Isolation and *X*-Ray Crystal Structure of a 2:1 Complex between Picric Acid and Dibenzo-24-crown-8; an Example of a Sandwich Structure†

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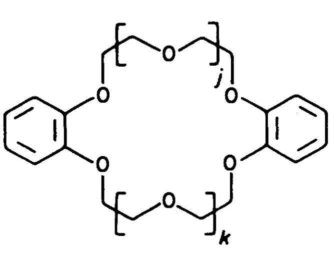
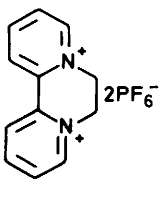
Despite the lack of strong intermolecular interactions in solution, picric acid (PicH) forms crystalline 2:1 complexes with both dibenzo-18-crown-6 (DB18C6) and dibenzo-24-crown-8 (DB24C8). An *X*-ray crystallographic study of 2PicH•DB24C8 reveals a continous layer structure comprising alternate PicH and DB24C8 molecules with stacking of the π-electron-deficient aromatic rings in the PicH molecules and the π-electron-rich aromatic rings in DB24C8 molecules.

The ability of dibenzo-crown ethers[1] of the general type DB3*n*C*n* (*n* = 6—10) to form stable 1:1 adducts in solution with substrates such as [Diquat][PF_6]$_2$[2] and [Pt(bipy)-(NH_3)$_2$][PF_6]$_2$[3] has been ascribed in part to charge-transfer interactions between the π-electron-deficient heterocyclic rings in the substrates and the π-electron-rich benzo rings in the crown ethers. The presence of charge-transfer absorption bands in the visible spectra, and the significant changes in ^{1}H chemical shifts experienced by both π-donor and π-acceptor aromatic rings in the ^{1}H n.m.r. spectra upon complexation, lend considerable support to the conclusion that the charge-transfer interactions in these 1:1 adducts provide a substantial part of their stabilisation energies (in acetonitrile, $\Delta G_{25}°$ = −4.9 and −7.2 kcal mol^{-1},‡ respectively). Although lithium picrate forms[4] a 2:1 crystalline complex with DB36C12 in which the two picrate ions are oriented nearly parallel to the benzo rings in the host, with a minimum inter-group separation of 3.37 Å, ^{1}H n.m.r. spectroscopy of a range of ethers DB3*n*C*n* (*n* = 9—12) reveals[4] little if any interaction between these two aromatic π-systems in solution. Presumably the formal negative charge on the picrate anion prevents it from behaving as a π-acceptor towards the electron-rich π-donating catechol units.

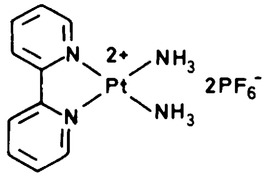
In view of the weak intermolecular charge-transfer complexes formed between macrocyclic polyethers, such as benzo-15-crown-5, DB18C6, and DB24C8, and neutral π-acceptors, such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone,[5] some tri- and tetra-nitrofluorenones,[6] and 8-dicyanomethylene-1,3-methanoindan,[7] we have examined the nature of the intermolecular interactions between the ethers DB3*n*C*n* and picric acid (PicH). The formation of charge-transfer complexes of PicH with aromatic species is a well established phenomenon.[8] In addition to the fact that a large number of charge-transfer complexes between n-alkylbenzenes and PicH have been prepared[9] as a means of separating substances and for purposes of identification, a number of complexes of nitrophenols with 18-crown-6 have been isolated and characterised.[10] The *X*-ray crystal structure of the (18-crown-6)•(2,4-dinitrophenol)•(water) (1:2:2) complex reveals that this π-electron-deficient phenol binds to the crown *via* its hydroxy group through the mediation of water molecules.[11]



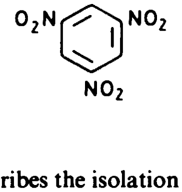
DB3*n*C*n*	*n*	*j*	*k*
DB18C6	6	1	1
DB21C7	7	2	1
DB24C8	8	2	2
DB27C9	9	3	2
DB30C10	10	3	3
DB33C11	11	4	3
DB36C12	12	4	4



[Diquat][PF_6]$_2$



[Pt(bipy)(NH_3)$_2$][PF_6]$_2$



PicH

This paper describes the isolation and characterisation of the 2:1 crystalline complexes, 2PicH•DB18C6 and 2PicH•DB24C8. The *X*-ray crystal structure of 2PicH•DB24C8 is reported and spectroscopic data (u.v. and ^{1}H n.m.r.) in solution are presented and evaluated with reference to the available solid-state structural information.

Experimental

Isolation of the 2:1 *Complex of* 2,4,6-*Trinitrophenol with Dibenzo*-24-*crown*-8 (2*PicH•DB*24*C*8) *and its* X-*Ray Structural Analysis*.—Approximately stoicheiometric amounts of picric acid (PicH) (50 mg) and dibenzo-24-crown-8 (DB24C8) (100 mg) were dissolved in acetone–dichloromethane (1:1) (5 ml), and the solution was filtered. Light petroleum (b.p. 60—80 °C) was allowed to diffuse slowly into the solution from the vapour phase.[12] After 44 h, large clusters of the 2:1 *complex*

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† *Supplementary data available* (SUP 56425, 3 pp.): H-co-ordinates, anisotropic thermal parameters. For details of Supplementary Publications see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, Issue 1, 1986. Structure factor tables are available from the editorial office on request.

‡ 1 kcal = 4.184 kJ.

Table 1. Atom co-ordinates (× 10^4) and temperature factors ($Å^2$ × 10^3)

Atom	x	y	z	U*
O(1)	−539(2)	−2 189(2)	1 676(1)	46(1)
C(2)	−1 292(3)	−3 303(2)	957(1)	45(1)
C(3)	−1 054(3)	−2 540(2)	70(1)	43(1)
O(4)	−2 418(2)	−1 804(2)	−74(1)	45(1)
C(5)	−2 633(3)	−1 375(2)	−992(1)	43(1)
C(6)	−4 185(3)	−2 614(2)	−1 539(1)	43(1)
O(7)	−4 517(2)	−2 200(2)	−2 447(1)	43(1)
C(8)	−3 246(3)	−2 387(2)	−3 058(1)	41(1)
C(9)	−2 390(3)	−986(2)	−3 560(1)	41(1)
O(10)	−1 140(2)	132(2)	−2 916(1)	45(1)
C(11)	−202(3)	1 535(2)	−3 229(1)	36(1)
C(12)	−111(3)	1 876(2)	−4 131(2)	47(1)
C(13)	910(3)	3 327(3)	−4 377(2)	55(1)
C(14)	1 817(3)	4 416(3)	−3 721(2)	56(1)
C(15)	1 733(3)	4 087(2)	−2 807(2)	48(1)
C(16)	722(3)	2 649(2)	−2 549(1)	37(1)
C(17)	3 935(3)	−2 886(2)	2 361(1)	40(1)
O(17)	2 554(2)	−4 225(2)	2 206(1)	58(1)
C(18)	4 665(3)	−2 039(2)	1 612(1)	37(1)
C(19)	6 022(3)	−629(2)	1 710(1)	39(1)
C(20)	6 709(3)	−32(2)	2 574(1)	40(1)
C(21)	6 058(3)	−809(3)	3 332(2)	45(1)
C(22)	4 683(3)	−2 219(3)	3 221(1)	44(1)
N(1)	3 902(2)	−2636(2)	691(1)	45(1)
O(18)	3 626(2)	−1 759(2)	142(1)	58(1)
O(19)	3 618(3)	−3 965(2)	518(1)	74(1)
N(2)	8 117(3)	1 486(2)	2 693(1)	50(1)
O(20)	8 678(2)	1 991(2)	3 470(1)	68(1)
O(21)	8 665(2)	2 164(2)	2 012(1)	63(1)
N(3)	4 009(3)	−3 005(2)	4 040(1)	61(1)
O(22)	2 861(3)	−4 311(2)	3 949(1)	78(1)
O(23)	4 581(3)	−2 363(3)	4 774(1)	95(1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

(2PicH·DB24C8) had formed as thin red platelets, m.p. 107.5—109 °C (Found: C, 47.3; H, 4.9; N, 8.4. $C_{36}H_{38}N_6O_{22}$ requires C, 47.7; H, 4.2; N, 9.3%). A single crystal of suitable quality was chosen for X-ray crystallographic investigation.

Crystal data. $C_{36}H_{38}N_6O_{22}$, $M = 906.7$, triclinic, $a = 7.493(1)$, $b = 9.427(2)$, $c = 14.747(3)$ Å, $\alpha = 90.27(2)$, $\beta = 94.97(1)$, $\gamma = 109.88(2)°$, $U = 975$ Å^3, $\mu(\text{Cu-}K_\alpha) = 11$ cm^{-1}, $\lambda = 1.541\,78$ Å, space group $P\bar{1}$, $Z = 1$, $D_x = 1.55$ g cm^{-3}, $F(000) = 472$. Approximate crystal dimensions: 0.38 × 0.15 × 0.15 mm.

Data collection and processing. 1 820 Independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $\theta \leqslant 50°$] were measured on a Nicolet R3m diffractometer with Cu-K_α radiation (graphite monochromator) and using ω-scans.

Structural analysis and refinement. The structure was solved by direct methods and all the non-hydrogen atoms were refined anisotropically. The hydroxy hydrogen atom in PicH was located from a ΔF map and was refined isotropically. All the other hydrogen atom positions were idealised (C–H 0.96 Å), assigned isotropic thermal parameters [$U(\text{H}) = 1.2U_{eq}$ (C)], and allowed to 'ride' on their parent carbon atoms. Refinement was performed by the block-cascade full-matrix least-squares method and converged to give $R = 0.034$, $R_w = 0.040$ [$\omega^{-1} = \sigma^2(F) + 0.001\,09F^2$]. Computations were carried out with an Eclipse S140 computer using the SHELXTL program system.[13]

Fractional atomic co-ordinates for the non-hydrogen atoms are given in Table 1. Tables 2 and 3 list bond lengths and angles, respectively.

Table 2. Bond lengths (Å)

O(1)–C(2)	1.425(2)		
C(2)–C(3)	1.491(3)	C(3)–O(4)	1.420(3)
O(4)–C(5)	1.427(2)	C(5)–C(6)	1.507(3)
C(6)–O(7)	1.422(3)	O(7)–C(8)	1.418(3)
C(8)–C(9)	1.490(3)	C(9)–O(10)	1.433(2)
O(10)–C(11)	1.373(2)	C(11)–C(12)	1.373(3)
C(11)–C(16)	1.400(3)	C(12)–C(13)	1.389(3)
C(13)–C(14)	1.361(3)	C(14)–C(15)	1.387(3)
C(15)–C(16)	1.383(3)	C(16)–O(1′)	1.363(2)
C(17)–O(17)	1.335(2)	C(17)–C(18)	1.406(3)
C(17)–C(22)	1.395(3)	C(18)–C(19)	1.369(3)
C(18)–N(1)	1.459(3)	C(19)–C(20)	1.373(3)
C(20)–C(21)	1.373(3)	C(20)–N(2)	1.459(2)
C(21)–C(22)	1.376(3)	C(22)–N(3)	1.457(3)
N(1)–O(18)	1.214(3)	N(1)–O(19)	1.219(3)
N(2)–O(20)	1.222(3)	N(2)–O(21)	1.219(3)
N(3)–O(22)	1.238(2)	N(3)–O(23)	1.208(3)

Table 3. Bond angles (deg.)

C(2)–O(1)–C(16′)	118.0(1)	O(1)–C(2)–C(3)	108.7(2)
C(2)–C(3)–O(4)	109.2(2)	C(3)–O(4)–C(5)	113.0(2)
O(4)–C(5)–C(6)	110.4(2)	C(5)–C(6)–O(7)	112.2(2)
C(6)–O(7)–C(8)	114.9(2)	O(7)–C(8)–C(9)	111.4(2)
C(8)–C(9)–O(10)	107.6(2)	C(9)–O(10)–C(11)	117.7(1)
O(10)–C(11)–C(12)	124.7(2)	O(10)–C(11)–C(16)	115.0(2)
C(12)–C(11)–C(16)	120.3(2)	C(11)–C(12)–C(13)	120.2(2)
C(12)–C(13)–C(14)	120.0(2)	C(13)–C(14)–C(15)	120.4(2)
C(14)–C(15)–C(16)	120.5(2)	C(11)–C(16)–C(15)	118.7(2)
C(11)–C(16)–O(1′)	115.5(2)	C(15)–C(16)–O(1′)	125.8(2)
O(17)–C(17)–C(18)	118.6(2)	O(17)–C(17)–C(22)	125.0(2)
C(18)–C(17)–C(22)	116.3(2)	C(17)–C(18)–C(19)	122.4(2)
C(17)–C(18)–N(1)	119.5(2)	C(19)–C(18)–N(1)	118.0(2)
C(18)–C(19)–C(20)	118.7(2)	C(19)–C(20)–C(21)	121.6(2)
C(19)–C(20)–N(2)	119.5(2)	C(21)–C(20)–N(2)	118.9(2)
C(20)–C(21)–C(22)	119.0(2)	C(17)–C(22)–C(21)	122.0(2)
C(17)–C(22)–N(3)	120.4(2)	C(21)–C(22)–N(3)	117.6(2)
C(18)–N(1)–O(18)	117.3(2)	C(18)–N(1)–O(19)	118.3(2)
O(18)–N(1)–O(19)	124.5(2)	C(20)–N(2)–O(20)	117.8(2)
C(20)–N(2)–O(21)	118.0(2)	O(20)–N(2)–O(21)	124.2(2)
C(22)–N(3)–O(22)	118.0(2)	C(22)–N(3)–O(23)	119.1(2)
O(22)–N(3)–O(23)	122.9(2)		

Isolation of the 2:1 *Complex of* 2,4,6-*Trinitrophenol with Dibenzo*-18-*crown*-6 (*2PicH·DB18C6*).—A mixture (*ca.* 2:1 molar) of picric acid (PicH) (50 mg) and dibenzo-18-crown-6 (DB18C6) (45 mg) was dissolved in acetone–dichloromethane (1:1) (4 ml) and the solution was filtered. Light petroleum (b.p. 60—80 °C) was allowed to diffuse slowly into the solution from the vapour phase.[12] After 36 h, the 2:1 *complex* (2PicH·DB18C6) crystallised out as very thin red platelets, m.p. 129—130 °C (Found: C, 46.5; H, 3.8; N, 10.0. $C_{32}H_{36}N_6O_{20}$ requires C, 47.0; H, 3.7; N, 10.3%); δ(CD_2Cl_2; 250 MHz) 2.11 (2 H, s, 2 OH), 3.94 (8 H, m, 2 CH_2OCH_2), 4.11 (8 H, m, 2 $CH_2CH_2OCH_2CH_2$), 6.87 (8 H, m, aromatic protons in the benzo rings), and 9.18 (4 H, s, aromatic protons in picric acid units). The integrated intensities of the signals in the spectra are consistent with a 2:1 stoicheiometry.

Results and Discussion

In the solid state, 2PicH·DB24C8 possesses a continuous layer structure comprising alternate PicH and DB24C8 molecules. The DB24C8 molecules adopt extended conformations so as to accommodate two PicH molecules positioned between any pair of DB24C8 molecules (Figure 1 and 2). The crystals have a pronounced red colour consistent with a charge-transfer interaction between the π-electron-rich catechol units of the DB24C8 and the π-electron-deficient PicH molecules. It is

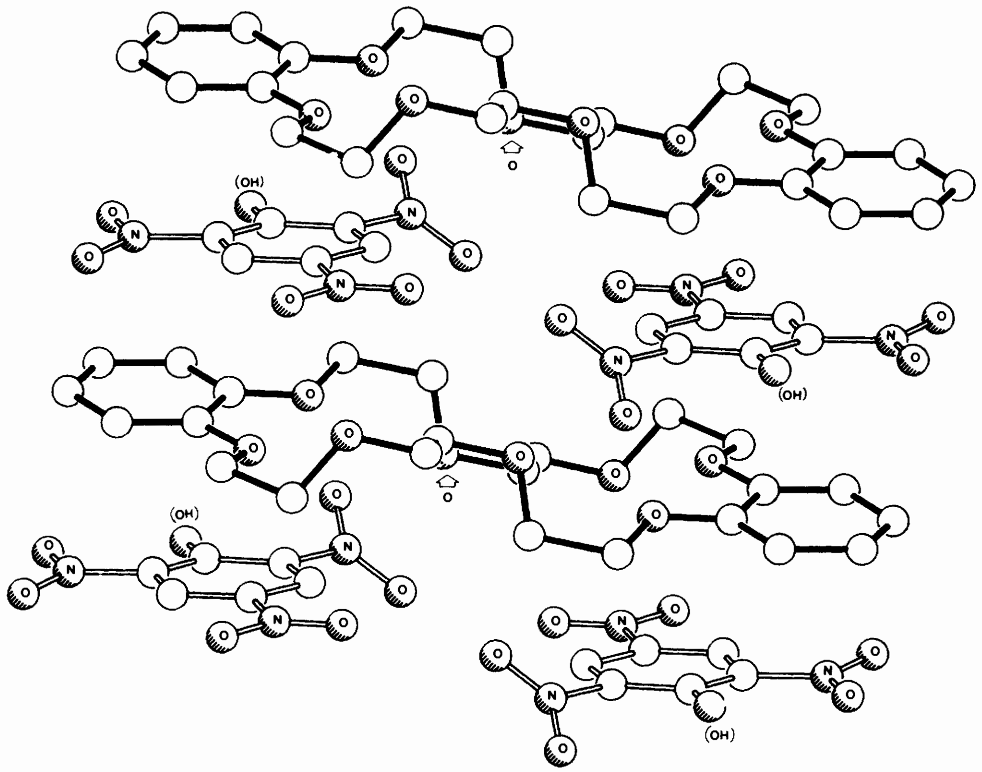

Figure 1. *X*-Ray crystal structure of 2PicH•DB24C8 showing the sandwiching of pairs of PicH molecules between adjacent DB24C8 molecules

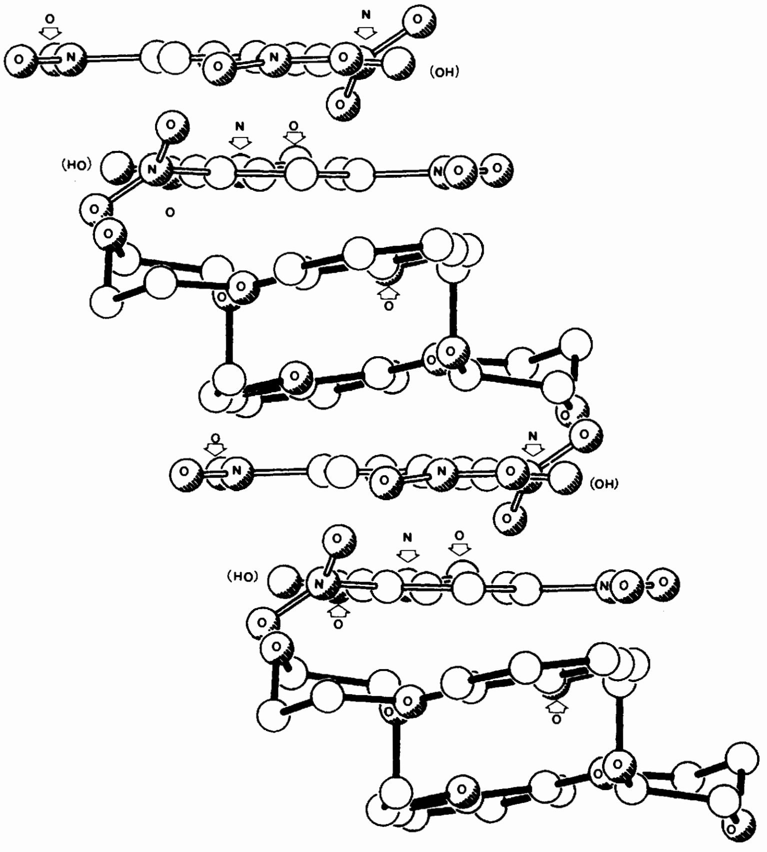

Figure 2. An end-on view of the stacking arrangement illustrated in Figure 1, showing the stagger of the continuous alternating array of PicH and DB24C8 molecules

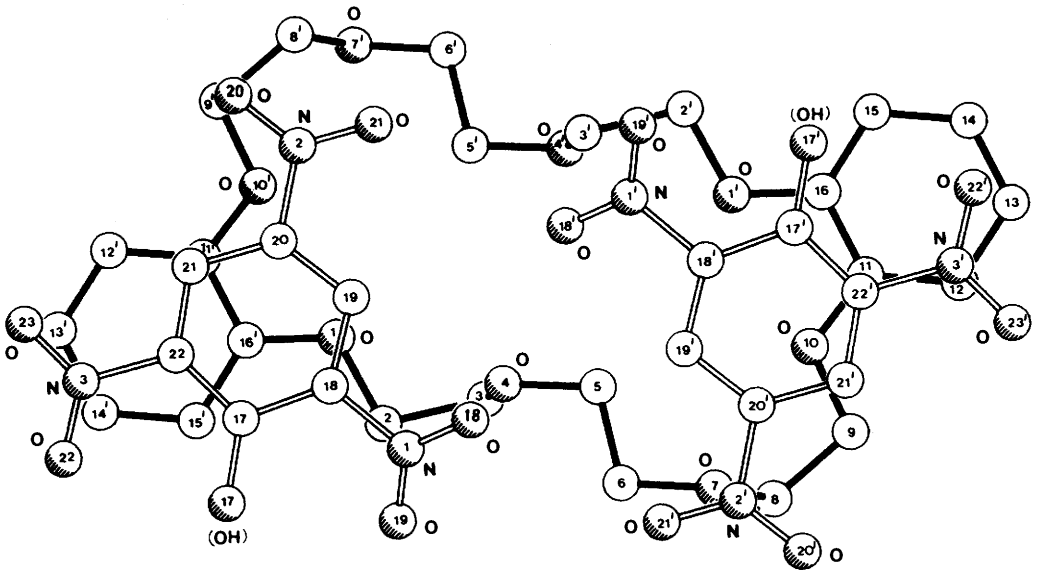

Figure 3. The supramolecular structure of 2PicH•DB24C8, giving the crystallographic numbering scheme and illustrating the relative overlap of the PicH molecules with the catechol units of the DB24C8 molecule.

Table 4. A comparison of the torsion angles in 2PicH•DB24C8 and in DB24C8[16]

Torsion angle	2PicH•DB24C8	DB24C8[a]
C(11')–C(16')–O(1)–C(2)	174	172
C(16')–O(1)–O(2)–C(3)	176	175
O(1)–C(2)–C(3)–O(4)	−75	78
C(2)–C(3)–O(4)–C(5)	−165	−144
C(3)–O(4)–C(5)–C(6)	91	−166
O(4)–C(5)–C(6)–O(7)	177	84
C(5)–C(6)–O(7)–C(8)	82	−177
C(6)–O(7)–C(8)–C(9)	−129	−85
O(7)–C(8)–C(9)–O(10)	68	78
C(8)–C(9)–O(10)–C(11)	−179	177
C(9)–O(10)–C(11)–C(16)	169	175
O(10)–C(11)–C(16)–O(1')	−1	1

[a] The torsion angles for DB24C8 are listed in accordance with the numbering scheme adopted in this paper for 2PicH•DB24C8.

Table 5. Dependence of the absorbances (*A*) at 400 nm of acetonitrile solutions (2×10^{-3}M; 1 cm cell) of PicH•DB3*n*C*n* at 25 °C upon ring sizes (3*n* = 18—36), and their changes in absorbance relative to PicH

DB3*n*C*n*	DB18C6	DB21C7	DB24C8	DB27C9	DB30C10	DB33C11	DB36C12
Absorbance (*A*)	0.81[b]	0.43[c]	1.45[b]	0.52[b]	0.46[b]	0.45[d]	0.50[d]
Δ*A*[a]	+0.35	−0.03	+0.99	+0.06	0.00	−0.01	+0.04

[a] Δ*A* = *A* − 0.46 (*N.B.* The absorbance for free PicH is 0.46.) [b] Average of two determinations. [c] Average of three determinations. [d] One determination.

evident from the relative positions (Figure 3) of the PicH molecules and catechol units that the coplanar portion [the ring, the nitro groups at N(2)/N(2') and N(3)/N(3'), and the hydroxy group] of PicH is involved in the intermolecular interactions with DB24C8. The third nitro group at N(1)/N(1') is twisted out of the plane of the ring, probably because of the short non-bonded contact between this group and the ether oxygen atom O(4). [The non-bonded distances involving O(4) are 2.93 and 3.02 Å to N(1) and O(18), respectively.] It is interesting that the planarity of the catechol units extends[2—4,14] to the first methylene carbon atoms [C(2)/(2') and C(9')/C(9)] in the polyether chains, thereby optimising the π-donating properties of these units. The minimum interplanar atomic separations between the catechol rings and the PicH rings immediately above and below them are 3.38 Å [between O(1) and C(19) in the PicH molecule on the opposite side of the catechol ring] and 3.44 Å [between N(3) and C(12')]. The hydroxy hydrogen atom on O(17)/O(17') is intramolecularly hydrogen bonded (2.57 Å) to the adjacent nitro oxygen atom, O(22)/O(22') (OHO angle 156°). Despite the presence of a hydroxy group in PicH, there is no hydrogen bonding between PicH and DB24C8 (*cf.* ref. 11). The torsion angles associated with the C–N and C–O bonds in the complexed PicH molecules of 2PicH•DB24C8 are similar in magnitude to those in free PicH molecules in the solid state.[15] Comparison of the torsion angles in complexed DB24C8 molecules in 2PicH•DB24C8 with those in crystalline free DB24C8 [16] (Table 4) reveals that, whilst both macrocycles have planar fragments associated with the catechol units (see before), the remainders of the polyether chains adopt significantly different conformations in the free and complexed states.

By contrast with 2PicH•DB24C8, the crystals of 2PicH•DB18C6 proved to be unsuitable for *X*-ray crystallography: they were very small, exceptionally thin plates which did not diffract sufficiently strongly.

Despite the evidence for charge-transfer complexation between PicH and the ethers DB3*n*C*n* (*n* = 6 or 8) in the solid state (enhanced colour, close approach, and parallel alignment of the π-systems in 2PicH•DB24C8), we could find only limited evidence for this type of interaction in solution. ^{1}H N.m.r. chemical shift changes relative to the separate components were extremely small (<0.07 p.p.m.; *cf.* >0.6 p.p.m. for 1:1 complexation of [Diquat] $[PF_6]_2$ by DB30C10[2]), and although acetonitrile solutions of PicH became noticeably deeper in colour on addition of DB3*n*C*n* ethers, the actual increase in absorbance (ΔA in Table 5) suggests that, in this solvent, the concentration of charge-transfer complex is very low indeed. Significantly, the largest ΔA values of +0.35 and +0.99, respectively, were observed for the two ethers DB18C6 and DB24C8 which have been demonstrated to form crystalline 2:1 complexes with PicH.

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