Cation Complexing Photochromic Materials involving Bisanthracenes linked by a Polyether Chain. Preparation of a Crown-ether by Photocycloisomerization

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Summary The first photochemically generated, 'cation-locked' crown-ether is reported.

X-RAY structure analysis has shown that, in contrast to the planar zig-zag arrangement of a polymethylene chain, a polyethylene oxide chain has a helical structure[1] in the crystalline state. It has also been shown experimentally[2] and by calculation[2,3] that, in organic solvents, the lowest energy structure of the polyethylene oxide resembles approximately the helical conformation occurring in the crystal. Also, in the cyclo-oligomerization of ethylene oxide,[4] the growing chain tends to adopt a helical shape thus facilitating the formation of crown-ethers.[5] The latter are known to be cation complexing agents and they are becoming increasingly important in organic chemistry.[6] Nevertheless, to our knowledge, no photochemical synthesis of a crown-ether has been reported. We anticipated that the conformational properties of a polyoxyethylene chain linking two anthracene molecules would provide an easy way to generate complexing agents by intramolecular photoaddition.

We thus prepared† the bisanthracene (I) having four oxygen atoms in the chain and, for comparison, the 1,10-bis-(9-anthryl)decane (II). U.v. irradiation of (II) in ether or benzene under preparative conditions only leads to recovered starting materials. The poor photoreactivity of (II) was confirmed by determination of the quantum yield of cycloisomerization in degassed benzene (Table). In contrast,

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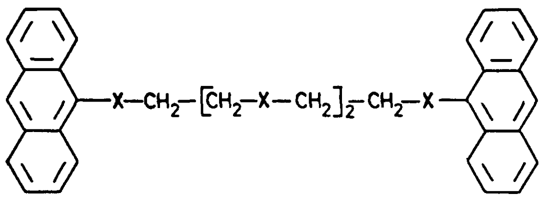
† (I) (m.p. 141—142 °C), (II) (m.p. 155—156 °C) and (III) gave satisfactory elemental analyses and spectroscopic data.

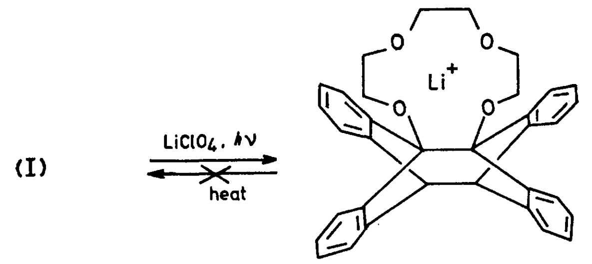
TABLE

	ϕ_C[a]		ϕ_C[a] (LiClO$_4$)		ϕ_F[b]	ϕ_F[b] (LiClO$_4$)	
	Benzene	Ether	Benzene	Ether	Benzene	Benzene	k_{diss}/s^{-1} [c]
(I)	0·32	0·27	0·29	0·29	0·14	0·15	4×10^{-3}
(II)	$\leqslant 10^{-4}$	—	—	—	0·75	—	—

[a] ϕ_C quantum yield of photocycloisomerization in degassed solvent (freeze–thaw–pump technique). [b] ϕ_F fluorescence quantum yield (ref. quinine sulphate). Concentration = *ca.* 3×10^{-5} M. [c] k_{diss}. rate constant of disappearance of the photocycloisomer of (I) in the absence of cation. All measurements were made at 25 °C.



(I) X = O
(II) X = CH$_2$



(III)

(I) photocycloisomerizes with a high quantum yield in benzene or ether but the photocycloisomer is not thermally stable and rapidly reverts to (I) ($t_{\frac{1}{2}}$ *ca.* 3 min). The striking difference between the photochemical behaviour of (I) and (II) is reflected in the fluorescence quantum yields (Table).

In the presence of a lithium salt (LiClO$_4$) used in slight excess (2—5 equiv.) irradiation of (I) gives the photocycloisomer (III)† with a similar quantum yield (Table), which is then 'cation locked;' it is thermally stable up to 206—210 °C and then decomposes with charring. Easy dissociation occurs by shaking it in a polar solvent such as acetonitrile which solvates the cation. The complex (III) is a particular example of a substituted 12-crown-4. That there is no cation effect on the yield of the intramolecular photoaddition is not surprising if we consider known chain conformations.[1,4] A modification of the photoreactivity by the cations is to be expected for longer chains. The present results will have far-reaching effects in bichromophore photochemistry[7] and in the study of chain dynamics.[8]

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