.

The shortest $H-H$ intermolecular distance is 2.49 (3) Å. The arrangement of the molecules in the unit cell is shown in Fig. 2.

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The Structure Determination and Molecular-Mechanics Calculation of 1,6-Anhydro- β -D-galactopyranose*

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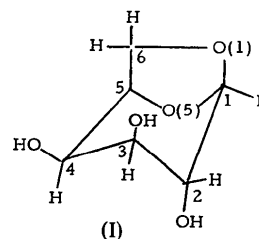
Abstract

1,6-Anhydro- β -D-galactopyranose, $C_6H_{10}O_5$, $M_r = 162.08$, m.p. = 498 K, is orthorhombic, $P2_12_12_1$, $a = 11.073$ (3), $b = 28.890$ (5), $c = 6.396$ (1) Å ($\lambda_{CuK\alpha} = 1.54051$ Å), $V = 2046.1$ Å³, $Z = 12$, $D_x = 1.578$, $D_m = 1.584$ Mg m⁻³. The structure was solved by *MULTAN* and refined to $R(F) = 0.056$ for 2033 independent reflections. The three symmetry-independent molecules have similar molecular dimensions, except for the orientations of the three hydroxyl groups. An extensive system of hydrogen bonds in the crystal structure involves three linear and six bifurcated $O-H\cdots O$ interactions. A molecular-mechanics program, *MMI-CARB*, parameterized for carbohydrates, gave a molecular fit such that the differences in

observed and calculated molecular dimensions were comparable to those observed between the symmetry-independent molecules.

Introduction

1,6-Anhydro- β -D-galactopyranose, (I), galactosan, is the tenth in a series of 1,6-anhydropyranose molecules for which crystal structure analyses are reported. Eight of these molecules have also been examined by



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molecular mechanics and their observed and calculated conformations have been compared (Jeffrey & Park, 1979). The ninth is a more recent report on 1,6-anhydro-2,4-deoxy-2,4-difluoro- β -D-glucopyranose (Choong, 1979).

This crystal structure is particularly interesting and unusual, in that it contains three symmetry-independent molecules in $P2_12_12_1$. A comparison of the dimensions of these three molecules, therefore, permits an assessment of the effect of the crystal-field forces on the bond lengths, valence angles, and conformations of the molecules.

Experimental

A sample of (I), obtained from the collection of Professor R. E. Reeves, was recrystallized from a mixture of benzene and tetrahydrofuran at room temperature. A crystal with dimensions $0.95 \times 0.40 \times 0.25$ mm was used to collect 2034 hkl intensities by θ - 2θ scans to $\theta_{\max} = 65^\circ$ on a CAD-4 X-ray diffractometer with graphite-monochromated Cu $K\alpha$ radiation. No absorption corrections ($\mu_{\text{Cu } K\alpha} = 1.222 \text{ mm}^{-1}$) were applied.

The structure was solved with the 1978 version of *MULTAN* (Germain, Main & Woolfson, 1971) using 340 normalized structure factors for phase generation. The E map of the correct solution revealed all 33 non-hydrogen atoms in the asymmetric unit. Refinement was by least squares, minimizing $\sum_i w_i (|F_o| - k|F_c|)^2$, with $w_i = (\sigma_{ci})^{-2}$, where σ_{ci} was from counting statistics. All H atoms were located from difference syntheses and refined anisotropically. One reflection (060) was removed from the set of experimental data because it was thought to be poorly measured. The final values of $R = \sum_i ||F_o| - k|F_c|| / \sum_i |F_o|$, $R_w = [\sum w(|F_o| - k|F_c|)^2 / \sum w|F_o|^2]^{1/2}$ were 0.056 and 0.071, respectively, for 2033 reflections. The atomic scattering factors for O and C were from Cromer & Waber (1965) and those for H were from Stewart, Davidson & Simpson (1965). Bond lengths and principal valence

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (\AA^2) for non-hydrogen atoms in 1,6-anhydro- β -D-galactopyranose

Estimated standard deviations given in parentheses refer to the least significant digit.

	x	y	z	B_{eq}
C(1A)	7731 (3)	1100 (1)	4496 (6)	1.83
C(2A)	8578 (3)	857 (1)	2952 (7)	1.77
C(3A)	7849 (3)	535 (1)	1497 (7)	1.50
C(4A)	6610 (3)	746 (1)	912 (6)	1.64
C(5A)	6024 (3)	996 (1)	2769 (8)	2.03
C(6A)	5905 (4)	721 (1)	4762 (8)	2.51
O(1A)	7105 (3)	766 (1)	5693 (5)	2.35
O(2A)	9145 (2)	1215 (1)	1764 (6)	2.38
O(3A)	7717 (3)	100 (1)	2564 (6)	2.30
O(4A)	5800 (3)	397 (1)	201 (6)	2.52
O(5A)	6860 (2)	1357 (1)	3408 (5)	2.21
C(1B)	9616 (4)	2882 (1)	-3707 (7)	1.94
C(2B)	10317 (3)	2742 (1)	-1756 (7)	1.76
C(3B)	9587 (3)	2437 (1)	-286 (7)	1.72
C(4B)	8759 (3)	2104 (1)	-1514 (7)	1.78
C(5B)	8195 (4)	2343 (1)	-3408 (7)	1.91
C(6B)	7580 (3)	2804 (1)	-2954 (8)	2.07
O(1B)	8560 (2)	3134 (1)	-3108 (5)	2.37
O(2B)	11374 (3)	2501 (1)	-2468 (6)	2.80
O(3B)	8881 (3)	2727 (1)	1069 (5)	2.39
O(4B)	7820 (3)	1925 (1)	-257 (6)	2.91
O(5B)	9183 (3)	2485 (1)	-4752 (5)	2.12
C(1C)	794 (4)	586 (1)	7420 (7)	2.18
C(2C)	1525 (3)	368 (1)	9171 (7)	1.86
C(3C)	2745 (3)	606 (1)	9453 (7)	1.77
C(4C)	2648 (3)	1131 (1)	9092 (7)	1.85
C(5C)	1806 (4)	1250 (1)	7304 (8)	2.26
C(6C)	2051 (4)	1006 (2)	5271 (8)	2.70
O(1C)	1417 (3)	568 (1)	5503 (5)	2.84
O(2C)	796 (3)	423 (1)	10980 (6)	2.78
O(3C)	3593 (2)	405 (1)	8052 (5)	2.20
O(4C)	3850 (3)	1298 (1)	8702 (6)	2.89
O(5C)	619 (2)	1061 (1)	7867 (5)	2.45

angles are shown in Fig. 1. The atomic coordinates are given in Tables 1 and 2.*

* Lists of structure factors, anisotropic thermal parameters and bond and torsion angles including H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34982 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

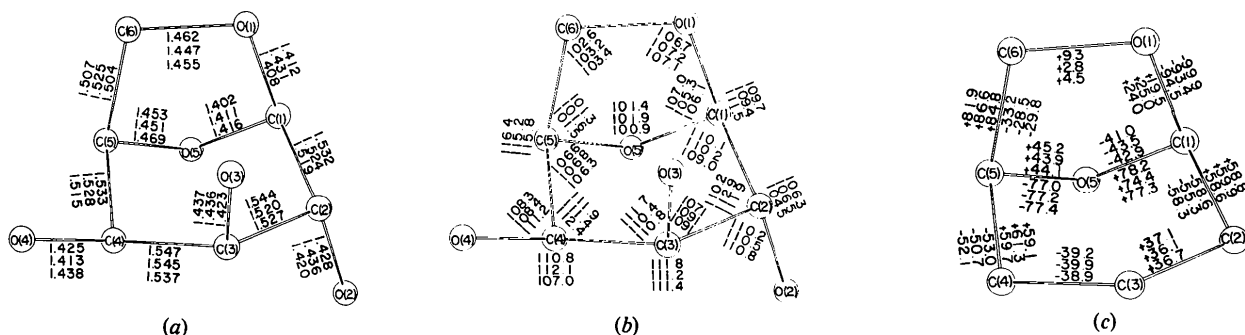


Fig. 1. (a) Bond lengths (\AA), (b) principal valence angles ($^\circ$) and (c) ring torsion angles ($^\circ$) in 1,6-anhydro- β -D-galactopyranose. The three values correspond to the three molecules in the asymmetric unit. The standard deviations are 0.005–0.006 \AA in bond lengths, 0.3–0.4 $^\circ$ in valence angles, and 0.3–0.5 $^\circ$ in torsion angles. The H atoms have been omitted.

Table 2. Fractional atomic coordinates ($\times 10^3$), isotropic temperature factors (\AA^2), and bond distances (\AA) for hydrogen atoms in 1,6-anhydro- β -D-galactopyranose

Estimated standard deviations in parentheses refer to the least significant digit. The temperature expression used is $T = \exp[-(B \sin^2 \theta/\lambda^2)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{iso}	(C, O)—H
H(C1A)	791 (5)	132 (2)	541 (9)	4 (1)	0.88 (5)
H(C2A)	924 (3)	69 (1)	394 (6)	1 (1)	1.08 (4)
H(C3A)	830 (4)	49 (1)	8 (7)	2 (1)	1.04 (4)
H(C4A)	674 (4)	102 (1)	-23 (8)	3 (1)	1.08 (5)
H(C5A)	544 (6)	115 (2)	185 (11)	7 (2)	0.99 (6)
H(C61A)	569 (4)	35 (1)	466 (7)	2 (1)	1.11 (4)
H(C62A)	539 (6)	99 (2)	559 (11)	6 (2)	1.10 (6)
H(O2A)	936 (5)	107 (2)	36 (12)	7 (2)	1.01 (6)
H(O3A)	759 (6)	-10 (2)	99 (11)	6 (2)	1.18 (7)
H(O4A)	630 (4)	19 (1)	-55 (8)	3 (1)	0.95 (5)
H(C1B)	1002 (4)	297 (2)	-492 (9)	4 (1)	0.93 (5)
H(C2B)	1051 (4)	299 (1)	-83 (7)	2 (1)	0.95 (4)
H(C3B)	1007 (4)	227 (1)	62 (7)	2 (1)	0.93 (4)
H(C4B)	931 (5)	181 (2)	-205 (10)	5 (1)	1.11 (6)
H(C5B)	763 (5)	210 (2)	-435 (10)	4 (1)	1.11 (6)
H(C61B)	714 (4)	285 (1)	-126 (7)	2 (1)	1.19 (4)
H(C62B)	696 (5)	286 (2)	-425 (9)	4 (1)	1.09 (5)
H(O2B)	1178 (6)	252 (2)	-127 (11)	8 (2)	0.89 (7)
H(O3B)	885 (3)	266 (1)	224 (7)	1 (1)	0.78 (4)
H(O4B)	795 (4)	172 (2)	51 (8)	3 (1)	0.78 (5)
H(C1C)	-5 (4)	46 (1)	692 (8)	3 (1)	1.05 (5)
H(C2C)	159 (3)	0 (1)	900 (6)	1 (1)	1.07 (4)
H(C3C)	305 (3)	58 (1)	1092 (6)	1 (1)	1.00 (4)
H(C4C)	238 (3)	127 (1)	1049 (6)	1 (1)	1.02 (4)
H(C5C)	180 (7)	164 (2)	690 (13)	8 (2)	1.15 (7)
H(C61C)	284 (5)	91 (2)	507 (9)	4 (1)	0.92 (5)
H(C62C)	165 (6)	115 (2)	422 (12)	7 (2)	0.90 (7)
H(O2C)	108 (6)	31 (2)	167 (10)	5 (2)	0.63 (7)
H(O3C)	437 (6)	43 (2)	875 (11)	7 (2)	0.98 (7)
H(O4C)	390 (6)	152 (2)	949 (12)	7 (2)	0.82 (7)

Discussion

The only major difference in the conformations of the three symmetry-independent molecules is in the orientations of the hydroxyl groups, as shown by the comparison of the relevant torsion angles given in Fig. 1(c) and Table 3. This is a consequence of the hydrogen bonding in the crystal and such significant differences as are observed in the other molecular dimensions are a consequence of this and related crystal-field effects. The pyranose and anhydro ring conformations are nearly identical in all three molecules, as shown by the

Table 3. Torsion angles ($^\circ$) of the hydroxyl groups in the three molecules of galactosan

Torsion angles involving methylene hydrogens in the three molecules differ by less than 4σ .

	<i>A</i>	<i>B</i>	<i>C</i>	Calculated value
C(1)—C(2)—O(2)—H(O2)	-153 (4)	+163 (4)	+174 (6)	+161
C(2)—C(3)—O(3)—H(O3)	-156 (3)	-137 (3)	-150 (4)	+171
C(3)—C(4)—O(4)—H(O4)	-36 (3)	-80 (4)	-131 (5)	-159

Table 4. Experimental vs theoretical puckering coordinates, and comparison of mean observed and calculated bond lengths and valence angles in galactosan

E.s.d.'s are 0.005–0.006 \AA for bond lengths and 0.3–0.4 $^\circ$ for valence angles. (I) and (II) refer to the calculations with unrestricted and restricted hydroxyl orientations referred to in the text.

Puckering coordinates (Cremer & Pople, 1975)	<i>A</i>	<i>B</i>	<i>C</i>	Theoretical (MMI-CARB) (I)
Pyranose ring				
Q (\AA)	0.638	0.629	0.644	0.633
θ ($^\circ$)	156.3	156.0	155.1	155.4
φ ($^\circ$)	175.9	168.3	175.2	174.1
Anhydro ring				
Q (\AA)	0.424	0.421	0.425	0.450
φ ($^\circ$)	346.8	355.1	353.1	356.3
Bond lengths (\AA)		Mean observed	Calculated (I)	(II)
C(1)—C(2)		1.525	1.532	1.534
C(2)—C(3)		1.530	1.527	1.531
C(3)—C(4)		1.543	1.529	1.531
C(4)—C(5)		1.525	1.530	1.531
C(5)—C(6)		1.512	1.526	1.529
C(6)—O(1)		1.455	1.412	1.418
C(1)—O(1)		1.417	1.407	1.404
C(1)—O(5)		1.410	1.422	1.414
C(2)—O(2)		1.428	1.418	1.419
C(3)—O(3)		1.432	1.418	1.419
C(4)—O(4)		1.425	1.417	1.418
C(5)—O(5)		1.458	1.423	1.426
Valence angles ($^\circ$)		Mean observed	Calculated (I)	(II)
C(1)—C(2)—C(3)		111.7	111.8	110.4
C(2)—C(3)—C(4)		111.5	110.5	110.7
C(3)—C(4)—C(5)		111.9	112.3	111.8
C(4)—C(5)—C(6)		115.8	115.9	115.6
C(2)—C(1)—O(5)		109.8	111.1	110.1
C(4)—C(5)—O(5)		106.5	108.6	107.7
C(6)—C(5)—O(5)		101.5	100.5	99.9
C(2)—C(1)—O(1)		110.2	112.7	111.6
C(5)—C(6)—O(1)		103.1	105.2	105.2
C(1)—C(2)—O(2)		105.8	108.3	108.1
C(3)—C(2)—O(2)		110.5	109.3	109.7
C(2)—C(3)—O(3)		108.4	108.9	108.4
C(4)—C(3)—O(3)		111.0	109.7	110.3
C(3)—C(4)—O(4)		110.0	108.3	110.8
C(5)—C(4)—O(4)		109.2	110.4	109.9
C(1)—O(1)—C(6)		107.0	104.3	104.7
C(1)—O(5)—C(5)		101.4	98.9	100.4
O(1)—C(1)—O(5)		106.1	107.0	107.5

puckering parameters given in Table 4. The pyranose rings are 1C_4 chairs distorted towards an E_0 sofa conformation (Jeffrey & Yates, 1979). The anhydro ring of molecule *A* is closest to a 0T_4 conformation. A calculation of the least-squares molecular fit (Nyburg,

1974), excluding the H atoms, between the three molecules gives the following maximum and mean differences (in Å): *A* to *B*, 0.084, 0.040; *A* to *C*, 0.074, 0.035; *B* to *C*, 0.095, 0.043. The differences in bond lengths, which may be significant, are 0.023 (7) Å, C(1)—O(1) *B*—C; 0.025 (7) Å, C(4)—O(4) *C*—B; 0.024 (8) Å, C(2)—C(3) *A*—B. In the valence angles, the largest differences are 5.1 (0.4)° in C(3)—C(4)—O(4) *B*—C; 3.8 (0.4)° in C(3)—C(4)—O(4) *A*—C; 2.9 (0.4)° in C(5)—C(4)—O(4) *C*—A, which are certainly significant. It is interesting to note that these angles all involve O(4), which is the oxygen of the hydroxyl group with the greatest difference in orientation in the three molecules, as shown in Table 3.

The hydrogen bonding is illustrated schematically in Fig. 2. It consists of a finite side chain, which originates at O(4C) and links to an infinite chain of hydrogen bonds between O(3A)H groups. A characteristic of this hydrogen bonding is the unusual number of bifurcated hydrogen bonds. There are three linear hydrogen bonds and six pairs of bifurcated hydrogen bonds, all but one of which involve ring oxygens. Their geometries are given in Table 5. All the oxygens except O(1A) are involved in the two hydrogen-bond chains. The bond lengths and angles of the three linear bonds are very close to the average values for O—H...O bonds in carbohydrate structures. They lie in the center of the distance *versus* angle plot of linear bonds observed in eighteen neutron diffraction angles of simple mono- and disaccharides (see Fig. 5, Newton, Jeffrey & Takagi, 1979). The bifurcated bonds are of the unsymmetrical type, as defined by Newton, Jeffrey & Takagi (1979) in their quantum-mechanical treatment. However, with these additional examples, it is apparent that there is no clear distinction between the symmetrical and unsymmetrical case. New studies of carbohydrate crystal structures and re-examination of some previous analyses are likely to provide examples of a continuous range of bifurcated interactions between the almost ideally symmetrical example (2.138, 2.185 Å) in methyl α -D-altropyranoside (Poppleton, Jeffrey & Williams, 1975) to the very unsymmetrical interaction (1.949, 2.715 Å) in α -L-rhamnose monohydrate (Takagi & Jeffrey, 1978).

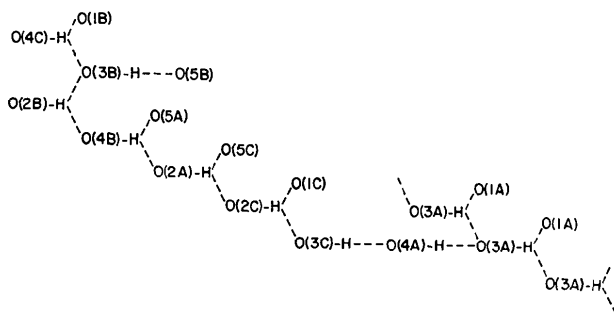


Fig. 2. Hydrogen-bonding scheme in the crystal structure of 1,6-anhydro- β -D-galactopyranose.

Table 5. Hydrogen bonds in the 1,6-anhydro- β -D-galactopyranose structure

The O—H bond lengths have been normalized to 0.97 Å.

Linear bonds	H...O	O—H...O	O...H...O
O(4A)—H...O(3A) ^a	1.81 Å	164°	
O(3B)—H...O(5B) ^b	1.83	166	
O(3C)—H...O(4A) ^b	1.84	173	
Bifurcated bonds			
O(2B)—H...O(3B) ^c	2.36	122	75°
...O(4B) ^c	2.12	135	
O(4C)—H...O(1B) ^d	2.41	149	81
...O(3B) ^d	2.12	127	
O(2A)—H...O(2C) ^e	2.51	109	71
...O(5C) ^e	2.14	149	
O(3A)—H...O(3A) ^a	2.40	152	79
...O(1A) ^a	2.08	128	
O(2C)—H...O(1C) ^b	2.40	120	93
...O(3C) ^f	2.01	139	
O(4B)—H...O(5A)	2.33	131	80
...O(2A)	1.96	149	

All atoms lacking superscripts are positioned at (*x*, *y*, *z*).

- | | | | |
|-----|--|-----|---|
| (a) | $\frac{1}{2} - x, \bar{y}, -\frac{1}{2} + z$ | (d) | $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$ |
| (b) | $x, y, 1 + z$ | (e) | $1 + x, y, -1 + z$ |
| (c) | $\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$ | (f) | $\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$ |

The application of the Allinger (1976) molecular-mechanics program *MMI* (Quantum Chemistry Program Exchange No. 318) predicted the conformation of the pyranose ring in good agreement with the observed molecules, but there were discrepancies arising from the assumed equilibrium distances of the C—O bonds, which were about 0.05 Å too small. This was improved by using *MMI-CARB*, a version of *MMI* in which the C—O equilibrium distances and some valence angles involving the anomeric C atom, C(1), had been changed to give a better fit to the molecular dimensions of pyranoses and methyl pyranosides determined by neutron diffraction (Jeffrey & Taylor, 1980). The energy-minimization method and functions used in *MMI* have been described by Allinger & Chung (1976, and references therein). The empirical constants are given in the program documentation of QCPE No. 318. The equilibrium bond lengths used were C—C 1.514, C—O 1.405, O—H 0.97 Å, except C(5)—O(5) 1.412, O(5)—C(1) 1.396, and C(1)—O(1) 1.380 Å. Oxygen lone pairs were treated as 'pseudo-atoms' with an equilibrium O—l.p. distance of 0.5 Å and an equilibrium l.p.—O—l.p. angle of 140°. The bond moments used were those chosen by Allinger & Chung (1976) to reproduce the dipole moments of ethers and alcohols.

The observed atomic parameters for each of the three molecules were used as starting coordinates for the molecular-mechanics energy minimization. With *MMI*, molecules *B* and *C* converged on the same minimum at

123.3 kJ mol⁻¹, but *A* converged on a slightly different minimum at 127.9 kJ mol⁻¹. Using *MMI-CARB*, all three molecules converged on the same minimum at 117.7 kJ mol⁻¹. A slightly better least-squares molecular fit was also obtained with the modified program, giving a mean difference of 0.04 Å, versus 0.05 Å for the *MMI* program.

The agreement between the mean observed and the calculated dimensions is given in Table 4 for comparison with the observed differences between the three molecules shown in Fig. 1. With the exception of the bond lengths C(6)—O(1) and C(5)—O(5), the *MMI-CARB* program reproduced the dimensions of the molecule to within 3σ for an individual molecule. The C(6)—O(1) and C(5)—O(5) bonds are the external bonds in a C—O—C—O—C sequence and have been observed to be longer than normal both in other 1,6-anhydro sugars (*cf.* Table 3 in Noordik & Jeffrey, 1977) and in the linkage bonds between residues in oligosaccharides (*cf.* Table 5 in Jeffrey, Pople & Radom, 1974). Although this is also believed to be a consequence of the 'anomeric effect', it was not parameterized as such in *MMI-CARB*, as were the better-understood C(1)—O bond lengths and torsion potentials.

The orientations of the three hydroxyl groups given in Table 3 depend on the intermolecular hydrogen bonding, which is not modelled by the molecular-mechanics calculations which refer to isolated molecules. The large discrepancies shown in Table 3 between the observed and calculated values of these torsion angles are therefore neither unexpected nor significant.

A further calculation was carried out with the three C—C—O—H torsion angles fixed at their observed value for the three molecules. This gave minimum energies of

147.6, 136.3 and 130.4 kJ mol⁻¹ for molecules *A*, *B* and *C* respectively, significantly greater than those of the unrestricted molecules. There were also small differences in the optimized bond lengths and valence angles which were less than the experimental standard deviations. The mean values for the three molecules are shown in Table 4.

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Crystal and Molecular Structures of Diazapolycyclic Compounds.

VI. 1*H*,4*H*- and 3*H*,4*H*-2,3-Dimethylpyridazino[1,2-*b*]benzo[*g*]phthalazine-6,13-dione

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Abstract

The crystal structures of 1*H*,4*H*- and 3*H*,4*H*-2,3-dimethylpyridazino[1,2-*b*]benzo[*g*]phthalazine-6,13-

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dione have been solved by direct methods. The molecules have been compared by half-normal probability plots. The rings to which the methyl groups are bonded present different conformations. The hybridization of the N atoms is almost *sp*². [Crystal data: C₁₈H₁₆N₂O₂, *M*_r = 292.34. Isomer 1*H*,4*H*: triclinic, *P*1, *a* = 13.1795 (9), *b* = 8.0356 (5), *c* = 7.8197 (5) Å,