The Geometrical Requirements for Fluorescent Intramolecular Exciplex Formation and Fluorescence Quenching

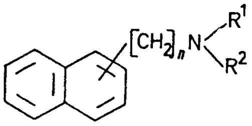
By R. Stephen Davidson* and Kenneth R. Trethewey
(*Department of Chemistry, The University, Leicester* LE1 7RH)

Summary From a study of intramolecular exciplex formation by the naphthylalkylamines (I)—(IV) it is concluded that the geometrical requirements for emissive complex formation are greater than those needed for intramolecular fluorescence quenching.

Many of the previous studies[1–4] on intramolecular exciplex formation between aromatic hydrocarbon and amines have been aimed at discovering the geometrical requirements for exciplex formation.[1,3,4] These requirements are far less stringent than those for intramolecular excimer formation between aromatic hydrocarbon nucleii.[5] In these cases, complex formation only occurs when the two aryl units can adopt a sandwich configuration. We now describe experiments designed to determine whether the geometrical requirements for intramolecular fluorescence quenching are the same for those for fluorescent exciplex formation.

Many of the compounds (I)—(IV) exhibit fluorescent intramolecular exciplex formation[2] and quantum yields and wavelength of the emissions are given in the Table. In every case substantial quenching of the fluorescence from the naphthalene unit was observed.

The finding that compounds (I)—(IV), $n = 1$, exhibit exciplex fluorescence in solvents of widely differing polarity is rather surprising in the light of the report that the corresponding compounds having $R^1 = R^2 = Me$ do not exhibit such fluorescence.[1] Furthermore the quantum yield of exciplex fluorescence is not particularly solvent dependent and the wavelength of their emission, in a number of solvents, is very similar to the corresponding compounds having $n = 2$, 3, and 4. From the solvent dependency of the wavelength of emission from (II, $n = 1$) and (IV, $n = 1$), the dipole moments of the complexes were calculated to be 14 D.[6] This is very similar to the value of 13 D obtained for (II, $n = 3$) and 16 D obtained for (IV, $n = 3$). In these compounds, the σ-bond framework can only allow at best an orthogonal interaction between the nitrogen lone



	Substitution	R^1	R^2
(I)	α	Et	Et
(II)	β	Et	Et
(III)	α	Me	Ph
(IV	β	Me	Ph

pair [(I) and (II)] or p-orbital of nitrogen [(III) and (IV)] and the π-system of the aromatic nucleus. The weakness of the exciplex emission attests to the unfavourability of this configuration for fluorescent exciplex formation. Nevertheless the results show that when the stability of an excited complex is mainly due to charge-transfer interactions, the relative orientation of the two interacting groups may not be particularly critical. From the fact that the quantum yields of exciplex and naphthalene unit emission are not particularly solvent sensitive, it appears that formation of the complex is not influenced by solvent polarity. For compounds such as p-(anthracen-9-ylmethyl)-NN-dimethylaniline,[3] fluorescent exciplex formation is dependent on solvent polarity.

TABLE

Quantum yields for fluorescence from naphthalene unit and exciplex, and wavelength of exciplex emission for compounds (I)—(IV)

		$n = 1$		$n = 2$		$n = 3$		$n = 4$	
Compound	Solvent	ϕ_M	ϕ_E	ϕ_M	ϕ_E	ϕ_M	ϕ_E	ϕ_M	ϕ_E
(I)	C_6H_{12}	0·005[a]	—	<0·001	0·406 (365nm)	0·01	0·20 (397nm)	0·03	0·034 (400nm)
„	MeCN	0·006	<0·001 (495nm)	0·008	0·040 (482nm)	0·012	0·015 (505nm)	0·008	0·002 (520nm)
(II)	C_6H_{12}	0·019[a]	—	0·186[a]	—	0·115	0·216 (393nm)	0·113	0·034 (430nm)
„	C_6H_6	0·001	0·006 (405nm)						
„	CH_2Cl_2	0·003	0·004 (440nm)						
„	EtOAc	<0·001	0·004 (440nm)						
„	EtOH	0·003	0·002 (480nm)						
„	MeCN	0·018	0·006 (495nm)	0·003	0·028 (470nm)	0·070	0·010 (470nm)	0·012	0·002 (500nm)
(III)	C_6H_{12}	0·005[a]	—	0·008	0·214 (377nm)	0·018	0·172 (377nm)	0·007	0·069 (383nm)
„	MeCN	0·006	<0·001	0·007	0·102 (465nm)	0·066	0·028 (510nm)	0·012	0·010 (490nm)
(IV)	C_6H_{12}	0·007[a]	<0·001 (390nm)	0·002	0·055 (390nm)	0·008	0·180 (380nm)	0·003	0·106 (375nm)
„	MeCN	0·005	0·007 (475nm)	0·005	0·143 (475nm)	0·009	0·050 (485nm)	0·011	0·016 (490nm)

[a] Quantum yield for total emission.

Another feature of compounds (I)—(IV), $n = 1$, is that the fluorescence from the naphthalene unit is strongly quenched even though fluorescent exciplex formation is inefficient. Thus the quenching process demands little in the way of orientation of the two groups relative to each other. With these compounds there is the possibility that the quenching occurs by the groups interacting *via* the C–H bonds of the interposing methylene group. The absorption spectra of the compounds give no indication of such an interaction. However the fact that the ionisation potential[7] of benzylamine (7·56 eV) is lower than that of either toluene (8·82 eV) or ethylamine (8·86 eV) suggests that such an interaction may occur and that it is not necessarily readily detected by absorption spectroscopy.

Through-bond interactions between the aryl and amino groups is unlikely to occur for compounds (I)—(IV), $n = 4$. For these compounds, fluorescence from the intramolecular complexes is weaker than for the corresponding compounds having $n = 3$. On the other hand quenching of the fluorescence from the aryl unit is very efficient. For compound (II, $n = 4$) in cyclohexane and acetonitrile and for (I, $n = 4$) in acetonitrile this quenching is more efficient than for the corresponding compounds having $n = 3$, *i.e.* lengthening the interposing chain from $n = 3$ to 4 has a much more profound effect upon fluorescent exciplex formation than the fluorescence quenching process. We conclude that the geometrical requirements for fluorescence quenching are far less than those for fluorescent exciplex formation and in fact the only factor of any importance may be the distance between the two groups. In the case of fluorescent exciplex formation, it is necessary for the molecule to adopt a favourable conformation and for the stability of the complex so formed to be significantly greater than that of the encounter complex.

Fluorescent exciplex formation for (I)—(IV), $n = 2$ and 3, is relatively efficient and this is probably a consequence of the molecules being able to adopt a conformation in which there is an in-line interaction of the nitrogen lone pair [in (I) and (II)] or p-orbital [in (III) and (IV)] with the aromatic π-system.

Since fluorescence quenching occurs so efficiently from a complex having little geometrical requirements, it is highly probable that chemical reactions can occur from such a complex.[8] It is established that triplet and radical ion formation[9] can take place from such complexes. Thus the question as to whether a particular reaction occurs from an exciplex or not has to be widened to asking whether reaction occurs from an encounter or fluorescent complex.

We thank the S.R.C. for funds to purchase a spectrofluorimeter.

(*Received, 5th August* 1976; *Com.* 907.)

---

[1] E. A. Chandross and H. T. Thomas, *Chem. Phys. Letters*, **1971**, **9**, 393.

[2] D. R. G. Brimage and R. S. Davidson, *Chem. Comm.*, **1971**, 1385; G. S. Beddard, R. S. Davidson, and A. Lewis, *J. Photochem.*, 1972/3, **1**, 491.

[3] T. Okada, T. Fujita, M. Kubota, S. Masaki, N. Mataga, R. Ide, Y. Sakata, and S. Misumi, *Chem. Phys. Letters*, 1972, **14**, 563; R. Ide, Y. Sakata, S. Misumi, T. Okada, and N. Mataga, *J.C.S. Chem. Comm.*, **1972**, 1009.

[4] T. J. Chuang, R. J. Cox, and K. B. Eisenthal, *J. Amer. Chem. Soc.*, 1974, **96**, 6828.

[5] E. A. Chandross and C. J. Dempster, *J. Amer. Chem. Soc.*, 1970, **92**, 3586.

[6] H. Knibbe, Ph.D. Thesis, University of Amsterdam, 1969; B. Stevens, *Adv. Photochem.*, 1971, **8**, 161. After examination of molecular models of these complexes, a value of 5·0 Å was chosen for the cavity radius.

[7] J. L. Franklin, J. G. Pillard, H. M. Rosenstock, J. T. Herron, K. Droxl, and F. H. Field, Ionisation Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions, NSRDS-NBS, No. 26, National Bureau of Standards, Washington D.C., 1964.

[8] For a recent review, R. S. Davidson, in 'Molecular Association,' ed. R. Foster, Academic Press, London, 1975, p. 215.

[9] M. Ottolenghi, *Accounts Chem. Res.*, 1973, **6**, 153.