Discussion. The disorder is due to the chemical equivalence of the P and As atoms. Weissenberg photographs of some further crystals showed extra weak reflexions corresponding to a doubling of c; these reflexions can be attributed to a supercell containing two ordered anions in opposite orientations.

There is evidence for hydrogen bonding between the N atoms of the cation and O atoms of the anion; several short $O \cdots N$ contacts from 2·55 to 2·8 Å are observed.

Reference

DIXON, H. B. F., SPARKES, M. J. & WEBSTER, D. (1977). *Biochem. Soc. Trans.* **5**, 209–210.

N-Iododimethylamine

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Abstract. $(CH_3)_2NI$, $M_r = 170·98$, orthorhombic, $Pnma$, $a = 10·50$ (2), $b = 7·59$ (2), $c = 5·76$ (1) Å, $V = 459·04$ Å^3, $Z = 4$. The structure is polymeric, with $-N-I-N-I-$ chains, very similar to the framework found in $NI_3.NH_3$.

Introduction. The compound was prepared by the reaction of $NI_3.NH_3$ with $(CH_3)_2NH$ and recrystallized from $(CH_3)_2NH$. The yellow needles decompose slowly at temperatures higher than $-30°C$. For the X-ray measurements the crystals were cooled to $-100°C$ with a Nonius low-temperature device. The cell parameters were determined from precession photographs calibrated with $Pb(NO_3)_2$. The systematic extinctions ($0kl$ for $k + l = 2n + 1$ and $hk0$ for $h = 2n + 1$) are consistent with either $Pnma$ or $Pn2_1a$. The intensities of the layers $h0l$ to $h10l$ were measured with a Stoe two-circle diffractometer (Mo $K\alpha$ radiation, graphite monochromator, ω scan) up to $\theta = 30°$. 800 measured hkl and $hk\bar{l}$ reflexions were averaged yielding 468 unique reflexions, of which 178 were considered unobserved with $\sigma_I > I$ [$\sigma_I = (S + 0·0009I^2)^{1/2}$, where

S is the sum of the scan and background counts, and I the net intensity]. The intensities were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by Patterson and Fourier syntheses and refined by least-squares methods minimizing $\Sigma w(|F_o| - |F_c|)^2$, where $w = \sigma_F^{-2}$ and $\sigma_F = 0·5\sigma_I F_o/I$.

Anisotropic temperature factors for I and isotropic for C and N were used. In the last cycle five individual scale factors (one for each two layers) were refined. The atoms lie on or near planes perpendicular to **b** at $y = 0·0$ or $0·25$. In $Pnma$, where the atoms must lie in these special positions, $R = 0·040$ and $R_w = 0·045$ (20 parameters) were obtained. Refinement in $Pn2_1a$, where the y coordinates are not fixed, did not yield better results ($R = 0·040$ and $R_w = 0·045$, 25 parameters). The refinement of the y coordinates did not converge, the e.s.d.'s were comparatively large, and the values oscillated by nearly this amount. Therefore $Pnma$ seems to be more probable. Scattering factors were taken from Cromer & Mann (1968); the anomalous dispersion correction for I was included (Cromer &

Table 1. *Positional and thermal parameters*

The anisotropic temperature factor is given by: $\exp[-0·25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

	x	y	z	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I	0	0	0	1·38 (2)	0·86 (1)	0·96 (2)	0·02 (8)	−0·04 (8)	0·13 (8)
N	0·1033 (13)	0·25	0·1195 (25)	0·75 (17)					
C(1)	0·2343 (13)	0·25	0·0363 (26)	0·72 (17)					
C(2)	0·1105 (20)	0·25	0·3808 (37)	1·79 (26)					

Liberman, 1970). The final parameters are listed in Table 1.*

Discussion. NI₃.NH₃ (Hartl, Bärnighausen & Jander, 1968), NI₃.pyridine (Hartl & Ullrich, 1974) and CH₃NI₂.½pyridine (Ullrich, 1972) are polymeric. The iodo-amine molecules are connected by intermolecular N—I bonds forming zigzag chains in the direction of **b**. Only one of the I atoms takes part in this bonding. The remaining I atoms form intermolecular bonds with I atoms of adjacent chains or with the N atom of the adduct amine. The compounds are deep red-brown and insoluble. For (CH₃)₂NI a structure with isolated or only weakly connected molecules was assumed. This was concluded from the solubility in (CH₃)₂NH and the IR spectrum (Jander, Knuth & Renz, 1972; Jander, 1976). The present determination, however, reveals a polymeric structure. The same framework of —N—I—N—I— chains as in NI₃.NH₃ is found (Fig. 1). Each I is bound to two N atoms. The N—I—N group is linear and the N—I distances have the same value, 2·29 (1) Å, which is greater than the sum of the covalent radii (2·09 Å), but much shorter than the sum of the van der Waals radii (3·55 Å). The N atom is tetrahedrally coordinated by two methyl groups and two I atoms. The angles deviate by no more than 3° from the tetrahedral value. The C—N distances [1·46 (2), 1·51 (2) Å] lie in the range found for aliphatic amines. The distances between atoms of adjacent chains are longer than the sum of the van der Waals radii.

It is very characteristic for I atoms to form intermolecular contacts with other donor atoms besides

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32764 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
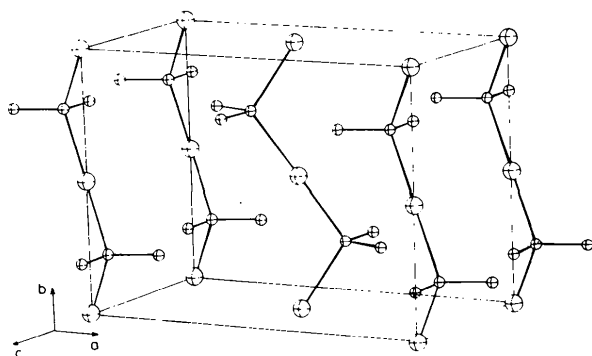

Fig. 1. View of the unit cell of (CH₃)₂NI.

covalent bonds, especially if the I atom is bound to a more electronegative atom. The intermolecular contact is also called a secondary bond (Alcock, 1972). The coordination of the I atom is linear and the lengths of the two bonds are strongly correlated: if the intermolecular bond becomes stronger, the intramolecular bond is weakened. The bonding can be described by a three-centre/four-electron bond.

In (CH₃)₂NI the two bonds have become equal and a distinction between an intra- and intermolecular bond is no longer possible. This symmetrical N—I—N group also occurs in some bis(amine)iodonium compounds, and the N—I distance lies at about 2·30 Å [NI₃.NH₃ 2·30 (1) (Hartl, Bärnighausen & Jander, 1968), NI₃.pyridine 2·36 (4) (Hartl & Ullrich, 1974), bis(hexamethylenetetramine)iodonium triiodide 2·30 (1) (Pritzkow, 1975), bis(quinuclidine)iodonium salts 2·29 (1) Å (Pritzkow, 1977)]. A somewhat shorter distance is found in bis(3-picoline)iodonium tetrafluoroborate [2·24 (2) Å (Osborn, 1972)] and in bis(pyridine)iodonium heptaiodide [2·16 (10) Å (Hassel & Hope, 1961)].

The —N—I—N—I— chain in NI₃.NH₃ cannot be the reason for the red-brown colour, as the same chain is also found in the pale-yellow (CH₃)₂NI. The I—I contacts between the chains, which are no longer possible in (CH₃)₂NI, probably cause the deep colour.

References

ALCOCK, N. W. (1972). *Advanc. Inorg. Chem. Radiochem.* **14**, 2–58.
CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
HARTL, H., BÄRNIGHAUSEN, H. & JANDER, J. (1968). *Z. anorg. allgem. Chem.* **357**, 225–237.
HARTL, H. & ULLRICH, D. (1974). *Z. anorg. allgem. Chem.* **409**, 228–236.
HASSEL, O. & HOPE, H. (1961). *Acta Chem. Scand.* **15**, 407–416.
JANDER, J. (1976). *Advanc. Inorg. Chem. Radiochem.* **19**, 1–64.
JANDER, J., KNUTH, K. & RENZ, W. (1972). *Z. anorg. allgem. Chem.* **392**, 143–158.
OSBORN, R. S. (1972). PhD Thesis, Univ. of London.
PRITZKOW, H. (1975). *Acta Cryst.* B**31**, 1505–1506.
PRITZKOW, H. (1977). Unpublished results.
ULLRICH. D. (1972). Thesis. Freie Univ. Berlin.