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with pyridine can provide added rigidity and modify the nature of the crown donor groups. In the course of this work, we have prepared and structurally characterized the title compound, (I), as a potential precursor to a pyridino-substituted crown ether extractant.

(I)
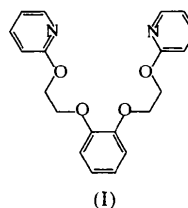
The title compound is illustrated in Fig. 1. All bond lengths and angles are in good agreement with standard values (Allen *et al.*, 1987). For example, the aromatic C═C bonds vary from 1.356 (3) to 1.405 (2) Å. The interplanar angles between the arene rings (N1, C1–C5 = A1; N2, C16–C20 = A2; C8–C13 = A3) are A1–A2 = 50.5 (1), A1–A3 = 73.9 (1), and A2–A3 = 83.0 (1)°. All three aromatic rings are planar, with the largest deviations from planarity being 0.007 (2) Å (C1 on A1, or C8 on A3).

1,2-Bis[2-(pyridin-2-yloxy)ethoxy]benzene

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Abstract

The structure of the title compound, $C_{20}H_{20}N_2O_4$, exhibits several intermolecular arene interactions. For example, π-stacking is observed between two arene rings, with an interplanar distance of roughly 3.6 Å.

Comment

Recent work in our group has focused on the substitution of relatively flexible ethylene linkages in crown ether molecules with more rigid groups such as benzo, cyclohexano and furano (Bryan *et al.*, 1998; Burns *et al.*, 1996). Making crown ether molecules more rigid limits conformational flexibility and can affect their extraction properties (Sachleben *et al.*, 1996; Vögtle & Weber, 1992). Replacement of crown ethylene groups
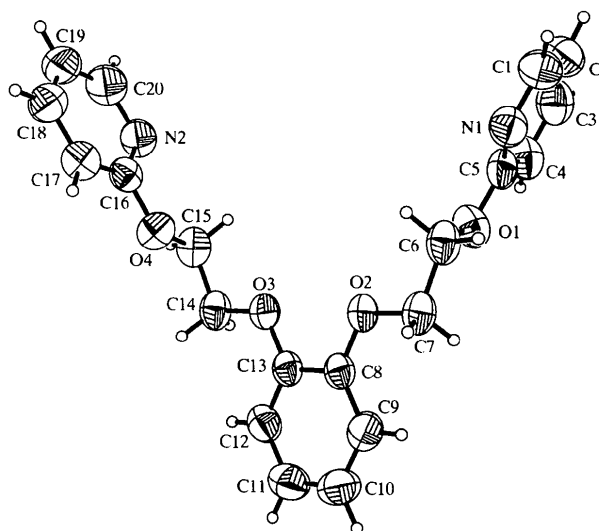

Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as spheres of an arbitrary radius.

Examination of the packing of this molecule reveals several edge-to-face interactions and one face-to-face interaction between arene rings, some of which are depicted in Fig. 2. The face-to-face ring interaction is between A1 and A3^{iii}, which stack in the lattice roughly along **b**, with an interplanar distance of roughly 3.6 Å and a centroid–centroid distance of 3.93 Å. Close edge-to-face arene contacts are observed between A2 and A3^i, and the equivalent pair A3 and A2^i, with an in-

terplanar angle of 83.0° and a centroid–centroid distance of 4.90 Å. Additionally, ring $A1^{ii}$ sits approximately in between rings $A1$ and $A2$, with interplanar angles of 78.7 and 87.3°, and centroid–centroid distances of 5.04 and 5.26 Å, respectively [symmetry codes: (i) $1 - x$, $2 - y$, $-z$; (ii) $-x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$; (iii) $1 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$].
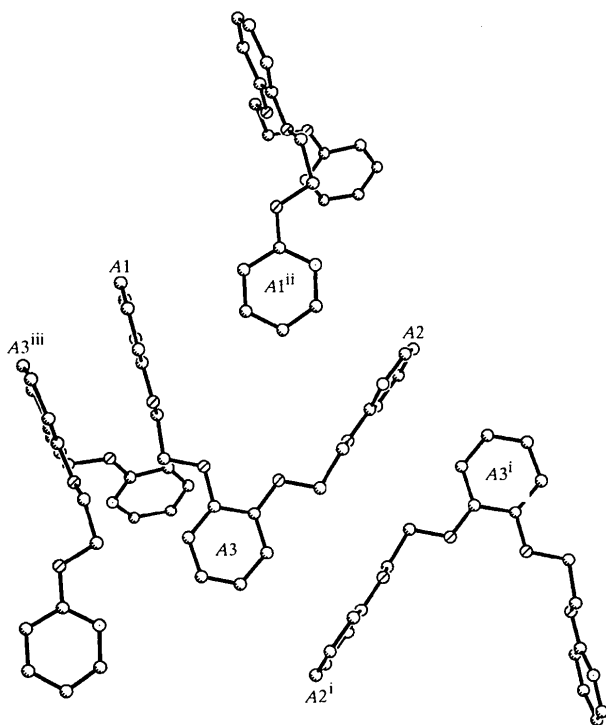

Fig. 2. Packing diagram showing intermolecular arene interactions for (I). For clarity, all atoms are represented as circles, and the H atoms are omitted [symmetry codes: (i) $1 - x$, $2 - y$, $-z$; (ii) $-x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$; (iii) $1 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$].

Despite the presence of good hydrogen-bond acceptors in this compound, no hydrogen bonding to O or N is observed, which is likely to be a consequence of the absence of good hydrogen-bond donors (O—H, N—H).

Experimental

The title compound was prepared by dissolving potassium metal (2.15 g, 55 mmol) in *tert*-butanol (100 ml), after which 1,2-bis(ethanoloxy)benzene (5.0 g, 25 mmol) was added and the solution was stirred until homogeneous. 2-Fluoropyridine (5.34 g, 55 mmol) was added, and the mixture was stirred overnight at 333 K. *tert*-Butanol was evaporated, and the residue dissolved in dichloromethane. The organic phase was successively washed with water and a solution of saturated sodium bicarbonate, then evaporated to dryness (yield: 99%). X-ray quality crystals of (I) were prepared from a 1,2-dichloroethane solution slowly diffused with heptane.

Crystal data

$C_{20}H_{20}N_2O_4$	Mo $K\alpha$ radiation
$M_r = 352.38$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
$a = 10.8956\,(9)$ Å	$\theta = 10.4$–$16.9°$
$b = 8.2532\,(5)$ Å	$\mu = 0.092$ mm^{-1}
$c = 20.2050\,(12)$ Å	$T = 295$ K
$\beta = 98.411\,(6)°$	Plate
$V = 1797.4\,(2)$ Å^3	$0.57 \times 0.34 \times 0.17$ mm
$Z = 4$	Colourless
$D_x = 1.30$ Mg m^{-3}	
D_m not measured	

Data collection

Nonius CAD-4 diffractometer	$R_{int} = 0.031$
ω scans	$\theta_{max} = 24°$
Absorption correction: none	$h = -12 \rightarrow 0$
5733 measured reflections	$k = -9 \rightarrow 9$
2819 independent reflections	$l = -22 \rightarrow 23$
1795 reflections with	3 standard reflections
$I > 2\sigma(I)$	frequency: 120 min
	intensity decay: 4%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R(F) = 0.036$	$\Delta\rho_{max} = 0.14$ e Å^{-3}
$wR(F^2) = 0.094$	$\Delta\rho_{min} = -0.17$ e Å^{-3}
$S = 1.01$	Extinction correction: none
2819 reflections	Scattering factors from
235 parameters	*International Tables for*
H atoms riding	*Crystallography* (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2]$	Absolute structure: none
where $P = (F_o^2 + 2F_c^2)/3$	

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

O1—C5	1.355 (2)	O4—C15	1.437 (2)
O1—C6	1.427 (2)	O4—C16	1.361 (2)
O2—C7	1.430 (2)	N1—C1	1.347 (3)
O2—C8	1.374 (2)	N1—C5	1.313 (2)
O3—C13	1.370 (2)	N2—C16	1.308 (2)
O3—C14	1.428 (2)	N2—C20	1.347 (3)
C5—O1—C6	118.0 (1)	C13—O3—C14	116.4 (1)
C7—O2—C8	116.6 (1)	C15—O4—C16	118.0 (1)
O1—C6—C7—O2	−72.2 (2)	O3—C14—C15—O4	−75.3 (2)
O2—C8—C13—O3	−2.2 (2)		

Data collection was terminated at $\theta = 24°$ due to lack of measurable intensity in the final shell ($I/\sigma = 1.8$ for resolution 0.90–0.87 Å).

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1993). Cell refinement: *CAD-4-PC Software*. Data reduction: *XCAD4* (Harms, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL* (Siemens, 1995). Software used to prepare material for publication: *PLATON* (Spek, 1998).

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A new strained angularly fused ring system: 8-hydroxy-1,2,3-trimethoxybenz[a]-anthracene-7,12-dione

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Abstract

The synthesis and crystal structure of the title compound ($C_{21}H_{16}O_6$) are reported. The introduction of a methoxy group at the 1-position brings two O atoms into close proximity with an O···O separation of 2.611 (3) Å. This interaction causes severe deformation of ring *B* but not ring *D*.

Comment

Recently, natural product researchers have determined the structures of tetracyclic aromatic compounds which are angularly fused. Some of these quinones, such as (1) and (2), exhibit significant activity (Rohr & Thiercke, 1992). Total syntheses have been recorded (Krohn, 1990). In our pathway, the angularly fused ring system was assembled by a strategy which is dramatically different from the previously reported pathways. Our original synthetic approach to this class of compounds will be published elsewhere.

(1)   (2)
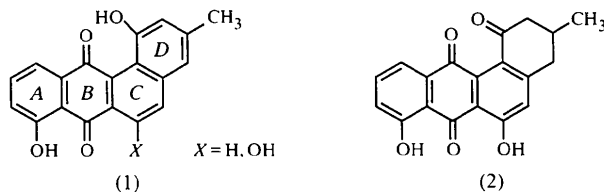
The reaction of (3) with 1-(trimethylsilyloxy)-1,3-butadiene in methylene chloride followed by Jones oxidation provided a single product in 84% yield which was characterized by ^1H and ^{13}C NMR spectroscopy. However, the position of the hydroxyl group remained unclear. To confirm the expected regioselectivity, the X-ray structural analysis of (4) was performed.

(3)   (4)
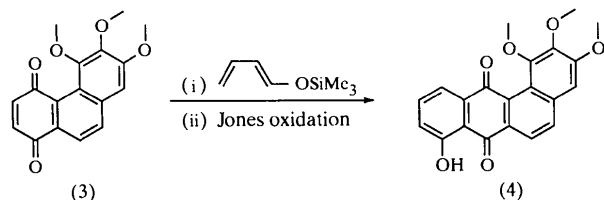
It is obvious from Fig. 1 and planarity calculations that the close proximity of atoms O1 and O6 introduces significant strain in the molecule. The strain is somewhat relieved by the subsequent deformation of the molecule, resulting in the excursion of atoms O1 and O6 to opposite sides of the plane defined by C1, C18, C17, and C16. The O1···O6 distance is 2.611 (3) Å, which is considerably smaller than the van der Waals separation of 3.02 Å (Bott *et al.*, 1980) and somewhat shorter than the corresponding O···O distance [average 2.534 (10) Å] reported for 4,5-dimethoxyphenanthrene, (5) (Cosmo *et al.*, 1990)

One measure of strain is the distance between atoms C3 and C4, and C9 and C10. In strained 4,5-disubstituted phenanthrenes, the relevant distances are in the range 1.452 (6)–1.469 (6) Å (Cosmo *et al.*, 1990), while in (4), C3—C4 and C9—C10 are 1.369 (3) and 1.455 (3) Å, respectively. Another measure of strain is the sum of the squares of the deviations from planarity through rings *D* and *B*. These sums were found to be