longer wave lengths than the corresponding ones of the single amide group. Thus we conclude that the conjugation effect is recognizable spectroscopically. This phenomenon resembles somewhat the effect of substitution on absorption by benzene or the conjugated polyenes.

The very weak absorption at about 2800–3300 Å may be explained by forbidden bands due to the transitions from Ψ_g to the triplet states of Ψ_{e1} and Ψ_{e2}, with the || absorption mainly attributed to the $\pi \rightarrow \pi$ transition ($\Psi_g \rightarrow \Psi_{e1}$) and the $\perp$ absorption to the $n \rightarrow \pi$ transition ($\Psi_g \rightarrow \Psi_{e2}$). However, for these very weak absorption bands, further investigation is necessary before drawing definite conclusions.

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Crystal Structure of Chlorobenzene and Bromobenzene at −180 °C

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The Debye–Scherrer photographs of chlorobenzene and bromobenzene frozen and cooled to −180 °C. have been taken and from the analysis both the crystals have been found to belong to the orthorhombic system. The unit-cell dimensions for chlorobenzene are $a = 13{\cdot}72$, $b = 11{\cdot}32$, $c = 7{\cdot}75$ Å and those for bromobenzene are $a = 14{\cdot}3$, $b = 11{\cdot}48$ and $c = 7{\cdot}5$ Å. The densities of the crystals have been found to be 1·225 and 1·654 gm.cm.$^{-3}$ respectively. The restrictions of reflections show that both substances belong to the space group Q_h^{13} having 8 asymmetric molecules per unit cell, which shows that neither molecule possesses a two-fold axis or a plane of reflection in the solid state at −180 °C.

Introduction

In continuation of the work on the structure of crystals of toluene (Biswas & Sirkar, 1957) and pyridine (Biswas, 1958), the present investigation was undertaken to study the Debye–Scherrer patterns of chlorobenzene and bromobenzene at −180 °C. to find out their crystal structures. As will be evident from the following sections the frozen masses have been found to give patterns resembling those due to fibres and it has therefore been possible to assign the indices unequivocally and to determine the space groups to which these two crystals belong.

Experimental

Chlorobenzene and bromobenzene used in the investigation were of chemically pure quality. Debye–

Scherrer photographs of the substances were taken with a low-temperature camera of special design (Biswas, 1958). The radius of the camera was derived from the Debye–Scherrer pattern of aluminium powder and was found to be 4·50 cm. The specimen was contained in a Lindemann glass capillary tube of bore 0·3 mm. A Seifert X-ray tube running at 32 kV. and 26 mA. was used, the photographs, of 3½ hr. exposure, being taken with Cu $K\alpha$ radiation.

Results and discussion

The patterns due to frozen chlorobenzene and bromobenzene are reproduced in Figs. 1(*a*) and (*b*). It can be seen from Fig. 1(*a*) that the Debye–Scherrer pattern of frozen chlorobenzene at −180 °C. resembles that of a fibre held vertically. Three layer lines are distinctly visible in the pattern and the spots in the layer lines are lengthened to form small arcs of circle. This shows that a large number of small single crystals are formed with a particular zone axis almost vertical in each of these crystals. Slight inclination (about ±8°) of this zone axis to the vertical is responsible for the elongation of the spots into small arcs. It was possible to calculate the primitive translation along this zone axis from the separation of the layer lines and this axis was assumed to be the *c*-axis; Lipson's (1949) method was then applied to find the other two axial lengths. It was found that the crystal belongs to the orthorhombic system.

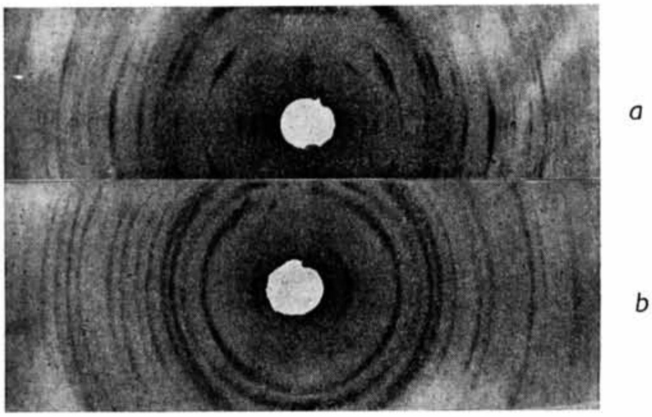

Fig. 1. X-ray diffraction patterns of frozen chlorobenzene (*a*) and bromobenzene (*b*) at −180 °C.

In the case of bromobenzene the rings were analysed by Lipson's method and this crystal was also found to belong to the orthorhombic system.

Structure of chlorobenzene

The values of $\sin^2\theta$ of the spots on the zero layer line and other different layer lines are given in Tables 1 and 2. The values of $\lambda^2/4a^2$, $\lambda^2/4b^2$ and $\lambda^2/4c^2$ which agree with the observed values of $\sin^2\theta$ are found to be

$$\lambda^2/4a^2 = 0\cdot00315,\ \ \lambda^2/4b^2 = 0\cdot00458,\ \ \lambda^2/4c^2 = 0\cdot00984. \tag{1}$$

Thus we get from (1)

$$a = 13\cdot72,\ \ b = 11\cdot32,\ \ c = 7\cdot75\ \text{Å}.$$

Table 1. *Chlorobenzene*

Zero layer line of chlorobenzene

$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	Indices & intensities
0·00780	0·00773	110 (*m*)
0·01260	0·01260	200 (*s*)
0·01830	0·01832	020 (*w*)
0·04420	0·04394	130 (*m*)
0·05080	0·05040	400 (*m*)
0·06930	0·06957	330 (*m*)
	0·06870	420 (*m*)
0·07340	0·07328	040 (*vw*)
0·08600	0·08588	240 (*s*)
0·1132	0·11340	600 (*s*)
0·1176	0·11764	150 (*s*)
0·1240	0·12368	440 (*w*)
0·1320	0·13172	620 (*w*)
0·1430	0·14285	350 (*w*)
0·1648	0·16488	060 (*m*)
0·1862	0·18670	640 (*w*)
0·1935	0·19320	550 (*m*)
0·2020	0·20160	800 (*m*)
0·2148	0·21528	460 (*w*)

Table 2. *Chlorobenzene*

First layer line of chlorobenzene

$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	Indices & intensities
0·01796	0·01757	111 (*w*)
0·03100	0·03131	121 (*vs*)
0·05480	0·05521	131 (*s*)
0·05620	0·05651	321 (*m*)
0·06380	0·06366	231 (*s*)
0·07900	0·07941	331 (*m*)
	0·07856	421 (*m*)
0·08870	0·08859	401 (*w*)
0·09620	0·09570	241 (*vw*)
0·10160	0·10146	431 (*w*)
0·10720	0·10691	521 (*w*)
0·11180	0·11147	341 (*m*)
0·12800	0·12782	611 (*s*)
	0·12749	151 (*s*)
	Second layer line	
0·03940	0·03936	002 (*vs*)

The calculated values of $\sin^2\theta$ and of the corresponding spacings of the different planes are also given in the tables. The visually estimated intensities are indicated by the letters in parentheses. As the order of the layer lines gives the values of the index *l* unequivocally it has been possible to assign all the indices correctly by trial. The density of the frozen substance at −180 °C. was measured by the method described earlier (Biswas & Sirkar, 1957) and was found to be 1·225 g.cm.$^{-3}$. The number of molecules per unit cell is therefore 7·90 which can be taken as 8.

The indices of the planes in the zero layer line listed in Table 1 show that *hk*0 is absent when $h+k$ is odd which suggests that the space group is *Pmmn* (Q_h^{13}).

It was found that the observed restrictions do not agree with those for any of the space groups with sixteen asymmetric molecules per unit cell. Thus the eight molecules in the unit cell of this crystal are all asymmetric and therefore the molecules has neither a two-fold axis passing through the C–Cl bond nor a plane of symmetry containing that axis.

Table 3. *Powder photograph of bromobenzene*

$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	Indices & intensities
0·00740	0·00739	110 (*s*)
0·01130	0·01156	200 (*w*)
0·01310	0·01340	101 (*w*)
0·01800	0·01800	020 (*w*)
0·03130	0·03139	121 (*s*)
0·04230	0·04220	002 (*s*)
0·04350	0·04339	130 (*w*)
0·04640	0·04626	400 (*m*)
0·05480	0·05451	321 (*s*)
0·06260	0·06251	231 (*s*)
0·07220	0·07200	040 (*w*)
0·07720	0·07700	331 (*m*)
	0·07675	510 (*m*)
0·08268	0·08225	041 (*w*)
	0·08250	032 (*w*)
	0·08280	501 (*w*)
0·08680	0·08730	511 (*w*)
	0·08621	322 (*w*)
0·10380	0·10404	600 (*s*)
0·11470	0·11539	150 (*w*)
	0·11420	042 (*w*)
0·11840	0·11824	440 (*w*)
0·13180	0·13204	621 (*m*)
	0·13225	522 (*m*)
0·13840	0·13850	350 (*m*)
0·14550	0·14601	710 (*w*)
	0·14524	413 (*w*)
0·16860	0·16880	004 (*s*)
0·18500	0·18496	800 (*m*)
0·19500	0·19530	551 (*w*)
0·20400	0·20404	062 (*w*)
	0·20300	820 (*w*)
0·23000	0·23000	362 (*m*)
	0·23060	071 (*m*)

Bromobenzene

The values of $\sin^2\theta$ calculated from the rings shown in Fig. 1(*b*) are listed in Table 3. The following values of $\lambda^2/4a^2$, $\lambda^2/4b^2$ and $\lambda^2/4c^2$ were obtained from Lipson's method:

$$\lambda^2/4a^2 = 0{\cdot}00289,\quad \lambda^2/4b^2 = 0{\cdot}00450,\quad \lambda^2/4c^2 = 0{\cdot}01055. \tag{2}$$

These give the following dimensions of the unit cell

$$a = 14{\cdot}3,\quad b = 11{\cdot}48,\quad c = 7{\cdot}5\ \text{Å}\,.$$

The values of $\sin^2\theta$ and of the spacings calculated from the unit-cell dimensions given in (2) are included in Table 3. The estimated approximate intensities of reflections are given in parentheses.

The density of bromobenzene at −180 °C. was found to be 1·654 g.cm.$^{-3}$. With these values of this density the number of molecules per unit cell comes out as 8. Now from the study of Table 3 it can be easily seen that the restrictions of reflection are the same as those in the case of chlorobenzene, i.e. *hk*0 is absent when $h+k$ is odd. Thus bromobenzene is also orthorhombic having the space group *Pmmn* (Q_h^{13}). In this case also the molecule has neither a two-fold axis nor a plane of symmetry.

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