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Geometrical Requirements for Fluorescent Intramolecular Excimer Formation and Fluorescence Quenching

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Summary From a study of fluorescence quantum yields for several α,ω-di-naphthylalkanes and related compounds it is concluded that the geometrical requirements for intramolecular fluorescence quenching are similar to those for fluorescent excimer formation.

PREVIOUS studies on the geometrical requirements for fluorescent excimer formation by aromatic hydrocarbons have shown that the two molecules making up the excimer adopt a sandwich configuration.[1] For compounds (I) and (II) Chandross and Dempster[2] showed that intramolecular

1-Np$[CH_2]_n$Np-1 (1-Np = 1-naphthyl)
(I)

2-Np$[CH_2]_n$Np-2 (2-Np = 2-naphthyl)
(II)

excimer formation takes place most readily when $n = 3$. The connecting chain having 3 methylene groups is one which most easily allows the two naphthalene groups to adopt a sandwich configuration. The question arises as to whether the fluorescence quenching which accompanies excimer formation takes place before the sandwich configuration is attained or whether it is due to radiationless decay of the excimer. This point is also relevant to the question of whether the photodimerisation of aromatic hydrocarbons, *e.g.* 9-cyanoanthracene,[3] involves excimers as intermediates.[4] Analyses of the kinetics of such reactions are consistent with them involving excimers as intermediates[5] but the data can also be rationalised as shown in the Scheme in which excimer formation is purely an energy wastage process.[6]

$$\text{Products} \longleftarrow \text{ArH}^* + \text{ArH} \rightleftharpoons \underset{\text{Excimer}}{(\text{ArH})_2^*}$$

SCHEME

We now report upon detailed measurements of the quantum yield of fluorescence from the naphthalene units and of excimer formation for compounds (I) and (II) and related compounds in degassed cyclohexane solutions at 18 °C. The results are shown in the Table.

TABLE. Quantum yields[a] for fluorescence from the naphthalene unit (Φ_M) and excimer (Φ_E) for α,ω-dinaphthylalkanes in degassed cyclohexane solution at 20 °C.

Compound[b]	1-Substituted naphthalenes		2-Substituted naphthalenes	
	Φ_M	Φ_E	Φ_M	Φ_E
$NpCH_2Np$	0·22	—	0·33	—
$Np[CH_2]_2Np$	0·19	—	0·23	—
$Np[CH_2]_3Np$	—	—	0·018	0·10
$Np[CH_2]_4Np$	0·19	—	0·21	—
$Np[CH_2]_6Np$	—	—	0·21	—
$NpCH(OH)CH_2CH_2Np$ . .	0·05	0·04	—	—
$NpCH_2OCH_2Np$ . .	0·015	0·033	0·0085	0·0375
$NpCH_2OCH_2CH_2Np$ . .	0·09	—	0·098	0·07
$NpCH_2OCH_2CH_2OCH_2Np$	0·10	—	0·14	—
$NpCH_2[OCH_2CH_2]_2OCH_2Np$	—	—	0·13	—

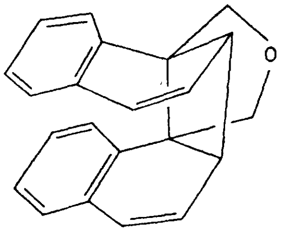
[a] Determined using 1- and 2-methylnaphthalenes as standards (Φ 0·21 and 0·30, respectively). The ethers 2-$NpCH_2OMe$ and 1-$NpCH_2OMe$ have quantum yields of 0·11 and 0·10 respectively.
[b] Np = naphthyl.

For compounds (I) and (II), little fluorescence quenching occurs except when $n = 3$ and for these compounds intramolecular excimer is observed. This result is in marked contrast to that reported for intramolecular fluorescence quenching in naphthylalkylamines (III) and (IV).[6,7] With

$1\text{-Np}[CH_2]_nNEt_2$ (III) $2\text{-Np}[CH_2]_nNEt_2$ (IV)

these compounds fluorescence quenching is efficient when $n = 1—4$.

Quantum yield measurements made on the ethers shown in the Table also demonstrate that little fluorescence quenching occurs except when excimer formation is observed. We therefore conclude that fluorescence occurs from a complex or complexes having a very similar configuration to an excimer. A further point of interest is that the only compounds which undergo intramolecular photocycloaddition reactions are those which exhibit excimer formation. Previously[2] (I, $n = 3$) has been shown to photodimerise. Di(1-naphthylmethyl) ether also forms a photodimer which undergoes thermal rearrangements to give (V). However not all compounds which form intramolecular excimers photodimerise, *e.g.* (II, $n = 3$)[2] and di(2-naphthylmethyl) ether. These results, together with the quantum yield data support the view that excimers are intermediates in the photodimerisation of aromatic hydrocarbons.



(V)

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[6] We are grateful to Professor M. D. Cohen for bringing this point to our attention.

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