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THE PHOTOCHEMISTRY OF INTRAMOLECULAR EXCIMERS: THE ROLE OF INTERSYSTEM CROSSING AND PRODUCT FORMATION

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Abstract - The quantum yields of triplet formation by some α,ω-dinaphthylalkanes and related compounds which exhibit intramolecular excimer fluorescence and/or intramolecular fluorescence quenching have been determined. Although most compounds have quite high quantum yields (∿ 0.4) others are much lower and no single reason could be found to explain this variance.

1. INTRODUCTION

Although it is known that excited complexes decay by a variety of routes [1], determination of the efficiency of these processes is proving quite difficult. Quantum yields and lifetimes of excimer and exciplex fluorescence have been determined for many systems [1] but other data such as quantum yield of triplet formation [2] and of radical ion formation [3] are less easy to obtain. Of particular interest is the efficiency with which excited complexes give rise to chemical products, especially the formation of intramolecular cycloaddition products by compounds which exhibit intramolecular excimer formation [4a,b]. Thus product studies have indicated that such compounds as di-(1-naphthylmethyl)ether can form two types of excimer which differ in conformation [5]. There is also considerable debate as to whether the excimers lie on the reaction path to products or whether the products are formed via biradical intermediates [6].

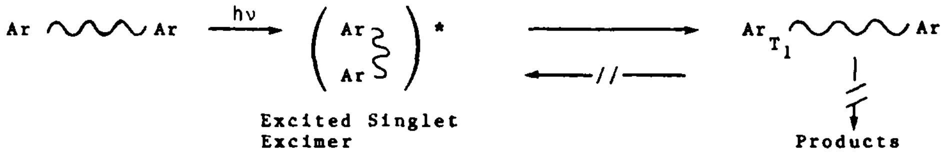
We now report upon the efficiency with which some α,ω-dinaphthylalkanes and related compounds, which exhibit intramolecular fluorescence quenching and in some cases exhibit intramolecular fluorescent excimer formation, undergo intersystem crossing to produce localised naphthalene triplets.

2. EXPERIMENTAL

A nanosecond laser flash photolysis system was used to determine the quantum yields of triplet formation details of which and the method have been previously described [7]. Quantum yields of fluorescence were determined for the compounds in degassed (freeze-pump-thaw process) cyclohexane solution by excitation at 310 nm where the optical density was 0.1. The quantum yields of fluorescence of 1- and 2-methylnaphthalenes were used as standards. The preparation of the compounds has been previously described [4a,8].

3. RESULTS AND DISCUSSION

Quantum yields of triplet formation were determined by the technique of laser flash photolysis and the results are presented in the Table. From this Table it can be seen that the lifetime of the localised naphthalene triplet state is independent of whether the system can form a fluorescent excimer (Entries 4 and 13) or shows extensive intramolecular fluorescence quenching (Entries 7 and 16). This leads to the conclusion that the localised triplet state cannot be acting as an efficient source of cycloaddition products and also that it is not in equilibrium with the excited singlet excimer.



Some of the compounds examined, e.g. di-(naphthylmethyl)ethers (Entries 4 and 13) and the 1-hydroxy-1,3-dinaphthylpropanes (Entries 8 and 17) form fluorescent intramolecular excimers. In some cases (Entries 4, 8 and 13) the quantum yield for triplet production is relatively low. This could be attributed to the excimer undergoing reaction to give cycloaddition products which effectively competes with intersystem crossing to give the localised triplet. However, only two of these three compounds (Entries 4 and 8) undergo intramolecular cycloaddition reactions [5,9]. Thus the low triplet yield exhibited by di-(2-naphthylmethyl)ether (Entry 13) cannot be attributed to chemical reaction. That chemical reaction may not have a major influence upon triplet yield is reinforced by the finding that 1-naphthylmethyl-2-(1-naphthyl)ethyl ether (Entry 5) which forms an intramolecular excimer and undergoes reaction inefficiently, has a high yield of triplet production [9].

1-Naphthylmethyl-1-naphthylacetate (Entry 7) shows substantial intramolecular fluorescence quenching but does not exhibit fluorescent excimer formation. This is rather surprising since the ester linkage allows the naphthyl groups to overlay each other in a sandwich configuration without giving rise to any undesirable non-bonded interactions in the linking chain. In this case, where fluorescent excimer formation is inefficient and the compound is photostable [10], the triplet yield is rather low. For the ester in the 2-naphthyl series (Entry 16) the quantum yield of triplet formation is quite respectable. This is true for other cases where fluorescence quenching but not excimer formation is observed (Entries 6 and 15).

The results show that one cannot identify a single factor which can influence the yield of triplet formation. Thus triplet formation doesn't necessarily have to occur via a fluorescent excimer. There is also no clear evidence that the propensity for an excimer to undergo chemical reaction plays an important part in determining triplet yield.

Although this work has not identified the factors which influence triplet formation by singlet excimers, it is clear that fluorescent and non-fluorescent excimers can give rise to quite high triplet yields. The triplets generated in this way may lead to chemical reaction, e.g. by sensitised singlet oxygen formation [11] or valence bond tautomerism [12].

Table Quantum yields of fluorescence and triplet formation, and triplet lifetimes for systems forming intramolecular excimers and some related systems in degassed cyclohexane solution.

Entry	Compound	1-substituted naphthalenes				Entry	2-substituted naphthalenes			
		ϕ_M^F	ϕ_E^F	ϕ_T	τ_T (μsec)		ϕ_M^F	ϕ_E^F	ϕ_T	τ_T (μsec)
1	$NpCH_3^*$	0.21	-	0.48	9.0	10	0.30	-	0.51	13.8
2	$NpCH_2Np$	0.22	-	0.37	13.1	11	0.33	-	0.20	22.0
3	$NpCH_2CH_2Np$	0.19	-	0.32	14.5	12	0.23	-	a	a
4	$NpCH_2OCH_2Np$	0.015	0.033	0.11†	14.0	13	0.009	0.038	0.087	11.5
5	$NpCH_2OCH_2CH_2Np$	0.09	-‡	0.42	12.8	14	0.098	0.07	0.35	17.7
6	$NpCH_2OCH_2CH_2OCH_2Np$	0.10	b	0.46	13.2	15	0.14	-	0.44	16.2
7	$NpCH_2CO_2CH_2Np$	0.038	-	0.18	10.0	16	0.11	-	0.38	13.7
8	$\underset{\substack{\vert \\ OH}}{NpCH}CH_2CH_2Np$	0.05	0.04	0.15	16.8	17	0.012	0.09	0.32	14.6
9	$Np(CH_2)_4\ Np$	0.19	-	0.28	15.1	18	0.21	-	0.46	15.5

a = Not determined. b = Fluorescence not detected.

*Quantum yields of fluorescence for 1- and 2-methylnaphthalene from I.B. Berlman in: Handbook of fluorescence spectra of aromatic molecules (Academic Press, New York, 1965): Quantum yields of triplet formation for 1- and 2-methylnaphthalene from A.A. Lamola and G.S. Hammond, J. Chem. Phys., 43, 2129 (1965).

†Quantum yield for intramolecular cycloaddition = 0.03
‡Excimer emission observed but ϕ_E^F not determined (Reference 9).
Np = Naphthyl.

ϕ_M^F = Quantum yield of fluorescence of naphthalene unit.

ϕ_E^F = Quantum yield of fluorescence of excimer.

ϕ_T = Quantum yield for production of the localised naphthalene triplet.

τ_T = Triplet lifetime.

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