

Refined Structure of Phenazine–Iodine Molecular Complex, C₁₂H₈N₂·I₂

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Abstract. $M_r = 434.0$, orthorhombic, $Pbcn$, $a = 12.901(3)$, $b = 11.602(3)$, $c = 8.303(3)$ Å, $V = 1243$ Å³, $Z = 4$, $D_m = 2.30$, $D_x = 2.32$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 5.097$ mm⁻¹, $F(000) = 800$, $T = 293$ K. From the photographically determined atomic coordinates [Uchida (1967), *Bull. Chem. Soc. Jpn.*, **40**, 2244–2248], the structure has been refined to $R = 0.039$ for 776 diffractometer data. The intramolecular I–I distance is 2.726(1) Å, and the two independent intermolecular N...I distances are 3.098(6) and 2.982(5) Å, respectively.

Introduction. The title complex is an n - σ -type donor–acceptor compound. Since its previous study was based on two-dimensional photographic data (Uchida, 1967), the results were inadequate to discuss the precise structure except for some distances including I atoms. This report concerns the refinement of the complex based on the counter data.

Experimental. Dark red prismatic crystal, grown from chloroform solution of constituents (1:1), approximate cross section 0.1 × 0.1 mm; D_m by flotation in aqueous K₂HgI₄; Rigaku four-circle diffractometer, Mo $K\alpha$; cell dimensions from least squares of setting angles of 12 reflections; ω – 2θ scan, scan speed 1° (2 θ) min⁻¹, scan width (1.0 + 0.45 tan θ)°, $2\theta_{\max} = 55^\circ$, $0 \leq h \leq 16$, $0 \leq k \leq 14$, $0 \leq l \leq 10$, two monitored reflections for every 50 measurements, intensity variation within 1% of F 's; 1662 unique reflections measured, 779 with no net intensities [$F_o < 3\sigma(F)$]; Lorentz and polarization corrections, no absorption correction; structure refined by anisotropic block-diagonal least squares (H isotropic), 108 parameters; $\sum w(|F_o| - k|F_c|)^2$ minimized, $w = [\sigma^2(F) - 0.015F_o + 0.0022F_o^2]^{-1}$; H from difference map, $B = 4.0$ Å²; in the final cycle, seven reflections (200, 310, 400, 041, 241, 002 and 202) given zero weight as being seriously affected by extinction; R , wR and S 0.039, 0.054 and 1.45, respectively; $(\Delta/\sigma)_{\max} = 0.29$, $(\Delta/\sigma)_{\text{av}} = 0.04$; in final difference map, $\Delta\rho$ excursions 0.6 and -1.1 e Å⁻³ near I atoms, not significant features; scattering factors with anomalous dispersion of I atom from *International Tables for X-ray Crystallography* (1974); computations at the Computer Centre of the University of Tokyo with

UNICS (1967) program system.*

Discussion. The final parameters and equivalent isotropic temperature parameters are listed in Table 1. The bond distances and angles are shown in Fig. 1 together with the numbering scheme. All the N and I atoms are on the twofold axis.

The phenazine and iodine molecules form an alternating linear chain parallel to the b axis (Fig. 2). The difference between the two intermolecular N...I distances implies that the charge-transfer interaction of N(2)...I(2) is stronger than that of N(1)...I(1). The I(1)–I(2) distance, 2.726(1) Å, is slightly elongated from the covalent bond length, 2.68 Å (*International Tables for X-ray Crystallography*, 1962), by the antibonding contribution. The geometry of the phenazine molecule is essentially similar to that of pure or complex-forming phenazines so far reported (Herbststein & Schmidt, 1955; Hirshfeld & Schmidt, 1957; Goldberg & Shmueli, 1973; Karl, Ketterer & Stezowski, 1982). The C(1)–N(1) distance, 1.326(9) Å, is significantly shorter than C(6)–N(2),

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38809 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters ($\times 10^4$ for non-H, $\times 10^3$ for H atoms) and the equivalent isotropic temperature parameters with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} (a_i \cdot a_j)$$

	x	y	z	$B_{\text{eq}}(\text{Å}^2)$
I(1)	0	600 (1)	2500	2.90 (2)
I(2)	0	–1750 (1)	2500	3.07 (2)
N(1)	0	3271 (6)	2500	2.7 (2)
N(2)	0	5676 (6)	2500	2.6 (3)
C(1)	742 (6)	3838 (6)	1731 (9)	2.1 (2)
C(2)	1565 (6)	3248 (6)	926 (10)	2.6 (2)
C(3)	2315 (6)	3842 (6)	119 (9)	3.0 (3)
C(4)	2305 (6)	5074 (8)	120 (10)	3.1 (2)
C(5)	1537 (6)	5665 (6)	843 (10)	3.0 (3)
C(6)	741 (5)	5074 (6)	1723 (9)	2.2 (2)
H(2)	153 (7)	245 (8)	91 (10)	
H(3)	274 (8)	347 (7)	–45 (10)	
H(4)	271 (8)	537 (7)	–78 (12)	
H(5)	152 (8)	647 (7)	86 (12)	

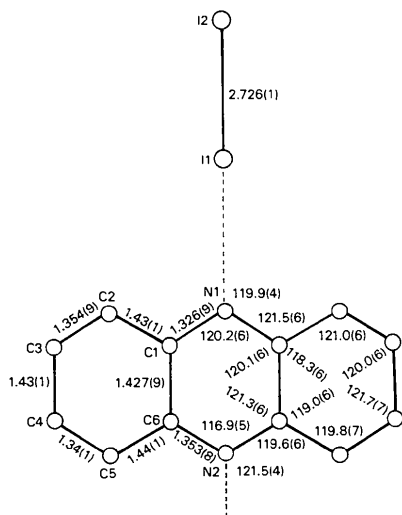


Fig. 1. Bond distances (Å) and angles ($^{\circ}$) with the numbering scheme. E.s.d.'s are in parentheses. Numbering of H atoms is the same as that of the attached carbon atoms.

1.353 (8) Å. In the case of several *N*-alkylphenazinium cations, the ring C—N bond distances adjacent to the alkyl groups are found to be longer than the non-alkylated C—N ring bonds (Morosin, Plastas, Coleman & Stewart, 1978; Endres, Keller, Moroni & Nöthe, 1979; Harms, Keller, Nöthe & Wehe, 1982). Although $N \cdots I$ is not a covalent bond in this complex, the stronger charge-transfer force about the N(2) atom elongates the N(2)—C(6) distance.

The average deviation of the ring atoms from the least-squares plane of phenazine is 0.02 (2) Å with maximum deviations of 0.05 (2) and 0.04 (2) Å for C(5) and C(2), respectively. The average distance between the planes of the two adjacent phenazine molecules is 3.46 (2) Å. The angle between the phenazine plane and the *c* axis is 56.3 (1) $^{\circ}$.

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Methyl (Diphenylmethylimino)acetate *N*-Oxide, $C_{16}H_{15}NO_3$

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Abstract. $M_r = 269.29$, monoclinic, $P2_1/a$, $a = 10.142$ (1), $b = 13.851$ (3), $c = 9.986$ (1) Å, $\beta = 99.961$ (9), $V = 1381.6$ (3) Å³, $Z = 4$, $D_m = 1.28$ (1),

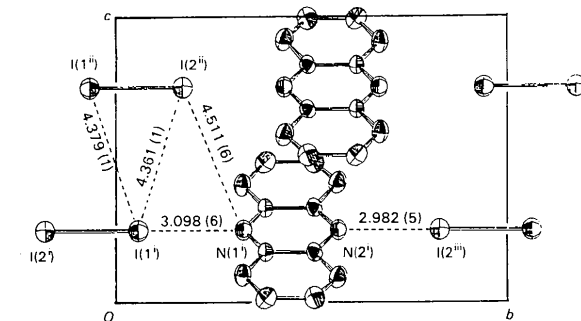


Fig. 2. The packing arrangement projected onto (100), with several intermolecular distances (Å). 50% probability ellipsoids are shown (Johnson, 1965). H atoms have been omitted. Symmetry code: (i) x, y, z ; (ii) $-x, -y, 1 - z$; (iii) $x, 1 + y, z$.

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