555. *An X-Ray Examination of the Crystal Structure of* p-*Iodonitrosobenzene.*

By Monica S. Webster.

Crystals of *p*-iodonitrosobenzene are green, and *X*-ray analysis confirms that they consist of the stable monomer. They are monoclinic, space-group *Aa*, with four monomeric units, $I\cdot C_6H_4\cdot NO$, per unit cell. Co-ordinates for all atoms have been obtained from [100] and [10$\bar{1}$] electron-density projections. The molecule is planar with a C–N–O angle of about 125°. A short iodine–oxygen contact distance suggests strong dipole–dipole attraction between molecules.

Crystal structure analyses of *p*-bromonitrosobenzene [1] and 2 : 4 : 6-tribromonitrosobenzene [2] have been reported. The crystals of both compounds are colourless, and the molecules are dimeric, joined by a nitrogen–nitrogen bond.

In 1952, Dr. Nakamoto observed that crystals of *p*-iodonitrosobenzene are green, indicating the presence of the monomer. He suggested an *X*-ray analysis of the structure and provided the material used in this research.

Preliminary Crystal Data.—*p*-$I\cdot C_6H_4\cdot NO$: Found, $d = 2{\cdot}20$ g./c.c. Calc., $d = 2{\cdot}20$ g./c.c. Grass-green monoclinic needles, much elongated along the V*a*-axis. Main {011} faces showing yellow-green to blue-green pleochroism. Unit-cell dimensions : $a = 7{\cdot}86$, $b = 9{\cdot}99$, $c = 10{\cdot}52$ Å, $\beta = 122°$. Space-group *Aa*. Four molecules of $I\cdot C_6H_4\cdot NO$ per unit cell.

Structure Analysis.—The crystals decompose fairly rapidly in air, but the decomposition of single crystals was retarded sufficiently to obtain satisfactory photographs by sealing them in capillary tubes. In view of the difficulty of correlating three-dimensional data obtained from a number of crystals, the analysis was limited to projections.

The space-group requires four asymmetric units per unit cell and forbids bonding to form dimers between two units. There is no centrosymmetric projection, and Fourier syntheses with observed structure amplitudes with heavy-atom phases have false symmetry. The iodine contributes one half of the scattering matter per molecule, so that light-atom positions cannot be accurately determined.

x and *z* co-ordinates of the iodine atom may be chosen arbitrarily; the *y* co-ordinate was found from an *a*-axis Patterson synthesis. Co-ordinates used for subsequent calculations were : $x = 0, y = 0{\cdot}203, z = 0$.

An electron-density projection along the *a*-axis, calculated from observed structure amplitudes with heavy-atom phases, gives the general distribution of the molecule (Fig. 1). The true structure is repeated by reflection across the false mirror plane along the *b*-axis. To reveal the nitroso-group it was necessary to remove the iodine atom peak from the electron-density distribution. A second Fourier synthesis with $(F_0 - F_{\text{calc. I}})$ values showed the nitrogen and oxygen atom peaks resolved but considerably distorted. However, the non-linearity of the oxygen atom with the carbon–nitrogen bond was clear. The projection was refined twice; the final $(F_0 - F_{\text{calc. I}})$ Fourier synthesis is shown in Fig. 2. The final *R* value for all 0*kl* terms is 0·12.

A further projection of electron density was calculated on the plane perpendicular to [10$\bar{1}$], at an angle of 76° with the plane of the first projection. The two projections were considered together, light-projection technique being used, and co-ordinates for all atoms except the oxygen were fixed. It was possible to keep the oxygen atom position unmoved in the [100] projection and to satisfy the [10$\bar{1}$] projection with the nitrogen–oxygen bond either in or perpendicular to the plane of the benzene ring. Sets of structure factors, followed by electron-density syntheses, were calculated on these alternative structures for the [10$\bar{1}$] projection. For the non-planar molecule the *R* value is 0·21, excluding unobserved reflections, and the corresponding Fourier synthesis gives the oxygen atom at only half

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[1] Darwin and Hodgkin, *Nature*, 1950, **166**, 827.

[2] Fenimore, *J. Amer. Chem. Soc.*, 1950, **72**, 3226.

weight. The planar molecule corresponds to an R value of 0·17, excluding unobserved terms, and the Fourier synthesis gives the oxygen atom at full weight (Fig. 3). The final R value, including all terms, is 0·18.

An electron-density projection along the b-axis, calculated from observed (010) amplitudes with iodine atom phases, confirms the planarity of the molecule (Fig. 4). The distribution contains a false centre of symmetry.

Final atomic co-ordinates for the structure are listed in Table 1. Corresponding bond lengths and angles are shown in Fig. 5. The C–N bond appears to be short, but other variations from expected interatomic distances are within the limits of reliability of the analysis. There is one short intermolecular contact distance of 3·2 Å between adjacent iodine and oxygen atoms along the b-axis.

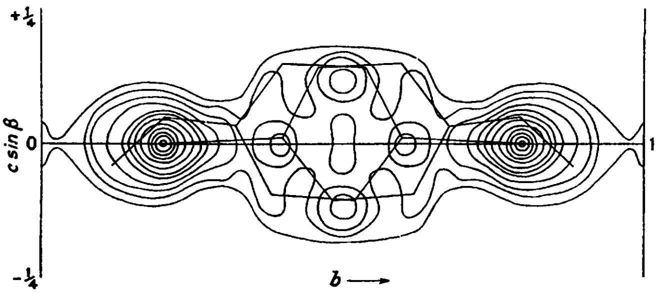


FIG. 1. *Electron density of* p-*iodonitrosobenzene projected on* (100); *calculated from observed amplitudes with iodine atom phases.*

(Contour lines begin at the 3e Å^{-2} contour and are drawn at intervals of 2e Å^{-2}, except for the iodine atom where the intervals are arbitrary.)

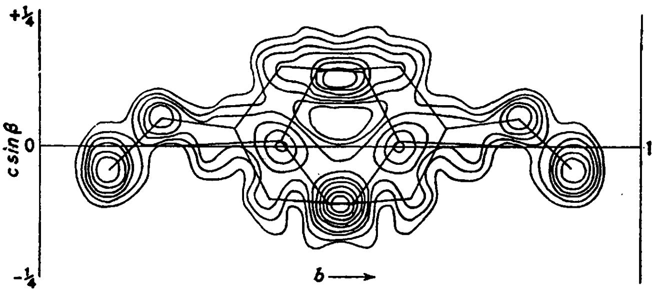


FIG. 2. *Electron density of* p-*iodonitrosobenzene projected on* (100); *calculated on the phases of all atoms but with the iodine atom subtracted.*

(Contour lines begin at the 3e Å^{-2} contour and are drawn at intervals of 1e Å^{-2} (F_{002} included using the calculated value.)

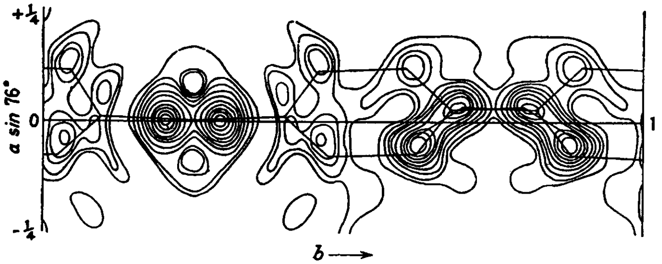


FIG. 3. *Electron density of* p-*iodonitrosobenzene projected along* [10$\bar{1}$]; *calculated on the phases of all atoms.*

(Contour lines begin at the 3e Å^{-2} contour and are drawn at intervals of 2e $^{-}$Å^{2}.)

TABLE 1. *Final co-ordinates.*

C at position	x	y	z	C at position	x	y	z		x	y	z
1	0·000	0·403	0·010	4	0·007	0·677	0·033	N	0·020	0·804	0·053
2	0·973	0·480	0·893	5	0·030	0·600	0·150	O	0·994	0·888	0·957
3	0·976	0·620	0·903	6	0·028	0·460	0·140	I	0·000	0·203	0·000

Discussion.—Two facts, in particular, emerge from the present structure analysis; p-iodonitrosobenzene is planar, and there is a short intermolecular iodine-to-oxygen contact distance. Short intermolecular contacts have also been reported in *p*-chloroiodoxybenzene [3] and in *N*-picryl-*p*-iodoaniline.[4]

The planar monomer may be compared with dimeric aromatic nitroso-compounds where there is steric hindrance between oxygen and the hydrogen atoms in *ortho*-positions [see (I)]. To achieve clearance, the planarity of the molecule is destroyed, and the structure analyses of *p*-bromonitrosobenzene and 2 : 4 : 6-tribromonitrosobenzene establish that the benzene rings turn out of the plane of the six central atoms. By contrast, the quinaldil molecule twists about the central bond.[5]

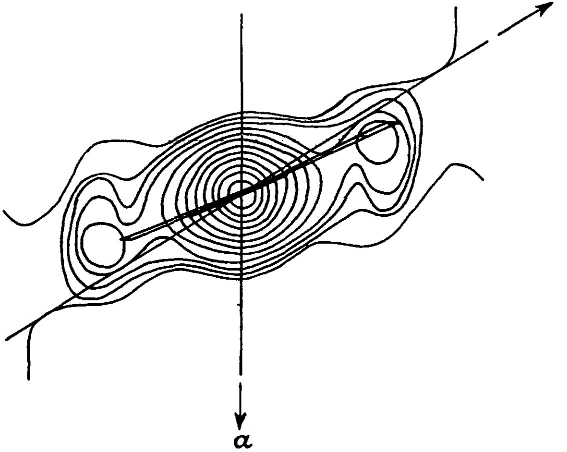


FIG. 4. *Electron density of* p-*iodonitrosobenzene projected on* (010); *calculated on the iodine atom phases.*

(Contours are drawn at arbitrary intervals.)

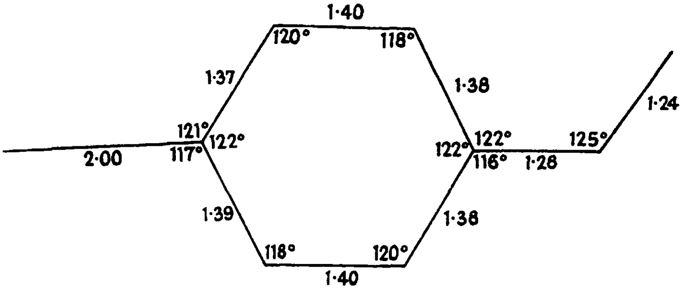
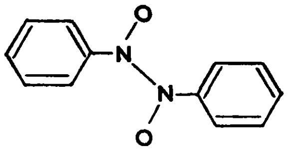
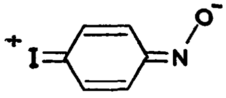


FIG. 5. *Bond lengths and angles calculated from atomic co-ordinates listed in Table* 1.

Dr. Lüttke [6] has recently suggested that electron-accepting groups in *para*-positions favour dimerisation of nitroso-compounds, while electron-donating groups stabilise the monomer. *p*-Iodo-, *p*-methoxy-, and *p*-dimethylamino-nitrosobenzene are monomeric, and in each case the substituent group is an electron donor. The planarity of *p*-iodonitrosobenzene suggests that contribution from a resonance structure of the type (II) stabilises the monomer, and when such a contribution is small or absent, dimerisation occurs. The short intermolecular contact is consistent with strong dipolar attraction

(I)





(II)

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[3] Archer, *Acta Cryst.*, 1948, **1**, 64.
[4] Grison, *ibid.*, 1949, **2**, 146.
[5] Davies and Powell, *Nature*, 1951, **168**, 386.
[6] Lüttke, verbal communication in Oxford.

between opposite ends of adjacent molecules. It is significant that *o*-iodonitrosobenzene, in which there is steric hindrance, is dimeric.

It is suggested that the monomer is stable only under these electronic and steric conditions. In all other cases dimers are formed, and the resulting molecule is stabilised by resonance localised in the central planar group. Similar conclusions have been reached by Mr. Mijs.[7]

EXPERIMENTAL

The crystals sent by Dr. Nakamoto were grass-green needles suitable for *X*-ray photography without recrystallisation. To improve their shape for the [010] and [10$\bar{1}$] axis photographs they were cut across the needle length. Each crystal was mounted on a glass fibre about the correct axis before being sealed in a thin-walled, Hysil capillary tube. Rapid decomposition occurred in the air, probably with loss of iodine, and a new crystal was required for each set of photographs. Approximate dimensions of crystals used were 0·07 × 0·07 × 0·15 mm.

X-*Ray Measurements*.—Unfiltered copper radiation was used. Intensities were estimated visually from Weissenberg photographs by using multiple-film technique. The number of reflections observed for the [100], [010,] and [10$\bar{1}$] projections were respectively 55 out of a possible 64, 41 out of 47, and 45 out of 55. For accurate cell-dimension measurements the films were calibrated at the edges with copper powder lines obtained from a fine wire. The lattice constant for copper was taken to be 3·60775 Å. The absolute scale was determined by correlation of final $F_{obs.}$ and $F_{calc.}$ values.

TABLE 2. *Temperature factors.*

		$10^{16}B_{(mol.)}$	$10^{16}B_{(iod.)}$			$10^{16}B_{(mol.)}$	$10^{16}B_{(iod.)}$
(100) projection :	$\parallel b$ ...	5·95	4·76	(10$\bar{1}$) projection :	$\parallel b$ ...	2·38	2·38
	$\perp b$ ...	5·95	6·40		$\perp b$ ...	2·38	6·40

TABLE 3. *Observed and calculated values of the structure factor (hydrogen contributions and unobserved reflections are not included).*

hkl	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$
020	36	32	042	8	7	097	1	2	31$\bar{3}$	29	27
040	7	6	044	7	7	0,10,2	10	9	33$\bar{3}$	20	18
060	6	4	046	5	4	0,10,4	6	6	35$\bar{3}$	7	4
080	8	10	048	3	3	0,10,6	4	4	37$\bar{3}$	10	8
0,10,0	11	10	04,10	1	1	0,11,3	2	0	39$\bar{3}$	14	15
0,12,0	6	5	051	29	31	0,12,2	4	4	3,11,$\bar{3}$	10	11
002	78	64	053	23	23	0,12,4	2	3	42$\bar{4}$	25	28
004	34	28	055	16	15	20$\bar{2}$	56	70	44$\bar{4}$	10	6
006	16	17	057	8	8	40$\bar{4}$	31	30	46$\bar{4}$	7	5
008	9	9	059	3	4	60$\bar{6}$	15	14	48$\bar{4}$	12	13
00,10	3	3	062	3	4	80$\bar{8}$	8	8	4,10,$\bar{4}$	9	13
011	3	3	064	1	3	11$\bar{1}$	27	30	51$\bar{5}$	20	19
013	19	18	071	18	18	13	26	27	53$\bar{5}$	10	11
015	7	9	073	12	14	15$\bar{1}$	18	12	55$\bar{5}$	7	1
022	34	36	075	7	8	17$\bar{1}$	14	16	57$\bar{5}$	9	5
024	31	29	077	5	5	19$\bar{1}$	16	16	59$\bar{5}$	9	10
026	11	12	079	2	2	1,11,$\bar{1}$	12	14	62$\bar{6}$	15	15
028	4	5	082	9	10	22$\bar{2}$	32	34	64$\bar{6}$	9	4
02,10	1	3	084	8	8	24$\bar{2}$	10	7	68$\bar{6}$	7	8
031	36	35	086	4	5	26$\bar{2}$	6	6	71$\bar{7}$	12	11
033	22	22	088	1	2	28$\bar{2}$	15	17	73$\bar{7}$	9	6
035	13	13	091	5	6	2,10,$\bar{2}$	16	19	82$\bar{8}$	9	5
037	7	8	093	5	5	2,12,$\bar{2}$	8	11	91$\bar{9}$	5	5
039	3	3	095	4	3						

Calculations.—Fourier summations were obtained with a Hollerith tabulator. The final [100] and [10$\bar{1}$] projections were calculated at intervals of 1/60 of the cell edge, and the [010] projection at intervals of 1/30. Structure factors for all atoms except iodine were calculated with a cross-product table, with atoms weighted as carbon 6, nitrogen 7, and oxygen 8. The sum for each reflection was multiplied by a value obtained from a normalised McWeeney scattering curve for nitrogen, and added to the iodine contribution. This was calculated from Buerger's tables and the Thomas–Fermi atomic scattering curve for iodine.

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[7] See Havinga, *Chem. Weekblad*, 1955, **51**, 125.

Temperature factors were obtained by plotting ln F_0/F_c against $\sin^2\theta/\lambda^2$ for all reflections. Consideration of axial reflections alone indicated that the temperature factor of the iodine atom was significantly anisotropic. Final temperature factors used are given in Table 2. Proportional values for the iodine atom at intermediate points, were obtained by distortion of the reciprocal lattice.[8] No direct correction was made for absorption and this is assumed to account for anomalies in temperature factor values obtained experimentally.

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CHEMICAL CRYSTALLOGRAPHY LABORATORY,
UNIVERSITY MUSEUM, OXFORD.

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[8] Cochran, *Acta Cryst.*, 1954, **7**, 503.