

266. *The Crystal Structure of Picryl Iodide.*

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The structure of tetragonal crystals of picryl iodide has been investigated by Fourier syntheses from *X*-ray data. The molecules are related by a four-fold screw axis and their arrangement approximates to cubic close-packing. The two nitro-groups in the *o*-positions to the iodine atom are rotated so that the three atoms in NO_2 lie in a plane almost at right angles to that of the benzene ring; the third nitro-group is coplanar with the ring and its two oxygen atoms are related by the two-fold axis which passes through the molecule.

THE investigation of the structures of a number of compounds of polynitro-compounds with aromatic hydrocarbons and other substances has been hampered by a lack of know-

ledge of the structures of the polynitro-compounds. In view of the existence of a series of these substances containing picryl halides and similar molecules, the structure of picryl iodide has been investigated. In this we are concerned particularly with the arrangement of the nitro-groups. This has been determined by Fourier analysis.

Picryl iodide crystallises from benzene in golden-yellow tetragonal bipyramids showing the forms {111}, {100}, and {001}. The crystals were measured by Fels (*Z. Krist.*, 1900, **32**, 384), who found the axial ratio $a : c = 1 : 1.958$. Some structure investigations have been carried out by Hertel and Römer (*Z. physikal. Chem.*, 1933, *B*, **22**, 273), who found the unit cell to be a simple one with $a = 7.03$ Å. and $c = 19.8$ Å. The diagonal spacing of 10 Å. is the one taken as a by Fels. The density of 2.285 shows that there are four molecules in the cell. The odd orders of reflection $h00$ (and $0k0$) are absent and $00l$ appears only when $l = 4n$. These absences correspond to the enantiomorphous space-groups $P4_12_1$ and $P4_32_1$, and, in agreement with this, the crystals show optical activity.

From these data the following conclusions regarding the structure were drawn. The general space-group position is eight-fold, and the only four-fold position, $xx0$, lies on the two-fold axis of symmetry across the diagonal of the face c . The iodine atom must thus be in this position with the two-fold axis of the molecule coinciding with the diagonal of the cell. There must be four layers, each occupying 5 Å., down the screw axis, and this spacing suggests that the plane of the molecules is inclined to the (001) plane.

The picryl iodide was prepared by the interaction of potassium iodide and picryl chloride in alcoholic solution (Hepp, *Annalen*, 1882, **215**, 361) and recrystallised from alcohol and benzene. The observations of Fels and of Hertel and Römer were confirmed, and the refractive indices were measured for sodium light by a prism method: $\omega = 1.756$, $\epsilon = 1.640$.

Weissenberg photographs were taken of approximately cubic crystal fragments, of dimensions about 0.15 mm., rotated about the axes [001], [100], and [110], and the intensities were read off the photographs by visual comparison with a prepared scale. Copper radiation from a Philips Metalix tube was used for the photographs.

The best view of the structure, for purposes of investigation, is that along the two-fold axis [110], and the structure determination was initially based on the photograph obtained by rotation about this axis. A Patterson-Fourier summation was carried out by using values of F_{MI}^2 deduced from this photograph, and the projection obtained showed clearly the co-ordinate of the iodine atom. A Fourier synthesis was then performed, the signs being calculated for the iodine contribution to F_{MI} , and the projection showed the slope and general arrangement of the molecules.

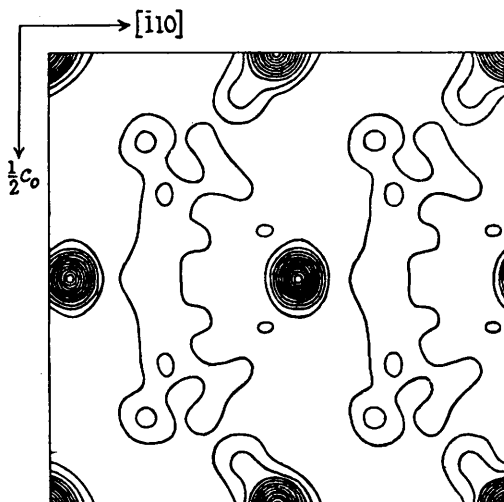
The iodine co-ordinate, x , is 0.045, and the rest of the molecule extends across the cell away from the origin; the plane of the molecules is inclined at about $51\frac{1}{2}^\circ$ to the (001) plane, and the two *o*-nitro-groups are turned up approximately at right angles to the plane of the benzene ring while the third (para) group remains flat. On this basis the Fourier projection can be explained very well, and from the apparent positions of the other atoms, their contributions to F_{MI} were calculated. It was found that the signs are almost entirely determined by the iodine contribution and the only ones changed were those of 550 and 1110.* With these altered signs another Fourier projection was prepared. Owing to the surprising hardness of the crystals, the terms of the Fourier series are not sufficiently convergent, and in order to eliminate spurious detail an artificial temperature factor, $e^{-B(\sin \theta/\lambda)^2}$, was applied, with $B = 4$, and the summation repeated. The peaks in the new projection were slightly more diffuse, but there was an improvement in the clarity of the projection, which is shown in Fig. 1.

Although the general configuration of the molecule is easily seen, it is not possible to deduce accurate details of bond lengths and angles from the Fourier projection, so an attempt was made to determine these more accurately by trial and error methods. Resonance with a possible quinonoid structure, in which the iodine atom and the nitrogen of the *p*-nitro-group are both doubly bound to the ring, may produce some distortion of the ring, since the resonance of the *o*-groups is greatly reduced by the steric influence of the iodine atom preventing their being coplanar with the ring. It is also possible that these *o*-groups will not be exactly at right angles to the ring, and a wire model of the cell indicated that,

* Italics are used to indicate that the indices are one-one-ten.

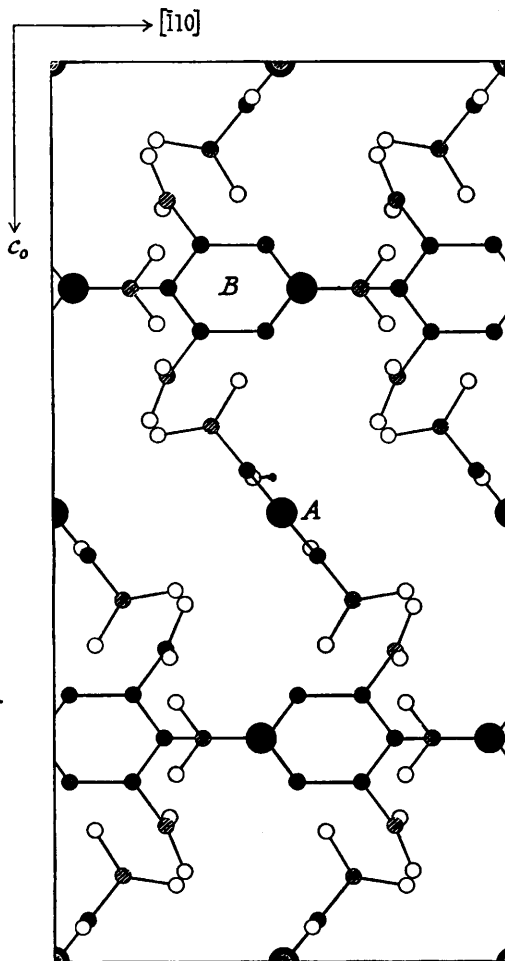
from the packing point of view, some movement from this position was desirable. Various distortions of the molecule and different bond-lengths and rotations of the nitro-groups were tried and checked by calculating F_{h0} but, although general agreement was obtained, it was impossible to remove some discrepancies and, in particular, the calculated value of F_{550} was always too small. There seemed to be no advantage in assuming any distortion of the benzene ring. The calculated F values in the table are those obtained by using the dimensions for the molecules which fitted the Fourier projection best; a temperature

FIG. 1.



Projection of relative electron density on face (110). Only half the cell down the c direction is shown. Contours are drawn at arbitrary equal intervals. The corresponding atomic projection is shown in Fig. 2.

FIG. 2.



● = I. ● = C. ● = N. ○ = O.

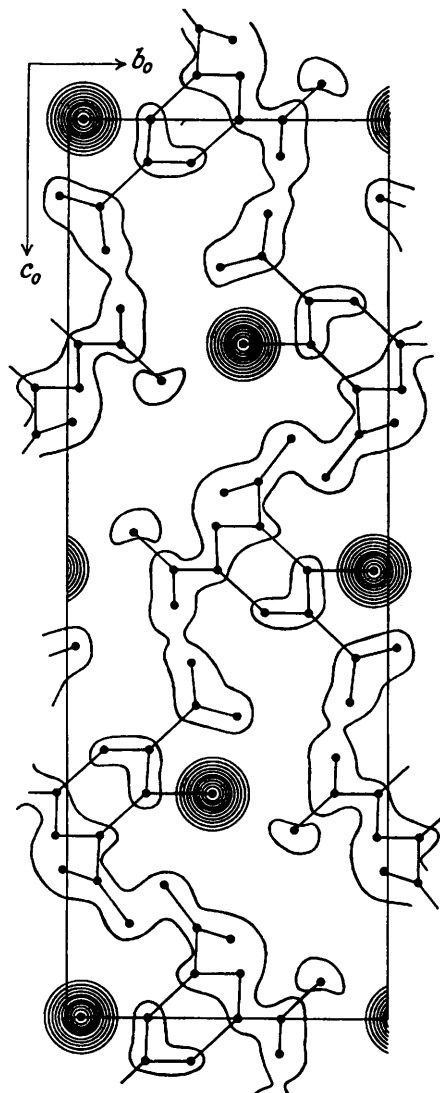
Structure projected on (110). Two views of the molecule are here presented: in one, *A*, the two-fold axis through the molecule is normal to the plane of projection, while in the other, *B*, the axis lies in this plane, but the plane of the ring is inclined to that of projection. In *A* the carbon and nitrogen atoms on the axis are obscured by the iodine atom, while in *B* the view is complicated by overlapping of neighbouring molecules, the iodine of one obscuring the para-carbon atom of the ring in the adjacent molecule. The turned-up ortho-nitro-groups and the flat para-group are seen plainly.

correction, $e^{-B(\sin \theta/\lambda)^2}$, has been applied, with $B = 2$, and the observed relative F 's have been adjusted approximately to an absolute scale by correlation with the calculated values. The projection of the molecules on the plane (110) is shown in Fig. 2, corresponding to the Fourier projection in Fig. 1.

A model of the structure shows plainly that the projection on the face (001) would be too much complicated by overlapping of the four layers of molecules to show the detail of the molecules, but the projection on (100) should show them clearly separated. Accordingly, a projection of electron density on this face was prepared by using values of F'_{0k} from a Weissenberg photograph and signs calculated from the atomic positions indicated by the [110] projection. The F' values were made more convergent by applying the same artificial temperature factor as in the previous case. The new projection agreed excellently

FIG. 3.

TABLE OF F_{hkl} .					
Indices.	$F_{obs.}$	$F_{calc.}$	Indices.	$F_{obs.}$	$F_{calc.}$
110	59	+ 68	2219	0	+ 9
220	113	+101	2220	26	+ 26
330	0	+ 4	2221	8	- 14
440	0	+ 12	331	58	- 45
550	22	- 5	332	40	+ 37
660	0	+ 10	333	34	+ 26
004	95	+106	334	36	+ 43
008	96	+ 85	335	42	- 23
0012	87	+ 70	336	30	+ 28
0016	39	+ 37	337	62	+ 46
0020	71	+ 64	338	34	+ 37
0024	28	+ 37	339	32	- 19
111	4	- 12	3310	60	+ 56
112	56	+ 53	3311	24	+ 25
113	57	+ 53	3312	17	+ 26
114	138	+136	3313	34	- 30
115	22	- 22	3314	20	+ 24
116	30	+ 25	3315	17	+ 13
117	61	+ 47	3316	17	+ 27
118	91	+ 79	3317	16	- 15
119	14	- 13	3318	11	+ 18
1110	7	- 6	3319	10	+ 14
1111	24	+ 22	3320	0	+ 12
1112	54	+ 44	441	20	- 10
1113	34	- 27	442	40	+ 35
1114	0	+ 1	443	30	+ 23
1115	14	+ 13	444	0	+ 5
1116	71	+ 60	445	28	- 19
1117	20	- 18	446	55	+ 46
1118	0	+ 5	447	14	+ 12
1119	0	+ 1	448	0	+ 17
1120	28	+ 35	449	45	- 35
221	26	- 14	4410	34	+ 36
222	6	+ 18	4411	32	+ 27
223	76	+ 58	4412	0	+ 24
224	79	+ 64	4413	10	- 10
225	22	- 22	4414	32	+ 35
226	34	+ 33	4415	25	+ 19
227	54	+ 45	4416	0	+ 5
228	57	+ 52	4417	7	- 14
229	30	- 22	551	14	- 15
2210	33	+ 29	552	52	+ 45
2211	34	+ 29	553	0	- 2
2212	65	+ 55	554	10	+ 2
2213	33	- 30	555	14	- 11
2214	16	+ 20	556	34	+ 37
2215	0	+ 18	557	0	0
2216	28	+ 29	558	0	+ 6
2217	26	- 28	559	0	- 3
2218	0	+ 15	5510	28	+ 35



The projection of the structure on (100) is here superposed on the relative electron density map. The molecules are clearly separated, but are viewed from an awkward angle. The bond joining the iodine to the benzene ring is inclined at 45° to the plane of projection, and the plane of the ring is rotated about this axis.

with the atomic positions previously deduced: in Fig. 3 these are shown superposed on the electron-density map, and the atomic co-ordinates are given below.

Four-fold positions: Iodine at (0.045, 0.045, 0).

Carbon at (0.255, 0.255, 0) and (0.533, 0.533, 0).

Nitrogen at (0.668, 0.668, 0).

Eight-fold positions: Carbon at (0.400, 0.250, 0.048) and (0.538, 0.388, 0.048).

Nitrogen at (0.405, 0.099, 0.098).

Oxygen at (0.790, 0.666, 0.040), (0.303, 0.115, 0.146), and (0.511, 0.971, 0.806).

These atomic co-ordinates correspond with the following dimensions for the molecules : I-C = 2.10 Å., symmetrical benzene ring with C-C = 1.39 Å.; para-C-N = 1.35 Å. and O-N-O angle 120° to allow for resonance effects; ortho-C-N = 1.45 Å. and O-N-O angle 127°. The three atoms of each *o*-nitro-group lie in a plane inclined at 80° to the plane of the ring, and these groups are assumed to be symmetrical. The oxygen atoms of the *p*-nitro-group are structurally equivalent, and this group is necessarily symmetrical.

The molecules are arranged in four layers related by the four-fold screw axis; each molecule is surrounded by twelve others so that the centres of the molecules lie approximately on a face-centred cubic lattice. It is particularly noticeable that the iodine atom fits into a large hole in the structure, so that its nearest neighbours are about 4 Å. away with the exception of the nitro-group of the adjacent molecule on the same two-fold axis, the I-O distance being here 3.3 Å.; this may be due to polarisation of the molecules, which would also explain the unexpected hardness of the crystals. The other shortest intermolecular distances are : O-C = 3.1 Å., O-N = 3.0 Å., O-O = 3.0 Å.

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