

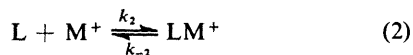
Ligands for the Alkali Metals. Part 7.¹ Synthesis and Characterisation of Crown Ether Macrocyces Containing the Di-1-naphthylmethyl Unit as a Novel Steric Barrier

Joyce C. Lockhart,* Martin B. McDonnell, and Philip D. Tyson

Department of Inorganic Chemistry, The University, Newcastle upon Tyne NE1 7RU

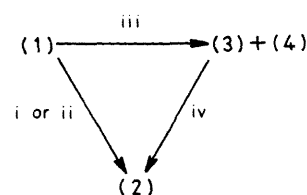
The first examples of crown ethers in which each end of the ether strand is fixed to one blade of a molecular propeller (a dinaphthylmethane) have been synthesised. The resultant steric barriers have been found to slow crown-flexing sufficiently for kinetic processes to be observed with ¹H or ¹³C n.m.r. in the temperature range 200–270 K. *vic*-Coupling constants for the ethylene oxide segments at ambient temperature indicate a very low proportion of *trans*-conformer in the conformational mix. The crowns also complex with the alkali cations in solution.

The mechanism by which macrocycles (L) complex alkali cations (M⁺) is of overwhelming chemical interest, many studies suggesting the dissociation step (labelled *k*₋₂ in the equation) as the main source of specificity in any macrocycle/cation interaction, see equations (1) and (2), while other studies have been concerned with the preliminary reorganisation of the ligand ^{1,2} [equation (1)]. An outstanding problem is to find and exploit ligands which undergo these processes at convenient rates, and which contain spectroscopic or other suitable reporter groups which could enable the kinetics of the various processes in equations (1) and (2) to be followed. Simple crown ethers such as 18-crown-6 undergo very fast conformational change [equation (1)] and cation association [equation (2)] which can be followed, at ambient temperature, in the absence of good spectroscopic labels only by ultrasonics, or at 130 K using ¹H or ¹³C n.m.r. spectroscopy.^{2,3} At the other extreme are the spherands, discussed by Cram and Trueblood which release cations too slowly for convenient kinetic study.⁴ This paper reports promising new macrocycle systems for which the conformational changes are on a more suitable timescale and which may enable a breakthrough in kinetic and mechanistic understanding of the overall complexation process.



Several crown ethers have been prepared in which each end of the ether strand is fixed to one blade of a molecular propeller⁵ [see compound (2) and Scheme 1], which should ensure that movement of the ether ring is correlated with that of the propeller blades. The resultant steric barriers have been found to slow crown-flexing sufficiently for n.m.r. observation in the 220–270 K region. Studies of related systems which are rich in n.m.r. reporter groups and have even higher steric barriers (n.m.r.-observable at 380 K and above) are underway.

Either the CsF^{1,6} or KH⁷ catalysed condensation of the appropriate ditosylate with the corresponding bis(naphthols) (1; X = H) gave rise to the series of dinaphtho crowns (2) plus the naphthoxazine (4). Direct reaction of (3) also gave the crowns (2) but the overall yield from bis(naphthol) (1) [which was used as the starting material for (3), see Scheme 1, route iii, iv] was less. The crowns were characterised by ¹H n.m.r. and mass spectroscopy. An estimation of the % *trans*-conformer in many of the ethylene oxide segments has been made based on the Karplus equation.



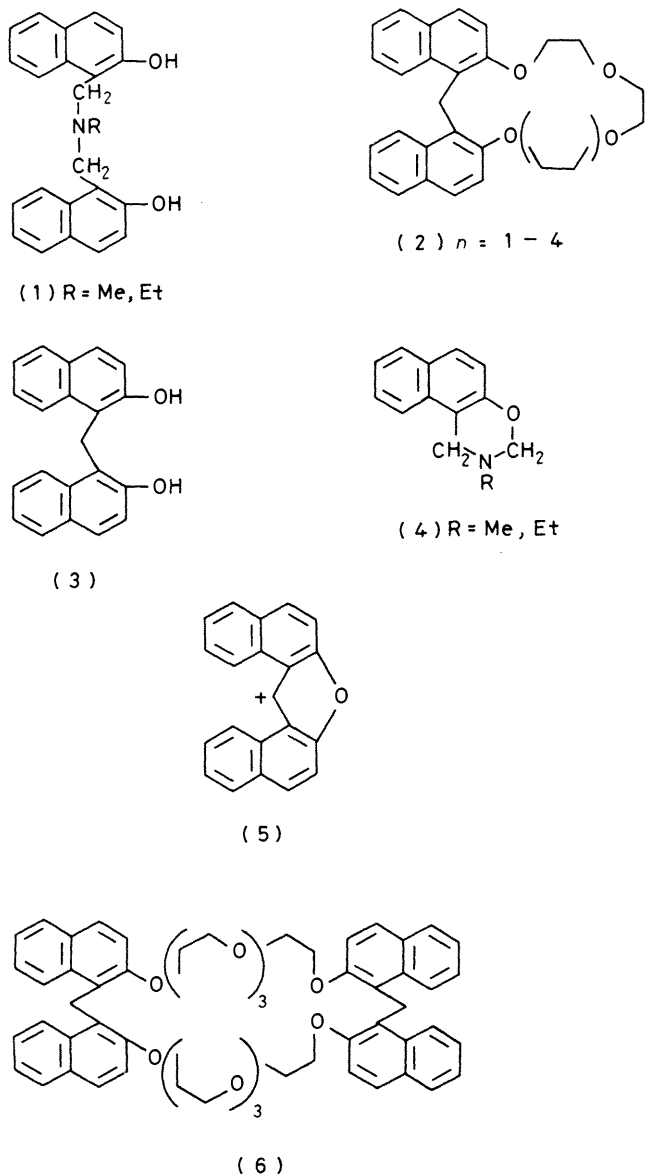
Scheme 1. Reagents: i, CsF, ditosylate; ii, KH, ditosylate; iii, base; iv, CsF, ditosylate

Experimental

The bis(naphthols) (1) and (3) were prepared by the method of Burke *et al.*⁸

General Syntheses of Crown Ethers (2).—CsF-Catalysed synthesis of (2; n = 1). This compound was prepared using CsF as catalyst by the method developed by Reinhoudt *et al.*⁶ for base-sensitive substrates. Caesium fluoride (12.2 g, 0.08 mol) dried for 24 h *in vacuo* at 100 °C and bis(naphthol) (1; R = Me, X = H) (6.58 g, 0.02 mol) were added to dry acetonitrile (600 ml) and heated under reflux in a nitrogen atmosphere until dissolved. Freshly prepared 1,8-bis(*p*-tolylsulphonyloxy)-3,6-dioxaoctane (9.16 g, 0.02 mol) was added to the solution and refluxing was continued for 24 h. Caesium salts which precipitated during the reflux period were filtered off from the cold mixture. The acetonitrile was removed on a rotary evaporator, and the oily residue dissolved in dichloromethane; this solution was washed with water and dried. The solvent was removed on a rotary evaporator and the residual brown syrup adsorbed on Celite⁹ and placed on top of an alumina column (Brockman Grade IV). Gradient elution with light petroleum–diethyl ether mixtures gave first the naphthoxazine (4), m.p. 64–65 °C (lit.,⁸ 66–67 °C) after recrystallisation from acetone, and further gradient elution gave white crystals of 8,9,11,12,14,15-hexahydro-23H-dinaphtho[2,1-k:1'-2'-n][1,4,7,10]tetraoxacyclopentadecin (2; n = 1), which were recrystallised from acetone (1.8 g), m.p. 169 °C (Found: C, 77.3; H, 6.3%; M⁺, 414. C₂₇H₂₆O₄ requires C, 78.2; H, 6.3%; M, 414) δ_H(CDCl₃) 8.2–7.0 (5.8 H, m, ArH), 5.13 (0.9 H, s, ArCH₂) 4.24 (2.0 H, ArOCH₂), 3.56 and 3.6 (4.5 H overlapping m and s, ether CH₂).

Synthesis of (2; n = 1) from (3). Compound (2; n = 1) was also prepared using the bis(naphthol) (3) as starting material instead of the bis(naphthol) (1). The reaction was carried out using the same molar quantities as before, but there was no unwanted oxazine by-product. The yield of (2) was 2.1 g.



Synthesis of (2; n = 2) using KH as basic condensing agent. The bis(naphthol) (1; R = Me, X = H) (6.58 g, 0.02 mol) and potassium hydride (1.6 g, 0.04 mol) were dissolved in n-butanol (350 ml), brought to reflux, then 1,11-bis(*p*-tolylsulphonyloxy)-3,6,9-trioxaundecane (10.04 g, 0.02 mol) was added under nitrogen. After 24 h at reflux, the mixture was placed on a rotary evaporator to remove solvent. The syrupy residue was taken up in dichloromethane (200 ml) and extracted with water to remove potassium salts. The dichloromethane was dried and evaporated to leave a brown oil which, after chromatography as previously described, gave off-white powdery crystals of the crown identified as 8,9,11,12,14,15,17,18-octahydro-26H-dinaphtho[2,1-n:1',2'-q][1,4,7,10,13]-pentaoxacyclo-octadecin, m.p. 164–165 °C, recrystallised from acetone (yield 0.9 g) (Found: C, 75.3; H, 6.6%; M^+ 458. $C_{29}H_{30}O_5$ requires C, 76.0; H, 6.6%; M , 458.6); $\delta_H(\text{CDCl}_3)$ 8.25–7.0 (11H, m, ArH) 5.175 (2 H, s, ArCH) 4.5–3.5 (15 H, overlapping s and m, ether CH_2). The compound was also obtained by the CsF route (a) from the bis(naphthol) (1; R = Me, and R = Et). Later fractions from the column gave the dimer (6), m.p. 152–154 °C; identified by its mass spectrum (M^+ ca. 916, confirmed by the doubly charged ions M^{2+} at

Table 1. Chemical shifts* of dinaphtho crown ethers

Crown	Solvent	(A) Protons	(B) Protons
(Segment i)			
(2; n = 1)	CDCl_3	4.2373	3.5683
(2; n = 2)	CDCl_3	4.3628	3.7435
(6)	CDCl_3	4.1441	3.6050
(2; n = 3)	CDCl_3	4.3685	3.8132
(2; n = 4)	CDCl_3	4.2908	3.7959
(2; n = 4)	$[\text{H}_7]\text{-DMF}$	4.4930	3.9504
(Segment ii)			
(2; n = 1)	CDCl_3	3.6293	3.6293
(2; n = 2)	CDCl_3	3.6521	3.6377
(6)	CDCl_3	3.4811	3.4548
(2; n = 3)	CDCl_3	3.6755	3.6459
(2; n = 4)	CDCl_3	3.6706	3.6184
(2; n = 4)	$[\text{H}_7]\text{-DMF}$	3.7005	3.5888
(2; n = 4) †	$[\text{H}_7]\text{-DMF}$	3.7330	3.6417
(Segment iii)			
(2; n = 3)	CDCl_3	3.5566	3.5566
(2; n = 4)	CDCl_3	3.5506	3.5017
(2; n = 4)	DMF	3.4970	3.4304
(2; n = 4) †	DMF	3.5619	3.5183

* Shifts in p.p.m. on δ scale (measured at 360.13 MHz and relative to CHCl_3). † Solution contained a tenfold molar excess of KNCS.

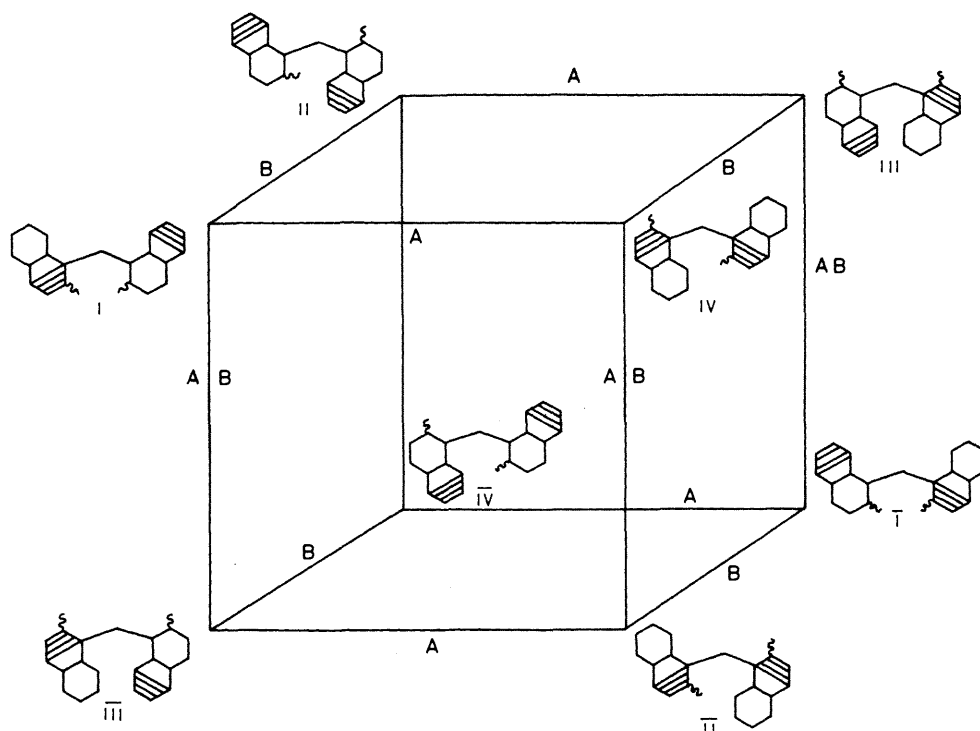
458 and 458.5) and its n.m.r. spectrum (Found: C, 75.1; H, 6.5%; M^+ , ca. 916. $C_{58}H_{60}O_{10}$ requires C, 76.0; H, 6.6%; M^+ , 917.2), $\delta_H(\text{CDCl}_3)$ 7.21–8.14 (12 H, m, ArH), 4.972 (2H, s, ArCH).

Also prepared by the CsF route were crown (2; n = 3) 8,9,11,12,14,15,17,18,20,21-decahydro-29H-dinaphtho[2,1-q:1',2'-t][1,4,7,10,13,16]hexaoxacycloheptacosin, m.p. 100–101 °C (Found: C, 72.2; H, 7.0; M^+ 502. $C_{31}H_{34}O_6$ requires C, 74.1; H, 6.8%; M , 502.6), $\delta_H(\text{CDCl}_3)$ 8.3–7.0 (12 H, m, ArH), 5.05 (2 H, s, ArCH₂), and 4.5–3.55 (20 H, m, ether CH_2); $\delta_C(\text{CDCl}_3)$ 69.4 (ether seg. iii), 69.9, 70.4 (seg. ii), 70.8, 71.3 (seg. i), 115.1, 123.2 (C-7), 124.5, (C-6), 125.5, 125.8, 127.8, 128.09, 129.65, 133.81, 151.4, 153.6, other aromatic carbons, not individually assigned; and crown (2; n = 4) 8,9,11,12,14,15,17,18,20,21,23,24-dodecahydro-32H-dinaphtho[2,1-t:1',2'-w][1,4,7,10,13,16,19]heptaoxacyclotetracosin, m.p. 111–113 °C (Found: C, 72.2; H, 7.0%; M^+ , 546. $C_{33}H_{38}O_7$ requires C, 72.5; H, 7.0%; M^+ , 546), $\delta_H(\text{CDCl}_3)$ 8.3–7.0 (12 H, m, ArH) 4.95 (2 H, s, ArCH₂), 4.4–3.5 (24 H, m, ether CH_2).

T.L.C.—The crown ethers were identified on t.l.c. plates as they were eluted from the alumina columns and had the following R_F values on silica gel (eluant CH_2Cl_2): (2) n = 1, 0.89; n = 2, 0.81; n = 3, 0.58; n = 4, 0.39.

KI Complex.—Equimolar solutions of crown (2; n = 4) and potassium iodide in acetone precipitated on standing a complex, m.p. 195–196 °C (Found: C, 55.7; H, 5.3%. $C_{33}H_{38}IKO_7$ requires C, 55.6; H, 5.4%).

Mass Spectra.—Electron impact induced mass spectra of the ligands (2; n = 1–4) indicated a common breakdown pattern. The main fragments were the parent ion M or m/z 281 [for which xanthenium structure (5) is suggested] as the base peak. The loss of neutral $\text{C}_2\text{H}_4\text{O}$ units (for which processes, several corroborative metastable peaks are observed) provided



Scheme 2. For clarity in Scheme 2 only the ends of the ether string are shown; the hatching indicates the pitch of the ring in the helical conformation

the other fragments of m/z greater than 281 for the larger rings ($2; n = 3,4$).

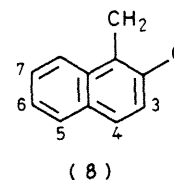
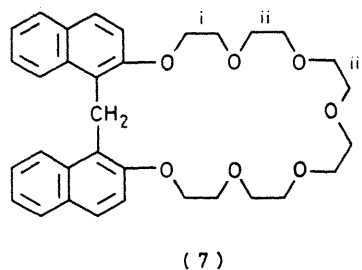
N.M.R. Spectra.— ^1H Spectra were run at 90 MHz on a Bruker HFX90 and are quoted on the δ scale relative to SiMe_4 , and 360 MHz also on the δ scale, but referred to a solvent absorbance unless otherwise stated. The ^{13}C spectra were referred to SiMe_4 and were run at r.f. 22.63 MHz on a Bruker HX90E. The program NUMARIT was used for simulating ^1H spectra.

Geometric calculations were made using the program PLUTO.

Discussion

Dinaphtho Crowns as Molecular Propellers.—The dinaphtho crowns (2) and (6), are examples of the two-bladed molecular propeller type Ar_2ZX (the methylene hydrogens being regarded as the pseudo-atom X), which, according to Gust and Mislow⁵ should have eight isomers ($4 \pm$ pairs) based on the dinaphthomethylene skeleton. These are shown in Scheme 2 with the eight possible isomers I,II,III,IV and $\bar{\text{I}},\bar{\text{II}},\bar{\text{III}},\bar{\text{IV}}$ at the vertices of a cube.

Interconversions of rotamers of simple crowns such as 12-crown-4 can be very fast (*e.g.* according to Krane, Dale and Daasvatn,³ the ^{13}C n.m.r. spectrum of the CsBPh_4 complex of 18-crown-6 ($2:1$ ligand: Cs) shows a coalescence temperature with a free energy of activation barrier ΔG^\ddagger of 7.0 ± 0.3 kcal/mol at -130°C . We examined spectra of benzo-15-crown-5 in CFCl_3 down to 194 K without success in locating a barrier to the ready interconversion of rotamers. Introduction of substituents with propeller motion may be expected to slow down such interconversions of the ether string to a more convenient rate for n.m.r. study. However each dinaphtho crown of the series was isolated apparently as a single compound of sharp m.p. The solutions were thus examined by the



solution n.m.r. technique, and at low temperatures, in a search for barriers to interconversion.

The ^1H n.m.r. spectra of the crowns were recorded at ambient temperature at 90 and 360 MHz. The shifts and coupling constant data from the latter spectra are shown in Tables 1—6 with the numbering shown in (7) and (8). Each crown gave a sharp spectrum indicating an apparent equivalence of protons which would be expected to differ in shift in different isomers, or even in a single isomer of the II or IV type (see Scheme 2 and later). On cooling, the 90 MHz spectra of dinaphtho crowns ($2; n = 2$) in $[\text{2H}]\text{-DMF}$ and CD_2Cl_2 (Figure 1) showed some separation of signals. The first signal to lose fine structure was the downfield part of segment i. In CD_2Cl_2 , the signal began to broaden at 240 K and was a broad signal with four resolved humps at 230 K. The resolution of the four humps at 220 K did not improve on further cooling. This resembled the downfield part of an ABCC' system, but each hump was *ca.* 10 Hz wide. The entire ABCC' envelope could be simulated with a range of trial parameters appropriate for a *gauche* segment of fixed conformation such as that shown in Figure 2 and coupling constants close to those shown for the frozen dioxan conformer in Table 7, but no reasonable fit was obtained with parameters appropriate to the other (Scheme 3) possible

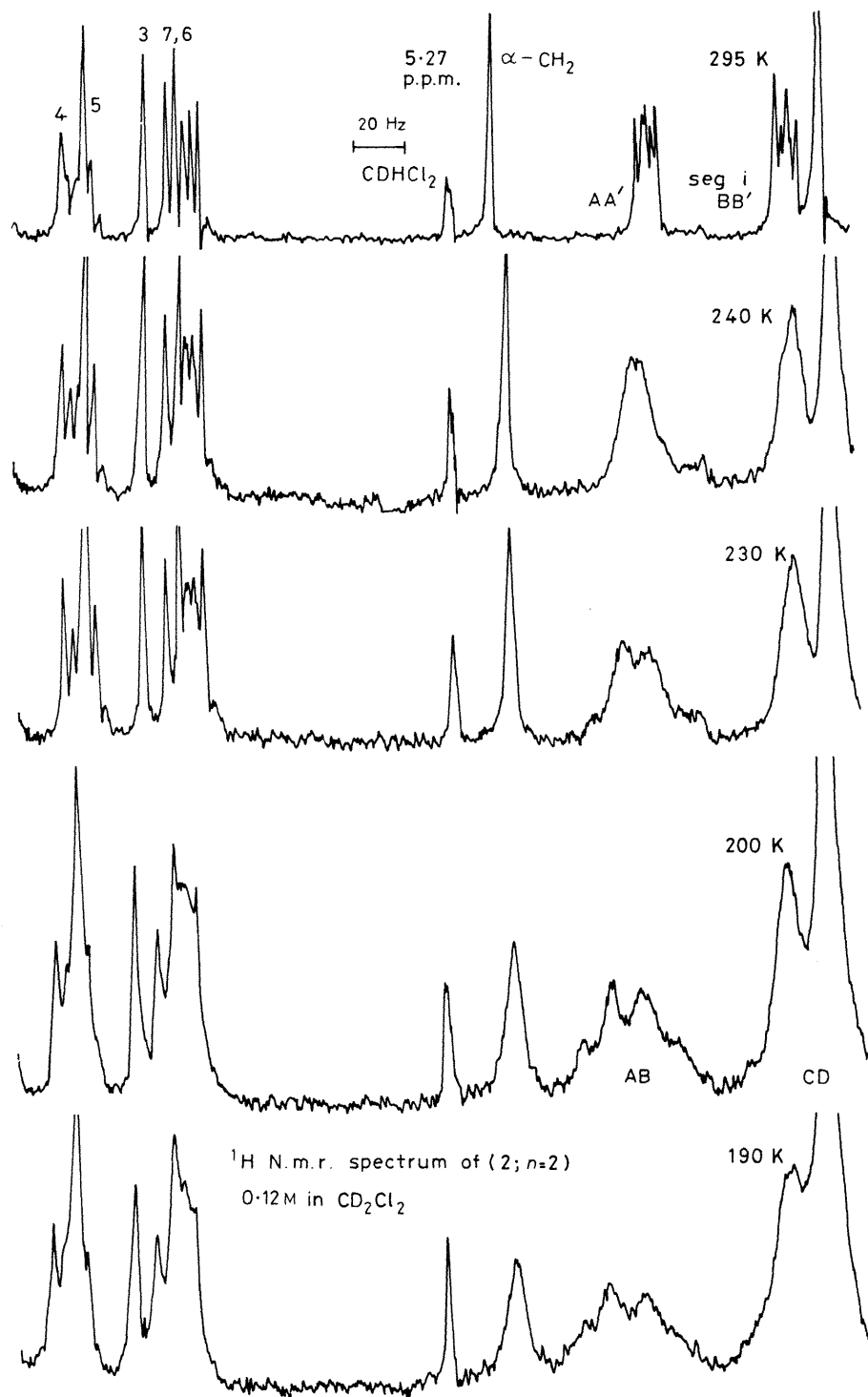


Figure 1. ^1H N.m.r. spectra for 0.12M-crown (2; $n = 2$) in CD_2Cl_2 solution at several temperatures

gauche or *trans* conformers for segment i. The segment i proton signals showed similar changes in $[^2\text{H}_7]$ -DMF; the downfield (AA') part of the signal gradually broadened to a half-width of *ca.* 30 Hz at 225 K in $[^2\text{H}_7]$ -DMF but did not show clear evidence of fine structure. Unfortunately, the solvent could not be cooled below this temperature. Concomitantly there was broadening of the $\alpha\text{-CH}_2$ singlet to *ca.* 10 Hz. The less readily interpreted signals of the aromatic protons showed associated changes at all temperatures below

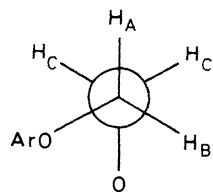


Figure 2.

Table 2. Coupling constants for ArOCH₂CH₂O (segment i) in dinaphtho crown ethers

Crown	Solvent	<i>J</i> /Hz *	<i>J'</i> /Hz *	M/Hz *	N/Hz *	L/Hz *
(2; <i>n</i> = 1)	CDCl ₃	6.19(0.05)	2.11(0.05)	0.74	8.30	4.07
(2; <i>n</i> = 2)	CDCl ₃	6.25(0.04)	2.73(0.04)	0	8.98	3.51
(6)	CDCl ₃	6.07(0.05)	3.75(0.03)	0.55	9.82	2.33
(2; <i>n</i> = 3)	CDCl ₃	6.00(0.04)	2.90(0.04)	0	8.90	3.10
(2; <i>n</i> = 4)	CDCl ₃	5.92(0.03)	3.38(0.03)	0	9.30	2.53
(2; <i>n</i> = 4) ‡	[² H ₇]-DMF	6.14(0.05)	2.78(0.05)	0	8.92	3.36

* The averaged coupling constants and spectral parameters as defined by R. J. Abraham, 'Analysis of High Resolution NMR Spectra,' Elsevier, Amsterdam, 1971. Calculated using NUMARIT, s.d. in brackets. This value was obtained by setting *J*_{gem} at -12.0 Hz. Standard deviation could be forced lower if *J*_{gem} was allowed to vary.

Table 3. Coupling constants for OCH₂CH₂O (segment ii) in dinaphtho crown ethers

Crown	Solvent	<i>J</i> /Hz *	<i>J'</i> /Hz *	M/Hz *	N/Hz *	L/Hz *
(2; <i>n</i> = 2)	CDCl ₃	6.26(0.02)	3.09(0.02)	0	9.35	3.17
(6)	CDCl ₃	6.22(0.02)	3.06(0.02)	0	9.28	3.16
(2; <i>n</i> = 3)	CDCl ₃	6.26(0.02)	2.76(0.02)	0.65	9.02	3.50
(2; <i>n</i> = 4)	CDCl ₃	6.19(0.04)	2.94(0.04)	0	9.13	3.25
(2; <i>n</i> = 4)	[² H ₇]-DMF	6.21(0.10)	3.07(0.10)	0	9.28	3.14
(2; <i>n</i> = 4) †	[² H ₇]-DMF	6.44(0.02)	2.74(0.04)	0	9.18	3.70

* See Table 2. † See Table 1.

Table 4. Coupling constants for OCH₂CH₂O (segment iii) in dinaphtho crown ethers

Crown	Solvent	<i>J</i> /Hz *	<i>J'</i> /Hz *	M/Hz *	N/Hz *	L/Hz *
(2; <i>n</i> = 3)	CDCl ₃	6.21(0.04)	2.80(0.03)	0	9.01	3.42
(2; <i>n</i> = 4)	DMF	6.20(0.02)	3.22(0.01)	0	9.41	2.48
(2; <i>n</i> = 4) †	DMF	6.39(0.02)	2.59(0.03)	0	8.97	3.80

* See Table 2. † See Table 1.

ambient in both DMF and CD₂Cl₂ but the aromatic envelopes could not be fully assessed at the resolution available. The ¹³C spectrum of the crown (2; *n* = 3) in CDCl₃ was also examined at lower temperatures. The aromatic carbon assigned as C-7 split at 240 K, into two equal lines, while two other aromatic carbon lines (possibly 3 and 8) became very wide.*

The spectrum of the seven-donor crown, (2; *n* = 4) with a 15-fold molar excess of KNCS (which ensures complete formation of the complex) also showed slow averaging on the time-scale, with 8-H, and protons of the downfield half of segment i not well resolved, at ambient temperature. The spectrum was fully resolved at 330 K in DMF (360 MHz). The lowest temperature to which this system was subjected was 195 K, when the multiplet for the methylenes of segment i adjacent to the naphthyl groups was resolved into two wide lines with *no* fine structure; these two lines persisted on heating † up to 214 K with a separation of *ca.* 250 ± 30 Hz. At the liminal temperature, *ca.* 236 K, there was one line *ca.* 100 Hz in half-width. Disappointingly, although all other signals lost fine structure, none split further.

The temperature dependent spectra suggest that there is just *one* averaged structure at higher temperatures, and that switching between the naphthyl environments for components is slowed at the lower temperatures. The separation of the segment i AA'BB' multiplets into an ABCC' type spectrum

Table 5. Aromatic proton chemical shifts * in dinaphtho crown ethers

Compd.	(4)	(2; <i>n</i> = 4)	(2; <i>n</i> = 3)	(2; <i>n</i> = 2)	(6)
3-H	7.0382	7.3089	7.3375	7.3255	7.2148
4-H	7.6445	7.6903	7.7275	7.69136	7.6234
5-H	7.7680	7.6911	7.7220	7.6871	7.6468
6-H	7.3536	7.2218	7.2512	7.2215	7.2013
7-H	7.4746	7.2569	7.2994	7.2513	7.2457
8-H	7.600	8.1410	8.2055	8.1231	8.1418

* Shifts in p.p.m. measured at 360.13 MHz and relative to CHCl₃ at 7.25 p.p.m., probably ± 0.0001 p.p.m. † Aromatic ring hydrogens numbered as in (8).

for crown (2; *n* = 2), indicates that the ether ring is no longer flexing at segment i. Further changes occur in the aromatic spectra at lower temperatures, for the carbon and proton at position 7, and the proton at position 8, which are in a salient position (see later) to experience a differential ring current in different isomers or an asymmetric isomer (II or IV, Scheme 2). The spectra we observe are consistent with correlated movement of crown and propeller entities being slowed in the range 270—190 K, either to a single rigid isomer, or to several distinct isomers having accidentally similar shifts. The spectra are not of sufficient quality for an unequivocal decision on this.

Ring Currents on the Naphthalene Rings.—The naphthalene ring protons gave a 6-proton spectrum which could be analysed in considerable detail at 360 MHz and ambient temperatures (Tables 5 and 6). Some of the small inter-ring coupling constants have not yet been obtained with satisfactory precision. The shifts of the aromatic protons can be a

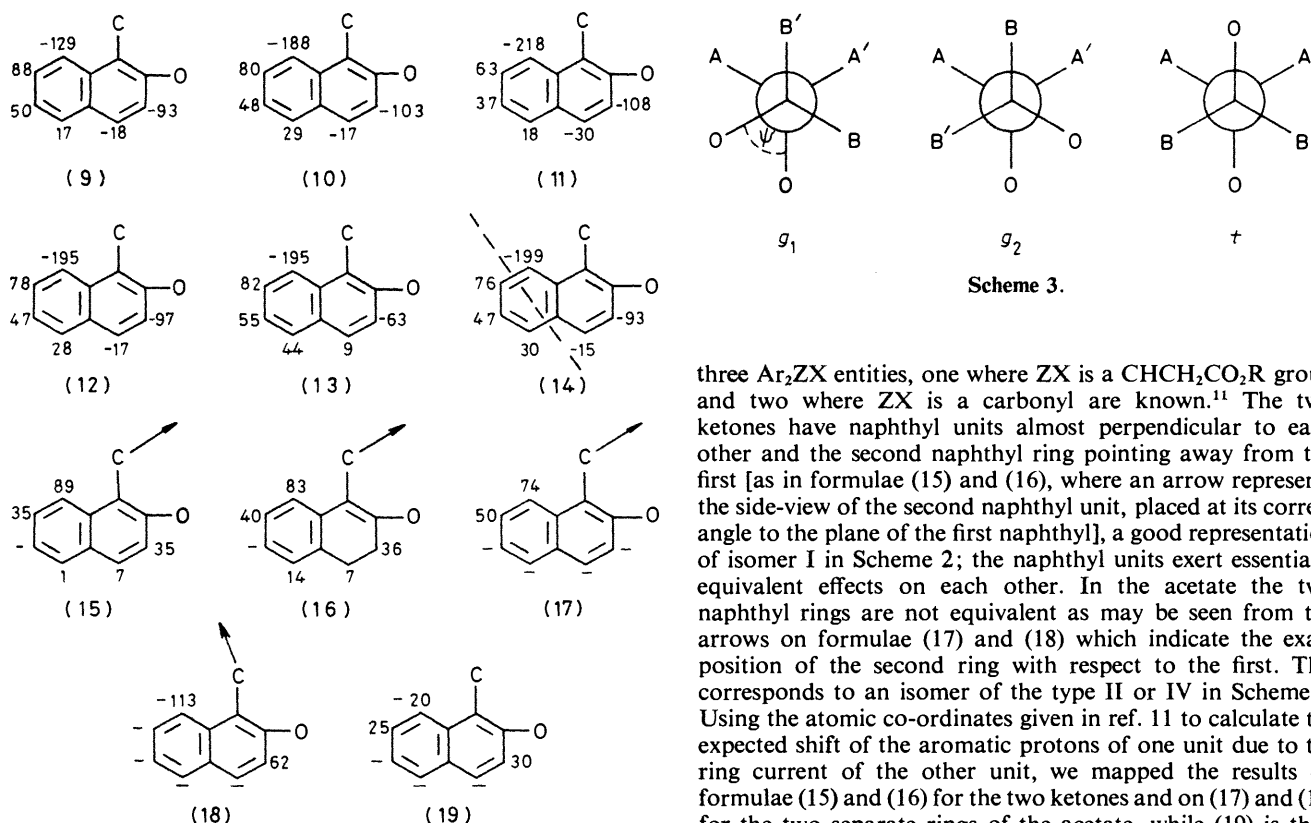
* The coalescence points in the ¹³C (aromatic C-7) and ¹H (seg. i) spectra correspond to an approximate Δ*G*‡ of 11.5—12.5 kcal mol⁻¹, at 225—240 K roughly, consistent with the same process, *i.e.* concerted motion of the ether and aromatic moieties.

† Approximate Δ*G*‡ of *ca.* 11.5—12.0 kcal mol⁻¹ may be estimated from this.

Table 6. Coupling constants in the naphthalene rings * of dinaphtho crown ethers

J^*	Naph †	(4)	(2; $n = 4$) (CDCl ₃)	Compound (2; $n = 4$) ([² H ₇]-DMF)	(2; $n = 3$)	(2; $n = 2$)	(6)
3,4	8.28	8.91	9.02	9.04	9.03	8.98	8.91
5,6	8.28	8.14	8.11	8.14	8.09	8.18	8.13
5,7	1.25	1.32	1.34	1.39	1.34	1.38	1.40
6,7	6.82	6.91	6.73	6.76	6.88	6.79	6.81
6,8	1.25	1.13	1.05	1.12	1.07	1.12	1.04
7,8	8.28	8.41	8.77	8.78	8.78	8.69	8.77

* Coupling constants obtained using NUMARIT probably ± 0.05 Hz. Numbering of aromatic hydrogen as in (8). † Naph = Naphthalene.



Scheme 3.

three Ar₂ZX entities, one where ZX is a CHCH₂CO₂R group and two where ZX is a carbonyl are known.¹¹ The two ketones have naphthyl units almost perpendicular to each other and the second naphthyl ring pointing away from the first [as in formulae (15) and (16), where an arrow represents the side-view of the second naphthyl unit, placed at its correct angle to the plane of the first naphthyl], a good representation of isomer I in Scheme 2; the naphthyl units exert essentially equivalent effects on each other. In the acetate the two naphthyl rings are not equivalent as may be seen from the arrows on formulae (17) and (18) which indicate the exact position of the second ring with respect to the first. This corresponds to an isomer of the type II or IV in Scheme 2. Using the atomic co-ordinates given in ref. 11 to calculate the expected shift of the aromatic protons of one unit due to the ring current of the other unit, we mapped the results on formulae (15) and (16) for the two ketones and on (17) and (18) for the two separate rings of the acetate, while (19) is their average. The shifts for each position of (19) approximate in sign to the observed shifts mapped on (9)–(13). The observed ring current pattern does not correspond to isomers like I or III alone, but could represent some net arrangement with contributing isomers in which the second ring differs from the first (isomers like II or IV, Scheme 2).

Conformational Analyses of Crown OCH₂CH₂O Segments using N.M.R. Spectroscopy.—There exist many qualitative methods of ligand conformational analysis of moieties with *vic* CH₂ groups (Scheme 3) based on the Karplus equation by which coupling constants obtained from the analysis of n.m.r. spectra are related to the dihedral angles in the absorbing system (ψ in the Newman projection, see g_1). It is a worthwhile aim to develop a qualitative method which can be applied to determine the conformation of crown segments (Scheme 3) in solution, so that a comparison of such structural data with the copious information available from X-ray crystallographic methods¹² may be made.

A common approach is to use a standard compound with known values of J for a fixed conformer to give type values for the OCH₂CH₂ segments (such a method has been used for the

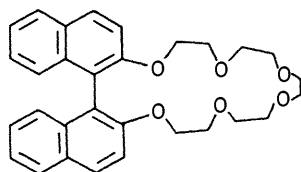
signpost indicating the relative positions of the two naphthyl units, since each naphthyl should itself suffer a ring current effect appropriate to its position relative to the other naphthyl unit. Experimental shieldings were estimated for comparison with those predicted by Tables:¹⁰ naphthoxazine (4) was chosen as a reference compound. The shieldings (in Hz) are mapped in the formulae (9)–(13) for the dinaphtho crowns (2; $n = 1$ –4) and crown (6) respectively; a negative number implies a downfield shift in Hz, and a blank a negligible effect. A definite pattern emerges, differing slightly, but not substantially, only for crowns (2; $n = 1$), and (6), with protons 8, 3, and 4 moving downfield, while 7, 6 and 5 show net upfield shifts. Formula (14) shows an approximate isoshielding line suggested by the data, with protons 8 and 3 in the deshielding zone, and proton 7 outside it. The small shieldings are not dealt with further and discussion is now confined to the 8, 7, and 3 protons.

We attempted to calculate the shifts of the aromatic ring protons for some known structures. The crystal structures of

Table 7. Coupling constants for an OCH₂CH₂O segment based on data for dioxan

Coupling constant (Hz)	Abraham/Gatti relation
J_g^g	2.78 * $J_g^g = 8.94 - 0.94 (E_x + E_y)$
$J_{g'g'} + J_{g't}$	12.5 * $J_{g'g'} + J_{g't} = 26.92 - 2.03 (E_x + E_y)$
J_t^g	5.65 † $J_t^g = 1.35 + 0.63 (E_x + E_y)$
J_t^t	12.06 † $J_t^t = 18.07 - 0.88 (E_x + E_y)$

* Observed values, ref. 14. † Calculated values, from the Abraham/Gatti relations¹⁵ with an average value of $E_x + E_y$.



(20)

amino acids¹³ RC(NH₂)H-CO₂H). As standard, we used dioxan¹⁴ coupling constants to calculate the coupling constants for a hypothetical *trans*-conformer using the equations of Abraham and Gatti¹⁵ (Table 7). Then substituting the values obtained for the averaged coupling constants of segments ii and iii (shown in Tables 3 and 4) we estimated the % of *gauche* conformer present in the segment. The results indicate a very small proportion of *trans*-conformer (< 5%) to be present.

Complexation with Cationic Species.—A spectrometric titration, performed by adding KNCS to a [²H₇]-DMF solution of crown (2; $n = 4$), indicated that a 10- to 20-fold excess of KNCS was required to give the limiting spectrum. Some of the shifts have been accurately determined and are shown in Tables 3 and 5. A solid complex of 1:1 stoichiometry was obtained from KI and the dinaphtho crown (2; $n = 4$) in acetone.

A brief comparison of the cation complexing ability of (2; $n = 3$) with that of the slightly more rigid ligand (20), synthesised by the Cram group¹⁶ was made. The association constants K_a for association of metal picrate and ligand in CHCl₃ measured and calculated by the technique of Cram *et al.*¹⁷ were 1×10^6 (Na) and 1×10^7 (K) comparable to 1×10^5 (Na) and 2×10^6 (K) for the slightly more rigid dinaphthyl crown (20).¹⁸ Despite the inherent chirality of the dinaphtho crowns, an attempt at chiral recognition in which (*S*)-1-phenylethylammonium thiocyanate as guest was allowed to react with the racemic host dinaphtho crown (2; $n = 3$), was unsuccessful. It should be marked that additional steric barriers will probably be required if the dinaphthyl crowns (2) are to provide effective chiral discrimination. The Cram group dinaphthyl ligands were more effective with two dinaphthyl units, and derivatives of crown (20) only showed chiral recognition when substituted with additional binding sites.¹⁸

The crowns reported in this paper are the first of a series of crowns intended to provide mechanistic information about macrocycle/cation interactions. The barrier to conformational averaging of the ether segments is several kcal mol⁻¹ higher than for unsubstituted crowns. We are currently engaged on the synthesis of related crowns (three-bladed propellers) which provide spectroscopic signposts and high steric barriers to conformational averaging. With appropriate substitution they may also provide chiral recognition.

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