Structure of 7-Methyl-1(2)a,1(6)a,3(4)a-trihomocubane-1(6)a,3(4)a-dione,* $C_{12}H_{12}O_2$.
A Case of Enantiomeric and Rotational Disorder

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Abstract. $M_r = 188 \cdot 22$, monoclinic, $P2_1/n$, $a = 6 \cdot 219$ (2), $b = 10 \cdot 508$ (2), $c = 7 \cdot 339$ (1) Å, $\beta = 107 \cdot 64$ (2)°, $V = 457$ Å^3, $Z = 2$, $D_m = 1 \cdot 360$ (3), $D_x = 1 \cdot 366$ (2) Mg m^{-3}, λ(Mo $K\alpha$) $= 0 \cdot 7107$ Å, $\mu = 0 \cdot 053$ mm^{-1}, $F(000) = 200$, $T = 293$ K. Final $R = 5 \cdot 8\%$ for 614 significant reflections. The molecule, which does not possess a centre of symmetry, occupies a crystallographic centre of symmetry because of the statistical enantiomeric and rotational disorder. Lattice-energy calculations, based on van der Waals attractive and repulsive potentials, clearly show minima at the observed disordered positions.

Introduction. In connection with synthetic investigations on polycyclic molecules as possible models for light-energy-storage systems, the molecules shown in Fig. 1 were synthesized by Mehta & Srikrishna (1982). The authors observed that the molecules underwent cyclobutane-ring cleavage upon heating, which upon irradiation yielded the starting material, and it is this aspect of these molecules that suggested themselves as possible candidates for the reversible storage of solar energy. Interestingly, to explain the products obtained, upon heating, required cleaving bonds *a* in (I), but bonds *b* in (II). X-ray crystallographic investigation was undertaken with the aim of correlating the observed chemical reactivity pattern with the molecular geometry. Although the original aim of the study could not be achieved for reasons detailed below, the crystal structure of (I) presented some interesting features.

Experimental. Single crystals of (I), kindly supplied by Professor G. Mehta, were obtained from a mixture of ethyl acetate and methanol by slow evaporation, D_m measured by flotation in KI solution. A crystal with approximate dimensions $0 \cdot 30 \times 0 \cdot 30 \times 0 \cdot 50$ mm used for data collection; preliminary Weissenberg photographs indicated that the crystals are monoclinic with two molecules in the unit cell; 12 reflections used for measuring lattice parameters; intensity data collected on a Nonius CAD-4 diffractometer, graphite-

monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ scan mode, scan speed 1° min^{-1}, $\theta < 23 \cdot 5$°; 713 unique reflections collected (range of *hkl*: $h\,0{\to}6$, $k\,0{\to}11$, $l\,{-}8{\to}8$) of which 614 judged significant ($|F_o| > 3\sigma|F_o|$); intensities not corrected for absorption; standard reflections $32\bar{1}$ and 031 varied in intensity by $\pm 1\%$ and $\pm 2\%$ respectively.

From the systematic absences ($h0l$, $h+l = 2n+1$; $0k0$, $k = 2n+1$) the space group was unambiguously determined to be $P2_1/n$. With $Z = 2$, there are two possibilities. Either the structure of the molecule possesses $\bar{1}$ symmetry and the molecule occupies a special position or there is an orientational disorder of the molecule about the crystallographic centre of inversion. The structure of the cage dione (I) was fully consonant with the spectral data (Mehta & Srikrishna, 1982), thus lending support to the latter possibility.

Structure determination was carried out using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The *E* map computed using the phases from the best set ($R_{Karle} = 20 \cdot 06\%$, ABSFOM $= 1 \cdot 1514$, PSIZERO $= 1 \cdot 541$, and COMFOM $= 3 \cdot 000$) in the space group $P2_1/n$ was too confusing to interpret. However, the *E* map calculated assuming the space group to be $P2_1$ revealed a centric distribution of peaks. Positional and isotropic least-squares refinement of these atoms converged at $R = 30\%$ and there were a number of parameters exhibiting high correlations. The centre of symmetry of the fragment was shifted to coincide with a centre of
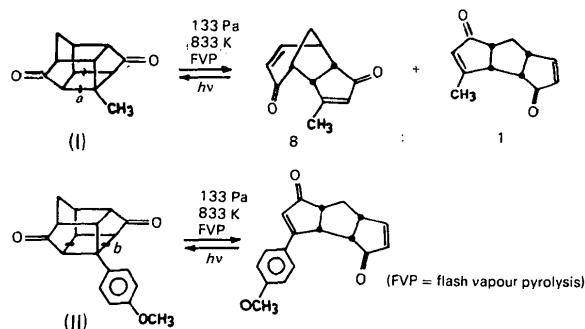

Fig. 1. Reactivity of molecules (I) and (II).

Table 1. *Fractional coordinates* $(\times 10^4)$, *occupancies and equivalent isotropic temperature factors* $(\times 10^2)$ *for non-*H *atoms with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	Occupancy	$U_{eq}(\text{Å}^2)$
O(1)	2471 (3)	2346 (2)	−1541 (3)	1·00	8·7 (1)
C(2)	1603 (4)	1485 (2)	−974 (4)	1·00	6·3 (1)
C(3)	1485 (4)	113 (3)	−1513 (4)	1·00	7·1 (1)
C(4)	−784 (9)	−289 (5)	−1450 (6)	0·51 (1)	4·3 (2)
C(5)	−2619 (14)	−398 (9)	−3396 (10)	0·45 (1)	8·2 (3)
C(6)	340 (6)	1497 (2)	438 (5)	1·00	8·2 (1)
C(7)	−1787 (7)	686 (3)	−277 (5)	1·00	9·9 (2)
C(8)	697 (16)	118 (9)	3302 (12)	0·35 (1)	5·1 (4)
C(9)	2166 (22)	380 (12)	2002 (17)	0·29 (1)	4·4 (4)
C(10)	1494 (26)	−130 (18)	2621 (33)	0·17 (1)	6·8 (9)
C(11)	1974 (27)	1073 (22)	2501 (28)	0·20 (1)	7·2 (8)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Average values for distances and angles involving disordered atoms are given.

O(1)—C(2)	1·192 (3)	C(6)—C(9) ⎫	
C(2)—C(3)	1·490 (4)	C(3')—C(10) ⎭	1·785 (16)
C(2)—C(6)	1·478 (5)	C(7')—C(9) ⎫	
C(3)—C(4)	1·487 (6)	C(7')—C(10) ⎭	1·765 (17)
C(3)—C(7')	1·523 (5)	C(3')—C(8) ⎫	
C(4)—C(5)	1·539 (9)	C(6)—C(11) ⎭	1·602 (15)
C(4)—C(6')	1·455 (6)	C(8)—C(9) ⎫	
C(4)—C(7)	1·583 (7)	C(11)—C(10) ⎭	1·421 (24)
C(6)—C(7)	1·527 (6)		
O(1)—C(2)—C(3)	129·3 (3)	C(2')—C(3')—C(8) ⎫	
O(1)—C(2)—C(6)	129·1 (3)	C(2)—C(6)—C(11) ⎭	109·4 (6)
C(3)—C(2)—C(6)	101·6 (2)	C(2')—C(3')—C(10) ⎫	
C(2)—C(3)—C(4)	103·7 (3)	C(2)—C(6)—C(9) ⎭	94·2 (6)
C(2)—C(3)—C(7')	108·7 (3)	C(7)—C(3')—C(8) ⎫	
C(4)—C(3)—C(7')	71·7 (3)	C(7)—C(6)—C(11) ⎭	116·2 (6)
C(3)—C(4)—C(5)	115·8 (5)	C(7)—C(3')—C(10) ⎫	
C(3)—C(4)—C(6')	103·2 (4)	C(7)—C(6)—C(9) ⎭	101·8 (6)
C(3)—C(4)—C(7)	111·5 (4)	C(3')—C(8)—C(9) ⎫	
C(5)—C(4)—C(7)	104·4 (5)	C(6)—C(11)—C(10)⎭	97·4 (1·2)
C(5)—C(4)—C(6')	112·4 (5)	C(6)—C(9)—C(8) ⎫	
C(6')—C(4)—C(7)	109·4 (4)	C(3')—C(10)—C(11)⎭	99·3 (1·2)
C(2)—C(6)—C(7)	110·1 (3)	C(6)—C(9)—C(7') ⎫	
C(2')—C(6')—C(4)	106·9 (3)	C(3')—C(10)—C(7')⎭	90·0 (8)
C(4)—C(6')—C(7')	72·5 (3)	C(7')—C(9)—C(8) ⎫	
C(3')—C(7)—C(4)	98·4 (3)	C(7')—C(10)—C(11)⎭	105·5 (1·2)
C(3')—C(7)—C(6)	98·3 (3)	C(3)—C(7')—C(9) ⎫	
C(4)—C(7)—C(6)	96·0 (3)	C(6')—C(7')—C(10)⎭	101·9 (6)
		C(6')—C(7')—C(9) ⎫	
		C(3)—C(7')—C(10) ⎭	125·0 (6)

symmetry at (000) in the space group $P2_1/n$. From a difference map calculated at this stage, two more positions [C(8) and C(9)] were identified (Fig. 2e), which clearly indicate the presence of enantiomeric disorder. Full-matrix least-squares refinement of the positional and isotropic thermal parameters of all the atoms, including C(8) and C(9), reduced the R value to 24%. Further refinements were carried out by assigning an occupancy value of 0·5 to the disordered atoms [C(4), C(5), C(8) and C(9)], with the remaining ones [O(1), C(2), C(3), C(6) and C(7)] carrying full occupancy. When the refinement was carried out treating the disordered atoms isotropically and the remaining atoms

anisotropically, R dropped to 17%. The occupancy parameters of atoms C(8) and C(9) showed a tendency to decrease considerably from the initial value of 0·5. From a difference map calculated at this stage, two more peaks [C(10) and C(11)] were selected (Fig. 2e). It was recognized that the presence of these additional peaks could be explained by a rotational disorder, arising from a 180° rotation about the axis passing through the two carbonyl groups. Further cycles of least-squares refinement were carried out in which the occupancy and isotropic thermal parameters of the disordered atoms were refined in alternate cycles of refinement allowing the former to vary while keeping the latter fixed at a time. The occupancy of atoms C(4) and C(5) was assigned a value of 0·5 whereas for the atoms C(8), C(9), C(10) and C(11) the value was 0·25. As for the other atoms, they were treated for positional and anisotropic thermal parameters. The final occupancies obtained are provided in Table 1. In the the light of the approximation involved in the refinement of occupancies and the interaction between these and the thermal parameters, the observed difference may not be very reliable. From the nature of the disorder recognized in
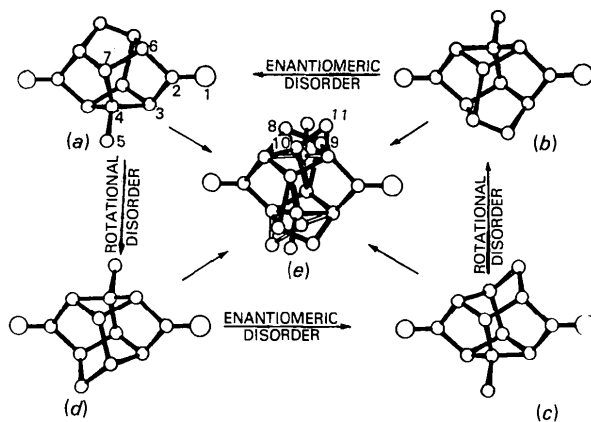

Fig. 2. Different disordered orientations observed and the final disordered crystal structure.
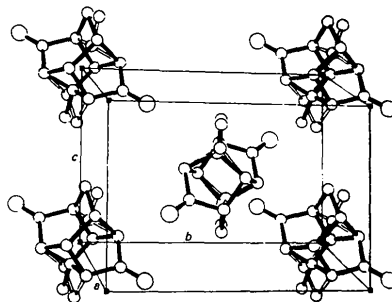

Fig. 3. Packing diagram for a pair of disordered enantiomers.

the crystal lattice, both C(4) and C(5) would be expected to carry an occupancy of 0·5. The occupancy values of C(8) and C(9), which should be equal, tend to have on average a value larger than that of C(10) and C(11). From this one may conclude that the atoms generated by the enantiomeric disorder have a higher probability of occurrence than those arising from the rotational disorder. However, potential-energy calculations do not lend support to this conclusion. The H atoms of the ordered atoms were determined from geometric considerations and these were also refined for their positional and isotropic thermal parameters. In the final cycles of refinement, all the non-H atoms were subjected to anisotropic-thermal-parameter refinement. The final R value was 5·8% ($R_w = 7·5\%$, $S = 1·793$). $(\Delta/\sigma)_{max} = 0·001$. The difference map calculated at this stage did not reveal any peaks of stereochemical significance and the peak of largest height was at about $0·2 \, e \, \text{Å}^{-3}$. It may be mentioned that *post-mortem* examination of the first E map calculated in the space group $P2_1/n$ showed that this map could now be interpreted.

Function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 1·0/(\sigma^2|F_o| + 0·002|F_o|^2)$. Scattering factors from *International Tables for X-ray Crystallography* (1974). Full-matrix least-squares program *SHELX76* (Sheldrick, 1976) used for the refinement.

Discussion. The final positional and thermal parameters are listed in Table 1;* bond lengths and angles are given in Table 2. The final disordered structure and the packing diagram for a pair of enantiomers are given in Figs. 2 and 3.

The crystal structure is highly disordered, exhibiting rotational as well as enantiomeric disorder and hence detailed discussion of the geometric parameters is not undertaken. Thus the purpose for which this investigation was undertaken, namely chemical reactivity–geometry correlations did not materialize. But then there remains the question: Have we considered at all the various possibilities of the orientational disorder? In this connection, it was considered worthwhile to carry out packing-energy calculations in which the orientations of the molecules may be allowed to vary and find out independently the kinds of orientational disorder possible on considerations of potential energy. The program *WMIN* developed by Busing (1981) was used for this purpose. As the molecule as such is not centrosymmetrical, the packing-energy calculations were carried out in the space group $P2_1$ assuming an ordered arrangement of molecules in

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39449 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the crystal lattice. The energy is calculated by a pairwise potential as follows:

$$E = \sum_i \; \sum_{j \neq i}(-A_iA_j/r_{ij}^6) + \sum_i \; \sum_{j \neq i}(D_{ij}/r_{ij}^{12}). \quad (1)$$

In equation (1), the first and second terms represent van der Waals attractive and repulsive contributions respectively. A contribution of Coulombic energy was not included. The constants used are taken from Mirsky (1978): A_i for $O = 33·0$, $C = 42·0$, $H = 11·0 \, \text{kJ}^{1/2} \, \text{mol}^{-1/2} \, \text{Å}^3$; $D_{ij} \times 10^3$ for $O \cdots O = 639·91$, $O \cdots C = 1271·53$, $O \cdots H = 146·16$, $C \cdots C = 2653·55$, $C \cdots H = 298·73$, $H \cdots H = 28·93 \, \text{kJ} \, \text{mol}^{-1} \, \text{Å}^{12}$. The molecules were treated as rigid bodies. The energy E was calculated by rotating the molecule about the $C(2) \cdots C(2')$ axis (Fig. 2a) and at intervals of 5° over a range of 360°, starting from crystal positions. In these calculations all the symmetry-related molecules were allowed to rotate together. The calculations were performed for both the enantiomers (Fig. 2a and b). From the calculations, it was observed that the energy minima occur at orientations corresponding to those determined from X-ray data (Fig. 4). Energy for orientations: $a = -77·9$, $b = -77·9$, $c = -77·0$, $d = -76·2 \, \text{kJ} \, \text{mol}^{-1}$. No other orientation was observed with energy nearer to the crystal minima, *i.e.* $-75·4 \, \text{kJ} \, \text{mol}^{-1}$.
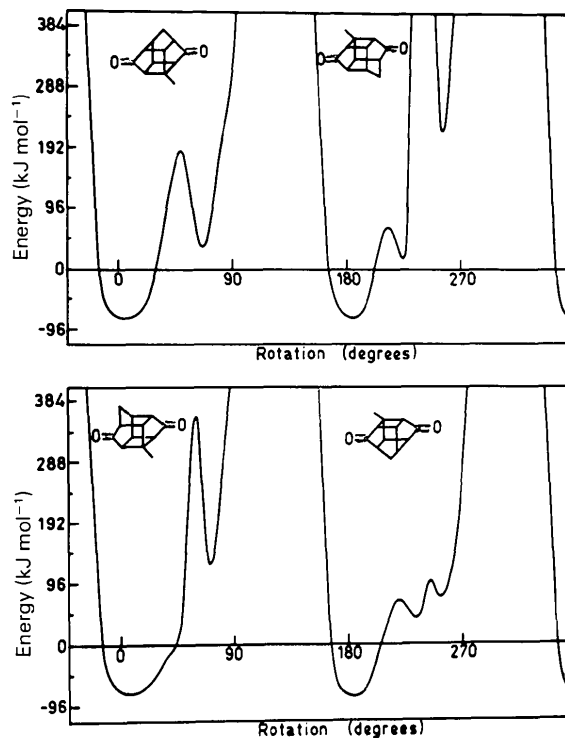

Fig. 4. Graph showing packing energy (kJ mol⁻¹) vs rotation (°) for both the enantiomers.

On the basis of the intermolecular distances, the crystal structure is stabilized by van der Waals interactions only. Enantiomeric disorder is sufficient to create a statistical centre of inversion, whereas the rotational disorder was not anticipated.

References

BUSING, W. R. (1981). WMIN. A computer program to model molecules and crystals in terms of potential-energy functions. Oak Ridge National Laboratory, Tennessee.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.

MEHTA, G. & SRIKRISHNA, A. (1982). J. Chem. Soc. Chem. Commun. pp. 218–219.

MIRSKY, K. (1978). Proceedings of an International Summer School in Crystallographic Computing, pp. 169–182. Delft Univ. Press.

SHELDRICK, G. M. (1976). SHELX76. A program for crystal structure determination. Univ. of Cambridge, England.

Bis(hydronium dichloropicrate)–1,4,7,10,13,16-Hexaoxacyclooctadecane Complex, 2[H₃O⁺.C₆(NO₂)₃Cl₂O⁻].(CH₂CH₂O)₆

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Abstract. $M_r = 896.35$, monoclinic, $P2_1/a$, $a = 8.369$ (3), $b = 25.538$ (6), $c = 9.562$ (2) Å, $\beta = 110.12$ (2)°, $Z = 2$, $V/Z = 959.5$ (8) Å³, $D_x = 1.551$ (1) g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, $\mu = 4.06$ cm⁻¹, $F(000) = 920$, $T = 297$ (2) K, $R = 0.056$ for 1618 reflections. The complex is centrosymmetric with the two hydronium ions weakly hydrogen bonded to O atoms of the crown ether (18-crown-6) and strongly hydrogen bonded to a dichloropicrate anion. The hydronium-ion positions are disordered. There are no unusual bond distances or angles.

Introduction. In the course of studying possible analytical uses of crown ethers (Kolthoff, Wang & Chantooni, 1983; Chantooni, Wang & Kolthoff, 1984) the title compound was prepared. A study of the binding of the two hydronium ions to the 18-crown-6 was the objective of this paper.

Experimental. The compound was prepared in water by precipitation of dichloropicric acid with an equivalent of hexaoxacyclooctadecane (18-crown-6). Crystals suitable for the diffraction experiments were obtained. D_m not measured. Crystal $0.1 \times 0.15 \times 0.4$ mm cut from a larger crystal and coated with a thin layer of epoxy cement to prevent loss of water. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. 22 reflections with $11° < \theta < 16°$ to determine the cell parameters. Systematic extinctions ($0k0$, k odd; $h0l$, h odd) uniquely determined space group $P2_1/a$. Data collected in the range $0° < \theta < 25°$ for one quadrant (ranges: h, 0 to 9; k, 0 to 30; l, −11 to 11). 3369 unique reflections measured; 1618 with $I > \sigma(I)$ used in the calculations. Three check reflections measured every 5000 s of exposure time showed no systematic change with time. No absorption corrections; ψ scans were run, max. variation in intensity 4%. Structure solved by direct methods (MULTAN, Germain, Main & Woolfson, 1971) and refined with full-matrix least-squares refinement of F's. Secondary-extinction coefficient 1.23 (3) ×10⁻⁷ included in the refinement. Methylene H atoms placed at idealized positions with fixed isotropic thermal parameters and not refined. Hydronium H atoms could not be located, presumably due to the disorder, and were not included. All remaining atoms given anisotropic thermal parameters. The O of a hydronium ion was found to be distributed over two positions and was included with partial occupancy at each position such that the total occupancy was 1.00; the occupancy was 0.55 (2) for OW(1), 0.45 (2) for OW(2). Refinement converged

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