Ligands for the Alkali Metals. Part 4.[1] Nuclear Magnetic Resonance of Crown Ethers with Alkali-metal Ions

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The solution ^1H n.m.r. spectra of the crown ligands 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin (benzo-15-crown-5) and 2,3,5,6,8,9,11,12,14,15,17,18-dodecahydro-1,4,7,10,13,16,19-benzoheptaoxacycloheneicosin (benzo-21-crown-7) as free ligands and in mixtures with alkali-metal iodides or thiocyanates are reported and analysed to provide shifts and coupling constants. The signals of some or all the hydrogens in the mixtures are upfield of those of the free ligands for complexes of 2 : 1 ligand : cation ratio, but downfield when only a 1 : 1 complex is present, and this finding may be used diagnostically. An empirical explanation of the direction of the shift on complexation is given in terms of the electric-field effect, ring-current variations, and specific ion pairing. The gross conformation of the two complexes in solution is shown to be similar to that found in the crystal by *X*-ray methods.

A NUMBER of n.m.r. studies have been reported [2-7] for alkali-metal complexes of crown ligands, and useful correlations of ^1H, ^{13}C, or alkali-metal nuclear resonance spectra with complex formation [5,6] or conformation [7] have been published. Our parallel work [8] provides a diagnostic use of ^1H n.m.r. spectra in the investigation of complex formation between crown ligands and alkali-metal ions and considers empirically the differences in

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[3] E. Shchori, J. Jagur-Grodzinski, and M. Shporer, *J. Amer. Chem. Soc.*, 1973, **95**, 3842.

[4] J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, 1974, **74**, 351; R. M. Izatt, R. E. Terry, D. P. Nelson, Y. Chan, D. J. Eatough, J. S. Bradshaw, L. D. Hansen, and J. J. Christensen, *J. Amer. Chem. Soc.*, 1976, **98**, 7626.

[5] D. Live and S. I. Chan, *J. Amer. Chem. Soc.*, 1976, **98**, 3769.

[6] A. I. Popov, in 'Solute–Solvent Interactions,' eds. J. F. Coetzee and C. D. Ritchie, Marcel Decker, New York, 1976, vol. 2, pp. 271—330.

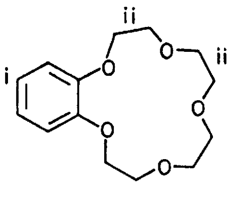
[7] F. A. L. Anet, J. Krane, J. Dale, K. Daasvatn, and P. O. Kristiansen, *Acta Chem. Scand.*, 1973, **27**, 3395.

[8] (*a*) A. C. Linsdell (Robson), Ph.D. Thesis, University of Newcastle upon Tyne, 1971; (*b*) J. C. Lockhart, A. C. Robson, and M. E. Thompson, *J.C.S. Perkin I*, 1973, 577; (*c*) J. C. Lockhart, presented in part at the September meeting of the Chemical Society, Sheffield, 1976.

shielding and conformation between free and complexed crowns.

RESULTS AND DISCUSSION

The ^1H n.m.r. spectra of Pedersen crowns[4] based on ethylene oxide oligomers consist of a series of AA'BB' spectra, some of which may be analysed to provide conformational information. In benzo-15-crown-5 (1), for example, one can expect at least three different AA'BB' spectra for (*i*) the symmetrical 1,2-disubstituted benzene segment [labelled i in formula (1)], (*ii*) the $ROCH_2CH_2O$ (R = aryl) segment (labelled ii) in which the A protons resonate downfield of those of the remaining segment and (*iii*), OCH_2CH_2O; the shifts of the A and B protons for segment (iii) are virtually the same, and we could not observe coupling for them even at 220 MHz. The aza-crown analogue (4) has a very similar spectrum, with the aryl protons forming an ABCD system and with a further segment OCH_2CH_2NH for which only the B protons resonate upfield of the segment iii protons.[8b] Benzo-21-crown-7 (2) has a spectrum very similar to that of (1), but contains another broad singlet, equal in intensity to that of segment iii, and a few hertz upfield [labelled iv in formula (2)]. Rapid conformational averaging takes place at ambient and greater temperatures for (1), giving the simple averaged AA'BB' spectra noted above, but spectra indicating slow averaging on the n.m.r. timescale were observed at lower temperatures. For (2), averaging was only sufficiently rapid to give simple spectra at 323 °C and above. The shifts and coupling patterns alter considerably in the presence of iodide or thiocyanate salts of alkali-metal ions (see Tables 1—4). Some of the shifts and coupling constants (for 'average conformations' of segments i and ii) were estimated as described by Abraham[9] and the values refined using the LAOCOON program, with the magnetic-equivalence modification.* The lines were relatively wide, leading to uncertainty, particularly in the coupling constants obtained from the program.



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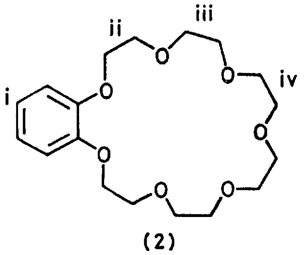

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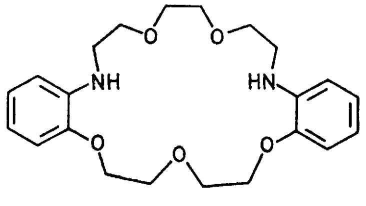

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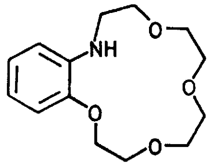

(4)

TABLE 1

Shifts [a] of the protons of benzo-15-crown-5 (0.5 mol dm^{-3}) plus salts (0.5 mol dm^{-3})

System	Shift Aryl (R) i	 $ROCH_2CH_2O$ ii	 OCH_2CH_2O iii
Free crown	6.900 (0)	3.944 (0.233)	3.678
Crown + LiBr	6.989	4.033	3.722
Crown + NaI	7.067 (0.236)	4.022 (0.324)	3.767
Crown + KI	6.878	3.838 (0.211)	3.678
Crown + RbI	6.922 (0)	3.869 (0.242)	3.644
Crown + CsI [b]	6.967 (0)	3.916 (0.309)	3.644

[a] Shifts are given in p.p.m., downfield from an internal $SiMe_4$ standard. Spectra were obtained at 90 MHz in CD_3OD solution at 298 K and were reproducible to ±0.002 p.p.m. The position of the centre of each AA'BB' multiplet (see text) is quoted together with (in parentheses) the separation in p.p.m. between the shifts of the A and B signals. [b] Each *ca.* 0.2 mol dm^{-3}; CsI is not sufficiently soluble for higher concentrations.

TABLE 2

Shifts [a] of the protons of benzo-15-crown-5 (0.5 mol dm^{-3}) plus salts (0.25 mol dm^{-3})

System	Shift Aryl (R) i	 $ROCH_2CH_2O$ ii	 OCH_2CH_2O iii
Free crown	6.900 (0)	3.944 (0.233)	3.678
Crown + NaI	7.000 (0.011)	4.000 (0.311)	3.722
Crown + KI	6.822 (0.169)	3.761 (0.129)	3.676
Crown + RbI	6.878 (0.098)	3.811 (0.178)	3.633
Crown + CsI [b]	6.967 (0)	3.868 (0.244)	3.611

[a] As in Table 1. [b] Diluted to achieve solution.

TABLE 3

Hydrogen-1 n.m.r. shifts * of protons of benzo-21-crown-7 (2) (0.5 mol dm^{-3}) plus salts in CD_3OD at 323 K

System	Shift Aryl (R) i	 $ROCH_2CH_2O$ i	 OCH_2CH_2O iii	 OCH_2CH_2O iv
Free crown	6.911	3.971 (0.283)	3.687	3.606
Crown + KI (0.5 mol dm^{-3})	7.000	4.051 (0.309)	3.693	3.643
Crown + RbI (0.25 mol dm^{-3})	6.954	4.007	3.680	3.613
Crown + RbI (0.5 mol dm^{-3})	6.967	4.044	3.683	3.622

* Shifts are given in p.p.m. downfield from an internal $SiMe_4$ standard, reproducible to ±0.002 p.p.m. The position of the centre of each AA'BB' multiplet (see text) is quoted with (in parentheses) the separation in p.p.m. between the shifts of the A and B signals.

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* The Bothner–Bye program LAOCOON 3, with magnetic-equivalence modification by Dr. C. W. Haigh, Swansea, obtained by courtesy of Dr. Haigh.

[9] R. J. Abraham, 'Analysis of High Resolution NMR Spectra,' Elsevier, Amsterdam, 1971.

Values of J_{gem} were not refined since they have little effect on the spectrum, and were not used in the further analysis presented here. Since the AA′BB′ spectra are symmetrical, the centres of the multiplets are quoted in Tables 1—4 as primary data and the derived shift separation of the A and B nuclei (usually calculated for segment ii) is given in parentheses. Not only the conformational equilibria of free crowns but also the equilibria between the crowns and cations are temperature dependent; spectra quoted in the Tables refer to temperatures above the rapid-exchange limit, and comparisons between the spectra of the free and complexed crowns are drawn at the same temperature.

TABLE 4

Hydrogen-1 n.m.r. shifts[a] of benzo-15-crown-5 in the presence of 0.1 mol dm^{-3} K[NCS] in CD_3OD

Mol ratio [KNCS] : [crown]	Shift Aryl (R) i	 $ROCH_2CH_2O$ ii	 OCH_2CH_2O iii
0.42	6.819	3.783 (0.131)	3.689
0.62	6.844	3.819 (0.168)	3.700
0.73	6.856	3.837 (0.173)	3.722
0.82	6.856	3.852 (0.181)	3.722
1.04	6.867	3.861 (0.197)	3.711
1.5	6.911 (0)	3.879 (0.223)	3.722
3.1	6.944 (0)	3.939 (0.293)	3.722
4.8	6.955 (0)	3.946 (0.321)	3.722
7.6[b]	6.978 (0)	3.960 (0.322)	3.744
Free crown	6.900 (0)	3.944 (0.233)	3.678
2 : 1 Complex[c]	6.807	3.753 (0.11)	3.691

[a] As in Table 1. [b] Taken as the limiting spectrum of the 1 : 1 complex. [c] Obtained assuming all the K^+ is complexed, and the observed spectrum is the average of the free crown (0.04 mol dm^{-3}) and sandwiched crown (0.2 mol dm^{-3} based on ligand) for the first entry in this Table.

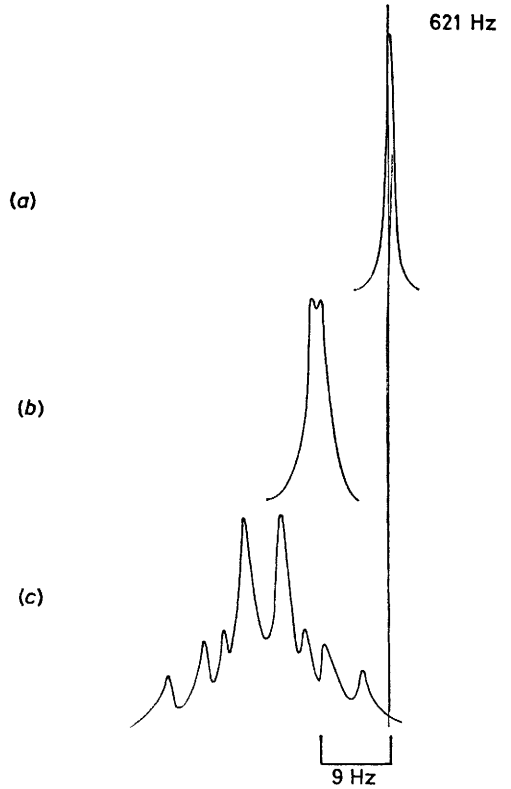

FIGURE 1 Hydrogen-1 n.m.r. spectra (aryl region) (in Hz downfield from $SiMe_4$ at 90 MHz on the Bruker Spectrospin) of benzo-15-crown-5 (initial concentration 0.5 mol dm^{-3} in CD_3OD) with varying concentrations of NaI such that R = [benzo-15-crown-5] : [NaI] takes the values (*a*) ∞, (*b*) 2, and (*c*) 0.3

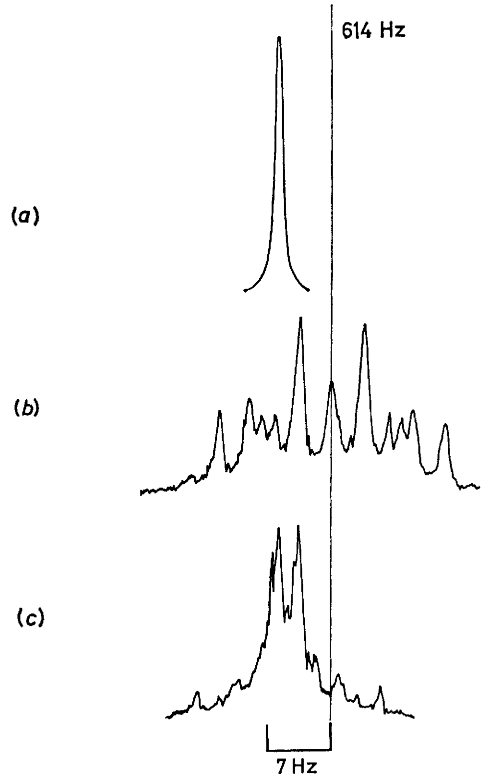

FIGURE 2 Hydrogen-1 n.m.r. spectra (aryl region) [in Hz downfield from $SiMe_4$ at 90 MHz (Bruker Spectrospin)] of benzo-15-crown-5 (initial concentration 0.5 mol dm^{-3} in CD_3OD) with varying concentrations of KI, such that R = [benzo-15-crown-5] : [KI] takes the values (*a*) ∞, (*b*) 2, and (*c*) 1

The changes in the spectra of crowns on addition of alkali-metal iodides are postulated to indicate complex formation [equations (1) and (2)]. The direction of the

$$L + M^+ \rightleftharpoons [ML]^+ \qquad (1)$$

$$2L + M^+ \rightleftharpoons [ML_2]^+ \qquad (2)$$

shift seems to be related to the stoicheiometry of the complex formed. Qualitatively it has been noted that, for ligand : cation combinations known or expected to give 1 : 1 complexes,[5,8a] the ^1H signals are downfield from those of the free crown at all crown : cation ratios investigated (Tables 1—4 and Figure 1). However, for combinations expected to give both 2 : 1 and 1 : 1 complexes, the shifts are upfield of the corresponding free-crown shifts at crown : cation ratios of 2 : 1 or more, and downfield at low crown : cation ratios (see Tables 1—4). The effect is different in degree for each type of proton, and is most pronounced for segments i and ii. The aryl signals (segment i) are shown in Figures 1 and

2 as typical evidence for the existence of more than one species in solution. The spectra for free (1) and for (1) in the presence of NaI (Figure 1) or KI (Figure 2) provide a contrast between a system in which a 1 : 1 ligand : cation stoicheiometry is expected * and one in which both 2 : 1 and 1 : 1 stoicheiometries are expected.[4] Although the effect of sodium iodide on the spectra is consistent with the presence of a 1 : 1 complex (or its coexistence with a weak 2 : 1 complex), since there is a smooth downfield shift of the signals with increasing sodium iodide concentration, the effect of potassium iodide is different: the spectrum in Figure 1(*b*) is an average of those in 1(*a*) and 1(*c*), whereas Figure 2(*b*) could not represent an average of 2(*a*) and 2(*c*). For the potassium solutions, at least three crown environments must be postulated to account for the spectra, probably free crowns, sandwich (2 : 1) complex, and 1 : 1 complex. This is confirmed by a study of the potassium thiocyanate–crown interaction, using a constant concentration of salt and varying amounts of crown as indicated in Table 4. The limiting spectrum of the crown in the 1 : 1 complex was obtained with a large excess of K[NCS], and the limiting 2 : 1 spectrum was calculated from the spectrum with the maximum possible concentration of crown permitted by its solubility. The spectrum of the 1 : 1 complex is similar to that of the firmly established 1 : 1 NaI complex except for the aryl region. From the series of spectra (Table 4) attempts were made to calculate formation constants β_1 and β_2 for the reactions (1) and (2), using an approximate graphical method.[10] The quotients obtained (β_1 30—50 dm^3 mol^{-1}, β_2 2 000 $\pm$ 500 dm^6 mol^{-2}) differed when determined using the shifts for different sets of protons [*e.g.* R or ROC*H*$_2$ (R = aryl)]. An apparent β_1 (6—30 dm^3 mol^{-1}) for the sodium iodide–ligand (1) system was smaller than that found in this work (*ca.* 500 dm^3 mol^{-1}) in u.v. spectral studies. The apparent β values for potassium and sodium are smaller than found for aqueous methanol solutions by a calorimetric method.[4] We suggest that the different methods are measuring different types of ion pair in different ways in the composite equilibria (1) and (2). The discrepancy between quotients measured from different sets of protons may arise from anion effects in a specific ' tight ' ion pair. The effect of ion pairing on the ^{1}H shifts of the complexed crowns may be largely responsible for the change in direction of the shifts in complexes of different composition, as suggested later in this paper. The calorimetric treatment [4] did not establish the existence of 2 : 1 as well as 1 : 1 complexes for certain salts and needs revision in the light of our n.m.r. data. The meaning of measured ' selectivities ' for benzo-15-crown-5 and cations which can form complexes of more than one stoicheiometry (and indeed for related ionophores which can do so) is open to question.

Assuming reasonable values (*ca.* 30—300 dm^3 mol^{-1}) for β_1 for formation of 1 : 1 complexes,[1,4] it can be estimated, for systems in which there is no likelihood of 2 : 1 complexes forming, that 1 : 1 complex formation is largely (>80%) complete in equimolar mixtures at the concentration of Table 1. The spectra described therein are substantially those of the 1 : 1 complexes. In the mixtures with 2 mol of crown per mol of cation the cation is >90% complexed and the spectrum is an average of the spectra of the free and complexed crown. In the remaining systems where 2 : 1 complexes are observed it is certain that the spectra quoted in Table 1 are not limiting spectra for the 1 : 1 complex. We infer, for the iodide spectra as for the thiocyanate, that the shifts are upfield for segments i and ii in 2 : 1 complexes, downfield for 1 : 1 complexes, and that in mixtures of free, 2 : 1, and 1 : 1 complexed ligands the averaged signal depends on the relative proportion of each present. Table 5 shows how the signals shift for ligands (3) and (4) in the presence of sodium and potassium iodides. The five-donor crown (4) shows upfield shifts with sodium, downfield with potassium, while the seven-donor crown (3) shows downfield shifts with both salts, following the trends found with the corresponding Pedersen all-oxo-crowns. From the equilibrium constant β_1 of *ca.* 4.2 dm^3 mol^{-1} obtained for (4) by u.v. spectrometry in MeOH (in this work) it can be estimated that *ca.* 27% of the crown is complexed to sodium, so the signals do not reflect a limiting shift as is the case for ligand (1). Nevertheless, the trends are clear and we propose that only complexes of 1 : 1 ligand : metal stoicheiometry are formed by (3) with sodium and potassium, and by (4) with sodium, while (4) can form a 2 : 1 complex with potassium.

TABLE 5

Shifts * of protons of dibenzo-21-diaza-crown-7 (3) plus salts (each 0.05 mol dm^{-3}) at 298 K

	Shift			
System	Aryl (R) *	$ROCH_2CH_2O$ A	$ROCH_2CH_2O$ B	OCH_2CH_2O *
Free crown	6.69	4.11	3.91	3.60
Crown + NaI	6.77	4.17	4.10	3.70
Crown + KI	6.90	4.17	3.83	3.65

Shifts of protons of benzo-15-aza-crown-5 (4) plus salts (each 0.1 mol dm^{-3})

	Shift		
System	Aryl (R) *	$ROCH_2CH_2O$ *	OCH_2CH_2O *
Free crown	6.73	4.00	3.68
Crown + NaI	6.80	4.05	3.80
Crown + KI	6.67	3.87	3.65

* Centre of multiplet is quoted. Shifts are given in p.p.m., downfield from $SiMe_4$ as internal standard, and were obtained at 60 MHz (*i*) in 1 : 1 CD_3OD–$CDCl_3$ for (3), (*ii*) in neat CD_3OD for crown (4). The methylene hydrogen signals of the aryl NCH_2CH_2O segments of these crowns show substantially no shift and are not included in the Table.

The coupling constants for the aryl segment i are typical of symmetrical 1,2-disubstituted benzenes,[9] and

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* Although one instance of a solid 2 : 1 ligand : Na$^+$ complex is known, this is attributable to the lack of alternative co-ordinating species and is not expected in a donor solvent like methanol (D. G. Parsons and J. N. Wingfield, *Inorg. Chim. Acta*, 1976, **17**, 625).

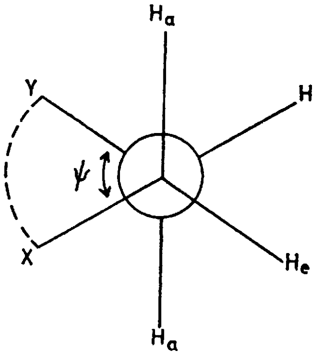
[10] F. J. C. Rossotti and H. Rossotti, ' The Determination of Stability Constants,' McGraw-Hill, New York, 1961.

do not vary between complexed ligands. [Values of J_{ortho} (8.1 and 7.7), J_{meta} (1.3), and J_{para} (0.5), all ±0.1 Hz, were obtained for the 2 : 1 mixture of crown : potassium iodide, the spectrum of which appears in Figure 2(*b*).] The dramatic differences in coupling pattern in Figures 1 and 2 arise solely from changes in chemical shift.

From the spectra of segment, ii, values of δ and J_{vic} averaged over all the conformations of free and complexed crown can be obtained. The range of values of J_{vic} (J and J') is shown in Table 6. For free crowns the values are very similar to those of dioxan,[11] suggesting that the main contributing conformations must have oxygens *gauche* in segment ii. The *gauche* conformation for $(OCH_2CH_2)_n$ units is calculated to be more stable by *ca.* 400 cal mol^{-1}.[12,*] There is a definite change to greater J and smaller J' in the salts. Whether this can be attributed to conformational changes (slight changes in dihedral angle) or to electronegativity changes (which must be considerable at oxygen) is not clear. The results of Live and Chan [5] cover three other benzo-crowns and different solvents, and their derived vicinal coupling constants correspond closely to ours, giving confidence in the trends observed for segment ii. Since crystal data are available for a number of the free crowns and alkali-metal complexes whose n.m.r. spectra have now been analysed, the Lambert–Buys $J : J'$ ratio method was considered as an aid to conformational analysis of large crown rings. Adopting Lambert's hypothesis [13a] that the ratio $R = J : J'$ is independent of the electronegativity of the X and Y substituents [defined in (5)] for six-membered rings and can be used as a criterion of conformational change relatively free from electronegativity effects, it is seen that the coupling in segment ii (and, by implication, the conformation) is different in free and complexed crowns (Table 6). For six-membered rings such as dioxan, where the oxygens can only be *gauche*, Buys [13c] derived [equation (3)] the torsion angle ψ. The relation should hold within the same bounds [13a] for

$$\psi = \cos^{-1} [3/(2 + 4R)]^{\frac{1}{2}} \tag{3}$$

individual OCH_2CH_2O segments of crown rings with the additional proviso that the oxygens of the segment are never in a *trans* relation. *X*-Ray studies of the free ligands 18-crown-6 [14] and dibenzo-18-crown-6 [15] indicate that *trans* oxygens are possible (OCCO torsion angles of 75.4, 67.6, and 174.7° for 18-crown-6, 77 and 105° for dibenzo-18-crown-6), although the larger dibenzo-30-crown-10 has only puckered *gauche* oxygens [16] (72, 70, 67, and 63°). The smaller 12-crown-4 is also reported to have only *gauche* oxygens in the solid state (i.r. evidence [7]). All the available evidence on alkali-metal complexes of crowns in the solid state indicates *gauche* oxygens.[14-20] Values of the torsion angle ψ for segment ii were calculated using equation (3) and are given in Table 6. Where available, the value of ψ from crystal-structure analysis is compared with that obtained by the Buys method in Table 7. The agreement is not as satisfactory as for six-membered rings, but nevertheless indicates the same gross conformation at segment ii in the crystal and in solution except for dibenzo-18-crown-6, which would from this analysis be supposed to have the *gauche* conformation in solution. More crystal data are needed to test the relation further.



(5)

TABLE 6

Average vicinal coupling constants (in Hz) for segment ii and derived torsional angles (°)

Ligand	Mol ratio [crown] : [salt]	Salt	J [a]	J' [a]	R [b]	ψ [c] (n.m.r.)
(1)			5.75	3.1	1.9	55
(2)			6.35	3.3	1.9	55
(3)			5.9	3.1	1.9	56
Dioxan			6.1	2.7	2.3	58.5
(1)	2.4	K[NCS]	6.4	1.9	3.4	64
(1)	2.0	KI	6.3	2.3	2.7	61
(1)	2.0	RbI	6.3	2.2	2.9	62
(1)	2.0	CsI	6.5	2.3	2.7	61
(1)	1.0	NaI	6.8	2.1	3.2	63
(1)	1.0	KI	6.05	1.7	3.5	64
(1)	0.13	K[NCS]	6.2	2.05	3.0	62.5
(1)	1.0	RbI	6.4	2.1	3.0	62.5
(1)	1.0	CsI	6.3	1.8	3.4	64
(2)	1.0	KI	6.3	1.8	3.4	64

[a] Generally ±0.2—0.3 Hz. [b] $R = J : J'$. [c] Derived by Lambert–Buys method, see ref. 13.

While an exact calculation of nuclear-screening constants in a molecule of crown size is out of the question for the present, it is possible to assess empirically certain differences in screening between benzo- and non-benzo-substituted crowns, and between free and complexed

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[*] Throughout this paper: 1 cal = 4.184 J.

[11] N. Sheppard and J. J. Turner, *Proc. Roy. Soc.*, 1959, **A252**, 506.

[12] R. Iwamoto and H. Wakano, *J. Amer. Chem. Soc.*, 1976, **98**, 3764.

[13] (*a*) J. B. Lambert, *Accounts Chem. Res.*, 1971, **4**, 87; (*b*) J. B. Lambert, J. J. Papay, S. A. Khan, K. A. Kappauf, and E. S. Magyar, *J. Amer. Chem. Soc.*, 1974, **96**, 6112; (*c*) H. R. Buys, *Rec. Trav. chim.*, 1969, **88**, 1003.

[14] J. A. Dunitz and P. Seiler, *Acta Cryst.*, 1974, **B30**, 2739.

[15] D. Bright and M. R. Truter, *J. Chem. Soc.* (*B*), 1970, 1544.

[16] M. A. Bush and M. R. Truter, *J.C.S. Perkin II*, 1972, 345.

[17] J. D. Dunitz, M. Dobler, P. Seiler, and R. P. Phizackerley, *Acta Cryst.*, 1974, **B30**, 2733.

[18] M. A. Bush and M. R. Truter, *J.C.S. Perkin II*, 1972, 341.

[19] P. R. Mallinson and M. R. Truter, *J.C.S. Perkin II*, 1972, 1818.

[20] M. A. Bush and M. R. Truter, *J. Chem. Soc.* (*B*), 1971, 1440.

crowns. If we make the usual approximation[21,22] that the total screening constant σ can be regarded as a sum of several contributions [equation (4)], then the main differences between the free and complexed ligands should be (*a*) an electric-field effect σ_e and (*b*) ring-current effects σ_r (σ_d and σ_p are the local diamagnetic and paramagnetic effects respectively). Under (*a*) we should

$$\sigma = \sigma_d + \sigma_p + \sigma_e + \sigma_r \qquad (4)$$

initially consider the electric-field effect of the cation, of the dipole induced on the ether oxygens, and of the anion, and under (*b*) ring-current effects, principally arising for the 2 : 1 ligand : cation complexes, from the benzo-group of the second ligand interacting with the protons of the first.

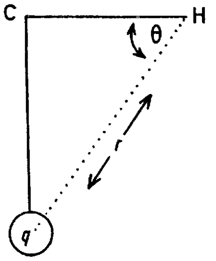
TABLE 7

Comparison of angles derived from the Lambert–Buys relation with those obtained from crystal structures

Ligand	Salt	$\psi/°$ n.m.r.	$\psi/°$ *X*-ray
Dibenzo-18-crown-6		54.5[a]	*trans*[b]
	NaBr	61[a]	63.3, 64.5[b]
Dibenzo-30-crown-10	KI		59 (av.)[c]
		56.5[a]	65[c]
(1)	KI	61[d] (64[e])	61[f]
(1)	NaI	63	58[g]

[a] *J* Values from ref. 5. [b] Refs. 15 and 20. [c] Ref. 16. [d] 2 : 1 crown : KI mixture. [e] Limiting 2 : 1 crown : K[NCS] spectrum. [f] Ref. 19. [g] Ref. 18.

The electric-field-effect contribution was calculated using the Buckingham model[22] [see (6) and equation (5)], and the ring-current effects using the Johnson–Bovey model[23] and the tabulated contributions for this model.[21] Distances and angles required for the calculations were computed * using the atomic co-ordinates published[18,19] for the sodium and potassium iodide complexes of benzo-15-crown-5 and co-ordinates derived for possible alternative conformations of the ligand.



(6)

$$\sigma_e = -12.5(q/r^2)\cos\theta - 17.0(q/r^2)^2 \qquad (5)$$

The shift differences observed for protons in benzo-15-crown-5 and benzo-21-crown-7 relative to those in the corresponding non-benzo-substituted analogue are given in Table 8. These shift differences can be accounted for if the free benzo-crown has a *gauche* conformation for the oxygens of segment ii, intermediate in detailed geometry between those found in the sodium benzo-crown-5 and potassium bis(benzo-crown-5) complexes[18,19] in the crystal. Shifts predicted for the A and B protons of segment ii for conformations of benzo-crown-5 with *trans* oxygens in segment ii or iii give less satisfactory agreement. Samples of calculated ring-current shifts are given in Table 8, excluding the effect of the second ring in the potassium bis complex (which is used only in Table 9).

TABLE 8

Estimation of ring-current contribution to the ^1H n.m.r. shifts of OCH_2CH_2O segments of benzo-crowns

Ligand	Contribution iiA	Contribution iiB	Contribution iii	Contribution iv
(1)[a]	0.3601	0.128	−0.022	
(1)[b]	0.368	0.203	0.049	
(1)[c]	0.408	0.126	0.030	
(1)[d]	0.292	0.212		
(2)[e]	0.472	0.149	0.007	−0.074

[a] The shifts (in p.p.m.) are those observed in CD_3OD in this work and are referred to the measured shift of benzo-15-crown-5 in $CDCl_3$ as reported by J. Dale and P. O. Kristiansen, *Chem. Comm.*, 1971, 670. Hydrogen-1 shifts of benzo-15-crown-5 are identical in $CDCl_3$ and CD_3OD. [b] Calculated on the basis of the conformation found in the crystalline NaI complex, ref. 18. [c] Calculated on the basis of the conformation found in the crystalline KI complex, ref. 19. [d] Calculated on the basis of conformation with *trans* oxygens on one of the segments ii. A number of such calculations gave low shifts for iiA but high for iiB nuclei. [e] Shifts observed in CD_3OD, downfield from the shift of benzo-21-crown-7 in $CDCl_3$, taken from the reference given in footnote *a*.

TABLE 9

Electric-field effect due to cations complexed to benzo-15-crown-5

Shift[a] observed or calculated relative to free crown	Segment i	Segment ii	Segment iii
1 : 1 NaI (calc.)	−0.272[b]	−0.59	−0.64
1 : 1 NaI (obs.)	−0.167	−0.084	−0.09
1 : 1 KI (calc.[c])	−0.236	−0.468	−0.431
1 : 1 K[NCS] (obs.)	−0.078	−0.016	−0.067
2 : 1 KI (calc.[d])	−0.236	−0.464	−0.201
2 : 1 K[NCS] (obs.)	+0.078	+0.192	−0.002

[a] It is not clear whether the A and B protons are reversed in shift between the free and complexed states, hence the average is quoted as for example in footnote *b*. Shifts and screening constants in p.p.m. [b] The average shift calculated for H(17,15), H(18,16), H(19,17), and H(20,18) as numbered in ref. 18 is given for segment i. [c] Assuming, for the 1 : 1 complex of K[NCS], the geometric location of K^+ relative to the single ring observed for either ring of the centrosymmetric bis complex in ref. 19. [d] Dimensions of ref. 19 were used. A correction was applied for the ring current of the second ring (only significant for segment iii).

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* Program IXRAY kindly made available by Dr. W. Clegg, University of Newcastle.

[21] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High-resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, Oxford, 1965, vol. 1, p. 595.

[22] A. D. Buckingham, *Canad. J. Chem.*, 1960, **38**, 300; L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, Oxford, 1969, p. 68; M. P. Schweizer, S. I. Chan, G. K. Helmkamp, and P. D. P. Ts'o, *J. Amer. Chem. Soc.*, 1964, **86**, 696.

[23] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.

Calculated shifts due to the electric-field effect of the cation, assuming a full positive charge on the metal ion [$q = +1$ in equation (5)] are shown in Table 9 and compared with the observed shift relative to the free crown. These calculated shifts are downfield for the 1 : 1 complexes of Na and K, but much greater than the observed shifts, while for the 2 : 1 complex of potassium they are downfield, in the opposite direction to the observed shifts, even when a correction is made for the second ring current. (The aromatic ring of the second ligand in the 2 : 1 complex is situated above the segment iii protons [19] and gives an upfield shift.) Consideration of other effects, (*a*) reduced charge on the metal ion, (*b*) significant induced dipole on oxygen, and (*c*) general and specific location of the counter anion or solvent, was not adequate to explain the observed shifts fully. A reduced charge (*ca.* one-seventh of a full positive charge) brings the calculated shifts for the 1 : 1 NaI complex into line in Table 9, but individual A and B shifts for segment i and ii would be wrong. The order of magnitude would be right for both the 1 : 1 complexes in Table 9. Allowing a charge of -0.01 on each ring oxygen makes a *ca.* 0.038—0.044 p.p.m. difference (upfield) operating evenly on all the ring protons for the NaI complex. Including the effect of the second-ring oxygens on the protons of the first ring for the bis complex of KI makes a difference of *ca.* 0.044—0.05 p.p.m., again a general upfield correction for all the protons and insufficiently selective to account for the observed shifts. The effect of the negatively charged anion can be evenly spread, if the anion is rapidly moving between ' loose ' ion pairs and if it may be located at any point on the periphery of the complex. However, in a ' tight ' or specific ion pair, the anion could be located asymmetrically and exert a differential upfield shift on certain protons. This may account for the segment ii protons of the bis complex. Ion pairing seems to have an effect on the n.m.r. spectrum, as noted in the discussion on stability constants, and this may be the nature of the effect. This argument could be extended to a specific or tight solvated complex with solvent OH. However, the explanation of upfield shifts for the 2 : 1 complexes is still uncertain and examination of other systems is necessary for a more detailed analysis.

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were run in CD_3OD solvent at 60 MHz (Varian EM 360), mostly at 90 MHz (Bruker Spectrospin HFK-6), and at 220 MHz (free benzo-15-crown-5 and its NaI complex only) using the S.R.C. service.

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