Acta Cryst. (1979). B**35**, 2367–2369

Preparation and X-ray Analysis of a 1:1 Adduct of Hexamethylenetetramine Oxide and Hydroquinone

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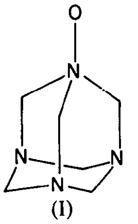
(*Received* 9 *March* 1979; *accepted* 8 *June* 1979)

Abstract

A 1:1 adduct of hexamethylenetetramine oxide and hydroquinone, $(CH_2)_6N_4O.C_6H_4(OH)_2$, has been prepared and subjected to crystal structure analysis. The crystals are triclinic, space group $P\bar{1}$, with a = 9·532 (2), b = 6·521 (1), c = 10·399 (2) Å, α = 102·13 (2), β = 83·09 (2), γ = 92·09 (2)°, and Z = 2. The structure was solved by a combination of direct phasing with packing considerations and refined to R = 0·053 for 2334 Mo $K\alpha$ diffractometer data. The $C_6H_4(OH)_2$ molecules occupy two non-equivalent sites of symmetry $\bar{1}$, and are linked by hydrogen bonds to form infinite zigzag chains. Two centrosymmetrically related $(CH_2)_6N_4O$ molecules are attached to every other $C_6H_4(OH)_2$ molecule in each chain through hydrogen bonding involving their *N*-oxide functions.

Introduction

X-ray analysis of the 1:1 adduct of hexamethylenetetramine with hydroquinone, $(CH_2)_6N_4.C_6H_4(OH)_2$, has shown that the two molecular components are linked by O—H···N hydrogen bonds to form infinite zigzag chains (Mak, Tse, Chong & Mok, 1977). Recently we isolated and studied hexamethylenetetramine oxide† (I) and a number of its molecular adducts (Lam & Mak, 1978; Yu & Mak, 1978; Mak, Ladd & Povey, 1979, and references therein). In the present work, the title compound was prepared and subjected to analysis to elucidate the nature of the molecular association. It constitutes part of our current structural investigation of hydrogen-bonded molecular complexes of hexamethylenetetramine and its *N*-oxide.


(I)

Experimental

Preparation of the hexamethylenetetramine oxide–hydroquinone 1:1 *adduct*

Hexamethylenetetramine oxide (I) was prepared by the reaction of hexamethylenetetramine with 30% aqueous hydrogen peroxide (Lam & Mak, 1978) and recrystallized from chloroform. Hydroquinone (II) was recrystallized from ethanol in an inert atmosphere. Compounds (I) (0·78 g, 5 mmol) and (II) (0·55 g, 5 mmol) were dissolved separately in the minimum amount of ethanol. The solutions were mixed at room temperature and set aside for crystallization, yielding colorless, air-stable crystals (III) of stoichiometry $C_{12}H_{18}N_4O_3$‡ [m.p. 466–468 K (in sealed tube) with decomposition]. The molecular formula of (III) was confirmed by its IR (KBr disc) and NMR [CD_3OD and $(CD_3)_2SO$] spectra, which consisted essentially of a superposition of those of (I) and (II).

The crystals were rather irregular in shape and a roughly spherical specimen of diameter *ca* 0·5 mm was selected. Unit-cell parameters were determined by least-squares refinement of the θ values of 22 reflections measured on a diffractometer with Zr-filtered Mo $K\alpha$ radiation (λ = 0·71069 Å).

Crystal data

$(CH_2)_6N_4O.C_6H_4(OH)_2$, M_r = 266·31, triclinic, space group $P\bar{1}$, a = 9·532 (2), b = 6·521 (1), c = 10·399 (2) Å, α = 102·13 (2), β = 83·09 (2), γ = 92·09 (2)°, V = 627·3 Å^3, Z = 2, D_m = 1·420 (5) (by flotation in CCl_4/benzene), D_x = 1·410 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·112 mm^{-1}.

Intensities for 2886 unique reflections with θ < 27·5° were collected on a Nonius CAD-4 diffractometer operating in the ω-scan mode. Three standard reflections were measured every hour to check the stability of the crystal and the electronics, and 2334 independent reflections had $I > 3\sigma(I)$, $\sigma(I)$ being calculated from counting statistics. Data were correc-

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† IUPAC name: 1,3,5,7-tetraazaadamantane *N*-oxide.

‡ Elemental analysis performed by the Australian Microanalytical Service, CSIRO, Parkville, Victoria, Australia.

0567-7408/79/102367-03$01.00

ted for Lorentz and polarization factors but absorption correction ($\mu R \sim 0{\cdot}028$) was considered unnecessary.

Structure determination and refinement

Initial attempts to solve the structure with *MULTAN* (Germain, Main & Woolfson, 1971) were unsuccessful. One of the *E* maps gave an indication of the orientation, but not the correct location, of the $(CH_2)_6N_4O$ molecule. Packing considerations led to the conclusion that the remainder of the asymmetric unit actually consists of two separated half-molecules of $C_6H_4(OH)_2$. The correct structure was derived by model building based on the known orientation of $(CH_2)_6N_4O$ and the fact that the $C_6H_4(OH)_2$ molecules are located on two non-equivalent sites of symmetry $\bar{1}$. Full-matrix anisotropic least-squares refinement of all 19 non-hydrogen atoms (Fig. 1) yielded a conventional *R* of 0·097 for 2334 observed data. Four very strong reflections (102, 202, 11$\bar{1}$, and $\bar{1}$10) consistently had $|F_o| < |F_c|$. A check of the intensity data showed that their scan profiles were quite asymmetric; they were therefore considered unreliable and assigned zero weight in further calculations. A Fourier difference map gave the positions of all 18 H atoms; inclusion of these with isotropic thermal parameters in subsequent refinement yielded a final *R* of 0·053.

Scattering factors for non-hydrogen atoms were generated from the analytical expressions of Cromer & Mann (1968), and those for H from Stewart, Davidson & Simpson (1965). Computations were performed on an Amdahl 470 system with a local adaptation of *ORFLS* (Busing, Martin & Levy, 1962). The function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F)$.

The final atomic parameters are listed in Table 1.* The atom numbering is shown in Fig. 1. Bond distances and angles are listed in Table 2. An *ORTEP* (Johnson, 1965) stereoplot of the molecular packing is shown in Fig. 2.

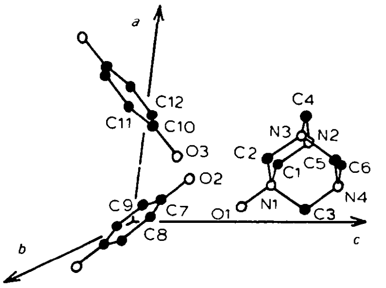

Fig. 1. Atom numbering of asymmetric unit in $(CH_2)_6N_4O.C_6H_4(OH)_2$.

Discussion

The present structure is unusual in that it comprises two types of hydroquinone molecules in non-equivalent sites of symmetry $\bar{1}$ (Fig. 2). These crystallo-

Table 1. *Final positional parameters (fractional* O, N, *and* C $\times 10^4$, H $\times 10^3$) *with estimated standard deviations in parentheses*

	Bonded to	*x*	*y*	*z*
O(1)		726 (2)	2148 (3)	4077 (1)
N(1)		1600 (2)	2549 (3)	5070 (2)
N(2)		3264 (2)	1065 (3)	6212 (2)
N(3)		3555 (2)	4680 (3)	5935 (2)
N(4)		1609 (2)	3738 (3)	7443 (2)
C(1)		2381 (2)	603 (3)	5153 (2)
C(2)		2682 (3)	4248 (4)	4869 (2)
C(3)		713 (2)	3294 (3)	6397 (2)
C(4)		4274 (2)	2745 (4)	5973 (2)
C(5)		2646 (3)	5360 (4)	7190 (2)
C(6)		2365 (3)	1831 (4)	7469 (2)
O(2)		1778 (2)	−64 (3)	1910 (2)
C(7)		899 (2)	−19 (3)	955 (2)
C(8)		323 (2)	1850 (3)	844 (2)
C(9)		582 (2)	−1868 (3)	99 (2)
O(3)		2799 (2)	6179 (3)	1986 (2)
C(10)		3884 (2)	5628 (4)	985 (2)
C(11)		4572 (2)	7064 (3)	311 (2)
C(12)		4315 (2)	3561 (4)	673 (2)
H(1)	C(1)	298 (3)	13 (4)	431 (3)
H(2)	C(1)	163 (3)	−47 (4)	529 (3)
H(3)	C(2)	327 (3)	372 (4)	401 (3)
H(4)	C(2)	214 (3)	551 (4)	484 (3)
H(5)	C(3)	25 (3)	457 (5)	633 (3)
H(6)	C(3)	−1 (3)	214 (4)	652 (3)
H(7)	C(4)	487 (3)	309 (4)	669 (3)
H(8)	C(4)	480 (3)	230 (4)	511 (3)
H(9)	C(5)	323 (3)	568 (4)	795 (3)
H(10)	C(5)	212 (3)	661 (4)	720 (3)
H(11)	C(6)	299 (3)	212 (4)	819 (3)
H(12)	C(6)	168 (3)	69 (4)	761 (3)
H(13)	C(8)	57 (3)	314 (4)	149 (3)
H(14)	C(9)	100 (3)	−321 (4)	18 (3)
H(15)	C(11)	429 (3)	851 (4)	51 (3)
H(16)	C(12)	380 (3)	258 (4)	113 (3)
H(17)	O(2)	141 (4)	80 (6)	272 (4)
H(18)	O(3)	255 (4)	752 (6)	195 (3)

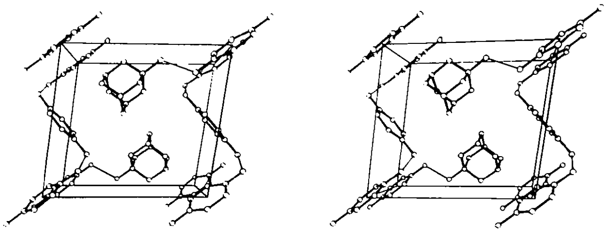

Fig. 2. Stereodrawing showing the molecular packing viewed approximately into **b** toward the origin of the unit cell at the lower left corner. The **a** and **c** vectors point upward and to the right respectively. Thinner lines represent the O···O hydrogen bonds.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34532 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *with their e.s.d.'s*

(i) Hexamethylenetetramine oxide			
O(1)–N(1)	1·381 (2)		
N(1)–C(1)	1·518 (3)	N(2)–C(4)	1·473 (3)
N(1)–C(2)	1·516 (3)	N(2)–C(6)	1·477 (3)
N(1)–C(3)	1·524 (3)	N(3)–C(4)	1·468 (3)
N(2)–C(1)	1·441 (3)	N(3)–C(5)	1·471 (3)
N(3)–C(2)	1·440 (3)	N(4)–C(5)	1·464 (3)
N(4)–C(3)	1·438 (3)	N(4)–C(6)	1·467 (3)
Around quaternary N atom (mean O–N–C = 110·9, C–N–C = 108·0)			
O(1)–N(1)–C(1)	111·9 (1)	C(1)–N(1)–C(2)	108·3 (2)
O(1)–N(1)–C(2)	111·5 (2)	C(1)–N(1)–C(3)	107·8 (2)
O(1)–N(1)–C(3)	109·3 (2)	C(2)–N(1)–C(3)	108·0 (2)
Around tertiary N atoms (mean C–N–C = 108·9)			
C(1)–N(2)–C(4)	108·9 (2)	C(4)–N(3)–C(5)	109·1 (2)
C(1)–N(2)–C(6)	108·8 (2)	C(3)–N(4)–C(5)	109·4 (2)
C(4)–N(2)–C(6)	108·3 (2)	C(3)–N(4)–C(6)	109·3 (2)
C(2)–N(3)–C(4)	108·7 (2)	C(5)–N(4)–C(6)	108·6 (2)
C(2)–N(3)–C(5)	108·8 (2)		
Around methylene C atoms (mean N–C–N = 111·1)			
N(1)–C(1)–N(2)	110·5 (2)	N(2)–C(4)–N(3)	111·9 (2)
N(1)–C(2)–N(3)	110·5 (2)	N(3)–C(5)–N(4)	111·7 (2)
N(1)–C(3)–N(4)	110·0 (2)	N(2)–C(6)–N(4)	111·8 (2)
(ii) Hydroquinone centered at (0,0,0)			
O(2)–C(7)	1·379 (2)	O(2)–C(7)–C(8)	120·8 (2)
C(7)–C(8)	1·388 (3)	O(2)–C(7)–C(9)	119·6 (2)
C(7)–C(9)	1·388 (3)	C(8)–C(7)–C(9)	119·5 (2)
C(8)–C(9)$^{\rm i}$	1·384 (3)	C(7)–C(8)–C(9)$^{\rm i}$	120·3 (2)
		C(7)–C(9)–C(8)$^{\rm i}$	120·1 (2)
(iii) Hydroquinone centered at $(\frac{1}{2},\frac{1}{2},0)$			
O(3)–C(10)	1·376 (3)	O(3)–C(10)–C(11)	122·6 (2)
C(10)–C(11)	1·386 (3)	O(3)–C(10)–C(12)	118·0 (2)
C(10)–C(12)	1·384 (3)	C(11)–C(10)–C(12)	119·4 (2)
C(11)–C(12)$^{\rm ii}$	1·391 (3)	C(10)–C(11)–C(12)$^{\rm ii}$	120·4 (2)
		C(10)–C(12)–C(11)$^{\rm ii}$	120·2 (2)
(iv) Hydrogen bonds			
O(2)···O(1)	2·522 (2)	O(2)···O(3)$^{\rm iii}$	2·689 (3)
H(17)···O(1)	1·58 (4)	O(2)···H(18)$^{\rm iii}$	1·77 (4)
N(1)–O(1)···O(2)	115·5 (1)	C(7)–O(2)···O(3)$^{\rm iii}$	116·9 (1)
N(1)–O(1)···H(17)	115 (1)	C(7)–O(2)···H(18)$^{\rm iii}$	119 (1)
O(1)···O(2)···O(3)$^{\rm iii}$	117·0 (1)	C(7)–O(2)···O(1)	109·0 (1)
O(2)–H(17)···O(1)	176 (3)	O(2)···H(18)$^{\rm iii}$–O(3)$^{\rm iii}$	170 (3)

Roman numerals refer to the following equivalent positions relative to the atom at *x,y,z*: (i) $-x,-y,-z$; (ii) $1-x$, $1-y$, $-z$; (iii) x, $-1+y$, z.

graphically distinct molecules are joined lengthwise by O(3)–H(18)···O(2) hydrogen bonds [2·689 (3) Å], resulting in infinite zigzag chains extending along $[\bar{1}10]$. Pairs of centrosymmetrically related $(CH_2)_6N_4O$ molecules are attached to every other hydroquinone molecule in each chain, with the *N*-oxide groups serving as proton acceptors in O(2)–H(17)···O(1) hydrogen bonds [2·522 (2) Å]. Due to the formally negative charge on O(1), this latter type of hydrogen bonding is stronger than that within a chain. The zigzag chains are arranged in layers parallel to (001), with the $(CH_2)_6N_4O$ groups protruding from both sides of each layer and fitting into hollows between neighboring layers. This mode of packing, in which the $(CH_2)_6N_4$ moiety is not involved in hydrogen bonding and relegated to a space-filling role, has been observed for $(CH_2)_6N_4O.H_2O_2.H_2O$ (Mak & Lam, 1978) and $(CH_2)_6N_4O.(NH_2)_2CS$ (Yu & Mak, 1978), and appears to be a structural feature common to molecular complexes of $(CH_2)_6N_4O$.

As a consequence of hydrogen bonding, the N(1)→O dative bond [1·381 (2) Å] in the present adduct is significantly longer than the corresponding distance [1·363 (6) Å] in crystalline hexamethylenetetramine oxide (Mak, Ladd & Povey, 1979). Other than this, the molecular dimensions of $(CH_2)_6N_4O$ in both parent compound and adduct are in excellent agreement, especially in regard to the pattern of bond alternation for C–N distances disposed successively further away from the polar *N*-oxide function.

Both types of hydroquinone skeletons, except for their phenolic H atoms, are each planar within experimental error; the normals to their best planes make an angle of 84·1 (2)°. In each molecule, the C–C–OH angle is somewhat larger on the side of the H atom, in accord with the observation for a variety of phenols studied by diffraction methods (Mahmoud & Wallwork, 1975).

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