

117. The Structure of Molecular Compounds. Part II.

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Evidence from melting points, and the intensities of reflexion of *X*-rays, including diffuse spectra, of crystals of intermolecular compounds is against the existence of ions in the structures. The structures of the intermolecular compounds of the picryl halides and hexamethylbenzene are very complex and disordered to some extent. They consist of alternate layers of the two components, and the binding between the layers, and therefore between the two kinds of molecule, is shown to be weak.

IN Part I (this vol., p. 153) it is shown that molecular-compound formation between *s*-trinitrobenzene and *p*-iodobenzene is not due to the production of any covalent bond between the molecules. There may be very weak hydrogen bonds between amino-groups and oxygen atoms of nitro-groups, but these do not seem to be an essential feature of the compound formation. It has been suggested (Weiss, J., 1942, 245) that all the properties of these molecular compounds may be explained by assuming the formation of a complex molecule, ionic in character, through transfer of an electron from a hydrocarbon, or its derivative, to the polynitro-compound. It is apparently envisaged that in the crystal structures of these compounds the carbon atoms of the component ions will be about 3.2 Å. from each other. This is not the case for the compound studied, and the interatomic distances observed are about normal for intermolecular distances in typical organic crystals. In this paper some evidence bearing on the ionic hypothesis is considered.

Whether or not the component parts in a crystal of a molecular compound are held together by ionic bonds may be considered independently of interatomic distances by a study of the strengths of the crystals. In general, a crystal in which electrostatic attraction between oppositely charged ions is one of the binding forces, will have greater strength than one containing geometrically comparable molecules held by weaker forces, *e.g.*, forces of van der Waals type. This reveals itself in the greater hardness and higher melting point of the ionic crystal. Since the thermal movements of the atoms are of greater amplitude in the weaker crystal, it also shows in the falling off in intensity of all *X*-ray reflexions as the Bragg angle θ increases, which is more marked in the weaker crystal. A further way in which the strength of the crystal may be revealed is in the production of "diffuse" *X*-ray reflexions. The origin of diffuse reflexions is disputed and such reflexions have been observed from crystals in which all kinds of interatomic binding are operative; but it is only in crystals where there are planes held by weak forces that the diffuse spectra are of such intensity that they may be observed with the relatively short exposures in an ordinary moving-crystal oscillation or Weissenberg photograph. The effect is readily interpreted on the elastic vibration theory as due to the large atomic movements perpendicular to a plane, as, *e.g.*, the basal plane in graphite, favoured by weak inter-layer binding. In this case the diffuse spectra may appear as backgrounds to the normal Bragg reflexions of the corresponding planes. In basing any

conclusions on the existence of such reflexions it is clearly necessary to consider the whole structure, since the interatomic forces, in a different direction may, as in graphite, be of a different kind.

The following table gives the melting-point data for a number of molecular compounds, together with the m. p.'s of the components. The m. p. of the compound is usually lower than that of one of the components, and if the two components have nearly the same m. p. the compound may melt at a lower temperature than either of them. This indicates that the intermolecular binding forces in the compound are not markedly greater than those in the molecular crystals of the component substances.

Melting points of A, B, and their molecular compound AB.

A.	B.	Melting points.		
		A.	B.	AB.
Aniline	<i>s</i> -Trinitrobenzene	-8°	122°	123°
2 : 4 : 6-Tribromoaniline	"	118.5	122	108.5
<i>p</i> -Chloroaniline	"	71	122	110
<i>p</i> -Iodoaniline	"	63	122	108
3 : 5-Di-iodo- <i>p</i> -toluidine	"	125.5	122	95.5
Hexamethylbenzene	Picryl chloride	164	83	148
"	" bromide	164	122	151
"	" iodide	164	165	145

X-Ray photographs do not show any evidence of increased hardness that would be expected for an ionic crystal. In Fig. 1 it may be seen that for picryl iodide, which is unusually hard for an organic crystal, the falling off in *X*-ray intensities as the Bragg angle θ increases is not so marked as for the molecular compound of *p*-iodoaniline and trinitrobenzene.

Diffuse *X*-ray reflexions have been observed from crystals of several molecular compounds. They were not observed for the *p*-iodoaniline-*s*-trinitrobenzene compound for which the structure is most completely known, and it should be noted that in this structure the planes of the molecules are not all parallel to any one plane of the crystal. When the molecular planes are all parallel, diffuse reflexions are observed, the most significant case being that of the compounds of hexamethylbenzene with picryl halides. These compounds have a structure which is to some extent disordered; the unit cell contains 336 (or possibly 1344) atoms, exclusive of hydrogen, and this complexity, added to the disorder, makes it difficult to determine the complete structure, but the essential part is known with certainty.

The compound of picryl chloride and hexamethylbenzene forms bright yellow, orthorhombic crystals, pseudo-hexagonal prisms showing the main forms {100}, {001}, {011}; m. p. 148°; d 1.37₅ g./c.c. They show strong negative double refraction, with acute bisectrix along [100] and optic axial plane parallel to (001), and there is marked dispersion ($v > \rho$) of the optic axial angle. *X*-Ray oscillation and Weissenberg photographs show an apparent unit cell with $a = 14.0$, $b = 9.0$, $c = 15.4$ A., having four molecules of each component per cell. From the absent spectra, the space group is *Ama* or *Amam*. In addition to the diffraction pattern due to this cell there are streaks which indicate irregularity in the a spacing, and suggest that the true b dimension should be three times that given above. The picryl bromide compound is very similar in morphology, optical properties, and the intensities of corresponding *X*-ray reflexions. The dimensions of the pseudo-cell are $a = 14.0$, $b = 9.13$, $c = 15.32$ A. Additional streaks similar to those given by the chloride are observed, but they are much more intense, and for certain positions they group into smudged-out spots on intermediate layer or row lines corresponding to the unit cell with trebled b spacing. The picryl iodide compound is similar in form and optical properties to the other two. The a and c dimensions are about the same as those of the bromide, and b has a definite value, approximately three times that of the pseudo-cells of the chloride and bromide. The irregular streaks and smudges have, in this compound, become sharp spots on intermediate layer lines, but there is still some irregularity shown by a tendency to continuous row lines in rotation photographs about the A axis. These lines tend to split into spots on layers corresponding to a fourfold enlarged a spacing. If this is disregarded, the cell dimensions are $a = 14.15$, $b = 27.98$, $c = 15.16$ A. The density is 1.6 g./c.c., and there are twelve molecules of each component in the unit cell: space group *Ama* or *Amam*.

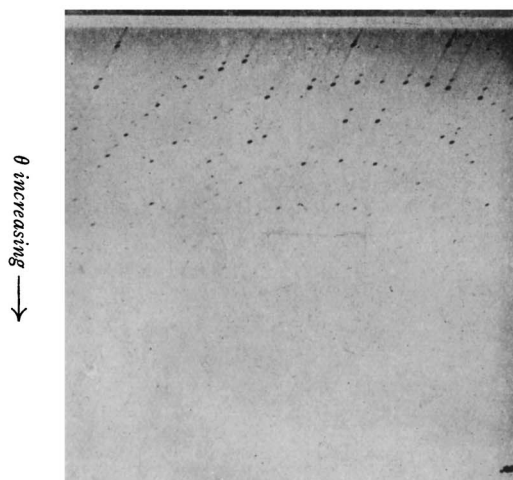
In addition to the extra reflexions, arising from the disorder in the lattice, diffuse reflexions are observed. These are not so sharp as many of the extra reflexions and there are few of them. There is one particularly intense diffuse reflexion which appears as background to the strong Bragg reflexion 400. It is easily observed in an ordinary oscillation photograph (Fig. 2).

If, in the first place, the apparent unit cell and space group of the chloride is taken as a basis, then the value of the a spacing, optical properties, and the alternation in intensities of $h00$ reflexions all combine to indicate that the structure consists of alternate layers of the two components parallel to (100). This is confirmed by the Patterson-Fourier projection normal to [001], which shows only four ridges of high $P(xy)$ value, spaced out at equal intervals of 3.5 A. along the a direction. The interatomic vectors with a components of zero or 7 A. combine to produce much higher ridges at those distances than at 3.5 and 10.5 A. In the Patterson-Fourier projection for the iodide, all the reflexions corresponding to the treble-size unit cell are used and a similar result is obtained (Fig. 3). The only interpretation possible is that there are four layers of molecules parallel to (100) equally spaced at 3.5 A. and that each layer consists of one kind of molecule only. This conclusion is confirmed completely by calculation of the intensities of reflexion $h00$. For these calculations the picryl

FIG. 1.



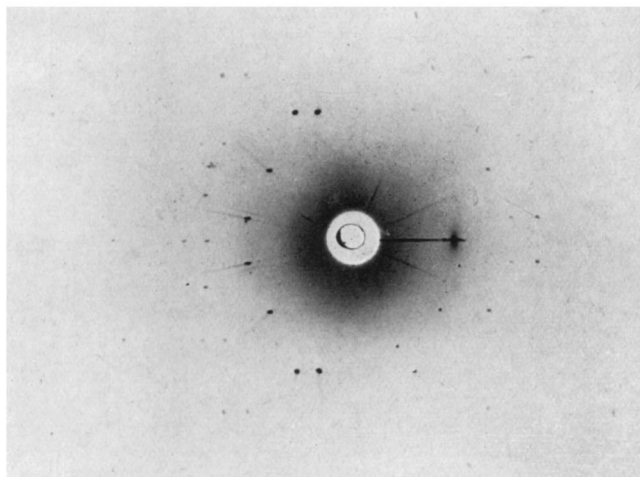
Part of Weissenberg photograph of picryl iodide. Reflexions extending to high values of θ .



Part of Weissenberg photograph of the compound of p-iodoaniline and s-trinitrobenzene. Reflexions fade off more rapidly with increasing θ .

FIG. 2.

Oscillation photograph of picryl chloride-hexamethylbenzene, showing diffuse reflexions 400 (strong) and 402 (faint).



halide molecules are assumed planar except for the oxygen atoms of the two nitro-groups in the *o*-positions to the halogen, which are taken to be turned up out of the plane as in picryl iodide (Huse and Powell, J., 1940, 1398). The agreement shown in the following table is destroyed if mixed layers are assumed. The structure is thus established as far as the relative disposition of the molecules along the *a* axis is concerned. It is easy

Calculated and observed values of F(h00). (Temperature correction with $B = 4$ applied.)

		$h =$	2.	4.	6.	8.	10.	12.
Picryl chloride-	F relative, obs.		30	91	13	43	6	16
hexamethylbenzene	F/12, calc.		32	94	4	34	1	16
Picryl iodide-	F relative, obs.		58	140	48	80	23	30
hexamethylbenzene	F/12, calc.		69	124	24	58	19	38

to arrange the hexamethylbenzene molecules in the available space so that the layer is almost identical with a single layer of the structure in hexamethylbenzene itself, and it seems probable that they have this arrangement.

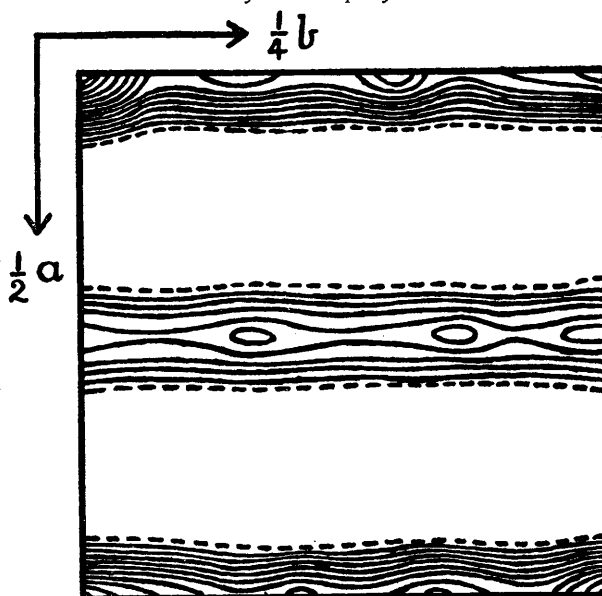
Very extensive trials made to determine the distribution of the picryl halide molecules in their layers will not be considered here since the problem has not been completely solved. A possible explanation of the complexities of the structure is that the sequence of layers is not a completely regular one, and that, owing to the great similarity of the structure of the hexamethylbenzene layer to that of the pure hydrocarbon, there are occasional regions where an extra layer of hexamethylbenzene is added, the crystal growing momentarily as though it were one of hexamethylbenzene only. This could result in the almost continuous distribution of *a* spacing represented by the observed streaks. Owing to the pseudo-hexagonal character of the hydrocarbon layers, there are three ways of placing a picryl halide molecule relative to the hexamethylbenzene molecules which are geometrically almost equivalent. One way of accounting for the trebling of the *b* dimension is to suppose that all three ways are used. A regular sequence of the molecules in the three alternative positions would give the true larger unit cell of the iodide, a less regular arrangement with a preponderance of molecules in regular array would produce the smudged-out spots on intermediate layer lines as in the bromide, and the pseudo-cell observed for the chloride would be due to the almost completely random distribution of molecules in the three positions.

The intense diffuse reflexion observed as background to 400 is readily explained in terms of the structure, since it is from the plane of the flat molecules. Another faint diffuse reflexion 402 is from a plane slightly inclined to the plane of the molecules. These reflexions are similar to those given by other molecular crystals containing flat parallel molecules, and show that there is weak binding between the layers. Since all molecules in a given layer are of one kind, and each layer is related in the same way to both its neighbouring layers, there must be weak binding between the two kinds of molecule; the conclusion is independent of the detailed structure in the layers. All the evidence on the strength of these crystals is thus against the existence of ions in the structure; what interaction there is between the component molecules does not appear to be greater than the mutual interaction of molecules of a nitro-compound such as picryl iodide, in its crystals, where the transfer of an electron with formation of oppositely charged ions would not be postulated.

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FIG. 3.
Hexamethylbenzene-picryl iodide.



Patterson-Fourier projection on (001) showing high ridges separated by $\frac{1}{3}a$ (7 Å.), and lower ridge half way between.