Molecular Complexes of Macrocyclic Polyethers with Fluoranil

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Fluoranil forms weak 1 : 1 molecular complexes with both benzene substituted and nonbenzenoid macrocyclic ethers. ^{19}FMR shifts have been used for the evaluation of association constants. The infrared and ^{1}HMR data of the complexes reveal relative orientations of the molecules in the complexes.

Little attention has been paid so far as to the ability of polyethers to form molecular complexes [1]. In view of their permselective conductance behaviour [2], it would be worthwhile to enquire whether the site of interaction of these polyethers with the membrane wall is governed by charge-transfer forces. It has been shown earlier [3] that hydrogen bonding and geometric factors govern the stabilisation forces in the molecular complexes of two polyethers. However, no information is available as to the nature of the binding sites and forces which govern the stability and structure of these complexes in solution.

We have examined here the ability of six polyethers (trivial names are used), 15-crown-5(I), 18-crown-6(II), 24-crown-8(III), benzo-15-crown-5(IV), dibenzo-18-crown-6(V) and dibenzo-30-crown-10(VI) to form molecular complexes with 2,3,5,6-tetrafluoro-1,4-benzoquinone, fluoranil(Fl).

Addition of Fl to the CH_2Cl_2 solutions of the benzene substituted ethers causes a red colouration while no perceptible colour change is observed in the nonbenzenoid ethers. It was found that on progressive addition of ethers in $CDCl_3$ to Fl, the ^{19}F resonance of Fl shifts to down field indicating acceptor behaviour of Fl. These shifts were analysed graphically (Fig. 1) using published procedures [4]. The linearity of the plots suggests 1 : 1 complexation of ethers with Fl. The association constants, k and Δ_0, the chemical shift of the ^{19}F signal in the complex relative to that of pure Fl, were evaluated and given in Table 1 along with ν_{CT}, the charge-transfer absorption bands of the complexes.

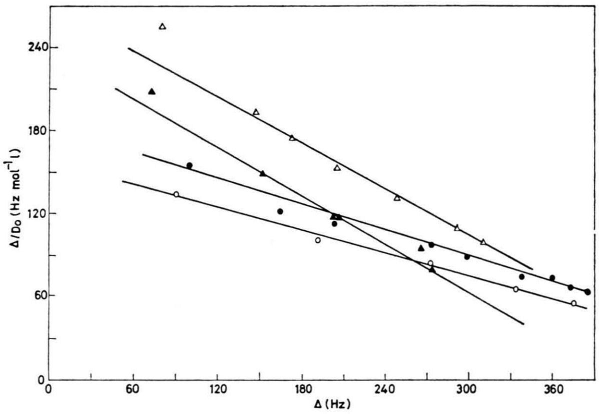

Fig. 1. Plot of Δ/D_0 versus △ for (a) ○-15-crown-5, (b) ●-18-crown-6, (c) △-24-crown-8 and (d) ▲-benzo-15-crown-5.

The magnitude of the association constants suggest low stability of these complexes. Limited comparison of the k values lead to the suggestion that among similar donors (I, II and III), the larger ring size favours higher stability and the enhanced stability in the (IV)-Fl complex is traced to the presence of the benzene ring in the system. The Δ_0 value, which is a measure of the amount of charge transferred, and the position of ν_{CT} in the complexes do not follow the donor strengths of the ethers as found in the *sym*trinitrobenzene complexes [5].

The infrared spectra of the 1 : 1 complexes (in solid state) of polyethers with Fl show only marginal changes in intensity and position of the frequencies of the component molecules. The two ν(C=O) and ν(C–F) of Fl occurring at 1705, 1685 and 1335 cm^{-1}, respectively, remain unchanged in the complexes while the ring breathing at 1000 cm^{-1} of Fl is lowered to 980 cm^{-1} in all the complexes except in (V). This suggests that the electronic effects of complexation are nonlocalised and the lowering is attributed to the postulation of alternate arrangement of acceptor (A) and donor (D) as –A–D–A–D– for the complexes. It is worthwhile to note the absence of the conformation sensitive band at 968 cm^{-1} of (IV) in the complex indicating *trans* configuration of the $O–CH_2–CH_2–O$ group [5]. In the (V) and (VI) complexes, the $–OCH_2–CH_2–O–$ group retains *gauche* configuration as that of the free ethers as shown by the presence of the 998 and 961 cm^{-1} bands, respectively.

The proton chemical shifts of ethers give some insight into the orientation of two molecules in the

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Donor	K l mol^{-1}	Δ_0 Hz	Concentration range	ν_{CT} cm^{-1}
(I) 15-crown-5	0.29	560	0.70 — 6.5 M	+
(II) 18-crown-6	0.30	592	0.60 — 6.0 M	+
(III) 24-crown-8	0.56	328	0.30 — 3.0 M	+
(IV) b-15-crown-5	0.62	410	0.34 — 3.5 M	20618
(V) db-18-crown-6	*			20533
(VI) db-30-crown-10	*			21276

Table 1. Measured properties of fluoranil complexes of macrocyclic polyethers.

* Inadequate solubility in $CDCl_3$.

\+ The charge transfer maxima lie beneath the absorption of fluoranil. Absorption maxima measured in CH_2Cl_2.

complexes. All the protons, aryl(Ar), Ar–O–CH_2 and CH_2–O–CH_2 of (V) and (VI) resonate at higher fields (2—8 Hz) when compared to the free ethers while a shift to lower field (8 Hz) of only the Ar protons is observed in the (IV) complex. The protons of the nonbenzenoid ethers are shifted to lower fields (2—8 Hz) in the complexes. On the basis of these observations, the logical choice for the structures of the (V) and (VI) complexes is to place Fl over the cavity of these ethers with oxygen atoms projecting inwards such that the protons experience shielding effects due to proximity of Fl. It is probable that in the (IV) complex, the Fl is located predominantly over the benzene ring of (IV) away from the diamagnetic shielding zone, similar to that of the *sym*trinitrobenzene system [5]. The deshielding effect experienced by the nonbenzenoid ether protons indicates an alteration of the electron density in the vicinity of oxygen atoms and it is likely that Fl is situated over the oxygen atoms of the ethers.

The Fl in the complexes behaves as π (aromatic) acceptor though it contains two potential carbonyl sites. The lone pair electrons of the oxygen atoms and the aryl groups of the ethers are the possible donor sites. The nonbenzeneoid complexes can be viewed as n-π type though the possibility of juxtaposed oxygen lone pair electrons forming a π system cannot be ruled out. The benzene substituted ether complexes are essentially of the π-π type. It is known that a biological membrane offers a variety of acceptor sites and it is tempting to suggest that the preferential location of these ethers on the membrane is governed by charge transfer forces.

Experimental

All the NMR measurements were carried out on a Varian XL 100 FT instrument using $CDCl_3$ as solvent at ambient temperature 31.6°. The ^{19}F and ^1H spectra were recorded at operating frequencies of 94 and 100 MHz, respectively. The ^{19}F and ^1H shifts (accuracy ± 0.1 Hz) were measured using internal ^2H lock and TMS as internal standard, respectively. The preparation of the ethers, purification of the solvents and spectrometers used are essentially the same as described elsewhere [5]. Fluoranil (Aldrich Chemicals, U.S.A.) was sublimed in *vacuo*, mp 177°.

[1] D. J. Cram and J. M. Cram, Science **183**, 803 (1974).

[2] G. Szabo, G. Eisenman, R. Laprade, S. M. Ciani, and S. Krasne, Membranes, **II**, 179 (1973).

[3] I. Goldberg, Acta Cryst. **B31**, 754 (1975).

[4] R. Foster and C. A. Fyfe, Trans. Faraday Soc. **61**, 1626 (1965).

[5] Y. Jayathirtha and V. Krishnan, Proc. Indian Acad. Sci. (in press).