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# The Crystal Structure of *cis*-D,L-8,9-Methyleneheptadecanoic Acid (Dihydromalvalic Acid)

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The crystal structure of dihydromalvalic acid, $C_{18}H_{34}O_2$, has been determined by a three-dimensional structure analysis. The molecule is shown to have the 'bent' chain configuration believed to be a characteristic of *cis* cyclopropyl fatty acids in which the three-membered ring is located near the center of the hydrocarbon chain.

Within the cyclopropane ring the mean C–C bond length is 1·508 Å, and the bond angles are 60°. The C–C bonds *exo* to the ring are 1·507 Å, and the corresponding external and internal angles formed by these bonds with the bonds of the ring are 123° and 119°. The other bond lengths and angles in the molecule are as expected for a long chain fatty acid, *viz.*

$$\mathrm{C}(sp^3)\text{–}\mathrm{C}(sp^3) = 1{\cdot}522\ \text{Å},\ \ \mathrm{C}(sp^3)\text{–}\mathrm{C}(sp^3)\text{–}\mathrm{C}(sp^3) = 113{\cdot}6°,\ \ \mathrm{C}(sp^3)\text{–}\mathrm{C}(sp^2) = 1{\cdot}487\ \text{Å},$$
$$\mathrm{C=O}\ \ 1{\cdot}244\ \text{Å},\ \ \mathrm{C\text{–}O}\ \ 1{\cdot}299\ \text{Å},\ \text{with e.s.d. of } 0{\cdot}004\ \text{Å}\ .$$

The three-membered rings and the hydrogen-bonded carboxylic acid dimer groups restrict the close-packing of the hydrocarbon chains and, in consequence, the cross-sectional area of the straight segments of the chain molecules is 19·7 Å$^2$, as compared with the 18·5 Å$^2$ usually quoted for the orthorhombic close-packing of *n*-paraffinic chains. A marked increase is observed in magnitude and anisotropy of the thermal motion of the atoms towards the non-polar end of the hydrocarbon chain.

## Introduction

Dihydromalvalic acid (Fig. 1) is one of a number of fatty acids containing the cyclopropane ring in the chain that have been studied in these laboratories over the past several years (Brotherton & Jeffrey, 1957; Brotherton, Craven & Jeffrey, 1958; Craven & Jeffrey, 1959*a*; Craven, 1959). A two-dimensional analysis of this substance was originally carried out by Craven & Jeffrey (1959*b*) in order to elucidate the chemical structure of its precursor, malvalic acid, a compound of interest in agricultural and food chemistry (Shenstone & Vickery, 1956). In that work dihydromalvalic acid was shown to be *cis*-D,L-8,9-methyleneheptadecanoic acid. The present three-dimensional analysis was then undertaken because a detailed stereochemical description of at least one representative member in this homologous series was desired. The quality of the crystals of this compound, although not good, was exceptional in that it permitted a reasonably accurate three-dimensional study.

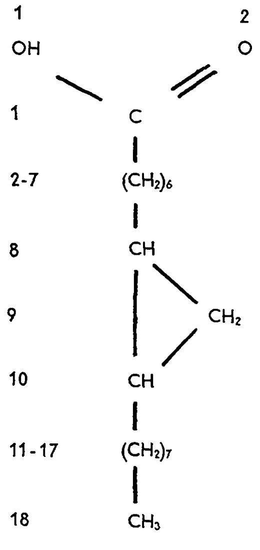

Fig. 1. Dihydromalvalic acid. The atomic numbering.

### Crystal data

*cis*-D,L-8,9-methyleneheptadecanoic acid, $C_{18}H_{34}O_2$; M.W. 282·45, m.p. 40 °C.
Monoclinic, with

$$a = 9{\cdot}20 \pm 0{\cdot}02,\ b = 5{\cdot}126 \pm 0{\cdot}007,$$
$$c = 81{\cdot}48 \pm 0{\cdot}06\ \text{Å};\ \beta = 100°\ 55' \pm 20'.$$

$V = 3773$ Å$^3$, $D_m = 1{\cdot}006$ g.cm$^{-3}$.
$Z = 8$, $D_x = 0{\cdot}995$ g.cm$^{-3}$.

Space group, from the extinctions $hkl$ absent $h+k$ odd, $A2/a$ or $Aa$; from the structure analysis $A2/a$.

## Experimental

The cell parameters were determined from $2\theta$ measurements using a single-crystal orienter on the General Electric XRD3. Because of the long $c$ axis, the three-dimensional intensity data were obtained most conveniently from single crystals mounted about the two other principal axes. These crystals were grown from aqueous acetone solutions as soft flat platelets with the $c^*$-axis direction normal to the plate and the cleavage plane. A trapezohedronally shaped crystal was used for the $a$-axis data. The approximate lengths of the edges bounding the trapezoidal face were 0·9, 0·4, 0·7 and 0·9 mm, and the thickness was 0·26 mm. The $b$-axis data were obtained from a similar crystal of approximate dimensions, 1 mm × 0·7 mm × 0·1 mm.

The reflections were recorded on multifilm equi-inclination Weissenberg photographs with Cu $K\alpha$ radiation. Long exposures, ranging from 95 to 125 hr, were required to record the very weak reflections. This was particularly necessary since extensive regions of accidental absences occurring along pendants of otherwise closely spaced reflections made difficult the indexing of isolated groups of high order reflections. Of the 4275 possible independent reflections within the limiting sphere for Cu $K\alpha$ radiation, 3859 were indexed and estimated, of which 974 were unobserved above the background.

The uncorrected intensities were estimated visually by comparison with a standard calibration scale. The intensities ranged from 1 to 31,000. The usual angle corrections were applied to 2843 intensities on nine layers about the $a$ axis and to 3268 intensities on five layers about the $b$ axis, using an IBM 7070 program (Craven, 1962). Of the 1889 reflections measured about both axes, 1252 were used for the interlayer correlation of the data by a least-squares method (Craven, 1962). The reflections with intensities less than 2 on the standard scale were omitted from this correlation procedure, as were seven reflections showing a large discrepancy between magnitudes measured in the two settings. No corrections were made for absorption or extinction.

## The structure determination

The initial three-dimensional coordinates were obtained from the two projections which include the long axis. Craven & Jeffrey (1959*b*) had solved the $(h0l)$ projection to obtain the first proof of the configuration of the naturally occurring malvalic acid. The solution to the $(0kl)$ projection remained to be solved. The very intense 020 reflection indicated that the projected chain direction must very nearly parallel the $c$ axis and from several trial and error calculations with low order reflections it was apparent that the molecules lie at $y=\frac{1}{4}$ and $\frac{3}{4}$, between the glide planes at $y=0$ and $\frac{1}{2}$. At first it was assumed that the molecules were dimerized across either an inversion center at the origin or a twofold axis at $(y, 0)$, but trial calculations based on these models led to no convergence by Fourier syntheses to a correct solution. A modulated Fourier series, $C(yz)$, was plotted, where

$$C(yz) = \frac{m}{A} \sum_0^\infty k \sum_0^\infty l \, \frac{|F_o|^2}{F_c} \cos 2\pi ky \cos 2\pi lz$$

omitting from the summation those terms where $|F_o|^2/|F_c|$ was greater than the largest observed amplitude (Sax, 1963). $A$ is the area of the projected cell and $m$ is the usual multiplicity factor.

The resulting map suggested a reversal of the molecule corresponding to a shift of the $z$ coordinates to $\frac{1}{4}-z$, with carboxyl groups dimerized by hydrogen bonding across either a symmetry center at $(\frac{1}{4}, \frac{1}{4})$ or a screw axis at $(y, \frac{1}{4})$. With this correct initial model, several cycles of Fourier refinement reduced the agreement index, $R$, to 0·35 for 220 observed $(0kl)$ reflections. The refinement in projection was continued with additional cycles of Fourier difference syntheses until the agreement index was 0·198. In this calculation the hydrogen atom contributions were included with coordinates determined from the difference Fourier synthesis and individual isotropic temperature factors were assigned to the heavier atoms. There still remained an ambiguity in the $x$ coordinates, since the screw diad and inversion center could not be distinguished in the projections. This ambiguity could not be resolved solely from packing considerations. However, two calculations of 353 of the $1kl$ structure factors demonstrated clearly that the dimer consisted of a pair of D and L isomers hydrogen-bonded across an inversion center, since this model yielded an $R$ of 0·3 compared to 0·8 for the other possibility which involved a spiral hydrogen-bonding scheme about the screw axes. The initial structure factor calculation on all the observed three-dimensional data gave an agreement index of 0·326.

## The structure refinement

Two three-dimensional $F_o$ syntheses were calculated, and the carbon and oxygen positional parameters estimated from the second synthesis with the individual isotropic temperature factors derived from the last $0kl$ difference map gave an $R$ index of 0·267 for 2882 observed reflections. The composite electron density map from this computation is shown in Fig. 2.

The refinement was continued by isotropic differential synthesis using the IBM 7070 program of Shiono (1962). Twelve cycles of refinement brought the $R$ value to 0·187 with assumed hydrogen parameters included. The hydrogen atom coordinates were calculated from those of the heavier atoms using the IBM 7070 program of Schapiro (1962*a*), assuming 1·09 Å as the CH bond length, 1·1 Å the OH bond, 107·6° the HCH angle in the chain and 112° *exo* to the cyclopropyl ring. The hydrogen atoms were assigned the same temperature factor as the atoms to which they were bonded. The carbon and oxygen atomic scattering factors were those given by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955). Those of McWeeny (1951) were used for the hydrogen atoms. The unobserved reflections were omitted from calculation of the $R$ values.

From the curvatures of the atomic peaks (Table 2)

Table 1(*a*). *The carbon and oxygen parameters*

The fractional atomic coordinates, the estimated standard deviations in the coordinates (Å), and the thermal parameters (Å$^2$), referred to the crystallographic axes

| Atom | $x$ | $\sigma(x)$ | $y$ | $\sigma(y)$ | $z$ | $\sigma(z)$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{23}$ | $B_{13}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| O(1) | 0·3636 | 0·003 | 0·0177 | 0·003 | 0·24732 | 0·003 | 4·7 | 5·0 | 4·8 | 0·9– | 0·9 | 0·4 |
| O(2) | 0·3946 | 0·003 | 0·3602 | 0·002 | 0·23138 | 0·003 | 3·7 | 5·0 | 4·8 | 1·3– | 0·7 | 0·9 |
| C(1) | 0·3208 | 0·003 | 0·1699 | 0·003 | 0·23458 | 0·003 | 2·9 | 3·1 | 2·6 | 0·3– | 0·1– | 1·5 |
| C(2) | 0·1771 | 0·004 | 0·0961 | 0·003 | 0·22391 | 0·004 | 4·0 | 3·4 | 4·1 | 0·6– | 0·3– | 0·5 |
| C(3) | 0·1312 | 0·004 | 0·2572 | 0·003 | 0·20793 | 0·004 | 3·6 | 3·4 | 4·2 | 0·5– | 0·2– | 0·5 |
| C(4) | 0·0180– | 0·005 | 0·1675 | 0·004 | 0·19822 | 0·005 | 4·3 | 3·9 | 4·1 | 0·7– | 0·1– | 0·7 |
| C(5) | 0·0667– | 0·005 | 0·3042 | 0·004 | 0·18154 | 0·005 | 4·4 | 3·7 | 4·0 | 0·5– | 0·2– | 0·8 |
| C(6) | 0·2128– | 0·005 | 0·2034 | 0·004 | 0·17173 | 0·004 | 4·8 | 4·1 | 4·4 | 0·3– | 0·5 | 0·5 |
| C(7) | 0·2596– | 0·005 | 0·3402 | 0·003 | 0·15478 | 0·005 | 5·2 | 3·4 | 4·7 | 0·1 | 0·1– | 0·2 |
| C(8) | 0·3980– | 0·005 | 0·2194 | 0·004 | 0·14458 | 0·005 | 4·2 | 3·9 | 4·2 | 0·2 | 0·2– | 0·4 |
| C(9) | 0·3843– | 0·005 | 0·0296– | 0·004 | 0·13512 | 0·005 | 4·1 | 3·8 | 5·2 | 0·6– | 0·1– | 0·7 |
| C(10) | 0·4278– | 0·005 | 0·2193 | 0·004 | 0·12569 | 0·005 | 4·2 | 4·3 | 4·0 | 0·5 | 0·0 | 0·2– |
| C(11) | 0·3253– | 0·006 | 0·3351 | 0·004 | 0·11540 | 0·005 | 5·5 | 3·7 | 4·2 | 0·5– | 0·2 | 0·1 |
| C(12) | 0·3316– | 0·007 | 0·2038 | 0·004 | 0·09850 | 0·006 | 6·7 | 4·8 | 4·7 | 0·3– | 0·2– | 0·6 |
| C(13) | 0·2218– | 0·008 | 0·3140 | 0·005 | 0·08864 | 0·007 | 7·2 | 5·4 | 5·2 | 0·6– | 0·6– | 0·7 |
| C(14) | 0·2261– | 0·008 | 0·1944 | 0·006 | 0·07148 | 0·007 | 6·5 | 6·4 | 5·2 | 0·4– | 0·4– | 1·3 |
| C(15) | 0·1134– | 0·011 | 0·3107 | 0·008 | 0·06213 | 0·008 | 9·8 | 8·0 | 6·8 | 0·2– | 0·2 | 2·7 |
| C(16) | 0·1194– | 0·015 | 0·1989 | 0·010 | 0·04477 | 0·009 | 11·2 | 9·7 | 5·3 | 0·5– | 1·0– | 2·0 |
| C(17) | 0·0110– | 0·018 | 0·3107 | 0·015 | 0·03538 | 0·012 | 12·9 | 11·4 | 6·2 | 0·2 | 0·2– | 5·0 |
| C(18) | 0·0074– | 0·035 | 0·2083 | 0·028 | 0·01835 | 0·017 | 17·6 | 16·9 | 7·5 | 2·5 | 1·2 | 6·9 |

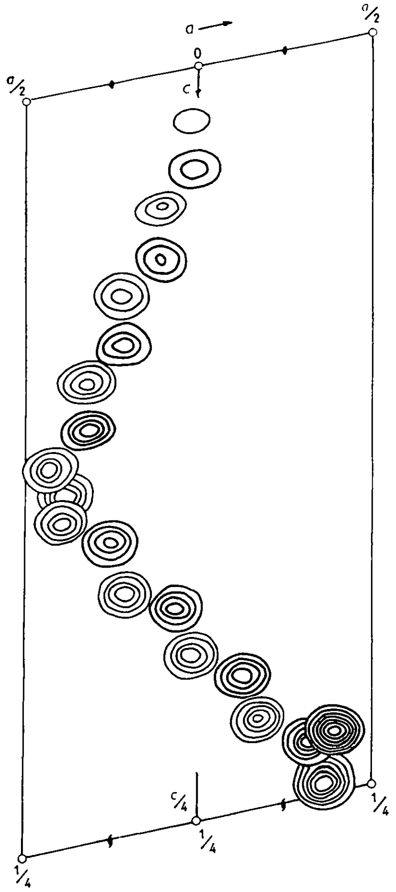

Fig. 2. Electron density distribution in a molecule of dihydromalvalic acid. Sections through atomic centers with contour intervals of ~1·5 e.Å$^{-3}$ (*cf.* Table 2 for peak heights).

Table 1(*b*). *The hydrogen atom parameters*

The fractional coordinates and isotropic temperature factors

| Atom | Bonded to | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|---|
| H(1) | C(2) | 0·090 | 0·113 | 0·2313 | 4·0 |
| H(2) | | 0·183 | 0·107– | 0·2204 | 4·0 |
| H(3) | C(3) | 0·215 | 0·239 | 0·2002 | 4·2 |
| H(4) | | 0·124 | 0·461 | 0·2112 | 4·2 |
| H(5) | C(4) | 0·103– | 0·199 | 0·2058 | 4·5 |
| H(6) | | 0·013– | 0·040– | 0·1960 | 4·5 |
| H(7) | C(5) | 0·078– | 0·511 | 0·1837 | 4·5 |
| H(8) | | 0·019 | 0·280 | 0·1741 | 4·5 |
| H(9) | C(6) | 0·300– | 0·231 | 0·1791 | 5·0 |
| H(10) | | 0·203– | 0·004– | 0·1697 | 5·0 |
| H(11) | C(7) | 0·169– | 0·329 | 0·1479 | 5·5 |
| H(12) | | 0·278– | 0·545 | 0·1568 | 5·5 |
| H(13) | C(8) | 0·491– | 0·242 | 0·1510 | 4·5 |
| H(14) | C(9) | 0·274– | 0·111– | 0·1353 | 5·5 |
| H(15) | | 0·468– | 0·180– | 0·1350 | 5·5 |
| H(16) | C(10) | 0·542– | 0·242 | 0·1189 | 4·5 |
| H(17) | C(11) | 0·211– | 0·324 | 0·1224 | 5·5 |
| H(18) | | 0·353– | 0·540 | 0·1134 | 5·5 |
| H(19) | C(12) | 0·444– | 0·224 | 0·0912 | 7·0 |
| H(20) | | 0·310– | 0·003– | 0·1005 | 7·0 |
| H(21) | C(13) | 0·110– | 0·289 | 0·0960 | 7·5 |
| H(22) | | 0·242– | 0·522 | 0·0871 | 7·5 |
| H(23) | C(14) | 0·338– | 0·220 | 0·0640 | 7·0 |
| H(24) | | 0·206– | 0·013– | 0·0729 | 7·0 |
| H(25) | C(15) | 0·002– | 0·281 | 0·0695 | 10·0 |
| H(26) | | 0·133– | 0·519 | 0·0610 | 10·0 |
| H(27) | C(16) | 0·231– | 0·227 | 0·0375 | 11·5 |
| H(28) | | 0·099– | 0·010– | 0·0460 | 11·5 |
| H(29) | C(17) | 0·100 | 0·286 | 0·0430 | 13·0 |
| H(30) | | 0·033– | 0·518 | 0·0342 | 13·0 |
| H(31) | C(18) | 0·078 | 0·309 | 0·0131 | 18·0 |
| H(32) | | 0·019 | 0·001 | 0·0192 | 18·0 |
| H(33) | | 0·116– | 0·236 | 0·0103 | 18·0 |
| H(34) | O(1) | 0·467 | 0·070 | 0·2564 | 5·0 |

it was apparent that the magnitude and anisotropy of the thermal motion of the atoms in the chain increased sharply in progressing from the cyclopropyl ring to the terminal methyl group. Since no full-matrix or block-matrix least-squares program which would deal with 180 coordinate and anisotropic temperature parameters in a reasonable computing

Table 2. *Observed and calculated atomic peak heights and curvatures*

| | | $\varrho$ (e.Å$^{-3}$) | $A_{hh}$ (e.Å$^{-5}$) | $A_{kk}$ (e.Å$^{-5}$) | $A_{ll}$ (e.Å$^{-5}$) | $A_{hk}$ (e.Å$^{-5}$) | $A_{kl}$ (e.Å$^{-5}$) | $A_{hl}$ (e.Å$^{-5}$) |
|---|---|---|---|---|---|---|---|---|
| O(1) | obs. | 10·8 | 84·2− | 85·8− | 80·2− | 8·5− | 7·4 | 11·3 |
| | calc. | 10·0 | 77·8− | 79·1− | 74·3− | 7·9− | 6·9 | 10·7 |
| O(2) | obs. | 11·2 | 93·8− | 89·0− | 84·4− | 12·6− | 7·3 | 15·6 |
| | calc. | 10·6 | 89·2− | 84·3− | 80·5− | 11·9− | 7·0 | 15·2 |
| C(1) | obs. | 8·8 | 79·7− | 81·7− | 78·9− | 3·4− | 1·4 | 20·8 |
| | calc. | 9·3 | 84·4− | 86·2− | 83·7− | 3·7− | 1·7 | 22·3 |
| C(2) | obs. | 7·7 | 61·4− | 66·9− | 58·5− | 5·0− | 0·1− | 12·5 |
| | calc. | 7·7 | 60·8− | 66·1− | 58·01− | 4·9− | 0·1− | 12·6 |
| C(3) | obs. | 7·9 | 64·9− | 68·2− | 61·4− | 3·6− | 0·8− | 11·9 |
| | calc. | 7·9 | 65·1− | 68·3− | 61·7− | 3·6− | 0·9− | 12·2 |
| C(4) | obs. | 7·4 | 57·6− | 62·1− | 55·1− | 3·6− | 0·3− | 12·3 |
| | calc. | 7·5 | 58·4− | 62·7− | 55·8− | 3·6− | 0·3− | 12·6 |
| C(5) | obs. | 7·4 | 58·8− | 61·4− | 55·5− | 2·5− | 0·7 | 12·5 |
| | calc. | 7·6 | 60·7− | 63·2− | 57·3− | 2·6− | 0·7 | 13·1 |
| C(6) | obs. | 7·5 | 58·8− | 59·8− | 56·8− | 1·1− | 3·1 | 12·1 |
| | calc. | 7·3 | 56·9− | 57·5− | 54·9− | 1·0− | 2·9 | 11·8 |
| C(7) | obs. | 7·4 | 55·1− | 63·8− | 54·4− | 0·1 | 0·9− | 8·6 |
| | calc. | 7·3 | 54·5− | 63·0− | 53·8− | 0·1 | 0·9− | 8·6 |
| C(8) | obs. | 7·3 | 54·4− | 57·2− | 53·9− | 1·5 | 1·0 | 8·6 |
| | calc. | 7·3 | 54·6− | 57·2− | 53·9− | 1·5 | 1·0 | 8·7 |
| C(9) | obs. | 7·1 | 55·5− | 55·7− | 48·7− | 4·2− | 0·2 | 7·4 |
| | calc. | 7·0 | 54·3− | 54·5− | 47·7− | 4·1− | 0·2 | 7·2 |
| C(10) | obs. | 7·2 | 53·5− | 56·6− | 50·3− | 2·6 | 0·8− | 2·4 |
| | calc. | 7·2 | 53·6− | 56·6− | 50·2− | 2·6 | 0·9− | 2·3 |
| C(11) | obs. | 6·9 | 49·1− | 57·2− | 49·2− | 2·1− | 0·9 | 5·2 |
| | calc. | 7·0 | 49·8− | 58·0− | 49·9− | 2·1− | 0·9 | 5·4 |
| C(12) | obs. | 6·3 | 38·6− | 49·4− | 43·7− | 0·7− | 0·5 | 4·4 |
| | calc. | 6·1 | 37·3− | 47·7− | 42·2− | 0·6− | 0·5 | 4·2 |
| C(13) | obs. | 5·7 | 35·4− | 40·8− | 38·8− | 1·3− | 1·7− | 4·4 |
| | calc. | 5·7 | 35·5− | 40·6− | 38·7− | 1·3− | 1·7− | 4·4 |
| C(14) | obs. | 5·6 | 35·3− | 37·3− | 37·4− | 0·5− | 1·3− | 5·7 |
| | calc. | 5·7 | 35·9− | 38·1− | 38·1− | 0·5− | 1·3− | 5·9 |
| C(15) | obs. | 4·8 | 26·1− | 28·7− | 31·6− | 0·2− | 0·3− | 7·0 |
| | calc. | 4·7 | 25·8− | 28·3− | 31·0− | 0·2− | 0·3− | 6·8 |
| C(16) | obs. | 4·1 | 18·4− | 21·6− | 27·0− | 0·4− | 1·2− | 3·7 |
| | calc. | 4·3 | 19·8− | 23·4− | 29·1− | 0·5− | 1·3− | 4·0 |
| C(17) | obs. | 3·3 | 15·0− | 14·4− | 22·1− | 0·4 | 0·6 | 6·7 |
| | calc. | 4·0 | 18·1− | 17·5− | 26·8− | 0·6 | 0·7 | 8·1 |
| C(18) | obs. | 2·4 | 7·8− | 7·8− | 14·7− | 1·4 | 0·2 | 5·1 |
| | calc. | 3·0 | 10·0− | 10·0− | 19·0− | 2·0 | 0·2 | 6·5 |
| e.s.d. (r.m.s.) | | 0·10 | 1·39 | 0·92 | 1·10 | 0·67 | 0·59 | 0·73 |

time was available to us, we continued the refinement by means of six additional cycles of anisotropic differential synthesis thereby ignoring the parameter interactions between different atoms. These computations were carried out with Shiono's IBM 7070 program (1962). The anisotropic structure factors were calculated on the IBM 7070 using a program of Schapiro (1962*b*). When the refinement was discontinued the coordinate shifts did not exceed one fifth of a standard deviation.

The final $R$ index for the 2882 observed reflections was 0·148. The final atomic parameters and their standard deviations are listed in Table 1. The peak electron densities and their first and second derivatives are given in Table 2, with the standard deviations, which were estimated by the Cruickshank method (1949, 1950). It is interesting to note that the larger differences between the observed and calculated peak electron densities and curvatures occur at the terminal atoms of the molecules, *i.e.* at atoms O(1), O(2), C(1), C(17) and C(18), as shown in Table 2. The limits of error in the bond lengths calculated from the estimated standard deviations of the coordinates are

Table 3. *Bond lengths and valence angles in the dihydromalvalic acid molecule*

| | Distance (Å) | e.s.d. (Å) | | (°) |
|---|---|---|---|---|
| C(1)–O(1) | 1·299 | 0·004 | O–C=O | 123·2 |
| C(1)–O(2) | 1·244 | 0·004 | C–C=O | 122·4 |
| C(1)–C(2) | 1·487 | 0·005 | C–C–OH | 114·4 |
| C(2)–C(3) | 1·532 | 0·005 | C(1)–C(2)–C(3) | 115·4 |
| C(3)–C(4) | 1·520 | 0·006 | C(2)–C(3)–C(4) | 110·7 |
| C(4)–C(5) | 1·519 | 0·006 | C(3)–C(4)–C(5) | 114·1 |
| C(5)–C(6) | 1·518 | 0·006 | C(4)–C(5)–C(6) | 113·2 |
| C(6)–C(7) | 1·536 | 0·006 | C(5)–C(6)–C(7) | 112·6 |
| C(7)–C(8) | 1·515 | 0·006 | C(6)–C(7)–C(8) | 111·5 |
| C(8)–C(9) | 1·508 | 0·006 | C(7)–C(8)–C(9) | 118·9 |
| C(8)–C(10) | 1·511 | 0·007 | C(7)–C(8)–C(10) | 122·0 |
| C(9)–C(10) | 1·504 | 0·006 | C(8)–C(9)–C(10) | 60·2 |
| C(10)–C(11) | 1·498 | 0·009 | C(9)–C(10)–C(8) | 60·0 |
| C(11)–C(12) | 1·524 | 0·008 | C(9)–C(8)–C(10) | 59·7 |
| C(12)–C(13) | 1·514 | 0·010 | C(8)–C(10)–C(11) | 123·9 |
| C(13)–C(14) | 1·520 | 0·009 | C(9)–C(10)–C(11) | 119·2 |
| C(14)–C(15) | 1·520 | 0·013 | C(10)–C(11)–C(12) | 114·0 |
| C(15)–C(16) | 1·517 | 0·013 | C(11)–C(12)–C(13) | 113·3 |
| C(16)–C(17) | 1·482 | 0·022 | C(12)–C(13)–C(14) | 115·5 |
| C(17)–C(18) | 1·490 | 0·024 | C(13)–C(14)–C(15) | 113·5 |
| O(1)H···O′(2) | 2·625 | 0·004 | C(14)–C(15)–C(16) | 114·4 |
| | | | C(15)–C(16)–C(17) | 115·2 |
| | | | C(16)–C(17)–C(18) | 118·5 |

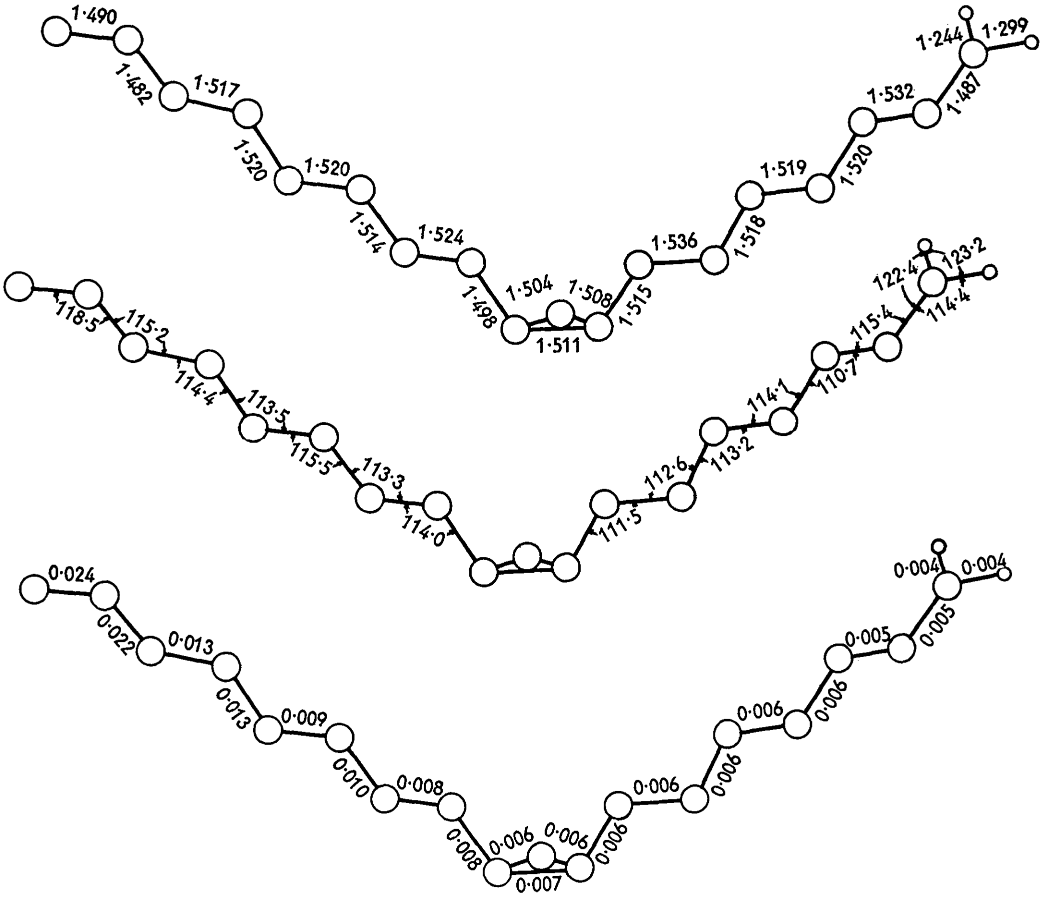

Fig. 3. Bond lengths, valence angles, and standard deviations of bond lengths in dihydromalvalic acid.

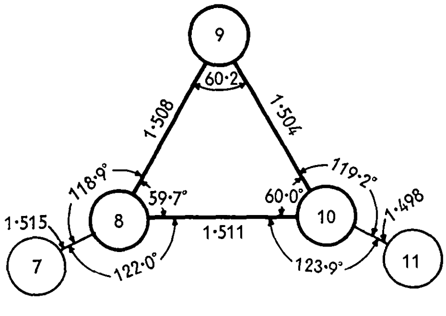

Fig. 4. Stereochemistry of cyclopropane ring in dihydromalvalic acid.

given with the bond lengths and angles in Table 3 and in Figs. 3 and 4. The table of observed and calculated structure factors was submitted with the paper and has been deposited with the American Documentation Institute, Auxiliary Publications Project, Washington 25, D.C.†

## Discussion of the structure

### *The geometry of the molecule*

The bent-chain conformation is the most noticeable stereochemical feature of the molecules in the crystal lattice. The two main hydrocarbon chain directions intersect at an angle of approximately 115°. They are, to an approximation, related by a mirror plane normal to the $c^*$ direction and bisecting the three-membered ring. This stereochemical feature had previously been noted in the structure of *cis*-D,L-11,12-methyleneoctadecanoic acid by Craven & Jeffrey (1959*a*). The general features of the geometry of both these molecules are quite similar despite the different positions of the cyclopropyl ring and the different lengths of the chains. There are, however, some differences in detail associated particularly with the different numbers of carbon atoms between the carboxyl group and the ring. The data relating to the stereochemical details with respect to the coplanarity of various segments of the molecule in this structure are given in Table 4.

The carboxyl group is coplanar with the next

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† Document No. 7484, available from Chief, Photoduplication Service, Library of Congress, Washington, D.C.

Table 4. *The atomic planes in the molecules*

| Atoms | Coefficients† in $AX+BY+CZ+D=0$ | | | | Max. distance from plane | Dihedral angle with (*a*, *c*) plane |
|---|---|---|---|---|---|---|
| | *A* | *B* | *C* | *D* | | |
| O(1), O(2), C(1), C(2) | −0·5941 | 0·5826 | 0·5547 | −11·309 | 0·005 Å | 54° 22′ |
| O(7), O(2), C(1), C(2), C(3) | −0·6096 | 0·5916 | 0·5276 | −10·813 | 0·044 | 53° 44′ |
| C(3), C(4), C(5), C(6), C(7) | −0·5618 | 0·7036 | 0·4351 | −9·308 | 0·027 | 45° 17′ |
| C(4), C(5), C(6), C(7) | −0·5832 | 0·6860 | 0·4351 | −9·351 | 0·005 | 46° 42′ |
| C(7), C(8), C(10), C(11) | −0·4802 | 0·8772 | −0·0074 | −3·731 | 0·001 | 28° 42′ |
| C(8), C(9), C(10) | 0·9793 | 0·2020 | 0·0112 | 5·414 | | 78° 21′ |
| C(10), C(11), C(12) to C(18) | −0·6200 | 0·6726 | −0·4042 | −0·333 | 0·038 | 47° 44′ |
| C(11), C(12) to C(18) inclusive | −0·6110 | 0·6814 | −0·4030 | −0·335 | 0·032 | 47° 3′ |
| C(12) to C(18) inclusive | −0·6032 | 0·6937 | −0·3936 | −0·3729 | 0·017 | 46° 5′ |

† These refer to the orthogonal axes *abc**. The equation referred to the crystallographic axes is obtained merely by substituting the following values for *C* in the order tabulated above: 0·6572, 0·6335, 0·5337, 0·5377, 0·0837, −0·1745, −0·2797, −0·2800, and −0·2723.

carbon atom in the chain, C(2). The plane of the carbon chain then twists about an angle of 8° and runs coplanar again from C(4) to C(7). As we approach the cyclopropyl ring, the main chain twists through a further 18° at C(7), and is coplanar through C(7), C(8), C(10), C(11). Beyond the ring, the chain then twists back again until from C(12) to C(18) the carbon atoms lie in a plane at the same inclination to the basal (*a*, *c*) plane as that of the C(4) to C(7) segment. These two planes C(12) · · · C(18) and C(4) · · · C(7) have the same inclination to the basal plane and are approximately mirror related, as mentioned above.

In the 11,12 acid, there is a twist of about 11° between the carboxylic acid plane and the main carbon chain from C(4) to C(11), and this twist appears to be distributed over the atoms C(1) to C(5). Then from C(4) to the cyclopropyl group at C(11) the chain is coplanar. The terminal part of the chain C(12) · · · C(18) is also in a plane inclined at the same angle to the basal plane as that of C(4) · · · C(11) and these two segments of the chain are approximately mirror related. Thus, except for the greater twist of carboxyl group, the stereochemistry of both molecules is very similar.

The dihedral angle of the plane of the cyclopropyl ring with the planes of the hydrocarbon chains flanking it is 63° for the 8,9 compound and 54° for the 11,12 compound. Since the latter analysis was based on two two-dimensional projections, in neither of which were the ring atoms completely resolved, there is no evidence of a real difference in this feature of the cyclopropyl stereochemistry, and this three-dimensional analysis is the more accurate. As previously noted, this geometry involves a comparatively short intramolecular non-bonded H · · · H interaction as illustrated in Fig. 4 of the paper by Craven & Jeffrey (1959*a*). If it is assumed that the C(7)–H and C(11)–H bonds have normal lengths and undistorted valence angles, the shorter H · · · H distance in this structure is 2·04 Å (it was estimated to be 2·15 Å in the 11–12 molecule). Nevertheless, it is not unlikely that this is the conformation of minimum energy with respect to the intramolecular forces around the cyclopropyl ring, since any rotation of the methylene chains about C(7)–C(8) or C(10)–C(11), which would increase these H · · · H distances, does so at the expense of causing the energetically unfavorable eclipsed configuration for the bonds C(8)–H and C(6)–C(7) or C(10)–H and C(11)–C(12).

It is generally accepted that the non-bonding forces in long-chain fatty acids are such as to make the polymethylene chains lie parallel in a single direction. This corresponds to the staggered configuration along the hydrocarbon chain, which is generally considered to minimize the exchange interactions between the electrons in adjacent bonds. The magnitude of the repulsion energy has been described as proportional to the amounts of *d* and *f* character in these bonds (Pauling, 1960). The only way for the carbon chain of a *cis* cyclopropyl fatty acid molecule to be in one principal direction is for one of the carbon atoms to depart from this normal straight-chain arrangement. Such configuration is illustrated in Fig. 3(*a*) of the paper by Craven & Jeffrey (1959*a*), in connection with the discussion of a 'false solution' to the phase problem. It has not, hitherto, been observed in any member of the *cis* cyclopropyl fatty acid series. The bond lengths in the molecule have the generally accepted values. The average $sp^3$–$sp^3$ C–C single bond is 1·522 Å with an estimated mean standard deviation of 0·004 Å. This value is not corrected for the effects of thermal motion. Because of the large thermal factors of the atoms at the non-polar end of the molecule, the lengths of the two terminal bonds are relatively less accurate and have been omitted from the average. The bonds *exo* to the cyclopropane ring have been excluded also, because of the stereochemical influence of the ring

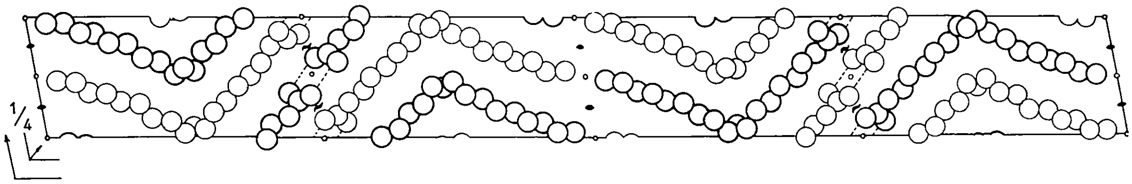

Fig. 5. Molecular packing in one unit cell of dihydromalvalic acid.

upon the bond length. The average bond angle between carbon atoms linked through $sp^3$–$sp^3$ bonds in the straight chain is 113·6°. The mean bond length in the cyclopropane ring is 1·508 Å, with an estimated mean standard deviation of 0·004 Å. The C–C bonds *exo* to the ring are 1·515 Å and 1·498 Å with standard deviations of 0·006 Å and 0·008 Å respectively. The former differs from 1·522 by one standard deviation and the latter by three standard deviations. Within the ring the bond angles are equal at 60°. The C–C bonds *exo* to the ring make angles of 123° and 119° with the C–C bonds in the ring (Fig. 4). The single bond between the carbon atom in the carboxyl group and the α carbon atom in the chain is 1·487 Å showing the expected decrease for an $sp^3$–$sp^2$ single bond involving a double-bonded carbon atom (Dewar & Schmeising, 1960).

Table 5. *Intramolecular distances between alternate carbon atoms in the hydrocarbon chain*

| Atoms | Distance | e.s.d. |
|---|---|---|
| C(1)–C(3) | 2·554 Å | 0·005 Å |
| C(2)–C(4) | 2·513 | 0·006 |
| C(3)–C(5) | 2·552 | 0·006 |
| C(4)–C(6) | 2·537 | 0·006 |
| C(5)–C(7) | 2·544 | 0·006 |
| C(6)–C(8) | 2·525 | 0·007 |
| C(7)–C(9) | 2·604 | 0·007 |
| C(7)–C(10) | 2·647 | 0·007 |
| C(8)–C(11) | 2·656 | 0·007 |
| C(9)–C(11) | 2·589 | 0·008 |
| C(10)–C(12) | 2·538 | 0·008 |
| C(11)–C(13) | 2·541 | 0·009 |
| C(12)–C(14) | 2·569 | 0·010 |
| C(13)–C(15) | 2·545 | 0·011 |
| C(14)–C(16) | 2·551 | 0·013 |
| C(15)–C(17) | 2·532 | 0·017 |
| C(16)–C(18) | 2·557 | 0·025 |

The distances between alternate carbon atoms within the hydrocarbon chain are given in Table 5. For the *n*-paraffin parts of the molecule, this distance averages 2·543 Å (e.s.d. = 0·004 Å). If one of the bonds is in the cyclopropane ring, this distance increases to 2·624 Å, which is clearly a reflection of the differences in the bond angle of 113·6° in the *n*-paraffinic chain segments and the bond angles of 121° *exo* to the ring. The dimensions of the carboxyl group are in agreement with the X-ray results for other carboxylic acid dimers (Nardelli, Fava & Giraldi, 1962).

The IBM 7070 programs of Chu (1962) were used for calculating these details of the molecular geometry.

### *The molecular packing*

Fig. 5 shows the arrangement of the molecules in the unit cell. The pairs of molecules are hydrogen-bonded across the inversion centers at either $\frac{1}{4}$ or $\frac{3}{4}$ along the *b* axis. The hydrogen-bonded oxygen atoms are separated by 2·625 Å. The two carboxyl groups involved in H bonding are not coplanar, but are in parallel planes 0·21 Å apart. This is a common feature of carboxylic acid groups dimerized across a center of symmetry (Jeffrey & Sax, 1963). At the non-polar end of the molecules the closest approach of neighboring methyl groups is 3·7 Å.

The straight chain segments of the molecule, C(4) · · · C(7) and C(12) · · · C(18), display the orthorhombic type of packing described by Bunn (1939) and Vainshtein & Pinsker (1950). The cross-sectional area per chain, estimated from the sub-cells of both chains is 19·7 Å. This is substantially in excess of the 18·5 Å usually reported for orthorhombically packed chains (Vand, 1953). Presumably, the loss of compactness in the packing of the straight chain segments is a consequence of the necessity to accommodate the three-membered rings and the carboxyl groups. The expansion in cross-sectional area is manifested almost equally (3–4%) in the $a_s$ and $b_s$ axes of the orthorhombic subcell.† These are $a_s = 5·12$ Å, $b_s = 7·70$ Å, in dihydromalvalic acid, compared with 4·96 Å and 7·40 Å usually found in orthorhombically packed chains (*cf.* Shearer & Vand, 1956).

Table 6 summarizes the distribution of the intermolecular distances between neighboring methylene groups and shows how the packing density varies along the chain. The structure is considerably more open in the part of the chain most remote from the carboxyl groups, *i.e.* from C(14) to C(18), the carbon atom of the terminal methyl group. In the region of the cyclopropane ring, particularly at the methylene bridge carbon, C(9), the density of packing increases noticeably. Corresponding to the twisting of the chain in the proximity of the carboxyl group, there is an

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† By convention the orthorhombic subcell is generally referred to the space group *Pbnm*. Therefore $a_s$ of the subcell is the *b* axis of the main cell; $c_s$, which is chosen parallel to the chain direction, equals 2·543 Å.

Table 6. *Distribution of intermolecular* C · · · C *and* C · · · O *distances less than* 5 Å, *between atoms in neighboring chains*

| Atom | Number of contacts 3·0–3·6 Å | 3·6–4·2 Å | 4·2–4·8 Å | Total, less than 5·0 Å |
|---|---|---|---|---|
| O(1)(hydroxyl) | 7 | 6 | 9 | 22 |
| O(2)(carbonyl) | 3 | 8 | 7 | 18 |
| C(1) | 3 | 8 | 8 | 19 |
| C(2) | 1 | 8 | 5 | 14 |
| C(3) | 0 | 3 | 9 | 12 |
| C(4) | 0 | 5 | 5 | 10 |
| C(5) | 0 | 0 | 9 | 9 |
| C(6) | 0 | 0 | 8 | 8 |
| C(7) | 0 | 1 | 7 | 8 |
| C(8) | 0 | 1 | 8 | 9 |
| C(9) | 0 | 4 | 10 | 14 |
| C(10) | 0 | 1 | 8 | 9 |
| C(11) | 0 | 1 | 7 | 8 |
| C(12) | 0 | 0 | 9 | 9 |
| C(13) | 0 | 0 | 9 | 9 |
| C(14) | 0 | 0 | 8 | 8 |
| C(15) | 0 | 0 | 8 | 8 |
| C(16) | 0 | 0 | 6 | 6 |
| C(17) | 0 | 0 | 6 | 6 |
| C(18) | 0 | 1 | 2 | 3 |

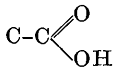
increase in the number of neighboring atoms at distances less than 5·0 Å, which reaches a maximum at the oxygen atoms. This distortion from planarity at the carboxylic acid end of the chain molecule appears to be analogous to that observed in the odd-membered dicarboxylic acids, and is discussed in relation to the planar even members of that series by Goedkoop & MacGillavry (1957). It is interesting to note that the variation of the atomic thermal parameters along the chain is consistent with a model in which the molecules are packed more rigidly at the carboxyl end and at the position of the cyclopropyl rings. The temperature factor increases only slightly from C(1) to C(10), but from C(10) to C(18) it increases from a mean value perpendicular to the chain direction of $B=4$ Å$^2$ to $B=17$ Å$^2$.

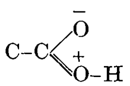
### *The chemical bonding*

The bent-bond model for describing the C=C double bond has been adapted to the description of the C–C bonds in a cyclopropane ring by Coulson (1953), who refers to them as 'banana' bonds. It is interesting that the simple way of calculating the length of multiple C–C bonds from the bent bond model (Pauling, 1960), when applied to the bonds within the cyclopropane ring, gives a calculated bond length of 1·49 Å in approximate agreement with the experimental value 1·508 Å. Because of bond-bending, it is to be expected that some shortening of the C–C single bonds *exo* to the cyclopropyl ring should occur to a degree somewhat less than for a single bond adjacent to a double bond. For this type of bond we found 1·507 Å with $\sigma=0{\cdot}005$ Å. This value is shorter by $3\sigma$ than the mean single-bond length in the chain. Thus our results are in qualitative agreement with the theoretical predictions on the basis of the bent-bond model for cyclopropane and for ethylene.

An elementary molecular orbital treatment of the bonding in cyclopropane involving non-orthogonal orbitals has been given by Handler & Anderson (1958). Two equivalent hybrid orbitals per carbon atom consisting of 35% $s$, 15% $p_x$, and 50% $p_y$ character and making a valence angle of 122° were used for the formation of the bonds *exo* to the ring. From the percentage of $s$ character in the hybrid orbitals used in bond formation, the length of the C–C bond formed by overlapping one of these hybrids with the $sp^3$ orbital of an external carbon atom is estimated to be in the range of 1·505 Å to 1·515 Å (Somayajulu, 1959; Dewar & Schmeising, 1960). Our results are also in agreement with these predictions, and quite clearly no distinction could be made between these alternative descriptions from information on bond lengths and valence angles alone.

The bond distances found in the carboxyl group agree with theory, taking into account the 2·625 Å O–H · · · O distance which indicates a greater delocalization of the double bond in the dimer than in the monomer. Pauling (1960) has estimated, for example, that in formic acid monomer the valence bond form (I) contributes 85% and (II) 15% to the structure.


(I)


(II)

In this structure, the C=O length of 1·244 Å is 0·02 Å longer and the C–OH length of 1·299 is 0·06 Å shorter than found in the formic acid monomer (Karle & Karle, 1954), corresponding to valence bond contributions of 65% of (I) and 35% of (II).

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# On the Least-Squares Analysis of the Rigid Body Vibrations of Non-Centrosymmetrical Molecules

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The need for refinement of the origin of the mean-square rotational tensor $\omega_{ij}$ for non-centrosymmetrical molecules is investigated. The equations for the least-squares procedure are given, but a cruder method is used to establish that the refinement is important to obtain meaningful results. This is used on results for azulene, maleic anhydride and succinimide. Azulene presents a particular problem for which a special refinement is suggested.

Robertson, Shearer, Sim & Watson (1962) use the method of Cruickshank (1956) to analyse the anisotropic temperature factors obtained from the least-squares refinement of azulene. This gives the translational and rotational mean-square displacement tensors $T_{ij}$ and $\omega_{ij}$.

Previously Cruickshank (1957*a*, *b*) had applied this method to naphthalene and anthracene with considerable success. In both of these examples the molecule is centrosymmetrical, and therefore there is no ambiguity of choice for the origin of the molecular axes. This origin must clearly be at the centre of symmetry. The rotational tensors obtained by Cruickshank are therefore in the inertial coordinate system, describing rotations about the centre of symmetry.

However, azulene presents a different problem. The crystal belongs to the space group $P2_1/a$, and as there are only two molecules in the unit cell, this suggests a centrosymmetrical molecule placed about one quarter of the crystal symmetry centres. But the azulene molecule has no centre of symmetry and is found to exist in the crystal randomly in two orientations related to each other by the crystal centre of symmetry.

Robertson *et al.* (1962) used this centre as the origin for the tensor $\omega_{ij}$, and obtained the results

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