

- LIDE, JR., D. R. (1962). *Tetrahedron*, **17**, 125.
 MATHIESON, A. McL. (1961). *Pure and Appl. Chem.* **2**, 505.
 MO, F. (1966). Thesis, The Technical Univ. of Norway, Trondheim.
 ROGERS, D. & MOFFETT, R. H. (1956). *Acta Cryst.* **9**, 1037.
 SIM, G. A. (1958). *Acta Cryst.* **11**, 420.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
 SØRENSEN, N. A., GILLEBO, T., HOLTERMANN, H. & SØRENSEN, J. S. (1951). *Acta Chem. Scand.* **5**, 757.
 SØRENSEN, N. A. & MEHLUM, J. (1948). *Acta Chem. Scand.* **2**, 140.
 SØRUM, H., BARSTAD, J. & DALE, J. (1956). *Acta Chem. Scand.* **10**, 1663.
 SØRUM, H. & DALE, J. (1955). *Acta Chem. Scand.* **9**, 141.
 WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151.

Acta Cryst. (1968). **B24**, 615

The Crystal and Molecular Structure of Cyclotetatriacontane [CH₂]₃₄

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Crystals of cyclic paraffins of long chain lengths have considerable interest in relation to the chain-folded nature of the crystallization of polymers in general. A three-dimensional analysis of [CH₂]₃₄ crystals indicates that the molecular rings are collapsed and are basically in the form of two roughly parallel zigzag chains of 15 atoms, linked at each end by two closure atoms, and conforming to a path traceable in the diamond structure. Small twists and bond distortions occur in the side chains as a result of steric hindrance at the closure atoms, which hindrance is also indicated by extensive strain at the molecule ends. The sub-cell is described in detail and related to other polymeric materials. A final *R* value of 0.16 was achieved with the use of 446 reflexion intensities.

Introduction

In recent years, the preparation of single crystals of a number of different polymers has been reported, for example, polyethylene (Keller, 1957; Fischer, 1957; Till, 1957), polyoxymethylene (Geil, 1960), cellulose (Manley, 1961), polypropylene (Morrow, Sauer & Woodward, 1965), establishing beyond doubt the general occurrence of the single-crystal phase in polymers. Such crystallization takes place by a folding of the main polymer chains at regular intervals, the distance between successive folds (the fold length) being constant for crystals prepared at a particular temperature. The crystals are thin platelets, the thickness being usually equal to one or a few of the fold lengths which are ~100 Å each. Such crystals are well suited for study by the electron microscope, investigations with which have revealed a wealth of morphological detail. The extreme fragility of these crystals has limited X-ray study to the more robust aggregates, and up to the present, the arrangement of atoms in the folded regions and the influence of this, if any, on polymer properties has not been established.

There is another class of compound in which sharp folds occur between carbon chains; this is the homologous series of large cyclic paraffins [CH₂]_{*n*} first prepared by Ruzicka, Plattner & Wild (1964). The work

of Ruzicka and co-workers, combined with the X-ray observations of Muller (1933), established that the large rings (*n* > 22) crystallized as two parallel linear chains, linked by a few closure atoms at either end.

It was considered that an X-ray analysis of the crystal structures of cyclic paraffins would be useful, in order to reveal features that might be applicable to polyethylene. With the same chain packing, the same fold configuration would be anticipated. It can be supposed that several fold configurations are possible for cyclic paraffins, depending on the number of members in the ring, and that one of these fold configurations

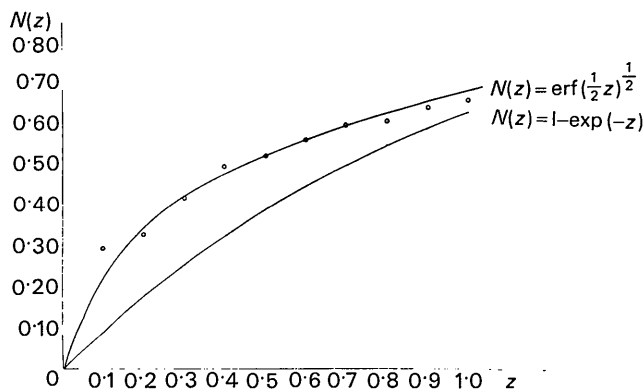


Fig. 1. Distribution of intensities for the *0kl* reflexions. *z* = intensity expressed as a fraction of local average intensity. *N(z)* = fraction of reflexions with intensity less than *z*.

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might be directly applicable to the polyethylene case. If not, then at least it is likely that a survey of the various fold configurations occurring in different cyclic paraffins would throw some light on those factors most influencing the fold configurations in polymers. The largest cyclic paraffin available to us was cyclotetatriacontane $[\text{CH}_2]_{34}$ (prepared by Wassermann (1960), Bell Telephone Laboratories, Murray Hill, New Jersey) and an X-ray crystal structure analysis of this compound was made.

Experimental

Crystals were grown by slow evaporation of xylene solution. Using a C. Supper Mark II precession camera and Cu $K\alpha$ radiation, it was found that the crystals were triclinic,

$$a = 8.172 \pm 0.016, \quad b = 5.470 \pm 0.010, \quad c = 18.91 \pm 0.04 \text{ \AA}$$

$$\alpha = 87^\circ 18' \pm 6', \quad \beta = 95^\circ 10' \pm 3', \quad \gamma = 106^\circ 04' \pm 6'$$

$$V = 808.8 \text{ \AA}^3,$$

1 molecule per unit cell; calculated density 0.979 g.cm^{-3} .

The density of the crystals as measured in a density gradient column was $0.979 \pm 0.001 \text{ g.cm}^{-3}$. Using a small crystal ($1 \text{ mm} \times 1 \text{ mm} \times 0.02 \text{ mm}$) the $h0l$, $h1l$, $h2l$, and $0kl$ reflexions were recorded by the multiple-film method with an Enraf-Nonius integrating Weissenberg camera. 446 independent reflexions were measured with a Joyce-Loebl microdensitometer, and corrected for Lorentz and polarisation effects, but not for absorption.

The statistical analysis of intensities suggested by Howells, Phillips & Rogers (1950) was used to distinguish between the space-groups $P1$ and $P\bar{1}$. By considering the fraction $N(z)$ of reflexions with intensities less than or equal to fractions (z) of the local average intensity, then for the non-centrosymmetric case, we have $N(z) = 1 - \exp(-z)$ and for the centrosymmetric case, $N(z) = \text{erf}(\frac{1}{2}z)^{1/2}$ where $\text{erf}(x)$ is the error function.

These two functions are shown plotted in Fig. 1. The experimental points obtained from the $(0kl)$ zone of reflexions are plotted also. This analysis indicates that the crystal is centrosymmetric.

Sub-cell determination

The $01\bar{2}$ and $20\bar{1}$ reflexions are the two most intense reflexions measured, and it seemed reasonable to sur-

mise that the chains of the molecule lay parallel to the intersection of these planes. (This was later confirmed from Patterson projections.) A second unit cell B was calculated, such that the c axis was parallel to the chain

direction, using the transformation $\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 1 & 4 & 2 \end{vmatrix}$ giving:

$$a_B = 8.172, \quad b_B = 5.470, \quad c_B = 43.58 \text{ \AA};$$

$$\alpha_B = 60^\circ 35', \quad \beta_B = 91^\circ 42', \quad \gamma_B = 106^\circ 04'.$$

with two molecules per unit cell.

From the distribution of intensities, the existence of a sub-cell was apparent, bounded approximately by (010) , (200) and $(1,0,17)$ planes as defined in the B unit-cell system. The dimensions of this sub-cell were calculated to be:

$$a_s = 4.246, \quad b_s = 5.470, \quad c_s = 2.564 \text{ \AA};$$

$$\alpha_s = 60^\circ 30', \quad \beta_s = 74^\circ 08', \quad \gamma_s = 96^\circ 47'$$

$$V_s = 47.53 \text{ \AA}^3, \quad 2 \text{ CH}_2 \text{ groups per sub-cell.}$$

Calculated density 0.980 g.cm^{-3} .

In linear paraffins and polyethylene the sub-cell most commonly encountered is the orthorhombic cell. However, triclinic cells have been observed in some long-chain fatty acids and also in the linear paraffins. More recently, workers with cold-worked polyethylene found reflexions which could not be indexed with the use of the usual orthorhombic cell, and Turner-Jones (1962) has ascribed a triclinic sub-cell to these reflexions. A thorough study of the possible packings of infinitely long hydrocarbon chains has been made by Segerman (1965), who showed that these triclinic sub-cells were in fact derived from a monoclinic form of chain-packing. Segerman interprets the small departures from this monoclinic cell as being caused by 'end effects'. Table 1 shows the triclinic sub-cells obtained from several compounds, those from $[\text{CH}_2]_{34}$ and polyethylene II being transformed for the purposes of comparison. Since the sub-cell obtained for $[\text{CH}_2]_{34}$ is similar to the sub-cell found in some forms of polyethylene, it is likely that the fold configuration in each case is essentially similar.

Derivation of trial structure

In the case of $[\text{CH}_2]_{34}$ described in terms of the B cell, the distance available for end to end packing of the molecules is $\frac{1}{2}c_B$. If the alternate carbon repeat distance along a chain is c_s then the length of a linear

Table 1. *Sub-cell constants of substances with long carbon chains*

| | Authors | a | b | c | α | β | γ |
|-----------------------------------|--------------------------|-------|------|-------|----------------|-----------------|-----------------|
| Trilaurin (β form) | Vand & Bell (1951) | 4.287 | 5.4 | 2.45 | $74^\circ 45'$ | $108^\circ 02'$ | $117^\circ 24'$ |
| n-Pentadecanoic acid (A' form) | von Sydow (1954) | 4.25 | 5.82 | 2.61 | 66° | 106° | 122° |
| Lauric acid (A form) | von Sydow (1956) | 4.42 | 5.41 | 2.63 | 74° | 109° | 122° |
| Lauric acid (A ₁ form) | Lomer (1963) | 4.25 | 5.41 | 2.54 | $74^\circ 54'$ | $108^\circ 24'$ | 120° |
| Potassium palmitate | Dumbleton & Lomer (1965) | 4.15 | 5.30 | 2.557 | $65^\circ 12'$ | $108^\circ 30'$ | $110^\circ 24'$ |
| Polyethylene II | Turner-Jones (1962) | 4.285 | 5.45 | 2.54 | $62^\circ 12'$ | $110^\circ 15'$ | $110^\circ 68'$ |
| $[\text{CH}_2]_{34}$ | Current work | 4.319 | 5.47 | 2.564 | $60^\circ 35'$ | $108^\circ 57'$ | $116^\circ 04'$ |

chain with N carbon atoms is $\frac{1}{2}(N-1)c_s$. Assuming that the linear sections of molecules packing end to end are collinear and that terminal carbon atoms in such adjacent chains are separated by q , we have then $\frac{1}{2}(N-1)c_s + q = \frac{1}{2}c_B$.

The value of q results from the close-packing of the ends of the molecules and depends on the details of the fold configuration. Using $c_s = 2.564 \text{ \AA}$, values of q for various N can be calculated. If we assume N to be 13, 14, and 15, then q is 6.41, 5.13 and 3.84 \AA . The distance between terminal carbon atoms (Shearer & Vand, 1956) in the case of the linear paraffin $C_{36}H_{74}$ is 3.91 \AA thus indicating that for $[\text{CH}_2]_{34}$ there are probably 15 atoms in each chain and two end atoms (atoms not lying on either straight chain, *i.e.* closure atoms) at either end. However, a value for q of 5.13 \AA with three closure atoms at either end, which would be expected to be a more bulky configuration, is also possible.

If the linear sections of the molecule are not to be seriously twisted in the middle then the centre of symmetry of the molecule would require the carbon-carbon zigzags to be roughly parallel and this then would make a comparison with the diamond structure appropriate. It would seem reasonable to suppose that

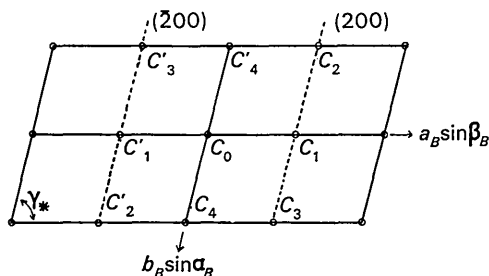


Fig. 2. Projection onto plane perpendicular to chain direction for $[\text{CH}_2]_{34}$. Small circles represent projected chains.

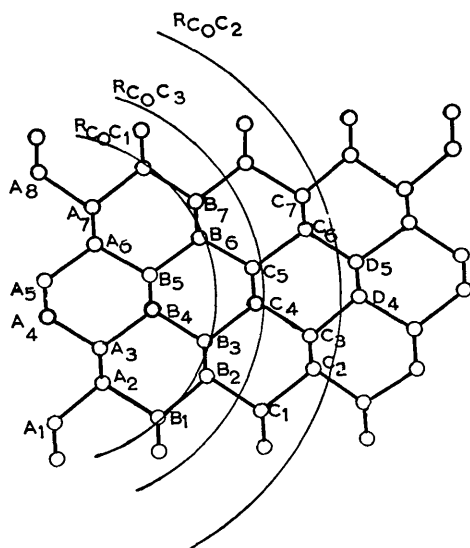


Fig. 3. Projection of diamond structure onto (110) plane.

configurations traceable on the diamond structure would be of lower energy than structures not traceable in such a way. For the orthorhombic phase of polyethylene, with non-parallel zigzag chains, the diamond structure would not be appropriate and this then would imply a fold configuration with a higher strain-energy than that considered here.

From a study of the diamond structure, it is clear that a large number of configurations are possible for a molecule of the cyclic paraffin $[\text{CH}_2]_{34}$, but in view of the packing considerations only those configurations with two, three, or four closure atoms were considered. Fig. 2 shows the projection of the molecular chains onto a plane perpendicular to the chain direction. The three possible linkages between chain C_0 placed at the origin and chains C_1, C_2, C_3 were considered; the repeat nature of the unit cell entailing linkages of C_0 with C_4 and C'_4 is impossible. The perpendicular distances between these chains are $R_{C_0C_1} = 4.08 \text{ \AA}$, $R_{C_0C_2} = 7.15 \text{ \AA}$, and $R_{C_0C_3} = 5.26 \text{ \AA}$.

Referring now to the diamond structure to consider configurations for the possible chain separations just quoted, Fig. 3 shows a projection of the diamond structure onto the (110) plane. Chains are perpendicular to this projection, and the planes of the carbon-carbon zigzags are represented by the vertical traces A_2A_3, B_2B_3, A_4A_5 etc. The possible linkages between the chain A_4A_5 and chains at the perpendicular distances $R_{C_0C_1}, R_{C_0C_2}$ and $R_{C_0C_3}$ are then considered; arcs centred on the mid-point of A_4A_5 with these expected separations are shown in the Figure. If chains C_0 and C_2 are linked, then Fig. 3 shows that at least four closure atoms are required. Moreover since there are no chains at the appropriate distance in the diamond structure, then considerable bond deformation would be involved in the fold configuration. The perpendicular distance between chains A_4A_5 and C_4C_5 is 5.05 \AA compared with the value for $R_{C_0C_3}$ of 5.26 \AA . These chains could be linked by a fold configuration of three atoms (A_3, B_4 and B_3). However, the best fit occurs for a linkage of only two closure atoms, A_3 and B_4 (or A_6 and B_5) between chains A_4A_5 and B_2B_3 (or B_6B_7) and the perpendicular separation of these chains in diamond is 4.18 \AA compared with the value for $R_{C_0C_1}$ in the structure of 4.08 \AA . With this configuration, there would be only eight *gauche* bonds per molecule and any of the other arrangements would involve more. Further, this latter arrangement meets the packing requirement of the measured sub-cell since the translation vector t between the chains is inclined to the chain axis by an angle of $\sim 72^\circ$ (compared with the measured value for $\beta_s = 74^\circ 08'$) and is of magnitude 4.12 \AA (compared with the measured value of $a_s = 4.25 \text{ \AA}$).

Analysis

Computations were made with the crystallographic programs of Daly, Stephens & Wheatley (1963) with the Elliott 503 computer, the quantity minimized in

the structure-factor least-squares program being $\sum_q W_q \Delta^2 = \sum_q W_q (|F_o| - |F_c|)^2$ where q is hkl , W a weighting factor and F_o, F_c the observed and calculated structure factors, the program following closely the procedure of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961). Scattering factors for carbon and hydrogen were taken from *International Tables for X-ray Crystallography*, Vol. III.

From the spatial argument given, it seemed likely that there would be two carbon atoms at either end of the molecule not lying on either of the two parallel chains. Comparison with the diamond structure has shown that two possibilities existed, corresponding essentially to two different orientations of the plane of the carbon-carbon zigzag in the unit cell. If the angle between the plane of the zigzag and b_B projected onto a plane perpendicular to the chain direction is θ , then these possibilities correspond to two values of θ (0° and $-42^\circ 30'$). Known structures of the triclinic sub-cell would not involve either of these two orientations. However, a study by Kitaigorodskii (1957) of the packing of infinite aliphatic chains in terms of optimum nearest neighbour fit pointed to a possible triclinic sub-cell (with dimensions similar to the [CH₂]₃₄ cell) which corresponded approximately to the packing entailed by an orientation $\theta = 0^\circ$. This possibility was considered first. The coordinates of all the atoms (including hydrogen) were calculated and an isotropic temperature factor $B = 5.0 \text{ \AA}^2$ assigned to each. When the calculated and observed F values for the $h0l$ reflexions were compared for this possibility a value for the reliability index $R = (\sum_q |F_o| - |F_c|) / \sum_q |F_o|$ of 0.55 was obtained. This high value for R indicated that this structure was probably incorrect.

The calculated structure factors were examined in greater detail and it was noticed that the most serious discrepancy occurred for the strong 108 and 10 $\bar{9}$ reflexions corresponding to sub-cell planes. The ratio $|F(108)_{\text{obs}}| / |F(10\bar{9})_{\text{obs}}|$ between the observed values was $\sim 3/4$, whereas the ratio between the calculated values was $\sim 5/3$. If all hydrogen atoms and closure atoms were neglected then $|F(108)_{\text{calc}}| = |F(10\bar{9})_{\text{calc}}|$. It was noticed that the positions of the closure atoms were such that they contributed to the 108 reflexion and detracted from the 10 $\bar{9}$ reflexion. These considerations pointed to the alternative possibility, $\theta = -42^\circ 30'$. The coordinates of all atoms for this case were calculated and used to compute the structure factors of $h0l$ reflexions. A comparison between $|F_{\text{calc}}|$ and $|F_{\text{obs}}|$ values indicated considerable improvement, a figure for $R = 0.40$ being obtained. All the data were included and after three cycles of the least-squares structure-factors program the value for R dropped to 0.27, only the coordinates of carbon and hydrogen atoms being refined, and an isotropic temperature factor ($B = 5.0 \text{ \AA}^2$) being assigned to each atom and maintained constant.

With a rescaling between different zones of reflexions, and a further three cycles, the value for R dropped to 0.18.

Since the proportion of scattering material in the folded regions is relatively small, some doubt was felt at this stage that the coordinates of the end atoms were sufficiently critical to distinguish between different fold configurations. For this reason various fold configurations (even though sterically unfavourable) were tried, without altering the coordinates of the bulk of the atoms in the chains. In all, six alternative folding schemes were attempted, and subsequent refinement failed to reduce the value for R to below 0.36 for any of these possibilities.

Isotropic temperature factors for the carbon atoms were included in the refinement, and with two more cycles the value for R dropped to 0.16. For long paraffinic chains a marked thermal anisotropy of vibration is common, large vibrations perpendicular to the chain direction and small vibrations in the chain direction being usual. Values of U_{ij} , the anisotropic thermal vibration parameters, which would describe such an effect were estimated and when the structure factors were recalculated some of them changed markedly, indicating that further least-squares refinement would be advantageous. It would have been desirable to use anisotropic temperature factors with the carbon atoms and isotropic temperature factors for the hydrogen atoms and to refine only the coordinates and the U_{ij} . However, the computer program used was not of sufficient flexibility to permit this procedure. With six temperature parameters and three positional parameters for each atom, the total number of independent parameters is 460, and the amount of data did not warrant the least-squares refinement of all these parameters together. Thus the refinement was concluded at this point. Table 2 shows the observed and calculated structure factors.

Table 2. Comparison of observed and calculated structure factors

| | F_o | F_c | | F_o | F_c |
|---------|-------|-------|---------|--------|--------|
| 0 0 2 | -927 | -261 | 2 0 1 | 1766 | 1758 |
| 0 0 3 | 1357 | 1502 | 2 0 2 | -1394 | -1626 |
| 0 0 4 | -1896 | -2066 | 2 0 3 | 781 | 1078 |
| 0 0 5 | 2010 | 1691 | 2 0 4 | -247 | -442 |
| 0 0 6 | -2068 | -1732 | 2 0 5 | 2 | -285 |
| 0 0 7 | 2198 | 1930 | 2 0 6 | -258 | -509 |
| 0 0 8 | -2368 | -1595 | 2 0 7 | 470 | 547 |
| 0 0 10 | 825 | 413 | 2 0 13 | -244 | -135 |
| 0 0 11 | -711 | -475 | 2 0 14 | 445 | 597 |
| 0 0 12 | 653 | 612 | 2 0 15 | -942 | -947 |
| 0 0 13 | -997 | -474 | 2 0 16 | -1304 | -1259 |
| 0 0 14 | 556 | 120 | 2 0 -1 | -11407 | -11131 |
| 0 0 15 | -535 | -499 | 2 0 -2 | -4784 | -5472 |
| 0 0 16 | 412 | 507 | 2 0 -3 | 1983 | 2312 |
| 0 0 17 | 808 | 797 | 2 0 -4 | -711 | -464 |
| 1 0 0 | 206 | 273 | 2 0 -6 | 470 | 627 |
| 1 0 1 | 789 | 827 | 2 0 -7 | -235 | -236 |
| 1 0 2 | -1853 | -1783 | 2 0 -8 | -678 | -444 |
| 1 0 3 | 1955 | 1700 | 2 0 -9 | 486 | 531 |
| 1 0 4 | -1410 | -1171 | 2 0 -10 | 1415 | 1313 |
| 1 0 5 | -578 | -332 | 2 0 -11 | -972 | -1068 |
| 1 0 6 | 321 | 40 | 2 0 -13 | 290 | 256 |
| 1 0 7 | -1666 | -1099 | 2 0 -14 | -460 | -426 |
| 1 0 8 | -3940 | -3224 | 2 0 -15 | 326 | 326 |
| 1 0 9 | -1176 | -948 | 2 0 -18 | -235 | -253 |
| 1 0 10 | 141 | 148 | 3 0 0 | 846 | 907 |
| 1 0 11 | -835 | -856 | 3 0 1 | -680 | -842 |
| 1 0 12 | 554 | 460 | 3 0 2 | 532 | 151 |
| 1 0 13 | -216 | -231 | 3 0 3 | -436 | -408 |
| 1 0 14 | 529 | 249 | 3 0 4 | 496 | 284 |
| 1 0 16 | -568 | -449 | 3 0 6 | -263 | -131 |
| 1 0 -1 | -216 | -268 | 3 0 7 | 569 | 367 |
| 1 0 -2 | 839 | -252 | 3 0 8 | 293 | 261 |
| 1 0 -3 | -2054 | -2622 | 3 0 14 | -172 | -154 |
| 1 0 -4 | 2254 | 2840 | 3 0 15 | 685 | 650 |
| 1 0 -5 | -1983 | -1964 | 3 0 -1 | 471 | 429 |
| 1 0 -6 | 1517 | 1196 | 3 0 -2 | -1828 | -2128 |
| 1 0 -7 | -1101 | -999 | 3 0 -3 | 1500 | 1997 |
| 1 0 -8 | 774 | 872 | 3 0 -4 | -1018 | -993 |
| 1 0 -9 | 6583 | 5493 | 3 0 -5 | 518 | 393 |
| 1 0 -10 | 762 | 721 | 3 0 -7 | -363 | -370 |
| 1 0 -12 | 322 | 284 | 3 0 -8 | 752 | 849 |
| 1 0 -18 | 529 | 364 | 3 0 -9 | -600 | -610 |
| 2 0 0 | -1321 | -1608 | 3 0 -10 | -2550 | -2326 |

Results and conclusions

Cruickshank's weighting scheme was used,

$$w_q = \frac{1}{a + |F_o| + c|F_o|^2}$$

with $a \sim 2|F_o \min|$ and $c \sim 2/|F_o \max|$. The greatest precision can be achieved by the least-squares procedure only if the assigned weights are correct. The precision of the weighting scheme was assessed by subdividing the reflexions into groups according to (a) magnitude of F_o , (b) value of $\sin^2\theta/\lambda^2$. It is generally assumed that if the averages of $w\Delta_q^2$ are constant for all the groups of reflexions, then the weights are correct. The results of this analysis are shown in Table 3, the averages being roughly constant except in those cases with only a few reflexions per group, when the results are not statistically reliable.

Table 3

(a) Analysis of weighting scheme in terms of $|F_o|$

| $\Sigma w\Delta_q^2/n$ | $\Sigma w\Delta_q^2$ | n | $ F_o $ |
|------------------------|----------------------|-----|-------------|
| 0.62 | 875 | 14 | 0-1.0 |
| 0.71 | 143 | 2 | 1.0-2.0 |
| 0.13 | 597 | 47 | <i>etc.</i> |
| 0.10 | 1548 | 150 | |
| 0.11 | 1286 | 112 | |
| 0.16 | 971 | 59 | |
| 0.38 | 607 | 16 | |
| 0.48 | 240 | 5 | |
| 0.02 | 2 | 1 | |

(b) Analysis of weighting scheme in terms of $(\sin \theta/\lambda)^2$

| $\Sigma w\Delta_q^2/n$ | $\Sigma w\Delta_q^2$ | n | $(\sin \theta/\lambda)^2$ |
|------------------------|----------------------|-----|---------------------------|
| 0.15 | 895 | 60 | 0-0.128 |
| 0.18 | 1782 | 99 | 0.128-0.256 |
| 0.16 | 1349 | 84 | <i>etc.</i> |
| 0.12 | 587 | 51 | |
| 0.14 | 640 | 47 | |
| 0.12 | 361 | 29 | |
| 0.05 | 99 | 18 | |
| 0.37 | 480 | 13 | |
| 0.0 | 0 | 0 | |
| 0.09 | 38 | 4 | |
| 0.38 | 38 | 1 | |

The coordinates of all the atoms and the average standard deviations in the carbon and hydrogen atom positions are shown in Table 4, where the designation of each atom is best seen from Fig. 4. The contribution of individual hydrogen atoms to the resulting structure amplitudes being relatively small, the standard deviations in these coordinates are correspondingly high (~ 0.1 Å). The standard deviations in the carbon atom coordinates are comparable with those obtained for structures of other long-chain compounds, for examples, potassium palmitate (Dumbleton & Lomer, 1965), lauric acid (Lomer, 1963) and oleic acid (Abrahamsson & Ryderstedt-Nahrngbauer, 1962). The effect of large temperature factors and crystal imperfection is to limit the number and accuracy of measurable reflexions, and

this combined with the large number of variable parameters leads to high values in the standard deviations encountered in this type of compound.

Table 4. Atomic coordinates (Å) and standard deviations

(a) Coordinates referred to primitive unit cell

| | X | Y | Z |
|--------|---------|---------|---------|
| Cl | -3.9751 | -4.4473 | -7.8824 |
| C(2) | -3.4211 | -3.0454 | -7.0548 |
| C(3) | -3.5375 | -3.2768 | -5.5765 |
| C(4) | -2.9217 | -1.9039 | -4.7566 |
| C(5) | -2.9732 | -2.2870 | -3.2795 |
| C(6) | -2.4385 | -0.9066 | -2.4218 |
| C(7) | -2.4549 | -1.0543 | -0.9349 |
| C(8) | -1.9539 | 0.3407 | -0.2436 |
| C(9) | -1.9128 | 0.1868 | 1.2766 |
| C(10) | -1.2483 | 1.6126 | 2.0099 |
| C(11) | -1.3815 | 1.5602 | 3.4627 |
| C(12) | -0.7219 | 2.9092 | 4.1853 |
| C(13) | -0.6753 | 2.7407 | 5.7065 |
| C(14) | -0.0836 | 4.2142 | 6.3615 |
| C(15) | -0.1658 | 4.1145 | 7.9278 |
| C(16) | -5.6101 | -5.0831 | -7.7556 |
| C(17) | -6.4020 | -3.8933 | -8.2265 |
| H(B1) | -4.1801 | -6.3727 | -6.6437 |
| H(R1) | -4.5092 | -4.5110 | -7.7849 |
| H(L2) | -6.0706 | -2.3092 | -6.7340 |
| H(R2) | -2.6198 | -2.7406 | -7.2239 |
| H(L3) | -4.3602 | -3.6401 | -5.6842 |
| H(R3) | -2.6711 | -4.0175 | -5.3311 |
| H(L4) | -3.6221 | -1.2721 | -4.7439 |
| H(R4) | -2.0433 | -1.6657 | -4.7983 |
| H(L5) | -3.6118 | -2.9629 | -2.8346 |
| H(R5) | -2.6648 | -2.2214 | -3.0661 |
| H(L6) | -3.2501 | -0.3163 | -2.7151 |
| H(R6) | -1.3762 | 0.0300 | -2.5054 |
| H(L7) | -3.3175 | -2.0284 | -0.6765 |
| H(R7) | -1.8105 | -1.0064 | -0.7047 |
| H(L8) | -2.4414 | 0.6836 | -0.3393 |
| H(R8) | -1.3054 | 0.8601 | -0.7150 |
| H(L9) | -2.5984 | -0.4038 | 1.5329 |
| H(R9) | -1.1911 | -0.0579 | 1.4804 |
| H(L10) | -2.0642 | 2.2225 | 1.9101 |
| H(R10) | 0.0610 | 2.0012 | 1.9389 |
| H(L11) | -2.4927 | 0.8198 | 3.6972 |
| H(R11) | -0.9403 | 1.6115 | 3.4160 |
| H(L12) | -1.6959 | 3.9824 | 3.2316 |
| H(R12) | 0.4324 | 3.1369 | 4.4548 |
| H(L13) | -1.3865 | 2.3071 | 5.9151 |
| H(R13) | -0.1795 | 2.8442 | 5.6268 |
| H(L14) | -0.1302 | 6.2426 | 4.7973 |
| H(R14) | 1.2451 | 4.0408 | 6.3714 |
| H(L15) | -0.7790 | 3.2155 | 8.9480 |
| H(T15) | 0.4330 | 4.5814 | 7.8996 |
| H(L16) | -5.6525 | -5.0952 | -6.7156 |
| H(T16) | -6.1866 | -0.4479 | -8.8915 |
| H(B17) | -6.2553 | -2.9147 | -8.3714 |
| H(T17) | -6.8725 | -3.3812 | -9.5334 |

(b) Average standard deviations

| | X | Y | Z |
|---|--------|--------|--------|
| C | 0.0228 | 0.0254 | 0.0209 |
| H | 0.1536 | 0.1675 | 0.1440 |

The C-C bond lengths, the C-C-C bond angles and the standard deviations in these quantities are shown in Table 5. *Trans* and *gauche* bond designations are

also given in Table 5, the assignment being made by considering an anti-clockwise sequence on Fig. 4. The mean value of those C-C bond lengths in the chain C(2)-C(14) is 1.531 \AA with a standard deviation of $\sim 0.01 \text{ \AA}$. The bond lengths in the fold regions seem to be systematically higher, the largest C-C bond being C(17)-C(16), which is $1.633 \pm 0.033 \text{ \AA}$. The mean value of those C-C-C bond angles in the chain C(2)-C(3)-C(4) to C(12)-C(13)-C(14) is $112^\circ 44' \pm 27'$, cf. the tetrahedral angle $109^\circ 28'$. The distance C_s between alternate carbon atoms in the chain is shown in Table 6, the mean value being $2.547 \pm 0.01 \text{ \AA}$. In order to assess the degree of twisting along the chain, the angle between each C-C bond and the b axis, projected onto a plane perpendicular to the chain direction was calculated. The standard deviation in these angles was estimated to be $\sim 4^\circ$. To this accuracy it appeared that the carbon atoms in the chain were coplanar. A mean value for $\theta = -26^\circ 45'$ was obtained.

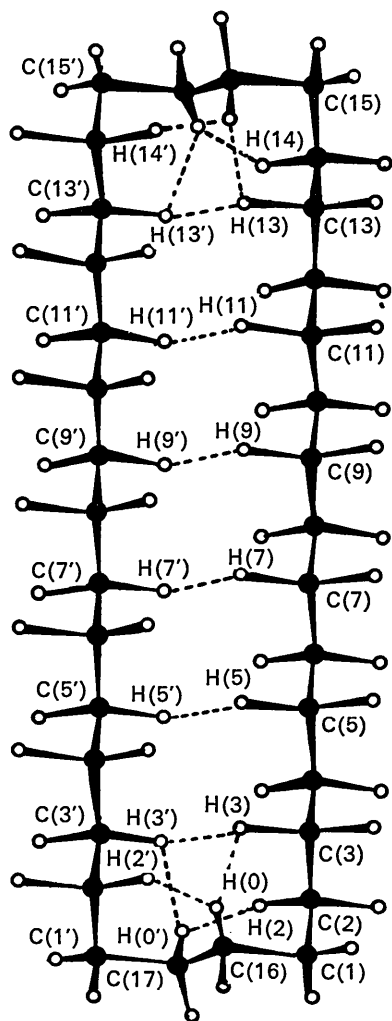


Fig. 4. Configuration of $[\text{CH}_2]_{34}$ (from diamond structure). Hydrogen atoms separated by less than $2R_H$ joined by dashed lines.

Table 5. Bond lengths and angles

| | | |
|-------------------|-------------------------------|---------------|
| C(1')-C(17) | $1.615 \pm 0.034 \text{ \AA}$ | <i>gauche</i> |
| C(17)-C(16) | 1.633 ± 0.033 | <i>gauche</i> |
| C(16)-C(1) | 1.596 ± 0.035 | <i>trans</i> |
| C(1)-C(2) | 1.598 ± 0.034 | <i>gauche</i> |
| C(2)-C(3) | 1.495 ± 0.033 | <i>gauche</i> |
| C(3)-C(4) | 1.576 ± 0.033 | <i>trans</i> |
| C(4)-C(5) | 1.510 ± 0.033 | <i>trans</i> |
| C(5)-C(6) | 1.596 ± 0.033 | <i>trans</i> |
| C(6)-C(7) | 1.488 ± 0.033 | <i>trans</i> |
| C(7)-C(8) | 1.522 ± 0.033 | <i>trans</i> |
| C(8)-C(9) | 1.519 ± 0.032 | <i>trans</i> |
| C(9)-C(10) | 1.581 ± 0.032 | <i>trans</i> |
| C(10)-C(11) | 1.468 ± 0.033 | <i>trans</i> |
| C(11)-C(12) | 1.513 ± 0.033 | <i>trans</i> |
| C(12)-C(13) | 1.521 ± 0.032 | <i>trans</i> |
| C(13)-C(14) | 1.577 ± 0.030 | <i>trans</i> |
| C(14)-C(15) | 1.573 ± 0.033 | <i>trans</i> |
| C(2')-C(1')-C(17) | $107.95^\circ \pm 1.5^\circ$ | |
| C(1')-C(17)-C(16) | 120.17 ± 1.5 | |
| C(17)-C(16)-C(1) | 108.75 ± 1.5 | |
| C(16)-C(1)-C(2) | 109.73 ± 1.5 | |
| C(1)-C(2)-C(3) | 113.45 ± 1.5 | |
| C(2)-C(3)-C(4) | 112.98 ± 1.5 | |
| C(3)-C(4)-C(5) | 108.12 ± 1.5 | |
| C(4)-C(5)-C(6) | 109.38 ± 1.5 | |
| C(5)-C(6)-C(7) | 117.93 ± 1.5 | |
| C(6)-C(7)-C(8) | 112.53 ± 1.5 | |
| C(7)-C(8)-C(9) | 112.53 ± 1.5 | |
| C(8)-C(9)-C(10) | 112.98 ± 1.5 | |
| C(9)-C(10)-C(11) | 114.98 ± 1.5 | |
| C(10)-C(11)-C(12) | 115.68 ± 1.5 | |
| C(11)-C(12)-C(13) | 113.43 ± 1.5 | |
| C(12)-C(13)-C(14) | 109.50 ± 1.5 | |
| C(13)-C(14)-C(15) | 111.47 ± 1.5 | |

Table 6. Distances between alternate carbon atoms in chain

| | |
|-------------|-------------------------------|
| C(2)-C(4) | $2.561 \pm 0.032 \text{ \AA}$ |
| C(3)-C(5) | 2.499 ± 0.033 |
| C(4)-C(6) | 2.535 ± 0.033 |
| C(5)-C(7) | 2.643 ± 0.033 |
| C(6)-C(8) | 2.503 ± 0.033 |
| C(7)-C(9) | 2.529 ± 0.033 |
| C(8)-C(10) | 2.585 ± 0.033 |
| C(9)-C(11) | 2.572 ± 0.033 |
| C(10)-C(12) | 2.524 ± 0.033 |
| C(11)-C(13) | 2.536 ± 0.033 |
| C(12)-C(14) | 2.530 ± 0.030 |
| C(13)-C(15) | 2.603 ± 0.034 |

The C-C bond lengths in the chains are approximately the same, the greatest deviation from the mean value being about twice the standard deviation, and thus not of statistical significance. Also the mean bond length in the chain $1.531 \pm 0.01 \text{ \AA}$ is not significantly different from the diamond C-C length of 1.5445 \AA . The mean bond angle C-C-C, equal to $112^\circ 44' \pm 27'$, in the chain is significantly greater than tetrahedral, in agreement with values obtained for other longchain compounds, and this is reflected in the mean distance between alternate carbon atoms in the chain $C_s = 2.547 \pm 0.01 \text{ \AA}$. The bond lengths in the fold configuration seem consistently longer than normal, but only for the bond length C(16)-C(17) can the increase in length be regarded as possibly significant.

Fig. 4 shows the molecular configuration of $[\text{CH}_2]_{34}$ obtained from the diamond structure. In deriving this model we assumed steric hindrance between hydrogen atoms to exist only if the hydrogen atoms, when placed at the C-C bond distance from the carbon atoms, occupied the same point in space. For the model proposed there was no such steric hindrance. However, the equilibrium van der Waals separation of hydrogen atoms is 2.6 Å. Assuming C-H bond lengths to be 1.09 Å, the hydrogen atoms H(3) and H(3'), H(5) and H(5'), etc. in Fig. 4 are separated by a distance of only 2.07 Å. In the fold regions the steric hindrance is even more severe, hydrogen atom H(0) being equidistant from atoms H(2') and H(3) at 1.55 Å, and hydrogen

atom H(0') being equidistant from atoms H(2) and H(3') at the same distance. In order to avoid this steric hindrance, small deformations of bond lengths and angles combined with small twists about C-C bonds would be expected, but without a detailed knowledge of the force constants involved it would be difficult to predict that deformed configuration with the minimum potential energy.

For comparison with this configuration, the coordinates of the carbon atoms obtained from the structure analysis were transformed to the set of orthogonal axes $x y z$, with z the chain direction, and x and y parallel to and perpendicular to the plane of the carbon-carbon zigzags. The x and y projections of these

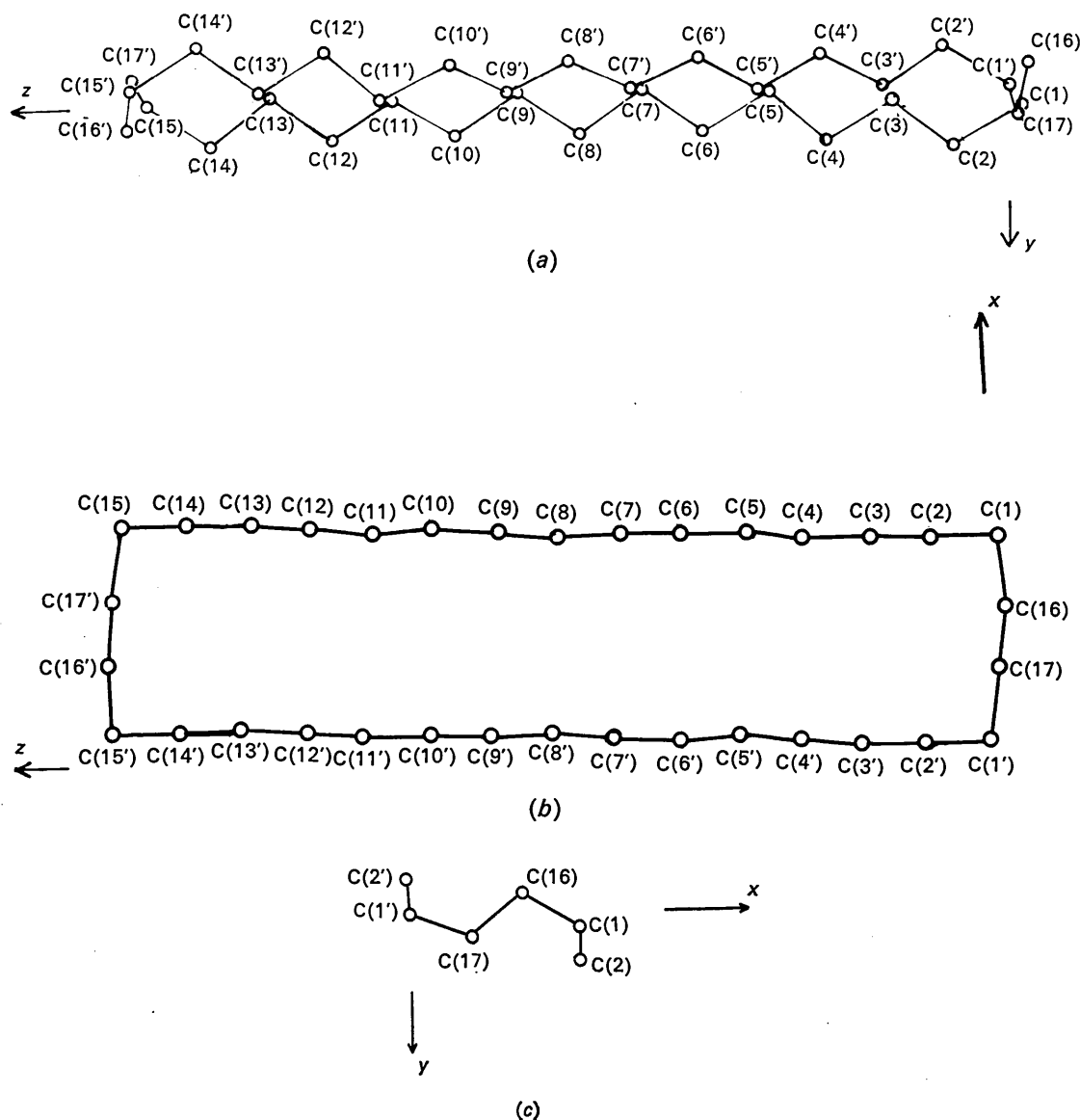


Fig. 5. (a) x projection (perpendicular to plane of C-C zigzag). (b) y projection (parallel to plane of C-C zigzag). (c) z projection of fold configuration (projection perpendicular to chain direction).

coordinates are shown in Fig. 5(a) and (b). Fig. 5(c) shows the z projection of those atoms involved in the fold configuration [C(2'), C(1'), C(17), C(16), C(1) and C(2)].

One can speculate that in order to reduce steric hindrance the molecular configuration is distorted in the following ways:

(a) The planes of the carbon-carbon zigzags are rotated about the chain direction by $\sim 16^\circ$ (from the proposed orientation of $\theta = -42^\circ 30'$ to the orientation $\theta = -26^\circ 45'$). This results in an increase in the hydrogen-hydrogen distances, H(3)-H(3'), H(5)-H(5') *etc.* of $\sim 0.56 \text{ \AA}$. The total distance between these atoms would now be 2.63 \AA compared with the van der Waals

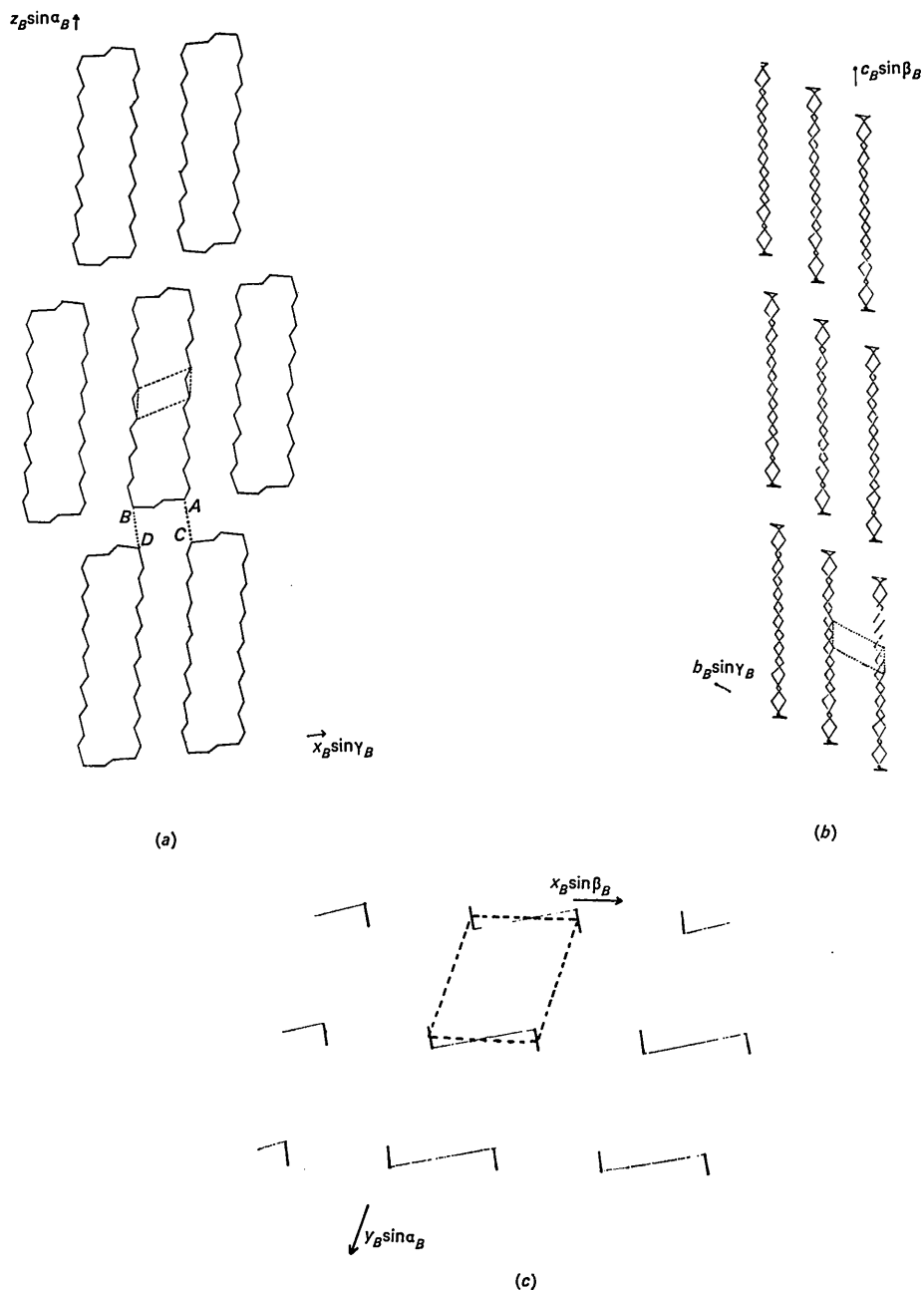


Fig. 6. (a) b_B projection showing molecular packing. Dashed lines represent sub-cell projection. (b) a_B projection showing molecular packing. Dashed lines represent sub-cell projection. (c) c projection showing molecular packing. (Only the traces of the central regions of the chains are shown.) Linked chains are joined by solid lines. Dashed lines represent sub-cell projection.

optimum separation 2.6 \AA , the resultant side-packing of the chains being approximately that packing suggested by Segerman.

(b) This rotation would have an effect tending to extend greatly the C(16)–C(17) bond length. This would be energetically unfavourable, and is avoided by a bend in the chain in the plane of the carbon–carbon zigzag, chiefly at the carbon atom C(6) [and C(10')] by an increase in C(7)–C(6)–C(5) valence angle to $117^\circ 56'$ [Fig. 5(a)]. The nearer to the chain end that this bend occurs, the less will be the *trans*-chain steric hindrance, but the greater will be the deformation of bond angle required. The observed bend in the chain presumably results from a balance of these two effects.

(c) In order to avoid steric hindrance in the fold regions, some torsion about the C(1)–C(2) and the C(1')–C(2') bonds is observed, being $\sim 7^\circ$ and $\sim 16^\circ$ respectively. This also has the effect of further reducing the C(16)–C(17) bond extension.

(d) The remaining strain appears to be taken up by an increase in the C(1')–C(17)–C(16) bond angle to $120^\circ 11'$, with a final extension of the C(17)–C(16) bond length to 1.633 \AA , although the errors in the structure determination render this latter result of doubtful significance.

The molecular packing is shown in Fig. 6. Fig. 6(a) is the projection perpendicular to b_B . The chains are all parallel, and are very nearly collinear, the angle of inclination to z_B being $\sim 3^\circ$. In order to achieve a close molecular end-to-end packing, the molecules are staggered so that atoms in the fold regions of the molecules are not adjacent. The closest end to end distances between molecules are between carbon atoms *A* and *C*, and *B* and *D*, shown dotted in Fig. 6(a). Owing to the bends in the chains of atoms, *A* and *C* are closer (3.765 \AA) than atoms *B* and *D* (4.083 \AA) and this accounts for the slight obliquity in the packing ($\sim 3^\circ$). The broken lines in Fig. 6 represent the projections of the sub-cell, and it can be seen that the chain packing is essentially that described by Segerman for the 'triclinic' sub-cell. The packing of chains in the same molecule is the same as the packing of chains in neighbouring molecules; the mean value of chain separation a_s (intramolecular) being $4.29 \text{ \AA} \pm 0.02 \text{ \AA}$ and the mean value of a_s (intermolecular) being $4.26 \text{ \AA} \pm 0.02 \text{ \AA}$, if only the central regions of the chains are considered. Fig. 6(b) shows the projection perpendicular to a_B . Adjacent molecules are displaced by c_s in the chain direction to achieve a close packing of the chains side by side without steric hindrance at the folded regions. The projection of the sub-cell is repre-

sented by dotted lines, the mean value for b_s being $4.86 \pm 0.01 \text{ \AA}$. Fig. 6(c) shows the projection perpendicular to c_B . The chains are inclined $\sim 3^\circ$ to the axis of projection with some chain bending in either molecular chain. Thus, for reasons of clarity, the average values of the *x* and *y* coordinates in projection of those atoms in the central regions of the chains have been used to define the traces of the carbon–carbon zigzags. Those chains which are in the same molecule are linked by solid lines. The sub-cell projection is shown by the dotted lines, and shows that the chain packing along b_s is that suggested by Segerman and not that of Kitaigorodskii. The planes of the carbon–carbon zigzags are approximately $(\bar{4}10)$ planes, whereas to give the triclinic packing suggested by Kitaigorodskii the planes of the carbon–carbon zigzags would be (200) planes.

The authors hope to extend these measurements to other members of the series to confirm the generality of the structural conclusions drawn from $[\text{CH}_2]_{34}$.

References

- ABRAHAMSSON, S. & RYDERSTEDT-NAHRINGBAUER, I. (1962). *Acta Cryst.* **15**, 1261.
- CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis* (Paper 6). Oxford: Pergamon Press.
- DALY, J. J., STEPHENS, F. S. & WHEATLEY, P. J. (1963). Monsanto Research S. A. Final Report no. 52.
- DUMBLETON, J. H. & LOMER, T. R. (1965). *Acta Cryst.* **19**, 301.
- FISCHER, E. W. (1957). *Z. Naturforsch.* **12a**, 753.
- GEIL, P. H. (1960). *J. Polymer Sci.* **44**, 449.
- HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
- KELLER, A. (1957). *Phil. Mag.* **2**, 1171.
- KITAIGORODSKII, A. I. (1957). *Organic Chemical Crystallography*. New York: Consultants Bureau.
- LOMER, T. R. (1963). *Acta Cryst.* **16**, 984.
- MANLEY, R. ST. J. (1961). *Nature, Lond.* **189**, 390.
- MORROW, D. R., SAUER, J. A. & WOODWARD, A. E. (1965). *J. Polymer Sci.* **B3**, 463.
- MULLER, A. (1933). *Helv. Chim. Acta.* **16**, 155.
- RUZICKA, L. VON, PLATTNER, P. A. & WILD, H. (1964). *Helv. Chim. Acta.* **29**, 1611.
- SEGERMAN, E. (1965). *Acta Cryst.* **19**, 789.
- SHEARER, H. M. M. & VAND, V. (1956). *Acta Cryst.* **9**, 379.
- SYDOW, E. VON (1954). *Acta Cryst.* **7**, 529.
- SYDOW, E. VON (1956). *Ark. Kemi*, **9**, 231.
- TILL, P. H. (1957). *J. Polymer Sci.* **24**, 301.
- TURNER-JONES, A. (1962). *J. Polymer Sci.* **62**, 553.
- VAND, V. & BELL, I. P. (1951). *Acta Cryst.* **4**, 465.
- WASSERMANN, E. (1960). *J. Amer. Chem. Soc.* **82**, 4433.