Photophysical and Photochemical Studies of Cyclophanes with Unsaturated Bridges

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Fluorescence spectra and quantum yields have been measured for the series of cyclophanes with unsaturated bridges, compounds *1—8*. The emission spectra are characterised by large shifts, interpreted as being due to increased planarity in the excited state. Photocyclisation of the cyclophanes to polycondensed aromatics is discussed, and the free-valence indices at the reactive positions in the excited states have been calculated.

Cyclic hydrocarbons with large conjugated perimeters such as the annulenes and the bridged annulenes have been extensively studied.[1-3] Recently, annulenes with aromatic rings built into the perimeter, *i.e.* unsaturated cyclophanes, have become readily available *via* multiple Wittig reactions.[4-7] The neutral cyclophanes can be regarded as normal aromatic compounds with no significant contributions from the large conjugated perimeter system. However, upon electrochemical reduction the unsaturated cyclophanes behave differently depending on the size of the perimeter. The cyclophanes with formally 4N π-electrons around the periphery give relatively stable dianions by a reversible two-electron process whereas those with 4N+2 perimeters are reduced to unstable species. The stable dianions (4N+2 perimeters) show large diatropic ring current effects equivalent to those of 4N+2 annulenes.[8-10] Simple Hückel calculations have been employed successfully to describe the delocalisation of the two extra electrons in the dianions,[11] the electrons entering a slightly antibonding, delocalized orbital. The calculations assume fairly planar π-systems in the

dianions, an assumption which seems to be valid. Thus, the reduction is accompanied by a considerable geometrical change (flattening of the π-system) as well as by an increased barrier to rotation of the benzene rings around the adjacent single bonds.
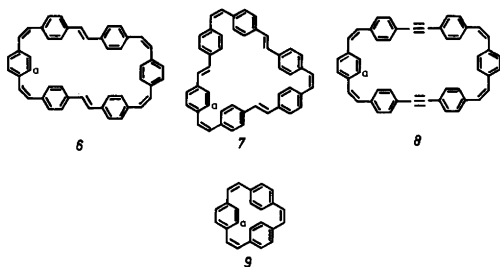
Within the Hückel approximation there is a formal similarity between the dianion and the first excited state (S_1), as the bond orders are the same in both states, thus implying similar geometries. To test this hypothesis we have investigated some photophysical and photochemical properties of the unsaturated cyclophanes.

RESULTS AND DISCUSSION

Fluorescence. The parent cyclophane for this series, [2$_4$]paracyclophanetetraene, *1*, is very stable towards irradiation, and no significant fluorescence emission is observed. If two of the benzene rings are exchanged for 2,6-naphthalene units as in *2*, a weak fluorescence is observed, while in *3*, with four 2,6-naphthalene units, the fluorescence is quite strong and shows a considerable shift (10 000 cm^{-1}).

1   *2*   *3*

4   *5*
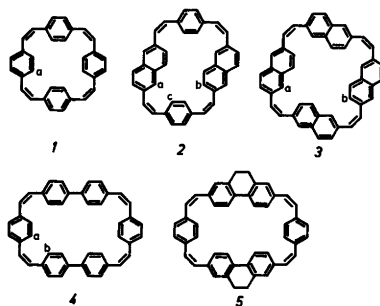
The general behaviour of the biphenyl cyclophanes, compounds 4 and 5, is similar with one main absorption band at 312 and 336 nm, respectively. The fluorescence band is broad and structureless for both compounds. Berlman has shown for biphenyl that substituents in the para position, particularly phenyl or vinyl groups, and bridging of the biphenyl unit produces a bathochromic shift as well as a higher fluorescence quantum yield.[12] Compound 5 exhibits this shift but not an increased quantum yield compared to 4. The fluorescence quantum yield of 5 is approximately the same as that of biphenyl (0.15), while that of 4 is higher, similar to that of 4-vinylbiphenyl (0.51). The large shift differences between absorption and emission maxima of 4 (12 000 cm^{-1}) and 5 (10 600 cm^{-1}) indicate that a certain degree of relaxation follows the excitation. The changes in calculated HMO bond orders in the excited state compared to the ground state suggest the possibility of a more planar quinoid excited state, an explanation similar to that put forward by Fischer et al. for stilbene compounds.[13]

Fig. 1. Excitation and emission spectra of 6 and 7.

The cyclophanes 6, 7 (Fig. 1) and 8 with 36 π-electron perimeters also show broad and unstructured emission spectra as well as large shifts of 9400, 10 000 and 10 400 cm^{-1}, respectively. Again, changes in bond orders upon excitation indicate extensive geometrical changes and relaxation processes, resulting in a more planar geometry of the excited state. The observed difference in quantum yields of fluorescence between 6 and 8 may result from different intersystem crossing efficiencies. Investigations of trans-stilbene[14] and tolan[15] have shown a more efficient intersystem crossing for trans-stilbene. Comparing compounds 6 and 7, one finds a difference in quantum yields of fluorescence (0.08 and 0.16 respectively). Inspection of models (CPK) reveals that 6 may attain a more
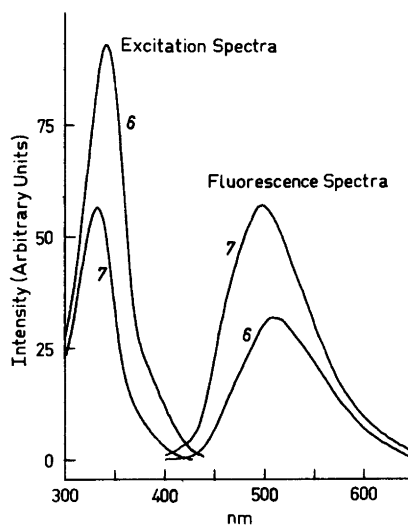
planar conformation with the two benzene rings of the respective trans-stilbene units in one plane. This is not possible for the corresponding three trans-stilbene units in 7. As a result, cyclophane 7 is somewhat more puckered, which also results in a hypsochromic shift of both the absorption and emission spectra as compared to 6.

^{1}H NMR investigations of the dianions of some of these cyclophanes show that they exhibit large diamagnetic ring currents, thus suggesting that the dianions must be relatively planar.[9–10] This is an important observation, since the HMO calculations infer that the reduction of the cyclophanes to their dianions has the same effect on the molecular geometry as the photo-excitation process. It therefore seems probable that photo-excitation triggers conformational changes resulting in a more planar, quinoid, first-excited state the geometry of which is reflected by the large Stokes' shifts observed.

Photocyclisation. Another interesting aspect of these paracyclophanes is their resistance to undergo the well-known intramolecular photocyclisation reaction to give phenanthrene derivatives. This lack of reactivity has also been observed for related heterosubstituted cyclophanes.[16] A frontier-orbital analysis of the paracyclophanes reveals this process to be allowed, yet it does not occur. The inertness of cis-1,2-diphenylethylene systems with additional anne-

Table 1. Spectroscopic properties of compounds *1–8*.

Compound	Absorption wavelength (nm)	Emission wavelength (nm)	Quantum yield of fluorescence
1	303	*a*	<0.001
2	320	535	0.01
3	337	507	0.30
4	312	499	0.55
5	336	523	0.20
6	345	510	0.09
7	332	498	0.17
8	325	490	0.24

a Impurity interference.

Table 2. Free-valence index and the sum of the free-valence indices between atoms of cyclisation of molecules *1–9* in the first excited state.

Compound	F_r^* value (site)	ΣF_r^* value (interaction)
1	0.453 (a)	0.906 (a–a')
2	0.524 (a)	0.966 (a–c)
	0.450 (b)	0.892 (b–c)
	0.442 (c)	
3	0.530 (a)	1.060 (a–a')
	0.450 (b)	0.980 (a–b)
		0.900 (b–b')
4	0.452 (a)	0.906 (a–b)
	0.454 (b)	
5	*a*	*a*
6	0.450 (a)	0.900 (a–a')
7	*b*	*b*
8	*b*	*b*
9	0.488 (a)	0.976 (a–a')

a Within the HMO approximation the same as for *4*. *b* Identical to *6*.

lated aromatic units towards irradiation has also been observed by Muszkat *et al.*, who interpreted this fact in terms of topological effects.[17] A thermochemical analysis of the conversion of *cis*-1,2-diphenylethylene to the corresponding 4a,4b-dihydrophenanthrene reveals that the ground state of the product is 188.1 kJ/mol higher than that of the reactant. Extension of the conjugated π-system of a *cis*-stilbene by proper substituents should eventually lower the energy of the first excited state to a point at which the energy becomes insufficient for the intramolecular cyclisation to dihydrophenanthrene to occur. The potential barrier of photocyclisation in *cis*-1,2-diphenylethylene is 12 kJ/mol.[18] Thus, the energy necessary for the cyclisation can be estimated to *ca.* 200 kJ/mol, which corresponds to the energy content of light of 600 nm. All of the paracyclophanes reported here have lowest singlet excited states of higher energy and should, therefore, undergo the photocyclisation. Blackburn and Timmons have shown that compounds which failed to photocyclize fell into two categories, those which readily undergo intersystem crossing and those which have insufficient electron availability at the reacting sites.[19] In determining the probability of photocyclisation we have used the HMO method to calculate the

value of the free-valence index (F_r^*) at each reacting atom and the sum of the free-valence indices (ΣF_r^*) between atoms of cyclisation of molecules in the first excited state. Both Blackburn et al.[19] and Laarhoven et al.[20] have found that, with few exceptions, only compounds with a ΣF_r^*-value greater than unity undergo cyclisation. The computed values of ΣF_r^* for compounds 1−8 are all below unity with one exception (Table 2). However, calculation of the ΣF_r^* value for [2.2.2.]paracyclophanetriene (9) also gives a value below unity (0.976) although this compound is known to photocyclize.[21−22] Inspection of models (CPK) as well as molecular mechanics calculations[23] shows that 9 cannot assume a planar geometry while cyclophanes 1−8 can adopt fairly planar conformations. Thus, the results from HMO calculations, assuming planar structures, must be evaluated with this fact in mind. HMO calculations on these cyclophanes show a certain degree of quinoid character even in the ground state, and this is confirmed for compound 1 by both molecular mechanics calculations[24] and X-ray analysis.[25] This quinoid character, which is accentuated in the first excited state, should represent resistance to an intramolecular photocyclisation since this reaction produces a dihydrophenanthrene intermediate of quinoid structure from the initial cis-stilbene system. Cyclophanes in which the conjugated periphery has been broken by saturation of one more of the bridging double bonds do in fact cyclize,[26] and this has been explained as being due to reduced steric interference in the more flexible, partly saturated compounds. Introduction of iodine substituents into the benzene rings of compounds 1 and 4 does lead to successful photocyclisation,[27] but this reaction is a radical type process and very different from the conrotatory concerted one discussed earlier.

cis−trans isomerisation. Photo-induced isomerisation is usually a facile process in open chain unsaturated compounds but is often hindered in more rigid cyclic olefins. cis−trans isomerisations occur upon irradiation of a number of cyclophanes of the general type discussed here when the isomers are relatively unstrained. For the more rigid cyclophanes 1−5 and 8 no isomerisation has been observed although isomers with one trans double bond seem to be only moderately strained from inspection of molecular models. The less rigid isomers of [2₆]paracyclophanehexaene, compounds 6 and 7, undergo a photoinduced interconversion upon prolonged irradiation.[28] Apparently, the photo-isomerisation is not a facile process in the unsaturated cyclophanes with a conjugated perimeter.

EXPERIMENTAL

Compounds 1,[4] 2,[6] 3,[6] 4,[4] 5,[29] 6,[7] 7,[28] and 8[7] were available from previous synthesis. UV spectra were measured on a Cary 210 recording spectrometer. Fluorescence spectra (corrected) were recorded on a Aminco SPF-500 and a Hitachi-Perkin-Elmer MPF-4 instrument with corrected spectra attachment. Fluorescence quantum yields were obtained using acenaphthalene as reference. Solvents used were spectrograde. The excitation spectra were in all cases identical with the corresponding absorption spectra. Photocyclisations and photoisomerisations were performed with a Rayonet reactor (RPR-100) equipped with various lowpressure mercury lamps having emission wavelength maxima at 254, 300 and 350 nm, respectively. Air was not excluded. The photoexperiments were carried out using a standard quartz vessel or quartz NMR tube with cyclohexane or benzene as solvent.

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