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Cellulose Organic Solvents.
II. The Structure of *N*-Methylmorpholine *N*-Oxide $2 \cdot 5H_2O$

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Abstract

$C_5H_{11}NO_2.2 \cdot 5H_2O$, $M_r = 162 \cdot 2$, is monoclinic, $P2_1/c$, with $a = 12 \cdot 803$ (6), $b = 6 \cdot 500$ (4), $c = 21 \cdot 913$ (8) Å, $\beta = 109 \cdot 99$ (10)°, $Z = 8$, $d_o = 1 \cdot 22$, $d_c = 1 \cdot 257$ Mg m^{-3}. The structure was solved by direct methods and refined to $R = 0 \cdot 042$ for 991 reflexions. The morpholine ring takes the chair form with N—O axial. The structure contains an intricate network of hydrogen bonding involving ten non-equivalent O···O distances in the range 2·661 (6)–2·810 (6) Å. The non-solvent character of the compound is attributed to the saturation of the *N*-oxide by hydrogen bonds.

Introduction

Cyclic amine oxides such as *N*-methylmorpholine *N*-oxide (abbreviated MMNO) have the capacity to dissolve cellulose in large quantities (Johnson, 1969; Franks & Varga, 1979). Cellulose dissolution is found to depend on: the temperature of the solution, the water content of the mixture, the concentration and the degree of polymerization of the cellulose (Chanzy, Péguy, Chaunis & Monzie, 1980). Of these, the water-content dependence can be resolved from the crystal structure, since MMNO occurs in a series of crystalline hydrates, depending on the drying conditions. Anhydrous MMNO, as well as its monohydrate, are both good solvents of cellulose. The crystal structures of these two forms have been investigated (Maia, Péguy & Pérez, 1981) and it was shown that the N—O bond of MMNO interacts through one hydrogen bond with a water molecule, yielding a polymer-like structure.

As the water content increases, the ability of MMNO to dissolve cellulose decreases. No cellulose can be dissolved when the molecular ratio of water to MMNO reaches 2, unless the water content is reduced by application of a vacuum. It was therefore of interest to investigate the molecular structure of such a hydrate, to elucidate the reasons for its non-solvent character.

Experimental

Anhydrous MMNO was obtained by vacuum sublimation of MMNO monohydrate (from Eastman Kodak) at 338 K and then dissolved in toluene. 2 mol of water per mol of anhydrous MMNO were added and the resulting solution was heated to about 323 K. The solution was cooled to 305 K and kept at this temperature, at which crystals grew. Crystals suitable for X-ray investigation (0·2 × 0·2 × 0·3 mm) were mounted in capillaries, all operations being performed in a drybox.

The space group was determined from precession photographs. The unit-cell dimensions were obtained as part of the alignment process on an automatic diffractometer by a least-squares fit to the settings of 16 well-centred reflexions. The density was measured by flotation in a mixture of anhydrous CCl_4 and cyclohexane.

Intensity data were collected on a Philips PW1100 diffractometer, using Ni-filtered Cu radiation and the θ–2θ scan mode up to $\theta = 60°$. The intensities of two reference reflexions, measured every 2 h, decreased by about 6% of their initial values over the duration of the data collection. Of the 2507 independent reflexions measured, only 991 $[I > 2 \cdot 5\sigma(I)]$ were employed for the structure determination and refinement. The high percentage of 'unobserved' reflexions is attributed to the fact that the data collection was performed at 293 K, only 16 K below the melting point of the crystals. Because of the small size of the crystals and the low value of the absorption coefficient ($\mu = 0 \cdot 75$ mm^{-1}) no absorption correction was applied. The X-ray scatter-

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ing factors were those of Cromer & Waber (1965) for O, N, C and of Stewart, Davidson & Simpson (1965) for H.

From the observed density of 1·22 Mg m^{-3}, it can be deduced that the asymmetric unit contains two independent MMNO molecules, the number of water molecules being either 4 (d_c = 1·187 Mg m^{-3}) or 5 (d_c = 1·257 Mg m^{-3}).

Table 1. *Fractional coordinates and their e.s.d.'s* (×10^4, ×10^3 *for* H) *and equivalent isotropic thermal parameters* (Å^2) *for the non-hydrogen atoms*

B_{eq} is one third the trace of the diagonalized anisotropic temperature factor matrix.

	x	y	z	B_{eq}/B_{iso}
O(1)	863 (2)	5570 (4)	9370 (1)	4·3 (4)
C(2)	1159 (3)	6867 (8)	8944 (2)	4·7 (4)
C(3)	2163 (4)	8114 (6)	9318 (2)	4·5 (4)
N(4)	3135 (2)	6745 (5)	9656 (1)	3·5 (3)
C(5)	2771 (3)	5192 (7)	10042 (2)	4·0 (4)
C(6)	1722 (4)	4140 (6)	9636 (2)	4·2 (4)
C(7)	4076 (5)	8023 (12)	10090 (3)	5·3 (5)
O(8)	3470 (2)	5801 (4)	9183 (1)	4·0 (4)
O(1′)	1724 (2)	5094 (5)	5706 (1)	4·7 (5)
C(2′)	895 (3)	6482 (7)	5758 (2)	4·2 (4)
C(3′)	1335 (3)	7662 (6)	6386 (2)	3·8 (3)
N(4′)	1687 (2)	6232 (4)	6957 (1)	3·1 (3)
C(5′)	2497 (3)	4718 (6)	6867 (2)	3·6 (4)
C(6′)	2020 (4)	3648 (7)	6220 (2)	4·4 (4)
C(7′)	2210 (4)	7410 (8)	7575 (2)	4·5 (4)
O(8′)	744 (2)	5192 (4)	6979 (1)	3·5 (3)
W(1)	5163 (2)	7395 (5)	8849 (1)	4·7 (4)
W(2)	5908 (3)	4627 (6)	8150 (2)	5·1 (5)
W(3)	4720 (3)	1050 (5)	8120 (2)	5·0 (5)
W(4)	3146 (3)	2148 (6)	8600 (2)	5·0 (5)
W(5)	1019 (3)	2002 (6)	7825 (2)	5·9 (5)
H(1)	47 (4)	789 (7)	870 (2)	7·5 (9)
H(2)	131 (3)	590 (6)	859 (2)	4·4 (8)
H(3)	236 (4)	919 (7)	901 (2)	7·9 (9)
H(4)	194 (3)	896 (6)	963 (2)	4·6 (8)
H(5)	340 (3)	416 (6)	1024 (2)	5·4 (9)
H(6)	264 (3)	618 (7)	1041 (2)	7·3 (9)
H(7)	150 (3)	310 (7)	992 (2)	7·2 (9)
H(8)	186 (3)	311 (7)	925 (2)	6·8 (9)
H(9)	475 (4)	715 (8)	1036 (2)	8·4 (9)
H(10)	387 (4)	904 (8)	1039 (2)	8.9 (9)
H(11)	440 (4)	901 (8)	986 (2)	8·3 (9)
H(1′)	68 (4)	755 (8)	536 (2)	8·2 (9)
H(2′)	20 (3)	568 (6)	572 (2)	4·3 (8)
H(3′)	69 (3)	880 (5)	642 (2)	4·0 (8)
H(4′)	199 (3)	868 (7)	638 (2)	6·5 (9)
H(5′)	274 (3)	363 (6)	728 (2)	5·4 (9)
H(6′)	323 (3)	571 (6)	691 (2)	4·3 (8)
H(7′)	263 (3)	267 (7)	615 (2)	6·7 (9)
H(8′)	127 (4)	268 (7)	622 (2)	8·1 (9)
H(9′)	175 (4)	864 (8)	764 (2)	8·2 (9)
H(10′)	286 (4)	830 (7)	755 (2)	5·9 (9)
H(11′)	253 (4)	644 (7)	802 (2)	7·4 (9)
H(*W*11)	469 (3)	708 (7)	895 (2)	5·2 (9)
H(*W*12)	494 (4)	859 (8)	862 (2)	7·3 (9)
H(*W*21)	570 (4)	539 (9)	828 (3)	7·0 (9)
H(*W*22)	559 (4)	313 (9)	816 (2)	9·5 (9)
H(*W*31)	427 (4)	144 (8)	817 (2)	5·9 (9)
H(*W*32)	422 (3)	44 (7)	768 (2)	7·9 (9)
H(*W*41)	254 (4)	161 (8)	835 (2)	7·9 (9)
H(*W*42)	318 (4)	331 (9)	878 (2)	8·5 (9)
H(*W*51)	52 (4)	157 (8)	798 (2)	7·3 (9)
H(*W*52)	93 (4)	315 (8)	766 (2)	8·5 (9)

The structure was solved by a straightforward application of *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). The *E* map computed with the best set of phases revealed 15 non-hydrogen atoms belonging to the two independent MMNO molecules. The remaining heavy atoms were located in a difference Fourier synthesis, and the number of water molecules in the asymmetric unit was found to be 5. Three cycles of full-matrix least-squares refinement led to a conventional *R* value of 0·15. The H atoms were located and included in the refinement with isotropic temperature factors. The final *R* values for the observed reflexions only and for all the measured reflexions were 0·042 and 0·081 respectively. The quantity minimized was $\sum w(F_o - F_c)^2$, each reflexion being assigned unit weight. A final electron density map showed no significant residual density, the extreme fluctuations being 0·28 and −0·30 e Å^{-3}.

Results and discussion

The positional parameters are presented in Table 1.* A view of the asymmetric unit with the numbering of atoms is given in Fig. 1 [*PITMOS* (Dheu & Pérez, 1980)].

The interatomic distances, bond angles and torsion angles are presented in Tables 2, 3 and 4. Corresponding values of the two morpholine rings compare well but minor differences are observed around the en-

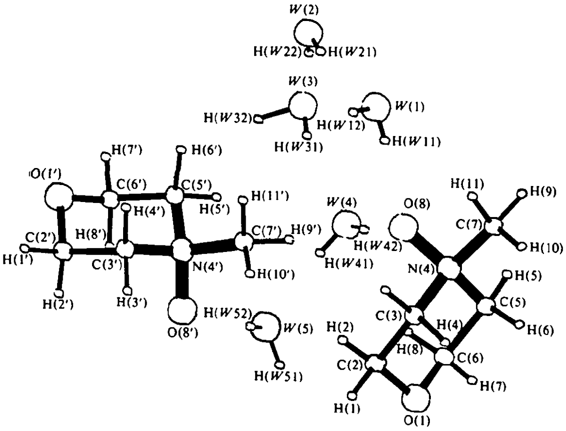

Fig. 1. View of the asymmetric unit (*PITMOS*) with the numbering of the atoms.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36408 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å)

	Unprimed molecule	Primed molecule
Endocyclic		
O(1)–C(2)	1·403 (5)	1·427 (5)
C(2)–C(3)	1·504 (6)	1·506 (6)
C(3)–N(4)	1·503 (5)	1·499 (4)
N(4)–C(5)	1·490 (5)	1·491 (4)
C(5)–C(6)	1·499 (6)	1·508 (6)
C(6)–O(1)	1·405 (5)	1·416 (5)
Exocyclic		
N(4)–C(7)	1·504 (5)	1·500 (5)
N(4)–O(8)	1·392 (3)	1·399 (3)

Table 3. *Bond angles* (°)

	Unprimed molecule	Primed molecule
Endocyclic		
C(6)–O(1)–C(2)	108·8 (3)	111·1 (3)
O(1)–C(2)–C(3)	109·7 (3)	109·8 (3)
C(2)–C(3)–N(4)	111·0 (3)	111·0 (3)
C(3)–N(4)–C(5)	108·3 (3)	108·9 (3)
N(4)–C(5)–C(6)	111·3 (3)	110.6 (3)
C(5)–C(6)–O(1)	111·1 (3)	110·7 (4)
Exocyclic		
C(3)–N(4)–C(7)	109·5 (4)	110·6 (3)
C(3)–N(4)–O(8)	107·9 (3)	108·1 (3)
C(5)–N(4)–C(7)	110·7 (4)	109·9 (3)
C(5)–N(4)–O(8)	111·1 (3)	109·5 (3)
C(7)–N(4)–O(8)	109·3 (3)	109·9 (3)

Table 4. *Torsion angles* (°)

	Unprimed molecule	Primed molecule
Endocyclic		
O(1)–C(2)–C(3)–N(4)	60·1 (4)	−57·9 (4)
C(2)–C(3)–N(4)–C(5)	−52·2 (4)	54·5 (4)
C(3)–N(4)–C(5)–C(6)	50·8 (4)	−53·9 (4)
N(4)–C(5)–C(6)–O(1)	−57·9 (4)	57·8 (4)
C(5)–C(6)–O(1)–C(2)	64·1 (4)	−61·1 (4)
C(6)–O(1)–C(2)–C(3)	−64·8 (4)	61·0 (4)
Exocyclic		
C(7)–N(4)–C(3)–C(2)	−173·0 (4)	175·3 (3)
C(7)–N(4)–C(5)–C(6)	170·8 (4)	−175·1 (3)
O(8)–N(4)–C(3)–C(2)	68·2 (4)	−64·2 (4)
O(8)–N(4)–C(5)–C(6)	−67·6 (4)	64·1 (4)

docyclic O atoms O(1) and O(1′). In both molecules, the rings assume an almost perfect chair conformation with smaller torsion angles about the C—N bonds. The exocyclic O atom is axial while the methyl group is equatorial, as in the anhydrous and monohydrate structures of MMNO. N—O bond lengths are 1·392 (3) and 1·399 (3) Å, and fall in the range of values for the molecules already studied (Maia *et al.*, 1981). It is worth observing that the N—O lengths are independent of hydrogen bonding to O.

There are five water molecules in the asymmetric unit, which form an intricate network of hydrogen bonds (Fig. 2). This work reveals that the O atom of a tertiary amine oxide can be the acceptor of two hydrogen bonds. Exocyclic O atom O(8) is hydrogen bonded to *W*(1) [2·718 (6) Å] and to *W*(4) [2·661 (6) Å], whereas O(8′) is linked to two symmetry-related *W*(5) water molecules [2·707 (6) and 2·722 (6) Å]. Thus, the two independent morpholine molecules have different environments and the overall structure is better described as $2MMNO.5H_2O$. The five water molecules are involved in ten different hydrogen bonds. The distribution of the proton donor–acceptor systems is well defined and summarized in Table 5. The O atoms of the water molecules, *W*(1), *W*(2), *W*(3), *W*(4), along with O(8), are arranged in a five-membered-ring fashion, with lateral bonding through *W*(4) and *W*(5) and additionally to O(8′). Two such quasi planar rings, derived from the symmetry operation, are linked through a *W*(3)···*W*(2) type hydrogen bond. There results a column of water molecules surrounded by MMNO molecules and a distinct segregation between the hydrophobic and the hydrophilic moieties in the structure.

Without any inference as to the nature of the initial step of the dissolution process of cellulose by a tertiary amine oxide (*i.e.* a swelling or peeling process) it may be envisaged as starting by breaking the hydrogen bonds between the cellulose chains. Hydrogen bonds are then formed between the cellulose hydroxyl groups and the amine oxide. In this scheme, the hydroxylic O atoms of the cellulose act as donors, the acceptor centres being the exocyclic O atoms of MMNO, as strongly indicated by the molecular arrangement found in the complex MMNO-*trans*-1,2-cyclohexanediol (Chanzy, Maia & Pérez, 1982). As shown from the present work, such a centre can act as the receptor of two hydrogen bonds. Therefore, it can be rationalized

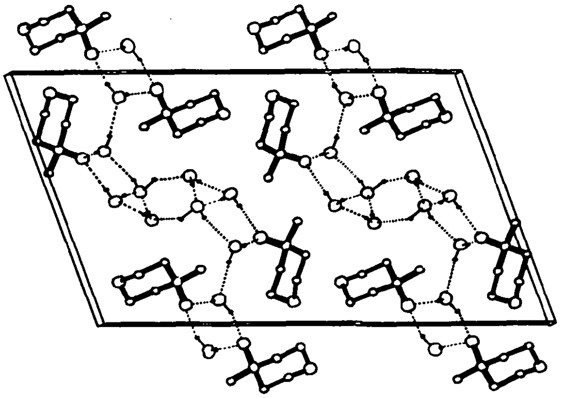

Fig. 2. View of the packing (*PITMOS*). The hydrogen bonds are shown as dashed lines. The H atoms of the MMNO molecules are omitted.

Table 5. *Hydrogen bonding in* MMNO.2·5H_2O

i j k	D_{ik} (Å)	D_{jk} (Å)	θ_{ijk} (°)
$W(1)$–H($W11$)···O(8)	2·718 (6)	1·98 (5)	171 (5)
$W(1)$–H($W12$)···$W(3)^{i}$	2·810 (6)	1·90 (5)	170 (5)
$W(2)$–H($W21$)···$W(1)$	2·739 (6)	2·08 (5)	169 (5)
$W(2)$–H($W22$)···$W(3)$	2·767 (6)	1·73 (5)	164 (5)
$W(3)$–H($W31$)···$W(4)$	2·669 (6)	2·02 (5)	161 (5)
$W(3)$–H($W32$)···$W(2)^{ii}$	2.778 (6)	1·85 (5)	148 (5)
$W(4)$–H($W41$)···$W(5)$	2·673 (6)	1·92 (5)	148 (5)
$W(4)$–H($W42$)···O(8)	2·661 (6)	1·82 (5)	172 (5)
$W(5)$–H($W51$)···$O(8')^{iii}$	2·707 (6)	1·88 (5)	159 (5)
$W(5)$–H($W52$)···O(8′)	2·722 (6)	1·95 (5)	157 (5)

Symmetry code: None x,y,z; (i) x, $1 + y$, z; (ii) $1 - x$, $-\frac{1}{2} + y$, $\frac{3}{2} - z$; (iii) $-x$, $-\frac{1}{2} + y$, $\frac{3}{2} - z$.

that when the molecular ratio of water bonded to MMNO is less than 2, such a bonding scheme is quite feasible. On the other hand, a molecular ratio equal to or greater than 2 would be sufficient to saturate the hydrogen-bond possibilities of the N—O linkage to cellulose and would hamper any solvent character. Indeed such a scheme is achieved in the present structure.

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Abstract

$C_5H_{11}NO_2.C_6H_{12}O_2$, M_r = 233·33, is monoclinic, $P2_1/c$, with a = 6·137 (3), b = 10·153 (4), c = 21·015 (6) Å, β = 94·33 (10)°, Z = 4, d_o = 1·19, d_c = 1·19 Mg m^{-3} and R = 0·042 for 1019 reflexions. The morpholine ring takes the chair form with N—O axial. In the *trans*-1,2-cyclohexanediol molecule, a distinct shrinkage of the bond between the two oxygen-bearing C atoms is observed [1·473 (5) Å]. The molecule is in a chair conformation with both hydroxylic O atoms equatorial. The N—O structuring site links, through hydrogen bonds, contiguous *trans*-1,2-cyclohexanediol molecules oriented along the a axis. The nature and the geometry of the intermolecular interactions in this

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