Intramolecular Exciplex Formation in Some Compounds Containing Condensed Aromatic Hydrocarbon and *NN*-Dimethylaniline Moieties

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Summary Effects of the geometrical restrictions on intramolecular exciplex formation have been studied for some systems containing anthracene or pyrene and *NN*-dimethylaniline moieties, and it is concluded that a parallel sandwich structure may be favourable but not necessary for intra- and inter-molecular exciplex formation.

There have been many investigations on exciplexes formed from singlet excited aromatic hydrocarbons and ground-state amines, but little information is available regarding the geometrical requirements for exciplex formation. Recently, it was reported that intramolecular exciplexes[1,2] containing aromatic hydrocarbon and aliphatic amine functions are less demanding so far as geometrical requirements are concerned. However, no such studies have hitherto been reported for aromatic hydrocarbon-aromatic amine systems.

$p\text{-Me}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot(\text{CH}_2)_n\text{–Ar}$

(I) Ar = 9-anthryl; $n = 0,1,2,3$

(II) Ar = 2-anthryl; $n = 3$

(III) Ar = 1-pyrenyl; $n = 1,2,3$

In order to obtain further information about the structure of the exciplexes, we have prepared eight compounds containing condensed aromatic hydrocarbon and *NN*-dimethylaniline (DMA) moieties in the same molecule, *i.e.*, (I; $n = 0$—3), (II; $n = 3$), and (III; $n = 1$—3). In the exciplex state of these compounds, the relative geometrical arrangements of the two moieties are more or less restricted, depending upon the number of methylene groups and the position of substitution in the hydrocarbon nuclei. The chemical structures of the compounds were determined by means of i.r., n.m.r., mass spectrometry, and elemental analysis. The electronic absorption spectra of (I), (II), and (III), except for (I; $n = 0$), indicate that there are no appreciable interactions between the two moieties in the ground state.

Fluorescence band maxima of (I) *and* (II) *in solution at room temperature.*

	(I)					(II)
	$n=0$	$n=1$	$n=2$	$n=3$	ref.[a]	$n=3$
Cyclohexane	430			480	483	503
Ether	465	490	493	518	515	532
Tetrahydrofuran ..	505	555	550	552	550	559

[a] "ref" = 9-ethylanthracene–DMT.

The positions of the fluorescence bands of (I; $n = 0$—3) and (II; $n = 3$) are shown in the Table. In cyclohexane, (I; $n = 3$) alone exhibits a typical exciplex fluorescence with the emission maximum in agreement with that of the exciplex formed from 9-ethylanthracene and *NN*-dimethyl-*p*-toluidine (DMT), while (I; $n = 1$ and $n = 2$) exhibit fluorescence spectra characteristic of 9-ethylanthracene, and not of exciplexes. The fluorescence spectra of (I; $n = 3$) show remarkable solvent effects, namely, a red-shift and a decrease of intensity with increasing solvent polarity, probably due, respectively, to the stabilization of the polar exciplex and the formation of a non-fluorescent ion radical in polar solvents.[3] The fact that the compound (I; $n = 3$) exhibits almost the same shift of maxima, in various solvents, as the 9-ethylanthracene–DMT system suggests that similar structures contribute to the intra- and inter-molecular exciplexes. The compounds (I; $n = 1$ and $n = 2$) in cyclohexane exhibit only the fluorescence spectra due to the anthracene nucleus, while in ether solutions the structureless spectra of the exciplexes can be observed. It is reasonable to suppose that the energy level of the charge-transfer (CT) state is higher than that of the singlet excited anthracene in non-polar solvents, but that the relative positions of these energy levels may be reversed in polar solvents. This assumption is supported by the fact that compounds (I; $n = 1$ and $n = 2$) exhibit only fluorescence bands due to the anthracene moiety in an EPA matrix at 77K, where reorientation of the solvent is impossible. Furthermore, the maxima of (I; $n = 1$ and $n = 2$) in ether appear at shorter wavelength than those of (I; $n = 3$) and of the 9-ethylanthracene–DMT system, while they appear at nearly the same wavelength in more polar solvents such as tetrahydrofuran and ethanol.

On the other hand, (I; $n = 0$) shows fluorescence spectra different from those of (I; $n = 1$—3), indicating the formation of an excited state different from an ordinary intermolecular exciplex. The fact that the maxima of (II; $n = 3$) appear at longer wavelength than those of (I; $n = 3$) and of the 9-ethylanthracene–DMT system can be explained in terms of more favourable overlapping of the two moieties in the excited state of the former. The behaviour of the pyrene system (III; $n = 1-3$) and of 1-ethylpyrene–DMT so far as exciplex fluorescence is concerned is similar to that of the anthracene system already described.

Thus, it is clear that not only the ($n = 3$) system but also the ($n = 1$ and $n = 2$) systems can emit the broad structureless fluorescence spectra attributable to the CT state. Hence, we conclude that, although the sandwich structure may be favourable for intermolecular exciplex formation in aromatic hydrocarbon–DMA systems, the two rings need not necessarily be parallel in the exciplex state.

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