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The Crystal Structure of Menthyl Trimethylammonium Iodide

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Menthyl trimethylammonium iodide ($[C_{10}H_{19}N(CH_3)_3]^+I^-$) crystallizes in the space group $P2_12_12_1$ with $a=8{\cdot}4$ $b=12{\cdot}4$ and $c=15{\cdot}0$ Å. The structure was solved by three-dimensional Fourier and vector-convergence methods and refined by Fourier methods. The six-membered ring is shown to be boat-shaped and somewhat distorted, so that the large substituents, the trimethylammonium and isopropyl groups, are directed away from each other and on opposite sides of the ring. The iodine and the trimethylammonium group are electrostatically linked to form a spiral along a screw axis parallel to *a*.

1. Introduction

Menthol is the naturally occurring alcohol of the monocyclic terpene menthene. The chemical study of menthol has been extensive and has been of some importance in the stereochemistry of cyclohexane (Simonsen, 1947). The chemical constitution of menthol is shown in Fig. 1(*a*) and the chemically most favourable of the 16 stereo-chemical forms is shown in Fig. 1(*b*), where the ring is shown as chair-shaped with the three substituents in the equatorial position. Menthol and a number of its derivatives have been examined by X-ray methods (Grant & Rogers, 1954) with a view to confirming this configuration. Of those examined, the only crystalline derivative suitable for X-ray structural analysis was the trimethylammonium iodide. This derivative has two serious disadvantages, namely that the presence of the large trimethylammonium group could well change the stereochemical configuration from that of the parent alcohol, and also that the presence of one iodine to only 14 'light' atoms would mean that the accuracy of the structure determination would not be high. The ratio of the sum of the squares of the atomic numbers of the iodines to that of the light atoms is 5·3 to 1; thus

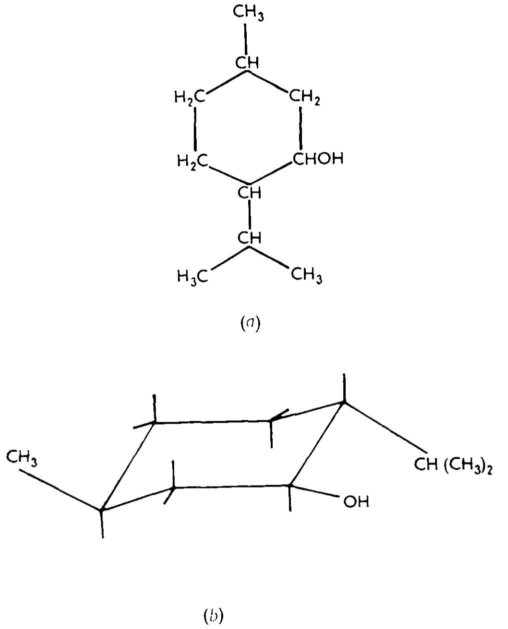


Fig. 1. (*a*) The chemical constitution of menthol. (*b*) Chair-shaped ring with the substituents in the equatorial position.

the average contribution of the light atoms is not much larger than the error in the estimation of the intensities.

2. Crystal data

Menthyl trimethylammonium iodide

$$[C_{10}H_{19}N(CH_3)_3]^+I^-;$$

molecular weight 325; m.p. 193–4 °C.

Orthorhombic,

$$a=8{\cdot}4,\ b=12{\cdot}4,\ c=15{\cdot}0\ \text{Å},\ V=1562\ \text{Å}^3,$$

$$d_o=1{\cdot}380\ \text{g.cm.}^{-3},\ d_c=1{\cdot}382\ \text{g.cm.}^{-3}\ \text{for}\ Z=4,$$
$$F(000)=664,\ \mu=178\ \text{cm.}^{-1}.$$

The space group was determined by means of oscillation and Weissenberg photographs taken with Cu $K\alpha$ radiation. Absent spectra were found to be $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd; hence the space group is determined uniquely as $P2_12_12_1-D_2^4$.

2. Intensity data

The intensities of the reflexions from spherical crystals ($r=0{\cdot}012$ cm.) were recorded for the layers $h=0\rightarrow 6$ and $k=0\rightarrow 3$ using multiple-film equi-inclination Weissenberg photographs with Cu $K\alpha$ radiation and the intensities were measured visually. Corrections for polarization and Lorentz factors were made in the usual way and for absorption using the tables of Evans & Ekstein (1952). The intensities were put on a common relative scale using the Weissenberg photographs about the b-axis for correlation. A Wilson plot gave a scale factor, which was revised later, and indicated an overall temperature factor of 6·2 Å^2.

Table 1. *Reflexions observed in each layer*

h	N(observed)	N(possible)	Ratio
0	101	249	0·406
1	121	266	0·454
2	139	257	0·541
3	133	247	0·539
4	106	230	0·461
5	73	212	0·344
6	62	189	0·328
> 6	48	423	0·112

The number of reflexions observed (about 800) represents only 42% of the number possible, the high temperature factor causing most of these to fall in the range $\sin^2\theta \leq 0{\cdot}6$. The number of reflexions observed in each layer of constant h is shown in Table 1.

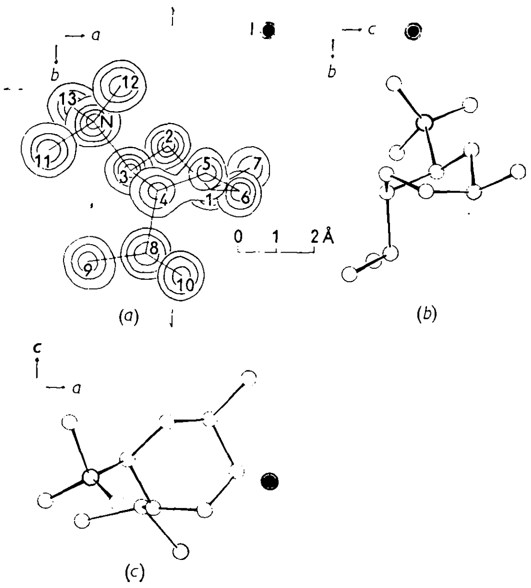
4. The structure determination

The (010) and (100) Patterson projections gave the iodine position. The scaling of the intensities on each layer was checked against the 'iodine only' structure factors and a three-dimensional electron-density map calculated. A comparison of this with two three-dimensional vector-convergence maps, based on the Patterson and sharpened Patterson functions, resulted in five of the light atoms being located. Three cycles of structure factors and electron-density maps were required to determine the positions of the remaining light atoms.

The cyclohexane ring was not complete until the last stage and was found to be in the less likely 'boat' form. A large spurious peak, related by symmetry to the iodine position, made the final location of the trimethylammonium group particularly difficult.

5. Refinement

The structure was refined using the electron-density maps alone. The large contribution of the iodine to the structure factors makes the 'organic' contribution not very much larger than the error in the $|F_o|$'s. Thus a method of refinement involving values of F_o-F_c would not have been reliable. Four cycles of structure factors and electron-density maps were calculated, the centres of each atom being located at each stage by a modification of the method of Booth (1948). After the second cycle the iodine was given anisotropic temperature factors in the following way. A set of 'iodine only' structure factors with an isotropic temperature factor was used to calculate a spherically symmetric iodine. Another electron-density map around the iodine was calculated using $|F_o|$ and the phases given by the last structure factors for the whole molecule. The difference between these two maps showed negative lobes parallel to the z-direction



(a) (b)

(c)

Fig. 2. (a) A composite diagram of sections nearest to the atomic positions in the final three-dimensional electron-density map. Contours are at 1 e.Å^{-3}, the first contour being that for 2 e.Å^{-3}. (b) The molecule viewed along a. (c) The molecule viewed along b.

Table 2. *Agreement summary*

769 observed reflexions $|F_o|$ min $\simeq 10$

$\lvert F_o\rvert$ range	$0 \le \lvert\Delta F\rvert < 2$	$2 \le \lvert\Delta F\rvert < 4$	$4 \le \lvert\Delta F\rvert < 6$	$6 \le \lvert\Delta F\rvert < 8$	$8 \le \lvert\Delta F\rvert < 10$	$10 \le \lvert\Delta F\rvert < 12$	$\lvert\Delta F\rvert \ge 12$
0–19	86	79	26	20	2	2	—
20–39	87	120	63	38	15	9	6
40–59	25	31	25	15	6	9	6
60–79	12	19	11	7	1	3	8
80–99	3	1	5	4	3	1	4
100–119	—	2	—	—	3	1	3
$\ge$ 120	—	—	—	—	1	—	7

Table 3. *Atomic coordinates and their standard deviations*

	x/a	x (Å)	$\sigma(x)$ (Å)	y/b	y (Å)	$\sigma(y)$ (Å)	z/c	z (Å)	$\sigma(z)$ (Å)
C_1	+0·6169	+5·182	0·056	+0·4674	+5·796	0·055	+0·2538	+3·807	0·054
C_2	+0·4822	+4·051	0·058	+0·3755	+4·656	0·057	+0·2467	+3·701	0·056
C_3	+0·3659	+3·074	0·053	+0·4260	+5·282	0·053	+0·1807	+2·711	0·052
C_4	+0·4423	+3·715	0·054	+0·4728	+5·860	0·055	+0·0961	+1·442	0·054
C_5	+0·6049	+5·081	0·055	+0·4347	+5·390	0·053	+0·0895	+1·343	0·052
C_6	+0·7119	+5·980	0·057	+0·4710	+5·840	0·049	+0·1677	+2·516	0·050
C_7	+0·7396	+6·213	0·050	+0·4192	+5·198	0·050	+0·3289	+4·934	0·050
C_8	+0·4152	+3·488	0·052	+0·6030	+7·477	0·055	+0·0984	+1·476	0·048
C_z	+0·2434	+2·045	0·048	+0·6200	+7·688	0·061	+0·0733	+1·099	0·047
C_{10}	+0·5324	+4·472	0·055	+0·6521	+8·086	0·054	+0·0251	+0·377	0·050
C_{11}	+0·1106	+0·929	0·050	+0·3903	+4·840	0·058	+0·1101	+1·652	0·047
C_{12}	+0·3364	+2·826	0·055	+0·2399	+2·975	0·053	+0·1057	+1·586	0·051
C_{13}	+0·1910	+1·604	0·060	+0·2865	+3·553	0·052	+0·2457	+3·686	0·050
N	+0·2491	+2·092	0·038	+0·3257	+4·039	0·037	+0·1522	+2·283	0·044
I	+0·8017	+6·734	0·004	+0·1240	+1·538	0·004	+0·1450	+2·175	0·004

only and the temperature factors $B_1 = B_2 = 6{\cdot}2$ Å and $B_3 = 5{\cdot}5$ Å^2, with the ellipsoid axes parallel to the cell axes, were then used. At the last stage of refinement a program (for Stantec 'ZEBRA' and available only then) was used to provide a least-squares fit of a spherical or ellipsoidal atom to the three-dimensional electron-density peaks and to give the final atomic coordinates (Grant, 1961).

The cycles of refinement were continued until the average shift found was less than one-third of the calculated standard deviations of the coordinates. The R-factor for the observed reflexions was then 12·7%; an agreement summary for the observed and calculated structure factors is shown in Table 2.* A representation of the final three-dimensional electron-density map viewed along c is shown in Fig. 2(a), and two other views of the molecule are shown in Figs. 2(b) and (c). These show the ring to be boat-shaped with the 'bow' and 'stern' at C_2 and C_5 respectively. The boat is however distorted in that the bond C_1–C_6 is not parallel to C_3–C_4. The substituents are arranged in such a way as to give minimum steric interference with one another and, in particular, the isopropyl and trimethylammonium groups are found one on each side of the ring. The final coordinates and their standard deviations are shown in Table 3.

6. Molecular geometry

The intramolecular bond lengths and bond angles and their standard deviations are shown in Table 4.

Table 4. *Bond lengths and angles and their standard deviations*

	l	$\sigma(l)$		θ	$\sigma(\theta)$
C_1–C_2	1·61 Å	0·12 Å	C_1–C_2–C_3	102°	6°
C_2–C_3	1·53	0·11	C_2–C_3–C_4	115	6
C_3–C_4	1·54	0·11	C_3–C_4–C_5	109	6
C_4–C_5	1·45	0·11	C_4–C_5–C_6	114	6
C_5–C_6	1·54	0·11	C_5–C_6–C_1	109	6
C_6–C_1	1·52	0·11	C_6–C_1–C_2	109	6
C_1–C_7	1·64	0·10	C_2–C_1–C_7	103	5
			C_6–C_1–C_7	106	5
C_4–C_8	1·63	0·10			
C_8–C_9	1·51	0·10	C_3–C_4–C_8	107	5
C_8–C_{10}	1·60	0·10	C_5–C_4–C_8	117	6
C_3–N	1·64	0·09	C_4–C_8–C_9	105	6
N–C_{11}	1·55	0·09	C_4–C_8–C_{10}	106	5
N–C_{12}	1·47	0·09	C_9–C_8–C_{10}	111	6
N–C_{13}	1·56	0·09			
			C_2–C_3–N	104	6
			C_4–C_3–N	109	5
			C_3–N–C_{11}	99	5
			C_3–N–C_{12}	112	5
			C_3–N–C_{13}	101	5
			C_{11}–N–C_{12}	124	5
			C_{11}–N–C_{13}	107	5
			C_{12}–N–C_{13}	111	5

As was expected, the dominance of the structure by the iodine and the lack of high-order reflexions have resulted in low accuracy for the coordinates of the light atoms; the standard deviations of the bond lengths are as much as 0·1 Å. However the significance levels of Cruickshank (1949) show that the bond lengths and angles which differ significantly from the accepted values occur only in the trimethylammonium

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* Photographic copies of the lists of observed and calculated structure factors may be obtained from the authors on request.

group, namely C_3–N = 1·64 Å and the angles C_3–N–C_{11} = 99°, C_{11}–N–C_{12} = 124°. The bulky methyl groups could account for these distortions in angles, and the lengthening of the C_3–N bond may be due to the distances C_{11}–C_4 = 2·94 Å and C_{13}–C_2 = 2·73 Å being short. These would be shorter still if the C_3–N bond was not stretched to reduce the hindrance between the trimethylammonium group and the ring atoms. This lengthening of the C–N bond has been noted in other substances with large substituent groups (Geller, Hoard & Owen, 1951).

7. Electrostatic arrangement

As would be expected the trimethylammonium group is involved in a network of electrostatic linkages with the iodine ions. The sum of the effective radius of a methyl group and the radius of an iodine ion is about 4·16 Å (Pauling, 1939). Some iodine–methyl distances are listed in Table 5. Calculation shows that C_{11}, C_{12}, N and I_3 lie within 0·25 Å of the best (least-squares) plane through them and C_{11}, C_{13}, N, I_2 lie within 0·5 Å of the best plane through them; this indicates which part of the trimethylammonium group is associated with each iodine, and results in a spiral arrangement of electrostatic linkages around the screw axes parallel to *a*. A view of this is shown in Fig. 3. An interesting feature is the way the distance I_2–C_{12} provides a spacing linkage between the trimethylammonium groups and the iodines.

Table 5. *Iodine-methyl distances*

I_1 at (x, y, z)	I_2 at $(x-1, y, z)$	I_3 at $(x-\frac{1}{2}, \frac{1}{2}-y, -z)$
	l	$\sigma(l)$
I_1–C_{12}	4·21 Å	0·075 Å
I_2–C_{11}	4·23	0·080
I_2–C_{13}	4·13	0·081
I_3–C_{11}	4·15	0·080
I_3–C_{12}	4·13	0·075

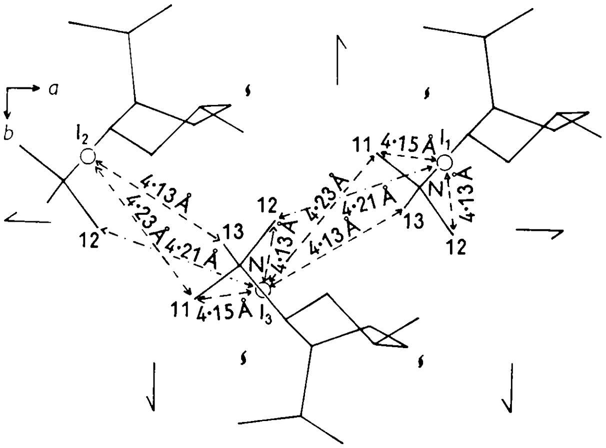

Fig. 3. The electrostatic linkage between the iodine and the trimethylammonium group viewed along *c*.

8. Summary

(i) The six-membered ring was found to have adopted a distorted boat-shaped form in order to reduce the steric hindrance between the bulky substituents.

(ii) If, however, the ring shape found was changed to chair-shaped by moving C_3 and C_5 without any rearrangement of the substituents, then the generally accepted form for menthol results (Fig. 1). This structure determination does not give direct evidence for the structure of menthol itself, but suggests that the form shown in Fig. 1 is possible.

(iii) The only significant changes in bond lengths and angles occur in the trimethylammonium group. The distortion of this group and, in particular, the lengthening of the C_3–N bond may be thought of as being due to the short distances between parts of this group and atoms in the ring itself.

(iv) The electrostatic arrangement shows an interesting spiral linkage about one screw axis parallel to *a* with iodine–methyl distances of about 4·2 Å.

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