C3—N3—C18	126.6 (2)	C19—C4—C21	86.6 (2)
C6—N5—C4	123.6 (3)	C4—C19—C20	88.4 (2)
N2—C3—N3	114.9 (3)	C19—C20—C21	87.8 (2)
N2—C3—C4	122.5 (2)	C4—C21—C20	88.7 (2)
N3—C3—C4	122.6 (2)		
C12—S1—N2—C3	−135.0 (3)	N3—C3—C4—N5	−107.0 (3)
N2—S1—C12—C11	60.3 (3)	N3—C3—C4—C21	27.8 (4)
S1—N2—C3—N3	168.8 (3)	C4—N5—C6—C7	−165.4 (3)
S1—N2—C3—C4	−11.3 (5)	N5—C6—C7—C8	109.0 (3)
C18—N3—C3—N2	178.3 (3)	C7—C8—C9—C10	96.2 (4)
C17—N3—C3—N2	3.6 (4)	C8—C9—C10—C11	−179.0 (3)
C6—N5—C4—C3	68.1 (3)	C7—C8—C9a—C10a	−87.1 (9)
N2—C3—C4—N5	73.1 (3)	C8—C9a—C10a—C11	175.7 (8)

Table 2. Hydrogen-bonding geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N5—H5⋯O2	0.870 (18)	2.10 (3)	2.773 (3)	133 (3)
C1—H11⋯O6[i]	0.99	2.23	3.192 (4)	163
C1—H12⋯O14[ii]	0.99	2.33	3.177 (4)	144
C1—H12⋯O15[ii]	0.99	2.42	3.274 (5)	144

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $1 - x, 1 - y, -z$.

The absorption corrections were based on the ψ scans of three reflections. Two methylene groups, C9 and C10, of the 12-membered ring are disordered. Two positions were defined for each of these atoms and their site occupation factors were refined. The major conformation has an occupancy of 0.743 (8). The conformation of the disordered region was restrained to maintain a reasonable geometry by applying DFIX restraints (Sheldrick, 1997) to all C—C bonds involving at least one of the atoms C9 and C10. The largest peaks and holes of residual electron density were 0.87 and 0.38 Å from C11 and C10a, respectively. The amide H atom was placed in the position indicated by a difference electron density map and its positional and isotropic displacement parameters were allowed to refine while the N—H bond length was restrained to 0.90 (2) Å. All of the remaining H atoms were placed in geometrically calculated positions. The methyl H atoms were refined as rigid groups which were allowed to rotate but not to tip, and U_{iso}(H) was set equal to $1.5U_{eq}$(parent atom). All other H atoms were allowed to ride on their parent atoms with U_{iso}(H) = $1.2U_{eq}$(C).

Data collection: MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1991). Cell refinement: MSC/AFC Diffractometer Control Software. Data reduction: TEXSAN PROCESS (Molecular Structure Corporation, 1989). Program(s) used to solve structure: SHELXS86 (direct methods) (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97. Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1482). Services for accessing these data are described at the back of the journal.

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Highly Rigid Crown Ether Fragments: Phenyl and Cyclohexyl Catechol Ethers

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Abstract

The structures of 1,2-bis(o-nitrophenoxy)benzene [(1), $C_{18}H_{12}N_2O_6$], 2,2'-o-phenylenedioxybis(phenylamine) [(2), $C_{18}H_{16}N_2O_2$] and meso-2,2'-o-phenylenedioxybis(cyclohexanol) [(3), $C_{18}H_{26}O_4$], potential precursors for rigid crown ether molecules, are presented. Each structure displays hydrogen bonding. Compound (1) exhibits weak C—H⋯O interactions, while (2) and (3) display extensive E—H⋯E and E—H⋯π (E = N, O) bonding.

Comment

Much of our recent work with crown ether molecules has focused on the substitution of their relatively flexible ethylene linkages with more rigid groups such as benzo, cyclohexano, or furano (Burns et al., 1996). Making crown ether molecules more rigid will limit their conformational flexibility and can affect their

extraction properties (Sachleben *et al.*, 1996; Vögtle & Weber, 1992). Synthetic convenience has allowed the substitution of only every other ethylene linkage around a crown ether ring. Our increasing desire to further inhibit conformational flexibility has compelled us to develop new synthetic methods towards more highly substituted crown ether molecules. In the course of this work, we have prepared and structurally characterized three new catechol diether molecules, (1), (2) and (3), as potential precursors to highly substituted crown ether extractants.
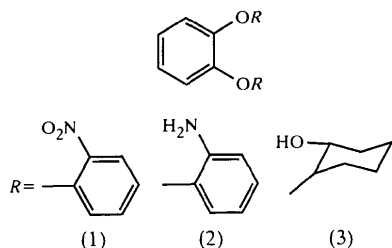
The three catechol diether compounds are shown in Figs. 1–3. All bond lengths and angles are in good

Fig. 3. Molecular structure of (3) showing 50% probability displacement ellipsoids.

agreement with standard values (Allen *et al.*, 1987). For example, the aromatic C=C bonds vary from 1.369 (2) to 1.399 (2) Å, with an average of 1.385 (3) Å.

All three compounds exhibit hydrogen bonding. Compound (1) displays the most subtle example as it has no strong hydrogen-bond donors. Only weak C—H···O interactions (Steiner, 1996) are observed (Table 2). Compound (2) exhibits N—H···N bonding as shown in Table 4 and Fig. 4. Additionally, one amine H atom
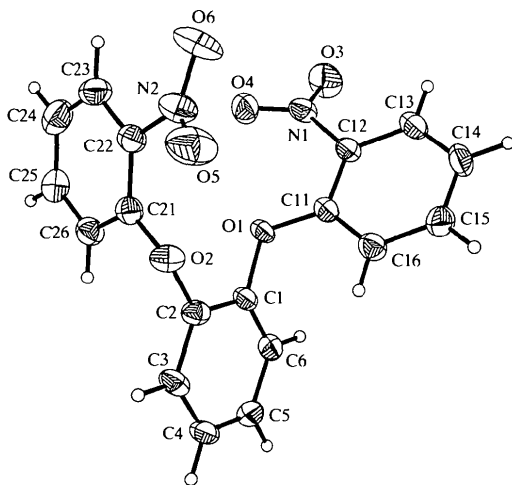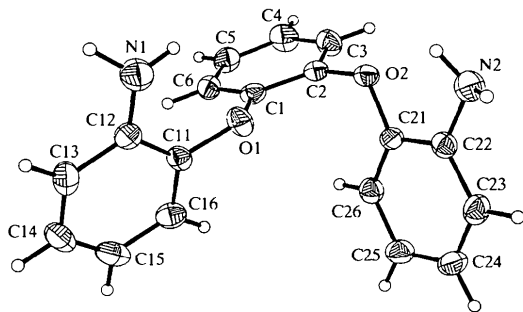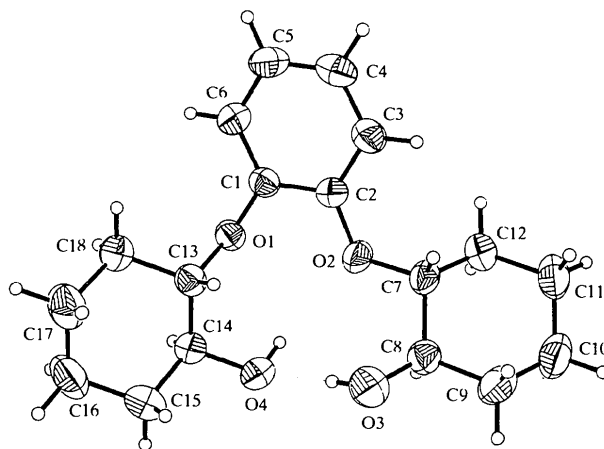

Fig. 1. Molecular structure of (1) showing 50% probability displacement ellipsoids.

Fig. 2. Molecular structure of (2) showing 50% probability displacement ellipsoids.
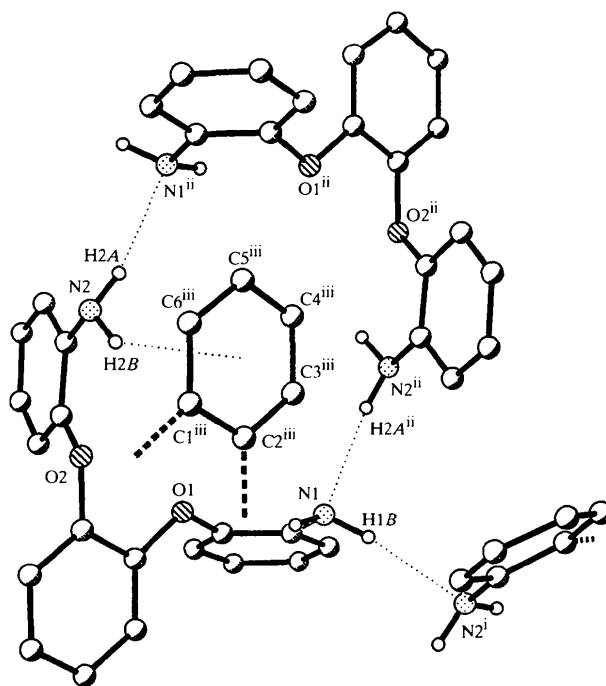

Fig. 4. Hydrogen-bond interactions in (2). For clarity, two of the symmetry-equivalent molecules are shown incomplete, all atoms are represented as circles, and only the amine H atoms are shown. Symmetry codes: (i) $2 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$; (ii) $2 - x$, $1 - y$, $1 - z$; (iii) $2 - x$, $1 - y$, $-z$.

is located near an arene ring center (H···centroid = 2.78 Å), suggesting an N—H···π interaction (Bakshi *et al.*, 1994). A few close C—H···π contacts are also observed, some of which may represent hydrogen bonds (Steiner *et al.*, 1996). The metrical parameters for these potential hydrogen bonds are also presented in Table 4, with ring centroids represented as $Cn1-n6$ (n = 0, 1, 2) for the C atoms that make up the ring.

Hydrogen bonds observed in compound (3) are presented in Table 6 and in Fig. 5. A conventional intramolecular hydrogen bond exists between H3A and O4 [H···O = 2.16(2) Å, O—H···O = 168(2)°]. The other hydroxy H atom (H4A) does not have good directionality towards any acceptor, yet it is surrounded by two ether O atoms (O1 and O2) and a phenyl ring (C1–6^i). In a sense, H4A is trifurcated by these three acceptors. On the opposite face of the molecule, H7 forms a hydrogen bond to a symmetry equivalent of

O1. Taken together, the intermolecular hydrogen bonds form one-dimensional chains along **c**.

Experimental

Preparations for compounds (1) and (2) have been previously reported (Kurita & Williams, 1974). X-ray quality crystals of (1) were grown from an Et₂O/hexane solution, and (2) and (3) were grown from acetonitrile solutions. Compound (3) was synthesized by reaction of catechol and cyclohexene oxide with potassium carbonate in refluxing ethanol (Szemes *et al.*, 1987). The *meso-* and D,L isomers were separated by silica gel chromatography.

Compound (1)

Crystal data

C₁₈H₁₂N₂O₆	Mo $K\alpha$ radiation
$M_r = 352.30$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 25
$P2_12_12_1$	reflections
$a = 7.9494\,(9)$ Å	$\theta = 10.6-14.9°$
$b = 13.3702\,(7)$ Å	$\mu = 0.11$ mm^{-1}
$c = 14.9355\,(8)$ Å	$T = 173\,(2)$ K
$V = 1587.4\,(2)$ Å^3	Square rod
$Z = 4$	$0.36 \times 0.32 \times 0.31$ mm
$D_x = 1.47$ Mg m^{-3}	Yellow
D_m not measured	

Data collection

Nonius CAD-4 diffractometer	$\theta_{max} = 26°$
	$h = -9 \rightarrow 9$
ω scans	$k = -16 \rightarrow 16$
Absorption correction: none	$l = -18 \rightarrow 18$
4410 measured reflections	3 standard reflections
1801 independent reflections	frequency: 120 min
1495 reflections with	intensity decay: 5%
$I > 2\sigma(I)$	
$R_{int} = 0.034$	

Refinement

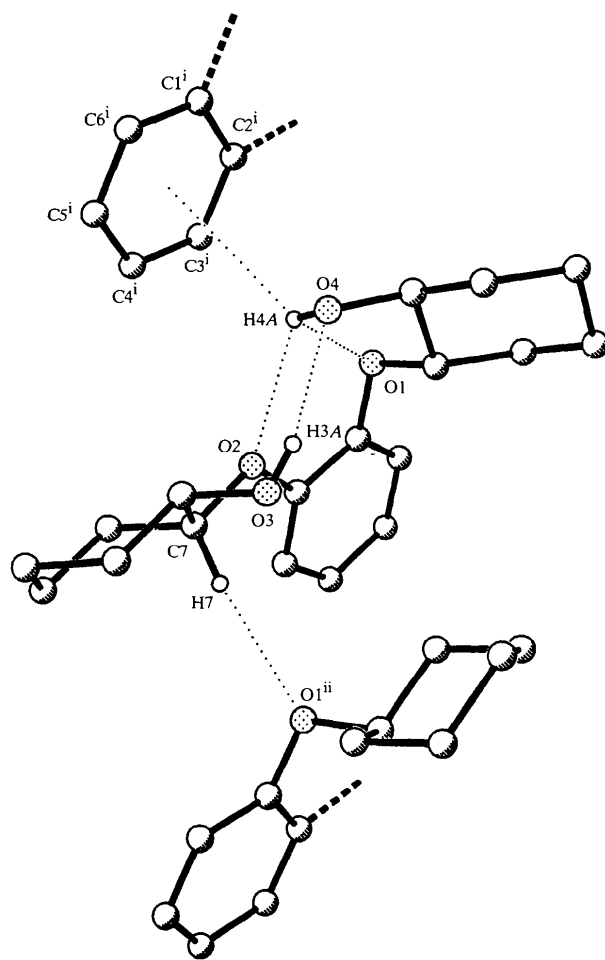|	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2$
$R(F) = 0.042$	$+ 0.4843P]$
$wR(F^2) = 0.114$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.000$
3117 reflections	$\Delta\rho_{max} = 0.38$ e Å^{-3}
235 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-3}
H-atom parameters not refined	Extinction correction: none
	Scattering factors from
	International Tables for Crystallography (Vol. C)

Fig. 5. Hydrogen-bond interactions in (3). For clarity, two of the symmetry-equivalent molecules are shown incomplete, all atoms are represented as circles, and only the amine H atoms are shown. Symmetry codes: (i) x, $\frac{3}{2} - y$, $-\frac{1}{2} + z$; (ii) x, $\frac{3}{2} - y$, $\frac{1}{2} + z$.

Table 1. *Selected geometric parameters (Å, °) for (1)*

O1—C1	1.403 (3)	O4—N1	1.224 (3)
O1—C11	1.370 (3)	O5—N2	1.229 (4)
O2—C2	1.385 (3)	O6—N2	1.214 (3)
O2—C21	1.371 (3)	N1—C12	1.463 (3)
O3—N1	1.223 (3)	N2—C22	1.459 (4)
C1—O1—C11	117.6 (2)	O4—N1—C12	118.5 (2)
C2—O2—C21	115.8 (2)	O5—N2—O6	122.9 (3)
O3—N1—O4	122.9 (2)	O5—N2—C22	118.3 (3)
O3—N1—C12	118.6 (2)	O6—N2—C22	118.4 (2)

Table 2. *Hydrogen-bonding geometry (Å, °) for (1)*

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···O5^i	0.95	2.57	3.402 (4)	147
C6—H6···O6^{ii}	0.95	2.52	3.400 (4)	155
C15—H15···O4^{iii}	0.95	2.44	3.324 (3)	154
C26—H26···O6^{iv}	0.95	2.56	3.340 (4)	140

Symmetry codes: (i) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $\frac{1}{2}-x, -y, z-\frac{1}{2}$; (iii) $x-1, y, z$; (iv) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Compound (2)

Crystal data

$C_{18}H_{16}N_2O_2$	Mo $K\alpha$ radiation
$M_r = 292.34$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
$a = 10.9111$ (7) Å	$\theta = 10.2-14.7°$
$b = 18.0088$ (9) Å	$\mu = 0.09$ mm^{-1}
$c = 7.5830$ (6) Å	$T = 173$ K
$\beta = 93.362$ (8)°	Chunk
$V = 1487.46$ (17) Å^3	0.54 × 0.51 × 0.35 mm
$Z = 4$	Colorless
$D_x = 1.30$ Mg m^{-3}	
D_m not measured	

Data collection

Nonius CAD-4 diffractom-eter	$\theta_{max} = 25°$
ω scans	$h = -12 \to 12$
Absorption correction: none	$k = -21 \to 13$
3470 measured reflections	$l = 0 \to 9$
2604 independent reflections	3 standard reflections
2044 reflections with	frequency: 120 min
$I > 2\sigma(I)$	intensity decay: 3%
$R_{int} = 0.023$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.000$
$R(F) = 0.039$	$\Delta\rho_{max} = 0.33$ e Å^{-3}
$wR(F^2) = 0.111$	$\Delta\rho_{min} = -0.17$ e Å^{-3}
$S = 1.04$	Extinction correction:
2603 reflections	SHELXL93 (Sheldrick,
212 parameters	1993)
H atoms treated by a	Extinction coefficient:
mixture of independent	0.019 (2)
and constrained refinement	Scattering factors from
$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2$	*International Tables for*
$+ 0.4572P]$	*Crystallography* (Vol. C)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 3. *Selected geometric parameters (Å, °) for (2)*

O1—C1	1.381 (2)	O2—C21	1.395 (2)
O1—C11	1.396 (2)	N1—C12	1.386 (2)
O2—C2	1.391 (2)	N2—C22	1.406 (2)
C1—O1—C11	118.6 (1)	C2—O2—C21	116.8 (1)

Table 4. *Hydrogen-bonding geometry (Å, °) for (2)*

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···N2^i	0.97 (3)	2.24 (3)	3.207 (2)	171.7 (19)
N2—H2A···N1^{ii}	0.94 (2)	2.53 (2)	3.429 (2)	160.2 (18)
N2—H2B···C1-6^{iii}	0.91 (2)	2.78	3.56 (1)	145

C4—H4···C21-26^{iv}	0.95	2.90	3.66 (1)	139
C5—H5···C11-16^{iv}	0.95	2.59	3.43 (1)	147
C24—H24···C21-26^v	0.95	3.05	3.76 (1)	133

Symmetry codes: (i) $2-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $2-x, 1-y, 1-z$; (iii) $2-x, 1-y, -z$; (iv) $x, y, z-1$; (v) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

Compound (3)

Crystal data

$C_{18}H_{26}O_4$	Mo $K\alpha$ radiation
$M_r = 306.40$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
$a = 8.6656$ (6) Å	$\theta = 10.2-14.2°$
$b = 17.7913$ (14) Å	$\mu = 0.09$ mm^{-1}
$c = 10.7602$ (6) Å	$T = 296$ K
$\beta = 97.548$ (6)°	Prism
$V = 1644.6$ (2) Å^3	0.54 × 0.41 × 0.24 mm
$Z = 4$	Colorless
$D_x = 1.24$ Mg m^{-3}	
D_m not measured	

Data collection

Nonius CAD-4 diffractom-eter	$\theta_{max} = 25°$
ω scans	$h = -5 \to 10$
Absorption correction: none	$k = -21 \to 21$
6685 measured reflections	$l = -12 \to 12$
2898 independent reflections	3 standard reflections
2057 reflections with	frequency: 120 min
$I > 2\sigma(I)$	intensity decay: 1%
$R_{int} = 0.026$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.000$
$R(F) = 0.033$	$\Delta\rho_{max} = 0.13$ e Å^{-3}
$wR(F^2) = 0.090$	$\Delta\rho_{min} = -0.13$ e Å^{-3}
$S = 1.04$	Extinction correction:
2898 reflections	SHELXL93 (Sheldrick,
206 parameters	1993)
H atoms treated by a	Extinction coefficient:
mixture of independent	0.0402 (2)
and constrained refinement	Scattering factors from
$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2$	*International Tables for*
$+ 0.2944P]$	*Crystallography* (Vol. C)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 5. *Selected geometric parameters (Å, °) for (3)*

O1—C1	1.382 (2)	O2—C7	1.445 (2)
O1—C13	1.449 (2)	O3—C8	1.426 (2)
O2—C2	1.369 (2)	O4—C14	1.426 (2)
C1—O1—C13	114.4 (1)	C2—O2—C7	119.1 (1)

Table 6. *Hydrogen-bonding geometry (Å, °) for (3)*

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···O4	0.84 (2)	2.16 (2)	2.9911 (19)	168 (2)
O4—H4A···O1	0.84 (3)	2.40 (2)	2.8109 (15)	111.0 (18)
O4—H4A···O2	0.84 (3)	2.54 (2)	3.1055 (18)	126.2 (18)
O4—H4A···C1-6^i	0.84 (3)	3.02	3.53 (1)	121
C7—H7···O1^{ii}	0.98	2.47	3.4465 (18)	172

Symmetry codes: (i) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (ii) $x, \frac{3}{2}-y, \frac{1}{2}+z$.

Anisotropic displacement parameters were used for all non-H atoms. All C-bound H atoms were placed in calculated positions, refined using a riding model, and given isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of the C atom to which they are attached. The C—H distances used depend on the temperature and type of C atom: for (1) and (2) $C_{aromatic}$—H = 0.95 Å at 173 K; for (3) $C_{tertiary}$—H = 0.98, $C_{secondary}$—H = 0.97, $C_{aromatic}$—H = 0.93 Å at 296 K. Positional parameters for all heteroatom-bound H atoms were refined. They were given isotropic displacement parameters equal to 1.5 times the equivalent isotropic displacement parameter of the atom to which they are attached. Two full octants of data $(-h, -k, +l$ and $+h, +k, -l)$ and one partial octant $(\theta \leq 15^\circ$ $+h, +k, +l)$ were collected for (1). The refinement of (1) was performed without averaging Friedel pairs. The absolute structure of (1) was not reliably determined as the Flack parameter (Flack, 1983) has a high s.u. for both structures, while the residuals were unchanged.

For all compounds, data collection: *CAD-4-PC* (Enraf–Nonius, 1993); cell refinement: *CAD-4-PC*; data reduction: *XCAD4* (Harms, 1995); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL* (Siemens, 1990); software used to prepare material for publication: *PLATON* (Spek, 1990).

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1,4-Bis(imidazol-1-ylmethyl)benzene Dihydrate

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Abstract

An analysis of the structure of 1,4-bis(imidazol-1-yl-methyl)benzene dihydrate, $C_{14}H_{14}N_4.2H_2O$, shows that the imidazole moieties hydrogen bond to water molecules to form an extended two-dimensional sheet.

Comment

Metal complexes of 1,4-bis(imidazol-1-ylmethyl)benzene, hereafter bix, have been shown recently to form coordination polymers incorporating unusual polyrotaxane interactions (Hoskins *et al.*, 1997a,b). Within each coordination polymer two distinct types of conformation are observed, *i.e.* a centrosymmetric conformation and a 'half-loop' conformation in which bix forms part of an $M_2(bix)_2$ macrocycle. As part of a more general investigation into the ligand and its conformational preferences, bix was isolated as its dihydrate, (I).

(I)
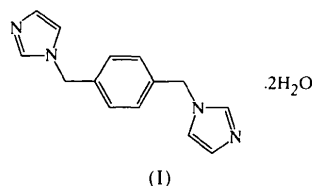
The midpoint of the phenylene ring lies on a centre of symmetry and the terminal N atoms of the imidazole rings form hydrogen bonds [N$\cdots$O 2.822(5) Å] to the O atoms of two water molecules, as shown in Fig. 1. Further hydrogen bonding between water molecules [O$\cdots$O 2.727(9) and 2.781(9) Å] results in a