

The Structures of Medium-Ring Compounds.

XVIII. X-ray and Neutron Diffraction Analysis of Cyclodecane-1,6-*trans*-diol*

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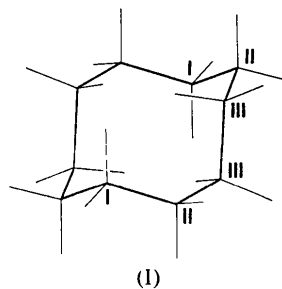
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The crystal structure of cyclodecane-1,6-*trans*-diol (monoclinic, $a = 11.168$, $b = 11.728$, $c = 8.072$ Å, $\beta = 110.86^\circ$, space group $P2_1/c$, $Z = 4$) has been determined by X-ray analysis and refined by least-squares analysis of neutron diffraction data. The crystal contains two crystallographically independent types of centrosymmetric molecules, which have similar ring conformations with the hydroxyl substituents at C(II) carbon atoms in the 'semi-axial' positions. The main difference is in the orientation of the O-H bonds, which are antiplanar to C(III)-C(II) in one type, synclinal in the other. The most important result is the experimental verification of short transannular H...H distances (*circa* 1.95 Å) in the cyclodecane ring, accompanied by significant deviations of the methylene groups involved from local C_{2v} symmetry.

Introduction

X-ray crystallographic studies of several cyclodecane derivatives (Dunitz, 1968) have established the existence of a single, fairly well defined conformation (I) for the cyclodecane ring. This stable conformation, which can be recognized as a distortion of a diamond-lattice conformation, is characterized by having very short transannular H...H distances. Indeed, with all CCC angles tetrahedral and all CCCC partial conformations exactly staggered, the transannular H...H distances would be so short as to lead to enormous repulsive forces. In the observed conformation the CCC angles have been widened to values of $115-118^\circ$, and the CCCC partial conformations deviate from staggered in such a way as to increase the transannular H...H distances to more tolerable values. However, although the carbon skeleton of the cyclodecane ring can be defined rather accurately from the available experimental evidence (Dunitz, 1968) it has not been possible so far to determine the hydrogen positions with the desired accuracy from the X-ray analyses mentioned above because of well known limitations of the method. Of course, the hydrogen positions can be estimated from stereochemical considerations, *e.g.* by assuming the methylene groups to have local C_{2v} ($mm2$) symmetry and known dimensions. Such considerations lead to transannular H...H distances as short as 1.85 Å, but since there is little doubt that strong repulsion is still effective at such distances, the actual distances

must be somewhat larger than those calculated in this way. A knowledge of the H...H distances that actually occur in such 'overcrowded' molecules as cyclodecane is important for defining some of the parameters used in empirical force-field calculations. In addition, to the best of our knowledge, no reliable information has been available up till now concerning the deviations from C_{2v} symmetry that occur in methylene groups under steric compression. A neutron-diffraction study of a suitable compound was clearly indicated to fill these gaps in our knowledge. A survey of cyclodecane derivatives showed that the 1,6-diols might be specially suitable for accurate structural studies. They have high melting points (*circa* 150°C) so that the effects of thermal vibration should not be too severe at room temperature, and they can be obtained as reasonably large single crystal specimens.



Because of the very large incoherent neutron scattering by protons, it would have been advantageous to use a perdeuterated sample for the neutron-diffraction study. However, the synthesis of perdeuterated compounds of this type would appear to be rather difficult

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and time-consuming (Sicher, 1970) so that we deemed it preferable to study the more easily available non-deuterated substances. The sample of *trans*-1,6-diol used for the present investigation was prepared by catalytic hydrogenation of cyclodecan-1,6-olone provided by Dr H. Westen. The product crystallized from acetone yielded two recognizably different types of crystal, which were eventually identified as the *trans*-diol and as a molecular compound of *cis*- and *trans*-diol in the ratio 2:1.

X-ray analyses have been carried out for the *trans*-diol, for the molecular compound mentioned above, and for the *cis*-diol. The structure of the *trans*-diol, as refined by neutron-diffraction analysis, was discussed in a preliminary communication (Ermer & Dunitz, 1971) and is described in detail in the present paper. Results for the other two crystals will be given elsewhere.

Crystallographic data

Cyclodecane-1,6-*trans*-diol, C₁₀H₂₀O₂; m.p. 152° (Prelog & Schenker, 1952); monoclinic, $a=11.168$, $b=11.728$, $c=8.072$ Å, $\beta=110.86^\circ$, $U=988.0$ Å³, $D_m=1.13$, $D_x=1.15$ g cm⁻³, $Z=4$, space group $P2_1/c$. Large, thick prismatic crystals were readily obtained from acetone solution. The volume of the crystal used for the neutron diffraction analysis was 15.6 mm³. The

cell dimensions given above were obtained from X-ray measurements on a 4-circle diffractometer (Mo $K\alpha$ radiation, $\lambda=0.71069$ Å) and have errors of the order of 0.1%.

X-ray intensities

The X-ray intensities of 1936 independent reflections were measured on a computer-controlled 4-circle diffractometer equipped with a graphite monochromator (Mo $K\alpha$ radiation: ω step-scan; $\sin \theta/\lambda$ limit 0.62).

Neutron intensities

The neutron intensity measurements ($\lambda=0.9958$ Å) were performed on a computer-controlled 4-circle diffractometer at the Brookhaven National Laboratory High Flux Beam Reactor. 1735 non-zero intensities in the range out to $\sin \theta/\lambda=0.60$ were measured with an $\omega/2\theta$ step-scan technique. Two standard reflexions were recorded every 30 measurements. Their intensities did not change significantly throughout the data collection. After correction for absorption (Gaussian numerical integration, $\mu=2.84$ cm⁻¹, assuming an incoherent scattering cross-section of 35 barns for H) and averaging over equivalent reflexions, 1596 independent intensity measurements remained.

Table 1. Atomic coordinates and vibration tensor components in crystal coordinate system (all $\times 10^4$)

The U_{ij} values have standard deviations in the ranges 0.0009–0.0020 for carbon and oxygen, 0.0021–0.0062 for hydrogen

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	913 (2)	-1237 (2)	-38 (3)	351	443	295	74	53	-29
C(2)	1202 (2)	-1422 (2)	1935 (3)	386	417	306	88	66	49
C(3)	620 (3)	-574 (2)	2854 (3)	535	644	297	218	166	111
C(4)	976 (3)	687 (2)	2906 (3)	548	590	337	192	-73	-125
C(5)	516 (2)	1365 (2)	1173 (3)	377	408	443	11	26	-67
C(11)	5074 (2)	-1475 (2)	-682 (3)	439	502	333	-100	70	-38
C(12)	4570 (2)	-1085 (2)	-2607 (3)	464	490	314	-137	126	-85
C(13)	4358 (2)	198 (2)	-2948 (3)	461	514	373	-103	117	-6
C(14)	3362 (3)	826 (3)	-2386 (3)	409	685	414	24	-9	-69
C(15)	3623 (2)	954 (3)	-411 (4)	305	747	459	-13	74	-110
O(1)	2562 (3)	-1423 (3)	2862 (4)	418	532	322	100	-3	-18
O(11)	3411 (3)	-1699 (3)	-3470 (4)	552	569	330	-257	46	-62
H(1A)	1266 (5)	-430 (5)	-242 (6)	555	687	470	6	135	74
H(1B)	1483 (5)	-1855 (5)	-459 (7)	640	784	545	260	112	-80
H(2)	841 (6)	-2266 (6)	2075 (7)	682	623	658	-17	133	214
H(3A)	913 (7)	-867 (6)	4238 (7)	1060	1043	373	386	272	182
H(3B)	-421 (6)	-666 (6)	2318 (8)	612	951	699	131	321	192
H(4A)	2026 (6)	759 (6)	3502 (9)	550	850	820	32	-189	-109
H(4B)	590 (8)	1100 (6)	3816 (8)	1386	1068	466	475	250	-151
H(5A)	1106 (5)	1116 (5)	381 (8)	486	822	694	44	200	-21
H(5B)	723 (6)	2266 (6)	1516 (9)	767	543	863	-14	-28	-92
H(O1)	2920 (5)	-2050 (5)	2399 (6)	517	666	415	127	80	19
H(11A)	4354 (5)	-1288 (5)	-117 (7)	524	848	459	-139	147	-36
H(11B)	5140 (6)	-2413 (5)	-698 (7)	933	567	630	-69	17	50
H(12)	5284 (5)	-1344 (5)	-3193 (7)	685	762	663	2	337	-87
H(13A)	4053 (6)	293 (5)	-4375 (7)	841	806	433	-71	138	33
H(13B)	5288 (5)	624 (5)	-2412 (8)	579	738	703	-196	180	-20
H(14A)	2433 (5)	402 (6)	-2980 (8)	367	1181	684	-102	-41	-210
H(14B)	3251 (7)	1681 (6)	-2959 (8)	991	897	642	159	152	163
H(15A)	3508 (5)	154 (7)	106 (8)	562	929	643	-125	159	-10
H(15B)	2853 (6)	1512 (6)	-266 (9)	529	1072	907	202	230	-173
H(O11)	3127 (5)	-1568 (4)	-4727 (7)	648	608	394	-102	35	-44

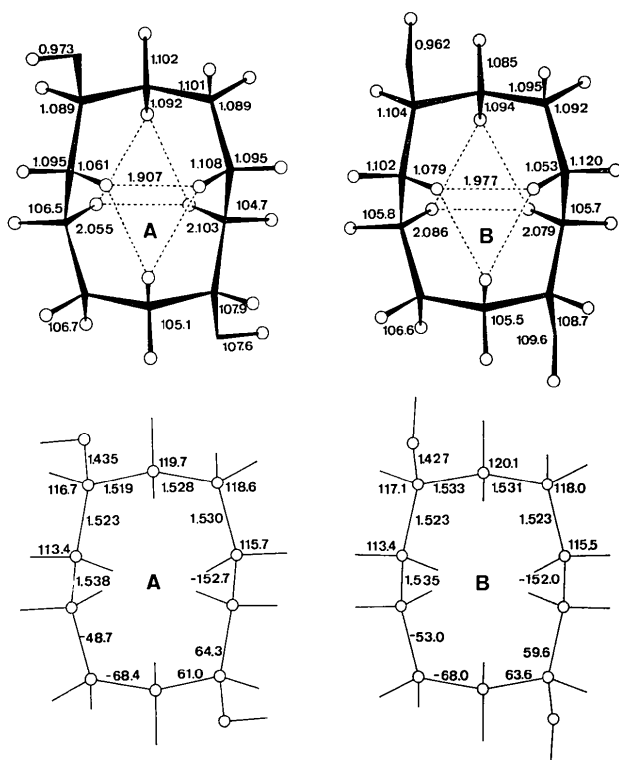


Fig. 2. Top: Interatomic distances (Å) and angles (°) involving hydrogen atoms (for HCC angles see Fig. 3). Average standard deviations: 0.006 Å for C-H and O-H, 0.008 Å for H...H, 0.5° for HCH, 0.4° for HCO and HOC. Bottom: Bond distances (Å), angles and torsion angles (°) involving heavy atoms only. Average standard deviations: 0.003 Å for C-C and C-O, 0.2° for bond angles, 0.3° for torsion angles.

Discussion

The four molecules in the unit cell are not in the general positions of the space group $P2_1/c$. Instead, there are two crystallographically independent kinds of molecule, one kind with its centre at the special positions (0,0,0), etc. the other at $(\frac{1}{2}, 0, 0)$, etc. Both kinds of molecule have the stable cyclodecane conformation with the hydroxyl substituents at type II carbons (Fig. 1), but there is a difference in the orientation of the hydroxylic protons. In molecule *A* the O-H bond is synclinal with respect to C(III)-C(II), antiplanar with respect to C(I)-C(II), whereas in molecule *B* these relations are reversed. This difference is associated with differences in the hydrogen-bonding behaviour of the two kinds of molecules, with quite definite changes in skeletal torsion angles and transannular H...H distances, and also with smaller differences between corresponding bond distances and bond angles (Figs. 2 and 3). For certain purposes we shall disregard these differences, averaging over the two sets of molecular parameters where it seems appropriate.

The shortest transannular H...H distances between pairs of type III methylene groups are 1.91 Å in molecule *A* and 1.98 Å in molecule *B*, significantly different. The next shortest are 2.05–2.10 Å in molecule *A* and 2.08–2.09 Å in *B*. This represents the first experimental verification that short transannular H...H distances occur in the cyclodecane ring. The observed distances are indeed somewhat longer than the earlier estimates of 1.84 Å (shortest) and 1.97 Å (next shortest) derived from the cyclodecane carbon skeleton by assuming local C_{2v} symmetry of the methylene groups with rea-

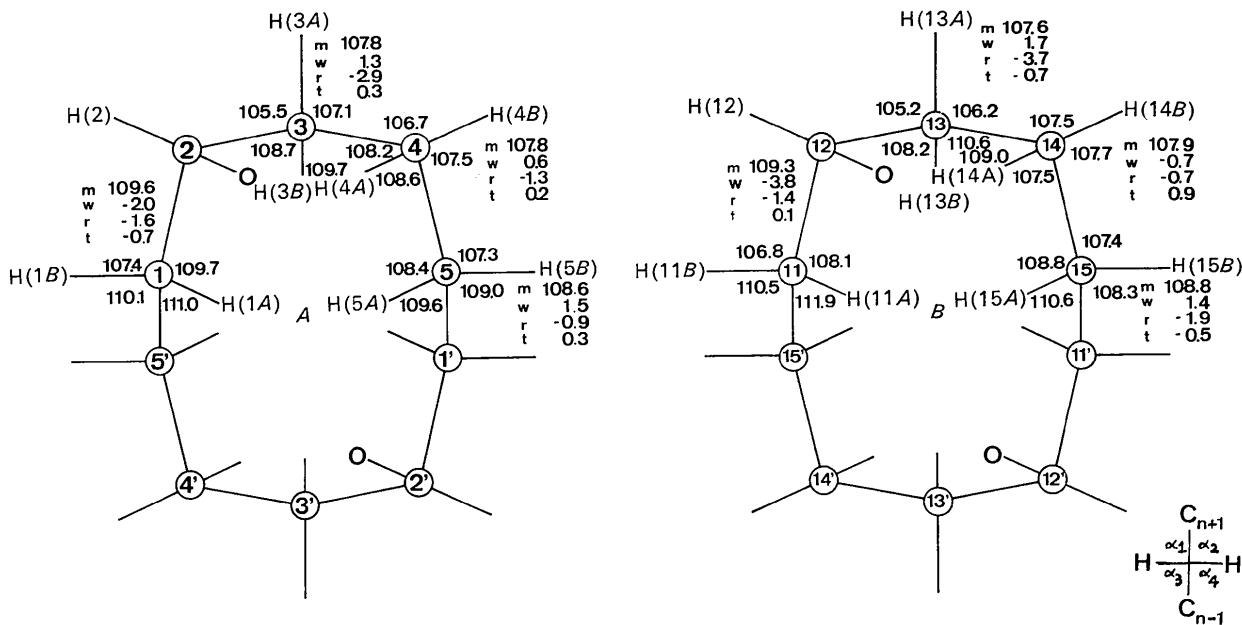


Fig. 3. HCC angles (standard deviations 0.4°) and various linear combinations: *m* (mean), *w* (wag), *r* (rock), and *t* (twist), as explained in text.

sonable C–H distances (1.10 Å) and HCH angles (107°). However, these earlier estimates were explicitly described (Dunitz, 1968) as lower limits, subject to an increase of unknown magnitude from the effects of non-bonded repulsion. The most striking effect of such repulsions on the molecular geometry is to cause significant deviations from local C_{2v} symmetry at some of the type I and III methylene groups. These deviations are conveniently discussed in terms of the following linear combinations

$$\begin{aligned} m &= \frac{1}{4}(\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4) \\ w &= \frac{1}{2}(\alpha_1 + \alpha_2 - \alpha_3 - \alpha_4) \\ r &= \frac{1}{2}(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4) \\ t &= \frac{1}{2}(\alpha_1 - \alpha_2 - \alpha_3 + \alpha_4) \end{aligned}$$

of the four HCC-angles, $\alpha_1, \alpha_2, \alpha_3, \alpha_4$, at a given methylene group (Fig. 3). These linear combinations (symmetry coordinates) provide a measure of the amount of distortion associated with the wag, rock and twist type of deformation, respectively. For the type I methylene groups the HCH bisector is markedly rocked out of the CCC plane ($r = 2.9^\circ$ for molecule *A* and 3.7° for molecule *B*). The rocking deformations at type III atoms are smaller (average 1.5°), those at type II still smaller (average 1.0°). Distortions corresponding to wagging motions of the methylene groups (HCH plane bent out of CCC bisector) are $w = 3.8^\circ$ at C(11) and 2.0° at C(1), [1.4° at C(15) and 1.5° at C(5)], all type III, while twisting distortions (HCH plane twisted round CCC bisector) are less than 0.9° and not significant. All the larger deviations are in such a sense as to increase the transannular H...H distances from the values they would have if strict C_{2v} symmetry were imposed on the methylene groups.

The effect of mutual repulsion between intra-annular hydrogen atoms also shows itself in other ways. The six independent intra-annular C–H distances (uncorrected for thermal motion) vary from 1.053 to 1.108 Å, mean value 1.081 Å, and the remaining 12 C–H distances vary from 1.085 to 1.120 Å, mean value 1.097 Å. The HCH angles cover the range 104.7 – 106.7° , with the two largest angles at C(4) and C(14), the only methylene groups with both hydrogen atoms extra-annular, and the smallest at C(1), presumably due to the influence of molecular packing (see below).

The CCC angles at type I are 119.7 and 120.1° , those at type II lie in the range 116.7 – 118.6° , those at type III in the range 113.4 – 115.7° . This angle pattern, with the marked widening at types I and II, agrees with the results of numerous earlier structural studies of cyclodecane derivatives (Dunitz, 1968).

One might expect from general considerations that increase in CCC (from the tetrahedral angle) should be accompanied by a decrease in HCH, even in the absence of specific non-bonded repulsions like those mentioned above. We have surveyed the dimensions of methylene groups (flanked by two carbon atoms) as determined by neutron diffraction in various crystals. The

observed HCH angles are plotted against CCC in Fig. 4. There is obviously no clear-cut trend and, in particular, the observations give no support for the view (Mislow, 1965) that the two angles are related by the equation

$$\cos(\text{HCH}) = \frac{\cos(\text{CCC}) + 1}{3 \cos(\text{CCC}) - 1}$$

derived from a simple hybridization model. The range of observed CCC angles extends over about 9° , whereas the HCH angles extend over less than 5° . With the limited information available the 'best' value for HCH would appear to be about 106° (for CCC in the range 111 – 120°). Neutron-diffraction analyses of perdeuterated polyethylene or other long-chain compounds would be of value for defining the dimensions of a 'standard' methylene group, while similar systematic investigations on strained molecules containing nonstandard methylene groups should also be carried out to provide the information required for useful comparison.

It is at least apparent that the magnitudes of the various effects of non-bonded repulsion depend on a complicated interplay of forces, the results of which are impossible to foresee intuitively. We have therefore carried out energy-minimization calculations using two recently developed consistent force fields (Warshel &

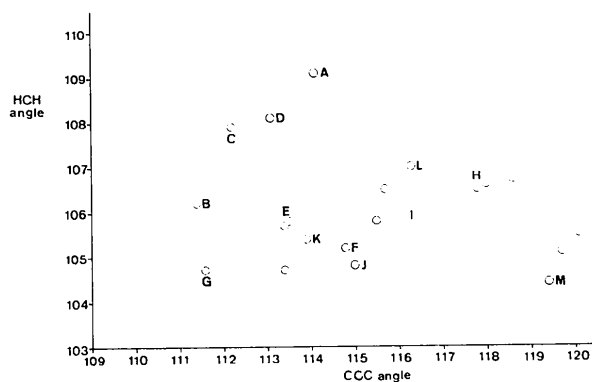


Fig. 4. Plot of HCH *vs.* CCC angles at methylene groups (flanked by two carbon atoms) from various neutron diffraction analyses. The labelled points are from:

- A–C* L-lysine HCl.2H₂O (Koetzle, Lehmann, Verbist & Hamilton, 1972).
- D* L-histidine (Lehmann, Koetzle & Hamilton, 1972*a*).
- E* L-asparagine.H₂O (Verbist, Lehmann, Koetzle & Hamilton, 1972).
- F, G* L-arginine 2H₂O (Lehmann, Verbist, Hamilton & Koetzle, 1973).
- H, I* L-glutamic acid (Lehmann, Koetzle & Hamilton, 1972*b*).
- J–L* (1,1'-trimethylene-dicyclopentadienyl)TiCl₂ (Epstein & Bernal, unpublished).
- M* KH malonate (Currie & Speakman, 1970).

The unlabelled points are from the present analysis.

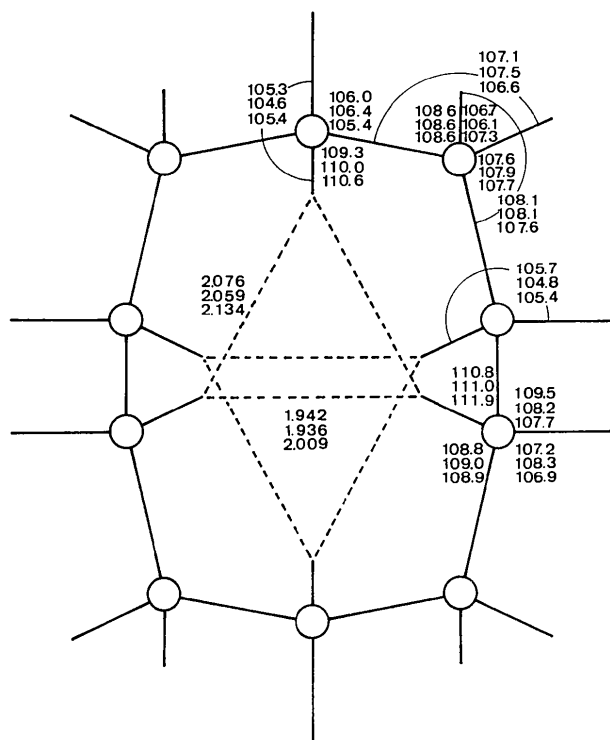


Fig. 5. Comparison of observed angles (averaged over molecules *A* and *B* and over C_{2h} molecular symmetry where appropriate) with angles derived from force-field calculations. The order is: observed (top), Warshel & Lifson, 1970 (middle), Ermer & Lifson, 1973 (bottom).

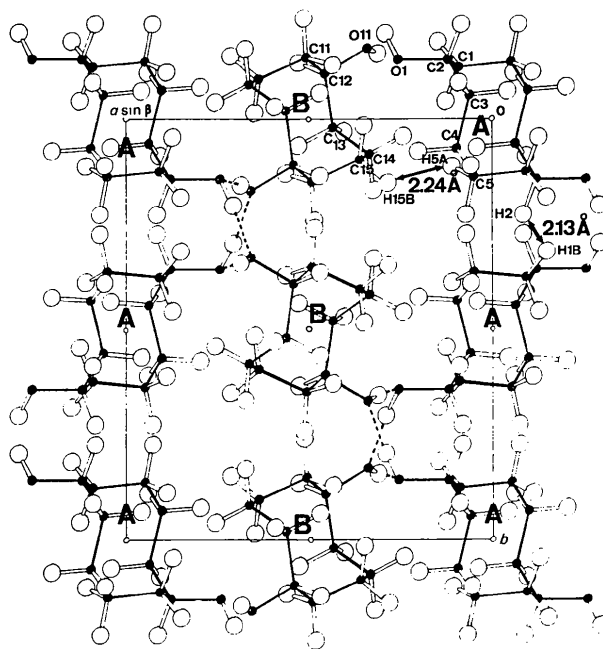


Fig. 6. Packing diagram. For clarity the heavy-atom skeletons are drawn in heavy line, hydrogen bonds dashed.

Lifson, 1970; Ermer & Lifson, 1973). The calculations were made for the unsubstituted cyclodecane molecule since potential functions of the required quality are not available for interactions involving the hydroxyl group. In Fig. 5 the resulting structural parameters involving hydrogen atoms are compared with the observed parameters averaged over the two molecules and over all atoms of a given conformational type. Considering that the two molecules are significantly different from one another and that both deviate markedly from C_{2h} molecular symmetry the agreement must be regarded as satisfactory in that the various distortions of CH_2 groups from local C_{2v} symmetry are reproduced by the force-field calculations. The averaged transannular $\text{H}\cdots\text{H}$ distances are reproduced better by the Warshel-Lifson CFF than by the Ermer-Lifson one: we shall return to this point after discussing the molecular packing.

The minimum-energy conformation of cyclodecane turns out to have exact C_{2h} symmetry in both calculations. The same result is also obtained using various other reasonable force fields. However, as mentioned above the present analysis leads to carbon skeletons that are significantly distorted from C_{2h} symmetry. Indeed the 16° difference between pairs of 'equivalent' torsion angles around $\text{C(II)}-\text{C(III)}$ in molecule *A* is much larger than that observed in any other cyclodecane derivative possessing the stable conformation. Typical differences between such pairs of equivalent torsion angles amount to $4-8^\circ$, as in molecule *B*. The unusually large distortions in molecule *A* are probably mainly due to intermolecular forces rather than to any intramolecular effects of the hydroxyl groups, as an analysis of the molecular packing shows.

The crystal structure (Fig. 6) is built from sheets in which each molecule of a given type (*A* or *B*) is surrounded by two molecules of its own type and by two of the other type. The $A\cdots A$ and $B\cdots B$ interactions involve only van der Waals contacts, but molecules of different types are linked by hydrogen bonds [$\text{O(11)}\cdots\text{O(1)}(x, y, z-1)$: 2.788 \AA ; $\text{O(11)H}\cdots\text{O(1)}$: 1.828 \AA], which run approximately parallel to *c*. The sheets are interlinked by the second kind of hydrogen bond [$\text{O(1)}\cdots\text{O(11)}(x, -\frac{1}{2}-y, \frac{1}{2}+z)$: 2.763 \AA ; $\text{O(1)H}\cdots\text{O(11)}$: 1.795 \AA] between hydroxyl groups of *A* molecules.

These hydrogen bonds between sheets bring pairs of hydrogen atoms belonging to different *A* molecules into very close contact [$\text{H(2)}\cdots\text{H(1B)}(x, \frac{1}{2}-y, -\frac{1}{2}+z)$: 2.127 \AA]. This short contact appears to be responsible for the large distortions of the carbon skeleton of molecule *A* from C_{2h} symmetry.

Inspection of the packing diagram (Fig. 6), preferably with the help of molecular models, shows that the repulsive force between these two hydrogen atoms has a large component perpendicular to both $\text{C}-\text{H}$ bonds and to the $\text{C(1)}-\text{C(2)}$ bond. This force tends to increase the absolute value of the $\text{H(1B)}-\text{C(1)}-\text{C(2)}-\text{H(2)}$ torsion angle and to decrease the HCH angle at C(1) . (The latter is indeed the smallest of all HCH angles;

see Fig. 2). If the methylene groups were completely rigid this motion would make the short transannular distance $H(1A)\cdots H(5A)$ even shorter than in the free molecule. Inspection of a molecular model indeed suggests that the molecule yields to this force mainly by a shearing motion of the two longer sides of the 10-membered ring, in qualitative agreement with the observed distortion from C_{2h} symmetry.

The shortening of the transannular distance $H(1A)\cdots H(5A)$ in molecule *A* is evident from the observed dimensions (Fig. 2) and one might infer that this distance in the free molecule is even slightly longer than observed for molecule *B*, which also deviates a little from the expected C_{2h} symmetry, in the same sense as molecule *A*. This slight distortion of molecule *B* may also result from intermolecular forces, in particular from the repulsion connected with the second shortest intermolecular contact (2.24 Å) between $H(5A)$ and $H(15B)$. (All other $H\cdots H$ intermolecular contacts are greater than 2.3 Å). The shortest transannular distance $H(1A)\cdots H(5A)$ is calculated to be 1.94 Å and 2.01 Å from force-fields I and II, respectively. Thus the force field II (Ermer & Lifson, 1973) may give a better estimate for gaseous cyclodecane.

The short intermolecular $H\cdots H$ distance of 2.13 Å is almost 0.3 Å shorter than the accepted van der Waals diameter of 2.4 Å for hydrogen. The potential function for non-bonded $H\cdots H$ interactions derived in the Ermer-Lifson calculation is:

$$V_{HH}(r) = 903.8/r^9 - 28.30/r^6$$

$(r \text{ in } \text{Å}, V_{HH} \text{ in kcal mole}^{-1})$

according to this function, $V(2.13) = 0.7 \text{ kcal mole}^{-1}$, a substantial amount but quite small in comparison with a hydrogen-bonding energy of about 5 kcal mole⁻¹.

This whole discussion of the effects of intermolecular forces would be on a much more tenuous basis without accurate experimental information about the hydrogen positions. Such information is a prerequisite for any significant confrontation between the results of structural studies in the solid phase and those obtained by calculations on isolated molecules.

Analysis of the experimental vibration tensors (Fig. 7) in terms of rigid-body translational and librational motions of the molecules according to the procedure of Schomaker & Trueblood (1968) gave very poor agreement between observed and calculated tensor components U_{ij} . The values of $Q = \langle (U_{ij}^{\text{obs}} - U_{ij}^{\text{calc}})^2 \rangle^{1/2}$ was about 0.0094 Å² for both molecules compared with e.s.d.'s of 0.0009–0.0062 Å² for the experimental values. This poor level of agreement was not altogether surprising since it is not self-evident that the cyclodecane ring system should behave as a rigid body. However, examination of the results of the rigid-body calculation revealed an interesting systematic behaviour. For the heavy atoms the calculated values of U_{ii} (diagonal elements of vibration tensors) were uniformly too large,

while for the hydrogen atoms they were too low. This suggested that the rigid-body approximation might hold better for the heavy-atom skeleton than for the attached hydrogen atoms. Accordingly, the calculations were repeated, whereby the least-squares fitting was carried out only on the vibrational tensors of the heavy atoms.

The values of Q dropped to 0.0017 for molecule *A* and to 0.0022 Å² for molecule *B*, as low as can be expected in view of the uncertainties in the experimental data. Both molecules thus appear to behave reasonably well as rigid bodies as far as the heavy-atom skeletons are concerned. The largest eigenvalues of the librational tensors are 6.3° for molecule *A* and 5.9° for molecule *B*. In both cases the corresponding librational axis is approximately coincident with the line interconnecting the alcoholic hydrogen atoms so that the hydrogen-bonding interactions are least affected by this libration mode.

The vibrational amplitudes of the hydrogen atoms, calculated from the rigid-body motion of the heavy-atom skeleton are consistently smaller than the observed ones (except for the hydroxyl hydrogens). The residual vibration tensors obtained by subtraction of the rigid-body motions were analysed. For seven out of the 20 hydrogen atoms, one eigenvalue of the residual thermal motion tensor turns out to be slightly negative, indicating that the subtraction of the rigid-body motion has been somewhat overdone.

In all cases the largest eigenvalue of the residual thermal motion tensor is nearly perpendicular to the C–H bonds. In no case is there any appreciable residual motion parallel to the C–H bonds (it is in these directions that the mean square amplitudes of vibration are negative in some cases). The residual motion thus corresponds mainly to internal modes involving angle bending, similar to that calculated from normal-coordinate analysis of spectroscopic data for benzene and cyclobutane (Johnson, 1970).

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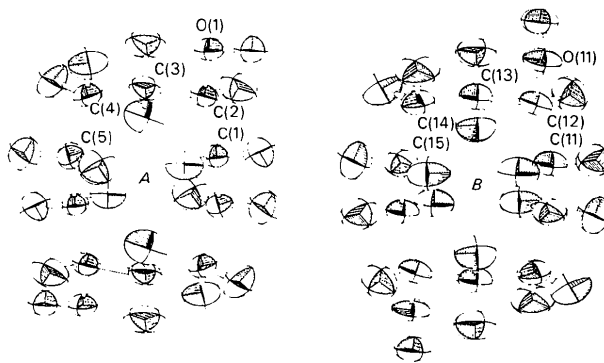


Fig. 7. Thermal ellipsoids based on parameters of Table 1 and drawn by ORTEP (Johnson, 1965).

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References

- BACON, A. E. (1962). *Neutron Diffraction*, p. 31. Oxford Univ. Press.
- COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.
- CURRIE, M. & SPEAKMAN, J. C. (1970). *J. Chem. Soc. (A)*, pp. 1923–1926.
- DUNITZ, J. D. (1968). *Perspectives in Structural Chemistry*, edited by J. D. DUNITZ & J. A. IBERS. Vol. 2, pp. 1–70. New York: John Wiley.
- EPSTEIN, E. F. & BERNAL, I. (1973). Unpublished results.
- ERMER, O. & DUNITZ, J. D. (1971). *Chem. Commun.* pp. 178–179.
- ERMER, O. & LIFSON, S. (1973). *J. Amer. Chem. Soc.* **95**, 4121–4132.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory. Oak Ridge, Tennessee.
- JOHNSON, C. K. (1970). *Thermal Neutron Diffraction*, edited by B. T. M. WILLIS, p. 149. Oxford Univ. Press.
- KOETZLE, T. F., LEHMANN, M. S., VERBIST, J. J. & HAMILTON, W. C. (1972). *Acta Cryst.* **B28**, 3207–3214.
- LEHMANN, M. S., KOETZLE, T. F. & HAMILTON, W. C. (1972a). *Int. J. Peptide Protein Res.* **4**, 229–239.
- LEHMANN, M. S., KOETZLE, T. F. & HAMILTON, W. C. (1972b). *J. Cryst. Mol. Struct.* **2**, 225–233.
- LEHMANN, M. S., VERBIST, J. J., HAMILTON, W. C. & KOETZLE, T. F. (1973). *J. Chem. Soc. Perkin II*, in the press.
- MISLOW, K. (1965). *Introduction to Stereochemistry*, p. 17. New York: Benjamin.
- PRELOG, V. & SCHENKER, K. (1952). *Helv. Chim. Acta*, **35**, 2044–2053.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- SICHER, J. (1970). Private communication.
- VERBIST, J. J., LEHMANN, M. S., KOETZLE, T. F. & HAMILTON, W. C. (1972). *Acta Cryst.* **B28**, 3006–3013.
- WARSHEL, A. & LIFSON, S. (1970). *J. Chem. Phys.* **52**, 582–594.

Acta Cryst. (1973). **B29**, 2285

The Structure of β -LiIO₃

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β -LiIO₃ crystallizes in space group $P4_2/n$ with $a = 9.7329$ (7), $c = 6.1566$ (7) Å, $Z = 8$. The intensities were collected with a diffractometer. The final R based on F is 0.059. The structure consists of discrete IO₃ groups in the form of distorted trigonal pyramids, and distorted LiO₄ tetrahedra. Each tetrahedron shares two corners with two other tetrahedra. The mean bond distances are I–O = 1.79, Li–O = 1.98 Å.

Introduction

Three modifications of LiIO₃ are known. α -LiIO₃ can be transformed reversibly into γ -LiIO₃ at about 250°C. The retransformation γ - α takes place at about 200°C. γ -LiIO₃ can be transformed irreversibly into β -LiIO₃ at about 300°C. β -LiIO₃ is stable up to the melting point (435°C) (Liebertz, 1969; Matsumura, 1971). The transformation behaviour is strongly influenced by contamination of LiIO₃ by small amounts of HIO₃ (Arend, Remoissenet & Staehlin, 1972). Furthermore, the α - and β -phases can be grown from neutral and acid aqueous solution at different temperatures (Desvignes & Remoissenet, 1971).

α -LiIO₃ crystallizes in space group $P6_3$ with $a = 5.18$, $c = 5.17$ Å. The iodine atoms are surrounded by six oxygens in a distorted octahedral arrangement. They form discrete trigonal IO₃ groups with I–O = 1.81 Å and O–I–O = 99°. Each oxygen is bonded to two iodine

atoms forming a three-dimensional network of I–O bonds (Rosenzweig & Morosin, 1966; de Boer, van Bolhuis, Olthof-Hazekamp & Vos, 1966). The features of the I–O network agree with other iodate structures. The lithium atoms have an octahedral coordination with Li–O = 2.12 Å.

The orthohexagonal cell of γ -LiIO₃ was determined from high temperature powder diffractometer values by Matsumura (1971): $a = 19.1$, $b = 11.14$, $c = 10.44$ Å. This cell is closely related to the cell of α -LiIO₃. The structure of γ -LiIO₃ is not yet known.

Experimental

Polycrystalline samples were prepared from large single crystals (diameter about 1 cm) of β -LiIO₃ for a determination of the lattice constants with a Jagodzinski–Guinier camera and Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å). Silicon was used as an internal standard. The lat-