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Neutron and New X-ray Study of 4,4′-Bis(dimethylamino)diphenylammoniumyl Iodide, $[(CH_3)_2\text{-}N\text{-}C_6H_4\text{-}\dot{N}H\text{-}C_6H_4\text{-}N\text{-}(CH_3)_2]^+.I^-$

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Abstract. $M_r = 382{\cdot}278$, monoclinic, $C2/c$, $a = 13{\cdot}114\,(2)$, $b = 14{\cdot}124\,(2)$, $c = 9{\cdot}633\,(1)$ Å, $\beta = 109{\cdot}914\,(9)°$, $V = 1677{\cdot}5$ Å^3, $Z = 4$, $D_x = 1{\cdot}526$ g cm^{-3}, $T = 295$ K. X-ray study: Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 19{\cdot}5$ cm^{-1}, $F(000) = 764$, $R(R_w) = 0{\cdot}070\ (0{\cdot}074)$ for 1741 unique observed reflections. Neutron study: $\lambda = 1{\cdot}0405\,(9)$ Å, $\mu = 1{\cdot}784\,(5)$ cm^{-1}, $F(000) = 24{\cdot}544 \times 10^{-12}$ cm, $R(R_w) = 0{\cdot}261\ (0{\cdot}085)$ for 467 unique observed reflections. The mean C—H distance in the methyl group is 1·03 Å, in the benzene ring 1·06 Å. The hydrogen bridge N—H···I is linear [all three atoms are in special positions (0, y, 0·25)] with N—H = 1·53 and H···I = 2·27 Å.

Introduction. The title substance is of interest because of its high electrical conductivity. Its molecular conformation and packing have been described and thoroughly discussed in a previous study by Toman & Očenásková (1966) (hereafter TO). However, positions of H atoms were not determined and some doubt about the position of one of the methyl C atoms remained. The aim of this study was to fill these gaps.

Experimental. Synthesis described by TO, growth of larger crystals suitable for neutron study by Tichý & Honzl (1968). Samples for X-ray and neutron measurements taken from the same batch.

X-ray. Spherical crystal, radius 0·1 mm. Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$. Lattice and orientation parameters by least squares on 25 reflections ($20{\cdot}6° < 2\theta < 24{\cdot}6°$). Intensities by $\omega{:}2\theta$ scan, $\sin\theta/\lambda < 0{\cdot}628$ Å^{-1}, hkl range $0,\overline{17},\overline{11}$ to 16,17,11. Absorption and Lorentz–polarization corrections, no extinction correction. Total of 3556 reflections measured, 1741 unique, 1387 observed [$I > 3\sigma(I)$]. Stability (within $\pm 1{\cdot}5\%$) monitored by three standards measured after intervals of 60 reflections during the whole data collection. Although the structure was known from TO, heavy-atom method and direct methods applied; their solutions converged to coordinates of TO within 1·0 e.s.d. Refinement on F, anisotropic temperature parameters for all atoms, $w = 1/\sigma^2(F)$, mean Δ/σ 0·12, max. 0·91 in the final cycle. Positions of H atoms not determined from X-ray data.

Neutron. Rectangular needle-like crystal, $0{\cdot}70 \times 0{\cdot}85 \times 4{\cdot}20$ mm. Orientation matrix from 10 reflections ($46° < 2\theta < 57°$) centred on a four-circle diffractometer at the Saphir reactor, Würenlingen. Graphite monochromator. Linear absorption coefficient μ determined from the attenuation of pinhole-collimated neutrons by the measured sample. Intensities by $\omega{:}g\theta$ scan [$g = 1{\cdot}5$ to 2·0 with increasing θ, such that diffracted beam always coincided with the detector centre-line (Werner, 1971) during the scan]. $\sin\theta/\lambda < 0{\cdot}468$ Å^{-1}, hkl range $\overline{12},0,0$ to 11,13,8. Corrections for Lorentz factors, transmission (range 0·862 to 0·899) and extinction [range of mean path length 0·59 to 0·83 mm; for strongest reflection 020 $y(020) = J_{\rm obs}/J_{\rm kin} = 0{\cdot}365$]. Total of 1007 reflections measured, 709 unique, 467 observed [$F > 2{\cdot}5\sigma(F)$]. High inherent background caused by incoherent scattering of neutrons on H atoms, peak/background count ratio 2:1 for medium reflections, background fitted by least squares. Stability (within $\pm 7\%$) monitored by one strong reflection after intervals of about 40 reflections.

X-ray data used in this study are, we believe, more accurate than those in the work by TO. First, we used a small spherical crystal which allowed accurate absorption corrections (these were neglected by TO), second, we collected our data in the four-circle geometry which is superior to the 'normal-beam' technique which was then available to TO.

For our neutron diffraction investigation we used a crystal with well developed faces. Unfortunately, the accuracy of our neutron measurement does not match the accuracy achieved in our X-ray work. The conventional R factor is rather high (0·265), but the weighted $R_w = 0{\cdot}085$ is approximately of the same magnitude as that for X-ray data ($R_w = 0{\cdot}074$).

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H positions from consecutive Fourier syntheses computed with signs based on final parameters for non-H atoms from X-ray refinement. Scattering lengths from Bacon (1972), all atoms refined with anisotropic temperature factors, refinement on F with $w = 1/\sigma^2(F)$. Secondary-extinction parameter $r^* = 2{\cdot}0\ (3) \times 10^4$ refined according to Zachariasen (1967). Anisotropic thermal parameters non-positive-definite for H(72) and H(73) atoms in the last cycle. Agreement factors at this stage $R = 0{\cdot}165$ and $R_w = 0{\cdot}035$. Mean Δ/σ 0·19, max. 0·82. On the final difference Fourier synthesis maximum positive (negative) peak = 63 (−60) nuclear density units, while nuclear density at the centre of C atoms was 492 units, in H atoms – 190 units.

The position of H(72) on the final Fourier map (0·66, 0·52, 0·09) was about 0·85 (8) Å from its position (0·66, 0·47, 0·13) in the final cycle of the refinement. The latter is very close [0·72 (5) Å] to the position of C(7) (0·61, 0·47, 0·14). In order to obtain more reliable information about positions of methyl H atoms a constrained refinement [with a local version of the program *ORFLS* modified according to Chesick & Davidon (1975)] was performed. Methyl groups were

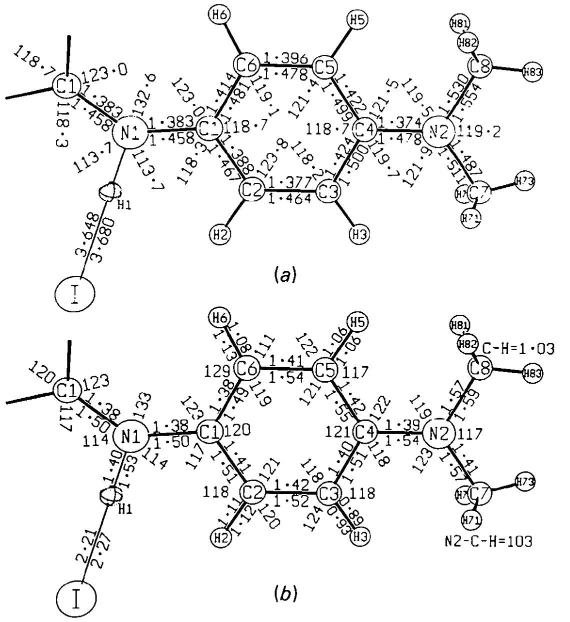

Fig. 1. *ORTEP* (Johnson, 1971) representation of the independent half of the molecule of the title compound showing its conformation, atom numbering, bond lengths (Å) and bond angles (°). Upper numbers are uncorrected bond distances, lower numbers are distances corrected for thermal motion [all for independent oscillation except for C(7), C(8) and H atoms which were corrected for riding motion]. (*a*) Results for X-ray measurement; e.s.d.'s 0·009–0·015 Å and 0·5–1·1°. (*b*) Results for neutron measurement; e.s.d.'s 0·03–0·06 Å (for H atoms 0·09–0·16 Å) and 2–4°. Methyl atoms were constrained to threefold symmetry along N(2)—C(7) and N(2)—C(8) bonds [C—H = 1·03 Å, N(2)—C—H = 103°].

Table 1. *Fractional atomic coordinates* (× 10⁴, H *atoms* × 10³) *and equivalent isotropic thermal parameters*

For I, N, C atoms: above X-ray data, below neutron data.
For methyl H atoms: above values from the unconstrained, below from the constrained neutron refinement.
For other H atoms: values from the unconstrained neutron refinement.
Equivalent isotropic temperature factors B_{eq}(Å²):
for X-ray data: $\frac{8}{3}\pi^2\sum U_{ij}\cos(a_i,a_j)$.
for neutron data: $\frac{4}{3}\sum b_{ij}a_ia_j\cos(a_i,a_j)$.
E.s.d.'s in parentheses refer to the last decimal digits.

	x	y	z	B_{eq}(Å²)
I	0	2037 (1)	2500	4·3 (0·1)
	0	2072 (55)	2500	13·0 (4·0)
N(1)	10000	5381 (7)	7500	3·5 (0·5)
	10000	5371 (14)	7500	6·4 (1·3)
N(2)	6924 (8)	3953 (6)	2380 (9)	5·0 (0·4)
	6922 (17)	3983 (13)	2367 (21)	8·3 (1·2)
C(1)	9266 (8)	4987 (6)	6241 (10)	3·4 (0·4)
	9266 (20)	4980 (13)	6244 (22)	5·9 (1·1)
C(2)	8488 (9)	5573 (7)	5291 (11)	3·9 (0·5)
	8501 (19)	5600 (14)	5299 (20)	4·7 (1·1)
C(3)	7712 (9)	5265 (7)	4008 (11)	4·0 (0·5)
	7706 (22)	5274 (16)	3982 (28)	5·0 (1·4)
C(4)	7698 (8)	4288 (7)	3641 (10)	3·7 (0·5)
	7709 (17)	4309 (15)	3650 (19)	5·7 (1·2)
C(5)	8524 (9)	3687 (7)	4561 (10)	4·1 (0·5)
	8520 (20)	3699 (22)	4564 (22)	6·8 (1·4)
C(6)	9302 (8)	4027 (6)	5848 (10)	3·6 (0·4)
	9303 (17)	4042 (17)	5863 (21)	5·3 (1·3)
C(7)	6097 (10)	4595 (9)	1385 (13)	6·1 (0·6)
	6105 (32)	4569 (21)	1423 (50)	6·9 (2·0)
C(8)	6868 (10)	2893 (7)	2041 (13)	5·4 (0·5)
	6830 (46)	2886 (30)	2054 (52)	10·4 (3·4)
H(1)	0	364 (22)	250	31·0 (14·7)
H(2)	856 (3)	636 (6)	559 (4)	10·2 (3·5)
H(3)	721 (7)	564 (8)	335 (8)	15·1 (6·6)
H(5)	854 (3)	300 (4)	419 (5)	7·4 (2·4)
H(6)	991 (6)	351 (3)	637 (5)	10·0 (3·3)
H(71)	573 (14)	470 (9)	183 (11)	20·8 (10·6)
	570	487	203	13·2
H(72)	662 (6)	468 (37)	135 (19)	*
	658	508	106	13·2
H(73)	575 (8)	425 (10)	56 (8)	*
	565	415	54	13·2
H(81)	763 (6)	262 (4)	220 (8)	12·3 (3·9)
	760	279	186	13·2
H(82)	672 (6)	243 (5)	291 (10)	15·3 (5·5)
	682	259	297	13·2
H(83)	629 (7)	274 (3)	110 (9)	15·4 (4·8)
	620	285	110	13·2

* The resultant anisotropic temperature factor was non-positive-definite.

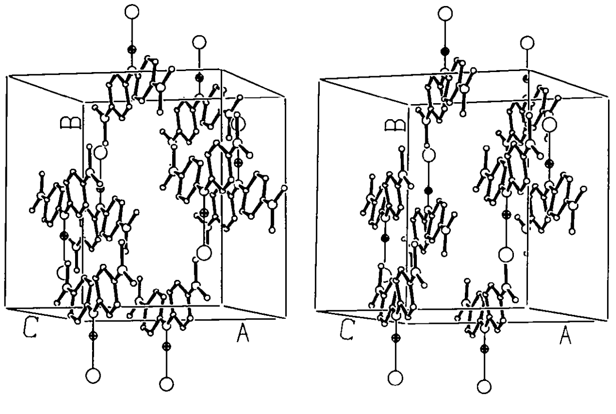

Fig. 2. *ORTEP* (Johnson, 1971) stereoview of the molecular packing. I atoms as large circles, H(1) atoms in hydrogen bridges as small black circles, all other H atoms omitted for clarity.

constrained to threefold symmetry about the N(2)—C bonds and C—H was constrained to 1·03 Å. Only the angles of rotation of the methyl groups about the N(2)—C bonds, the N—C—H angle and the overall isotropic temperature factor for the methyl H atoms were allowed to vary. The resultant angle N—C—H = 103 (3)°; the resultant angles of rotations of methyl groups brought H(73) and H(83) into the plane defined by the benzene ring (see Fig. 1). The position of H(72) from this refinement is (0·66, 0·51, 0·10) which is in a good agreement with its position from the final Fourier map. With the methyl groups thus constrained, the agreement factors ($R = 0{\cdot}165$ and $R_w = 0{\cdot}035$ for all atoms freely refined) rose to $R = 0{\cdot}261$ and $R_w = 0{\cdot}085$. Fractional coordinates of methyl H atoms differ by an average 1·6σ [max. 4·4σ for H(72)] from their unconstrained counterparts. Max. shift = 0·62 Å [for H(72)], mean [without H(72)] = 0·27 Å. Computer programs: *XRAY* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972), *ORFLS* (Busing, Martin & Levy, 1962), *ORFFE* (Busing, Martin & Levy, 1964), *ORTEP* (Johnson, 1971).

Discussion. Fractional coordinates for both X-ray and neutron measurements are listed in Table 1;* the bond distances and angles are plotted in Fig. 1, which also shows the molecular conformation and the numbering of the atoms. The molecular packing is shown in Fig. 2.

The hydrogen bridge I···H(1)—N(1) is linear because all three atoms are in special positions (0, y, 0·25). Although the anisotropy of the thermal ellipsoid of H(1) is very high and its largest amplitude is in the direction of the I···H(1)—N(1) bond, attempts to introduce statistically disordered H(1) positions failed on a very high correlation and the divergence of the refinement.

Comparison of three available sets of atomic coordinates (the X-ray study of TO, and the present X-ray and neutron measurements) shows that for non-hydrogen atoms the average estimated standard deviations are in the ratio 12·7:1:2·4 respectively. Atomic positions of I, N, C atoms resulting from these three refinements agree on average within 0·75σ (σ taken for neutron data) and differ by 2·1σ at the most.

The lower accuracy of the neutron measurement was imposed by the allocated time, the small size of the sample and a very high background caused by the incoherent scattering of H atoms in the sample.

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References

Bacon, G. E. (1972). *Acta Cryst.* A**28**, 357–358.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.

Chesick, J. P. & Davidon, W. C. (1975). *Acta Cryst.* A**31**, 586–591.

Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. W. & Hall, S. R. (1972). The *XRAY* system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Tichý, K. & Honzl, J. (1968). *J. Cryst. Growth*, **2**, 369–372.

Toman, K. & Očenásková, D. (1966). *Acta Cryst.* **20**, 514–520.

Werner, S. A. (1971). *Acta Cryst.* A**27**, 665–669.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

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* Lists of anisotropic thermal parameters, structure factors and a more detailed table of interatomic distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39259 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 6-Chloro-4-phenyl-1,2,3-benzoxathiazine 2,2-Dioxide, $C_{13}H_8ClNO_3S$

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Abstract. $M_r = 293{\cdot}7$, orthorhombic, $Pbca$, $a = 8{\cdot}418$ (1), $b = 14{\cdot}708$ (6), $c = 20{\cdot}564$ (3) Å, $V = 2546{\cdot}1$ Å^3, $Z = 8$, $D_m = 1{\cdot}50$, $D_x = 1{\cdot}53$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}407$ mm^{-1}, $F(000) = 1200{\cdot}0$, room temperature, $R = 0{\cdot}060$ for 1272 observed reflections. Bond lengths and angles are in agreement with expected values. The oxathiazine ring exhibits a distorted half-chair conformation; the chlorophenyl and benzo groups are each planar, with a dihedral angle between these planes of −150·3 (2)°. There are no intermolecular contacts less than van der Waals distances.

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