

## Propeller Substituents imposing Steric Restraint on Crown Ethers

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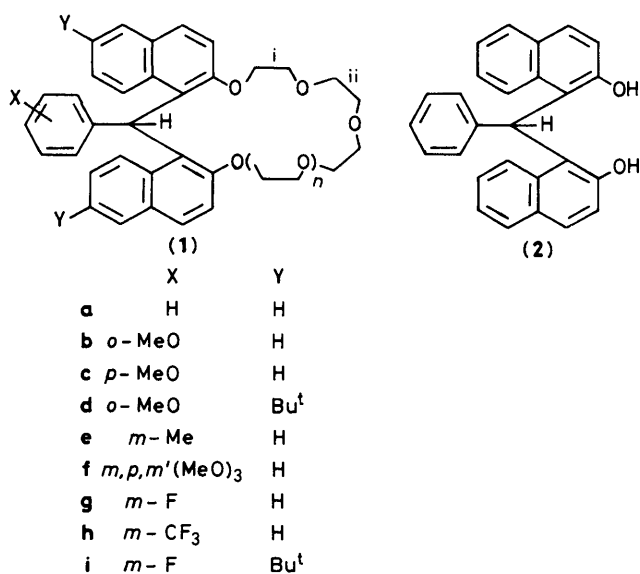
Crown ethers with steric restraint imposed by a three-bladed propeller substituent have been synthesised and the X-ray crystal structures of one example and its NaNCS complex indicate approximately the same conformation of the propeller but quite different conformations of the ether ring in the two; n.m.r. solution spectra indicate that the flipping of the propeller and of the crown moieties are mutually restricted in these crown ethers.

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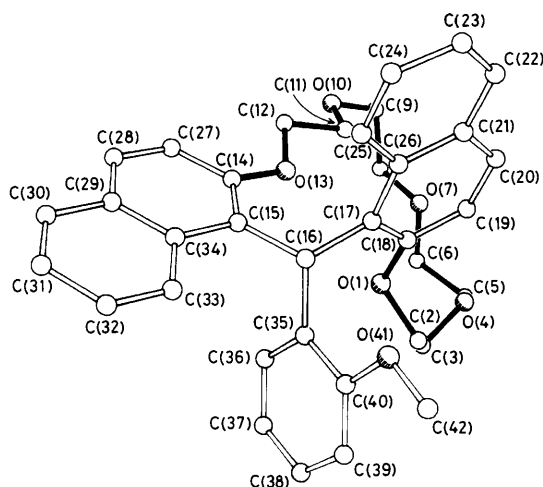
The flexibility of simple crown ethers (*e.g.* 12-crown-4) is such that it is rapid down to 140 K on the <sup>13</sup>C n.m.r. timescale.<sup>1</sup> In a search for ethers in which conformational change could be slowed for examination at more convenient temperatures,<sup>2</sup> we synthesised a class<sup>†</sup> of crown ethers with a triarylmethyl

propeller incorporated in the ether ring to provide control of ether flexing. Such three-bladed propellers are subject to correlated rotation of the aryl rings. Thus if each end of a polyether strand is attached to a different ring of the propeller [see (1)] the flexing of the polyether strand should likewise be correlated. This strategy for slowing down ether flexing was successful.

<sup>†</sup> Dinaphthopolyoxacycloalkin.

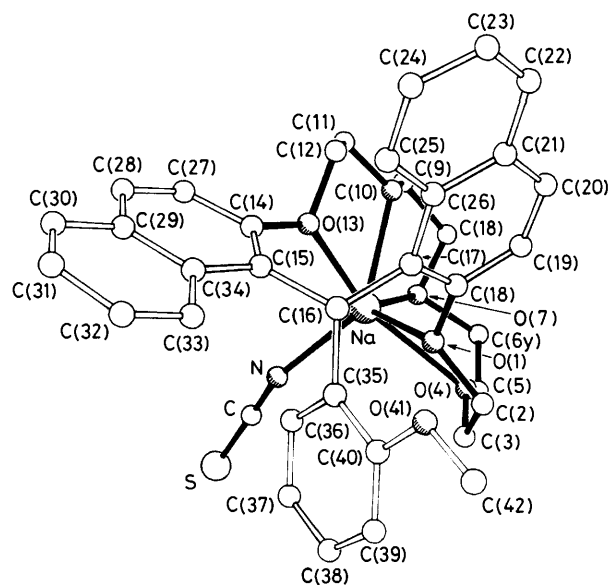


Compound (1a) is 26-phenyl-8,9,11,12,14,15,17,18-octahydro-26H-dinaphtho[2,1-*n*,1',2'-*q*][1,4,7,10,13]pentaoxacyclo-octadecin. Compounds (1) were all prepared with Y = H, *n* = 1. Some were also prepared with *n* = 2,3 or with Y = Bu<sup>t</sup>.



**Figure 1.** Molecular structure of (1b) projected on the reference plane: propeller section with open bonds, crown ring with filled bonds. *Crystal data:* space group  $P\bar{1}$ ,  $a = 11.243(2)$ ,  $b = 12.009(2)$ ,  $c = 12.716(3)$  Å,  $\alpha = 112.04(2)$ ,  $\beta = 103.81(2)$ ,  $\gamma = 99.54(2)^\circ$ ,  $Z = 2$ ,  $R = 0.066$  for 3367 reflections with  $F > 4\sigma(F)$ .

The compounds† (1) were made by standard routes from the benzylidene bis(naphthols) (2). The crystal structures‡ of the most sterically hindered of these crown ethers (1b) (Figure 1) and its NaNCS complex (Figure 2) showed each to be isolated as a single pair of enantiomers. A single molecule of each is drawn perpendicular to the reference plane of the propeller to bring out the strikingly similar propeller skeletons. The ring tilt angles of the two structures are 55.3, 50.2,



**Figure 2.** Molecular structure of NaNCS complex of (1b) projected on the reference plane as for (1b) in Figure 1. *Crystal data:* space group  $P\bar{1}$ ,  $a = 10.165(3)$ ,  $b = 10.955(4)$ ,  $c = 16.594(6)$  Å,  $\alpha = 91.11(2)$ ,  $\beta = 93.80(3)$ ,  $\gamma = 94.14(2)^\circ$ ,  $Z = 2$ ,  $R = 0.070$  for 3346 reflections with  $F > 4\sigma(F)$ . The crystal structure also contains disordered acetone molecules.

and 50.1° for (1b), and 50.1, 62.9, and 52.9° for the sodium complex. The ether ring which has an unusually distorted *aaa*, *g<sup>+</sup>g<sup>-</sup>a*, *ag<sup>+</sup>g<sup>+</sup>*, *ag<sup>+</sup>a* sequence of ether segments in Figure 1 is quite different in Figure 2, where the rough pentagonal-based pyramidal co-ordination of the sodium forces an *ag<sup>+</sup>a*, *ag<sup>-</sup>a*, *ag<sup>+</sup>a*, *ag<sup>-</sup>a* sequence.

Thermal motion is high in both structures, with some particularly large  $U_{11}$  components for crown ether atoms in the sodium complex. Although this could indicate some disorder of the flexible  $-\text{CH}_2\text{CH}_2\text{O}-$  segments, such disorder could be resolved only for one C atom. The minor component of the disorder (with occupancy factor 0.36) is not shown in Figure 2, and is not considered in the torsion angle sequence given above. In general, the high thermal motion means that the geometry of the ether chain is less well determined than that of the propeller.

The symmetrically substituted phenyl derivative (1c) showed in its <sup>1</sup>H n.m.r. spectrum a process coalescing the ether signals at ambient temperature: above 380 K one ABCD spectrum was seen for segment i, and one AA'BB' spectrum for segment ii, and there were only four <sup>13</sup>C n.m.r. signals for the polyether carbon atoms. At the same time, only one naphthyl ABCDEF spectrum and a symmetrical methoxyphenyl AA'BB' pattern were observed and fourteen <sup>13</sup>C n.m.r. aromatic signals. This implies a process which makes the two sides of the molecule equivalent, averaging the segment ii, naphthyl, and methoxyphenyl ring protons over all stable rotamers, while leaving the segment i protons averaging through two non-equivalent rotamers (*gauche* and *trans*).

Thus the two sets of segment i protons on each side of the effective two-fold symmetry axis are equivalent but the protons on any one carbon atom are anisochronous. Flip processes in which the naphthyl rings can only twist *part* of the way round their bonds to the central methine carbon atom (models show that the naphthyl rings cannot pass through the ether ring) are a reasonable explanation. Similar spectroscopic observations were made for the symmetrical (1a) or (1f), *n* = 1 or 2, where the phenyl group makes little steric demand.

† All compounds had satisfactory elemental analyses, accurate masses, and the expected n.m.r. spectra.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Crown ethers with an asymmetric phenyl ring were made with various n.m.r. active X groups, as in (**1b**), (**1d**), (**1g-i**). Only one set of signals for each of these labels was observed under all conditions, suggesting either that they are accidentally isochronous in their respective isomers, or that a low energy process (probably the two-ring flip, see refs. 3 and 4) is averaging their environments. The crystal structure in Figure 1 emphasises the asymmetry of the ether ring. This asymmetry persists in solution where just one (averaged) species appears to be present with single methine and methoxy signals in the  $^{13}\text{C}$  and  $^1\text{H}$  n.m.r. spectra; 12 different naphthyl protons, seven proton multiplets in the segment i region (corresponding to a different ABCD spectrum for each segment i), two asymmetric proton multiplets for the segment ii protons, eight  $^{13}\text{C}$  n.m.r. signals for the ether, one each for the methine and methoxy groups, and 23 aromatic  $^{13}\text{C}$  n.m.r. signals were observed at 297 K. The two-ring flip can average the naphthyl rings of the symmetric benzylidene crown ethers, but not those of the asymmetric ones. The t-butyl derivative (**1d**) showed a collapse and averaging of the  $^1\text{H}$  n.m.r. signals for the t-butyl groups which can only happen if the two naphthyl rings become equivalent. This process, seen to have an activation energy of  $19.1 \pm 0.1 \text{ kcal mol}^{-1}$ ¶ at 93 °C in [ $^2\text{H}_5$ ]pyridine, is

¶ 1 kcal = 4.184 kJ.

expected to be a one-ring flip. Processes averaging the *m*-MeO and *o*-H signals of the trimethoxybenzylidene compound (**1f**) had activation energies around 11–12 kcal mol $^{-1}$ . Collapse of some naphthyl multiplets occurs for the *m*-Me derivative (**1e**) with activation energy *ca.* 17 kcal mol $^{-1}$ . Detailed dynamic n.m.r. studies of the importance of the ether flexing in the overall process of complexation of alkali cations are now underway.

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