

Comparison of the Steric Barriers in Three- and Two-Bladed Propeller Crowns

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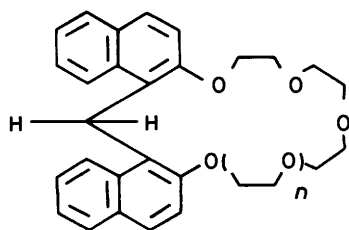
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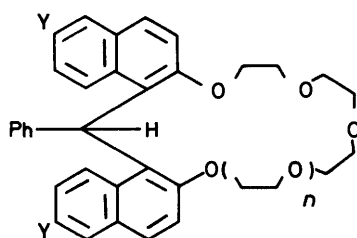
The propeller crowns (2) and (4) (dinaphthopolyoxacycloalkanins) have been characterised by single crystal *X*-ray structure determinations. Only one enantiomeric pair of isomers is present in each crystal structure. The presence of the trimethoxyphenyl substituent in (4) has remarkably little effect on the conformation of the ether ring. The propeller skeleton of (4) is different from that observed previously in the *o*-methoxyphenyl propeller; these two skeletal isomers are related by a two-ring flip of one naphthyl and the phenyl ring. Room-temperature ¹H n.m.r. spectra of (4) and of the 6-*t*-butyldinaphthylpolyoxacycloalkanin correspond to one 'averaged' species with a rapid averaging of naphthyl rings *via* a two-ring flip, slowed at 220 K. The relative steric demands of the propeller and the ether moieties are discussed.

We have recently prepared crown ethers¹ containing a propeller substituent² designed as a steric barrier to the flexing of the ether ring. Two- and three-bladed propellers (1) and (3) based on the dinaphthyl¹ and phenyldinaphthyl-methane³



(1)

(2) *n* = 2



(3)

(4) *n* = 2, X = C₆H₂(OMe)₃-3,4,5, Y = H

(5) *n* = 1, X = C₆H₄OMe-*o*, Y = H

(6) *n* = 2, X = C₆H₂(OMe)₃-3,4,5, Y = Bu[†]

skeletons were introduced. The ether ring is tied to two blades of the propeller and so its flexing motion is governed, in part, by movement of the propeller ring. The extent to which the propeller and ether movements are correlated is of importance to our kinetic investigations, and information on the crystal structure is vital in order to assess the relative steric demands of propeller and polyether moieties.

Experimental

Synthesis of Benzyldenedinaphthols.—The benzyldenedinaphthols were prepared by a known method.⁴

Preparation of Dinaphthyl-crown (2).—This crown compound was prepared as described in ref. 1, using CsF as the condensing agent in acetonitrile solution.

Synthesis of Crown (4).—To a solution of 3,4,5-trimethoxybenzyldenedinaphthol (9.2 g, 0.02 mol) in dry nitrogen-purged tetrahydrofuran (500 ml) was added sodium hydride (1.65 g, 0.07 mol). The mixture was kept for 20 min at a gentle reflux, after which, a solution of 1,14-bis(*p*-tolylsulphonyloxy)-3,6,9,12-tetraoxatetradecane (10.9 g, 0.02 mol), dissolved in tetrahydrofuran (40 ml), was added dropwise. The final mixture was refluxed for 20 h. On cooling, the solution was filtered free of residual sodium salts and treated with a small amount of water to destroy unused hydride; solvent was then removed on a rotary evaporator. The oily residue was taken up in dichloromethane, and the solution washed with water, dried (MgSO₄), and treated with Celite; solvent was then removed on a rotary evaporator. The Celite plus its adsorbates was placed on the top of an alumina column (Brockman Grade IV). Gradient elution (light petroleum–diethyl ether) produced a white solid; recrystallisation from acetone–dichloromethane (1:1) gave 2.78 g (21%) of 29-(3,4,5-trimethoxyphenyl)-8,9,11,12,14,15,17,18,20,21-decahydro-29*H*-dinaphtho[2,1-*g*:1',2'-*t*][1,4,7,10,13,16]hexaoxacycloheneicosin, m.p. 180 °C (Found: C, 71.7; H, 6.7%; *M*⁺, 668.3000. C₄₀H₄₄O₉ requires C, 71.8; H, 6.6%; *M*, 668.2985); δ_H(CDCl₃) 7.9–7.2 (12 H, m, ArH), 7.0 (1 H, s, ArCH), 6.45 (2 H, s, Ph), 3.57 [6 H, s, 3,5-Ar(OMe)₂], 3.82 [3 H, s, (ArOMe)], 3.34–3.9 (16 H, m, ether CH₂), 3.19–3.27 (2 H, m, ether CH₂), and 3.01–3.09 (2 H, m, ether CH₂).

*Synthesis of the *t*-Butyl-crown (6)*.—This crown was made from 3,4,5-trimethoxybenzyldenebis(6-*t*-butylnaphthol) by the same route, as a white powder, recrystallised from acetone–dichloromethane (1:1), m.p. 192 °C (Found: C, 74.1; H, 7.8; *M*⁺, 780.4128. C₄₈H₆₀O₉ requires C, 73.8; H, 7.7%; *M*, 780.4237; δ_H(CDCl₃) 7.790 (m, 8-H), † 7.703 (m, 4-H), 7.662 (m, 5-H), 7.36 (m, 7-H), 7.25 (m, 3-H), 6.45 (2 H, s, Ph-H), 3.32 (3 H, s, MeO) 3.6 (6 H, s, MeO), 3.3–3.9 (16 H, m, ether CH₂), and 1.357 (9 H, s, Bu[†]).

† Naphthyl proton assignments 8-H *etc.* use the numbering scheme previously used in ref. 1.

Crystal Data for (2).— $C_{31}H_{34}O_6$, $M = 502.6$, Monoclinic, m.p. 101–102 °C, $a = 10.011(1)$, $b = 12.736(2)$, $c = 20.986(3)$ Å, $\beta = 98.56(1)^\circ$, $V = 2645.9$ Å³ (by least-squares refinement on 2θ angles for 29 reflections, $\lambda = 0.71069$ Å), space group $P2_1/c$, $Z = 4$, $D_x = 1.262$ g cm⁻³. Colourless crystal, $0.35 \times 0.35 \times 0.20$ mm, $\mu(\text{Mo-K}\alpha) = 0.81$ cm⁻¹.

Data Collection and Processing.—Stoe-Siemens AED diffractometer, ω/θ scan mode, graphite-monochromated Mo-K α radiation, on-line profile fitting.⁵ 4145 reflections measured ($2\theta < 48^\circ$, $k, l \geq 0$), 2650 with $F > 3\sigma(F)$; no significant intensity variation for three standard reflections. No absorption or extinction corrections.

Structure Solution and Refinement.⁶—Multisolution direct methods, blocked-cascade refinement on F , with all non-hydrogen atoms anisotropic, hydrogens in calculated positions with C–H = 0.96 Å, $U(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. Weighting scheme, $w^{-1} = \sigma^2(F) + 0.00077F^2$. Final $R = 0.076$, $R_g = (\Sigma w\Delta^2 / \Sigma wF_o^2)^{1/2} = 0.075$. Slope of normal probability plot = 1.35, largest peak in final difference synthesis = $0.56 \text{ e } \text{Å}^{-3}$, largest hole = $-0.40 \text{ e } \text{Å}^{-3}$. Scattering factors from ref. 7.

Crystal Data for (4).— $C_{40}H_{44}O_9$, $M = 668.8$, Monoclinic, m.p. 192 °C, $a = 19.389(2)$, $b = 11.704(1)$, $c = 31.556(3)$ Å, $\beta = 90.95(1)^\circ$, $V = 7160.0$ Å³ (from 32 reflections, $\lambda = 0.71069$ Å), space group $C2/c$, $Z = 8$, $D_x = 1.241$ g cm⁻³. Colourless crystal, $0.75 \times 0.75 \times 0.60$ mm, $\mu(\text{Mo-K}\alpha) = 0.81$ cm⁻¹.

Data Collection and Processing.—This was carried out as for compound (2). 6283 Reflections with $2\theta < 50^\circ$, $h \geq 0$, $k \leq 0$, 4424 reflections with $F > 4(F)$, no decay or absorption corrections.

Structure Solution and Refinement.—This was carried out as for compound (2). Weighting scheme, $w^{-1} = \sigma^2(F) + 0.00036F^2$. Extinction $x = 3.6(4) \times 10^{-7}$ [$F_c' = F_c / (1 + xF_c^2 / \sin 2\theta)^{1/4}$]. Final $R = 0.050$, $R_g = 0.054$. Slope of normal probability plot = 1.50, largest peak in final difference synthesis = $0.22 \text{ e } \text{Å}^{-3}$, largest hole = $-0.17 \text{ e } \text{Å}^{-3}$.

Solution N.m.r. Spectra.—Spectra were obtained on a Bruker HFX90 or a Bruker WM-300/WB. Versions of DNMR3 and NUMAR1 obtained via the SERC NMR Program Library were used for the processing of spectral data on an IBM370 computer.

Results and Discussion

The results presented here allow a discussion of the effectiveness of the extra benzylidene substituent in (4) as a barrier to the flexing of the ether ring, and allow us to identify some of the steric requirements for slow flexing on the n.m.r. timescale.

We report first the single crystal X-ray structure determinations for the two representative crowns (2) and (4), which have respectively an H and a 3,4,3'-trimethoxyphenyl substituent on the central carbon of the propeller.

The numbering scheme for the crown (2) structure is shown in Figure 1, and the extra atoms in crown (4) are labelled in Figure 2. Atomic co-ordinates for non-hydrogen atoms are given in Tables 1 and 2. The bond lengths and angles are as expected for aryl rings and crown ethers, and are available as part of a supplementary publication [SUP no. 56178 (9 pp.)].* This publication also contains the thermal parameters and the atomic co-ordinates for the hydrogen atoms of compounds (2)

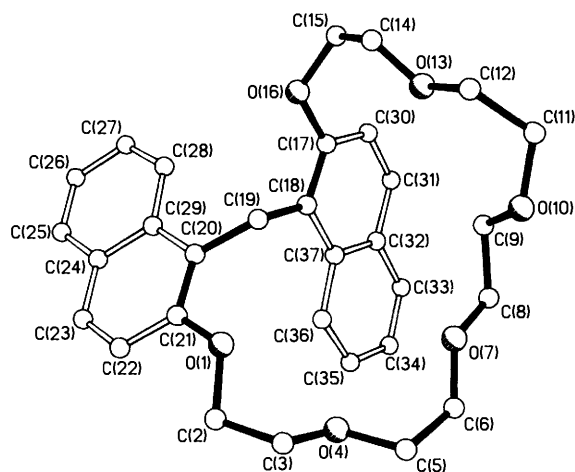


Figure 1. The structure of (2), showing the labelling of the atoms. Bonds are filled in the macrocyclic ring, open in the propeller substituents. H Atoms omitted.

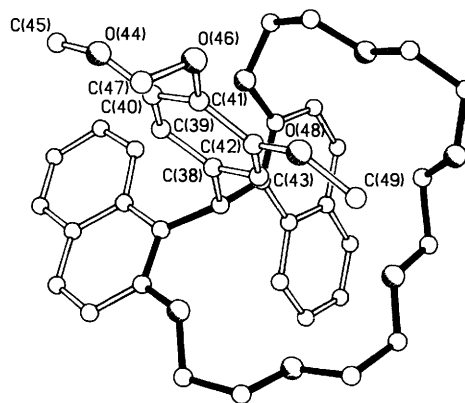


Figure 2. The structure of (4), showing the labelling of the additional atoms: unlabelled atoms are numbered as in (2).

and (4).^{*} The structure factor listings for the X-ray determinations are available on request from the Editorial office. Torsion angles for the macrocyclic ring, including the propeller portion, are shown in Figure 3.

The cyclic ether parts of the two crowns (2) and (4) are remarkably similar. The distances of the ether oxygens above and below their mean plane are compared for (2) and (4) in Table 3, while the actual torsion angles are compared in Figure 3. The crowns (2) and (4) have remarkably similar conformations of the ether ring with g^-g^+a , ag^-g^+ , ag^+a , ag^+a , ag^-a torsion angles in each (a sequence not so far observed in any other 6-donor crown,⁸ and resulting probably from the presence of the propeller). Figure 3 shows that none of the comparable ether torsion angles differ by more than 17°. An attempt to calculate the relative energies of the two was made using empirical force field calculations (molecular mechanics) using the MM2 program (as implemented in Chemgraf). For purposes of calculation, the input data consisted of the atomic co-ordinates from the crystal structure, modified with the Chemgraf program to generate comparable ether fragments [the section from O(1) to O(16) only]. The conformation of the ether fragment from (2) was found to be ca. 1.12 kcal mol⁻¹ more stable than that from (4), as expected. The extra strain of the substituent is accommodated particularly in the propeller torsion angles, and the torsion angles around O(13) and O(4),

* For details of the Supplementary publication scheme, see Instructions for Authors (1985), *J. Chem. Soc., Perkin Trans. I*, 1985, Issue 1.

Table 1. Atomic co-ordinates ($\times 10^4$) for (2)

	x	y	z
O(1)	2 869(3)	4 889(2)	5 544(1)
C(2)	2 358(4)	4 406(3)	4 933(2)
C(3)	3 253(4)	4 735(3)	4 467(2)
O(4)	3 156(3)	5 832(2)	4 389(1)
C(5)	3 982(4)	6 255(4)	3 960(2)
C(6)	4 232(4)	7 379(4)	4 118(2)
O(7)	5 149(3)	7 451(2)	4 694(1)
C(8)	5 323(4)	8 484(3)	4 928(2)
C(9)	6 215(4)	8 495(3)	5 560(2)
O(10)	7 542(3)	8 189(2)	5 481(1)
C(11)	8 540(4)	8 415(4)	6 021(2)
C(12)	8 576(4)	7 684(4)	6 574(2)
O(13)	7 446(3)	7 923(3)	6 906(2)
C(14)	7 468(5)	7 483(5)	7 477(2)
C(15)	6 407(4)	7 820(4)	7 825(2)
O(16)	5 107(3)	7 441(2)	7 552(1)
C(17)	4 349(4)	7 997(3)	7 057(2)
C(18)	3 623(3)	7 422(3)	6 567(2)
C(19)	3 750(3)	6 238(3)	6 543(2)
C(20)	2 470(3)	5 592(3)	6 529(2)
C(21)	2 068(4)	4 915(3)	6 019(2)
C(22)	911(4)	4 297(3)	5 989(2)
C(23)	144(4)	4 347(3)	6 462(2)
C(24)	488(4)	5 002(3)	7 004(2)
C(25)	-302(4)	5 042(4)	7 508(3)
C(26)	76(4)	5 654(4)	8 030(2)
C(27)	1 252(4)	6 263(4)	8 075(2)
C(28)	2 035(4)	6 249(3)	7 599(2)
C(29)	1 680(3)	5 625(3)	7 038(2)
C(30)	4 269(4)	9 104(3)	7 080(2)
C(31)	3 493(4)	9 633(3)	6 602(2)
C(32)	2 757(4)	9 099(3)	6 071(2)
C(33)	1 993(4)	9 643(3)	5 547(2)
C(34)	1 359(4)	9 114(4)	5 028(2)
C(35)	1 446(4)	8 031(4)	5 007(2)
C(36)	2 148(3)	7 473(3)	5 498(2)
C(37)	2 827(3)	7 991(3)	6 054(2)

Table 2. Atomic co-ordinates ($\times 10^4$) for (4)

	x	y	z
O(1)	7 565(1)	1 703(1)	427(1)
C(2)	7 525(1)	808(2)	121(1)
C(3)	6 783(1)	638(2)	20(1)
O(4)	6 450(1)	284(1)	390(1)
C(5)	5 730(1)	218(2)	340(1)
C(6)	5 414(1)	-42(2)	756(1)
O(7)	5 412(1)	962(1)	1 010(1)
C(8)	5 203(1)	721(2)	1 427(1)
C(9)	5 202(1)	1 778(2)	1 689(1)
O(10)	4 649(1)	2 494(2)	1 556(1)
C(11)	4 505(1)	3 402(2)	1 838(1)
C(12)	4 977(1)	4 408(2)	1 812(1)
O(13)	5 624(1)	4 141(1)	2 006(1)
C(14)	6 100(1)	5 044(2)	1 967(1)
C(15)	6 770(1)	4 732(2)	2 178(1)
O(16)	7 147(1)	3 890(1)	1 948(1)
C(17)	7 016(1)	2 740(2)	1 995(1)
C(18)	7 161(1)	2 042(2)	1 658(1)
C(19)	7 350(1)	2 453(2)	1 213(1)
C(20)	8 092(1)	2 232(2)	1 071(1)
C(21)	8 164(1)	1 819(2)	666(1)
C(22)	8 805(1)	1 557(2)	492(1)
C(23)	9 392(1)	1 733(2)	726(1)
C(24)	9 364(1)	2 170(2)	1 137(1)
C(25)	9 971(1)	2 360(2)	1 379(1)
C(26)	9 953(1)	2 788(2)	1 774(1)
C(27)	9 319(1)	3 073(2)	1 946(1)
C(28)	8 716(1)	2 899(2)	1 727(1)
C(29)	8 706(1)	2 431(2)	1 317(1)
C(30)	6 803(1)	2 290(2)	2 388(1)
C(31)	6 728(1)	1 149(2)	2 437(1)
C(32)	6 863(1)	381(2)	2 106(1)
C(33)	6 793(1)	-823(2)	2 156(1)
C(34)	6 904(1)	-1 548(2)	1 831(1)
C(35)	7 095(1)	-1 115(2)	1 439(1)
C(36)	7 184(1)	29(2)	1 383(1)
C(37)	7 080(1)	831(2)	1 712(1)
C(38)	7 092(1)	3 625(2)	1 071(1)
C(39)	7 510(1)	4 586(2)	1 066(1)
C(40)	7 261(1)	5 611(2)	910(1)
C(41)	6 589(1)	5 683(2)	748(1)
C(42)	6 178(1)	4 710(2)	740(1)
C(43)	6 426(1)	3 693(2)	905(1)
O(44)	7 637(1)	6 599(1)	889(1)
C(45)	8 302(1)	6 604(2)	1 081(1)
O(46)	6 318(1)	6 719(1)	613(1)
C(47)	6 539(2)	7 100(2)	213(1)
O(48)	5 540(1)	4 841(1)	551(1)
C(49)	5 099(1)	3 876(2)	529(1)

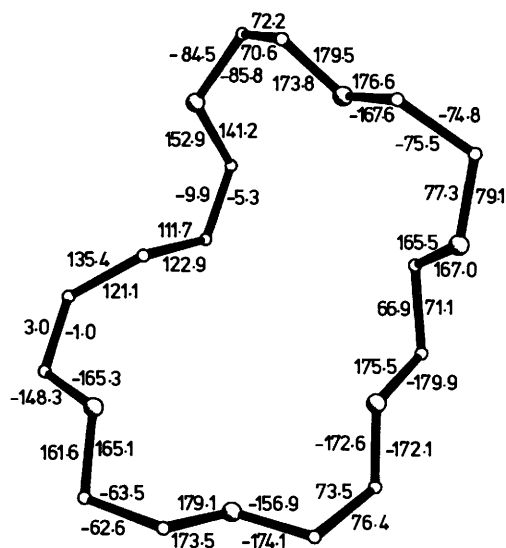


Figure 3. Torsion angles in the macrocyclic rings of (2) and (4). Values for (2) are shown inside the ring, for (4) outside. The view direction is as for Figure 1.

with the C(3), O(4), C(5), C(6) angles being 17.2° different. We suggest that there is little steric barrier provided by this trimethoxybenzylidene substituent when present in a dinaphthopolycycloalkanin of this size (6 donor atoms). Since the

Table 3. Distances (in Å) of ether oxygens from the mean oxygen plane for (2) and (4)

Atom	(2)	(4)
O(1)	0.549	0.468
O(4)	-0.172	-0.186
O(7)	-0.506	-0.362
O(10)	0.267	0.225
O(13)	0.440	0.321
O(17)	-0.579	-0.465

ether ring is little affected the propeller is also likely to be closer to its minimum energy conformation.

The crystal structures of the related 5-donor dinaphthopolycycloalkanin (5) (*o*-methoxybenzylidene substituent) both in free and complexed form³ provide a comparison with another three-bladed propeller structure. This has two features absent in (4), namely the *ortho* substituent on the benzylidene,

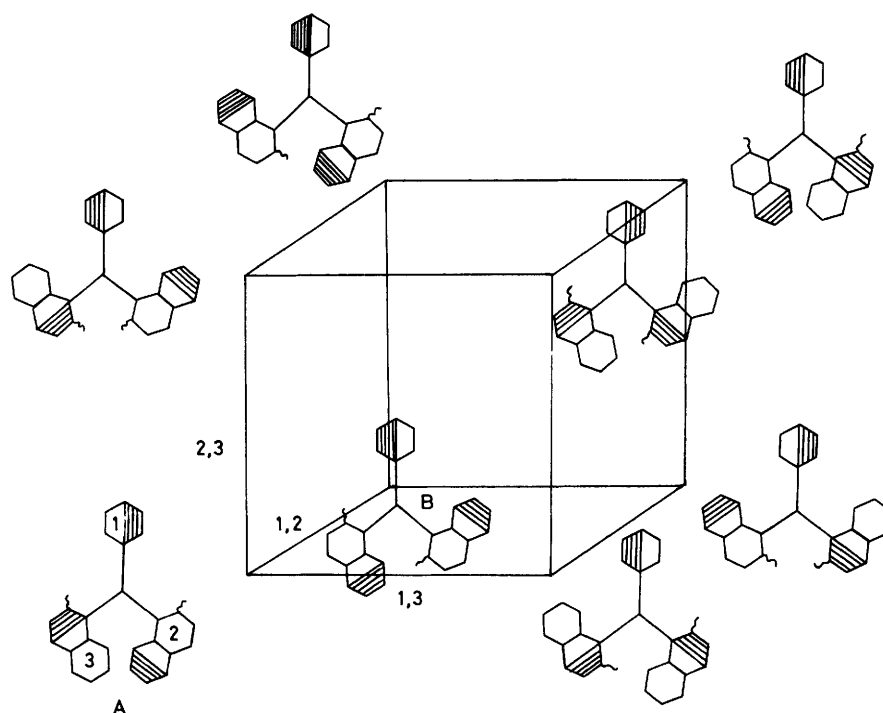
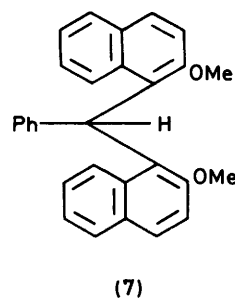


Figure 4. The eight diastereoisomers of the phenylbinaphthyl skeleton, having the same chirality at the central carbon. Isomer A is that reported in this paper for crown (4), while isomer B is that reported in ref. 3 for crown (5). The edges of the cube are labelled to show which two rings (labelled in structure A) are involved in the two-ring flip.

and the shorter ether strand, which are expected to offer additional steric restraint. Consequently, the observation of a more strained ether ring (torsion angles indicate considerable strain for a 5-donor ether crown) is to be expected, as is the occurrence of a different, more strained skeletal isomer for the propeller moiety.

The possible skeletal isomers of the two-bladed propeller were sketched in Scheme 2 of ref. 1, and discussed in detail there. The possible skeletal isomers of the three-bladed propeller of crown (4) are sketched in Figure 4 (following the analysis of Gust and Mislow⁹). These are depicted at the corners of a cube. Each can be interconverted by three different 2-ring flips (1,2; 1,3; 2,3) to the three isomers connected to the first by the three adjacent cube edges. The edges of the cube are labelled 1,2 *etc.* according to the rings involved. For the symmetric benzylidene, these 8 isomers are enantiomers of those on a second cube, with opposite chirality at the chiral carbon. The number of diastereoisomers is raised to 16 (with 16 enantiomers) for an asymmetric benzylidene. If we consider the skeleton of the benzylidene dinaphtho moiety (ignoring substituents on the benzylidene phenyl residue) we can compare the isomers found in (4) and the *o*-MeO crown (5) (and for the latter crown in its salt complex). These are labelled appropriately in Figure 4. It is clear that the two are related by a single two-ring flip (a 1,2 flip as drawn on this cube). An attempt to calculate the relative energies of the two was made using molecular mechanics. For purposes of calculation, the input structure consisted of the atomic co-ordinates from the crystal structure, modified with the Chemgraf program¹⁰ to generate fragments of identical molecular formulae shown in (7). The structures for crown (5) had the lowest energy, that in the conformation found in its NaNCS salt (which is the same skeletal isomer, but with different torsion angles) was 5.4 while the crown (4) fragment was 2 kcal mol higher in energy.

The *t*-butyl substituted version of (4) shown in (6) was synthesized to provide a convenient ¹H n.m.r. singlet as a

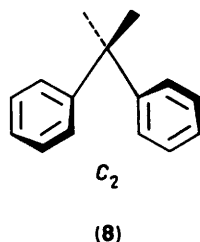


probe. This crown had one apparent *t*-butyl signal at room temperature in its 300 MHz spectrum, which split into two approximately equal intensity singlets at *ca.* 220 K; unfortunately, by 200 K these lines had merged again, although there was evidence of other species in low concentrations with signals in this range. For crowns (4) and (6), another convenient probe of the exchange process is provided by the *ortho* hydrogens of the phenyl substituent. These appear as a singlet at room temperature, and separate to two broad lines of equal intensity at *ca.* 220 K. Although these lines sharpen considerably at 190 K [as expected for an AB system with a large chemical shift separation and a small (*meta*) coupling constant] the quantitative analysis of the lineshapes is complicated by the emergence of additional signals in this range. The low-temperature spectra give additional signals in all proton regions, a doubling of most signals indicating the presence of one rigid isomer while there are new signals in addition to and *ca.* 1/5 of the intensity of those described, which indicate another rigid isomer to be present. The chemical shifts of individual protons (*e.g.* the naphthyl 8-H, or the phenyl 2-H,2'-H) are very different for the isomer present in low concentration. Examination of the n.m.r. spectra of (4) and (6) over the temperature range 180–300 K indicates rapid averaging of the two naphthyl rings at room

temperature, probably *via* a two-ring flip. However at the same time separation of signals of different intensities indicates that other isomers are present, certainly at 200 K and below. The occurrence of other two-ring flips with closely related activation energies is suggested. The curious behaviour of the *t*-butyl signals probably reflects accidental isochrony amongst *t*-butyl signals of the two different naphthyl rings of the major isomer. More clearcut evidence on related three-bladed propellers is currently being sought.

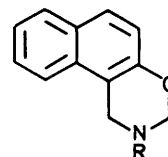
The dinaphthopolycycloalkanin (4) has apparently the least strained skeletal isomer found so far for these three-bladed propeller crowns. Accordingly, to find further strained isomers one should, (i) create steric hindrance in the propeller, probably with *ortho* substituents, (ii) shorten the ether chain further, and (iii) alter ether conformation with substituents or by formation of salt complexes. A number of compounds with some or all of these features have been produced and are under investigation by X-ray and multinuclear n.m.r. methods to determine the validity of this hypothesis.

Comparison of the propeller skeleton of (2) may be made with those of the bis(2-methyl-1-naphthyl)methanols¹¹ and of several substituted diphenylmethanes¹² and a dibenzocrown analogue of (1).¹³ Diphenylmethane itself has a helical structure (8). The dihedral angles which the naphthyl rings in the helical

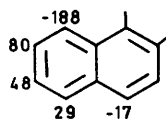


structure (2) make with the reference plane [defined according to ref. 12 by C(18), C(19), and C(20) in the numbering scheme in Figure 1] are each 59.9°, as compared with the angles of 63.9 and 71.1° made by the phenyl planes with the reference plane in diphenylmethane itself.

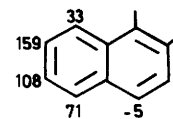
The structure of dinaphtho crown (2) may also be probed in solution, by considering the ring current shifts for the protons on the two naphthalene rings. In ref. 1, we gave the experimentally determined ring-current shieldings for this crown relative to the simple naphthoxazine (9). These are mapped on formula (10) (in Hz at 360 MHz) and are compared with those shown on formula (11), which are calculated from the positions of the naphthalene rings in the crystal structure of (2), and are an average over the two naphthalene rings. The observed ring-current pattern does not correspond to that expected if the



(9)



(10)



(11)

isomer in the crystal structure is the sole isomer in solution, particularly for the 5,6,7 and 8 protons.

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