Molecular and Crystal Structure of Hexamethylenetetramine Oxide †

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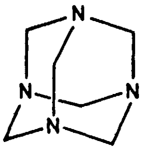
The crystal and molecular structure of hexamethylenetetramine oxide, $(CH_2)_6N_4O$, has been determined by *X*-ray analysis and the structure refined by full-matrix anisotropic least squares to *R* 0.053 for 228 diffractometer data. Crystals are trigonal, space group *R*3*m*, with $Z = 3$ in a hexagonal unit cell of dimensions: $a = 9.464(1)$ and $c = 6.789(1)$ Å. The cage molecule retains its idealized 3*m* symmetry in the crystal. The $N\rightarrow O$ dative bond of 1.363(6) Å is the shortest formal single bond between nitrogen and oxygen yet reported. The three sets of C–N bonds disposed successively further away from the polar *N*-oxide function vary in the order long, short, and normal, relative to the C–N bond in hexamethylenetetramine. Values of C–N–C angles at tertiary and quaternary nitrogen atoms suggest that the formally negative exocyclic oxygen atom is comparable to a lone pair in regard to stereochemical significance.

RECENTLY it has been shown that aqueous hydrogen peroxide readily oxidizes hexamethylenetetramine, $(CH_2)_6N_4$ (I) to its *N*-oxide, 1,3,5,7-tetra-aza-adamantane *N*-oxide, $(CH_2)_6N_4O$ (II).[1] In the present work, we determined the *X*-ray structure of (II) in order to assess the perturbation of the polar *N*-oxide group on the highly symmetric $(CH_2)_6N_4$ cage system. The analysis is of additional interest since it provides a direct comparison, through the measured interior angles at the tertiary and quaternary N atoms, of the relative repelling powers of the formally negative exocyclic oxygen atom *versus* a lone pair, in the context of the valence-shell electron-pair repulsion (VSEPR) theory.



(I)

EXPERIMENTAL

Crystals of hexamethylenetetramine oxide were prepared as described in ref. 1. As the compound is very hygroscopic, roughly spherical single crystals, diameter 0.5 mm, were mounted for *X*-ray study in Lindemann glass capillaries filled with paraffin wax. Accurate unit-cell parameters were determined by a weighted ($w = \tan\theta$) least-squares fit to the θ values of 14 reflections.

Crystal Data.—$C_6H_{12}N_4O$, $M = 156.16$. Trigonal, hexagonal axes $a = 9.464(1)$, $c = 6.789(1)$ Å, $U = 526.6$ Å^3, $D_m = 1.472(5)$ g cm^{-1} (by flotation), $Z = 3$, $D_c = 1.477$ g cm^{-3}. Space group *R*3*m* (No. 160),‡ from systematic absences $-h + k + l \neq 3n$. Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) = 8.4 cm^{-1}.

The intensities of 228 unique reflections with $\theta \leqslant 70°$ were collected at the University of Surrey on a Siemens four-circle diffractometer with Cu-K_α radiation. Data were corrected for Lorentz and polarization factors but absorption correction was considered unnecessary.

Of the three possible space groups consistent with the systematic absences, only *R*3*m* is compatible with the allowed point-group symmetry (3*m*) of the hexamethylenetetramine oxide molecule. From the known molecular dimensions of hexamethylenetetramine,[3] a set of trial co-ordinates was deduced for the carbon and nitrogen atoms, the *z* co-ordinate of N(1) being arbitrarily fixed at zero in order to define the cell origin. The *z* parameter of the oxygen atom was assigned by taking the $N(1)\rightarrow O$ bond as 1.388 Å, the observed value in Me_3NO.[4] Full-matrix anisotropic refinement of all five non-hydrogen atoms (Figure 1) yielded a conventional *R* of 0.061. The positions of the methylene hydrogen atoms were next generated by (i) assuming local *mm*2 (C_{2v}) symmetry for each methylene group, (ii) taking the C–H bond distance as 1.00 Å, and (iii) relating the angles H–C–H (α) and N–C–N (β) at each carbon atom through the relation $\cot^2(\alpha/2) + \cot^2(\beta/2) = 1$ for tetrahedral sp^3 hybrids.[5] Inclusion of these hydrogen atoms with *B* 4.0 Å^2 in another two cycles gave a final *R* of 0.053. A calculated Fourier difference map was featureless.

X-Ray scattering factors for non-hydrogen atoms were taken from ref. 6, whereas for hydrogen the form factor for a bonded hydrogen in the hydrogen molecule[7] was used. Structure-factor and least-squares calculations were carried out on an ICL 1904A computer with a local adaptation of ORFLS.[8] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, the weighting scheme being that of ref. 9 with $w = (2A + |F_o| + 2|F_o|^2/B)^{-1}$, where *A* and *B* were taken as 1.5 and 120.0 respectively. Anisotropic thermal parameters and structure factors are listed in Supplementary Publication No. SUP 22427 (5 pp., 1 microfiche).§

DISCUSSION

Description of Molecular Structure.—Final positional parameters are listed in the Table, and bond lengths and angles in Figure 1. Oxidation of hexamethylenetetramine (I) to its *N*-oxide (II) results in a reduction in molecular symmetry from $\bar{4}3m(T_d)$ to $3m(C_{3v})$ and markedly differentiates the C–N single bonds into three

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† 1,3,5,7-Tetra-aza-adamantane *N*-oxide.

‡ The corresponding primitive rhombohedral unit cell, with $a_{rh} = 5.914$ Å, $\alpha = 106.3°$, and $Z = 1$, is in the obverse setting adopted as standard in ref. 2.

§ See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.

types. Type 1 bonds, which involve the formally positive quaternary N(1) atom, are unusually long [1.514(2) Å]. However, the next set of C–N bonds (Type 2), away from the *N*-oxide functional group, are considerably shorter [1.445(7) Å]. Type 3 bonds, being most remote from the site of perturbation, have a normal length of 1.474(4) Å which corresponds to the observed value [1.476(2) Å] in crystalline hexamethylenetetramine.[3] The three types of C–N bonds thus vary in the order: long, short, normal. Similar perturbation of ring geometry has been reported recently for cycloheptasulphur oxide[10] and cyclo-octasulphur oxide.[11] The general trend of bond alternation in a ring system caused by an exocyclic oxygen atom may be rationalized as follows. In the present molecule, the formally positive N(1) atom induces its neighbouring C(1) atom to rehydridize so as to shift more *p* character into its hybrid atomic orbital towards N(1). In consonance with the idea of isovalent hybridization,[12] C(1) will direct enhanced *s* character into its remaining hybrids towards N(2) and the methylene H atoms. The C(1)–N(1) (Type 1) and C(1)–N(2) (Type 2) bonds are thus respectively lengthened and shortened relative to the C(2)–N(2) (Type 3) bond which, being farthest from the polar *N*-oxide group, remains virtually unaffected by the perturbation.

Final positional parameters and, in parentheses, estimated standard deviations of those varied in the least-squares refinement

Atom	Equivalent set	Point symmetry	x	y	z
O	3(*a*)	3*m*	0	0	−0.200 7(9)
N(1)	3(*a*)	3*m*	0	0	0
N(2)	9(*b*)	*m*	−0.085 9(2)	0.0859	0.294 3(8)
C(1)	9(*b*)	*m*	−0.086 0(2)	0.0860	0.081 5(7)
C(2)	9(*b*)	*m*	0.083 6(2)	−0.0836	0.366 8(10)
H(1)	18(*c*)	1	−0.2018	0.0270	0.0343
H(2)	9(*b*)	*m*	0.1412	−0.1412	0.3157
H(3)	9(*b*)	*m*	0.0820	−0.0820	0.5126

The N(1)→O dative bond [1.363(6) Å] is the shortest formal single bond yet established between nitrogen and oxygen. Bond alternation in the heterocyclic ring system provides a means of piling up more positive charge on N(1), resulting in enhanced polarity of the N(1)→O bond. Absence of such a synergic mechanism in Me_3NO accounts for the fact that its N–O bond is significantly longer [1.388(5) Å].[4] The N(1)→O bond is also shorter than corresponding N→O distances of 1.380—1.391 Å in three crystalline adducts of composition $(CH_2)_6N_4O{\cdot}HCO_2H$ (ref. 13), $(CH_2)_6N_4O{\cdot}H_2O_2{\cdot}H_2O$ (ref. 14), and $(CH_2)_6N_4O{\cdot}(NH_2)_2CS$ (ref. 15). This difference is understandable in view of the fact that the oxygen atom of the $(CH_2)_6N_4O$ molecule serves as proton acceptor in hydrogen bonding in all three adducts.

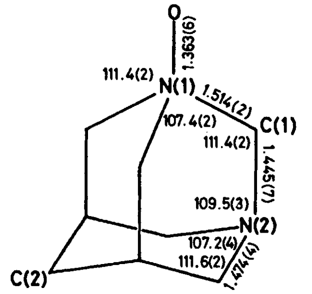

FIGURE 1 Molecular dimensions of (II), bond lengths (Å) angles (°). Atom numbering as for Table

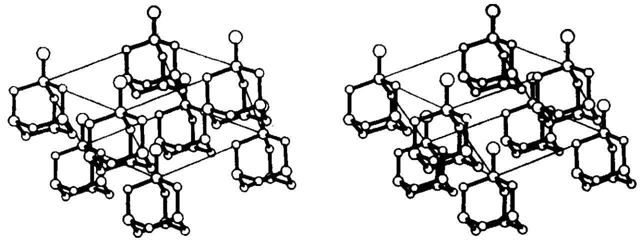

FIGURE 2 Stereodiagram showing a rhombohedral unit cell of (II)

The mean C–N–C bond angle is smaller than the mean N–C–N angle, in accord with the general trend in hexamethylenetetramine,[3] its molecular adducts,[16] and the aforesaid molecular adducts of hexamethylenetetramine oxide. Around the quaternary nitrogen atom N(1), O–N–C is considerably larger than C–N–C. The similar C–N–C angles at the tertiary and quaternary nitrogen atoms suggest that the formally negative exocyclic oxygen atom behaves like a lone pair in regard to stereochemical significance.

Description of Crystal Structure.—Figure 2 shows a PLUTO[17] stereoplot of the molecular packing. The present crystal structure is isostructural with that[18] of hexamethylenetetramine–borine, $(CH_2)_6N_4{\cdot}BH_3$, and is related to that of hexamethylenetetramine (space group $I\bar{4}3m$, $Z = 2$)[3] in a simple way. Starting with a cubic unit cell of $(CH_2)_6N_4$, one can arrive at the $(CH_2)_6N_4O$ structure by first removing the $(CH_2)_6N_4$ molecule at the body-centre, then introducing the N→O function in the [111] direction to each remaining molecule, and finally compressing the resulting primitive lattice along [111] until the oxygen atom of each $(CH_2)_6N_4O$ molecule nests comfortably in a recess formed by three hydrogen atoms of a neighbouring molecule.

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