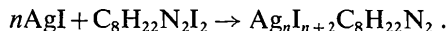


have conductivities approaching those of liquid electrolytes. When AgI is reacted with hexamethylenediamine diiodide, several compounds are formed according to the reaction (Coetzer & Thackeray, 1975)



An investigation into the conductive properties and crystal structures of these compounds is in progress at this laboratory. Here we report the structure of the compound $\text{Ag}_2\text{I}_4\text{C}_8\text{H}_{22}\text{N}_2$ in which the AgI concentration is 67 mol. %.

The structural features of the compound are illustrated in Fig. 1. The I^- ions form tetrahedra, each of which contains an Ag^+ ion at its centre. The mean Ag-I distance within each tetrahedron is $2.857(3)$ Å. The tetrahedral bond angles are listed in Table 2.

Each I^- tetrahedron shares two of its edges to form chains parallel to c . The Ag^+ ions at the centres of the tetrahedra are separated by 3.81 Å.

The amine chain lies along a on a mirror plane at $z = \frac{1}{2}$. It is also situated about a symmetry centre at $(0, \frac{1}{2}, \frac{1}{2})$. The bond lengths and angles within the amine chain are normal (Table 2).

References

- COETZER, J. & THACKERAY, M. M. (1975). Results to be published elsewhere.
 CROMER, D. T. & MANN, J. (1968). *Acta Cryst.* A24, 321-324.

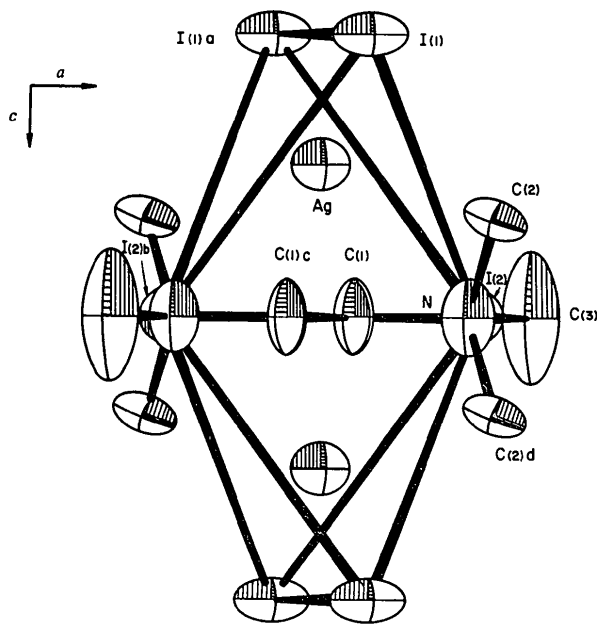


Fig. 1. [010] projection of the structure. The symmetry code for the atoms is given in Table 2.

- GELLER, S. & OWENS, B. B. (1972). *J. Phys. Chem. Solids*, 33, 1241-1250.
 OWENS, B. B. (1970). *J. Electrochem. Soc.* 117, 1536-1539.
 OWENS, B. B. & ARGUE, G. R. (1967). *Science*, 157, 308-309.
 STEWART, J. M., KRUGER, G. J., AMMON, H., DICKINSON, C. H. & HALL, S. R. (1972). Univ. of Maryland Comput. Sci. Tech. Rep. TR-192.

Acta Cryst. (1975). B31, 2342

2-(Nitromethylene)piperidine

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(Received 14 October 1974; accepted 29 March 1975)

Abstract. $\text{C}_6\text{H}_{10}\text{O}_2\text{N}_2$, M.W. 142.2, orthorhombic, $Pbca$, $a = 6.963(1)$, $b = 10.459(3)$, $c = 19.717(7)$ Å, $Z = 8$, $D_x = 1.30$ g cm $^{-3}$, $\mu(\text{Cu } K\alpha) = 0.845$ mm $^{-1}$. The pale-yellow transparent crystals are elongated along [001]. The nitro group is *cis* to the ring N atom.

Introduction. Crystals were supplied by Dr C. Boyce. Preliminary precession photographs of two crystals in different orientations showed the extinction rules: $0k1$: $k = 2n$, $h0l$: $l = 2n$, $hk0$: $h = 2n$, unambiguously defining the space group as $Pbca$. A crystal with approximate dimensions $0.20 \times 0.25 \times 0.18$ mm was glued to a Lindemann glass capillary and mounted on a Nonius

automatic three-circle diffractometer equipped with scintillation counter and pulse-height discriminator. The c axis coincided with the φ axis of the diffractometer. Cell dimensions were obtained from a least-squares fit on θ , $-\theta$ values of 13 reflexions with $\theta \leq 15^\circ$, measured with Cu $K\alpha$ radiation ($\lambda = 1.54182$ Å). In the range $0 \leq \sin \theta/\lambda \leq 0.497$ Å $^{-1}$, 564 unique reflexions, out of a possible 905, were observed using Ni-filtered Cu $K\alpha$ radiation and a $\theta, 2\theta$ scan. Attenuation filters were automatically inserted if the intensity of a reflexion exceeded 2000 c.p.s. A reflexion was considered to be observed when $\frac{1}{2}I > \sigma(I) = [C + B_1 + B_2 + (0.05I)^2]^{1/2}$, in which $\sigma(I)$ is the standard deviation of

the net intensity I , C is the total integrated count, B_1 and B_2 are the background counts measured for half the scan time at each side of the scan, and $I = C - B_1 - B_2$. The normal Lorentz and polarization corrections were applied and structure factors were obtained on a common arbitrary scale.

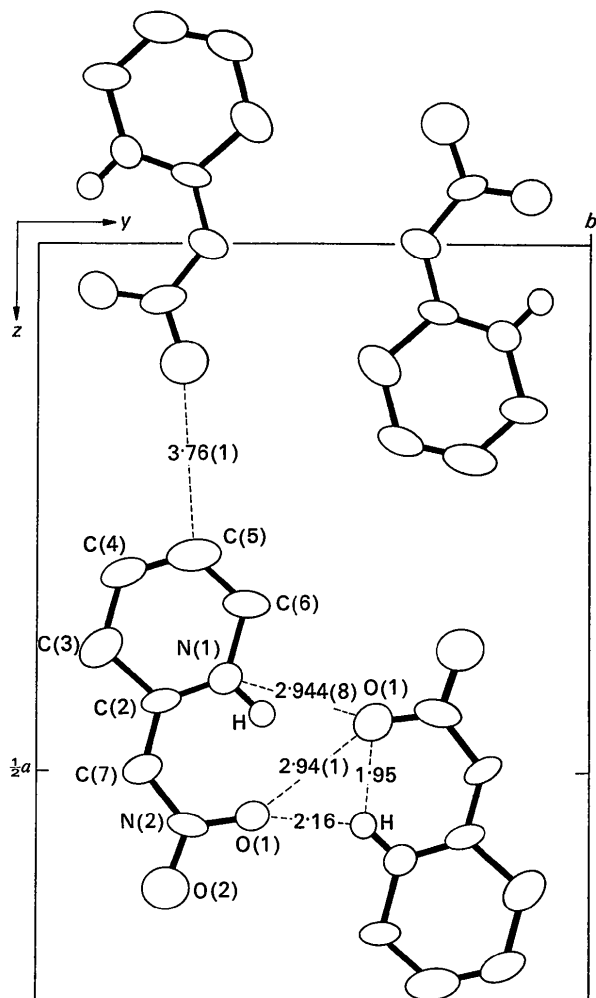


Fig. 1. Projection of the atoms with $-0.07 \leq x \leq 0.07$ on (100). (Shortest intermolecular distances are given in Å.) Figure drawn with ORTEP (Johnson, 1965).]

The Fourier transform method described by Tollin (1970) was employed to obtain the orientation of the molecules with respect to the unit-cell axes; the positions of the molecules within the cell were determined by finding the minimum R value as a function of molecular translation (Bright, Plessius & de Boer, 1973). Refinement of atomic coordinates, scale factor and isotropic temperature factors, using carbon scattering factors for all ring atoms, resulted in a conventional R value, based on F , (observed reflexions only) of 0.34, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|)^2]^{1/2} = 0.45$ (function minimized: $\sum w(|F_o| - |F_c|)^2$), in which $w = [\sigma(F_o)]^{-2}$.

The ring 'carbon' atom *cis* with respect to the nitro group had a temperature factor of 3.6 \AA^2 , while the average value for the other ring atoms was above 6.5 \AA^2 . Therefore we included this atom as nitrogen in the next cycle, resulting in a decrease of R to 0.33 and of R_w to 0.44. Upon refinement this measure reduced R to 0.215 and R_w to 0.265. Allowing for anisotropic vibration and omitting the poorly determined 200 and 002 reflexions resulted in $R = 0.11$, $R_w = 0.14$. The alternative *trans* model with the same parameters refined to this stage gave $R = 0.12$, $R_w = 0.15$.

The largest and roundest peak in a difference electron density map calculated at this stage for the *cis* model, using reflexions with $\sin \theta / \lambda \leq 0.35 \text{ \AA}^{-1}$ only, was consistent with a hydrogen atom attached to the ring nitrogen. The nitromethylene hydrogen was also visible, but the other hydrogens could not be located owing to an apparent conformational disorder of the ring carbon atoms. In the next cycles of refinement all the hydrogen atoms were included at their calculated positions ($C-H = 0.95 \text{ \AA}$, $H-C-H = 110^\circ$). Furthermore a weighting analysis suggested that the standard deviations of the structure factors should be modified as follows: for $\sin \theta / \lambda < 0.335 \text{ \AA}^{-1}$: $\sigma(\text{new}) = \sigma(\text{old}) \times 5.59$; for $\sin \theta / \lambda \geq 0.335 \text{ \AA}^{-1}$: $\sigma(\text{new}) = \sigma(\text{old}) \times 3.660$. Refinement with the new weighting scheme yielded the final values of $R = 0.101$, $R_w = 0.130$;^{*} the error in an observation of unit weight was

^{*} A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31036 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Final least-squares parameters ($\times 10^4$)

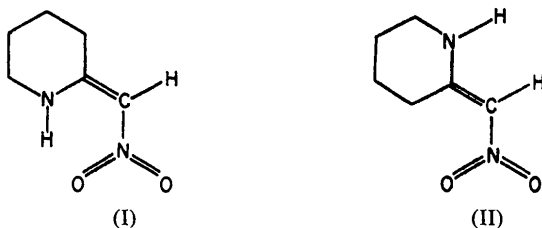
The form of the anisotropic thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Numbers in parentheses here and elsewhere are the estimated standard deviations in the least significant digits.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(2)	547 (9)	7755 (7)	5646 (3)	284 (15)	178 (10)	19 (2)	37 (10)	-7 (4)	-21 (3)
C(3)	672 (12)	8835 (9)	6151 (4)	513 (26)	208 (11)	52 (3)	-12 (15)	6 (7)	-33 (5)
C(4)	496 (22)	8439 (11)	6868 (5)	1098 (59)	252 (16)	35 (3)	150 (25)	-43 (9)	-35 (6)
C(5)	353 (19)	7178 (13)	7036 (4)	730 (42)	363 (22)	34 (3)	-160 (24)	14 (8)	-19 (6)
C(6)	75 (15)	6215 (9)	6564 (3)	746 (37)	229 (11)	23 (2)	119 (16)	4 (6)	1 (4)
N(1)	302 (9)	6581 (6)	5860 (3)	432 (18)	144 (8)	34 (2)	44 (9)	2 (4)	-6 (3)
C(7)	688 (9)	8073 (6)	4996 (3)	325 (18)	176 (8)	29 (2)	13 (10)	-6 (5)	-22 (3)
N(2)	548 (8)	7258 (7)	4460 (2)	286 (14)	231 (10)	21 (2)	12 (9)	4 (4)	19 (3)
O(1)	438 (8)	6081 (5)	4549 (3)	590 (19)	160 (7)	40 (2)	-23 (9)	11 (4)	-7 (3)
O(2)	589 (8)	7662 (6)	3857 (3)	419 (15)	249 (8)	46 (2)	-17 (9)	5 (4)	2 (3)

0.98. A weighting analysis based on ranges of F_o and of $\sin \theta/\lambda$ indicated that the new weighting scheme was satisfactory. The atomic numbering scheme is shown the Fig. 1; the final atomic parameters are listed in Table 1.

Throughout the refinement neutral atomic scattering factors from *International Tables for X-ray Crystallography* (1962) were used. For the refinement and the Fourier maps we used Ibers's version of *ORFLS* (Busing, Martin & Levy, 1962) and Zalkin's (1962) Fourier program.

Discussion. This investigation was undertaken to determine whether the nitro group is *cis* (I) or *trans* (II) to the ring nitrogen atom.



We conclude that the conformation is *cis* for the following reasons: (i) The *cis* model fits the diffraction data significantly better than the *trans* model. With the same number of degrees of freedom $R(cis)=0.11$, $R(trans)=0.12$ and $R_w(cis)=0.14$, $R_w(trans)=0.15$. (ii) Refinement with all the ring atoms included as carbon resulted in too low a temperature coefficient for the atom *cis* with respect to the nitro group. (iii) The hydrogen-atom configuration found is consistent with the *cis* model.

As a result of conformational disorder, the positions of the atoms C(4), C(5), and C(6), although determined with reasonable precision, have not been accurately located. Since our least-squares model is based on spherical atoms and the electron density function in the region of these atoms shows banana-shaped peaks, these atoms appear to be displaced from their expected positions towards the centre of the ring with a consequent shortening of the C–C distances and a widening of the C–C–C angle (Table 2). The N(1)–C(2)–C(3)–C(7)–N(2) group is planar within experimental error (Table 3), and bond lengths and angles in this fragment are within the normal ranges.

The structure consists of layers of molecules with x approximately equal to 0, and $\frac{1}{2}$. The shortest intermolecular distance between the layers is 3.421(8) Å, between O(2) and N(1'). The shortest distances within one layer are shown in Fig. 1.

Table 2. Bond distances (Å) and bond angles (°)

N(1)–C(2)	1.309 (9)*	N(1)–C(2)–C(3)	119.8 (6)†
C(2)–C(3)	1.509 (10)†	C(2)–C(3)–C(4)	114.6 (8)†
C(3)–C(4)	1.478 (14)†	C(3)–C(4)–C(5)	120.6 (7)†
C(4)–C(5)	1.363 (16)†	C(4)–C(5)–C(6)	123.5 (9)†
C(5)–C(6)	1.385 (14)†	C(5)–C(6)–N(1)	115.8 (9)†
C(6)–N(1)	1.448 (9)†	C(6)–N(1)–C(2)	124.8 (6)†
C(2)–C(7)	1.327 (9)	C(3)–C(2)–C(7)	116.5 (7)
C(7)–N(2)	1.362 (8)	N(1)–C(2)–C(7)	123.7 (6)
N(2)–O(1)	1.246 (7)	C(2)–C(7)–N(2)	126.0 (7)
N(2)–O(2)	1.262 (7)	C(7)–N(2)–O(1)	120.9 (5)
		C(7)–N(2)–O(2)	121.4 (7)
N(1)⋯O(1)	2.638 (9)	O(1)–N(2)–O(2)	117.7 (6)

* Estimated standard deviation calculated with *ORFFE* (Busing, Martin & Levy, 1964).

† These parameters are of doubtful accuracy because of the systematic errors in the coordinates of atoms C(4), C(5) and C(6) due to disorder.

Table 3. Distances (Å) to the N(1)–C(2)–C(3)–C(7)–N(2) plane

N(1)	0.002 (6)	N(2)	–0.010 (6)	C(4)	–0.039 (15)
C(2)	0.004 (6)	O(1)	0.073 (6)	C(5)	0.037 (14)
C(3)	–0.016 (9)	O(2)	–0.075 (6)	C(6)	–0.060 (10)
C(7)	0.016 (6)				

On the basis of the distances between the H atom bonded to the ring atom and neighbouring oxygen atoms [$H \cdots O(1) = 1.95$ Å, $H \cdots O(1') = 2.15$ Å] it is difficult to assess whether this atom is involved in inter- or intramolecular hydrogen bonding. Nevertheless, the electronic structure of the –NO₂ group is such that one would expect the oxygen lone pairs to be in the molecular plane. If so, O(1), unlike O(1'), would be in a very favourable position to form an intramolecular hydrogen bond with atom H. The presence of an intramolecular hydrogen bond would moreover explain the preferential formation of the *cis* isomer.

References

- BRIGHT, D., PLESSIUS, H. & DE BOER, J. J. (1973). *J. Chem. Soc. Perkin II*, pp. 2106–2109.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Oak Ridge National Laboratory Report ORNL-TM-306.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202–203. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
- TOLLIN, P. (1970). *Crystallographic Computing*, edited by F. R. AHMED, pp. 90–95. Copenhagen: Munksgaard.
- ZALKIN, A. (1962). *FORDAP, A Fortran Program for Crystallographic Fourier Synthesis*. Personal communication.