The Effect of Neighbouring Cyclopropyl Groups on the Luminescence of Aromatic Molecules

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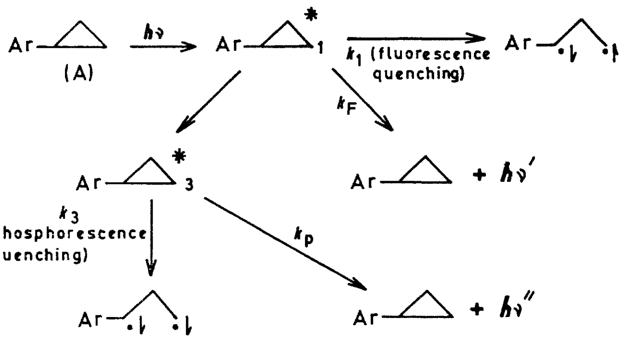
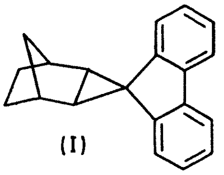
Summary The luminescence of benzenoid and naphthalenic compounds is quenched by neighbouring cyclopropyl groups.

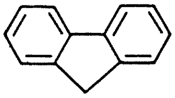
THE fluorescence yield of (I) ($\phi_F = 0{\cdot}005$) is low relative to that of (II) ($\phi_F = 0{\cdot}6$).[1] We report the effect of neighbouring cyclopropyl groups on the luminescence of some aromatic compounds, and show that introduction of a cyclopropyl group near a chromophore which absorbs in the near-u.v. region can result in both fluorescence- and phosphorescence-quenching. The degree of quenching is shown to be dependent on temperature and on the energy and lifetime of the emitting state. The compounds studied will be discussed in pairs; the fluorescence and phosphorescence yields (ϕ_F and ϕ_P) of the cyclopropane derivative being compared to those of its open-chain analogue within the framework of the following scheme.†

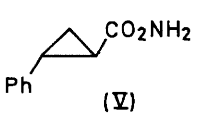


The phosphorescence yield (ϕ_P) for phenylcyclopropane[4] in EPA‡ or isopentane glass at 77°K is *ca.* 50 times less than ϕ_P for n-propylbenzene (IV). Under these conditions no large differences in their respective fluorescence yields (ϕ_F) were observed. At room temperature, in isopentane, ϕ_F for (III) is less than a factor of two lower than ϕ_F for (IV). The 77°K data suggest that the rate constant for ring-opening in the triplet state of (III) (k_3) is large compared to k_P while k_1 is insignificant relative to k_F (*ca.* 10^7 sec.$^{-1}$).[5] Although a slight decrease in ϕ_F for (III) relative to (IV) was observed at room temperature it would be presumptuous to assign this reduction to competitive ring-opening.

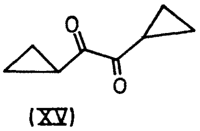
The comparison of the luminescence properties of *trans*-2-phenylcyclopropanecarboxamide (V)[6] and β-phenylpropionamide (VI) is more dramatic than that of (III) and (IV): ϕ_P for (V) at 77°K in EPA is >100 times less than that of (VI). Under these conditions ϕ_F for (V) and (VI) are essentially equal. At room temperature, in fluid EPA, ϕ_F for (V) is a factor of ten less than ϕ_F for (VI). These data imply that the rate constant for ring-opening in the excited singlet state of (V), at room temperature, is competitive with k_F. Using 10^7 sec.$^{-1}$ as approximation for k_F, k_1 for (V) at room temperature is estimated at 10^8 sec.$^{-1}$. The lack of fluorescence attenuation in (V) at 77°K is consistent with a quenching mechanism involving an activated process


(I)


(II)



(V)



(XV)

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† There is ample precedent for assigning the luminescence deactivation steps to ring opening reactions (ref. 2). The fact that diradicals are drawn as the ring-opened structures is not meant to exclude the possibility that the openings are ionic (ref. 3). (A) is meant to connote any structure containing an aromatic group and a cyclopropane ring, not necessarily directly bonded to one another.

‡ Ethyl ether : isopentane : ethyl alcohol, 5 : 5 : 2 by volume.

(*i.e.* ring rupture). The ability for ring-opening to compete with fluorescence in (V) and not in (III) is explicable in terms of the relative stabilities of the respective diradicals† generated in the two cases.

The ϕ_P for *N*-cyclopropylbenzamide (VII)[7] at 77°K in EPA is 50 times less than ϕ_P for *N*-ethylbenzamide (VIII). No fluorescence ($\phi_F < 10^{-4}$) was observed from either (VII) or (VIII) at room temperature or at 77°K.

At 77°K in EPA, the total emission spectra (fluorescence and phosphorescence) of *N*-cyclopropyl-α-naphthamide (IX) and α-naphthamide (X) were found to be essentially identical with respect to energy, band shape, and intensity. At room temperature in fluid EPA ϕ_F for (IX) was, however, *ca.* 5 times less than that of (X).§ We feel that the apparent lack of ring opening in the triplet state of (IX) at 77°K is related to the fact that E_T for (IX) and (X) (59 kcal/mole) is comparable to the bond-dissociation energy for cyclopropane (53·4 kcal/mole).[8] Ring rupture in this case might be expected to be inefficient since all of the energy of the triplet state of (IX) would not be localized in the cyclopropane ring.

A comparison of the fluorescence spectra of *N*-cyclopropyl-9-anthramide (XI) and *N*-ethyl-9-anthramide (XII) at room temperature in methylcyclohexane revealed no differences in their respective fluorescence yields. Both spectra were similar to that of anthracene with respect to energy and vibrational structure.

The phosphorescence spectra of cyclopropyl phenyl ketone (XIII) and acetophenone (XIV) in EPA at 77°K are very similar. The bands due to the long-lived component analogous to those reported by Yang[9] for indan-1-one are more prevalent in (XIII) than in (XIV). The ϕ_P's for (XIII) and (XIV) are essentially equal. The lack of effect of the cyclopropyl group in (XIII) puts an upper limit on the rate-constant for ring-opening in its triplet state at 77°K. The mean phosphorescence rate constant for (XIII) is *ca.* 10^2 sec.$^{-1}$. The value of k_3 for (XIII) at 77°K must therefore be $< 10^2$ sec.$^{-1}$. This result is in harmony with the data reported for (III), (V), (VII), and (IX), all of which have π,π^* triplet states with relatively small k_P's (*ca.* 10^{-1} sec.$^{-1}$).

We are extending this study to the luminescence properties of the α-diketone (XV).[10]

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§ The absolute fluorescence yield of (X) is very low (0·005). Further attenuation of this emission in (IX) is difficult to measure accurately due to background emission from solvent.

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