Acta Cryst. (1954). **7**, 301

X-ray studies of the terpenes. II. (−)-Menthylamine hydrochloride and hydrobromide, and (−)-menthyltrimethylammonium iodide.

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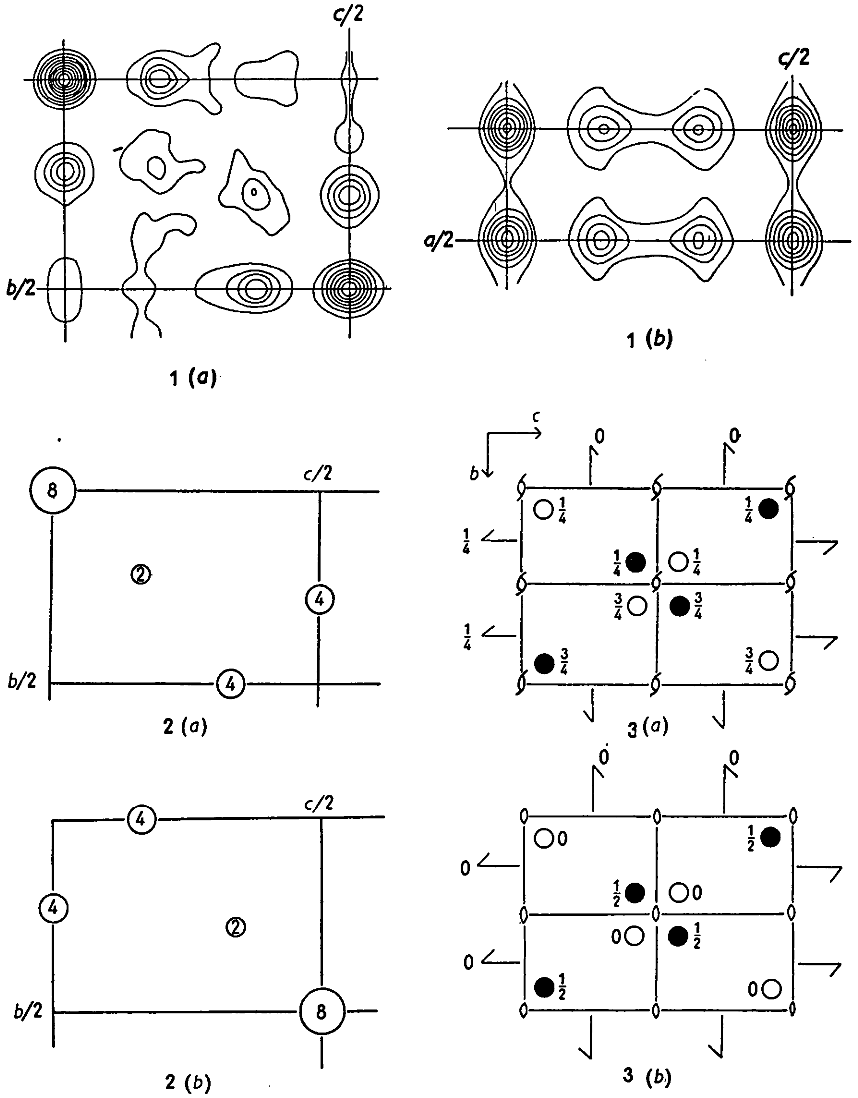
(*Received* 17 *December* 1953)

(−)-Menthylamine hydrochloride and hydrobromide, $C_{10}H_{22}NX$

This pair of isomorphous substances was chosen as a likely means of verifying the stereochemistry of the menthyl radical and also of determining the ring configuration in the crystalline state. Despite their high melting points (> 280° C.) and the ionic character of some of the bonds the crystals were found to have very large 'temperature' coefficients. This rapid attenuation in reciprocal space and certain structural peculiarities to be described later have so far defeated all attempts to determine the detailed structures. The results achieved are, however, here set on record.

The specimens were recrystallized from water and several other solvents as colourless orthorhombic needles elongated along [100]. The principal faces are {011} with occasionally {010}, and there is a ready though rather imperfect cleavage along (100). The inter-optic-axial angle is small and has for its acute bisectrix α, which is parallel to a. The birefringence, $(\gamma-\beta)$, for transverse sections of the prisms is very small, but α differs considerably from β and γ. The crystals are, in fact, nearly uniaxial negative.



1 (*a*)

1 (*b*)

2 (*a*)

3 (*a*)

2 (*b*)

3 (*b*)

Figs. 1–3. The determination of the space group of (−)-menthylamine hydrobromide.

Fig. 1. Patterson projections (*a*) (100), (*b*) (010).

Fig. 2. Schematic Harker sections (*a*) $x = 0$, (*b*) $x = \frac{1}{2}$.

Fig. 3. The two sets of halogen positions in (*a*) $P2_12_12_1$, (*b*) $P22_12_1$.

X-ray photographs gave the cell dimensions, which are listed in Table 1 and are of limited accuracy because of the absence of high-angle reflexions.

Table 1. *Data for (−)-menthylamine hydrochloride and hydrobromide*

	(−)-Menthylamine hydrochloride	(−)-Menthylamine hydrobromide
a (Å)	$7{\cdot}9_4$	$8{\cdot}0_6$
b (Å)	15·4	15·4
c (Å)	21·0	20·9
d_o (g.cm.$^{-3}$)	0·987	1·208
d_c (g.cm.$^{-3}$)	0·984	1·210
Mol.wt.	192	236
Z	8	8

The only systematic absences are the odd orders of the ($h00$), ($0k0$) and ($00l$) reflexions, confirmed up to $h = 7$, $k = 13$ and $l = 17$. Although this result leads uniquely to the space group $P2_12_12_1$, it was found necessary to discard this space group after the positions of the halogens had been found.

As there are two molecules in the asymmetric unit, eight halogen atoms had to be arranged in the unit cell in two independent sets of four. The (100) and (010) Patterson projections (Fig. 1) were interpreted in terms of space group $P2_12_12_1$ to give the halogen positions shown in Fig. 3(*a*). This arrangement also satisfied the observation that the reflexions for which $(h+k+l) = 2n$ were on the average considerably stronger than those for which $(h+k+l) = 2n+1$, to which the halogens make no contribution. Such an arrangement requires the non-equivalent halogen ions to occur in pairs separated by a mere 3·5 Å, which is less than twice the ionic radius of either chlorine or bromine.

Further information was sought from the Harker sections at $x = 0$ and $\frac{1}{2}$, which are shown schematically in Fig. 2. These are quite incompatible with the space group $P2_12_12_1$, but could have come from a number of other space groups. All these, except $P222$ and $P22_12_1$, require additional systematic absences and were, therefore, rejected. In view of the systematic absences quoted above, $P222$ was also rejected. The other, $P22_12_1$, leads to the arrangement of Fig. 3(*b*) in which the two sets of halogens occur in separate sheets, each containing ions separated by a minimum distance of 4·9 Å. These sheets appear, from the coordinates of the peaks in the Patterson projections and sections, to be identical and related so as to give a body-centred arrangement of halogen ions. But this arrangement is certainly not true of the eight menthylamine ions, which are alone responsible for the odd $(h+k+l)$ reflexions. In a similar way it may be shown that the two sheets of menthylamine ions are not related in any simple way, for all such ways would require various sets of additional systematic absences.

From a consideration of the optics, the cleavage, the Patterson projections and sections, and the above remarks, the space group must be regarded as being $P22_12_1$, and the structure as built up of two alternating and unrelated sheets of molecules all lying roughly parallel to (100), and with all three ring substituents in the thermodynamically more stable equatorial positions (Barton, 1953) (Hassel's $\varkappa$ positions, see Fig. 4). Such a structure would give very weak odd orders of ($h00$) and would explain our observation of a pseudoscrew. It might also be susceptible to layer-sequence faults which would contribute to the abnormally high temperature coefficients (B from 6 to 11 Å^2). It is not easy to see why the two sets of halogens should conform so closely to a body-centred arrangement when their environment so little resembles that, but it is quite likely that small discrepancies would become evident if only the odd $(h+k+l)$ reflexions could be incorporated into the electron-density maps.

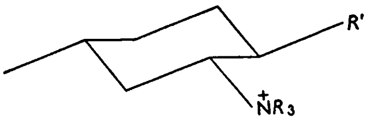


Fig. 4. (1) Menthylamine radical, R' = *iso*propyl, R = H. (2) Menthyltrimethylammonium radical, R' = *iso*propyl, $R = CH_3$.

The position at present is that all the signs of the even $(k+l)$ reflexions have been determined by isomorphous replacement and thus maps of projections containing sixteen half-weight molecules have been prepared. None of the odd $(k+l)$ signs could be determined by inequalities, and the indications given by Sayre's method (Sayre, 1952) have not led to interpretable maps, mainly because of poor resolution. If this can be improved by photography at low temperatures, the structure may yet be solved.

(−)-Menthyltrimethylammonium iodide, $C_{10}H_{19}N(CH_3)_3I$

(Molecular weight: 325.)

This substance was recrystallized in two forms:

I. The crystals as supplied, or after recrystallization from ethanol, are ragged plates usually thin and often in the form of lamellar overgrowths. The principal face is (011). The crystals are yellowish but darken on exposure to light. The birefringence is small for light passing normally through the plates. Some single crystals were successfully ground to spheres (diameter ~ 0·25 mm.) with the device described by Bond (1951) and these were used for the X-ray photography. The crystals are orthorhombic with absences denoting uniquely the space group $P2_12_12_1$. The axial lengths are

$$a = 8{\cdot}4_5,\ b = 12{\cdot}3_0,\ c = 15{\cdot}5_5\ \text{Å}\ ,$$

and the cell contains 4 molecules (d_o = 1·343 g.cm.$^{-3}$, d_c = 1·333 g.cm.$^{-3}$). A detailed analysis of this structure is now proceeding. The melting point of this form is 193–194° C. (McNiven & Read, 1952). ((−)-Menthyltrimethylammonium chloride has been obtained in apparently similar form, but as it is so very deliquescent no X-ray study of it has been made.)

II. The crystals formed by recrystallization from water or acetone are orthorhombic laths (m.p.: 189–190° C.) which grow perfectly to a considerable size as single crystals. They are initially colourless and acquire only a faint yellow tint on prolonged exposure to light. The larger prism faces are (001), the narrower are (010). The laths cleave readily along (010) and (100).

The axes of the indicatrix are $\alpha \parallel c$, $\beta \parallel b$, $\gamma \parallel a$; the difference $(\gamma-\alpha)$ is not large and $(\gamma-\beta)$ is very small.

The optic axes lie in (010) and, when viewed normal to (001), have a fairly large interaxial angle which exhibits marked dispersion. Weissenberg photographs gave the axial lengths

$$a = 7{\cdot}38,\ b = 14{\cdot}75,\ c = 56{\cdot}74\ \text{Å}\,.$$

The observed density is 1·305 g.cm.$^{-3}$, so that the cell contains 16 (15·85) molecules. The only systematic absences lead uniquely to the space group $P2_12_12_1$, but there are marked pseudo glides: b in the $0kl$ and a in the $hk0$ zones. The $0kl$ and $1kl$ layers also approximate closely to B-face centring, but the approximation fades out in the second and higher layers. No further work is to be done on this form as the asymmetric unit comprises 4 molecules.

We wish to thank Dr N. L. McNiven who kindly prepared these specimens and Prof. J. Read who supplied them to us. We also wish to thank Dr A. J. C. Wilson for encouragement and for the use of equipment purchased with a Royal Society grant. One of us (D.R.) is indebted to the University of Wales for an I.C.I. Research Fellowship.

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Metallurgical Equilibrium Diagrams. By W. Hume-Rothery, J. W. Christian and W. B. Pearson. Pp. 311 with 239 figs. London: Institute of Physics, 1952. Price 50*s*.

The title of this monograph is perhaps a little misleading, for it deals mainly with the accurate determination of metallurgical equilibrium diagrams, and not with the diagrams themselves. It is the only comprehensive account of these methods known to the reviewer, and as such it is a valuable contribution to metallurgical literature. The book commences with a section on the principles of binary systems, while later sections describe general experimental methods, the determination of the liquidus, the solidus, and reactions below the solidus. The book concludes with the consideration of the special problems of ternary systems. Throughout the monograph emphasis is laid on the limitations of the methods and on the precautions necessary to achieve maximum accuracy. The chapter on X-ray methods, which is of particular interest to crystallographers, deals only with X-ray powder methods for both normal and elevated temperatures. Much of the chapter is devoted to the methods of preparing a powder sample which is representative of the alloy and free from contamination. There is a comparison of the relative merits of the X-ray and microscopical methods which puts into perspective the value of X-ray techniques in this field. A later chapter contains a valuable discussion of the use of X-ray methods in the establishment of ternary diagrams.

The value of this book to crystallographers is difficult to assess. The chapter on X-ray methods can certainly be recommended, but the major value of the book, in the opinion of the reviewer, is as an invaluable guide to the preparation of metallic materials free from contamination and uniform in composition.

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