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Cellulose Organic Solvents.
I. The Structures of Anhydrous *N*-Methylmorpholine *N*-Oxide and *N*-Methylmorpholine *N*-Oxide Monohydrate

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Abstract

N-Methylmorpholine *N*-oxide (MMNO) appears to be one of the most potent organic solvents for cellulose. Anhydrous MMNO ($C_5H_{11}NO_2$, $M_r = 117{\cdot}1$) is monoclinic, $P2_1/m$; $a = 9{\cdot}886\ (5)$, $b = 6{\cdot}621\ (5)$, $c = 5{\cdot}112\ (4)$ Å, $\beta = 111{\cdot}54\ (10)^\circ$, $Z = 2$, $d_{\rm obs} = 1{\cdot}25$, $d_{\rm calc} = 1{\cdot}25$ Mg m^{-3}. The crystal structure has been solved by direct methods and refined to a final *R* value of 0·047 for 512 measured reflexions. MMNO monohydrate ($C_5H_{11}NO_2.H_2O$, $M_r = 135{\cdot}2$) is monoclinic, $P2_1/c$; $a = 25{\cdot}481\ (9)$, $b = 6{\cdot}04\ (5)$, $c = 9{\cdot}186\ (6)$ Å, $\beta = 99{\cdot}88\ (10)^\circ$, $Z = 8$, $d_{\rm obs} = 1{\cdot}28$, $d_{\rm calc} = 1{\cdot}29$ Mg m^{-3}. The structure has been solved by direct methods and refined to a final *R* value of 0·042 for 1993 measured reflexions. In both structures the morpholine ring occurs in a chair conformation with N–O axial. In the anhydrous state, the molecules are arranged so that the dipolar N–O bonds for nearest-neighbour molecules are antiparallel. For the monohydrate state of MMNO, the water molecules are structured in a polymer-like fashion through an extensive hydrogen-bonding scheme, linking the N–O groups of MMNO. This finding is related to the ability of MMNO molecules to dissolve cellulose materials.

Introduction

Among the various organic solvents for cellulose which have been recently investigated (Johnson, Nicholson & Haigh, 1975; Philipp, Schleicher & Wagenknecht, 1977; Turbak, Hammer, Davies & Portnoy, 1977), *N*-methylmorpholine *N*-oxide (abbreviated MMNO) appears to be of particular interest (Johnson, 1969; Chanzy, Dubé & Marchessault, 1979). MMNO occurs in a series of crystalline hydrates, depending on the drying conditions; when heated to about 373 K, MMNO containing about 5% of water is able to dissolve up to 30% of high-molecular-weight cellulose. Cellulose mesophases are normally obtained under these conditions. These anisotropic solutions can be readily oriented, thus yielding films or fibres, which upon regeneration exhibit a high degree of orientation (Chanzy, Peguy, Chaunis & Monzie, 1980). In general, the occurrence of cellulose dissolution is found to depend on: the temperature of the solution, water content of the mixture, and concentration and degree of polymerization of the cellulose (Chanzy *et al.*, 1980). The importance of the water content in the solution of cellulose and MMNO has been demonstrated by Franks & Varga (1979) and Chanzy *et al.* (1980). In view of their data, the binding of MMNO (with or without water) to cellulose through hydrogen bonding can be realized. Although these different properties begin to be well documented, neither the structural characterization of MMNO, nor the nature of its interactions with cellulose chains or water have yet been considered. This paper reports the structural and molecular characterization of MMNO in its anhydrous and monohydrate states. The present work has been undertaken in order to investigate the basic geometry and conformation of MMNO, and the nature of its interactions with water molecules.

Experimental

MMNO monohydrate from Eastman Kodak was recrystallized in dry acetone. It melted at 348 K and contained 13·3% water, *i.e.* one water molecule per MMNO. Anhydrous MMNO was obtained by vacuum sublimation of MMNO monohydrate at 338 K. It was a white crystalline hygroscopic powder melting at 445 K. Anhydrous MMNO was then dissolved in cyclohexane at about 353 K. Crystallization occurred at about 313 K. The density was measured by flotation in a mixture of anhydrous CCl_4 and cyclohexane.

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Table 1. *Measurement conditions*

	Anhydrous MMNO	MMNO monohydrate
Crystal dimensions	0·2 × 0·2 × 0·3 mm	0·3 × 0·3 × 0·4 mm
Scan mode	θ–2θ	θ–2θ
Intensity stability	95%	90%
Number of reflexions measured	512	1993
Significance, $I/\sigma(I)$	2·5	2·5
Number of observed reflexions	457	1796

For both crystal structures, preliminary work was performed on a precession camera, the single crystals being mounted in capillaries. 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. Intensity data were collected on a Philips PW 1100 diffractometer using Ni-filtered Cu radiation. The data were corrected for Lorentz and polarization effects and reduced in the usual manner. The measuring conditions are listed in Table 1. The X-ray scattering factors were obtained from Cromer & Waber (1965) for O, N, C, and from Stewart, Davidson & Simpson (1965) for H.

Structure determination and refinement

For both structures *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977) was used, along with the refinement program *ORFLS* (Busing, Martin & Levy, 1962); the quantity minimized was $\sum (F_o - F_c)$, each reflexion being assigned unit weight.

Anhydrous MMNO

The systematic absences ($0k0$, $k \neq 2n$) were compatible with space groups $P2_1$ and $P2_1/m$. Analysis of the E statistics was slightly in favour of the centrosymmetric space group. However, it was decided to try to solve the structure in the noncentrosymmetric $P2_1$. This was performed by a straightforward application of *MULTAN*. The E map computed with the best set of phases revealed the eight nonhydrogen atoms of the molecule. Three cycles of full-matrix isotropic least-squares refinement led to a conventional R of 0·16. The correlation matrix computed at this stage indicated a fairly strong correlation between the coordinates of some atoms in the molecule. Thus, it was confirmed that the compound was centrosymmetric, $P2_1/m$. After a change of origin, the full-matrix refinement proceeded smoothly. All the H atoms were located on a difference Fourier synthesis, and included in the refinement with isotropic temperature factors. The final R values (for observed reflexions only and for all reflexions, respectively) were 0·043 and 0·047.* A final electron density map showed no significant residual density, the extreme fluctuations being −0·25 and +0·20 e Å^{-3}.

Monohydrate MMNO

Two independent MMNO monohydrate entities per asymmetric unit had to be located. The structure was solved by application of *MULTAN*. The E map computed with the best set of phases revealed all the nonhydrogen atoms within the asymmetric unit. Three cycles of full-matrix least-squares refinement led to a conventional R value of 0·18. At this stage a difference Fourier synthesis yielded all the H atoms covalently bonded to the MMNO molecules. The H atoms of the water molecules were located later on a difference Fourier map performed after several cycles of refinement. The nonhydrogen atoms were given anisotropic temperature factors, while the H atoms were included with isotropic temperature factors. The final R values (for observed reflexions only and for all reflexions, respectively) were 0·039 and 0·042.* A final electron density map showed no significant residual density, the extreme fluctuations being 0·16 and −0·14 e Å^{-3}.

Results and discussion

The positional parameters are presented in Tables 2 and 3. A view of the molecule along with the numbering

Table 2. *Anhydrous MMNO: fractional coordinates* (×10^4, *for* H ×10^3) *and isotropic thermal parameters* (Å^2)

For nonhydrogen atoms $B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i . \mathbf{a}_j$.

	x	y	z	B_{eq}/B
O(1)	4454 (3)	2500	6501 (7)	6·2
C(2)†	3657 (4)	753 (6)	6627 (7)	5·8
C(3)†	2214 (3)	673 (4)	4273 (6)	4·0
N(4)	1344 (3)	2500	4388 (6)	3·1
C(7)	−52 (4)	2500	1948 (7)	4·2
O(8)	1073 (3)	2500	6872 (4)	3·5
H(1)†	351 (3)	63 (5)	849 (7)	7·3 (8)
H(2)†	422 (3)	−39 (5)	654 (6)	7·0 (8)
H(3)†	162 (3)	−55 (4)	433 (5)	4·5 (6)
H(4)†	235 (3)	79 (4)	241 (5)	4·8 (5)
H(9)†	−57 (3)	388 (5)	222 (6)	7·0 (8)
H(10)	19 (4)	250	10 (9)	6·3 (9)

† Equivalent atoms C(6), C(5), H(7), H(8), H(5), H(6) and H(11) are derived by mirror-symmetry operation (x, $\frac{1}{2} - y$, z) from the atomic coordinates given.

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* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35994 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *MMNO monohydrate: fractional coordinates* ($\times 10^4$, *for* H $\times 10^3$) *and isotropic thermal parameters* (Å^2)

For nonhydrogen atoms $B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i . \mathbf{a}_j$.

	x	y	z	B_{eq}/B
O(1)	4684 (1)	9275 (3)	6640 (2)	4·1
C(2)	4315 (1)	11048 (4)	6272 (3)	4·2
C(3)	3757 (1)	10326 (4)	6375 (1)	3·4
N(4)	3594 (1)	8452 (3)	5338 (2)	2·6
C(5)	4000 (1)	6653 (4)	5702 (2)	3·1
C(6)	4548 (1)	7514 (4)	5633 (3)	3·7
C(7)	3063 (1)	7595 (5)	5533 (3)	3·9
O(8)	3575 (1)	9154 (2)	3896 (1)	3·2
W(1)	2820 (1)	12388 (3)	3343 (2)	4·2
O(1′)	313 (1)	9346 (3)	6919 (2)	4·1
C(2′)	468 (1)	7578 (4)	6064 (2)	4·0
C(3′)	1019 (1)	6773 (4)	6710 (2)	3·4
N(4′)	1415 (1)	8622 (3)	6746 (2)	2·7
C(5′)	1229 (1)	10491 (4)	7604 (3)	3·1
C(6′)	670 (1)	11144 (4)	6919 (3)	3·8
C(7′)	1944 (1)	7821 (5)	7500 (3)	3·8
O(8′)	1445 (1)	9319 (2)	5329 (1)	3·3
W(1′)	2171 (1)	12690 (3)	5527 (2)	4·2
H(1)	443 (1)	1217 (4)	705 (3)	5·1 (6)
H(2)	433 (1)	1157 (5)	520 (3)	5·8 (6)
H(3)	347 (1)	1145 (4)	604 (2)	4·1 (5)
H(4)	373 (1)	990 (4)	728 (3)	4·2 (5)
H(5)	388 (1)	550 (4)	500 (2)	3·3 (4)
H(6)	398 (1)	610 (3)	670 (2)	3·2 (4)
H(7)	479 (1)	630 (4)	593 (3)	4·6 (5)
H(8)	457 (1)	800 (4)	459 (3)	3·7 (5)
H(9)	277 (1)	870 (5)	521 (3)	6·4 (6)
H(10)	308 (1)	723 (4)	649 (3)	3·8 (5)
H(11)	297 (1)	630 (6)	487 (4)	7·3 (8)
H(12)	305 (1)	1167 (6)	349 (4)	7·0 (9)
H(13)	266 (1)	1222 (5)	249 (4)	5·2 (7)
H(1′)	19 (1)	648 (4)	605 (2)	4·6 (5)
H(2′)	43 (1)	818 (5)	506 (3)	5·1 (5)
H(3′)	112 (1)	567 (4)	601 (3)	4·9 (5)
H(4′)	106 (1)	615 (4)	775 (3)	3·7 (4)
H(5′)	147 (1)	1166 (4)	751 (2)	4·0 (4)
H(6′)	124 (1)	1000 (4)	858 (3)	3·7 (4)
H(7′)	56 (1)	1240 (5)	756 (3)	6·4 (7)
H(8′)	67 (1)	1177 (4)	580 (3)	5·0 (5)
H(9′)	203 (1)	664 (9)	695 (3)	5·6 (6)
H(10′)	192 (1)	748 (4)	846 (3)	5·0 (5)
H(11′)	220 (1)	900 (5)	751 (3)	5·0 (5)
H(12′)	193 (1)	1168 (6)	540 (3)	6·8 (8)
H(13′)	233 (1)	1262 (5)	481 (4)	6·9 (7)

of the atoms is given in Fig. 1 (*PITMOS*, Dheu & Pérez, 1980). In the following discussion, the atoms belonging to the two independent entities occurring in MMNO monohydrate are labelled as unprimed and primed.

Geometry and conformation

The interatomic distances, bond angles and torsion angles are presented in Tables 4, 5 and 6. The bond distances, angles and torsion angles of the morpholine rings in both structures compare extremely well. The ring assumes an almost perfect chair conformation with the torsion angles nearly equal in magnitude. The results are also consistent with those recently reported by Swaminathan, Sundaralingam, Chattopadhyaya & Reese (1980), for the already studied morpholino and morpholinium rings. The only minor differences involve the N atom, where a smaller C(3)—N(4)—C(5) angle is observed, along with smaller torsion angles about the two C—N bonds. These features arise from the difference in nature of the substituents at N.

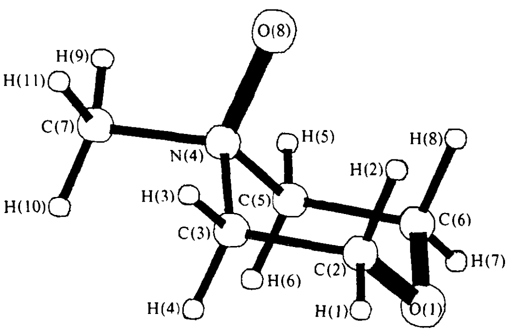

Fig. 1. A molecule of *N*-methylmorpholine *N*-oxide with the numbering of the atoms.

Table 4. *Bond distances* (Å)

The standard deviations are 0·003 Å.

	Anhydrous MMNO	MMNO monohydrate Unprimed residue	MMNO monohydrate Primed residue
O(1)—C(2)	1·414	1·427	1·421
C(2)—C(3)	1·492	1·506	1·508
C(3)—N(4)	1·498	1·492	1·502
N(4)—C(5)	1·498	1·498	1·499
C(5)—C(6)	1·492	1·502	1·508
C(6)—O(1)	1·414	1·413	1·417
N(4)—C(7)	1·482	1·488	1·487
N(4)—O(8)	1·391	1·384	1·383

Table 5. *Bond angles* (°)

The standard deviations are 0·2°.

	Anhydrous MMNO	MMNO monohydrate Unprimed residue	MMNO monohydrate Primed residue
C(6)—O(1)—C(2)	109·8	109·4	109·7
O(1)—C(2)—C(3)	112·1	111·0	110·7
C(2)—C(3)—N(4)	109·4	110·0	110·2
C(3)—N(4)—C(5)	107·9	107·6	107·4
N(4)—C(5)—C(6)	109·4	110·5	109·8
C(5)—C(6)—O(1)	112·1	111·0	111·1
C(3)—N(4)—C(7)	109·7	110·2	108·7
C(3)—N(4)—O(8)	110·0	109·8	110·6
C(5)—N(4)—C(7)	109·7	109·3	110·1
C(5)—N(4)—O(8)	110·0	110·2	109·8
C(7)—N(4)—O(8)	109·5	109·8	110·2

Table 6. *Torsion angles* (°)

The standard deviations are 0·5°.

	Anhydrous MMNO	MMNO monohydrate Unprimed residue	MMNO monohydrate Primed residue
Endocyclic			
O(1)–C(2)–C(3)–N(4)	−59·3	−59·8	−59·6
C(2)–C(3)–N(4)–C(5)	56·9	55·9	56·3
C(3)–N(4)–C(5)–C(6)	−56·9	−55·9	−56·2
N(4)–C(5)–C(6)–O(1)	59·3	59·5	60·0
C(5)–C(6)–O(1)–C(2)	−59·3	−60·9	−61·5
C(6)–O(1)–C(2)–C(3)	59·3	61·2	61·0
Exocyclic			
C(7)–N(4)–C(3)–C(2)	176·3	174·8	175·4
C(7)–N(4)–C(5)–C(6)	−176·3	−175·5	−174·4
O(8)–N(4)–C(3)–C(2)	−63·0	−64·1	−63·5
O(8)–N(4)–C(5)–C(6)	63·0	63·8	64·1

In both structures, the exocyclic oxygen atom O(8) is axial while the methyl group is equatorial. N—O bond lengths in the three molecules studied compare extremely well: 1·391 (3), 1·384 (3) and 1·383 (3) Å. These values are in good agreement with the value of 1·388 (5) Å in trimethylamine oxide (Caron, Palenik, Goldish & Donohue, 1964) which is one of the rare reports of structural studies on a tertiary amine oxide. It is worth mentioning that the N—O lengths are independent of hydrogen bonding of O.

Molecular packing

A stereoview of the packing of anhydrous MMNO is shown in Fig. 2. None of the intermolecular distances is shorter than 3·60 Å. Consequently, the molecules are held in the crystal by van der Waals forces. The molecules are arranged in such a way that the N—O bonds belonging to neighbouring molecules are antiparallel. Such a feature minimizes in a perfect manner any dipolar interactions between nearest N—O bonds.

For MMNO monohydrate, a projection of the structure onto the plane (010) is shown in Fig. 3. It can be seen that the molecules are held by a network of hydrogen bonds. Table 7 lists the intermolecular distances and angles of interest. The water molecules link MMNO molecules in a polymer-like fashion, oriented along the *z* axis. Very comparable hydrogen bonds emanate from the two independent MMNO molecules in the asymmetric unit [O(8)···*W*(1) = 2·728 (5), O(8′)···*W*(1′) = 2·734 (5) Å]. The water molecules are further linked together through hydrogen bonds which are also very comparable: *W*(1)···*W*(1′) = 2·821 (5) and *W*(1′)···*W*(1) = 2·816 (5) Å. The result is a polymer-like ribbon of nearly coplanar water molecules with only weak interactions between neighbouring ribbons. This indicates a distinct segregation between the hydrophobic and the hydrophilic moieties of the structure. This finding is important because it enhances the ability of MMNO molecules to complex to other molecules and further order them. The polar N—O part of the molecule seems to be responsible for this phenomenon. The MMNO molecules can be visualized as ordering a given set of molecular entities and then acting as a 'protective layer'. Since the external part of the protective layer does not allow any strong molecular interactions, the polymer-like structured entities are free to move with respect to one another. Such a freedom of motion would be a necessary step towards a dissolution process. This would tend to explain why the intracyclic O(1) does not play a major role; in fact, this atom can be replaced by a CH_2 group, and still the dissolution of cellulose occurs in *N*-methylpiperidine *N*-oxide (Johnson, 1969,1970).

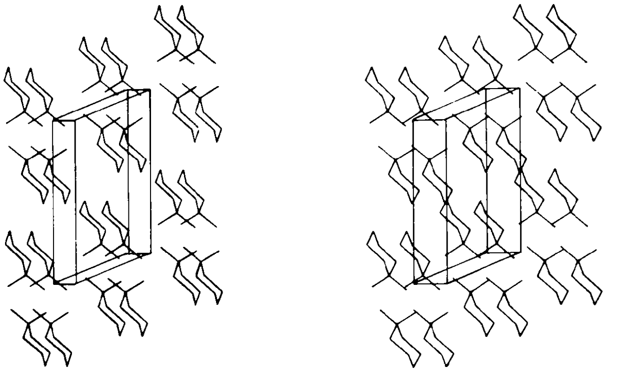

Fig. 2. Stereoview of the packing of anhydrous *N*-methylmorpholine *N*-oxide (*PITMOS*, Dheu & Pérez, 1980).

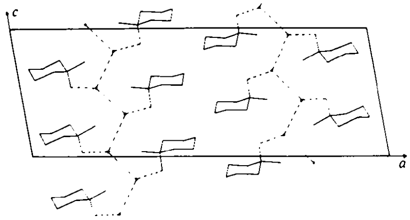

Fig. 3. Projection down the *b* axis of the structure of *N*-methylmorpholine *N*-oxide monohydrate (*PITMOS*, Dheu & Pérez, 1980). The hydrogen bonds are shown as dashed lines. The H atoms have been omitted.

Table 7. *Hydrogen bonding in MMNO monohydrate*

i *j* *k*	D_{ik} (Å)	D_{jk} (Å)	θ_{ijk} (°)
W(1)–H(12)···O(8)(x,y,z)	2·728 (5)	2·01 (5)	168 (4)
W(1)–H(13)···*W*(1′)($x, \frac{5}{2}-y, -\frac{1}{2}+z$)	2·821 (5)	2·01 (5)	168 (4)
W(1′)–H(12′)···O(8′)(x,y,z)	2·734 (5)	1·88 (4)	173 (4)
W(1′)–H(13′)···*W*(1)(x,y,z)	2·816 (5)	1·99 (5)	170 (4)

Also: *W*(1)–H(12) = 0·73 (3), *W*(1)–H(13) = 0·83 (3) Å, H(12)–*W*(1)–H(13) = 111 (3)°; *W*(1′)–H(12′) = 0·86 (3), *W*(1′)–H(13′) = 0·83 (3) Å, H(12′)–*W*(1)–H(13′) = 107 (3)°.

These results remain insufficient to understand fully the interaction of MMNO with cellulose materials. More information about the nature and the geometry of the interactions between MMNO and, for example, a glucose residue or relevant model compounds, is required. The structural elucidation of such crystalline adducts would obviously enlighten the understanding, at a molecular level, of the process of cellulose dissolution and mesomorph formation. Further work along this line is in progress in our laboratory and will be reported later.

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The Structure of Dibenzoyldiazomethane*

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Abstract

The structure of dibenzoyldiazomethane has been determined from three-dimensional X-ray diffraction data collected by counter methods. $C_{15}H_{10}N_2O_2$, M_r = 250·26, crystallizes in the space group $P2_1/n$ with a = 9·5631 (9), b = 14·564 (2), c = 10·154 (1) Å, β = 118·184 (9)°, V = 1246·6 Å^3 and Z = 4. The observed and calculated densities are 1·32 (1) and 1·333 Mg m^{-3}, respectively. A full-matrix least-squares refinement on 1471 unique observed reflections converged at R = 0·036 and R_w = 0·052. The dibenzoyldiazomethane molecule has an *s-trans-s-cis* conformation which is skewed significantly owing to non-bonded contacts. When a riding-motion correction is applied to the N—N distance [1·113 (2) Å, uncorrected] a value of 1·151 (2) Å results which is intermediate between an N—N triple and double bond. Other metrical parameters in the molecule indicate some π delocalization over the carbonyl and diazomethylene groups.

Introduction

Diazoalkane molecules have been the subject of investigation for many years owing, in part, to their utility as synthetic reagents (Fridman, Ismagilova,

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* 2-Diazo-1,3-diphenyl-1,3-propanedione.

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