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The Crystal Structure of Longifolene Hydrochloride

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Longifolene hydrochloride crystallizes in the space group $P2_12_12_1$ with $a = 8.505$, $b = 9.760$ and $c = 16.674$ Å. The structure, originally solved in projection by the isomorphous replacement method, has been confirmed by three-dimensional methods. Coordinates have been given to the 25 hydrogen atoms in the molecule, and the structure has been refined by least-squares methods. New values for the bond lengths and bond angles are given and the strain in the molecule is discussed.

1. Introduction

Longifolene, $C_{15}H_{24}$ (Fig. 1(b)), is a sesquiterpene whose molecular constitution was virtually unknown (Simonsen & Barton, 1952) until it was determined by Moffett & Rogers (1953) (Moffett, 1954) from the X-ray study in projection of the crystal structure of longifolene hydrochloride (Fig. 1(a)) and confirmed by the chemical evidence of Naffa & Ourisson (1953) (Simonsen & Ross, 1957). As a result of considerable overlap in the projections of the structure, some aspects of this X-ray work were not satisfactory (see below), and Barton & Mayo (1957) suggested that further chemical evidence was needed to confirm the proposed structure. More recently, longifolene has been synthesized by Corey, Ohno, Vatakechery & Mitra (1961), who state that the chemical facts alone did not constitute a proof of the molecular structure.

In this paper, a complete three-dimensional analysis of the crystal structure of longifolene hydrochloride is described, removing the possible doubts about the previous X-ray work and confirming in detail the structure previously found. As only a brief account of the two-dimensional work has been given, it is reviewed in the next paragraph.

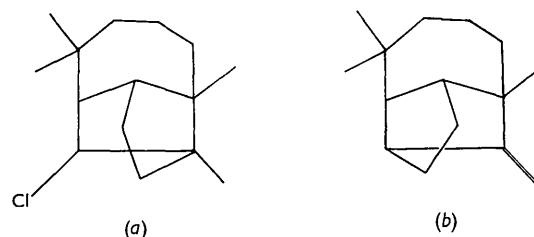


Fig. 1. (a) Longifolene hydrochloride. (b) Longifolene.

2. The previous work by Moffett & Rogers

The crystals of longifolene hydrochloride and hydrobromide were found to be isomorphous in the space group $P2_12_12_1$. The coordinates of the chlorine and bromine atoms were found from the (100) and (010) Patterson projections and the method of isomorphous replacement was used to determine the signs of 130 out of the 154 observed $0kl$ reflexions and the signs of 104 out of 126 observed $h0l$ reflexions. The electron density maps for these two projections were calculated for the hydrochloride. It was not possible to fit any of the then proposed chemical models to these maps.

Moffett & Rogers proceeded without making any assumptions about the chemical structure and,

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starting from the chlorine atom, attempted to build up the molecule by placing atoms on electron-density peaks so that the usual bond lengths and angles prevailed. The two five-membered rings were first located but the remaining part of the molecule was more difficult to establish. Error syntheses were required to decide between two possible models before a final chemical model which fitted both the projections was obtained. It was a considerable achievement to carry out this process with the use of two projections in which there is a great deal of overlap.

The refinement of the projections was carried out by difference syntheses, and at a late stage anisotropic temperature factors were applied to the chlorine atom. The final R indices for the $0kl$ and $h0l$ reflexions were 0.14 and 0.15 respectively. However, the z coordinates of the atoms which were not resolved in either projection were found to differ by as much as 0.12 Å and thus the bond lengths calculated from the final coordinates showed some very large deviations from the accepted values, for example C(1)–C(2) = 1.49 Å, C(2)–C(3) = 1.61 Å, C(5)–C(6) = 1.70 Å, C(6)–C(7) = 1.61 Å, C(9)–C(10) = 1.68 Å.

It was not possible in this projection work to take into account the 25 hydrogen atoms in each molecule which would have a significant effect on the refinement of the structure. For these reasons and those given in § 1, it was apparent that a three-dimensional analysis and refinement of the structure of longifolene hydrochloride was necessary and desirable.

3. Crystal data

Longifolene hydrochloride (C₁₅H₂₅Cl):

Orthorhombic

$$a = 8.505 \pm 0.003, \quad b = 9.760 \pm 0.002, \\ c = 16.674 \pm 0.003 \text{ \AA}.$$

$$d_o = 1.157 \text{ g.cm}^{-3}, \quad d_c = 1.154 \text{ g.cm}^{-3} \text{ for } Z = 4. \\ \mu = 22 \text{ cm}^{-1}.$$

The space group was determined by oscillation and Weissenberg photographs, taken with Cu $K\alpha$ radiation. Absent spectra were $h00$ for h odd, $0k0$ for k odd and $00l$ for l odd; the space group is determined uniquely as $P2_12_12_1 (D_2^2)$. The lattice parameters were determined by the method of Farquhar & Lipson (1946). The crystals of longifolene hydrobromide were found to be isomorphous with those of the hydrochloride and the cell dimensions of the hydrobromide are $a = 8.52$, $b = 9.52$, $c = 16.75$ Å.

4. Intensity data

The intensities of the reflexions from spherical crystals ($r \approx 0.015$ cm) were recorded for the layers $h = 0 \rightarrow 7$ using equi-inclination Weissenberg photographs with Cu $K\alpha$ radiation and the intensities were estimated

visually. Corrections for the polarization and Lorentz factors were made in the usual way. No corrections were made for absorption.

The number of reflexions observed, 1219, represents about 77% of the number possible in the layers recorded and 67% of all possible reflexions. The number of reflexions observed in each layer of constant h is shown in Table 1. The various layers were correlated initially using the $h0l$ reflexions.

Table 1. Reflexions observed in each layer

h	$N(\text{observed})$	$N(\text{possible})$
0	156	215
1	189	229
2	168	226
3	157	215
4	155	203
5	154	187
6	131	166
7	109	140
8	—	112
9	—	83
10	—	47

5. The structure determination and refinement

A set of structure factors were calculated by use of the coordinates of the chlorine and carbon atoms found by Moffett & Rogers and an overall temperature factor obtained from a Wilson plot. After the layers had been individually rescaled, the R values for the observed reflexions in each layer of constant h were between 0.24 and 0.28. A three-dimensional electron map was calculated with the phases of these calculated structure factors, and a careful examination of the map showed that there were no peaks of any significance other than those where the atoms had been placed. The R values and this map were sufficient to show that the structure obtained by Moffett & Rogers from the interpretation of the projections was substantially correct.

The refinement was continued with successive electron-density maps and structure factor calculations until, with an R index of 0.25 for the observed reflexions, it was possible to identify 25 small electron-density peaks as the hydrogen atoms. These positions were checked by calculation to ensure that the hydrogen atoms were correctly disposed with respect to the carbon atoms to which they were bonded; it was particularly difficult to locate the hydrogen atoms in the four methyl groups. Approximate values for the anisotropic thermal parameters for the chlorine atom were obtained at this stage by the fit of a Gaussian ellipsoid to the electron-density peak.

The refinement was further continued by least-squares methods, the positional parameters of the chlorine and carbon atoms, the anisotropic temperature parameters of the chlorine atom, and the individual isotropic temperature parameters of the carbon atoms all being refined. Neither the positional

Table 3. Atomic coordinates and their standard deviations

	x (Å)	$\sigma(x)$ (Å)	y (Å)	$\sigma(y)$ (Å)	z (Å)	$\sigma(z)$ (Å)
Cl	+2.861	0.004	-0.677	0.004	+3.397	0.003
C(1)	+2.555	0.011	+1.066	0.011	+5.559	0.010
C(2)	+1.269	0.015	+1.906	0.014	+5.571	0.013
C(3)	+0.111	0.019	+1.354	0.018	+6.445	0.017
C(4)	+0.467	0.017	+0.781	0.018	+7.783	0.015
C(5)	+1.235	0.013	-0.536	0.013	+7.827	0.012
C(6)	+2.772	0.012	-0.468	0.011	+7.438	0.010
C(7)	+3.211	0.012	-1.241	0.011	+6.125	0.011
C(8)	+2.322	0.013	-0.396	0.013	+5.111	0.012
C(9)	+4.674	0.015	-0.883	0.016	+5.993	0.014
C(10)	+4.711	0.015	+0.532	0.016	+6.564	0.014
C(11)	+3.293	0.012	+0.901	0.012	+6.934	0.010
C(12)	+1.618	0.017	+3.343	0.015	+6.050	0.015
C(13)	+0.720	0.019	+2.001	0.019	+4.159	0.018
C(14)	+3.599	0.016	-1.002	0.017	+8.649	0.015
C(15)	+2.758	0.017	-2.761	0.015	+6.034	0.014

Table 4. Hydrogen atom coordinates

	Attached to	x (Å)	y (Å)	z (Å)
H(1)	C(8)	+1.301	-0.654	+5.202
H(2)	C(1)	+3.215	+1.542	+4.886
H(3)	C(9)	+5.001	-0.908	+4.986
H(4)		+5.299	-1.552	+6.537
H(5)	C(10)	+5.103	+1.210	+5.853
H(6)		+5.341	+0.576	+7.420
H(7)	C(3)	-0.383	+0.615	+5.903
H(8)		-0.570	+2.128	+6.603
H(9)	C(4)	+1.038	+1.493	+8.287
H(10)		-0.425	+0.654	+8.320
H(11)	C(5)	+0.770	-1.201	+7.187
H(12)		+1.165	-0.917	+8.787
H(13)	C(14)	+4.644	-0.947	+8.454
H(14)		+3.300	-1.952	+8.754
H(15)		+3.402	-0.439	+9.538
H(16)	C(13)	+1.140	+2.801	+3.818
H(17)		+0.978	+1.142	+3.585
H(18)		-0.349	+2.079	+4.158
H(19)	C(12)	+1.242	+4.050	+5.386
H(20)		+2.713	+3.397	+6.103
H(21)		+1.199	+3.523	+6.986
H(22)	C(11)	+3.189	+1.718	+7.603
H(23)	C(15)	+1.659	-2.879	+6.136
H(24)		+3.308	-3.260	+6.953
H(25)		+3.070	-3.240	+5.086

Table 5. Temperature factors

C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
2.69	4.28	6.41	5.75	4.06	3.36	2.98	3.59
C(9)	C(10)	C(11)	C(12)	C(13)	C(14)	C(15)	
4.93	5.35	3.26	5.66	5.97	5.24	5.14	

Chlorine

Magnitude and direction cosines of the vibration ellipsoid axes

$B_1 = 4.96$	+0.466	-0.714	+0.523
$B_2 = 1.68$	-0.305	+0.425	+0.852
$B_3 = 7.33$	+0.831	+0.556	+0.020

nor the temperature parameters of the hydrogens were refined. After three cycles, the hydrogen positions

were adjusted by calculation and a final set of structure factors calculated for which the R index for all observed reflexions is 0.13. The observed and calculated structure factors are shown in Table 2, the atomic coordinates, and their standard deviations, of the chlorine and carbon atoms in Table 3, the coordinates of the hydrogen atoms in Table 4 and the temperature parameters in Table 5. A representation of the final electron-density map viewed along a is shown in Fig. 2.

6. Discussion

The three-dimensional determination and refinement shows the molecule of longifolene hydrochloride to be an elaboration of that of bornyl chloride, in that the third isoprene unit completes a seven-membered ring. This confirms the previous X-ray work of Moffett & Rogers and supports the chemical evidence referred to in § 1.

There are no abnormally short intermolecular distances, the shortest being 3.84 Å between C(14)

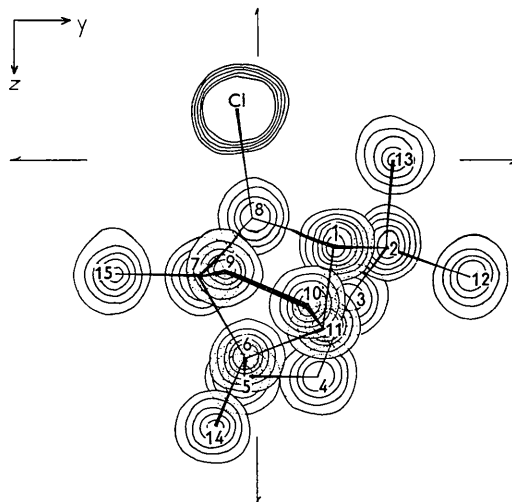


Fig. 2. A representation of the final three-dimensional electron-density map of longifolene hydrochloride, viewed along a .

Table 6. Bond lengths and angles and their standard deviations

	l	$\sigma(l)$		θ	$\sigma(\theta)$		θ	$\sigma(\theta)$
Cl-C(8)	1.821 Å	0.012 Å	Cl-C(8)-C(1)	112°	0.7°	C(5)-C(6)-C(11)	116	0.9
C(1)-C(2)	1.536	0.018	Cl-C(8)-C(7)	111	0.7	C(5)-C(6)-C(14)	108	0.9
C(1)-C(11)	1.570	0.015	C(1)-C(8)-C(7)	104	0.9	C(7)-C(6)-C(11)	94	0.8
C(1)-C(8)	1.546	0.017	C(8)-C(1)-C(2)	113	0.9	C(11)-C(6)-C(14)	112	0.9
C(2)-C(3)	1.552	0.023	C(8)-C(1)-C(11)	103	0.8	C(7)-C(6)-C(14)	109	0.9
C(2)-C(12)	1.557	0.020	C(2)-C(1)-C(11)	116	0.8	C(6)-C(7)-C(8)	97	0.8
C(2)-C(13)	1.519	0.023	C(1)-C(2)-C(3)	116	1.1	C(6)-C(7)-C(9)	103	0.9
C(3)-C(4)	1.498	0.023	C(1)-C(2)-C(13)	109	1.1	C(6)-C(7)-C(15)	116	0.9
C(4)-C(5)	1.524	0.022	C(1)-C(2)-C(12)	109	1.1	C(8)-C(7)-C(9)	111	0.9
C(5)-C(6)	1.587	0.017	C(12)-C(2)-C(13)	108	1.1	C(8)-C(7)-C(15)	108	0.9
C(6)-C(11)	1.550	0.016	C(3)-C(2)-C(12)	109	1.1	C(9)-C(7)-C(15)	120	1.0
C(6)-C(7)	1.586	0.015	C(3)-C(2)-C(13)	106	1.2	C(7)-C(9)-C(10)	102	1.1
C(6)-C(14)	1.560	0.019	C(2)-C(3)-C(4)	117	1.3	C(9)-C(10)-C(11)	107	1.1
C(7)-C(8)	1.591	0.017	C(3)-C(4)-C(5)	119	1.2	C(10)-C(11)-C(1)	105	0.9
C(7)-C(9)	1.511	0.019	C(4)-C(5)-C(6)	116	1.0	C(10)-C(11)-C(6)	100	1.0
C(7)-C(15)	1.590	0.018	C(5)-C(6)-C(7)	117	0.8	C(1)-C(11)-C(6)	103	0.9
C(9)-C(10)	1.526	0.022						
C(10)-C(11)	1.511	0.019						

and C(6) of a neighbouring molecule across a screw axis parallel to a .

The bond lengths and bond angles and their standard deviations are shown in Table 6. The very large differences in the bond lengths found in the two-dimensional work have been removed, but the bond angles in particular show the molecule to be considerably strained. In the tricyclic nucleus of the molecule the internal ring angles of the two five-membered rings are 94, 102, 102, 107 and 100°, and 94, 97, 104, 103 and 103°, all but one being significantly less than the tetrahedral value of 109.5°. This strain would be expected in the formation of the tricyclic arrangement. In contrast, in the seven-membered ring C(1)C(2)C(3)C(4)C(5)C(6)C(11) all the internal ring angles (except that at C(11)) are significantly greater than the tetrahedral value (117, 116, 117, 118, 114, and 118°) possibly to increase the distances between the atoms C(2), C(3), C(4), C(5) and the tricyclic system. (C(2) to C(5) = 2.65 Å, C(5) to C(11) = 2.66 Å, C(4) to C(11) = 2.95 Å and C(3) to C(1) = 2.62 Å.)

The external angles to the ring at C(2) where the dimethyl group is attached have the usual tetrahedral value, but at C(6) the angle C(7)-C(6)-C(5) has a value of 117° to assist in holding the seven-membered ring away from the nucleus. At C(7), the external angles to the rings are large but this is a consequence of the diminution in the size of all the ring angles at this atom. At C(8), there is some evidence that the angles involving the chlorine atom have been increased slightly, possibly to increase the distances between

the chlorine and the methyl carbon atoms C(15) and C(13) (3.36 Å and 3.51 Å).

The carbon-carbon bond lengths just significantly different from 1.541 Å are C(7)-C(6), C(7)-C(8), and C(7)-C(15), and these elongations may help to reduce the strain in the tricyclic nucleus.

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