

on the line joining the oxygen atoms of two neighbouring ether molecules. A similar structure is not to be expected if bromine is replaced by iodine monochloride, but we would expect the iodine atom to be directly linked to an ether oxygen and the angle O—I—Cl to be 180°. So far, we have not investigated this compound, but determined the structure of another compound which we obtained in the form of yellow needles (m. p. 103° C) directly from the vapours of the two compounds. Here the ratio of iodine monochloride and dioxan molecules is 2:1 as could easily be shown by dissolving the solid substance in an aqueous solution of potassium iodide and titrating the amount of iodine thereby set free.

The crystals of the new compound are *monoclinic* with  $\beta = 95.2^\circ$  and the space group is  $C2/m$ . The unit cell containing four molecules of iodine monochloride and two molecules of 1,4-dioxan have the constants  $a = 14.62$ ,  $b = 8.00$ ,  $c = 4.56$ . Approximate coordinates of the heavy iodine atoms could easily be found by conventional trial and error methods and Fourier maps computed using the signs of structure factors resulting from these coordinates. Only one refinement was necessary in order to arrive at the final maps reproduced in Fig. 1. The I and Cl coordinates thus obtained are: I: 0.242; 0; -0.290; Cl: 0.389; 0; -0.424. The coordinates of the light atoms derived from the maps are of course less accurate, but it is obvious that the centrosymmetrical dioxan molecules are of the "chair" form and the location of the oxygen atoms are good enough to show that each of them is linked to an iodine atom which has on its opposite side a chlorine atom, the O—I—Cl arrangement being linear or at least very nearly so. The O—I distance may safely be given as 2.6 Å, the I—Cl distance is 2.3 Å. The nearest Cl—Cl-approach, on the other side, is 3.38 Å showing that van der Waals forces only exist between chlorine atoms. The structure of the new compound thus provides a second example of a solid ether-halogen compound displaying a linear arrangement of the type O—Hal—Hal.

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2. Hassel, O. and Hvorslef, J. *Acta Chem. Scand.* **8** (1954) 873.

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## Structure of an Addition Compound Containing *two* Bromine Molecules and one Molecule of Hexamethylene Tetramine

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As part of a research programme dealing with crystal structures of addition compounds between ethers, amines *etc.* and inorganic molecules, a bromine compound which, according to analyses, contains two molecules of bromine on every molecule of hexamethylene tetramine has been investigated. The result of the X-ray work shows that each bromine molecule is linked to one of the four tertiary nitrogen atoms, the arrangement of both groups being the same. The N-Br-Br group is *linear* and the line through the three atoms in question is symmetrically situated with respect to the three C—N bonds of the nitrogen atom. Four tetrahedral bonds are thus found by each nitrogen atom involved. The bond angles do not deviate much from the "regular" angle (109.5°). The fact that the N-Br-Br angle is 180° (or at least very nearly so) rules out the possibility that resonance effects in the NBr<sub>2</sub> group based on equivalence of the two bromine atoms are of any significance. The two N-Br-Br groups of a molecular complex are crystallographically independent and the fact that they are found (within the limits of error) to be identical in shape is of considerable interest. The Br-Br distance is found equal to 2.4 Å; for the N-Br distance the value 2.3 Å was obtained. These findings point to a strong interaction between the nitrogen atom and the nearest bromine atom and indicate a very marked weakening of the Br-Br bond. It would appear rather probable that in addition compounds of amines showing markedly stronger basic properties than hexamethylene tetramine, a dissociation of the bromine molecule may even occur. Investigations dealing with addition compounds of such amines are now in progress in our laboratory.

The yellow crystals of the compound between hexamethylene tetramine and two molecules of bromine are *monoclinic* and belong to the space group  $P2_1/c$ .

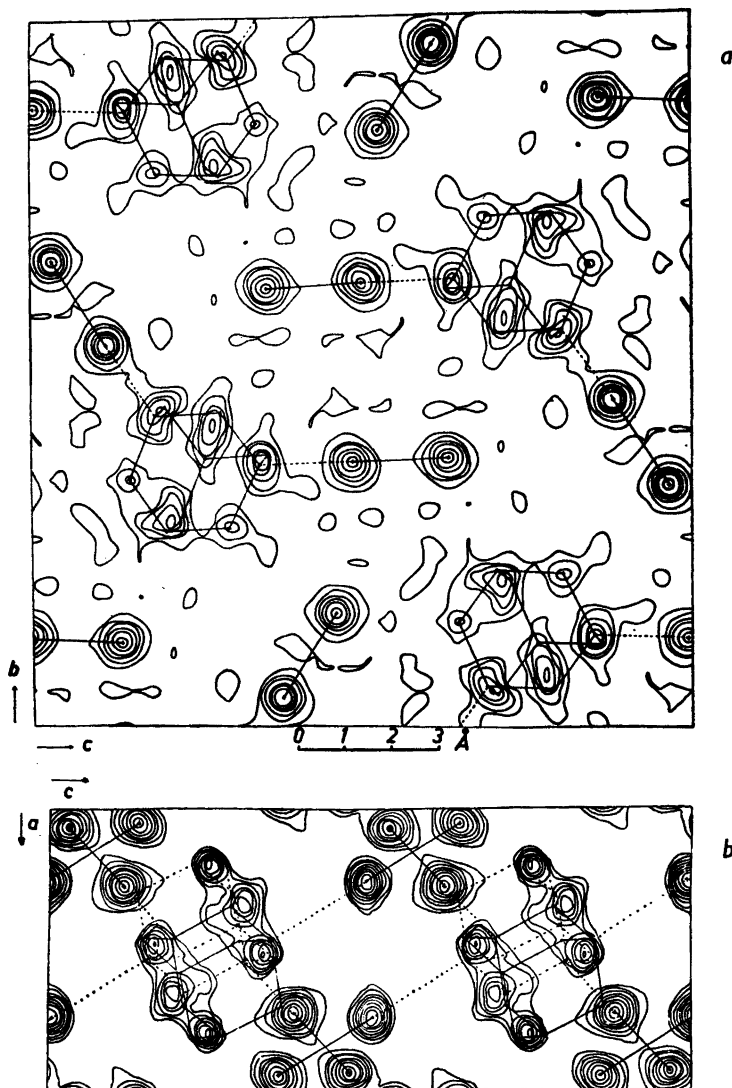


Fig. 1. Electron density maps projected a. along [100], b. along [010]. Interval between drawn contour lines four times larger for bromine than for carbon and nitrogen atoms.

From the observed density (2.35) and the lattice parameters:  $a = 6.05$ ;  $b = 14.90$ ;  $c = 13.88$  and  $\beta = 91.4^\circ$  follows that the unit cell must contain four molecules of hexamethylene tetramine and eight molecules of bromine. Patterson Charts com-

bined with "trial and error" calculations resulted in approximate values of the bromine parameters which could be used as a basis for two dimensional Fourier syntheses. Reproductions of electron density maps, projected along [100] (Fig. 1 a) and

along [010] (Fig. 1 b) are given. The form of the organic part of the complex necessarily leads to overlapping in any projection. In the [010] projection overlapping of two amine molecules occurs. A difference synthesis — with subtraction of the bromine atoms — led to a chart in which the organic part was better resolved than in Fig. 1 a. All further details of the investigation — now practically finished — will be given in a forthcoming publication.

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### *iso*Thiocyanates XVII. *o*-Methoxybenzyl *iso*Thiocyanate and some Derivatives

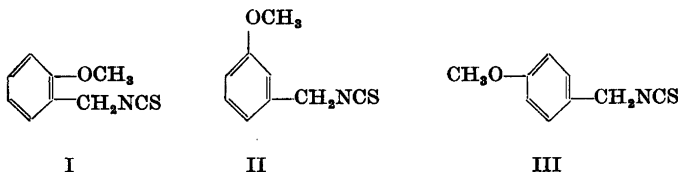
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Recently, Ettlinger and Lundeen<sup>1</sup> isolated *m*-methoxybenzyl *iso*thiocyanate (II) from seeds of the American plant *Limnanthes douglasii* R.Br. Coincidentally, *p*-methoxybenzyl *iso*thiocyanate (III) was recognised in this laboratory as the aglucone of a glucoside, named glucosubrietin, occurring in various species of the crucifer genus *Aubrietia*<sup>2</sup>. Both (II) and (III) were synthesised in the course of these investigations.

Ettlinger<sup>1</sup>, and used also for the synthesis of (II)<sup>1</sup> and (III)<sup>2</sup>. Contrary to the latter two, which are liquids at ordinary temperature, the mustard oil (I) appeared as a low-melting solid. Its ultra-violet absorption spectrum in 2,2,4-trimethylpentane has a shoulder at about 255  $m\mu$  ( $\epsilon$  ca. 1550), maxima at 271  $m\mu$  ( $\epsilon$  2400) and 277  $m\mu$  ( $\epsilon$  2400) and minima at 236  $m\mu$  ( $\epsilon$  850) and 275  $m\mu$  ( $\epsilon$  2200). These data are in accord with those reported for the *meta*-isomeride (II)<sup>1</sup>, but differ considerably from the values determined for (III) in the same solvent, *viz.* shoulders at about 250  $m\mu$  ( $\epsilon$  2300) and 285  $m\mu$  ( $\epsilon$  1000), maxima at 228  $m\mu$  ( $\epsilon$  11600) and 276  $m\mu$  ( $\epsilon$  1730) and a broad minimum around 269  $m\mu$  ( $\epsilon$  1550). In the wave-length region below 11  $\mu$ , the infra-red spectrum of (I) was comparable to that of (III), both displaying bands which deviated considerably from those reported for the *meta*-compound<sup>1</sup>.

For the purpose of characterisation, (I) was converted into *N*-*o*-methoxybenzylthiourea and *N*-benzyl-*N'*-*o*-methoxybenzylthiourea on reaction at room temperature with ammonia and benzylamine, respectively. The mustard oil reacted much more sluggishly than generally experienced for *iso*thiocyanates, a fact suggesting a certain sterical influence of the neighbouring methoxy-grouping. In an attempt to enforce the reaction between (I) and benzylamine under more drastic conditions, amine exchange occurred, resulting in the formation of *N,N'*-dibenzylthiourea. This reaction presents no novelty in thiourea chemistry. Recently, Ettlinger and Hodg-



On this background it became of interest to prepare the heretofore unknown *o*-methoxybenzyl *iso*thiocyanate (I). The requisite *o*-methoxybenzylamine was obtained by Leuckart-reaction on *o*-methoxybenzaldehyde, according to Lewis<sup>3</sup>, but in somewhat better yield (40 %). The amine was converted into (I) by the convenient modification of the Kaluza-synthesis which was recently introduced by Hodgkins and

kins<sup>4</sup> observed the formation of thio-carbanilide in the reaction of *N*-*t*-butyl-*N'*-phenylthiourea with aniline in boiling benzene, and referred to further examples in the literature. In the present case, it seems likely that sterical factors interfere with the usual thiamide-resonance, thus favouring the displacement of *o*-methoxybenzylamine. This view is supported by the infra-red spectra of the thioureas corresponding