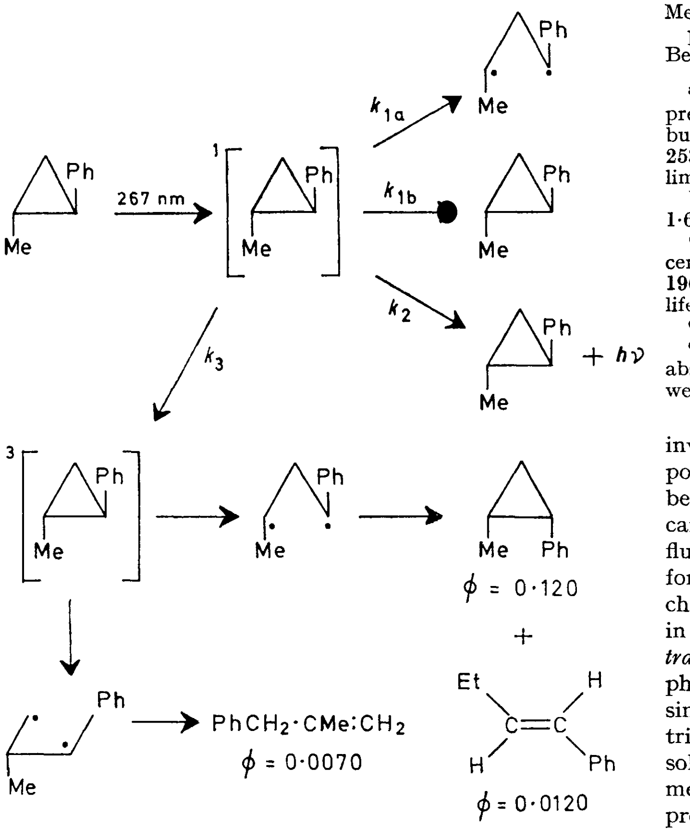
The Fluorescence of Phenylcyclopropanes

By K. SALISBURY

(*Department of Chemistry, The University of Texas at Austin, Austin, Texas* 78712)

Summary The increase in the gas-phase fluorescence quantum yields of phenylcyclopropanes relative to other monoalkylbenzenes is explained by a decrease in the inter-system crossing rate constants.

O'CONNELL and his co-workers[1] recently reported the quenching effect of a neighbouring cyclopropyl group on the luminescence of some benzenoid compounds. I report that, in the gas phase, a neighbouring cyclopropyl group *enhances* the fluorescence of benzenoid compounds.



SCHEME

The Table shows the gas-phase fluorescence quantum yields, Q_F, at the 0–0 bands and at a few other wavelengths and the radiative lifetimes, τ_{rad}, of phenylcyclopropane, *trans*-1-methyl-2-phenylcyclopropane (1), benzylcyclopropane, and some monoalkylbenzenes.

TABLE

		Q_F[a]			τ_{rad}(ns)
λ(nm)	260[b]	267	272	275	
Ethylbenzene	0·27	0·28	—	—	150[c]
n-Propylbenzene	0·28	0·29	—	—	145[c]
s-Butylbenzene	0·28	0·28	—	—	170 ?[c]
Phenylcyclopropane	0·40[e]	0·47	0·48	—	130[d]
Methylphenylcyclopropane	0·38[e]	0·47	0·47	0·47	140[d]
Benzylcyclopropane	0·25	0·25	—	—	150[d]

[a] Measured at 130—400 N m^{-2} of gas; the absence of low-pressure effects was proved by the addition of 6,700 N m^{-2} of butane. Benzene was used as the standard ($Q_F = 0{\cdot}18$ at 253 nm; ref. 2.) Neglecting any error in Q_F of benzene, the error limit in each of these Q_F values is $\pm 10\%$.

[b] The linear reciprocal dispersion of the monochromator was 1·6 nm per mm; in this work 1 mm slits were used.

[c] Derived from Berlman (I. B. Berlman, 'Handbook of Fluorescence Spectra of Aromatic Molecules,' Academic Press, New York, 1965) by multiplying them by the ratio of Burton and Noyes' lifetime[3] of toluene to that of Berlman's).

[d] Obtained from the integrated absorption spectra.[4]

[e] The decrease in Q_F with decrease in wavelength in benzenoid absorption bands is well documented, although perhaps not so well understood.[3,5]

The above results clearly indicate the enhancing effect of a neighbouring cyclopropyl group on the fluorescence quantum yields. The effect is not small (a factor of *ca.* 1·5 is involved) but is eliminated when a single methylene is interposed between the benzene and cyclopropyl rings. It has been suggested[1] that, in solution, cyclopropyl ring-openings can compete with phosphorescence and sometimes with fluorescence in arylcyclopropanes, thus providing a rationale for the decreased emission quantum yields relative to open-chain analogues. However, we have recently shown[6] that in the gas-phase photolysis (*cf.* solution photolysis[7]) of *trans*-1-methyl-2-phenylcyclopropane there is little, if any, photochemical reaction occuring from the first excited singlet state, but that very efficient processes occur from the triplet state (Scheme). These triplet reactions, as in the solution photochemistry, involve cleavage to a phenyl trimethylene species. It seems then that in the gas phase, processes involving a cyclopropane ring-fission from the triplet state can compete efficiently with any other process while in the case of the first excited singlet state this may not be so.

In considering the variation of Q_F in a series of compounds we must analyse the effects of molecular changes on all the rate constants of which Q_F is a function [$Q_F = k_2/(k_{1b} + k_{1a} + k_2 + k_3)$]. The radiative lifetime

$\tau_{\text{rad}} = 1/k_2$ may be obtained directly from the absorption spectra of the molecules[4] and from the Table we see that there is only a small decrease in τ_{rad} of the phenylcyclopropanes. Since internal conversion (k_{1b}) is unimportant in monoalkylbenzenes,[3] any decrease of k_{1b} in the phenylcyclopropanes would have little effect upon Q_F. The increase in Q_F must be attributed to a decrease in k_3, the intersystem crossing rate constant.† The reason for this decrease is being sought in modern theories of radiationless transitions.

I thank the Camille and Henry Dreyfus Foundation and the Robert A. Welch Foundation for financial support. The helpful guidance of Professor G. J. Fonken and Professor W. A. Noyes, jun., is gratefully acknolwedged.

(*Received, May 10th*, 1971; *Com.* 728.)

---

† If a rapidly reversible ring cleavage of the singlet molecule is taking place then it means that the decrease in k_3 must be even larger.

[1] E. J. O'Connell, jun., G. Martin, and J. T. Lis, *Chem. Comm.*, **1970**, 95.
[2] J. A. Poole, *J. Phys. Chem.*, 1965, **69**, 1343; W. A. Noyes, jun., D. Harter, and W. A. Mulac, *J. Chem. Phys.*, 1966, **44**, 2100.
[3] C. S. Burton and W. A. Noyes, jun., *J. Chem. Phys.*, 1968, **49**, 1705.
[4] S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, 1962, **37**, 814.
[5] K. Salisbury, *J. Chem. Soc.* (*B*), 1971, 931.
[6] K. Salisbury, in preparation.
[7] H. Kristinsson and G. W. Griffin, *Tetrahedron Letters*, **1966**, 3259; G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *J. Amer. Chem. Soc.*, 1964, **86**, 2532.