Acta Cryst. (1975). B**31**, 1505

Bis(hexamethylenetetramine)iodonium Triiodide

By H. Pritzkow

Anorganisch-Chemisches Institut, Universität Heidelberg, 69 Heidelberg, Germany (BRD)

(*Received* 15 *January* 1975; *accepted* 29 *January* 1975)

Abstract. $[(C_6H_{12}N_4)_2I]I_3$, $M=788\cdot0$, monoclinic, $P2_1$, $a=9\cdot790$ (2), $b=18\cdot592$ (4), $c=5\cdot988$ (2) Å, $\beta=102\cdot81$ (2)°, $V=1062\cdot8$ Å^3, $Z=2$, $D_m=2\cdot40$, $D_c=2\cdot462$ g cm^{-3}. The structure consists of almost centrosymmetric cations $(C_6H_{12}N_4)_2I^+$ and asymmetric triiodide anions. The N–I distances within the cation are significantly longer than in the corresponding bis(pyridine)iodonium cations.

Introduction. The compound was prepared by the method of Bowmaker & Hannan (1971). The systematic absences ($0k0$ for $k=2n+1$) are consistent with either of the space groups $P2_1$ or $P2_1/m$. The former was confirmed by an acentric intensity distribution and by the structure determination. The reflexions of the layers $hk0$ to $hk7$ were measured with a Stoe two-circle diffractometer (Mo $K\alpha$ radiation, graphite monochromator, ω-scan) up to $\theta=28°$. 79 of the 1833 measured reflexions were considered to be unobserved, with $\sigma_I > I[\sigma_I=\{S+(0\cdot03I)^2\}^{1/2}$, S is the sum of the scan and background counts, I is the net intensity]. The intensities of some reflexions, which were measured after every layer, decreased by 12% during the data collection. A scale factor for each layer was calculated according to the decrease. In the last cycle the scale factors were refined. The intensities were corrected for Lorentz and polarization effects and absorption ($\mu=59\cdot5$ cm^{-1}, crystal dimensions $0\cdot050\times0\cdot028\times0\cdot160$ mm). The structure was solved by Patterson and Fourier syntheses and refined by the least-squares method minimizing $\sum w(|F_o|-|F_c|)^2$ (the weight w was set equal to σ_F^{-2}, $\sigma_F=0\cdot5\sigma_I F_o/I$). Anisotropic temperature factors for iodine and isotropic temperature factors for carbon and nitrogen were used. The calculated positions of the hydrogen atoms ($r_{C-H}=0\cdot95$ Å) were included, but not refined. The final conventional R value for the observed reflexions is 0·039 (for all reflexions 0·043), the weighted R value is 0·037. The scattering factors for I, N and C were taken from the tables of Hanson, Herman, Lea & Skillman (1964), for H from *International Tables for X-ray Crystallography* (1968). The final parameters are listed in Table 1.*

Discussion. The reaction of hexamethylenetetramine (HMT) and iodine at room temperature in a concentrated solution yields a brown product, bis(hexamethylenetetramine)iodonium triiodide $[(HMT)_2I]I_3$ and not hexamethylenetetramine-1-diiodine (HMT.I_2). This was shown by careful analyses of the vibrational

Table 1. *Positional and thermal parameters with their e.s.d.'s in parentheses*

	x	y	z	B
I(1)	0·15421 (12)	0·19197 (6)	0·70252 (20)	
I(2)	0·27572 (11)	0·09538 (7)	0·41184 (19)	
I(3)	0·40233 (13)	0·0	0·13229 (22)	
I(4)	0·40606 (9)	0·33547 (6)	0·20065 (14)	
N(1)	0·5797 (11)	0·2717 (6)	0·0856 (18)	2·32 (21)
N(2)	0·8315 (12)	0·2628 (6)	0·1223 (19)	3·08 (24)
N(3)	0·6861 (11)	0·1555 (6)	0·0604 (18)	2·78 (22)
N(4)	0·6698 (11)	0·2424 (6)	−0·2474 (18)	2·58 (21)
C(1)	0·5750 (14)	0·1916 (8)	0·1386 (22)	2·83 (26)
C(2)	0·7212 (14)	0·3002 (8)	0·1995 (23)	2·79 (27)
C(3)	0·8207 (15)	0·1868 (8)	0·1688 (24)	3·43 (29)
C(4)	0·5616 (14)	0·2799 (8)	−0·1676 (22)	2·66 (26)
C(5)	0·8046 (16)	0·2743 (9)	−0·1271 (25)	3·49 (30)
C(6)	0·6680 (15)	0·1661 (9)	−0·1919 (26)	3·53 (29)
N(1′)	0·2328 (11)	0·4045 (6)	0·2991 (17)	2·32 (20)
N(2′)	−0·0193 (12)	0·4206 (6)	0·2181 (18)	2·78 (22)
N(3′)	0·1361 (12)	0·5239 (6)	0·2879 (18)	2·76 (22)
N(4′)	0·1201 (12)	0·4430 (6)	0·6003 (18)	2·68 (22)
C(1′)	0·2494 (14)	0·4819 (8)	0·2365 (23)	2·77 (26)
C(2′)	0·0940 (14)	0·3776 (8)	0·1656 (23)	3·05 (27)
C(3′)	−0·0012 (15)	0·4975 (9)	0·1593 (24)	3·22 (28)
C(4′)	0·2341 (14)	0·3999 (8)	0·5466 (22)	2·89 (27)
C(5′)	−0·0169 (15)	0·4139 (8)	0·4631 (23)	3·01 (27)
C(6′)	0·1364 (16)	0·5183 (8)	0·5339 (24)	3·18 (29)

Table 1 (*cont.*)

The form of the anisotropic temperature factor is

$$\exp\left[-0\cdot25(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)\right].$$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I(1)	3·53 (7)	3·67 (5)	5·17 (6)	−0·51 (4)	0·95 (4)	−0·42 (5)
I(2)	2·83 (4)	3·24 (4)	4·15 (5)	−0·62 (4)	0·18 (4)	0·43 (4)
I(3)	3·76 (6)	3·76 (6)	6·75 (7)	0·29 (5)	0·24 (5)	0·90 (5)
I(4)	2·20 (3)	2·46 (4)	2·67 (3)	0·22 (4)	0·83 (3)	−0·20 (4)

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30893 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

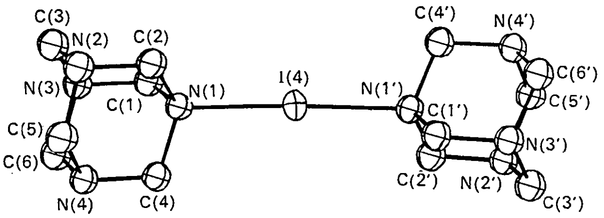

Fig. 1. View of the cation $[(C_6H_{12}N_4)_2I]^+$.

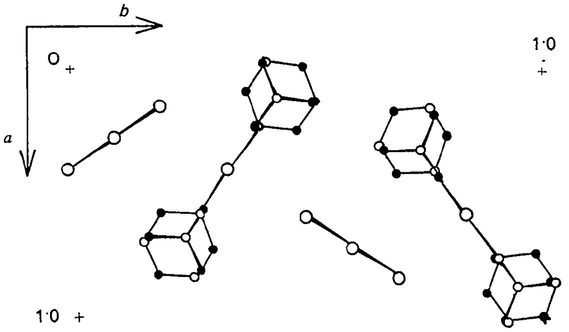

Fig. 2. Projection of the structure on the *ab* plane.

spectra of the brown compound (Bowmaker & Hannan, 1971). The calculated N–I force constant appeared to be considerably bigger than those for the bis(pyridine)iodonium compounds. The present structure determination was undertaken in order to elucidate the N–I bond length.

The structure contains discrete triiodide anions and $[(HMT)_2I]^+$ cations. The intermolecular distances are longer than the sum of the van der Waals radii. The cation is not strictly centrosymmetric. The group N(1)–I(4)–N(1′) is almost linear [176·5 (4)°]. The angles I(4)–N–C at the two nitrogen atoms N(1) and N(1′) have values between 108·0 and 112·5°.

This geometrical configuration can be explained by a simple MO model: a three-centre four-electron (3c, 4e) bond formed by the two lone electron pairs of the nitrogen atoms and an empty 5*p* orbital (parallel to the bond axis) of the iodine atom. The two N–I distances have the same length [2·30 (1) Å], but are significantly longer than those in the bis(pyridine)iodonium cation [2·16 (10) Å: Hassel & Hope, 1961] and in the bis-(3-picoline)iodonium cation [2·24 (2) Å: Osborn, 1972]. The shorter bond in the aromatic compounds can be rationalized in terms of π bonding between the nitrogen and iodine atoms. One of the 5*p* orbitals (perpendicular to the ring planes) overlaps with the π systems of the two rings and forms an additional bond (Sabin, 1971). This is not possible in the $[(HMT)_2I]^+$ cation. These results are in contrast to the calculated force constant for $[(HMT)_2I]^+$ (Bowmaker & Hannan, 1971). The disagreement may be caused by the model used for the force constant calculation. Furthermore the Raman spectra of the triiodide and perchlorate salts are quite different (Jander & Maurer, 1975). A calculation based on the values for the perchlorate salt revealed a valence force constant which is almost identical with those reported for the bis(pyridine)iodonium cations. A still lower value is to be expected for the comparatively long N–I bond in $[(HMT)_2I]^+$.

The arrangement found in $[(HMT)_2I]^+$ is very similar to the N–I–N group in the chains of nitrogen triiodide-1-ammonia $NI_3.NH_3$, which is centrosymmetric and has N–I bonds of the same length [2·30 (1) Å: Hartl, Bärnighausen & Jander, 1968]. The N–I distance in $[(HMT)_2I]^+$ is shorter by 0·14 and 0·20 Å respectively than the N–I distances in the 1:1 and 1:2 adducts of HMT and iodine (Pritzkow, 1975). This is also found for the pyridine compounds (Hassel & Hope, 1961; Hassel, Rømming & Tufte, 1961) and is predicted by the 3c,4e model. The formation of the cation has no marked effect on the HMT molecules. The N–C distances range from 1·435 to 1·525 Å with an estimated standard deviation of 0·02 Å. The mean value (1·475 Å) is in good agreement with the N–C distance found in HMT [1·476 (2) Å: Becka & Cruickshank, 1963)]. The angles N–C–N (range: 109·1 to 113·7°, e.s.d. 1·2°, mean value 110·7°) and C–N–C (range: 106·9 to 111·2°, e.s.d. 1·1°, mean value 108·9°) show more pronounced deviations from the values in HMT [113·2 (2) and 107·5 (2)° respectively]. As the estimated standard deviations are comparatively large, these differences are not significant.

The triiodide anion is almost linear [178·62 (6)°] and the two I–I distances are different [2·899 (2) and 2·931 (2) Å]. This is in agreement with the structures of other triiodides (Runsink, Swen-Walstra & Migchelsen, 1972, and references therein). The observed asymmetry may be due to the electrostatic field in the crystal.

I thank Professor Jander for his interest in this work and the VW-Stiftung for financial support.

References

Becka, L. N. & Cruickshank, D. W. J. (1963). *Proc. Roy. Soc.* A**273**, 435–454.

Bowmaker, G. A. & Hannan, S. F. (1971). *Aust. J. Chem.* **24**, 2237–2248.

Hanson, H. P., Herman, F., Lea, J. D. & Skillman, S. (1964). *Acta Cryst.* **17**, 1040–1044.

Hartl, H., Bärnighausen, H. & Jander, J. (1968). *Z. anorg. allgem. Chem.* **357**, 225–237.

Hassel, O. & Hope, H. (1961). *Acta Chem. Scand.* **15**, 407–416.

Hassel, O., Rømming, C. & Tufte, T. (1961). *Acta Chem. Scand.* **15**, 967–974.

International Tables for X-ray Crystallography (1968). Vol. III, p. 202. Birmingham: Kynoch Press.

Jander, J. & Maurer, A. (1975). In preparation.

Osborn, R. S. (1972). Ph.D. Thesis, Univ. of London.

Pritzkow, H. (1975). *Acta Cryst.* In the press.

Runsink, J., Swen-Walstra, S. & Migchelsen, T. (1972). *Acta Cryst.* B**28**, 1331–1335.

Sabin, J. R. (1971). *J. Mol. Struct.* **7**, 407–419.