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Distortion of the Hexamethylenetetramine Cage System by Protonation: X-ray Structure of 1,3,5,7-Tetraazaadamantan-1-ium Bromide,* $[(CH_2)_6N_4H]Br$

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Abstract. $M_r = 221{\cdot}11$, rhombohedral, $R3m$, $a = 8{\cdot}986\ (1)$, $c = 9{\cdot}276\ (1)$ Å (hexagonal axes, obverse setting), $U = 648{\cdot}7$ Å^3, $Z = 3$, $D_m = 1{\cdot}704$, $D_x = 1{\cdot}698$ g cm^{-3}, μ(Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å) = 46·5 cm^{-1}. Final $R = 0{\cdot}016$ for 210 unique data. The protonated hexamethylenetetramine cage retains its idealized $3m$ symmetry in the crystal, and the three equivalent C—N bonds involving the quaternary N atom are significantly longer than the remaining C—N bonds in the saturated heterocycle. These structural features provide an insight into the mechanism of acid hydrolysis of hexamethylenetetramine in aqueous solution.

Introduction. Crystallographic studies (Hanic & Šubrtová, 1969; Mak, Ladd & Povey, 1979, and references cited therein; Hon, Mak & Trotter, 1982, and references cited therein; Shao, Wang, Zheng & Tang, 1982) have shown that quaternization of one N atom of hexamethylenetetramine $[(CH_2)_6N_4]$, as in adduct and salt formation, profoundly distorts its highly symmetric cage structure. In all cases the endocyclic C—N$_{\text{quaternary}}$ bonds and adjacent C—N$_{\text{tertiary}}$ bonds are significantly lengthened and shortened, respectively, relative to the remaining bonds in the hexamethylenetetramine cage system. These results have an important bearing on the mechanisms of the Delépine and Sommelet reactions in organic synthesis (Blažević, Kolbah, Belin, Šunjić & Kajfež, 1979). As hexamethylenetetramine generally behaves as a monoacidic base and readily undergoes various acid-catalyzed fragmentation processes (Walker, 1964; Blažević *et al.*, 1979), we decided to investigate the effect of protonation on its molecular geometry through an X-ray analysis of 1,3,5,7-tetraazaadamantan-1-ium bromide, $[(CH_2)_6N_4H]Br$.

Experimental. Prepared by mixing an aqueous solution of $(CH_2)_6N_4$ and 47% HBr in 1:1 molar ratio, slow evaporation in air at room temperature, D_m measured by flotation in *n*-hexane/CCl$_4$, transparent prisms elongated along **c**, preliminary Weissenberg and precession photographs indicated rhombohedral symmetry, single crystal, approximately 0·12 × 0·20 × 0·25 mm, least squares, 20 high-angle reflections, Nicolet $R3m$ automated four-circle diffractometer, graphite-monochromatized Mo $K\alpha$, 565 total, 210 unique with $I > 1{\cdot}5\sigma(I)$, $0° < 2\theta < 55°$, ω–2θ scan technique, variable scan speeds between 2·5 and 8° min^{-1}, no absorption correction.

Symmetry considerations show that both the $[(CH_2)_6N_4H]^+$ and Br^- ions are located in sites of $3m$ symmetry. With the Br atom arbitrarily fixed at the origin, trial coordinates for the two C and two N atoms were deduced from the known molecular dimensions of $(CH_2)_6N_4$ (Becka & Cruickshank, 1963) and a reasonable estimate of the N—H···Br ionic separation. These five atoms were refined anisotropically to $R = 0{\cdot}027$, and the highest peaks in the resulting difference Fourier map corresponded to H atoms of the methylene groups. In subsequent calculations, the methylene H atoms were generated on the basis of sp^3 hybridization of their respective C atoms, and were allowed to ride on them with U_{iso} fixed at 0·05 Å^2. $R_w = 0{\cdot}021$, $S = 0{\cdot}840$; maximum parameter shift to error ratio in final cycle was −0·042, average ratio was 0·013, final difference

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* Adamantane is tricyclo[3.3.1.1^{3,7}]decane.

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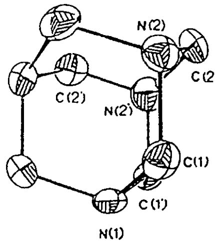
map essentially flat, maxima and minima between 0·28 and −0·18 e Å^{-3}, $F(000) = 335{\cdot}90$; Nova 3 minicomputer, *SHELXTL* program package (Sheldrick, 1981), complex neutral-atom scattering factors taken from *International Tables for X-ray Crystallography* (1974), weighting scheme employed for blocked cascade least-squares refinement and analysis of variance was $w = [\sigma^2(F) + 0{\cdot}0005|F|^2]^{-1}$.

Discussion. The final positional parameters for the non-H atoms are given in Table 1.* Atom labelling and dimensions of the $[(CH_2)_6N_4H]^+$ ion are shown in Fig. 1. Packing of the ions in a rhombohedral unit cell is depicted in Fig. 2.

To our knowledge the structure of the 1,3,5,7-tetraazaadamantan-1-ium cation (Fig. 1) has been determined for the first time. Although the acidic H atom could not be located from the final difference map, it is undoubtedly bonded to N(1) and directed towards Br^-. Protonation of hexamethylenetetramine results in a reduction in molecular symmetry from $\bar{4}3m$ to $3m$, and the N(1)—C(1) bond [1·512 (8) Å] is considerably lengthened relative to the other two unique C—N bonds and the standard bond length of 1·476 (2) Å in crystalline hexamethylenetetramine (Becka & Cruickshank, 1963). The precision of the present analysis is insufficient to differentiate between the N(2)—C(1) and N(2)—C(2) bonds, but the overall bond-length variation in the protonated cage does conform to the general trend for $(CH_2)_6N_4.BH_3$ (Hanic & Šubrtová, 1969), $(CH_2)_6N_4O$ (Mak *et al.*, 1979), $(CH_2)_6N_4O.H_2O_2$ (Mak & Lam, 1978), $(CH_2)_6N_4O.HCO_2H$ (Lam & Mak, 1978), $(CH_2)_6N_4O.(NH_2)_2CS$ (Yu & Mak, 1978), $[(CH_2)_6N_4CH_3]_2I_8$ (Hon, Mak & Trotter, 1979), $[(CH_2)_6N_4CH_3]I_3$ (Hon *et al.*, 1982), and $[(CH_2)_6N_4CH_2C_6H_5]Cl$ (Shao *et al.*, 1982). On the other hand, the C(1)—N(1)—C(1′) and N(1)—C(1)—N(2) bond angles (Fig. 1) are significantly larger and smaller, respectively, than the corresponding angles in the aforementioned adducts and salts of hexamethylenetetramine. This result is in accord with the VSEPR expectation that the exocyclic H atom exerts a much weaker repulsion on the neighboring C—N bonds in comparison with a nitrogen lone pair.



C(1)—N(1)—C(1′)	109·7 (3)	[109]
C(1)—N(2)—C(2)	108·8 (3)	[112]
C(2)—N(2′)—C(2′)	108·4 (4)	[111]
N(1)—C(1)—N(2)	108·5 (5)	[106]
N(2)—C(2)—N(2′)	112·7 (6)	[106]
N(1)—C(1)	1·512 (8)	[1·56]
N(2)—C(1)	1·458 (7)	[1·46]
N(2)—C(2)	1·465 (5)	[1·50]

Fig. 1. A perspective view of the $[(CH_2)_6N_4H]^+$ ion with the non-H atoms shown as 40% thermal ellipsoids. Bond lengths (Å) and bond angles (°) are given with e.s.d.'s in parentheses, and the corresponding MNDO values are enclosed in square brackets.

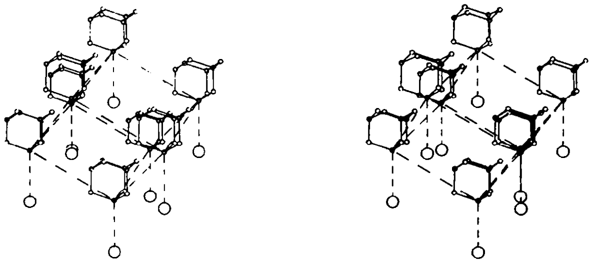


Fig. 2. Stereoscopic view of the packing of the $[(CH_2)_6N_4H]^+$ and Br^- ions. The edges of a rhombohedral unit cell [origin shifted from Br to N(1) for the sake of clarity] is outlined and N-H···Br ionic interactions are indicated by broken lines.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

U_{eq} calculated as $\frac{1}{3}$ of the trace of the orthogonalized **U** matrix.

	Site symmetry	x	y	z	U_{eq}(Å^2)
Br	$3m$	0	0	0	0·0381 (2)
N(1)	$3m$	0	0	0·3421 (5)	0·036 (1)
N(2)	m	0·1809 (4)	0·0905 (2)	0·5529 (4)	0·036 (1)
C(1)	m	0·1834 (10)	0·0917 (5)	0·3958 (6)	0·037 (2)
C(2)	m	0·0881 (5)	0·1762 (10)	0·6027 (6)	0·041 (2)

The equilibrium geometry of the $[(CH_2)_6N_4H]^+$ cation has been calculated in a recent MNDO study of hexamethylenetetramine and related cage systems (Ip, Li & Mak, 1982). Comparison of the calculated and experimental molecular dimensions (Fig. 1) shows that the MNDO model correctly reproduces the pattern of C—N bond-length variation albeit exaggerating the differences. Agreement of the bond angles is, however, far from satisfactory, and the MNDO values fail to reflect the stereochemical significance of the nitrogen lone pairs.

When an aqueous solution of hexamethylenetetramine is heated in the presence of strong acids, hydrolysis to ammonia and formaldehyde proceeds at a rate which depends on the temperature and the acid strength. The reaction

$$(CH_2)_6N_4 + 2H_2SO_4 + 6H_2O \rightarrow 2(NH_4)_2SO_4 + 6CH_2O$$

is quantitative and constitutes the basis of several standard methods of analysis of the heterocyclic amine. In view of the present finding, the hydrolysis mechanism most likely involves an initial step in which rupture of a C—N$_{\text{quaternary}}$ bond is assisted by nucleophilic

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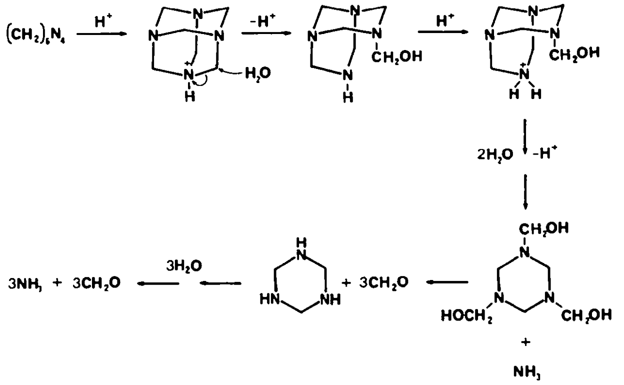
* Lists of structure factors, anisotropic thermal parameters, and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38121 (5 pp). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

attack of a water molecule on the α-carbon atom, as illustrated in the scheme below.



The present crystal structure (Fig. 2), which is isostructural with those of $(CH_2)_6N_4.BH_3$ and $(CH_2)_6N_4O$, can be derived from a cubic unit cell of hexamethylenetetramine (space group $I\bar{4}3m$, $Z = 2$) by first removing the $(CH_2)_6N_4$ molecule at the body-center, then introducing the proton and Br^- ion in the [111] direction to each remaining molecule, and finally extending the resulting primitive rhombohedral lattice along [111] until optimum packing is achieved. The observed N(1)···Br separation of 3·173 (5) Å is in good agreement with the mean value of 3·37 (15) Å for weak hydrogen bonds of the type $N—N^+\cdots Br^-$ (Joesten & Schaad, 1974). All van der Waals contacts of Br^- with neighboring C and H atoms are longer than 3·80 and 3·02 Å, respectively.

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Structure of 2,3-Diphenylpyrazine, $C_{16}H_{12}N_2$

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Abstract. $M_r = 232·28$, monoclinic, $C2/c$, $a = 25·849$ (4), $b = 10·277$ (4), $c = 19·011$ (3) Å, $\beta = 97·51$ (1)°, $V = 5007·0$ Å^3, $D_x = 1·233$ Mg m^{-3}, $Z = 16$, $F(000) = 1952$, μ (Cu $K\alpha$) = 0·58 mm^{-1}. The final R was 0·0605 for 4149 unique reflections. Each of the two independent molecules has approximate 2 (C_2) symmetry and the molecular geometries are nearly the same; the two pyrazine rings are essentially planar and the dihedral angles between the two phenyl substituents and the pyrazine rings are 51·4 and 40·2° for one molecule and 51·0 and 38·0° for the other.

Introduction. Since pyrazine derivatives are of interest due to their pharmacological activity and natural occurrence (Sammes, 1975; Cheeseman & Werstiuk, 1972), syntheses and reactivities of a series of pyrazines

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