47. *The Structure of Molecular Compounds. Part I. The Crystal Structure of* p-*Iodoaniline–*s-*Trinitrobenzene.*

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All the atomic positions have been determined by two- and three-dimensional Fourier analysis. It is found that there are no intermolecular distances less than the usual separations in molecular crystals. All formulæ for the compounds involving a covalency between the molecules are excluded. The closest approach of the two molecules is between the amino-group and some oxygen atoms of nitro-groups, which at most can correspond to a very weak hydrogen bond. One nitro-group approaches the aromatic ring of the *p*-iodoaniline molecule, but not closer than in crystals of picryl iodide, and interaction of the molecules may occur here.

The nature of the compounds formed between aromatic polynitro-compounds and other aromatic substances has been much disputed. Some of the theories proposed could be tested at once by consideration of the crystal structures of the compounds, but hitherto there has been no information as to the relative positions of the atoms in these structures. *X*-Ray crystallographic methods have been used to examine a large number of these compounds in our laboratory, with different degrees of completeness of the structure determination for various compounds. It is impossible to publish the results in their logical order, since many portions of the work are postponed; but since the results for one compound in particular are especially significant and sufficiently complete, they are now presented out of their natural order.

A wide search, including many preliminary Fourier analyses of these compounds, showed that the molecular compound of *p*-iodoaniline and *s*-trinitrobenzene was suitable for a complete structure determination. The compound was obtained in dark red, monoclinic crystals elongated along [100], and developing mainly the forms {001}, {011}, {100} and {101}. They show strong negative double refraction with the optic axial plane parallel to (001) and the acute bisectrix almost parallel to [100]. The usual type of oscillation photographs revealed the approximate cell dimensions, number of molecules per unit cell, and space group. For the detailed structure determination Weissenberg photographs were obtained for rotation about the three principal axes. The zero layers were obtained for rotation about [100] and [001], and for rotation about [010] all practicable layer lines were also determined by the equi-inclination method. Copper-$K\alpha$ radiation was used throughout, and the apparatus employed was the camera of Buerger's design (*Z. Krist.*, 1936, **94**, 87). Intensities were estimated visually for over 500 reflexions, and structure factors derived in the usual way. By Patterson–Fourier synthesis for the projections perpendicular to [010] and [100] the positions of the iodine atoms were obtained. This procedure gave for the unit cell: $a = 7{\cdot}43$, $b = 7{\cdot}39$, $c = 28{\cdot}3$ A.; $\beta = 103°\ 25'$; space group $P2_1/c$; four molecules of each of the components per unit cell; all atoms are in the general positions of the space group, and the approximate parameters of an iodine atom are 0·113, 0·151, 0·063, there being three other iodine atoms in the cell in the related space group positions.

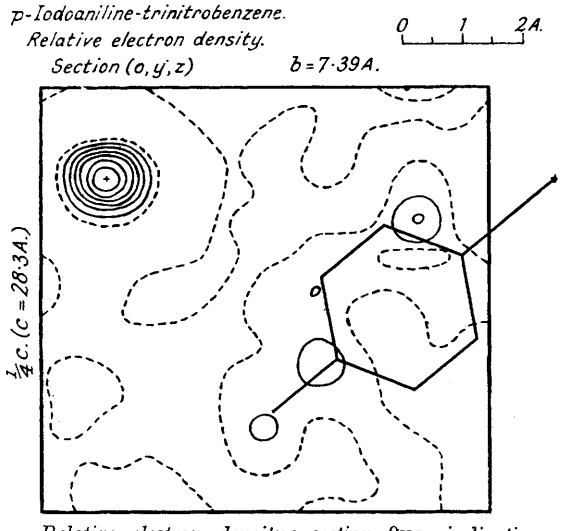
The signs for F($h0l$) and F($0kl$) were calculated from the iodine contributions alone, and the Fourier series for electron density projected perpendicular to [010] and [100] evaluated. These contained some spurious

detail but suggested approximate orientations for the rest of the molecules. As would be expected from packing considerations and from the optical properties of the crystal, the planes of the aromatic rings appeared to be inclined at fairly small angles to (100), and the best view of the structure would be expected when the plane of projection is perpendicular to [100]; but it became clear that the ring systems of a *p*-iodoaniline and a trinitrobenzene molecule were so nearly, but not exactly, superposed in this projection, that a great refinement of the parameters by repeated synthesis with revised signs could only be possible by this process for the oxygen atoms and two of the nitrogen atoms of the trinitrobenzene molecule. The structure was accordingly developed further by three-dimensional Fourier syntheses, since the difficulty of overlapping molecules disappears if the electron density at points in the cell is calculated instead of the projected density on one of the planes of the structure. For the three-dimensional syntheses over 400 F(*hkl*) coefficients were used to sum the series

$$\rho(xyz) \propto \Sigma\Sigma\Sigma F(hkl) \cos 2\pi(hx/a + ky/b + lz/c)$$

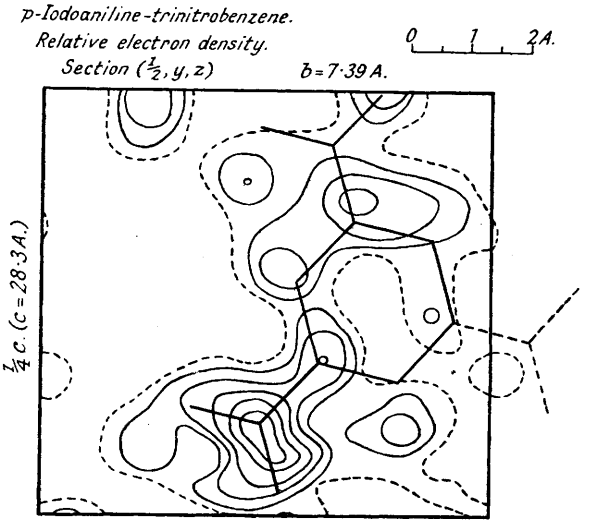
the signs of all the F's being computed from the iodine contributions alone. The relative electron density was calculated for all points 0*yz* and $\frac{1}{2}yz$ at intervals of $\frac{1}{30}$, $\frac{1}{60}$ for *y* and *z*, to give two sections passing approximately through the *p*-iodoaniline and the trinitrobenzene molecules; these are shown in Figs. 1 and 2. In them, the

FIG. 1.



Relative electron density; section 0yz, *indicating approximate position of* p-*iodoaniline molecule.*

FIG. 2.



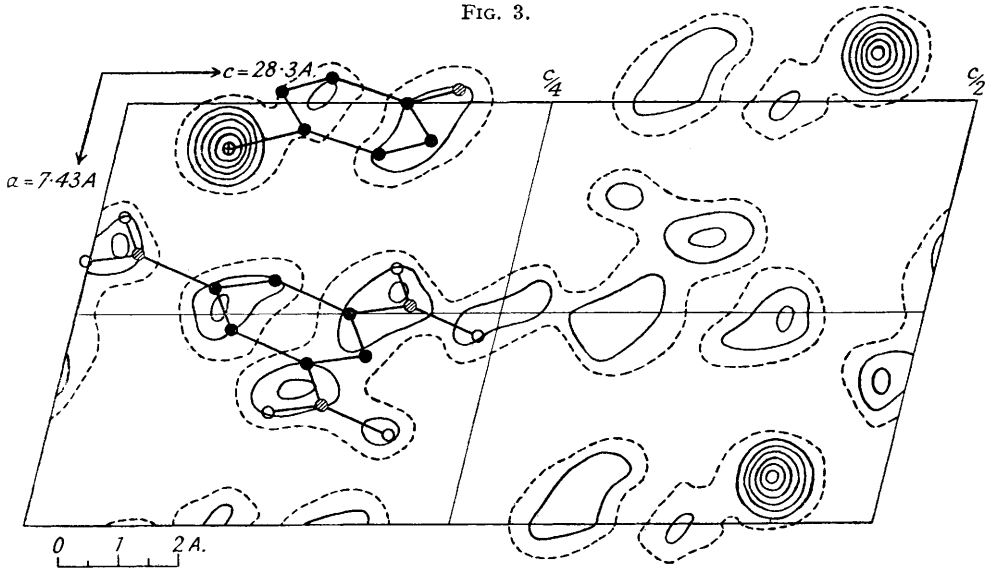
Relative electron density; section at $\frac{1}{2}$yz, *indicating approximate position of* s-*trinitrobenzene molecule. Both Figs.* 1 *and* 2 *are based on signs of* F_{hkl} *derived from the iodine contributions only and contain some spurious detail.*

pictures of the molecules are distorted, first because a certain number of the F(*hkl*) coefficients have been introduced with incorrect signs owing to neglect of the lighter atoms, and secondly because the peaks correspond, not to the centres of atoms, but to the centres of sections through the atoms which are at various displacements out of the plane. For example the nitro-group indicated by broken lines is a considerable distance from the plane of section and therefore does not appear. To supplement the information obtainable from the sections the electron density was also computed on lines through *xy'z'* with *y'* and *z'* constant and selected so that the lines passed through or near to suspected atomic centres. In this way a complete set of 69 co-ordinates for the 23 atoms in the symmetric unit (92 atoms in the cell) was obtained.

The projections on (010) and (100) were repeated with signs revised by inclusion of the contributions to the structure factors of all atoms, and these new projections were used in the final choice of parameters. Since reflexions used in these projections extend out to $\sin\theta/\lambda = 0{\cdot}59$, whereas the F(*hkl*) values in the three-dimensional work do not reach beyond $\sin\theta/\lambda = 0{\cdot}34$, the revised projections are to this extent more reliable than the sections or lines, apart from the improvement brought about by revision of the signs. It may be possible, later, to get further refinement of the parameters by extending the range of $\sin\theta/\lambda$ for F(*hkl*) with revision of all signs for the lighter atoms and allowance for the diffraction effects of the iodine. The extremely lengthy table of structure factors is not reproduced, but the results of the Fourier analysis are given in Figs. 3—6, of which Fig. 5 summarises the results as far as interatomic distances are concerned.

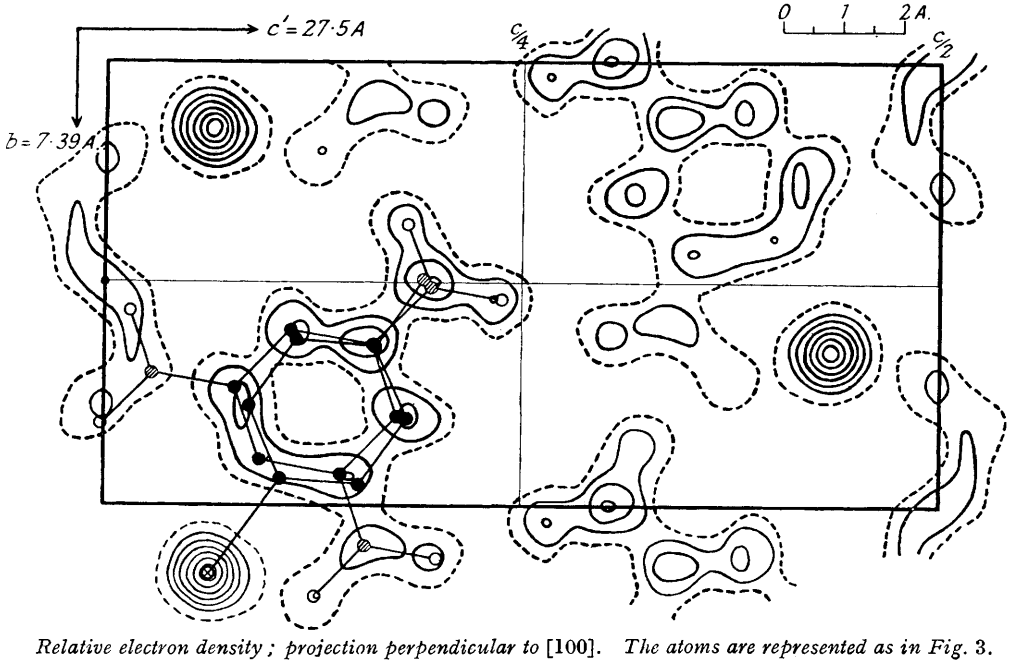
In general terms, the structure may be said to consist of alternate planar molecules of *s*-trinitrobenzene and *p*-iodoaniline arranged in rows with the normals to the planes of the molecules somewhat inclined to the general direction of the row. In the structure there are four such rows which run parallel to the *a* axis of the cell; these four rows consist of two pairs; in any pair the molecules of a row are related to the molecules of the other row by symmetry centres, and hence are parallel to them, but the molecules in the first pair of rows are not parallel to those in the other pair; the plane of a molecule in the second pair is related to that of a molecule

FIG. 3.



Relative electron density; projection on (010). *Black circles represent carbon, shaded circles nitrogen, open circles oxygen, the cross iodine.*

FIG. 4.



Relative electron density; projection perpendicular to [100]. *The atoms are represented as in Fig.* 3.

in the first pair by rotation of 180° about the *b* axis. Viewed along the direction of the rows, the two aromatic rings are not quite superposed atom for atom (see Fig. 4).

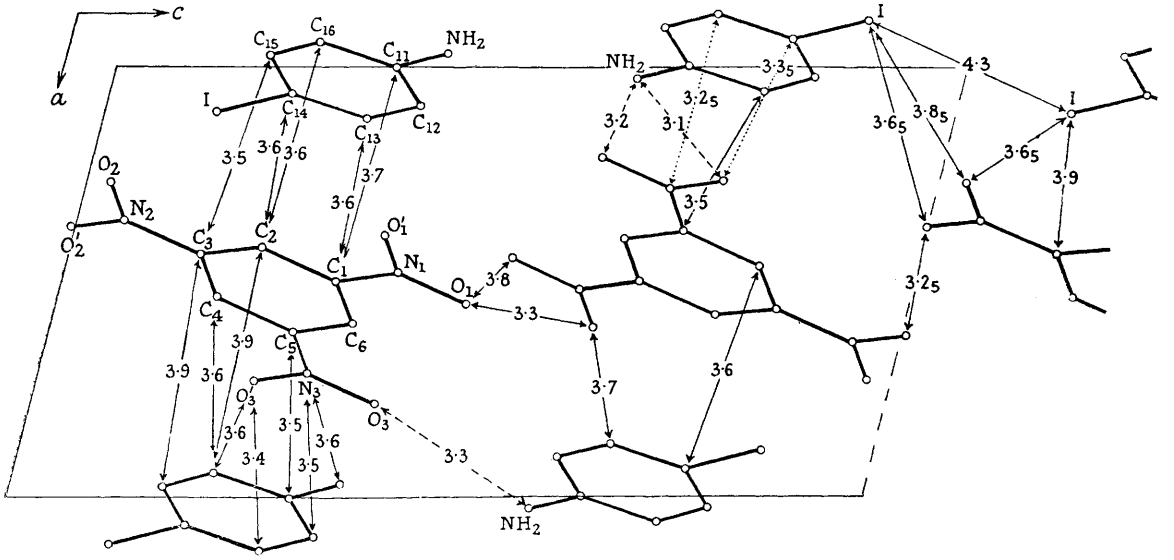
Estimated atomic positions for one asymmetric unit.

	p-Iodoaniline.				*s*-Trinitrobenzene.					
	x.	*y*.	*z*.		*x*.	*y*.	*z*.		*x*.	*y*.	*z*.
I	0·110	0·153	0·064	C_1	0·498	0·637	0·161	O_1'	0·395	0·366	0·182
C_{11}	0·003	0·642	0·162	C_2	0·420	0·605	0·112	O_2	0·277	0·562	0·015
C_{12}	0·090	0·802	0·182	C_3	0·439	0·735	0·078	O_2'	0·378	0·817	0·998
C_{13}	0·121	0·949	0·153	C_4	0·535	0·895	0·093	O_3	0·778	0·115	0·200
C_{14}	0·065	0·935	0·106	C_5	0·613	0·927	0·142	N_1	0·479	0·507	0·195
C_{15}	0·976	0·775	0·087	C_6	0·594	0·797	0·176	N_2	0·361	0·703	0·028
C_{16}	0·946	0·627	0·115	O_1	0·548	0·535	0·238	N_3	0·709	0·087	0·157
N	0·974	0·491	0·191								

Seen along the direction of the *b* axis (Fig. 3), the structure shows *s*-trinitrobenzene and *p*-iodoaniline molecules whose centres lie in alternate planes parallel to (100), cutting the *a* axis of the cell roughly at the origin and half way along the cell; the planes of the molecules themselves are inclined at about 30° to this face of the unit cell.

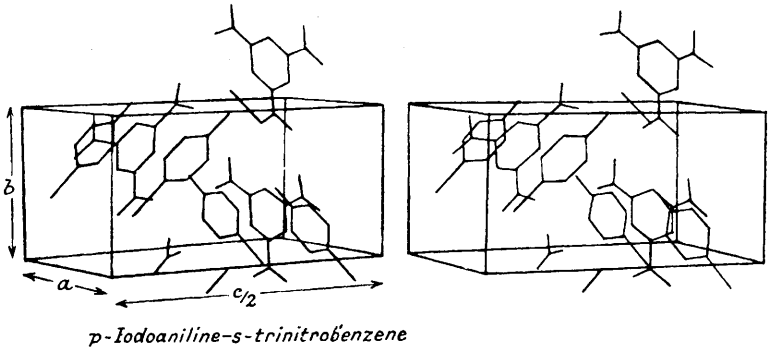
The positions assigned to the atoms are consistent with the following dimensions of the molecules: *s*-trinitrobenzene, planar with C–C 1·4, C–N 1·4, N–O $1{\cdot}2_3$, O–N–O angle 120°, planar *p*-iodoaniline with C–C 1·4, C–N $1{\cdot}4_3$, C–I 2·1 A. The distances between atoms in different molecules are recorded in Fig. 5. In this very complex structure all the co-ordinates are not known with the same accuracy, but since a knowledge of a

FIG. 5.



The atomic positions projected on (010) *corresponding to Fig.* 3. *The full length of the unit cell along* a *is shown and half the cell along* c. *To avoid confusion, all the principal intermolecular distances are not shown in any one part of the figure. Some of the distances specially referred to in the text are distinguished by broken lines.*

FIG. 6.



Stereoscopic drawing of part of the structure. The observer is looking through ($\bar{1}$00) *at the right-hand half of the unit cell, with the positive direction of the* b*-axis pointing downwards.*

few of them fixes the others, unless improbable distortions of the molecules are assumed, it is unlikely that there are any large errors. One possibility that it is difficult to eliminate entirely is that there might be slight rotation of the nitro-groups about the bond to the benzene ring. It is unlikely on chemical grounds owing to the resonance with the benzene ring, and in any case it could only be through a small angle, as the Fourier projections show.

The type of binding between the molecules may for convenience be considered under binding in the planes of *s*-trinitrobenzene or *p*-iodoaniline molecules, and binding between the two sorts of molecule. The *s*-trinitrobenzene molecules are arranged with an approximately hexagonal packing of molecular centres, and have the nitro-groups disposed so as to avoid any close approach of atoms in neighbouring molecules; Fig. 5 shows that the shortest interatomic distances (between oxygen atoms) are not less than 3·25 A. The smaller *p*-iodoaniline

molecules are also in a rough hexagonal packing and are more loosely packed; no distances within the planes of molecules are incompatible with the normal van der Waals separations between unlinked atoms. Between the *p*-iodoaniline and *s*-trinitrobenzene molecules the atomic separations are many of them equal to or greater than 3·5 A., as expected for unlinked atoms, and there is no distance between atoms in neighbouring molecules of the order of 1·5 A., as would be required for any covalent bond between the molecules. All structural formulæ proposed for these compounds which involve such a bond are therefore excluded at once, and there is no need to discuss the various earlier proposals in detail. The shortest interatomic distances, which are the ones of interest from the chemical viewpoint, prove to be those between the nitrogen atom of the amino-group and its oxygen neighbours. Each such nitrogen atom is at 3·1 A. from an oxygen of a nitro-group, 3·2 A. from the other oxygen of the same nitro-group, and at 3·3 A. from one of the oxygen atoms in a nitro-group of another neighbouring molecule; the last two oxygen atoms are structurally equivalent atoms of different molecules. The disposition of these atoms may be seen in Fig. 5. Distances NH . . . O of 2·98, 3·03 A. have been attributed to weak hydrogen bond formation in urea crystals (for the stronger bonds in glycine the distances are 2·76, 2·88 A.) and a similar weak bond may be assumed here.

Although the formation of such a bond provides a mechanism for the interaction of the two molecules concerned, it does not appear to be an essential feature of intermolecular compound formation; dimethylaniline, with no hydrogen atom on its nitrogen, forms molecular compounds, and hydrogen-bond formation by hydrocarbons such as hexamethylbenzene seems unlikely. The only other close approach of the two molecules arises from the position of one of the nitro-groups. All the carbon–carbon distances are large, 3·5 A. or more, and no atom of two of the nitro-groups is near to a carbon atom, but the third nitro-group is pointed in a direction which brings it nearer to a part of the carbon ring of the *p*-iodoaniline. The nitrogen of this group is at 3·25 A. from a carbon atom, and one of the oxygens is at 3·35 A. from the next carbon atom in the ring. These are not less than the minimum van der Waals distances permissible for the atoms involved, and the oxygen–carbon distance is greater than corresponding distances in the structure of picryl iodide (Huse and Powell, J., 1940, 1398). Whether this particular approach of the two molecules has any special significance, or is merely incidental to the packing of a selected pair of molecules, may be settled by detailed determination of similar structures.

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