Orbital Levels of Crown Ethers and Related Macrocycles studied by Ultraviolet Photoelectron Spectroscopy; Relationship to Complexation Studies

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Ultraviolet photoelectron spectroscopy has been used to measure the valence-shell ionization potentials of several crown ethers and other macrocyclic ligands. A comparison is made with results for corresponding open-chain and other model compounds. In general, evidence is found for appreciable through-bond or through-space interactions among the heteroatom lone-pair orbitals in the macrocyclic molecules, making these molecules softer ligands than would otherwise be anticipated.

A powerful aspect of ultraviolet photoelectron spectroscopy (u.p.s.) is its ability to quantitate the interactions among separated 'lone-pair' or π orbitals in molecules. Since the highest occupied molecular orbital (h.o.m.o.) of a substance is frequently of lone-pair or π type, it is not surprising that relatively subtle changes in these orbital energies or characteristics (orientation, size, *etc.*) can affect chemical properties in significant ways. Thus, u.p.s. provides a means of understanding chemical properties in a more complete and satisfactory way than was previously possible. For example, in an earlier study[1] we showed that the site of attack of singlet oxygen on molecules containing more than one olefinic site, *e.g.* α- and β-myrcene, correlated with the site of the h.o.m.o. We were also able to discover a new reaction for arylazoxy compounds based on u.p.s. results.[2] While arylazoxy compounds are generally unreactive compared to arylnitrones, raising of the h.o.m.o. level increases reactivity. Thus 4,4′-azoxyanisole but not azoxybenzene reacts with thionyl chloride or oxalyl chloride, resulting in *ortho* chlorination.

In the present study, our attention has focused on crown ethers and related macrocyclic ligands. In these molecules, the presence of several heteroatom lone-pairs introduces the possibility of rather extensive lone-pair interactions *via* through-space and/or through-bond mechanisms. Such interactions, if present, would lead to a raising of the h.o.m.o. energy and an increase in the 'softness' of the ligand, which would be significant in complexation studies.

Table. Photoelectron spectroscopic data

Compound	Band maxima (eV)
(1) dme[a]	9.9, 11.7, 12.9
(2) diglyme[b]	9.8[c]
(3) triglyme[d]	9.8[c]
(4) 12-crown-4	9.3, 10.0, 11.4[c]
(5) 15-crown-5	9.6, 11.3[c]
(6) 18-crown-6[e]	9.7, 10.4[c]
(7) Cyclohexyl-14-crown-4	9.2[c]
(8) Benzo-14-crown-4	8.1, 9.8[c,f]
(9) Benzo-15-crown-5	8.0, 9.6, 10.7
(10) Dibenzo-18-crown-6	7.8, 8.7, 9.5[c]
(11) 'Furano-crown'	7.1, 7.5, 9.3, 10.8
(12) Kryptofix 21	8.4, 9.7, 11.3
(13) Kryptofix 22	8.4, 9.7, 11.3[c]
(14) Kryptofix 221	7.7, 9.3, 11.0, 12.3[c]
(15) Kryptofix 222[g]	7.8, 9.5, 11.3
(16) cyclam[h]	8.5, 11.2[c]
(17) Trimethylcyclam	8.0, 10.8[c]
(18) Tetramethylcyclam	8.0, 10.8
(19) Benzocyclam	8.1, 9.0, 9.6, 9.9[c]

[a] dme = 1,2-dimethoxyethane. [b] diglyme = 2,5,8-trioxanonane. [c] Merging of bands at higher energy. [d] triglyme = 2,5,8,11-tetraoxadodecane. [e] Example of systematic nomenclature: 18-crown-6 = 1,4,7,10,13,16-hexaoxacyclo-octadecane. [f] Contains overlapping components. [g] Example of systematic nomenclature: Kryptofix 222 = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8.]-hexacosane. [h] cyclam = 1,4,8,11-tetra-azacyclotetradecane.

Experimental

All compounds were purchased from commercial chemical suppliers, or were synthesised using procedures available in the chemical literature. Photoelectron spectra were measured on a modified Perkin-Elmer PS18 instrument.

Results and Discussion

Photoelectron data are summarised in the Table. The spectra of some of the compounds are shown in Figures 1—3.

Harada and co-workers[3] have previously reported briefly on the photoelectron spectra of some of the crown ethers, but not on any of the cryptates. Although our u.p.s. results on the crown ethers common to both studies are in substantial agreement with those of the earlier group, our approach to interpretation is different. While Harada and co-workers based their interpretations chiefly on CNDO/2 calculations, we have favoured using, in addition, the photoelectron spectra of model compounds as a guide. We feel that in general this is the best approach for the interpretation of photoelectron spectra, since inspection of the spectra of a family of compounds often highlights features that may be obscured by approximations or deviations from Koopmans' theorem implicit in the molecular orbital (m.o.) calculation. For example, the CNDO/2 method used by Harada and co-workers often destabilizes σ type orbitals relative to π.

Interaction of the Heteroatom Lone-pairs in Open-chain and Unsubstituted Cyclic Polyethers.—Every oxygen atom in polyethers can be considered as having two lone-pairs. For u.p.s. studies, it is appropriate to consider the two lone-pairs as being energetically non-equivalent. The higher energy (lower i.p.) lone-pair $n_O(\pi)$ corresponds to an oxygen 2*p* orbital aligned parallel to a plane defined by the oxygen atom and the two carbon atoms formally bonded to it, while the lower energy lone pair $n_O(\sigma)$ is in this C–O–C plane, and contains some oxygen 2*s* character. These simplified descriptions, while not strictly valid for a proper m.o. description of a large molecule containing several oxygen atoms and other functionalities, are nevertheless useful since these π and σ lone-pairs can be viewed as localized 'basis' orbitals whose

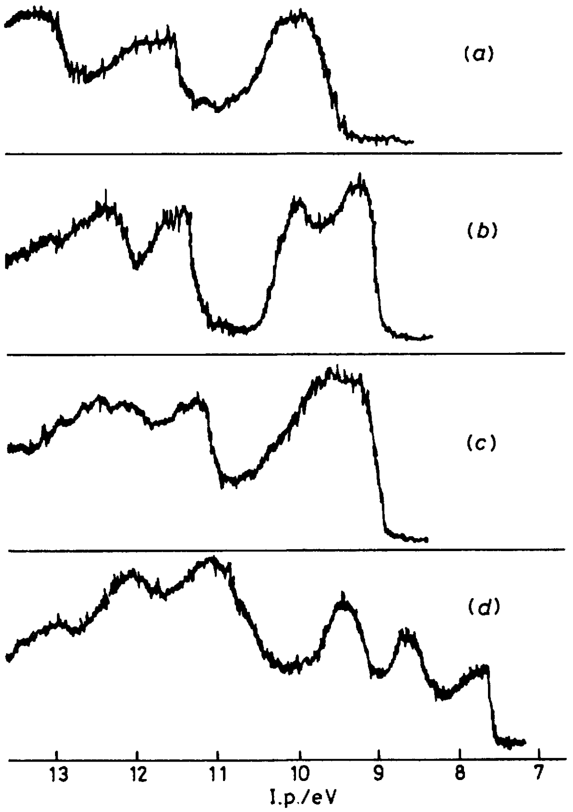
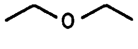


Figure 1. Ultraviolet photoelectron spectra (21.2 eV) of (*a*) 1,2-dimethoxyethane, (*b*) 12-crown-4, (*c*) 18-crown-6, and (*d*) dibenzo-18-crown-6

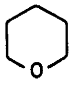
interaction with other localized orbitals leads to a valid m.o. description.

In an ideal case, interactions of the heteroatom lone-pairs would be revealed by multiple bands in the oxygen lone-pair region. The spectra of polyethers do not, however, conform to this ideal. Rather, a broad band, sometimes with shoulders apparent, is observed in the region expected for the lone-pairs. Thus, evidence for interactions must come from comparisons with photoelectron spectra of suitable models. In particular, appreciable interactions would result in an ionization potential (i.p.) lower than that for a model compound, and a photoelectron band broader than that of a model compound.

Several compounds were considered as models. Vertical i.p. data (eV) for the compounds below are: (I), 9.70; (II), 9.46; (III), 9.43 and 10.65.[4–6] For most simple mono-oxa compounds such as diethyl ether and tetrahydropyran, the lowest i.p., in the region 9—10 eV, corresponds to the $n_0(\pi)$ lone-pair, and the second i.p., close to 11 eV, corresponds to a molecular orbital with appreciable $n_0(\sigma)$ lone-pair character. In 1,4-dioxane, which in a sense is the simplest of the crown ethers (' 6-crown-2 '), the situation is more complex. There are two $n_0(\pi)$ and two $n_0(\sigma)$ lone-pairs. The in-phase combinations, $n_+(\pi)$ and $n_+(\sigma)$, but not the out-of-phase combinations of these orbitals can interact with the ideally oriented central C–C σ-bond orbitals to give a strong through-bond coupling.[6] Thus, for 1,4-dioxane,[6a] the first band of the photoelectron spectrum is safely assigned to the through-bond destabilized $n_+(\pi)$ combination, $n_0(\pi_+ - \sigma_{cc})$. The second and third bands, with i.p.s of *ca.* 10.7 and 11.3 eV, correspond to the similarly destabilized $n_+(\sigma)$ combination, $n_0(\sigma_+ - \sigma_{cc})$, and to the $n_-(\pi)$ combination, unaffected by through-bond coupling with the σ_{cc} orbital. The relative ordering is uncertain. It can be noted, however, that the unaffected $n_-(\pi)$ i.p. is certainly much higher than the $n_0(\pi)$ i.p. of tetrahydropyran. Some of this increase is expected in terms of the substitution of the second electronegative oxygen atom into the molecule in place of the $-CH_2-$ group, but a considerable part must be due to stabilization by way of through-bond interaction with C–C antibonding relay orbitals. In fact, it appears that the amount of destabilization of the h.o.m.o. due to through-bond interaction with relay C–C bonding orbitals may be of about the same order as the stabilization of the deeper n_0 orbital *via* through-bond interaction mediated by the orbitals.



(I)



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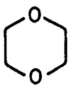
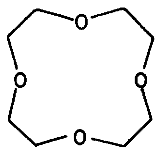


(III)

$CH_3{-}O{-}[CH_2{-}CH_2{-}O]_n{-}CH_3$

(1) *n* = 1
(2) *n* = 2
(3) *n* = 3



(4)

In common with 1,4-dioxane, the open-chain polyethers (1)—(3) and the crown ethers (4)—(6) contain the $-O-CH_2-CH_2-O-$ unit. Despite obvious conformational and other differences 1,4-dioxane serves as an appealing model in view of this fundamental similarity. Basically, if there are no lone-pair/lone-pair interactions, through-bond or through-space, it is expected that for the polyethers and crowns a $n_0(\pi)$ band centred near 10 eV, *i.e.* higher than that of tetrahydropyran, but lower than that of the $n_-(\pi)$ band of 1,4-dioxane, which as just noted, is probably stabilized significantly by through-bond interactions *via* relay orbitals. Through-bond or through-space interactions would be expected to produce a split of the $n_0(\pi)$ lone-pairs about this 10 eV region.

The open-chain polyethers (1)—(3) all show a broad first i.p. band, with a maximum at 9.9 eV. However, the first band in the spectrum of the polyether (4) has its maximum close to 9.3 eV. There is also a pronounced shoulder at 10.0 eV. Apparently, a rather significant interaction among the lone-pairs has taken place. In their earlier work, Harada and co-workers had attempted to correlate photoelectron peaks with particular m.o.s resulting from the combination of the oxygen lone-pairs. They based their conclusions on CNDO calculations. These calculations suggest that orbital interactions lead to a clustering of m.o.s resulting from oxygen 2*p* interactions into two groups, one with i.p. between 9 and 10 eV, and one in the region 11—13 eV. Thus, following this line of argument, the band at 11.4 eV in the spectrum of (4) would have to be assigned to the higher cluster of interacted oxygen 2*p* orbitals.

The spectra of compounds (5) and (6) are somewhat similar to that of (4), but the lowest i.p. band contains no clear shoulder, and the band maxima are at slightly higher i.p., close to 9.7 eV in both cases. However, with the loss of the clear shoulder seen in the spectrum of (4), the photoelectron band maximum will simply reveal the mean of the interacted oxygen lone-pair orbitals, which should be close to 9.9 eV,

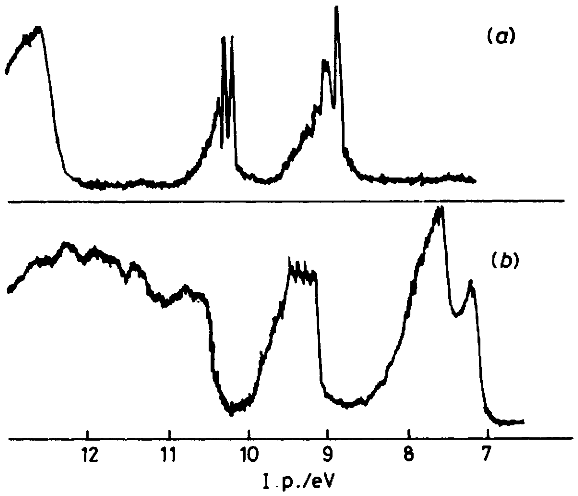
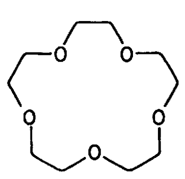


Figure 2. Ultraviolet photoelectron spectra (21.2 eV) of (*a*) furan and (*b*) ' furano-crown ' (11)



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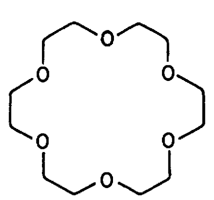

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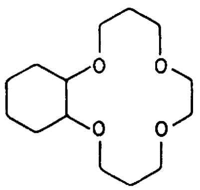

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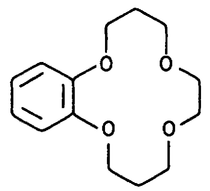

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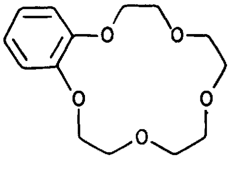

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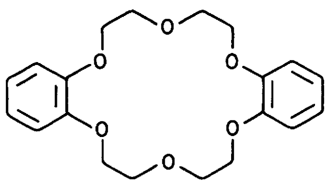


(10)

as discussed above. Since the lowest i.p. bands for all the crown ethers are approximately equally broad, it is probable that a similar degree of interaction is present in every case.

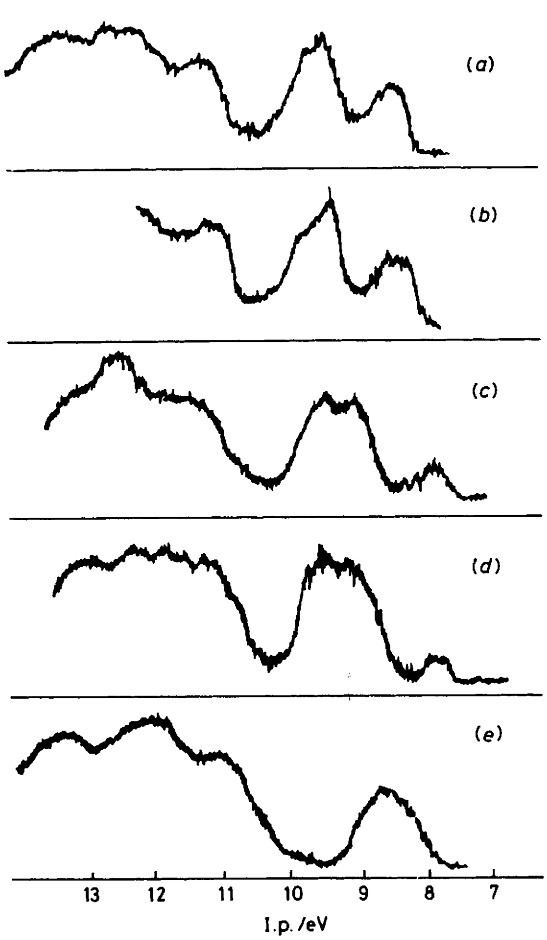
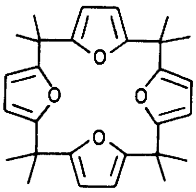


Figure 3. Ultraviolet photoelectron spectra (21.2 eV) of a number of the kryptofixes (*a*) (12), (*b*) (13), (*c*) (14), (*d*) (15), and (*e*) cyclam (16)

Substituted Crown Ethers.—The compounds (7)—(10) were examined. The photoelectron spectrum and hence the basic orbital structure of the cyclohexyl-substituted polyether (7) is quite similar to that of the crown ethers referred to in the previous section. A slightly lower first i.p. is recorded, reflecting the greater degree of alkyl substitution, but no other major differences are noticeable. By contrast, the benzo-substituted crown ethers (8)—(10) have significantly different photoelectron spectra than their unsubstituted parents. This finding was anticipated since through-space interactions of matched-symmetry benzenoid π orbitals and oxygen lone-pair orbitals can occur. Since these orbital types have similar ' pre-interaction ' energies, this effect is expected to be significant. Thus the h.o.m.o. of the benzo-substituted crown ethers should reflect appreciable mixing of benzenoid π and oxygen lone-pair character. This mixing also results in an appreciably lower i.p. for the benzo-substituted crown ethers. An INDO calculation on compound (9) confirmed this mixing in the h.o.m.o. of this compound. This calculation also suggested that the second highest orbital in this compound resides mainly on oxygen atoms not adjacent to the benzene rings, while the third orbital is partly benzenoid and partly ' adjacent oxygen ' in character. The photoelectron spectra of the monobenzo-substituted crowns, however, contain strongly overlapping bands in the region to higher i.p. of the h.o.m.o., and definitive assignments or correlations with m.o. calculations are essentially meaningless. Better separation of individual photoelectron bands is observed in the spectrum of compound (10). Three relatively narrow and quite well resolved bands are seen in the region between 7 and 10 eV, with band maxima at *ca.* 7.8, 8.7, and 9.5 eV. The relative intensities of these bands are not the same: the band at 8.7 eV is roughly twice the area of that at 7.8 eV, and the band at 9.5 eV is even larger. Again, it is inappropriate to make definitive assignments.



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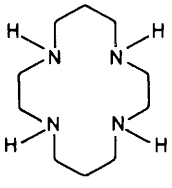

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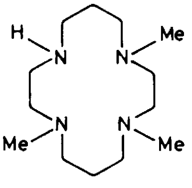

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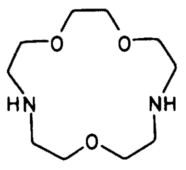

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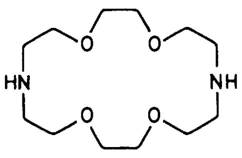

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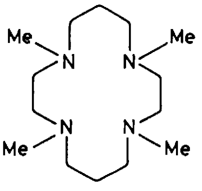

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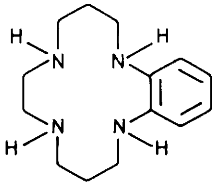

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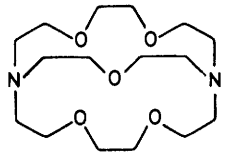

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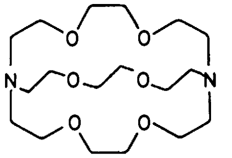

(15)

1,1,7,7,13,13,19,19-*Octamethyl*[1.1.1.1](2,5)*furanophan*.—The spectrum of this furano-crown compound is shown in Figure 2. It is appropriate to compare this spectrum with that of furan itself, also shown in Figure 2. The first three bands in the spectrum of furan relate to the three occupied π molecular orbitals of this molecule.[7] The vertical i.p.s characteristic of these three orbitals are 8.89, 10.30, and 12.63 eV. This same basic pattern of three bands would be expected for (11) if no interactions among the furan systems occurred. The spectrum of (11), however, indicates that a fairly major interaction must have occurred. The most striking feature in the spectrum of (11), as compared to the spectrum of furan, is the splitting into two major components of the first band. The first i.p. derived from the spectrum is exceptionally low, near 7 eV (nearly 2 eV lower than that of furan itself). It is quite remarkable that strong interactions among the ' individual ' furan h.o.m.o.s are seen when it is considered that this h.o.m.o. has a node at the oxygen atom of the furan ring. This means that the interactions can not be simply attributed to the proximity of the oxygen atoms around the periphery of the cavity in (11). A through-bond coupling of the furan π systems may be involved or the oxygens may be pointed away from the cavity.* A further study of this type of interaction would be useful.

Kryptofixes.—The kryptofixes (12)—(15) are analogues of the crown ethers in which two non-adjacent oxygen atoms have been replaced by nitrogen functionalities. The presence of a secondary or tertiary amine functionality requires that different model compounds be used than those used for the crown ethers. U.p.s. data on diethylamine (i.p. = 8.63 eV)[8] and morpholine (i.p. = 8.95 eV)[9] were accordingly used to model the secondary amine functionality.

The presence of the electronegative oxygen atom γ to the secondary nitrogen atom evidently raises the nitrogen lone-pair i.p. by between 0.3 and 0.4 eV. Turning now to the tertiary amine functionality, we note that triethylamine[10] and 1-azabicyclo[2.2.2]octane[11] have been shown to have i.p.s in the range 8.0—8.1 eV (8.07 and 8.02 eV respectively). The presence of an electronegative atom γ to the nitrogen can be expected to raise this value. There has been no u.p.s. study of a compound containing the $\gt N{-}CH_2{-}CH_2{-}O{-}$ unit, however 1,4-diazabicyclo[2.2.2]octane has been studied. In this compound there is a γ-nitrogen atom in place of a γ-oxygen atom. Strong through-bond interaction of the two nitrogen lone-pairs leads to two nitrogen lone-pair bands (i.p. = 7.52 and 9.65 eV) in the u.p.s. spectrum.[11] The mean, about 8.6 eV, is approximately 0.5 eV greater than the i.p. of triethylamine or of 1-azabicyclo[2.2.2]octane.

The spectra of the kryptofixes can now be examined with these numbers in mind. The most striking feature in the photoelectron spectra of the kryptofixes (Figure 3) is the presence of two distinct low-i.p. bands. The first of these bands is seen to decrease in intensity as the ratio of oxygen to nitrogen in the cryptands increases. Thus the first bands in the spectra appear to be interpretable in terms of orbitals largely associated with nitrogen atoms, and the second band in terms of orbitals associated mainly with oxygen atoms. The first (vertical) i.p.s for the compounds are consistently lower than those of the model compounds referred to above, which may mean that interactions among the various heteroatoms are taking place. For example, the first i.p. of kryptofix 222, compound (15) (7.80 eV), is only slightly higher than that of 1,4-diazabicyclo[2.2.2]octane (see above) where a very large through-bond interaction shifted the first nitrogen lone-pair peak to a very low ionization potential.

Cyclams.—The photoelectron spectra of cyclam (16), trimethylcyclam (17), and tetramethylcyclam (18) all show one distinct relatively broad lowest i.p. band, assigned to an orbital of mainly nitrogen character, and a group of overlapping bands at higher i.p. The first band leads to a vertical i.p. of *ca.* 8.5 eV for the parent compound. This is several tenths of an electronvolt lower than the vertical first ionization potential of diethylamine, and in this regard the situation is very similar to that of the cryptands discussed in the previous section. Methyl substitution on the nitrogen atoms has the expected effect of shifting the first band to still lower i.p.

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* Thus allowing through-space interactions of the C–C π components of the furan m.o.s.

Nature of the Heteroatom Lone-pair Interactions.—An important question concerns the extent to which through-bond interactions affect the energy levels of the macrocyclic substances discussed here. The cavity sizes in the crown ethers are as follows: 1.2—1.5 Å for (4), 1.7—2.2 Å for (5), and 2.6—3.2 Å for (6).[12]

It would be expected that through-space interactions would diminish as the size of the macrocyclic ring increases. However the photoelectron spectra show that large interactions are present even in compound (6). This is evidence for considerable through-bond interactions. The photoelectron spectrum of the furano-crown compound (11) is also strongly suggestive of appreciable through-bond interactions. As pointed out above, the π h.o.m.o. orbitals of individual furan rings have nodes at the oxygen atoms which are to be found around the periphery of the cavity. These orbitals have electron density only in the vicinity of the carbon atoms of the furan rings, and these would seem to be too far apart for efficient through-space couplings. In any event, all the macrocyclic compounds have lower i.p.s, sometimes appreciably lower, than those of corresponding open-chain or model compounds. This can be expected to play a role in the chemistry, particularly the co-ordination chemistry, of these compounds.

Conclusions and Applications to Complexation Studies.—There are appreciable interactions among the heteroatom lone-pair orbitals in crown ethers and cryptands. It seems likely that through-bond effects play an important role. The result of these interactions is to produce a relatively high energy h.o.m.o. for the macrocyclic compound, compared to corresponding open-chain compounds. This should make the macrocyclic compounds softer ligands than would have been anticipated if no orbital interactions had occurred. Although many factors other than softness are important in the complexation properties of crown ethers, it should certainly be taken into consideration.

The relative softness of crown compounds may, for example, be a significant factor in the pronounced preference of hard actinide metal ions for oxygen sites in water and nitrate ion rather than in crowns.[13] There is also a connection in some cases between stability constants [14] of complexes of crown ethers with ionization potential of the ligand, but other factors such as cavity size and flexibility of the ligand prevent any general correlation being given between the two sets of data.

Increased softness may also contribute to the stoicheiometries of crown complexes. For example, 1 : 2 complexes of cations smaller than the macrocycle cavity are known, *e.g.* Mg^{2+} forms a sandwich complex with compound (9).[15] It is not unreasonable that a relatively hard ion such as Mg^{2+} would require a larger number of co-ordination sites to achieve stability with a softer ligand. On the other hand, binuclear complexes are observed in cases where the ligand is a very large macrocycle and the cation is relatively polarizable.

A final point can be made concerning binuclear complexes. The fact that appreciable delocalization of electron density takes place around the periphery of the macrocycle should be taken into consideration in studies of the redox chemistry of such binuclear complexes. Particularly in the cases where through-bond effects are present, there may be an unexpected coupling of the redox centres in these compounds. A recent publication has noted for example that through-bond interactions lead to the observation of an intervalence charge-transfer transition in Ru^{II}/Ru^{III} binuclear complexes where the ligand is completely saturated and the ligating atoms are almost 18 Å apart.[16] Photoelectron spectroscopy is clearly a most useful tool for probing these through-bond effects, and we are currently using this technique to explore the types of molecular structure which lend themselves to this effect.

Acknowledgements

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References

1 L. A. Paquette, D. C. Liotta, and A. D. Baker, *Tetrahedron Lett.*, 1976, 2681.
2 G. H. Armen, C. Braunstein, M. I. Weinstein, and A. D. Baker, *Tetrahedron Lett.*, 1979, 4119.
3 M. Kajitani, A. Sugimori, N. Sato, K. Seki, H. Inokuchi, and Y. Harada, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 2199.
4 W. C. Tam and C. E. Brion, *J. Electron Spectrosc. Relat. Phenom.*, 1974, **3**, 263.
5 A. Planckacrt, J. Doucet, and C. Sandorfy, *J. Chem. Phys.*, 1974, **60**, 4846.
6 (*a*) D. A. Sweigert and D. W. Turner, *J. Am. Chem. Soc.*, 1972, **94**, 5599; (*b*) D. S. C. Yee, A. Hamnett, and C. E. Brion, *J. Electron Spectrosc. Relat. Phenom.*, 1976, **8**, 291.
7 A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Anal. Chem.*, 1970, **42**, 1064.
8 D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, 1975, **97**, 4137.
9 A. D. Baker, unpublished work.
10 D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, 1975, **97**, 4136.
11 P. Bischof, J. Hashmall, E. Heilbronner, and V. Hornung, *Tetrahedron Lett.*, 1969, **40**, 25.
12 C. J. Pedersen, in ' Synthetic Multidentate Macrocyclic Compounds,' eds. R. M. Izatt and J. J. Christiensen, Academic Press, New York, 1978, p. 25.
13 P. G. Eller and R. A. Penneman, *Inorg. Chem.*, 1976, **15**, 2439.
14 R. M. Izatt, *J. Am. Chem. Soc.*, 1976, **98**, 7620.
15 C. J. Pederen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, 1972, **16**, 11; N. S. Poonia, B. P. Yadav, V. W. Bhagwat, V. Naik, and H. Manohar, *Inorg. Nucl. Chem. Lett.*, 1977, **13**, 119.
16 C. A. Stein, N. A. Lewis, and G. Seitz, *J. Am. Chem. Soc.*, 1982, **104**, 2596.

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