

Table 5. *Hydrogen bonding in MMNO.2.5H<sub>2</sub>O*

<i>i</i>	<i>j</i>	<i>k</i>	<i>D<sub>ik</sub></i> (Å)	<i>D<sub>jk</sub></i> (Å)	$\theta_{ijk}$ (°)
W(1)—H(W11)...	O(8)		2.718 (6)	1.98 (5)	171 (5)
W(1)—H(W12)...	W(3) <sup>i</sup>		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) <sup>ii</sup>		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') <sup>iii</sup>		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*, -½ + *y*, ½ - *z*; (iii) -*x*, -½ + *y*, ½ - *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.

The authors thank Dr A. Péguy for growing the single crystals studied, and Professor D. Gagnaire and

Dr H. Chanzy for their continuous interest in this work. The data collection was performed within the 'Groupe Grenoblois de Diffractométrie'.

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## Cellulose Organic Solvents.

### III. The Structure of the *N*-Methylmorpholine *N*-Oxide—*trans*-1,2-Cyclohexanediol Complex

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#### Abstract

$C_5H_{11}NO_2 \cdot C_6H_{12}O_2$ ,  $M_r = 233.33$ , is monoclinic,  $P2_1/c$ , with  $a = 6.137$  (3),  $b = 10.153$  (4),  $c = 21.015$  (6) Å,  $\beta = 94.33$  (10)°,  $Z = 4$ ,  $d_o = 1.19$ ,  $d_c = 1.19$  Mg m<sup>-3</sup> 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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complex provide information about the interaction of  $C_3H_{11}NO_2$  with cellulose chains and their resultant stiffening.

### Introduction

*N*-Methylmorpholine *N*-oxide (abbreviated as MMNO) appears to be of particular interest as a solvent for cellulose and polysaccharide materials. The importance of the water content bonded to MMNO with respect to the dissolution of cellulose has been demonstrated by Franks & Varga (1979) and Chanzy, Péguy, Chaunis & Monzie (1980). Previous structural investigations (Maia, Péguy & Pérez, 1981; Maia & Pérez, 1982) have provided information about and a rationalization of the amount of water bonded to MMNO for cellulose dissolution. However, more information about the nature and the geometry of interactions between MMNO and, for example, a glucose residue (the cellulose monomer) or a relevant model compound remained to be found. A preliminary step for such an investigation is a study of the complex of MMNO with any molecule exhibiting structural similarities with the repeating unit of cellulose. In this connexion, the molecule *trans*-1,2-cyclohexanediol was selected. This molecule, which is supposed to occur in a chair conformation, has two hydroxyl groups in equatorial positions, similar to the two hydroxyl groups OH(2) and OH(3) found in the glucose units.

### Experimental

An equimolar mixture of MMNO monohydrate and *trans*-1,2-cyclohexanediol was prepared at room temperature. It was then dissolved in cyclohexane and heated to about 353 K yielding a viscous solution. When this solution was cooled to about 325 K crystal nuclei were formed and further cooling to 310 K at a rate of 1 K per day yielded well formed crystals suitable for X-ray work. A crystal of dimensions 0.25 × 0.30 × 0.30 mm was sealed in a capillary. All operations were 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 setting angles of 20 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 PW 1100 diffractometer with Ni-filtered Cu radiation, using the  $\theta$ - $2\theta$  scan mode up to  $\theta = 52^\circ$ . The intensities of two reference reflexions, measured every 2 h, were found to decrease by about 35% of their initial values over the duration of the data collection. Of the 1403 indepen-

dent reflexions measured, only 1019 [ $I > 2.5\sigma(I)$ ] were employed for the structure determination and refinement. Because of the small size of the crystal and the low value of the absorption coefficient ( $\mu = 0.62 \text{ mm}^{-1}$ ) no absorption correction was applied. The X-ray scattering factors were those from Cromer & Waber (1965) for O, N, C, and Stewart, Davidson & Simpson (1965) for H.

The structure was solved by application of *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). The *E* map computed with the best set of phases revealed the 16 non-hydrogen atoms within the asymmetric unit. 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 and for all the measured reflexions were 0.042 and 0.053. 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  $-0.20$  and  $0.15 \text{ e \AA}^{-3}$ .

### Results and discussion

The positional parameters are presented in Table 1.\* A view of the asymmetric unit with the numbering of the 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 morpholine ring compare well with those found in other MMNO-containing structures (Maia *et al.*, 1981; Maia & Pérez, 1982). The ring assumes an almost perfect chair conformation, with smaller torsion angles about the two C—N bonds. The exocyclic O atom O(8) is axial, and the N—O bond length of 1.383 (3) Å is in the range of distances already found. As for the *trans*-1,2-cyclohexanediol

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36410 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

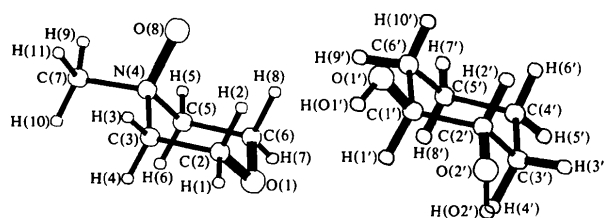


Fig. 1. View of the molecules of *N*-methylmorpholine *N*-oxide and *trans*-1,2-cyclohexanediol with the numbering of atoms (*PITMOS*).

Table 1. Fractional coordinates and their e.s.d.'s ( $\times 10^4$ ,  $\times 10^3$  for H) and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) for the non-hydrogen atoms

$B_{\text{eq}}$  is one third of the diagonalized anisotropic temperature factor matrix.

	x	y	z	$B_{\text{eq}}/B_{\text{iso}}$
<i>N</i> -Methylmorpholine				
O(1)	4016 (5)	9317 (3)	8726 (1)	6.6 (9)
C(2)	5709 (7)	9621 (4)	8334 (2)	5.5 (6)
C(3)	4946 (6)	10506 (4)	7801 (2)	4.6 (5)
N(4)	3053 (4)	9915 (2)	7411 (1)	4.1 (4)
C(5)	1334 (6)	9550 (4)	7845 (2)	4.9 (5)
C(6)	2290 (8)	8684 (5)	8365 (2)	6.4 (8)
C(7)	2168 (10)	10867 (4)	6927 (2)	6.3 (8)
O(8)	3734 (4)	8797 (2)	7107 (1)	4.6 (5)
H(1)	721 (6)	1006 (3)	860 (2)	6.9 (9)
H(2)	635 (5)	885 (3)	819 (2)	5.9 (9)
H(3)	612 (5)	1067 (3)	753 (1)	4.9 (8)
H(4)	449 (5)	1131 (3)	793 (1)	4.0 (7)
H(5)	14 (6)	904 (3)	757 (2)	7.1 (9)
H(6)	91 (5)	1038 (3)	800 (2)	6.0 (9)
H(7)	90 (6)	848 (3)	863 (2)	7.2 (9)
H(8)	282 (6)	784 (4)	820 (2)	7.1 (9)
H(9)	335 (6)	1108 (3)	663 (2)	7.0 (9)
H(10)	148 (6)	1163 (4)	717 (2)	7.3 (9)
H(11)	82 (6)	1053 (4)	672 (2)	7.6 (9)
<i>trans</i> -1,2-Cyclohexanediol				
O(1')	1033 (5)	7155 (3)	6435 (1)	6.0 (8)
O(2')	-2387 (4)	8926 (3)	6593 (1)	6.2 (8)
C(1')	-159 (6)	7783 (3)	5916 (2)	4.7 (5)
C(2')	-2432 (6)	8063 (4)	6053 (1)	4.7 (5)
C(3')	-3730 (8)	8687 (5)	5486 (2)	6.1 (7)
C(4')	-3749 (9)	7787 (6)	4907 (2)	7.3 (9)
C(5')	-1471 (10)	7479 (7)	4761 (2)	7.5 (9)
C(6')	-135 (9)	6884 (5)	5334 (3)	6.6 (9)
H(O1')	167 (7)	772 (4)	664 (2)	7.8 (9)
H(O2')	-383 (5)	886 (4)	677 (2)	5.6 (7)
H(1')	58 (5)	863 (3)	584 (1)	4.9 (8)
H(2')	-314 (5)	715 (3)	616 (1)	5.4 (8)
H(3')	-528 (6)	883 (3)	560 (2)	7.1 (9)
H(4')	-298 (6)	965 (4)	539 (2)	7.5 (9)
H(5')	-489 (6)	820 (3)	451 (2)	7.9 (9)
H(6')	-439 (6)	696 (4)	500 (2)	7.1 (9)
H(7')	-146 (6)	684 (3)	441 (2)	7.8 (9)
H(8')	-72 (7)	823 (4)	468 (2)	8.1 (9)
H(9')	131 (7)	674 (4)	527 (2)	8.2 (9)
H(10')	-72 (7)	608 (4)	543 (2)	8.2 (9)

Table 2. Bond distances ( $\text{\AA}$ )

(a) MMNO		(b) <i>trans</i> -1,2-Cyclohexanediol	
Endocyclic			
O(1)—C(2)	1.408 (5)	C(1')—C(2')	1.473 (5)
C(2)—C(3)	1.484 (5)	C(2')—C(3')	1.520 (5)
C(3)—N(4)	1.496 (4)	C(3')—C(4')	1.523 (6)
N(4)—C(5)	1.492 (6)	C(4')—C(5')	1.487 (7)
C(5)—C(6)	1.488 (6)	C(5')—C(6')	1.528 (7)
C(6)—O(1)	1.410 (5)	C(6')—C(1')	1.528 (5)
Exocyclic			
N(4)—C(7)	1.477 (5)	C(1')—O(1')	1.418 (4)
N(4)—O(8)	1.383 (3)	C(2')—O(2')	1.432 (4)

Table 3. Bond angles ( $^\circ$ )

(a) MMNO		(b) <i>trans</i> -1,2-Cyclohexanediol	
Endocyclic			
C(6)—O(1)—C(2)	110.0 (3)	C(6')—C(1')—C(2')	109.8 (3)
O(1)—C(2)—C(3)	111.7 (3)	C(1')—C(2')—C(3')	112.1 (3)
C(2)—C(3)—N(4)	111.0 (3)	C(2')—C(3')—C(4')	110.4 (4)
C(3)—N(4)—C(5)	108.7 (3)	C(3')—C(4')—C(5')	109.9 (4)
N(4)—C(5)—C(6)	109.7 (3)	C(4')—C(5')—C(6')	112.3 (4)
C(5)—C(6)—O(1)	111.4 (4)	C(5')—C(6')—C(1')	110.9 (4)
Exocyclic			
C(3)—N(4)—C(7)	110.1 (3)	C(1')—C(2')—O(2')	108.1 (3)
C(5)—N(4)—C(7)	110.1 (3)	C(3')—C(2')—O(2')	110.1 (3)
C(3)—N(4)—O(8)	109.4 (3)	C(2')—C(1')—O(1')	112.2 (3)
C(5)—N(4)—O(8)	109.3 (3)	C(6')—C(1')—O(1')	108.2 (3)
C(7)—N(4)—O(8)	109.1 (3)		

Table 4. Torsion angles ( $^\circ$ )

(a) MMNO		(b) <i>trans</i> -1,2-Cyclohexanediol	
Endocyclic			
O(1)—C(2)—C(3)—N(4)	-56.7 (4)	C(1')—C(2')—C(3')—C(4')	58.6 (5)
C(2)—C(3)—N(4)—C(5)	53.3 (4)	C(2')—C(3')—C(4')—C(5')	-56.1 (6)
C(3)—N(4)—C(5)—C(6)	-54.3 (4)	C(3')—C(4')—C(5')—C(6')	55.5 (7)
N(4)—C(5)—C(6)—O(1)	59.5 (5)	C(4')—C(5')—C(6')—C(1')	-55.3 (7)
C(5)—C(6)—O(1)—C(2)	-61.5 (5)	C(5')—C(6')—C(1')—C(2')	55.0 (6)
C(6)—O(1)—C(2)—C(3)	59.9 (4)	C(6')—C(1')—C(2')—C(3')	-57.4 (5)
Exocyclic			
C(7)—N(4)—C(3)—C(2)	174.0 (4)	O(1')—C(1')—C(2')—O(2')	60.8 (4)
C(7)—N(4)—C(5)—C(6)	-175.0 (4)	O(1')—C(1')—C(2')—C(3')	-177.7 (3)
O(8)—N(4)—C(3)—C(2)	-66.1 (4)	O(1')—C(1')—C(6')—C(5')	177.8 (4)
O(8)—N(4)—C(5)—C(6)	65.2 (4)	O(2')—C(2')—C(1')—C(6')	-178.9 (4)
		O(2')—C(2')—C(3')—C(4')	178.9 (4)

molecule, a severe shrinkage of the bond between the two oxygen-bearing C atoms C(1') and C(2') [ $1.473(5) \text{\AA}$ ] is observed. This bond shrinkage, which is accompanied by an opening of C(1')—C(2')—C(3') to  $112.1(3)^\circ$ , is also found for the C(4')—C(5') bond with the accompanying opening of C(4')—C(5')—C(6'). The ring assumes an almost perfect chair conformation with the torsion angles nearly equal in magnitude and varying about a mean absolute value of  $56.3^\circ$ . This is in agreement with the predicted value of  $\pm 54.7^\circ$  given by Bixon & Lifson (1967). The hydroxyl atoms O(1') and O(2') are both equatorial, and correspond to the conformation predicted to be the more stable for 1,2-*trans*-substituted cyclohexanediol (Zhdanov & Malysheva, 1972).

A projection of the structure onto the (010) plane is shown in Fig. 2. The *trans*-1,2-cyclohexanediol molecules are linked through two hydrogen bonds to the exocyclic O atom O(8) of two different MMNO molecules. Comparable distances are found for the hydrogen bonds: O(1')...O(8) =  $2.677(4) \text{\AA}$  and O(2')...O(8) =  $2.691(4) \text{\AA}$ ; O(1')—H...O(8) =  $167(4)^\circ$ , O(2')—H...O(8) =  $178(3)^\circ$  and O(1')...O(8)...O(2') =  $110.5(6)^\circ$ . This results in polymer-like ribbons oriented along the *a* axis with only weak interactions between neighbouring ribbons.

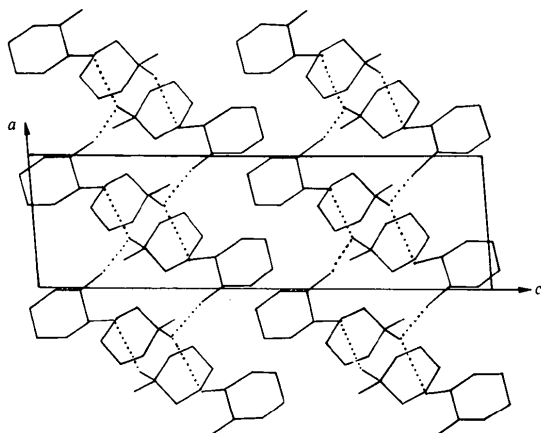


Fig. 2. Projection of the structure down the *b* axis (PITMOS). The hydrogen bonds are shown as dashed lines. The H atoms have been omitted.

There is an indication from this work that MMNO would not interact through its structuring N—O site with both the secondary hydroxyl groups OH(2) and OH(3) of the same glucose unit, merely on account of steric hindrance. Of the different ways of interaction of MMNO with cellulose, an interaction with hydroxyl groups belonging to two consecutive glucose residues of the cellulose backbone can be envisaged. Because of the overall  $2_1$  symmetry of the cellulose chain, this interaction would occur through hydrogen bonding between either the primary hydroxyl OH(6') and the secondary hydroxyl OH(2) or between the primary hydroxyl OH(6) and the secondary hydroxyl OH(3') of a contiguous glucose residue. This would result in a

stiffening of the cellulose chain. Examination of the possible modes of interaction between MMNO and cellulose is under study in our laboratory and will be reported later.

The authors thank Dr A. Péguy for growing the single crystals studied, and Professor D. Gagnaire for his continuous interest in this work. The data collection was performed within the 'Groupe Grenoblois de Diffractométrie'

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## Polarized Ethylenes: Structures of (1,3-Dimethyl-2-imidazolidinylidene)malononitrile and (1,3-Dimethyl-2-perhydropyrimidinylidene)malononitrile

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#### Abstract

Crystal structures of the title compounds, (I) and (II), have been determined by three-dimensional diffraction methods. Crystals of  $C_8H_{10}N_4$  (I) are monoclinic, space group  $P2_1/a$  with  $Z = 4$ ,  $M_r = 162$ ,  $a = 7.965$  (1),  $b = 16.232$  (2),  $c = 7.343$  (1) Å,  $\beta = 113.54$  (1)°,  $V = 890.7$  Å<sup>3</sup>,  $D_m = 1.218$ ,  $D_x = 1.208$  g cm<sup>-3</sup>,  $\mu(\text{Cu } K\alpha, \lambda = 1.5418 \text{ Å}) = 6.47$  cm<sup>-1</sup>,  $F(000) = 344$ . The

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crystals of  $C_9H_{12}N_4$  (II) are orthorhombic, space group  $P2_1cn$ , with  $Z = 4$ ,  $M_r = 176$ ,  $a = 7.983$  (3),  $b = 8.075$  (2),  $c = 14.652$  (3) Å,  $V = 944.43$  Å<sup>3</sup>,  $D_m = 1.219$ ,  $D_x = 1.237$  g cm<sup>-3</sup>,  $\mu(\text{Mo } K\alpha, \lambda = 0.7107 \text{ Å}) = 0.868$  cm<sup>-1</sup>,  $F(000) = 376$ . Both structures were solved by direct methods and refined to  $R = 5.8\%$  for (I) and  $5.3\%$  for (II). The C—C double-bond distances are 1.407 (3) in (I) and 1.429 (6) Å in (II), appreciably longer than normal. The steric and push-pull effects

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