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The Crystal Structure of Bromoform, $CHBr_3$

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The crystal structure of bromoform has been determined by the X-ray diffraction method at about −20°C. There are two molecules per cell in the structure with hexagonal space group $P6_3$ (C_6^6). Unit-cell constants are $a = 6{\cdot}335 \pm 0{\cdot}003$ and $c = 7{\cdot}214 \pm 0{\cdot}003$ Å. The structure is statistically disordered, with molecules oriented upwards and downwards along the *c* axis at random. The order parameter *w* was found to be nearly $\frac{1}{2}$ and hence the symmetry of the crystal can approximately be represented by $P6_3/m$ (C_{6h}^2). The structure is isomorphous with that of iodoform, while it is quite different from that of chloroform.

Introduction

Several theoretical treatments have been proposed to explain intermolecular interactions, but none of them is sufficiently accurate to predict the crystal structure of a methane derivative. The crystal structure of methyl chloride, CH_3Cl (Burbank, 1953), is quite different from those of methyl bromide, CH_3Br, and methyl iodide, CH_3I (Hijikigawa, Hayafugi, Ikeda, Fukushima Kawaguchi & Tomiie, 1972). The crystal structure of chloroform, $CHCl_3$ (Fourme & Renaud, 1966), is different from that of iodoform, CHI_3 (Nitta, 1926; Kitaigorodskii, Khotsyanova & Struchkov, 1951). It is the purpose of this investigation to ascertain what kinds of interactions determine various crystal structures composed of molecules which are quite similar in their physical and chemical properties. In order to collect information for this purpose, the authors have undertaken a series of studies on the determination of crystal structures of various halogenated derivatives of methane. In this paper, the crystal structure of bromoform, $CHBr_3$, will be reported and molecular interactions for these trihalogenated methanes will be considered.

Experimental

Bromoform (containing 6 vol. % ethanol), prepared by Wako Pure Chemical Industries, Ltd was purified repeatedly by recrystallization by cooling and by vacuum distillation. Bromoform purified in this way was sealed in thin glass capillary tubes (0·3 mm internal diameter and 0·01 mm wall thickness). The specimen was placed on the goniometer head of a Weissenberg camera, and crystallization was done carefully in a cold gas stream from liquid nitrogen. Because bromoform is liable to supercool, it was required to freeze the sample rapidly, followed by heating it up just below its melting point (8·05°C) and by keeping it at that temperature for a long time in order to grow a seed of the crystal as near to the size of the capillary as possible. The single crystal was then cooled down slowly to about −20°C to prepare oscillation and Weissenberg photographs.

Since these crystals do not last for a long time, it was necessary to replace one specimen by another until sufficient diffraction data to carry out the analysis had been collected. In almost all cases it was observed that there were only two kinds of zone axes along the capillary. They were first thought to be to the [100] and [101] axes of a monoclinic lattice, but were found later to correspond to the [100] and [110] axes of a hexagonal lattice.

Oscillation and Weissenberg photographs around these two axes were accounted for assuming the structure to be monoclinic. The integrated intensities were collected by means of the normal beam and the multiple-film methods using Ni-filtered Cu $K\alpha$ radiation. Four and five layers were obtained around these two axes.

Systematic extinctions (none for *hkl*, and 0*k*0 with *k* odd) showed that the crystal belongs to space group $P2_1$ or $P2_1/m$. The cell constants were calculated to be $a' = 6{\cdot}338$, $b' = 7{\cdot}214$, $c' = 6{\cdot}331$ Å and $\beta' \simeq 120°$. These constants strongly suggested that the lattice is hexagonal. Actually sixfold symmetry was observed, at least qualitatively, in the intensity distributions. The transformation of the axes gave $a = 6{\cdot}335 \pm 0{\cdot}003$ and $c = 7{\cdot}214 \pm 0{\cdot}003$ Å for a hexagonal lattice and the systematic extinctions none for *hkl*, and 00*l* with *l* odd, showed the space group to lie $P6_3$ or $P6_3/m$.

The resulting volume of the unit cell is $250{\cdot}7 \pm 0{\cdot}3$ Å^3, and there are two molecules per cell. The X-ray density is $3{\cdot}346 \pm 0{\cdot}003$ g.cm^{-3}. This value, when compared with the observed value 2·8905 g.cm^{-3} for the liquid at 20°C (Desreux, 1935), indicates that a rather large contraction of volume takes place upon solidification.

The unit-cell constants described above are similar to those of iodoform and the extinction rules are the same, which suggests that the structure of bromoform is isomorphous with that of iodoform. Iodoform has been assigned the space group symmetry $P6_3$, and a recent neutron-diffraction study on iodoform has shown that the structure is disordered and its symmetry approximately corresponds to $P6_3/m$ (Iwata, Oyama, Kawaguchi & Watanabé, 1972).

Structure determination

It is in fact impossible to place two molecules in the unit cell of $P6_3/m$. It is possible, however, to attain the symmetry if molecules are assumed to be oriented statistically upwards and downwards along the c axis.

By introducing an order parameter w, where w denotes the fraction of the molecules oriented in one way and $1-w$ the fraction oriented in the other way, the structure factor can be expressed by the equation as cited in the paper of Iwata *et al.*;

$$F(hkl)=A(hkl)+i(1-2w)B(hkl),$$

where

$$A(hkl)=\sum_j f_jT_j\cos 2\pi(hX_j+kY_j+lZ_j)\,,$$

$$B(hkl)=\sum_j f_jT_j\sin 2\pi(hX_j+kY_j+lZ_j)\,. \quad (1)$$

This equation represents the ordered, the perfectly disordered, and the partially disordered structures, when $w=0$ or 1, $\frac{1}{2}$, and other values respectively.

The intensity data measured visually were corrected for Lorentz–polarization and absorption effects with the cylindrical approximation ($\mu=249{\cdot}78$ cm^{-1} for Cu $K\alpha$ radiation). Here, the actual diameters of the specimens used may have various values even though the capillaries used all had internal diameters of 0·3 mm. This is mainly due to the striking contraction of volume of the material upon solidification. Although the actual value of the diameter for each specimen could not be measured, it was possible to estimate by trial and error the value of μR for each specimen from comparison between the intensities of equivalent reflexions obtained from different specimens. The intensity data, after making the above corrections, were brought into a common scale and were averaged for symmetrically equivalent reflexions. There were 160 independent reflexions, including 12 of zero intensity, used in the refinement of the structure.

With the aid of the three-dimensional Patterson function, approximate coordinates of the bromine atoms around the threefold rotation axes were immediately located. The reliability factor, $R=\sum||F_o|-|F_c||/\sum|F_o|$, was 30% with these coordinates of the bromine atoms alone. The least-squares refinement based upon equation (1) was applied, omitting the hydrogen atoms. The R value reduced to 23% for the ordered structure ($w=0$) and to 16% for the perfectly disordered structure ($w=\frac{1}{2}$), each with an isotropic temperature factor. It was discovered that the bromoform crystal prefers a disordered structure rather than an ordered one as does the iodoform crystal. Keeping the symmety of the crystal as $P6_3/m$, the structure was refined by using anisotropic temperature factors for the bromine atoms ($R=14{\cdot}7$%).

The refinement, including the order parameter w, was carried out assuming the structure to be partially disordered. Although the R value did not decrease, the resulting w converged a value of 0·43. It is concluded that the actual crystal is statistically disordered and its symmetry can approximately be described by $P6_3/m$.

Results

The observed and calculated structures factors are listed in Table 1, and the final values of the positional and thermal parameters are given in Table 2. The crystal structure is found to be isomorphous with that of iodoform. Since the order parameter w was found to be 0·43, the symmetry of the crystal should be represented by the space group C_6^6–$P6_3$. However, since w is close to $\frac{1}{2}$, the symmetry of the crystal can be approximately represented by the space group C_6^2–$P6_3/m$.

The crystal structure of bromoform is shown schematically in Figs. 1 and 2, which are the projections on the (001) and on the (010) planes respectively. In Fig. 2 the molecules oriented upwards are drawn with thick lines and those oriented downwards with thin lines. Some of the interatomic distances and angles are shown in the Figures and also listed in Table 3, where the bond distance between the carbon and hydrogen atoms was assumed to be 1·07 Å [referred to 1·068 Å for $CHBr_3$ given by a microwave study (Williams, Cox & Gordy, 1952)].

Table 1. *Observed and calculated structure factors*

The columns are *hkl*, $|F_o|$, $|F_c|$.

hkl	$\lvert F_o\rvert$	$\lvert F_c\rvert$	hkl	$\lvert F_o\rvert$	$\lvert F_c\rvert$	hkl	$\lvert F_o\rvert$	$\lvert F_c\rvert$	hkl	$\lvert F_o\rvert$	$\lvert F_c\rvert$
0 0 4	101.73	109.12	6 0 3	11.40	11.98	1 2 2	59.06	43.14	2 3 0	37.69	35.05
0 0 6	55.23	55.67	1 1 0	58.92	69.08	1 2 3	27.61	27.79	2 3 1	16.12	14.91
0 0 8	19.27	15.45	1 1 1	95.71	127.97	1 2 4	35.99	28.88	2 3 2	34.87	32.27
1 0 0	16.01	11.47	1 1 2	68.60	62.50	1 2 5	17.07	13.29	2 3 3	14.18	14.27
1 0 1	39.28	40.93	1 1 3	99.79	96.90	1 2 6	17.66	14.73	2 3 4	22.95	24.68
1 0 3	26.32	24.97	1 1 4	51.69	46.92	1 2 7	8.41	6.49	2 3 5	9.83	11.70
1 0 5	14.05	11.99	1 1 5	61.76	60.05	1 2 8	4.89	3.72	2 3 6	10.56	14.36
1 0 7	6.40	3.64	1 1 6	30.22	27.84	2 2 0	34.67	31.49	3 3 0	23.51	21.04
2 0 1	51.84	47.94	1 1 7	27.07	26.84	2 2 1	63.74	63.26	3 3 2	19.94	18.32
2 0 3	49.88	40.23	1 1 8	9.82	9.51	2 2 2	34.25	29.99	3 3 3	5.58	1.61
2 0 4	0.00	1.76	2 1 0	50.76	70.14	2 2 3	53.83	51.53	3 3 4	11.32	12.15
2 0 5	30.28	27.51	2 1 1	0.00	3.27	2 2 4	27.25	24.73	3 3 5	0.00	1.38
2 0 6	0.00	0.25	2 1 2	61.45	64.76	2 2 5	33.05	33.93	3 3 6	4.88	6.15
2 0 7	14.17	13.29	2 1 3	0.00	0.36	2 2 6	14.64	16.01	1 4 0	8.36	7.40
2 0 8	0.00	0.37	2 1 4	47.62	47.22	2 2 7	13.10	12.13	1 4 1	39.46	33.75
3 0 0	91.61	98.86	2 1 5	0.00	2.72	2 2 8	4.77	6.06	1 4 2	11.59	9.11
3 0 1	6.32	4.20	2 1 6	23.33	26.45	3 2 0	42.89	42.08	1 4 3	32.60	27.92
3 0 2	95.71	86.37	2 1 7	3.83	2.87	3 2 1	64.68	67.39	1 4 4	10.24	8.81
3 0 3	4.47	3.30	2 1 8	7.75	7.52	3 2 2	37.86	35.63	1 4 5	10.35	18.61
3 0 4	66.65	59.41	3 1 0	47.15	35.99	3 2 3	57.82	55.86	1 4 6	6.59	7.54
3 0 6	33.99	31.52	3 1 1	42.16	32.43	3 2 4	25.70	24.93	2 4 0	44.20	66.06
3 0 7	0.00	0.76	3 1 2	42.19	33.27	3 2 5	32.60	38.81	2 4 1	0.00	6.40
3 0 8	8.43	9.36	3 1 3	28.16	24.12	3 2 6	8.59	12.91	2 4 2	46.83	60.67
4 0 0	44.36	71.01	3 1 4	29.65	25.88	4 2 0	24.05	25.36	2 4 3	0.00	3.[illegible]
4 0 1	76.79	63.67	3 1 5	15.33	13.44	4 2 1	10.10	7.60	2 4 4	33.88	41.29
4 0 2	36.15	27.20	3 1 6	16.97	14.83	4 2 2	24.24	21.72	2 4 5	0.00	0.60
4 0 3	54.99	49.82	3 1 7	4.40	4.77	4 2 3	3.69	5.07	3 4 0	10.92	12.27
4 0 4	21.38	18.33	4 1 0	30.26	22.43	4 2 4	15.11	16.26	3 4 1	14.61	20.37
4 0 5	28.91	30.05	4 1 1	25.32	24.71	5 2 0	13.93	13.04	3 4 2	6.60	10.54
4 0 6	7.69	8.60	4 1 2	27.74	21.64	5 2 1	6.55	3.81	3 4 3	9.64	15.70
4 0 7	9.73	11.89	4 1 3	19.12	20.69	5 2 2	12.79	10.97	3 4 4	4.04	6.58
5 0 0	28.05	16.90	4 1 4	19.15	18.55	5 2 3	4.02	3.51	1 5 0	24.59	22.28
5 0 1	53.99	44.83	4 1 5	12.18	14.26	1 3 0	57.90	50.13	1 5 1	40.50	38.40
5 0 2	16.73	14.82	4 1 6	9.29	12.63	1 3 1	71.84	59.05	1 5 2	22.44	19.85
5 0 3	41.76	38.79	5 1 0	66.45	62.49	1 3 2	46.01	44.31	1 5 3	30.94	32.99
5 0 4	8.66	9.94	5 1 2	60.23	57.34	1 3 3	51.86	45.67	1 5 4	14.36	13.94
5 0 5	21.67	27.75	5 1 3	0.00	3.23	1 3 4	36.25	30.91	1 5 5	16.27	23.10
6 0 0	6.65	4.69	5 1 4	33.52	43.52	1 3 5	27.46	27.34	1 6 0	21.21	20.04
6 0 1	17.85	14.65	1 2 0	60.90	50.07	1 3 6	15.55	16.23	1 6 1	25.26	35.20
6 0 2	6.46	3.57	1 2 1	26.15	19.50	1 3 7	8.[illegible]	10.96	1 6 2	27.65	18.03

Molecular structure

Because the crystal structure is disordered, having a pseudo mirror plane, there remain two possibilities for the molecular structure. The first model, which is shown in Fig. 2, has the bond length 1·86 Å for Br–C and the valence angle 116° for Br–C–Br. The second model comprises bromine atoms (drawn with heavy circles) and carbon and hydrogen atoms (drawn with light circles in Fig. 2). This model gives corresponding values of 1·97 Å and 106°. However, the intensities of the reflexions do not draw any definite distinction between these two models.

Table 2. *Positional and thermal parameters of bromine and carbon atoms, with e.s.d.'s in parentheses*

The temperature factor is of the form $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{23}kl+2B_{31}lh)]$ for the bromine atom, and of the form $\exp[-B(\sin\theta/\lambda)^2]$ for the carbon atom.

Bromine atom			
X	0·690$_8$ (1)	B_{11}	0·019$_9$ (2)
Y	0·632$_5$ (1)	B_{22}	0·011$_3$ (2)
Z	0·277$_4$ (2)	B_{33}	0·001$_7$ (4)
		B_{12}	0·011$_1$ (2)
		B_{23}	−0·000$_6$ (1)
		B_{31}	−0·000$_1$ (1)
Carbon atom			
X	$\frac{2}{3}$	B	0·7$_9$ (14) Å^{-2}
Y	$\frac{1}{3}$		
Z	0·325$_8$ (14)		

Order parameter w = 0·42$_8$ (2)

The microwave study has given the corresponding bond length and valence angle 1·930 Å and 110·8° for the gaseous state of bromoform (Williams *et al.*, 1952). These values lie between those of the two models. Because the positions of the carbon atoms determined were not sufficiently correct, the final result should be postponed until a neutron diffraction study is carried out. It is suggested, however, that the first model is more likely the case because the second model gives too small a value for the valence angle Br–C–Br. In the following, we shall discuss the crystal structure on the basis of the first model.

Table 3. *Interatomic distances and angles with e.s.d.'s in parentheses*

Intramolecule			
Br···Br	3·15$_9$ (1) Å	Br–C–Br	116·5 (1)°
Br—C	1·85$_7$ (2)	Br–C–H	100·8 (3)
C—H	1·07 (assumed)		

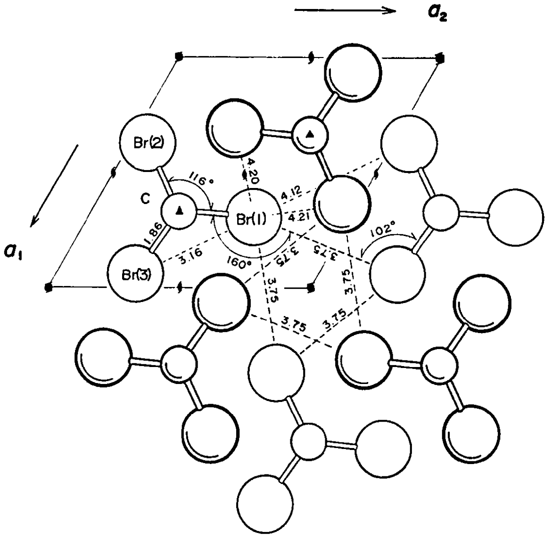

Fig. 1. Schematic crystal structure of bromoform, in the (001) plane. Some of interatomic distances and angles are shown.

Crystal structure

In the calculation of intermolecular distances two kinds of molecular arrangements must be considered because the structure is disordered. A molecule is oriented with its neighbour either parallel or antiparallel to it. The interatomic distances and angles between the neighbouring molecules for the two arrangements are listed in Table 3 and also shown in Figs. 1 and 2.

It can be seen in either case that most of the interatomic distances between neighbouring molecules are expressed by sums of the van der Waals radii (hereafter referred to as VDW distances). However, there are exceptions. Very close Br···Br contacts are observed between molecules lying side by side perpendicular to the *c* axis. They are 3·75 Å for the parallel arrangement and 3·78 Å for the antiparallel arrangement. These values are significantly smaller than the VDW distance, 3·90 Å. By virtue of these close contacts molecules lying on a plane perpendicular to the *c* axis appear as a two-dimensional network, and hence the crystal can be taken as a layer structure.

Table 3 (*cont.*)

Intermolecule*

In the parallel arrangement		In the antiparallel arrangement	
Br(1)$^{+}$ ······ Br(1)$^{+\prime}$	4·19$_7$ (2) Å	Br(1)$^{+}$ ······ Br(1)$^{-\prime}$	3·86$_3$ (2) Å
Br(1)$^{+}$ ······ Br(2)$^{+\prime}$	4·20$_7$ (2)	Br(1)$^{+}$ ······ Br(2)$^{-\prime}$	3·87$_4$ (2)
†Br(1)$^{+}$ ······ H$^{+\prime}$	3·23$_3$ (7)	†Br(1)$^{+}$ ······ H$^{-\prime}$	2·98$_7$ (6)
Br(1)$^{+}$ ······ Br(2)$^{+\prime\prime}$	4·12$_3$ (2)	Br(1)$^{+}$ ······ Br(2)$^{-\prime\prime}$	4·14$_7$ (2)
Br(1)$^{+}$ ······ Br(3)$^{+\prime\prime}$	3·75$_3$ (1)	Br(1)$^{+}$ ······ Br(3)$^{-\prime\prime}$	3·77$_5$ (1)
Br(1)$^{+}$ ······ Br(3)$^{+\prime\prime}$–C$^{+\prime\prime}$	102·4 (1)°	Br(1)$^{+}$ ······ Br(3)$^{-\prime\prime}$–C$^{-\prime\prime}$	103·5 (1)°
C^{+}–Br(1)† ···· Br(3)$^{+\prime\prime}$	159·6 (1)	C^{+}–Br(1)$^{+}$ ··· Br(3)$^{-\prime\prime}$	162·2 (1)

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* Atoms Br(1), Br(2) and Br(3) are those of the reference molecule shown in Fig. 1. Signs + and − indicate the orientations of the molecules. Single prime shows the molecule generated from the reference molecule by the 2_1 screw axis, and double prime shows the molecule generated by the translation along the a_2 axis.

† Calculation based on the assumed C–H bond distance, 1·07 Å.

Discussion

Approximate calculations for molecular interactions were made both for the ordered molecular arrangement and the statistically disordered one by using the 6–exp potentials, the dipole–dipole interactions and the induced effects, as described by the following equation.

$$\begin{aligned}E_{ab}= & -\sum_{i,j}\frac{C_{ij}}{r_{ij}^6}+\sum_{i,j}A_{ij}\exp\left(-B_{ij}r_{ij}\right)\\ & -\frac{14\cdot393\mu_a\mu_b}{r_{ab}^3}\{2\cos\theta_a\cos\theta_b-\sin\theta_a\sin\theta_b\\ & \times\cos(\varphi_a-\varphi_b)\}\\ & -\frac{14\cdot393}{r_{ab}^6}(\alpha_a\mu_a^2+\alpha_b\mu_b^2)\ [\text{kcal.mole}^{-1}]\,,\qquad(2)\end{aligned}$$

where molecules a and b have a separation r_{ab}, dipole moments μ, molecular polarizabilities α and a mutual geometry of the dipoles θ and φ, and r_{ij} indicates the interatomic distance between the ith atom of the molecule a and the jth atom of b. In this equation the dispersion and the exchange repulsive terms between molecules are described assuming the additive property of each interatomic interaction. The parameter C_{ij} is derived by the Slater–Kirkwood equation and B_{ij} is taken from Scott & Scheraga (1965). The parameter

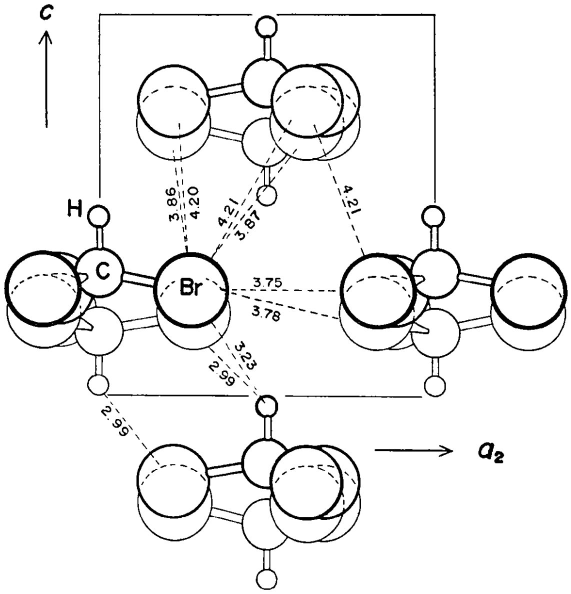

Fig. 2. Schematic crystal structure of bromoform, in the (010) plane. Molecules orienting upwards and downwards are drawn with thick lines and with thin lines, respectively. Some of interatomic distances are shown.

Table 4. *Parameters used for the calculations of the molecular interactions of equation* (2)

Molecule	Dipole moment (debye)	Molecular polarizability (10^{-24} cm^3)
$CHCl_3$	1·02	8·23
$CHBr_3$	0·99	11·11
CHI_3	0·91	16·42

Table 4 (*cont.*)

Interacting pair of atoms	Van der Waals radii sum (Å)	A_{ij} (kcal.mole^{-1})	B_{ij} (Å^{-1})	C_{ij} (Å^6. kcal.mole^{-1})
H···H	2·40	$0\cdot802\times10^4$	4·54	51·6
C···H	2·90	$0\cdot554\times10^5$	4·56	131
C···C	3·40	$0\cdot493\times10^6$	4·58	341
Cl···H	3·00	$0\cdot462\times10^5$	4·13	293
Cl···C	3·50	$0\cdot337\times10^6$	4·14	752
Cl···Cl	3·60	$0\cdot249\times10^6$	3·75	1670
Br···H	3·15	$0\cdot184\times10^5$	3·55	464
Br···C	3·65	$0\cdot107\times10^6$	3·57	1215
Br···Br	3·90	$0\cdot350\times10^5$	2·78	4351
I···H	3·35	$0\cdot204\times10^5$	3·38	652
I···C	3·85	$0\cdot112\times10^6$	3·39	1686
I···I	4·30	$0\cdot372\times10^6$	2·52	8366

Table 5. *Calculated lattice energies arising from the dispersion forces, the exchange repulsive forces, the dipole–dipole couplings and the induced effects* (*in* kcal.mole^{-1})

Compound	Space group	Total	Dispersion	Exchange repulsive	Dipole–dipole	Induced effect
CHI_3	$P6_3$ (w=0)	−18·39	−31·01	13·12	−0·43	−0·07
	$P6_3/m$	−18·28	−31·86	14·10	−0·44	−0·08
$CHBr_3$	$P6_3$ (w=0)	−16·73	−23·80	7·74	−0·59	−0·08
	$P6_3/m$	−16·69	−24·84	8·83	−0·59	−0·09
$CHCl_3$	*$P6_3$ (w=0)	−11·33	−13·46	2·80	−0·59	−0·08
	*$P6_3/m$	−11·25	−14·25	3·50	−0·59	−0·09
	Pnma	−13·47	−15·05	3·17	−1·50	−0·09

* Hypothetical crystal structures as described in the text; a=6·03 Å and c=7·10 Å.

A_{ij} is obtained by minimizing the 6–exp potential function at the VDW distance from the atoms i to j. All parameters used are listed in Table 4.

Calculations of the dipole–dipole interactions were carried out for every pair of molecules within a range of 40 Å and those of the other three interactions were carried out for every pair of atoms within a range of 20 Å. The lattice energies calculated from the four kinds of interactions were nearly the same for the two arrangements, namely 16·7 kcal.mole^{-1} (see Table 5). Most of the energies came from the dispersion and the exchange repulsive terms between the bromine atoms. It is to be noted that the difference of the lattice energies between the two molecular arrangements is unexpectedly small, and moreover, the contribution of the dipole–dipole interactions to the lattice energies is quite small for both arrangements in spite of the fairly large dipole moment of the molecule.

It was shown in the previous section that the crystal can be taken as a layer structure. This aspect is enhanced in the crystal of iodoform. It has close-contact distances of 3·94 and 3·96 Å for I$\cdots$I in the parallel and in the antiparallel arrangements respectively, both of which are much smaller than the VDW distance, 4·30 Å. Indeed, iodoform gives hexagonal and planar crystals, which can be cleaved easily along the (001) plane. It is to be noted that the chloroform crystal has no layer-like structure. This will be described later.

The crystals of chlorine, bromine and iodine are isomorphous, forming a layer structure. The intermolecular distances within the layer are increasingly shorter than the respective VDW distances going from chlorine to bromine to iodine. Further, the two kinds of angles X–X$\cdots$X, where X denotes the halogen atom, are approximately 90° and 180°. On these bases Tomiie (1961) suggested that in these crystals there occur intermolecular bondings between the halogen atoms arising from the charge transfer from $p\pi^*$ to $p\sigma^*$ orbitals. From his calculations it was concluded that the charge transfer and the bond order between the molecules are appreciable for iodine and bromine but are negligible for chlorine.

In the layer-like structures of iodoform and bromoform, there are also found very short intermolecular distances for X$\cdots$X and two kinds of angles C–X$\cdots$X for the two arrangements (see Table 3 for bromoform), which might favour the charge transfer between molecules. These aspects strongly suggest that the same sort of intermolecular bondings, as have been suggested by Tomiie in the crystals of iodine and bromine, may play an important role in other interactions.

It is expected that the interaction energies of this intermolecular bonding for the two kinds of molecular arrangements may be similar, because of the similar geometries and separations of the bromine atoms. Therefore, the hexagonal arrangement of bromoform (and also iodoform) gives a molecule two kinds of stable locations where the lattice energy is minimized to almost the same extent. It follows that when a crystal grows molecules moving in the immediate vicinity of a surface of the crystal may take either of the two orientations to become part of the crystal, thus forming the statistically disordered structure.

It is of considerable interest to try to explain why the crystal structure of chloroform is different from those of bromoform and iodoform in its molecular arrangement. The crystal structure of chloroform belongs to the orthorhombic system with space group D_{2h}^{16}–$Pnma$ and has four molecules per unit cell (Fourme & Renaud, 1966). Two of these molecules lie on a mirror plane and the other two lie on the succesive mirror plane. The orientations of the molecules in successive planes are antiparallel. The shortest intermolecular distances are 2·95 Å for H$\cdots$Cl and 3·59 Å for Cl$\cdots$Cl, and they are nearly equal to the corresponding VDW distances, 3·00 and 3·60 Å.

Here, the main intermolecular attraction of chloroform may arise from the dispersion forces as in the cases of bromoform and iodoform. However, the dipole–dipole couplings might also be effective in this molecular arrangement. It is worth while comparing the lattice energies of chloroform for the actual crystal structure and a hypothetical one which is isomorphous with the crystals of bromoform and iodoform. In deriving the structure, the sequence of the crystal structures of boron trichloride, tribromide and triiodide is also referred to and unit-cell constants are assumed to be $a=6\cdot03$ and $c=7\cdot10$ Å. The approximate calculations of the molecular interactions [equation (2)] were made for the actual orthorhombic crystal and for the hypothetical one in the same way as for the crystal of bromoform.

The calculated lattice energies are found to be about 13·5 and 11·3 kcal.mole^{-1} for the orthorhombic and for the hexagonal crystals, respectively (see Table 5). The differences in energies due to the exchange repulsive forces and the induced effects are small. The contribution of the dipole–dipole interactions is negligible in the hexagonal crystal as is found in the crystals of bromoform and iodoform, while it is significant in the orthorhombic crystal, 1·5 kcal.mole^{-1}. The contribution of the dispersion term in the orthorhombic crystal is about 1 kcal.mole^{-1} larger than that in the hexagonal crystal. It is concluded that these differences may cause chloroform to crystallize with an orthorhombic structure rather than a hexagonal one.

Boron trichloride, tribromide and triiodide all crystallize in the hexagonal system and their crystal structures are closely related to those of bromoform and iodoform (Wyckoff, 1964). Molecules of these boron trihalides are of the regular triangle type and hence they have no dipole moment. Comparing the structures of these boron trihalides with those of chloroform, bromoform and iodoform, it can be said that the dipole moment may play an important role in the difference between the structure of chloroform and those of bromoform and iodoform.

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The Crystal and Molecular Structure of Chromium(III) Tris-(*O*-ethylxanthate)

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Chromium(III) tris-(*O*-ethylxanthate) crystallizes in the rhombohedral space group $R\bar{3}$, with two molecules per unit cell, $a=9{\cdot}72$ Å, $\alpha=100°48'$. The crystal structure of the chromium xanthate has been refined by the least-squares method, starting from the atomic positions determined for the isostructural cobalt(III) tris-(*O*-ethylxanthate). The final agreement index for the observed reflexions was $R_1=0{\cdot}069$. Each molecule is formed by three ethylxanthate ligands coordinated to a chromium atom through the sulphur atoms; the molecule has trigonal symmetry C_3–3. The intermolecular interactions are of the van der Waals type. Mean bond lengths are Cr–S 2·393 (3) Å, S–C 1·691 (7) Å, C–O 1·297 (11) Å. The $\cdots S_2{}^{(-)}C=O^{(+)}R$ form makes an important contribution to the structure of the xanthate radical.

Introduction

This work is part of the program of research carried out in our laboratory on the crystal structures of dithiocarbamates and xanthates, with the aim of gaining information on metal–sulphur bonds and on the structure of dithiocarbamate and xanthate ligands.

Recently the crystal structures of cobalt(III) tris-(*O*-ethylxanthate) (Merlino, 1969) and of iron(III) tris-(*O*-ethylxanthate) (Hoskins & Kelly, 1970; Watanabe & Yamahata, 1970) were determined. It seemed useful to investigate the crystal structure of chromium(III) tris-(*O*-ethylxanthate) in order to specify which differences arise in the structure of the xanthate ligand by coordinating it to different metal atoms.

Experimental

The morphological, optical and X-ray crystallography of chromium(III) tris-(*O*-ethylxanthate) was investigated by Franzini & Schiaffino (1962); the cell data of this compound, as reported by these authors, are:

$Cr(III)(S_2COC_2H_5)_3$, M.W.415·60;
$a_{rh}=9{\cdot}72\pm0{\cdot}01$ Å, $\alpha_{rh}=100°48'\pm10'$;
$a_{hex}=14{\cdot}98$ Å, $c_{hex}=13{\cdot}31$ Å;
$U_{rh}=862{\cdot}4$ Å^3;
$D_m=1{\cdot}59$ g.cm^{-3}, $D_c=1{\cdot}591$ g.cm^{-3},
$Z=2$;
Space group $R\bar{3}$.

Throughout the present paper the rhombohedral (obverse setting) indices and coordinates will always be used.

Three-dimensional intensity data were recorded on Buerger precession photographs with the multiple-exposure technique and integration process; zirconium-filtered Mo $K\alpha$ radiation was used.

A crystal, prepared according to the method described by Franzini & Schiaffino (1962), was ground to a nearly spherical shape with a mean diameter of 0·84 mm. ($\mu R=0{\cdot}58$ for Mo $K\alpha$ radiation).

On the photographs of six layers, with [010] as the precession axis ($k=0$ to 5), a total of 902 independent reflexions were observed. The intensities, measured with a Nonius microdensitometer, were corrected for Lorentz, polarization and absorption factors by means