X-Ray Crystal Structure of 1,3,6,8-Tetraoxacyclodecane

By **Ivaro W. Bassi,* Raimondo Scordamaglia,** and **Leonardo Fiore**, Montedison Co., 'G. Donegani' Research Institute, Via del Lavoro 4, 28100 Novara, Italy

The molecular and crystal structure of the title compound has been determined from *X*-ray diffractometer data. The structure was solved by direct and Fourier methods and refined by least-squares techniques to R 0.064 for 391 independent reflections. Crystals are triclinic, space group $P\bar{1}$, or $P1$ (pseudo $P\bar{1}$), with $Z = 1$ in a unit cell of dimensions: $a = 6.947(2)$, $b = 6.441(5)$, $c = 4.855(5)$ Å, $\alpha = 91.31(7)°$, $\beta = 105.35(5)°$, $\gamma = 121.30(3)°$. The ring structure resembles that of cyclodecane as derived from the diamond lattice.

As previously reported[1,2] we have synthesized some large-membered-ring oxygen-containing cycloalkanes, whose molecular structures are of interest for comparison with those of cycloparaffins. The crystal structure of 1,3,6,8-tetraoxacyclodecane, (I), is now reported.

EXPERIMENTAL

Preliminary unit-cell dimensions and space group were obtained from equi-inclination Weissenberg photographs. A crystal, essentially a parallelepiped, having dimensions *ca.* 0.30 × 0.20 × 0.40 mm was mounted on a Picker, FACS 1 four-circle computer-controlled diffractometer equipped with a scintillation counter and a pulse-height analyser. The orientation-matrix and cell dimensions were obtained from a least-squares fit of χ, ϕ, ω, and 2θ values from 12 independent reflections.

Crystal Data.—$C_6H_{12}O_4$, $M = 148.16$, Triclinic. $a = 6.947(2)$, $b = 6.441(5)$, $c = 4.855(5)$ Å, $\alpha = 91.31(7)°$, $\beta = 105.35(5)°$, $\gamma = 121.30(3)°$, $U = 175.59$ Å^3, $D_m = 1.38$, $Z = 1$, $D_c = 1.40$. Space group $P\bar{1}$ or $P1$ (pseudo $P\bar{1}$), from structure determination. Cu-K_α radiation, $\lambda = 1.54178$ Å; $\mu(\text{Cu-}K_\alpha) = 10.1$ cm^{-1}.

Intensity data were collected by use of nickel-filtered Cu-K_α radiation with $2\theta \leqslant 120°$. The moving-crystal moving-counter technique was used with a 2θ scan rate of 1° min^{-1} and a scan range of 2.0—2.50° in order to allow for the greater separation of the α_1 and α_2 peaks at increasing 2θ values. Background counts of 10 s were measured at each end of every 2θ scan. The intensities of 3 standard reflections monitored every 50 reflections, decreased slightly and uniformly, with time *ca.* 20% at the end of data collection. The centring of the crystal was checked twice during data collection and no appreciable evidence of miscentring was detected. The diminution in intensity of the monitoring reflections has been attributed to crystal sublimation. Consequently the measured intensity of each reflection was multiplied by the ratio between the intensities of the monitoring reflections at the beginning of the collection, and the intensities of the monitoring reflections pertaining to the group of 50 reflections to which that reflection belonged. Of 468 independent reflections measured, 391 were considered observed, having $I \geqslant 3\sigma(I)$. An arbitrary intensity equal to 0.5 of the observable limit was assigned to non-significant reflections. All intensities were corrected for Lorentz and polarization effects. No absorption correction was introduced.

Determination and Refinement of the Structure.—The structure was solved by direct methods, by use of the MULTAN program.[3] Observed structure factors were converted into normalized structure factor amplitudes, $|E|$ values, by use of the scale factor and overall temperature factor obtained from Wilson's statistics. The distribution of $|E|$ values indicated the centrosymmetric $P\bar{1}$ space group as the most probable. All normalized structure-factor amplitudes >1.5 (72 reflections) were introduced into the calculations which were performed according to this space group. A further 40 reflections with very low $|E|$ were input to the program, in order to define also the ψ_0 figure of merit which is the most significant for triclinic space groups.

The ' discriminating power ' of the three figures of merit furnished by the program (ABS FOM, ψ_0, and RESID) for eight solutions was very poor. Exactly the same figures of merit were found for different solutions, furthermore these were very close to each other. Two three-dimensional Fourier-maps gave unsatisfactory results.

A clearer situation was achieved by performing the calculations according to a non-centrosymmetric structure (space group $P1$). The starting set automatically chosen by the program is reported in Table 1. The program furnished 32 solutions according to the phase angles attributed to A, B, and C $\left(\pm\frac{\pi}{4} \text{ and } \pm\frac{3}{4}\pi\right)$. The ABS FOM figures of merit were ineffective in indicating a solution having the same value of 1.16 for all 32 solutions. The ψ_0 figures of merit had their lowest values for solutions 10 and 27 (0.968×10^3 and 0.986×10^3 respectively) while the others were ten times higher. The corresponding phase angles for A, B, and C are 135, 45, and 135° for solution (10), and 45, 135, and 315° for solution (27).

TABLE 1

Starting set for the tangent formula

hkl	$\lvert E\rvert$	Phase	
$6\bar{3}\bar{2}$	3.13	0	Origin-fixing
$32\bar{2}$	2.31	0	
$1\bar{5}1$	1.93	0	
$20\bar{4}$	2.69	*A*	
$23\bar{1}$	2.47	*B*	
020	1.66	*C*	

The enantiomorph is fixed by the $20\bar{4}$ reflection.

A three-dimensional Fourier synthesis was performed for each solution but that from solution (27) showed stereochemically acceptable features of the molecule. A successive three-dimensional Fourier map performed with all reflections on the basis of the atomic co-ordinates obtained yielded a clear picture of the whole ring and enabled definite identification of the oxygen and carbon

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[1] I. W. Bassi, R. Scordamaglia, and L. Fiore, *J.C.S. Perkin II*, 1972, 1726.

[2] L. Fiore and G. Nissim, Italian P. 903271.

[3] G. Germain, P. Main, and M. M. Wolfson, *Acta Cryst.*, 1971, **A27**, 368.

atoms. Positional and the isotropic thermal parameters of the ring skeleton atoms were refined by full-matrix least-squares.[4] Atomic scattering factors were calculated from the expression in ref. 5, by use of values for the parameters in ref. 6. The weighting scheme of ref. 7 was adopted: $1/W = A + B|F_o| + C|F_o|^2$, where $A = 2F_o(\text{min})$, $B = 1.0$, and $C = 2F_o(\text{max})$. At this point R was 0.120 for the 391 non-zero reflections.

Some cycles of full-matrix refinement were then run, assuming anisotropic thermal parameters for all ring skeleton atoms; hydrogen atoms were introduced into the calculations, but not refined, their co-ordinates being defined on stereochemical grounds and in agreement with a difference-Fourier synthesis. In order to avoid oscillations in the refinement the last cycles of least-squares were run assuming as fixed the positional and thermal parameters of O(1), which were not refined further. The refinement converged to R 0.059 for the 391 non-zero reflections. Since the ring conformation was found to be nearly centrosymmetric, the baricentre of the ring was shifted in $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ of the unit cell and some cycles of least-squares anisotropic refinement were run according to the centrosymmetric space group $P\bar{1}$. The R value reached in this case was 0.066. Four further cycles of full-matrix refinement were performed, with only the hydrogen atoms being refined isotropically in order to obtain some indication of their σ values. The final R was 0.064 for the 391 non-zero reflections.

TABLE 2

Final fractional co-ordinates, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	$B/\text{Å}^2$
(*a*) Centrosymmetric				
O(1)	0.6402(4)	0.6989(5)	0.3239(5)	
C(2)	0.4549(7)	0.7419(7)	0.2303(9)	
O(3)	0.2815(4)	0.6296(5)	0.3688(6)	
C(4)	0.1223(7)	0.3658(8)	0.2793(10)	
C(5)	0.2379(7)	0.2228(7)	0.3686(9)	
H(2)	0.514(6)	0.929(7)	0.258(8)	3.0(8)
H(21)	0.387(8)	0.670(9)	−0.006(10)	5.1(11)
H(4)	−0.002(8)	0.328(9)	0.386(10)	4.6(10)
H(41)	0.043(8)	0.319(8)	0.047(10)	4.2(10)
H(5)	0.095(7)	0.029(7)	0.312(9)	3.2(8)
H(51)	0.348(6)	0.238(6)	0.245(8)	2.5(8)
(*b*) Non-centrosymmetric				
O(1)	0.6983(0)	0,8019(0)	0.2980(0)	
C(2)	0.5219(25)	0.8524(27)	0.2111(35)	
O(3)	0.3384(18)	0.7301(17)	0.3371(24)	
C(4)	0.1793(22)	0.4644(23)	0.2546(30)	
C(5)	0.2928(24)	0.3204(25)	0.3466(30)	
O(6)	0.4166(9)	0.4024(9)	0.6488(11)	
C(7)	0.6114(23)	0.3687(25)	0.7520(31)	
O(8)	0.7741(18)	0.4702(16)	0.6006(24)	
C(9)	0.9368(25)	0.7332(27)	0.6963(31)	
C(10)	0,8173(24)	0.8753(27)	0.6092(29)	
H(2)	0.594	0.023	0.238	5.00
H(21)	0.417	0.763	−0.025	5.00
H(4)	0.048	0.422	0.363	5.00
H(41)	0.083	0.419	0.013	5.00
H(5)	0.173	0.150	0.296	5.00
H(51)	0.402	0.329	0.219	5.00
H(7)	0.522	0.181	0.695	5.00
H(71)	0.702	0.453	0.975	5.00
H(9)	0.023	0.788	0·925	5.00
H(91)	0.081	0.796	0.588	5.00
H(10)	0.720	0.869	0.721	5.00
H(101)	0.963	0.083	0.613	5 00

The structure obtained corresponds to a solution furnished by the Multan program input according to space group $P\bar{1}$. This solution had the highest values of ψ_0 and ABS FOM while RESID was one of the minima of the set.

Table 2 reports the final fractional co-ordinates and the corresponding estimated standard deviations of the atoms of the independent unit of (I), resulting from both the non-centrosymmetric and the centrosymmetric refinements. Table 3 lists anisotropic thermal parameters of non-hydrogen atoms for both refinements. Calculated and observed structure amplitudes are listed in Supplementary Publication No. SUP 21334 (4 pp.).*

TABLE 3

Anisotropic thermal parameters ($\times 10^2$) * for non-hydrogen atoms

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
(*a*) Centrosymmetric						
O(1)	421(11)	441(12)	364(14)	236(10)	139(10)	078(10)
C(2)	493(19)	497(19)	486(23)	299(17)	221(17)	176(17)
O(3)	432(11)	450(13)	459(15)	265(10)	163(10)	086(10)
C(4)	390(17)	468(19)	533(23)	213(16)	093(16)	061(15)
C(5)	398(15)	382(17)	394(20)	172(13)	102(14)	002(13)
(*b*) Non-centrosymmetric						
O(1)	409(0)	417(0)	370(0)	213(0)	144(0)	054(0)
C(2)	524(52)	411(45)	515(63)	148(39)	247(46)	125(42)
O(3)	425(32)	392(37)	497(44)	229(29)	092(30)	043(27)
C(4)	362(48)	346(45)	523(80)	130(39)	058(45)	−019(41)
C(5)	391(47)	374(43)	378(65)	186(38)	174(43)	063(38)
O(6)	432(21)	489(24)	379(27)	284(20)	140(19)	112(20)
C(7)	402(42)	527(52)	452(56)	346(41)	129(38)	171(39)
O(8)	450(31)	488(37)	439(42)	286(30)	245(31)	129(28)
C(9)	451(54)	626(62)	464(80)	318(49)	128(48)	115(49)
C(10)	461(55)	418(51)	412(68)	204(47)	020(45)	−033(42)

* The temperature factor has the form: $T_i = \exp - \frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)$.

RESULTS AND DISCUSSION

Views of the molecule of (I), on the basis of a non-centrosymmetric structure,[8] are shown in Figure 1. The geometric parameters of the independent units of both structures, with their estimated standard deviations, are reported in Table 4.

The overall shape and conformation of the ring skeleton of (I) can be recognized as a slight distortion of the ideal cyclodecane ring which may be derived from the diamond structure. As shown by Dunitz[9] the structure of an n-membered cycloparaffin with $n = 4m + 2$ derived from the diamond lattice, has $2/m$ symmetry, all bond angles being tetrahedral and the bonds being staggered. The $2/m$ symmetry of the ideal cyclodecane ring is lost, in the actual ring of (I); the mirror plane and the two-fold axis cannot exist

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* See Notice to Authors No. 7 in *J.C.S. Perkins II*, 1974, Index issue.

[4] A. Immirzi, *Ricerca Sci.*, 1967, **37**, 743.

[5] V. Vand, P. E. Eiland, and R. Pepinsky, *Acta Cryst.*, 1957, **10**, 303.

[6] F H. Moore, *Acta Cryst.*, 1963, **16**, 1169.

[7] D. W. J. Cruikshank, D. E. Pilling, A. Buiosa, F. M. Lovell, and M. R. Truter, 'Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis,' Pergamon, Oxford, 1961, p. 32.

[8] C. K. Johnson, Oak Ridge National Laboratory, Report ORNL 3794, Oak Ridge, Tennessee, 1970.

[9] J. D. Dunitz and J. A. Ibers, *Perspectives in Structural Chem.*, 1968, **2**, 1.

owing to the presence and the positions assumed by the four oxygen hetero-atoms. The presence in the molecule of (I) of a centre of symmetry is questionable.

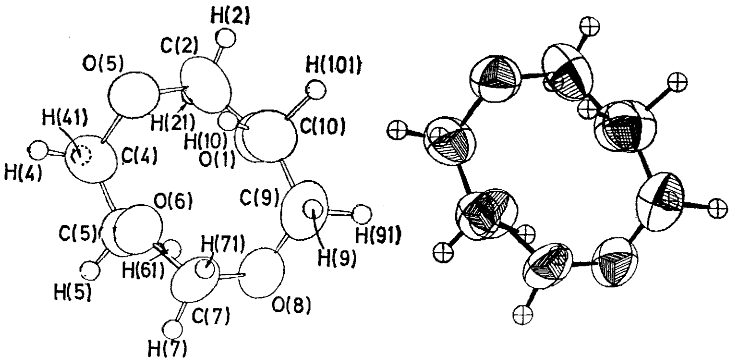

FIGURE 1 The molecule of (I), showing the atom labelling scheme, and 30% probability thermal vibrations ellipsoids

As shown by our least-squares refinements the centrosymmetric and the non-centrosymmetric structures of (I) are practically equivalent. Figure 2 shows the bond lengths and angles and the torsion angles for the two structures. The geometrical parameters found for the centrosymmetric structure are the mean of corresponding values found for the non-centrosymmetric structure. Furthermore, results for the centrosymmetric structure are in good agreement with data quoted by Dunitz for the tri- and mono-clinic forms of cyclodecane-1,6-*trans*-diamine dihydrochloride,[10-12] in which

TABLE 4

The most significant geometric parameters of the molecule of (I). Values for the non-centrosymmetric structure precede those for the centrosymmetric structure

(*a*) Bond lengths (Å)

O(1)–C(2)	1.39(0), 1.416(6)	O(6)–C(7)	1.44(2), 1.416(6)
C(2)–O(3)	1.42(2), 1.404(6)	C(7)–O(8)	1.39(2), 1.404(6)
O(3)–C(4)	1.44(2), 1.435(7)	O(8)–C(9)	1.43(2), 1.435(7)
C(4)–C(5)	1.51(3), 1.511(7)	C(9)–C(10)	1.53(3), 1.511(7)
C(5)–O(6)	1.41(2), 1.433(7)	C(10)–O(1)	1.45(0), 1.433(7)

(*b*) Bond angles (deg.)

O(1)–C(2)–O(3)	114.1(0), 113.93(17)
C(2)–O(3)–C(4)	118.9(7), 115.49(20)
O(3)–C(4)–C(5)	115.3(7), 114.41(19)
C(4)–C(5)–O(6)	108.0(6), 108.04(20)
C(5)–O(6)–C(7)	115.3(6), 113.44(20)
O(6)–C(7)–O(8)	113.2(6), 113.93(17)
C(7)–O(8)–C(9)	112.6(7), 115.49(20)
O(8)–C(9)–C(10)	112.6(7), 114.41(19)
C(9)–C(10)–O(1)	108.1(0), 108.04(20)
C(10)–O(1)–C(2)	112.2(0), 113.44(20)

(*c*) Torsion angles (deg.)

O(1)–C(2)–O(3)–C(4)	−68, −73
C(2)–O(3)–C(4)–C(5)	66, 68
O(3)–C(4)–C(5)–O(6)	53, 53
C(4)–C(5)–O(6)–C(7)	−155, −157
C(5)–O(6)–C(7)–O(8)	53, 57
O(6)–C(7)–O(8)–C(9)	79, 73
C(7)–O(8)–C(9)–C(10)	−70, −68
O(8)–C(9)–C(10)–O(1)	−54, −53
C(9)–C(10)–O(1)–C(2)	159, 157
C(10)–O(1)–C(2)–O(3)	−60, −57

(*d*) Most relevant intramolecular distances between non-bonded atoms (Å)

O(1) · · · C(4)	3.03(0), 3.023(6)	O(3) · · · C(9)	4.04(3), 4.043(7)
O(1) · · · C(5)	2.99(0), 2.951(6)	O(3) · · · C(10)	2.84(2), 2.841(6)
O(1) · · · O(6)	3.18(0), 3.172(6)	C(4) · · · C(7)	3.66(3), 3.642(6)
O(1) · · · C(7)	3.50(0), 3.503(6)	C(4) · · · O(8)	4.01(3), 4.043(7)
O(1) · · · O(8)	2.81(0), 2.813(5)	C(4) · · · C(9)	4.42(3), 4.423(7)
C(2) · · · C(5)	3.11(3), 3.050(6)	C(4) · · · C(10)	3.63(3), 3.637(6)
C(2) · · · O(6)	3.52(2), 3.503(6)	C(5) · · · O(8)	2.84(2), 2.841(6)
C(2) · · · C(7)	4.30(3), 4.305(8)	C(5) · · · C(9)	3.66(3), 3.637(6)
C(2) · · · O(8)	3.96(2), 3.968(6)	C(5) · · · C(10)	3.39(3), 3.385(6)
C(2) · · · C(9)	3.64(3), 3.642(6)	O(6) · · · C(9)	3.03(2), 3.023(6)
O(3) · · · O(6)	2.82(2), 2.813(5)	O(6) · · · C(10)	2.93(2), 2.951(6)
O(3) · · · C(7)	3.98(2), 3.968(6)	C(7) · · · C(10)	2.99(3), 3.050(6)

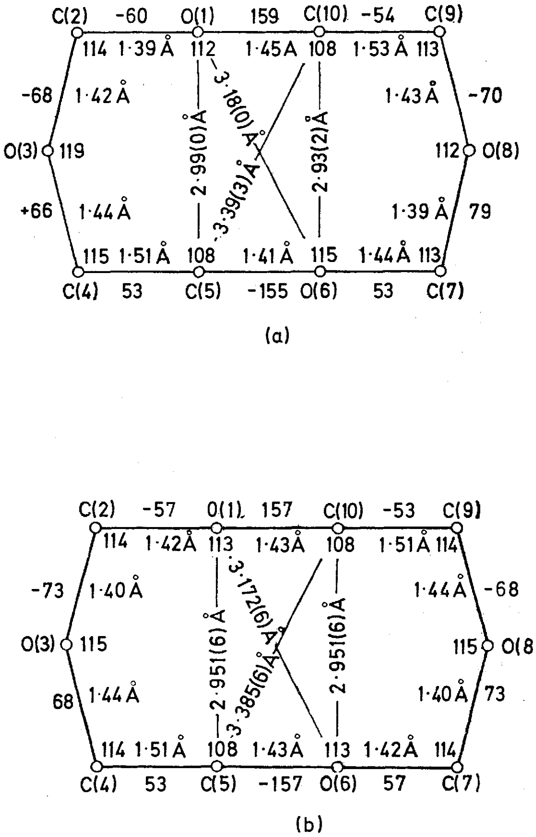

FIGURE 2 Bond lengths, bond angles, and torsion angles for the molecule (I) obtained with the refinement in space groups (a) *P*1, and (b) *P*$\bar{1}$

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[10] E. Huber-Buser and J. D. Dunitz, *Helv. Chim. Acta*, 1960, **43**, 760.

[11] E. Huber-Buser and J. D. Dunitz, *Helv. Chim. Acta*, 1961, **44**, 2027.

[12] E. Huber-Buser and J. D. Dunitz, *Helv. Chim. Acta*, 1966, **49**, 1821.

the ring baricentres are placed on the centres of symmetry of the unit cell. The non-centrosymmetric structure is in good agreement with data reported for cyclodecanamine hydrochloride sesquihydrate [13,14] and cyclodecane-1,6-*cis*-diamine dihydrochloride dihydrate,[15] in which the ring baricentres are in general positions.

Application of Hamilton's statistical test [16] on the R ratio, as suggested by a referee, has shown that the centrosymmetric structure can be rejected at the 0.005 significance level. We note however (see Table 4) that the internal co-ordinates, as refined in the non-centrosymmetric structure through our program,[4] appear to be nearly coincident, within the calculated standard deviations, with those derived from the centrosymmetric structure refinement.

For a discussion of the main features of the structure at least, an assumption of non-centrosymmetry does not appear to be relevant. Insertion of the oxygen atoms into the ideal cyclodecane ring at the observed positions may be considered as substitution of extremely strained type (2) and (3) CH_2 groups (see ref. 9) by less bulky oxygen atoms. As a result, the six intra-annular H $\cdots$ H short interactions present in the ideal cyclodecane ring are absent in molecule (I). In (I), all H $\cdots$ H interactions between hydrogen atoms separated by four or more bonds are >2.5 Å, except for H(21) $\cdots$ H(41) and the centrosymmetric H(9) $\cdots$ H(71) which are 2.37 Å (2.29 and 2.23 Å for the non-centrosymmetric structure). A similar substitution by oxygen atoms of the most strained CH_2 groups of the ideal ring was found for 1,3,8,10-tetraoxacyclotetradecane.[1]

Deviations of the ring skeleton of (I) from the ideal structure may be tentatively accounted for on the basis of intramolecular van der Waals repulsions between the facing oxygen and carbon atoms five or four bonds apart (see Figure 2). This latter ($CH_2 \cdots CH_2$) intramolecular separation, which would be 2.52 Å in the ideal cyclodecane ring, becomes 3.29 Å in the 'averaged' cyclodecane ring derived by Dunitz from experimental data [9] and is 2.95 Å [O(1) $\cdots$ C(5) = C(10) $\cdots$ O(6)] for (I); corresponding distances for the non-centrosymmetric structure are 2.99 and 2.93 Å.

The shortest value of the intramolecular O $\cdots$ CH_2 separation (2.95 Å) in respect of the $CH_2 \cdots CH_2$ separation (3.29 Å), present in the 'averaged' cyclodecane ring, may suggest that the intra-annular unshared electron pair on the oxygen occupies far less room than the intra-annular hydrogen atom of a methylene group. A similar shortening (O $\cdots$ C=O 2.83 Å) was also seen in 2-oxacyclodecane-1,6-dione,[17] which has a ring structure like that of (I).

The O $\cdots$ O and $CH_2 \cdots CH_2$ intramolecular separations between atoms five bonds apart in the ring of (I), are 3.17 [O(1) $\cdots$ O(6)] and 3.39 Å [C(5) $\cdots$ C(10)], corresponding distances for the non-centrosymmetric structure being 3.18 and 3.39 Å.

The intermolecular van der Waals interactions are also acceptable for both structures (see Figure 3), no C $\cdots$ C and O $\cdots$ O distance being <3.60 or <3.39 Å respectively, while the shortest C $\cdots$ O intermolecular distance between molecules superposed along the c axis is 3.49 Å.

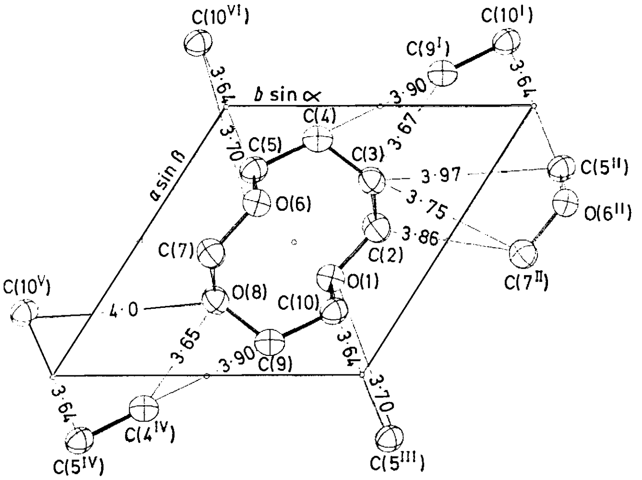

FIGURE 3 Structure of (I) viewed down the c axis, showing some of the most significant intermolecular contact distances (Å) (space group $P\bar{1}$). Roman numeral superscripts denote the following equivalent positions of the atoms, relative to the reference molecule at x, y, z:

I $x - 1, y, z$
II $x, y + 1, z$
III $x + 1, y + 1, z$
IV $x + 1, y, z$
V $x, y - 1, z$
VI $x - 1, y - 1, z$

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