Molecular Complexation of Arenediazonium and Benzoyl Cations by Macrocyclic Polyethers

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Summary Macrocyclic polyethers (crown ethers) of the proper dimensions solubilize in non-polar media arenediazonium tetrafluoroborate and benzoyl hexafluorophosphate salts by molecular complexation.

Examination of molecular models (CPK) of [18]-crown-6 cyclic polyether (**1**)[1] and of arenediazonium or arylacylonium cations suggested the crown might complex the rod-like cations by insertion of their heteroatoms into the hole of the macrocycle [see (**2**)]. We have examined the ability of crowns to solubilize arenediazonium and arylacylonium salts in non-polar media, and the ability of the solubilized salt to change the crown's ^1H n.m.r. spectra. Cation–oxygen interactions between crown ethers and metal or alkylammonium salts are strong enough to solubilize these salts in non-polar media.[2]

A solution of binaphtho[20]-crown-6 cyclic ether[2b] (**3a**) in $CDCl_3$ gave a n.m.r. spectrum (100 MHz) whose four $ArOCH_2$ protons provided an eleven-line multiplet centred at 4·06 p.p.m. This solution dissolved 0·9 mol of solid *p*-toluenediazonium tetrafluoroborate[3] (**4**) per mol of crown (n.m.r.). The four $ArOCH_2$ protons of the new solution appeared as two multiplets, one of six lines at 3·89 p.p.m. and one of seven lines at 4·21 p.p.m. Similarly, (**1**) solubilized (**4**) (mol salt/mol crown $\simeq$ 0·8), slightly shifting the methylene singlet of (**1**) from 3·62 to 3·58 p.p.m. Similarly (**3a**) solubilized *p*-hydrogen-, *p*-methoxy-, *p*-chloro-, and *p*-nitro-benzenediazonium tetrafluoroborate salts,[3] in salt to crown mol ratios of 0·3, 0·9, 0·8, and 0·9, respectively. The open-chain analogue of (**3a**), 2,2′-bis-(1,3,6-trioxo-octyl)-1,1′-binaphthyl†‡ (m.p. 55·5—56·5°) failed to solubilize these salts under the same conditions.

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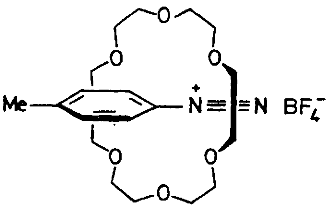
† Carbon and hydrogen analyses were within 0·20% of theory.

‡ ^1H n.m.r. and i.r. spectra were as expected.

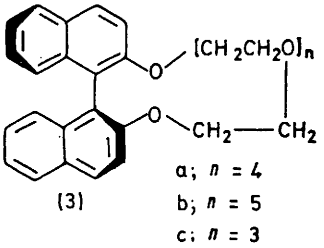
We conclude that the solubilization and ^{1}H n.m.r. shifts are caused by complexation, the linear $\mathrm{Ar{-}\overset{+}{N}{\equiv}N}$ inserting into the hole of the crown with its oxygen atoms turned inward toward the positive charge as in (**2**). With the methylenes in gauche conformations,[4] the hole of CPK models of (**3a**) averages (different directions) ~2·8 Å in diameter, and that of (**1**), ~2·6 Å. The crowns' holes easily accommodate the diazonium groups, whose cylindrical diameter is ~2·4 Å (estimated from the *X*-ray contour map of benzenediazonium chloride).[5] The diameter of binaphtho[23]-crown-7 (**3b**) measured ~3·75 Å (average), and that of binaphtho[17]-crown-5, (**3c**), ~2·2 Å. Experimentally, (**3b**) complexed 0·6 mole of (**4**), and (**3c**) failed to complex any (**4**). Further, 3,4-dimethylbenzenediazonium tetrafluoroborate (m.p. 89·5—90·0°, decomp.)[4b] was complexed by (**3a**) (one-to-one) but the sterically hindered 2,6-isomer‡ (m.p. 80·0—80·5°, decomp.) was not complexed by (**3a**) or (**1**). These results were expected from CPK molecular model examinations.

Both oxygen basicity (aryl *vs.* alkyl attachment) and the character of the aryl groups influenced the crown's complexing ability. Thus (**4**) was complexed by dibenzo[18]-crown-6[6] (**5**) in $\mathrm{CDCl_3}$ (salt to crown mol ratio of 0·4), acetone [acetone-soluble (**4**) complexes essentially acetone-insoluble (**5**), *crown to salt* molar ratio of 0·23], and dimethyl sulphoxide (*crown to salt* molar ratio of 0·12). The analogue of (**5**), (±)-dibinaphtho[22] crown-6,[2c] did not complex (**4**) in chloroform, possibly for steric or lattice energy reasons. Interestingly, the complexes of (**3a**) exhibited π–π charge-transfer type colours (yellow to red) not observed in (**1**–**4**) complexes.

Attempts to form azoarene-crown rotaxanes[7] by treating the (**3a**–**4**) complex in dichloromethane with *NN*-dimethylaniline,[8] *p*-tolyl-lithium,[3b] *p*-tolylmagnesium bromide, [3b] or di-*p*-tolylzinc[9] in ether at 25° or −78° failed. Only non-encircled, conventional products were obtained. For example, essentially quantitative yields of 4-chloro-4′-*NN*-dimethylaminoazobenzene were obtained in dichloromethane solution at −78° with two equivalents of (**1**) present to solubilize the *p*-chlorobenzenediazonium tetrafluoroborate. The solubilization rate of this salt by crown in dichloromethane was dramatically increased by lowering the temperature, a fact that suggests a large negative entropy for dissolution–complexation. Crown was readily recovered. Attempts to stabilize diphenylmethyldiazonium trifluoroacetate in $\mathrm{CDCl_3}$ with (**3a**) gave equivocal results. No complexation between (**3a**) and methyl isocyanide in $\mathrm{CDCl_3}$ was observed.



(2)



(3)

Benzoyl hexafluorophosphate (**6**) was solubilized in $\mathrm{CDCl_3}$ by both (**3a**) [mol (**6**)/mol (**3a**) = 0·5] and (**1**) [mol (**6**)/mol (**1**) = 0·25], and expected ^{1}H n.m.r. spectral changes were observed at 25° when (**3a**) became complexed. Benzoylation of the naphthalene rings of (**3a**) accompanied complexation. Complexation probably involves insertion of the linear $\mathrm{{-}\overset{+}{C}{=}O}$ group into the crown's hole, as with the $\mathrm{{-}\overset{+}{N}{\equiv}N}$ group. These results may be of synthetic use in reactions that involve arenediazonium or arylacylonium salts as reactants, and where homogeneity is desired. The crowns lipophilize the salts, and act as dispersing agents at a molecular level.

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