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The Crystal and Molecular Structure of a 1:1 Adduct of Hexamethylenetetramine Oxide and Formic Acid

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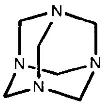
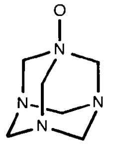
The 1:1 adduct $(CH_2)_6N_4O.HCOOH$ is monoclinic, space group $P2_1/c$, with $a = 6{\cdot}845\ (4)$, $b = 6{\cdot}847\ (4)$, $c = 20{\cdot}07\ (2)$ Å, $\beta = 104{\cdot}8\ (1)°$, $Z = 4$. The structure was refined with 2031 visual reflections to $R = 0{\cdot}105$. Moving away from the quaternary to the tertiary N atoms in hexamethylenetetramine oxide, the average lengths of the three non-equivalent C—N bonds vary in the order long–short–normal relative to that in hexamethylenetetramine. The two molecular components are linked by an $\geq$NO···H—O hydrogen bond and the two C—O bonds in the formic acid moiety are unequal in length.

Introduction

Recently it has been shown that hexamethylenetetramine, $(CH_2)_6N_4$ (I), reacts with 30% H_2O_2 in a neutral medium to give hexamethylenetetramine oxide, $(CH_2)_6N_4O$ (II), as the principal product (Lam & Mak, 1978).



(I)



(II)

Besides $(CH_2)_6N_4O$, two crystalline adducts of composition $(CH_2)_6N_4O.H_2O_2.H_2O$ and $(CH_2)_6$-$N_4O.HCOOH$ were isolated under different reaction conditions. In the present work, the last compound was subjected to X-ray analysis. The objective was threefold: to study the effect of the *N*-oxide function on $(CH_2)_6N_4O$ cage geometry, to establish the mode of attachment of the formic acid moiety to the $(CH_2)_6N_4O$ skeleton, and to determine whether there is indeed proton transfer in the hydrogen bonding, *i.e.* whether the formic acid molecule has given up a proton to a donor atom of $(CH_2)_6N_4O$ and become a formate ion.

Experimental

The adduct was prepared as described by Lam & Mak (1978). The crystals were colorless prisms elongated along **b** and well developed on the (100) face. As the compound is very hygroscopic, roughly spherical single crystals of diameter 0·6 mm were mounted in quartz capillaries filled with paraffin wax for the X-ray measurements. Cell dimensions were determined from high-angle reflections on all three zero-layer Weissenberg photographs calibrated with superimposed NaCl powder lines and refined by minimizing the sum of the residuals $|\sin^2\theta_m - \sin^2\theta_c|$.

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Crystal data

$(CH_2)_6N_4O.HCOOH$, M_r = 202·21, m.p. (with decomposition) 115 °C. Monoclinic, a = 6·845 (4), b = 6·847 (4), c = 20·07 (2) Å, β = 104·8 (1)°. V = 909·3 Å^3, Z = 4, D_m (by flotation in hexane/CCl_4) = 1·478 (2), D_c = 1·477 g cm^{-3}. Space group $P2_1/c$, μ(Cu $K\alpha$) = 10·0 cm^{-1}.

Intensities were collected about **a** for reflections 0*kl*–6*kl* and about **b** for *h*0*l*–*h*6*l* by the multiple-film equi-inclination Weissenberg method with Cu $K\alpha$ (λ = 1·5418 Å) radiation. The visually-estimated intensities were corrected for Lorentz and polarization factors but not for absorption. A set of scaled structure amplitudes was derived by least squares (Hamilton, Rollett & Sparks, 1965). The data after reduction consisted of 2031 independent observed and 382 unobserved reflections.

Structure determination and refinement

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) from 375 reflections with E > 1·25. Full-matrix isotropic and anisotropic least-squares refinement of all 14 non-hydrogen atoms yielded R = 0·118. The positions of all 13 C-bonded H atoms were then generated with a computer program (Mak, Mok & Tse, 1977). Inclusion of these H atoms with B = 5·0 Å^2 in another cycle gave a final R of 0·105. A final difference map was featureless and did not reveal the acidic H atom.

Scattering factors for non-hydrogen atoms (numbering shown in Fig. 1) were taken from *International Tables for X-ray Crystallography* (1974), and that for H from Stewart, Davidson & Simpson (1965). Structure factor and least-squares calculations were carried out on an ICL-1904A computer with a modification of *ORFLS* (Busing, Martin & Levy, 1962). The function minimized was $\sum w(|F_o| - |F_c|)^2$, the weighting scheme being that of Cruickshank (1961) with $w = (2F_{\min} + |F_o| + 2|F_o|^2/F_{\max})^{-1}$, where $F_{\min}$ and $F_{\max}$ were 1·0 and 145·0 respectively. The final atomic parameters are listed in Table 1.*

Table 1. *Fractional atomic coordinates* (×10^4) *with e.s.d.'s in parentheses*

	x	*y*	*z*
O(1)	5079 (4)	−915 (4)	896 (2)
N(1)	4384 (4)	944 (4)	988 (2)
N(2)	3606 (5)	3222 (5)	1811 (2)
N(3)	4719 (5)	4415 (5)	821 (2)
N(4)	1375 (5)	2956 (5)	652 (2)
C(1)	4438 (6)	1315 (6)	1743 (2)
C(2)	5576 (6)	2548 (6)	739 (2)
C(3)	2183 (5)	1073 (6)	567 (2)
C(4)	1482 (6)	3307 (7)	1382 (2)
C(5)	4777 (6)	4716 (6)	1553 (2)
C(6)	2599 (7)	4460 (6)	415 (2)
O(2)	8733 (5)	−1254 (6)	1298 (2)
C(7)	9436 (7)	−1807 (7)	1923 (2)
O(3)	11182 (5)	−2082 (6)	2206 (2)

Discussion

In the present adduct the two molecular components are linked by a short hydrogen bond of 2·435 (4) Å between O(1) and O(2). An *ORTEP* (Johnson, 1965)

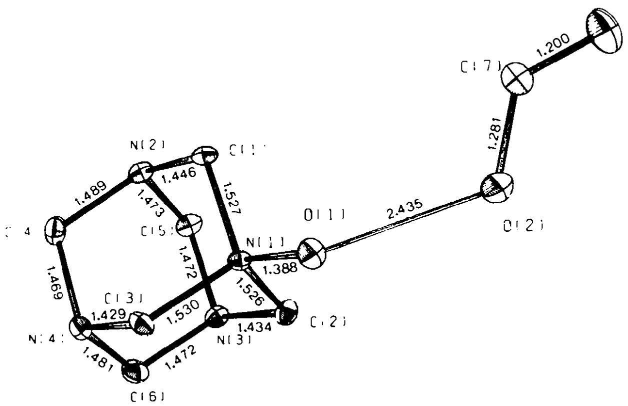

Fig. 1. *ORTEP* plot of $(CH_2)_6N_4O.HCOOH$ showing atom numbering and bond distances. The e.s.d.'s of individual bond lengths lie in the range 0·004–0·006 Å.

Table 2. *Bond angles* (°)

The e.s.d.'s of individual bond angles lie in the range 0·3–0·5°.

Around quaternary nitrogen (average O—N—C = 110·5, C—N—C = 108·4)			
O(1)–N(1)–C(1)	111·3	C(1)–N(1)–C(2)	109·0
O(1)–N(1)–C(2)	112·7	C(1)–N(1)–C(3)	108·0
O(1)–N(1)–C(3)	107·6	C(2)–N(1)–C(3)	108·1
Around tertiary nitrogens (average C—N—C = 109·0)			
C(1)–N(2)–C(4)	109·3	C(5)–N(3)–C(6)	108·7
C(1)–N(2)–C(5)	109·3	C(3)–N(4)–C(4)	110·1
C(4)–N(2)–C(5)	107·9	C(3)–N(4)–C(6)	108·8
C(2)–N(3)–C(5)	109·4	C(4)–N(4)–C(6)	108·6
C(2)–N(3)–C(6)	109·2		
Around methylene carbons (average N—C—N = 110·7)			
N(1)–C(1)–N(2)	109·5	N(2)–C(4)–N(4)	111·3
N(1)–C(2)–N(3)	109·6	N(2)–C(5)–N(3)	112·1
N(1)–C(3)–N(4)	110·1	N(3)–C(6)–N(4)	111·5
Around sp^2 carbon and in adduct linkage			
O(2)–C(7)–O(3)	126·1	C(7)–O(2)···O(1)	116·7
		N(1)–O(1)···O(2)	113·7

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* Tables of generated hydrogen positions, anisotropic temperature factors, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33294 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

plot of the adduct giving the atom numbering and bond distances is shown in Fig. 1. Bond angles are listed in Table 2. A stereoplot of the molecular packing is shown in Fig. 2.

Oxidation of hexamethylenetetramine to its *N*-oxide results in a reduction in molecular symmetry from T_d to C_{3v}. A PMR study of the *N*-oxide and its acid adducts has demonstrated the non-equivalence of the methylene protons (Lam & Mak, 1978). In the present adduct, three types of C—N bonds are disposed differently with respect to the *N*-oxide functional group. Type 1 bonds, which involve the formally positive quaternary N(1), have an average length of 1·528 (4) Å. Type 2 bonds are much shorter, with a mean length of 1·436 (4) Å. Type 3 bonds, being most remote from the *N*-oxide group, have a mean length of 1·476 (3) Å which coincides with the corresponding value of 1·476 (2) Å observed in hexamethylenetetramine (Becka & Cruickshank, 1963). The three types of C—N bonds thus vary in the order long–short–normal. This trend may be rationalized in terms of perturbation caused by the *N*-oxide group. Based on ^{13}C—H coupling constants, Haake, Miller & Tyssee (1964) have shown that the electronegativity of N in $(CH_3)_3NO$ is nearly the same as that of N^+ in quaternary ammonium salts and much larger than that of N in $(CH_3)_3N$. The N→O bond in *N*-oxides is thus highly polar. In hexamethylenetetramine oxide, the formally positive N(1) induces C(1), C(2) and C(3) to rehybridize so as to shift more *p* character into their hybrid atomic orbitals towards it (Bent, 1961). In accordance with the concept of isovalent hybridization, these three methylene C atoms will direct enhanced *s* character into their remaining hybrids towards N(2), N(3), N(4) and the H atoms. These effects account for the long type 1 C—N bonds in the proximity of the *N*-oxide group and the shortness of the type 2 bonds. Type 3 bonds, being farthest from the polar *N*-oxide group, are virtually unaffected by the perturbation and agree closely with the mean C—N length in hexamethylenetetramine and its molecular adducts (Mak, Tse, Chong & Mok, 1977).

The N(1)—O(1) length of 1·388 (4) Å is the same as the 1·388 (5) Å observed in $(CH_3)_3NO$ (Caron, Palenik, Goldish & Donohue, 1964), but is shorter than the 1·425 (11) Å reported for $(CH_3)_3NO.HCl$ (Rérat, 1960; Caron & Donohue, 1962). As the relative lengths of the N—O bonds in $(CH_3)_3NO$ and its hydrochloride are explicable in terms of the difference in formal charge between $\geqslant N^+—O^-$ and $\geqslant N^+—OH$, the two components of the present adduct are expected to be linked by a hydrogen bond of the type $\geqslant N^+—O^-\cdots H—O$ rather than $\geqslant N^+—O—H\cdots O^-$. The average C—N—C angle involving the tertiary N(2), N(3) and N(4) is smaller than the average N—C—N angle (Table 2), in accord with the general trend in hexamethylenetetramine and its molecular adducts. Around N(1), the average O—N—C angle is larger than the average C—N—C angle. The formally negative O(1) thus behaves like a lone pair in regard to steric repulsion. The significantly smaller O(1)—N(1)—C(3) angle might result from the particular way in which the formic acid molecule pairs up with the *N*-oxide (Fig. 1).

Crystalline formic acid has a zigzag chain structure with non-equivalent C—O bonds of 1·23 (3) and 1·26 (3) Å (Holtzberg, Post & Fankuchen, 1953). The corresponding values for monomeric and dimeric formic acid as determined by electron diffraction are 1·217 and 1·361 Å, and 1·220 and 1·323 Å respectively (Almenningen, Bastiansen & Motzfeldt, 1969). The C—O bonds are necessarily equivalent in the formate ion because of resonance, with lengths close to 1·26 Å and the O—C—O angle in the range 125–130°. The formic acid molecule in the present adduct is in a situation where the OH group is involved in hydrogen bonding while the C=O group remains intact. Its measured dimensions are similar to those of the free acid, and the unequal C—O lengths substantiate the conclusion that there is no proton transfer in the adduct as deduced from the N(1)—O(1) distance.

The formic acid moiety lies approximately normal to the mean plane containing O(1), N(1), C(3), N(4) and C(5) (Fig. 1) as defined by the equation $-0{\cdot}5189X - 0{\cdot}3349Y + 0{\cdot}7865Z = 0{\cdot}006$, where X,Y,Z are Cartesian coordinates in Å referred to a set of axes directed along **a**, **b** and **c***. The deviations of the atoms from this plane are 0·003, −0·004, −0·001, 0·001 and

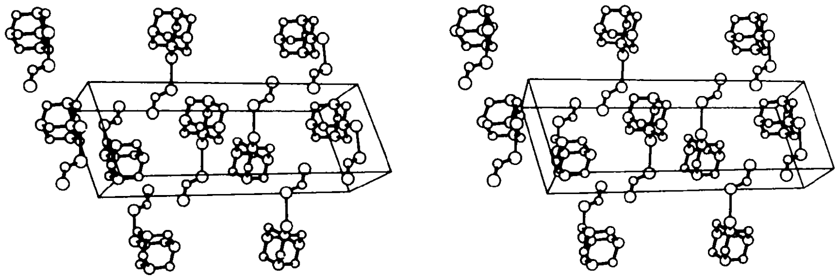

Fig. 2. Stereodrawing showing the molecular packing viewed approximately along **b**. The origin of the unit cell is at the lower left corner.

0·000 Å respectively. The plane equation for the formic acid moiety is $-0{\cdot}0007X - 0{\cdot}9528Y - 0{\cdot}3037Z = 0{\cdot}0532$. The angle between the two planes is 85·4°.

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The Structure of Octafluoronaphthalene at High Pressures Investigated by Neutron Powder Diffraction

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The structure of the molecular crystal octafluoronaphthalene at high pressures has been studied by neutron powder diffraction. Evidence was found at about 0·8 kbar for a structural phase transition similar to that which occurs at 266·5 K at atmospheric pressure. The structures at atmospheric pressure and at 2 and 4 kbar have been refined using the powder-profile-refinement program *EDINP*. There is evidence for a further structural change between 4 and 6 kbar, but there are insufficient data for a detailed analysis of this change.

Introduction

Neutron powder diffraction is well suited to the study of the variation of crystal structure with temperature and pressure where conventional single-crystal measurements are either difficult or impossible. Essential to the analysis of the diffraction data has been the development of the total-profile-refinement method (Rietveld, 1969). Recent work on this method has shown that the structures of relatively complicated