X-Ray Crystal Structure of 1,3,8,10-Tetraoxacyclotetradecane

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The molecular and crystal structure of the title compound has been determined from *X*-ray diffractometer data. The structure was solved by Patterson and Fourier methods and refined by least-squares techniques to R 0·058 for 775 independent reflections. Crystals are monoclinic, space group $P2_1/n$, with $Z = 2$ in a unit cell of dimensions: $a = 8{\cdot}107(3)$, $b = 14{\cdot}721(6)$, $c = 4{\cdot}724(1)$ Å, $\beta = 100{\cdot}25(8)°$. The ring structure resembles that of cyclotetradecane as derived from the diamond lattice.

WE have recently synthesised some large-membered oxygen-containing cycloalkanes.[1] The structure of these heterocyclic compounds is of interest both for comparison with those of cycloparaffins and in view of the possible correlations with the chain-folding phenomenon in polymeric materials. The crystal structure of 1,3,8,10-tetraoxatetradecane (I) is now reported.

EXPERIMENTAL

Preliminary space group and unit-cell dimensions were obtained from Weissenberg photographs.

A crystal, essentially a parallelepiped, having dimensions *ca.* 0·30 × 0·25 × 0·50 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.—$C_{10}H_{20}O_4$, $M = 204{\cdot}32$. Monoclinic $a = 8{\cdot}107(3)$, $b = 14{\cdot}721(6)$, $c = 4{\cdot}724(1)$ Å, $\beta = 100{\cdot}25(8)°$, $U = 554{\cdot}48$ Å^3, $D_m = 1{\cdot}20$, $Z = 2$, $D_c = 1{\cdot}22$. Space group $P2_1/n$ from systematic absences: $0k0$ for k odd, $h0l$ for $h + l$ odd. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; $\mu(\text{Mo-}K_\alpha) = 0{\cdot}95$ cm^{-1}.

Intensity data were collected by use of zirconium-filtered Mo-K_α radiation, with $2\theta \leqslant 70°$. 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 $K_{\alpha 1}$ and $K_{\alpha 2}$ peaks at increasing 2θ values. Background counts of 10 s were measured at each end of every 2θ scan. Three standard reflections, measured after every 50 reflections, showed no fluctuation $> \pm 3\%$ during data collection. 2372 Independent reflections were measured of which 775 were considered observed and had $I \geqslant 3\sigma$. An arbitrary intensity equal to 0·5 the observable limit was assigned to the 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 Patterson and trial methods. A two-dimensional Patterson map was performed with the ($hk0$) reflections. The set of interatomic vectors is consistent with the overlapping of two atoms at $x \approx 0{\cdot}700$ and $y \approx 0{\cdot}367$ in Fourier space.

As shown by Dunitz[2] the structure of an n membered cycloparaffin with $n = 4m + 2$ may be directly derived from the diamond structure. A fourteen-membered ring is built up from two parallel chains (lateral chains) each containing 5 methylene groups, similar in structure to the planar zig-zag chains of the crystalline normal paraffins; the bridges (folds) linking the ends of these chains contain two methylene groups. Also the arrangement of the four carbon atoms of the bridges is a planar zig-zag chain. The symmetry of the ring is $2/m$. This has been verified by the structures found for 1,8-diazacyclotetradecane dihydrobromide[3] and for 1,8 diazacyclotetradecane-1,8-diol.[4]

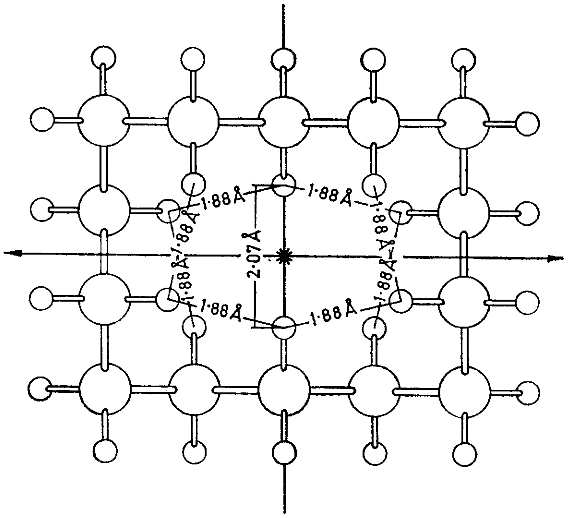

FIGURE 1 Conformation of cyclotetradecane as derived from the diamond lattice, showing some of the shortest H · · · H contact distances

A model of (I) was constructed on this basis, by considering all members of the ring skeleton as carbon atoms and involving bond angles and torsion angles undistorted in respect of those derived from the diamond lattice (Figure 1).

The x and y co-ordinates of the ring skeleton atoms were derived from the Patterson map and from the structure-factor graph of the (5,15,0) outstanding reflection. Some structure-factor calculations performed on the $hk0$ reflections confirmed the validity of the assumed ring structure.

Tentative z co-ordinates for the ring atoms were derived from packing considerations.

A three-dimensional Fourier synthesis based on the x,y,z co-ordinates derived in this way, yielded a clear picture of the whole ring and enabled definite identification of the oxygen and carbon atoms.

The positional and the isotropic thermal parameters of

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[1] L. Fiore and G. Nissim, Italian P. 903,271.

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

[3] J. D. Dunitz and E. F. Meyer, *Helv. Chim. Acta*, 1965, **48**, 1441.

[4] C. J. Brown, *J. Chem. Soc.* (*C*), 1966, 1108.

the ring skeleton atoms were refined by some cycles of full-matrix least-squares, by use of a program of Immirzi.[5] Atomic scattering factors were calculated from the expression in ref. 6, using values for the parameters given in ref. 7. The weighting scheme of ref. 8 was adopted: $1/W = A + B|F_o| + C|F_o|^2$, where $A = 2\ F_o(\text{min})$, $B = 1{\cdot}0$, and $C = 2/F_o(\text{max})$. At this point R was 0·140 for the 775 non-zero reflections.

Four cycles of full-matrix refinement were run, assuming anisotropic thermal parameters for all ring carbon and oxygen atoms, the hydrogen atoms being introduced into the calculations but not refined, their co-ordinates being defined on stereochemical grounds and according to a difference-Fourier synthesis.

The refinement converged to $R = 0{\cdot}064$. The final shifts of the atomic parameters were negligible, all being well below the corresponding σ. Four further cycles of full-matrix refinement were performed, only the hydrogen atoms being refined isotropically in order to obtain some indication of their σ values. The final R was 0·058 for the 775 non-zero reflections.

TABLE 1

Final fractional co-ordinates with estimated standard deviations in parentheses

	x	y	z	B/Å^2
O(1)	0·1890(2)	0·4740(1)	0·3778(4)	
O(2)	0·7216(2)	0·3769(1)	0·6714(4)	
C(1)	0·1456(3)	0·5617(2)	0·2673(6)	
C(2)	0·3143(3)	0·4315(2)	0·2473(6)	
C(3)	0·3711(4)	0·3473(2)	0·4180(6)	
C(4)	0·5198(4)	0·2997(2)	0·3260(6)	
C(5)	0·6783(4)	0·3555(2)	0·3718(6)	
H(1)	0·119(4)	0·559(2)	0·050(6)	2·8(6)
H(1′)	0·051(4)	0·578(2)	0·366(7)	2·8(7)
H(2)	0·416(4)	0·472(2)	0·254(7)	3·0(7)
H(2′)	0·271(4)	0·418(2)	0·044(7)	3·3(7)
H(3)	0·278(4)	0·305(2)	0·403(7)	2·8(6)
H(3′)	0·404(4)	0·363(2)	0·617(7)	2·6(6)
H(4)	0·492(4)	0·285(2)	0·111(7)	3·4(7)
H(4′)	0·537(4)	0·242(2)	0·429(7)	3·2(7)
H(5)	0·660(3)	0·411(2)	0·237(6)	2·1(6)
H(5′)	0·765(4)	0·322(2)	0·305(6)	2·2(6)

TABLE 2

Anisotropic thermal parameters * for the non-hydrogen atoms

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	3·85(7)	3·59(7)	4·99(9)	−0·12(6)	1·49(7)	0·57(7)
O(2)	3·69(7)	3·59(7)	3·65(7)	−0·29(6)	0·45(5)	0·13(6)
C(1)	3·30(9)	3·75(10)	5·40(13)	−0·17(9)	0·75(9)	0·46(10)
C(2)	4·04(10)	3·82(10)	4·08(11)	0·38(9)	1·04(8)	0·16(9)
C(3)	4·06(11)	3·23(9)	4·60(12)	−0·69(9)	0·17(9)	0·58(9)
C(4)	5·37(14)	3·15(9)	4·79(13)	0·25(10)	0·11(10)	−0·64(9)
C(5)	4·64(12)	4·46(12)	3·66(11)	0·75(10)	1·05(9)	−0·27(9)

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

Table 1 reports the final fractional co-ordinates and the corresponding estimated standard deviations of the atoms of the independent unit. Table 2 lists the anisotropic thermal parameters of the non-hydrogen atoms. Calculated and observed structure amplitudes are listed in Supplementary Publication No. SUP 20452 (7 pp., 1 microfiche).[†]

RESULTS AND DISCUSSION

Views of the molecule of (I) are shown in Figures 2 and 3. The geometric parameters of the molecule with their estimated standard deviations are reported in Table 3.

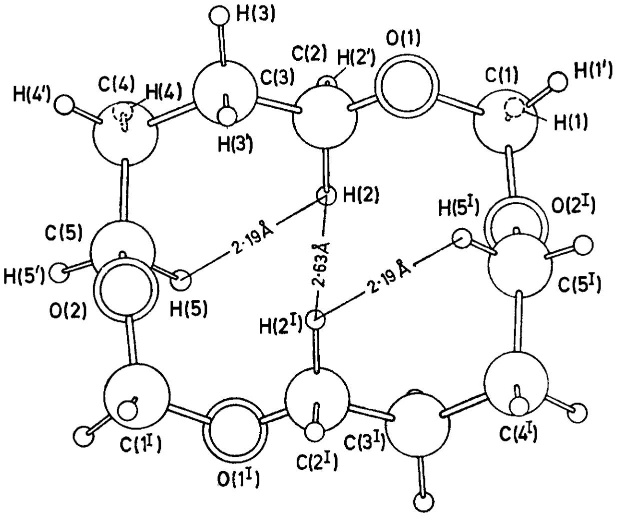

FIGURE 2 Projection along the c axis of the actual ring of (I)

TABLE 3

Most significant geometric parameters of the molecule (I); atoms labelled with a Roman I are related to the others in the molecule by a centre of inversion

(*a*) Bond lengths (Å)

O(1)–C(1)	1·414(3)
O(1)–C(2)	1·423(3)
C(2)–C(3)	1·506(4)
C(3)–C(4)	1·523(4)
C(4)–C(5)	1·508(4)
C(5)–O(2)	1·431(3)
O(2)–C(1^{I})	1·395(3)
C(1)–H(1)	1·00(3)
C(1)–H(1′)	0·99(3)
C(2)–H(2)	1·00(3)
C(2)–H(2′)	0·98(3)
C(3)–H(3)	0·97(3)
C(3)–H(3′)	0·95(3)
C(4)–H(4)	1·02(3)
C(4)–H(4′)	0·98(3)
C(5)–H(5)	1·03(3)
C(5)–H(5′)	0·95(3)

(*b*) Bond angles (deg.)

O(1)–C(1)–O(2^{I})	112·48(10)
C(1)–O(1)–C(2)	113·02(10)
O(1)–C(2)–C(3)	107·66(09)
C(2)–C(3)–C(4)	114·09(11)
C(3)–C(4)–C(5)	113·96(11)
C(4)–C(5)–O(2)	108·32(10)
C(5)–O(2)–C(1^{I})	113·09(11)
H(1)–C(1)–H(1′)	117(2)
H(2)–C(2)–H(2′)	107(2)
H(3)–C(3)–H(3′)	107(2)
H(4)–C(4)–H(4′)	108(2)
H(5)–C(5)–H(5′)	104(1)

(*c*) Torsion angles (deg.)

O(1)–C(2)–C(3)–C(4)	187
C(2)–C(3)–C(4)–C(5)	64
C(3)–C(4)–C(5)–O(2)	59
C(4)–C(5)–O(2)–C(1^{I})	188
C(5)–O(2)–C(1^{I})–O(1^{I})	68
O(2)–C(1^{I})–O(1^{I})–C(2^{I})	65
C(1^{I})–O(1^{I})–C(2^{I})–C(3^{I})	190
O(1^{I})–C(2^{I})–C(3^{I})–C(4^{I})	173
C(2^{I})–C(3^{I})–C(4^{I})–C(5^{I})	−64
C(3^{I})–C(4^{I})–C(5^{I})–O(2^{I})	−59
C(4^{I})–C(5^{I})–O(2^{I})–C(1)	172
C(5^{I})–O(2^{I})–C(1)–O(1)	−68
O(2^{I})–C(1)–O(1)–C(2)	−65
C(1)–O(1)–C(2)–C(3)	170

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

C(5) · · · C(2)	3·11(1)
C(5) · · · O(1)	4·34(1)
C(5) · · · C(2^{I})	3·61(1)
O(2) · · · C(2)	3·63(1)
O(2) · · · C(3)	2·91(1)
O(2) · · · C(3^{I})	4·14(1)
C(2) · · · C(2^{I})	4·03(1)
C(2) · · · O(1^{I})	4·33(1)
C(2) · · · C(3^{I})	4·26(1)
C(2) · · · C(1^{I})	4·57(1)
H(2) · · · H(5)	2·19(4)
H(2) · · · H(2^{I})	2·63(4)

[†] For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

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

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The overall shape and conformation of the ring of (I) is similar to that of the cyclotetradecane ring which may be derived from the diamond structure. The 2/*m* symmetry of ideal cyclotetradecane (Figure 1) is lost; in the actual ring of (I) only the inversion centre is maintained owing to the presence and the position of the four oxygen heteroatoms. The carbon and oxygen atoms of the independent unit of (I) roughly define two nearly perpendicular planes (83°), one of them defined by C(1),O(1),C(2),C(3),C(4), the five atoms of the lateral chain (root-mean-square distance 0·158 Å) the other containing C(4),C(5),O(2),C(1), the four atoms of the fold (root-mean-square distance 0·091 Å). Comparing the experimentally determined atomic positions of the ring skeleton of (I) and the atomic positions of the ideal ring with a proper set of molecular axes, the similarity between the two structures is immediately apparent (Table 4). The root mean-square deviation in an atomic position is *ca.* 0·11 Å. Figure 4 reports the projections of the actual ring of (I) and of the ideal ring, in a plane perpendicular to the zig-zag lateral chain direction [the best line through C(4), C(2), and C(1) in the case of (I)]. The torsion angles of (I) are also similar to those (±60 or 180°) of the structure derived from the diamond lattice. The 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 hydrogen atoms five bonds apart, and for the presence of heteroatoms in the ring. As shown in the ideal structure (Figure 3), there are many H · · · H contact distances <2 Å.

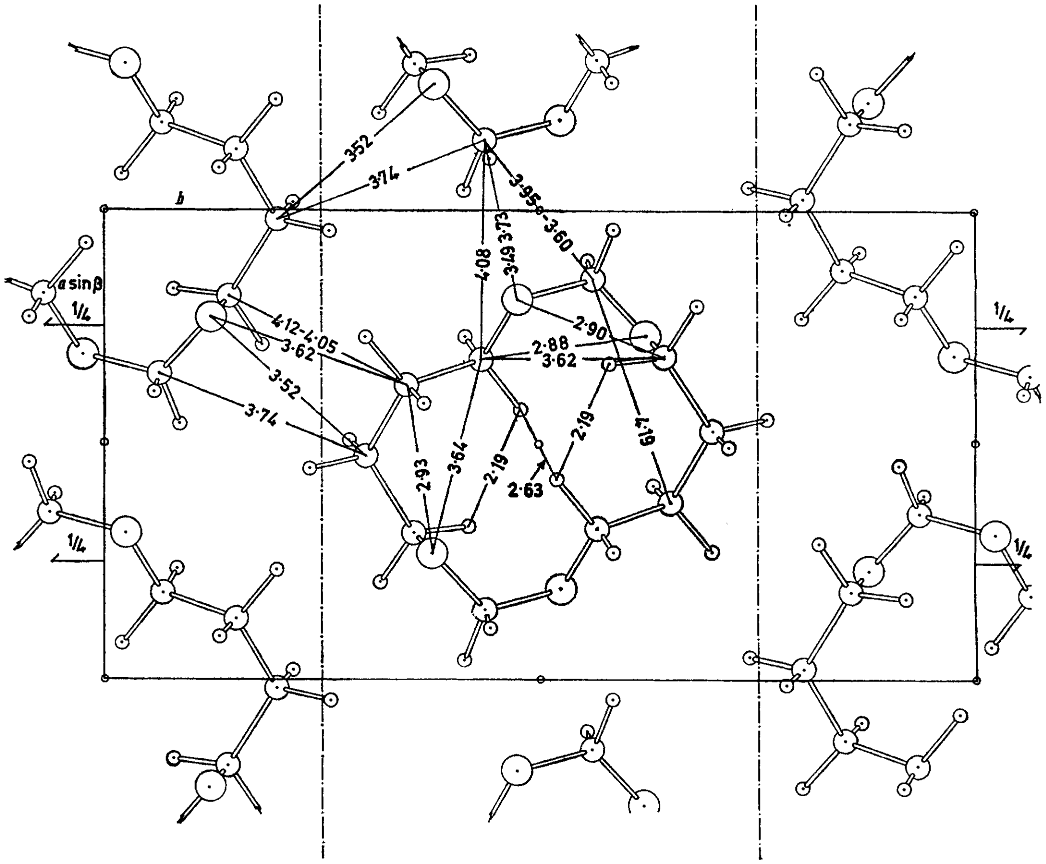

Figure 3 Structure of 1,3,8,10-tetraoxacyclotetradecane as viewed down the *c* axis, showing some of the most significant intra- and inter-molecular contact distances

The insertion in the ideal ring of the oxygen atoms, according to the experimentally found positions, removes all but one H · · · H short interactions, in each fold region. The residual steric crowding of the hydrogen atoms is released by the distortion of the ring skeleton in respect of the ideal structure. As a result, all H · · · H interactions in the actual ring of (I) are >2·5 Å

Table 4

Comparison between the atomic co-ordinates (Å) of the actual ring of (I) and those of the corresponding atoms of the cyclotetradecane ring as derived from the diamond lattice

	(I)			Diamond		
	x	*y*	*z*	*x*	*y*	*z*
C(1)	0·49	1·83	2·44	0·445	1·892	2·522
O(1)	1·23	1·90	1·22	1·333	1·892	1·261
C(2)	0·45	2·00	0·04	0·445	1·892	0
C(3)	1·30	1·90	−1·14	1·333	1·892	−1·261
C(4)	0·49	1·83	−2·46	0·445	1·892	−2·522
C(5)	−0·40	0·68	−2·64	−0·445	0·631	−2·522
O(2)	0·38	−0·60	−2·54	0·445	−0·631	−2·522

with the exception of two interactions [H(5) ··· H(2) and H(5′) ··· H(2′)] which are 2·19 Å. All C ··· C and C ··· O intramolecular contact distances reach acceptable values (see Figure 2). The intermolecular van der Waals interactions are also acceptable, no C ··· C distance being <3·60 Å, while the shortest C ··· O intermolecular distance between molecules superposed along the *c* axis is 3·40 Å.

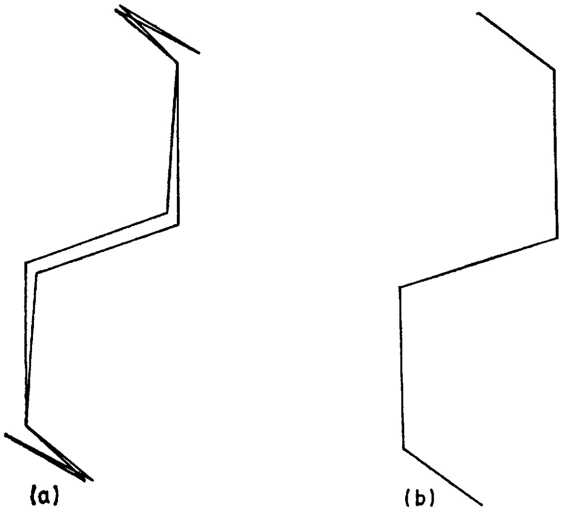

FIGURE 4 (*a*) Projection of the actual ring of (I) in a plane perpendicular to the best line through C(4), C(2), and C(1). (*b*) Projection of the ideal cyclotetradecane ring as derived from the diamond lattice, in a plane perpendicular to the zig-zag lateral chain direction

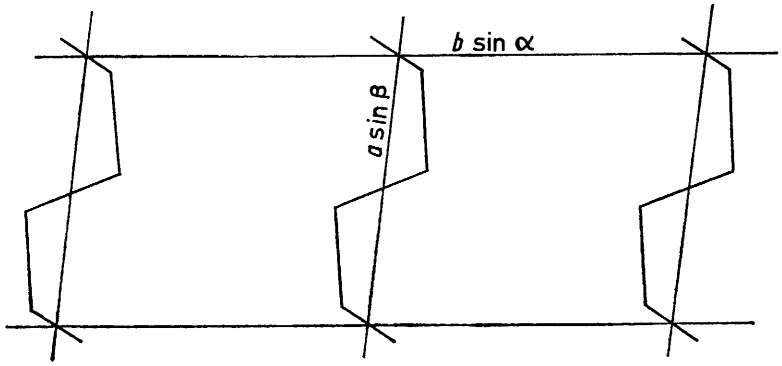

FIGURE 5 Projection on a plane perpendicular to c_0 axis of the triclinic subcell of 1,3,8,10-tetraoxacyclotetradecane

The packing of the rings face to face along the *c* axis of the unit cell, resembles that foreseen by Kitaigorodskii for triclinic even-numbered alkanes[9] and later found for triclinic polyethylene,[10] for triclinic *trans*-polyalkenamers[11] and for cyclic $[CH_2]_{34}$.[12] By considering the lengths of the lateral zig-zag chains as infinite and constituted by CH_2 methylene groups only, we can derive for (I) a triclinic subcell, the parameters of which are: $a_s = 4{\cdot}3$, $b_s = 4{\cdot}724$ (*c* axis of the monoclinic cell), $c_{os} = 2{\cdot}52$ Å, $\alpha_s = 90$, $\beta_s = 107$, $\gamma_s = 103°$. The corresponding values for triclinic polyethylene are: $a = 4{\cdot}285$, $b = 4{\cdot}82$, $c = 2{\cdot}54$ Å, $\alpha = 90$, $\beta = 110$, $\gamma = 107°$.

In both cases, the lateral zig-zag chains, which are adjacent in the direction of the a_s axis, are displaced along the *c* axis by $c_{os}/2$ (*i.e.*, one CH_2 group) whereas those which are adjacent in the direction of the b_s axis are not displaced along *c* (Figure 5). Using this (or any other) triclinic subcell, the $a_s \sin \beta$ and $b_s \sin \alpha$ lengths of 4·1 and 4·7 Å, are almost identical with the corresponding values quoted for the triclinic cells of polyethylene, of *trans*-polyalkenamers and of cyclic $[CH_2]_{34}$.

The extrapolation of these findings to polymeric materials in order to explain the chain-folding phenomenon, cannot be made directly in a simple way. Nevertheless, we consider this present work sheds light on the possible structures of the folds in polymeric materials. Our results confirm that the chain-folding in triclinic polyethylene may be actuated by a succession of torsion angles nearly of the type $G+G+T$ $G+G+$ or $G-G-T$ $G-G-$ (T = *trans* and G = *gauche*) and by additional deformations of the bond angles, without sensibly altering the chain packing in the crystals. This agrees also with the results of minimum potential-energy calculations performed, for the *A* type of folding in orthorhombic polyethylene.[13]

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[2/808 *Received*, 10*th April*, 1972]

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