Synthesis and Crystal Structure of *N,N'*-Dicyclohexylpiperazine *N,N'*-Dioxide Octahydrate

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Abstract. *N,N'*-Dicyclohexylpiperazine *N,N'*-dioxide octahydrate, $C_{16}H_{46}N_2O_{10}$, $M_r = 426.55$, monoclinic, space group $C2/m$ (No. 12), $a = 12.961(4)$, $b = 11.533(4)$, $c = 7.907(1)$ Å, $\beta = 98.37(2)°$, $V = 1169.3(6)$ Å^3, $Z = 2$. The structure was solved by the direct method and refined to $R = 0.045$ for 1192 observed MoK$_\alpha$ reflections. The *N,N'*-dioxide molecule occupies a site of symmetry $2/m$. The piperazine ring takes the chair form with the two N—O bonds oriented axially in a *trans* configuration. Hydrogen bonding between the water molecules, as well as between the *N*-oxide groups and water molecules, gives rise to a puckered layer composed of edge-sharing four-membered, five-membered, six-membered, and eight-membered rings. Adjacent layers are cross-linked by the *N,N'*-dicyclohexylpiperazine moieties lying between them, thereby generating a 'sandwich' structure consolidated by covalent and hydrogen bonding.

Key words. *N,N'*-dicyclohexylpiperazine, *N*-oxide, hydrate, crystal structure, hydrogen bonding.

1. Introduction
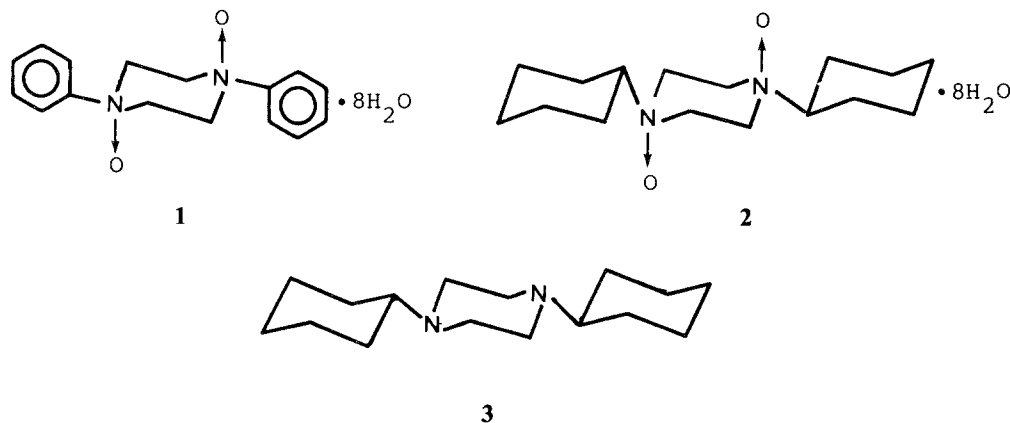
In a previous paper, we described the crystal structure of *N,N'*-diphenylpiperazine *N,N'*-dioxide octahydrate, **1** [1], which is characterized by strong hydrogen bonding between the water molecules, as well as between the *N*-oxide groups and water molecules, giving rise to

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a three-dimensional network structure composed of edge-sharing four-membered, five-membered, six-membered, and fourteen-membered rings. Synthesis and structure determination of the title compound **2** (replacing the phenyl rings in **1** by cyclohexyl rings) was undertaken as part of our systematic study of hydrated tertiary amine N-oxides. Our principal aim was to investigate how variations of N,N'-disubstitution in the piperazine ring would affect the structural chemistry and hydrogen bonding features of **1**.

2. Experimental

All reagents or solvents used are general purpose grade. Proton NMR spectra were recorded on a Brucker Cryospec WM250 (250 MHz) spectrometer. Deuterated methanol was used as solvent and δ (ppm) was measured with TMS as an internal standard. Mass spectra were recorded on a VG Micromass 70-70F spectrometer. Solid-state IR spectra were recorded on a Beckman AccuLab 1 spectrometer, and the KBr discs were prepared according to the standard procedure [2].

2.1. SYNTHESIS

The preparation of N,N'-dicyclohexylpiperazine, **3**, was carried out according to the scheme of Ionescu, [3], but the procedure of product isolation was modified. A mixture of cyclohexylamine (6 mL), NaOH (20 g) and dibromoethane (21 mL) was refluxed at 90—130°C for about 6 hours. The product was extracted with chloroform and washed thrice with about 200 mL of 10% NaOH. After the chloroform was removed by evaporation, the product (46.4% yield) was recrystallized from 60% ethanol.

The oxidation of **3** to **2** was effected by the procedure of Bennett [4]. Compound **3** was dissolved in a mixture of glacial acetic acid and hydrogen peroxide (30% aqueous). The mole ratio of **3** : acetic acid : hydrogen peroxide was 1 : 24.0 : 12.6. The mixture was kept at 50—70°C for about 16 hours. After removing the excess hydrogen peroxide and acetic acid, the crude product was dissolved and recrystallized from water at ~60°C several times. Well-formed crystals of **2** were obtained from slow evaporation of an aqueous solution in a desiccator containing silica gel placed in a refrigerator.

IR of **2** (KBr disc), 3215–3440 sbr, 2940–2960s, 2880s, 1710m, 1480m, 1462m, 1455m, 1442m, 1398m, 1360m, 1338m, 1310m, 1190w, 1050w, 1025w, 1010m, 980s, 962s, 932s, 900m, 858w, 822m, 775s, 700–738 sbr, 670s (cm^{-1}). ^{1}H NMR, 1.18–1.74 (m, 12H), 1.97 (d, 4H, $J = 9$ Hz), 2.35 (d, 4H, $J = 9$ Hz), 3.17 (d, 4H, $J = 9$ Hz), 3.24 (s, 2H, $J = 9$ Hz), 4.05 (d, 4H, $J = 9$ Hz) (ppm). MS (m/e), 281.9 (0.6%), 266.0 (2.2%), 250.0 (3.4%), 235.0 (11.7%), 167.0 (23.2%), 138.0 (11.3%), 85.1 (18.2%), 83.1 (45.4%), 82.0 (87.3%), 67.1 (100%) 56.1 (100%).

2.2. X-RAY DATA COLLECTION

The density was measured by flotation in n-hexane/carbon tetrachloride. A single crystal was cut to a suitable size and attached directly to a glass fiber with epoxy glue. Determination of the crystal class and orientation matrix, on a Nicolet R3m diffractometer using Mo$K\alpha$ radiation, was performed according to established procedures [5]. Accurate unit-cell dimensions were derived from a least-squares fit of the refined angular settings of 21 high-angle reflections. Intensity data were collected at 22°C following established procedures in our laboratory [6, 7]. The crystal remained stable throughout the diffraction

Table I. Data collection and processing parameters.

Molecular formula	$C_{16}H_{30}H_2O_2 \cdot 8H_2O$ (2)
Molecular weight	426.54
Cell parameters	$a = 12.961(4)$ Å $\quad \beta = 98.37(2)°$
	$b = 11.533(4) \quad\quad V = 1169.3(6)$
	$c = 7.907(1) \quad\quad Z = 2, F(000) = 471.9$
Density (exptl.)	1.24 g cm^{-3} (flotation in CCl_4/n-hexane)
Density (calcd.)	1.211 g cm^{-3}
Space Group	$C2/m$ (No. 12)
Radiation	graphite-monochromatized MoK_α, $\lambda = 0.71069$ Å
Absorption coefficient	0.92 cm^{-1}
Crystal size	$0.44 \times 0.40 \times 0.24$ mm
Mean μr	0.016
Transmission factors	0.926 to 0.945
Scan type and speed	ω-2θ; 2.02–8.37 deg min^{-1}
Scan range	$1°$ below $K\alpha_1$ to $1°$ above $K\alpha_2$
Background counting	stationary counts for one-half of scan time at each end of scan range
Collection range	$h, k, \pm l$: $2\theta_{max} = 60°$
Unique data measured	1515
Observed data with $|F_0| > 3\sigma(|F_0|)$, n	1192
Number of variables, p	70
$R = \Sigma \, ||F_0| - |F_c||/\Sigma \, |F_0|$	0.045
Weighting scheme	$w = [\sigma^2(|F_0|) + 0.0012|F_0|^2]^{-1}$
$R_w = [\Sigma \, w|F_0| - |F_c|)^2/\Sigma \, w|F_0|^2]^{\frac{1}{2}}$	0.065
$S = [\Sigma \, w(|F_0| - |F_c|)^2/(n - p)]^{\frac{1}{2}}$	1.395
Residual extrema in final difference map	$+0.24$ to $-0.26 \, e$ Å^{-3}

experiment as two standard reflections monitored every 125 data measurements showed only random fluctuations within $\pm 1\%$ of their mean values. The raw intensities were processed with the learnt-profile procedure [8], and absorption corrections were based on a pseudo-ellipsoidal fit to the azimuthal scans of selected strong reflections over a range of 2θ-values. The statistical distribution of the normalized structure factors was consistent with that expected for a centrosymmetric space group. The data collection and processing are summarized in Table I.

2.3. STRUCTURE DETERMINATION AND REFINEMENT

Structure solution was achieved by direct phase determination guided by negative quartets [9]. All non-hydrogen atoms were varied anisotropically in structure refinement. The methylene H atoms were generated geometrically (C—H bond length fixed at 0.96 Å) and assigned isotropic thermal parameters. Water H atoms, some of which exhibited two-fold disorder, were located from successive difference Fourier maps; they were assigned isotropic temperature factors and held stationary in subsequent least-square cycles. Computations were performed on a Data General Corporation Nova 3/12 minicomputer using the SHELXTL program package [10]. Analytic expressions of neutral-atom scattering factors were employed, and anomalous dipersion corrections were incorporated [11]. Blocked-cascade least-squares refinement [12] converged to the R indices listed in Table I. The numbering of atoms in the asymmetric unit is shown in Figure 1, and the refined atomic parameters are given in Tables II–IV.
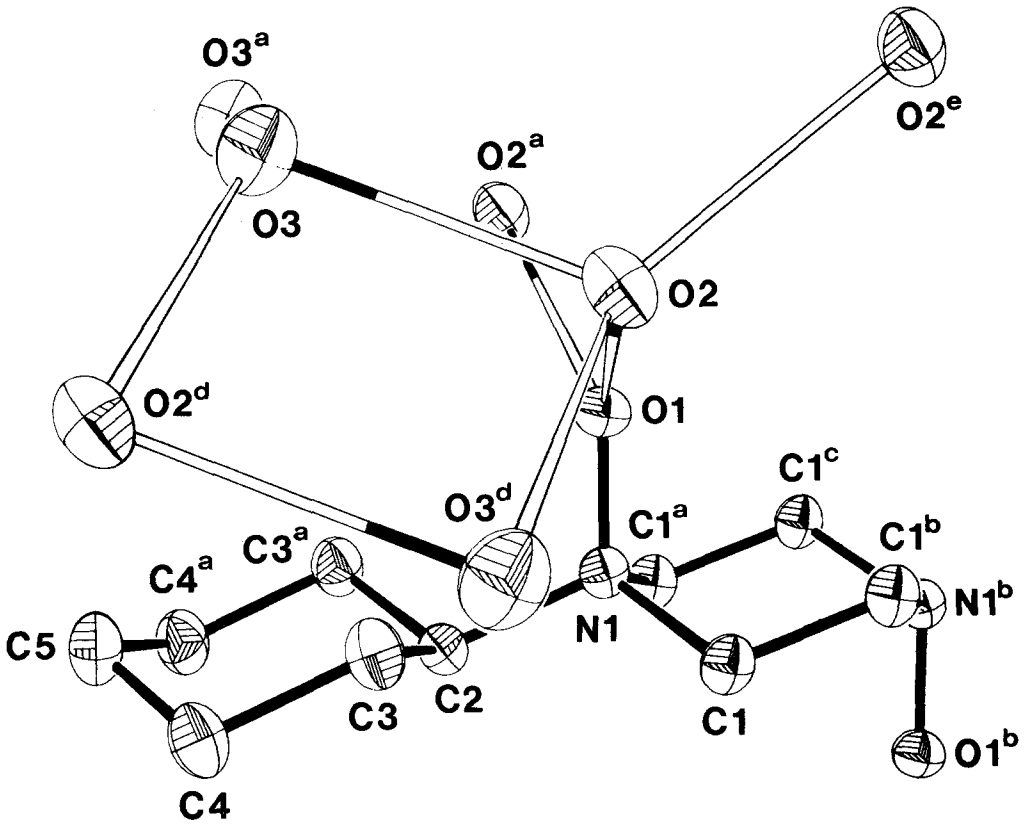
Fig. 1. Numbering of atoms in the asymmetric unit of **2**. The thermal ellipsoids are drawn at the 25% probability level.

Table II. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature ($\text{Å}^2 \times 10^3$) for the non-hydrogen atoms in the asymmetric unit of N,N'-dicyclohexylpiperazine N,N'dioxide octahydrate (**2**).

Atom	x	y	z	U_{eq}[a]
N,N'-dioxide				
O(1)	880(1)	0	2612(2)	39(1)
N(1)	1087(1)	0	933(2)	32(1)
C(1)	584(1)	1046(1)	22(2)	36(1)
C(2)	2271(1)	0	863(2)	33(1)
C(3)	2782(1)	1087(1)	1694(2)	44(1)
C(4)	3957(1)	1081(1)	1604(2)	49(1)
C(5)	4480(2)	0	2410(3)	53(1)
Water molecule				
0(2)	981(1)	1967(1)	4475(1)	54(1)
0(3)	2793(1)	1229(1)	6759(2)	64(1)

[a]Equivalent isotropic temperature factor U_{eq} defined as 1/3 of the trace of the orthogonalized U matrix.

Table III. Anisotropic thermal parameters[a] ($\text{Å}^2 \times 10^3$) for non-hydrogen atoms of N,N'-dicyclo-hexylpiperazine N,N'-dioxide octahydrate (2).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N,N'-dioxide						
O(1)	41(1)	42(1)	35(1)	0	10(1)	0
N(1)	33(1)	29(1)	35(1)	0	5(1)	0
C(1)	38(1)	27(1)	43(1)	2(1)	2(1)	0(1)
C(2)	31(1)	34(1)	35(1)	0	7(1)	0
C(3)	38(1)	39(1)	54(1)	−7(1)	7(1)	−2(1)
C(4)	38(1)	47(1)	62(1)	−6(1)	8(1)	−8(1)
C(5)	37(1)	62(1)	59(1)	0	−1(1)	0
Water molecules						
O(2)	46(1)	50(1)	67(1)	−12(1)	17(1)	−5(1)
O(3)	69(1)	49(1)	69(1)	5(1)	−1(1)	−1(1)

[a]The exponent takes the form: $-2\pi^2 \, \Sigma\Sigma \, U_{ij} h_i h_j a_i^* . a_j^*$.

3. Discussion

In the crystal structure of **2**, the N,N'-dioxide molecule occupies a site of symmetry $2/m$. A two-fold rotation axis (parallel to b) passes through the mid-points of the two carbon-carbon bonds in the central piperazine ring, so that the C(5), C(2), C(2)[b], C(5)[b] atoms and the two N—O bonds lie in the same mirror plane. The bond lengths and bond angles of **2** are tabulated in Table V. The measured N → O dative bond length of 1.392(2) Å is in good agreement with the corresponding values in N,N'-diphenylpiperazine N,N'-dioxide octahydrate, **1** [1.387(2) Å] [1], the 1 : 3 molecular complex of triethylenediamine N,N'-dioxide

Table IV. Hydrogen atomic coordinates ($\times 10^4$) and thermal parameters[a] ($\text{Å}^2 \times 10^3$) for N,N'-dicyclo-hexylpiperazine N,N'-dioxide octahydrate (2).

Atom	x	y	z	U
N,N'-dioxide				
H(1A)	734	1050	−1131	44
H(1B)	867	1732	602	44
H(2)	2365	0	−319	40
H(3A)	2472	1759	1110	53
H(3B)	2679	1112	2871	53
H(4A)	4270	1749	2196	57
H(4B)	4058	1114	426	57
H(5A)	4437	0	3611	61
H(5B)	5199	0	2244	61
Water molecules				
HO(2A)	921	1339	3804	70
HO(2B)*	1360	2445	4158	70
HO(2C)*	413	1973	4784	70
HO(3A)	2794	3527	3920	70
HO(3B)*	1818	3306	3351	70
HO(3C)*	2174	4456	3437	70

[a]The exponent of the isotropic temperature factor U takes the form $-8\pi^2 U \sin^2 \theta / \lambda^2$. Asterisk indicates half site occupancy.

Table V. Bond distances (Å), bond angles (deg), and selected torsion angles (deg) in N,N'-dicyclo-hexylpiperazine N,N'-dioxide octahydrate (**2**).

O(1)—N(1)	1.392(2)	N(1)—C(1)	1.505(1)
N(1)—C(2)	1.544(2)	C(2)—C(3)	1.522(2)
C(1)—C(1)[b]	1.509(2)	C(3)—C(4)	1.535(2)
C(4)—C(5)	1.514(2)	O(2)...O(3)[d]	2.874(2)
O(2)⋯O(3)	2.875(2)	O(1)⋯O(2)	2.698(2)
O(2)⋯O(2)[e]	2.788(2)	O(3)⋯(3)[a]	2.834(2)
O(1)—N(1)—C(1)	109.0(1)	O(1)—N(1)—C(2)	111.4(1)
C(1)—N(1)—C(2)	110.3(1)	N(1)—C(2)—C(3)	110.9(1)
C(1)—N(1)—C(1)[a]	106.7(1)	C(3)—C(2)—C(3)[a]	111.0(1)
N(1)—C(1)—C(1)[b]	112.0(1)	C(3)—C(4)—C(5)	111.8(1)
C(2)—C(3)—C(4)	110.4(1)	C(4)—C(5)—(4)[a]	110.8(2)
N(1)—O(1)⋯O(2)	121.3(2)	O(3)⋯O(2)⋯O(3)[d]	89.2(3)
O(2)[d]⋯O(3)⋯O(3)[a]	136.4(3)	O(2)⋯O(1)⋯O(2)[a]	114.5(2)
O(1)⋯O(2)⋯O(3)	93.7(3)	O(3)⋯O(2)⋯O(2)[e]	120.7(3)
O(1)⋯O(2)⋯O(3)[d]	114.1(3)	O(3)[d]⋯O(2)⋯O(2)[e]	132.4(3)
O(2)⋯O(3)⋯O(3)[a]	107.2(3)	O(1)⋯O(2)⋯O(2)[e]	100.9(3)
C(1)—N(1)—C(2)—C(3)	59.3(2)	O(1)—N(1)—C(2)—C(3)	−61.9(1)
O(1)—N(1)—C(1)—C(1)[b]	−60.5(1)	C(1)[a]—N(1)—C(1)—C(1)[b]	57.1(2)
C(3)—C(4)—C(5)—C(4)[a]	55.3(2)	N(1)—C(2)—C(3)—C(4)	−179.6(1)
C(2)—C(3)—C(4)—C(5)	−56.1(2)	C(3)[a]—C(2) − C(3)—C(4)	56.6(2)

Symmetry transformations:

[a] $x, -y, z$;	[b] $-x, y, -z$;	[c] $-x, -y, -z$;
[d] $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$;	[e] $-x, y, 1 - z$;	[f] $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$;
[g] $x, 1 - y, z$:	[h] $-x, 1 - y, 1 - z$;	[i] $-\frac{1}{2} + x, \frac{1}{2} + y, z$;
[j] $-\frac{1}{2} + x, \frac{1}{2} - y, z$;	[k] $-x, -y, 1 - z$.	

Table VI. The N—O bond lengths in some related amine derivatives

Compound	N—O bond length (Å)	Reference
N,N'-diphenylpiperazine N,N'-dioxide octahydrate	1.387(2)	[1]
N,N'-di(o-tolyl)piperazine N,N'-dioxide tetrahydrate	1.402(2)	[25]
N,N'-di(p-tolyl)piperazine N,N'-dioxide tetrahydrate	1.392(2)	[25]
N,N'-di(p-chlorophenyl)piperazine N,N'-dioxide tetrahydrate	1.395(1)	[25]
Me_3NO	1.388(5)	[26]
$Me_3NO \cdot 2H_2O$	1.398(1)	[14]
$Me_3NO \cdot HCl$	1.425(11)	[27]
$(CH_2)_6N_4O$	1.363(6)	[16]
$(CH_2)_6N_4O \cdot H_2O \cdot H_2O$	1.376(6)	[28]
$ON(CH_2CH_2)_3NO \cdot 3H_2O$	1.395(8)	[13]
NH_2OH	1.453(3)	[29]
$(NH_3OH)Cl$	1.411(2)	[30]

with water [1.395(8) Å] [13], and trimethylamine N-oxide dihydrate [1.398(1) Å] [14]. The N—O bond lengths in some related amine derivatives are listed for comparison in Table VI. The N(1)–C(1) bond [1.505(1) Å] is apparently longer than the corresponding bonds in piperazine hexahydrate [1.459(4) Å] [15]. This may be rationalized by the fact that the formally positive N(1) atom in **2** induces its neighbouring C(1) atom to rehybridize so as to shift more p-character into its hybrid atomic orbital towards N(1) [16]. All the covalent bonds in **2** are arranged in nearly staggered conformations according to the values of torsion angles shown in Table V.

From Figure 2, it can be seen that the water molecules and the O atoms of the N-oxide groups are connected by hydrogen bonding in the pattern of a puckered layer composed of edge-sharing four-membered (type A, Figure 3), five-membered (type B involving one N-oxide group, Figure 3), six-membered (type C involving the N-oxide groups of two N,N'-dioxide molecules, Figure 3), and eight-membered rings (type D, Figure 3). Ring A is centrosymmetric, ring B has symmetry m, whereas the other two have symmetry $2/m$. The water protons which are not involved in hydrogen bonding with the N-oxide groups are two-fold disordered.

This puckered layer, which is parallel to the ab plane, may be considered as composed of two novel types of edge-sharing, ribbon-like arrangements of hydrogen bonded rings (Figure 2). One ribbon-like arrangement is formed by four- and five-membered hydrogen bonded rings (A and B respectively), and the other type by six- and eight-membered hydrogen bonded rings (C and D respectively). Both of them extend parallel to the b axis, and the puckered layer is generated by arranging these ribbons alternately and side-by-side normal to the a direction. Adjacent puckered layers are further cross-linked by the N,N'-dicyclohexylpiperazine moieties lying between them, thereby generating a three-dimensional network structure consolidated by covalent and hydrogen bonding. The resulting structure (Figure 4) bears a close resemblance to the 'sandwich' structure of the tetrahydrates of
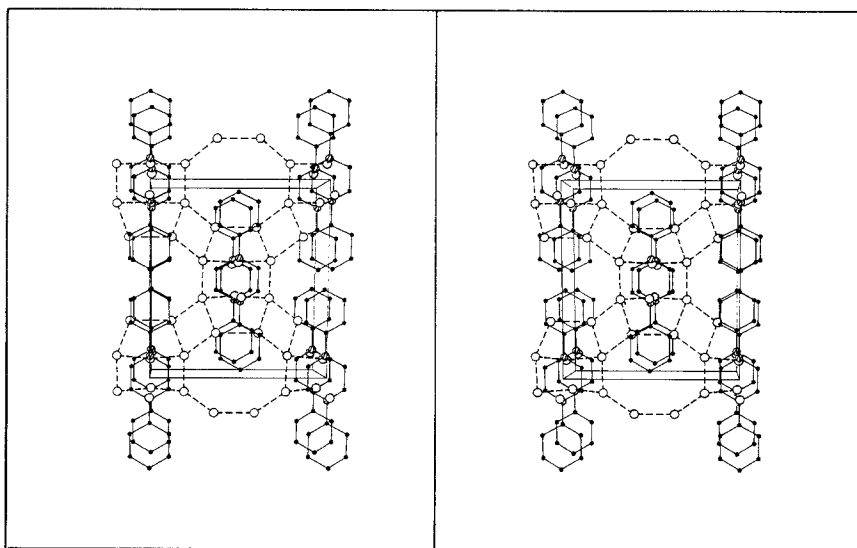

Fig. 2. Stereodrawing showing a puckered layer in the crystal structure of **2**. The origin of the unit cell lies at the lower left corner, with a pointing upwards, c away from the reader, and b from left to right. The hydrogen bonds are represented by broken lines.
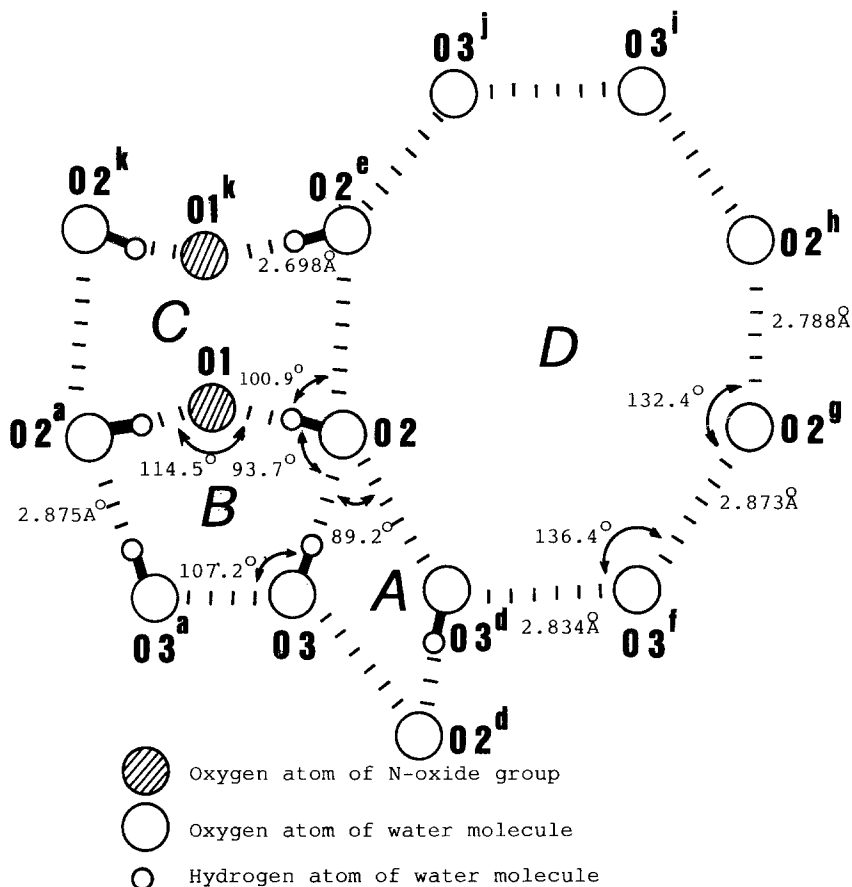
Fig. 3. Geometries of the four-, five-, six-, and eight-membered hydrogen bonded rings of a puckered layer in **2**. The symmetry transformations are as given in Table V.

2,5-dimethyl-2,5-hexanediol [17] and 2,7-dimethyl-2,7-octanediol [18], in which layers of puckered edge-sharing pentagons (formed by the water and hydroxyl groups) are separated by the hydrocarbon chains.

Compound **2**, like that of **1** [1], is a novel type of hydrate inclusion compound in which the host lattice is constructed of water molecules and the O atoms of *N*-oxide groups. In view of the polar nature of the *N*-oxide bond, the host framework bears a partial negative charge, which may be considered as filling the gap between the neutral water lattices in the gas hydrates [19–21] and the negatively charged water-anion lattices in the peralkylated onium salt hydrates [19–24]. The guest species in **2** are the *N*,*N*′-dicyclohexylpiperazine moieties, so that the dominant host-guest interaction comprises coordinate covalent N → O bonding.

Although **1** and **2** have the same stoichiometry, the difference in size between the phenyl and cyclohexyl groups leads to very different crystal structures. In **1** the *N*,*N*′-diphenylpiperazine moiety lies within a void in a three-dimensional hydrogen bonded framework formed by the water molecules and the *N*-oxide groups, whereas in **2** there are insufficient water molecules to enclose the *N*,*N*′-dicyclohexylpiperazine portion of the guest species. A comparison of the principal types of hydrate inclusion compounds in terms of host-lattice composition and host-guest interaction is given in Table VII.

Table VII. Hydrate inclusion compounds differing in host-lattice composition and host-guest interaction.

| Hydrate	Host lattice	Crystal structure	Guest species	Host-guest interaction	Reference
$6Cl_2 \cdot 46H_2O$	water molecules	clathrate	Cl_2	van der Waals	[31]
$(CH_2)_6N_4 \cdot 6H_2O$	water molecules	clathrate-like framework	$(CH_2)_6N_4$	hydrogen bonding and van der Waals	[32]
$(CH_3)_4N^+OH^- \cdot 5H_2O$	water molecules and hydroxide ions	clathrate	$(CH_3)_4N^+$	ionic and van der Waals	[33]
$(C_2H_5)_4N^+CH_3COOO^- \cdot 4H_2O$	water molecules and acetate ions	layer	$(C_2H_5)_4N^+$	ionic and van der Waals	[23]
2,5-dimethyl-2,5-hexanediol tetrahydrate	water molecules and hydroxyl groups	sandwich	$-C(CH_3)_2CH_2CH_2(CH_3)_2C-$ moiety	convalent and van der Waals	[17]
Compound 1	water molecules and N-oxide groups	clathrate-like framework	N,N'-diphenylpiperazine moiety	coordinate covalent (partially ionic) and van der Waals	[1]
N,N'-diaryl]piperazine N,N'-dioxide tetrahydrate (aryl = o-tolyl, p-tolyl, p-chlorophenyl)	water molecules and N-oxide group	layer	N,N'-diarylpiperazine moiety	coordinate covalent and van der Waals	[25]
Compound 2	water molecules and N-oxide groups	sandwich	N,N'-dicyclohexyl-piperazine moiety	coordinate covalent and van der Waals	This work
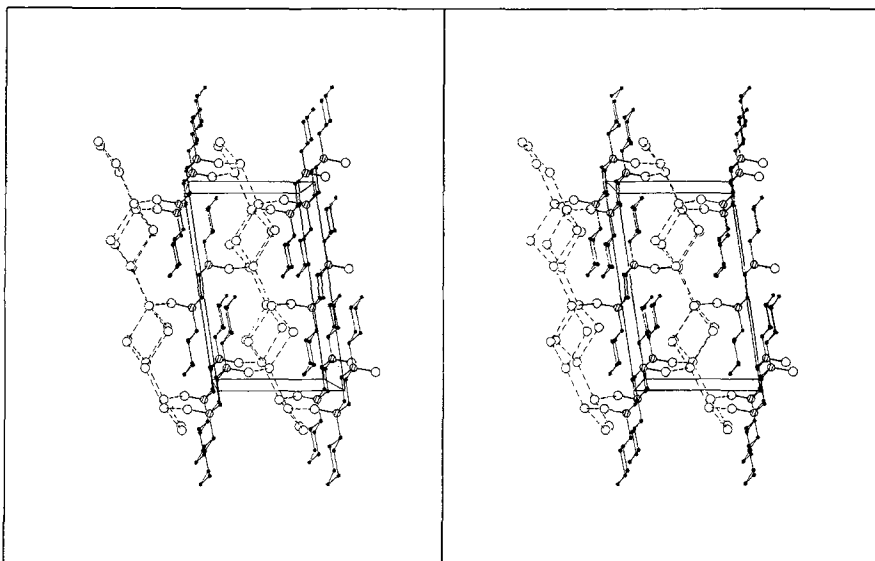
Fig. 4. Stereodrawing of the crystal structure of **2**. The origin of the unit cell lies at the lower left corner, with *a* pointing upwards at a slant, *b* towards the reader, and *c* from left to right. The hydrogen bonds are represented by broken lines.

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