Effect of Intramolecular Exciplex Formation upon the Photoreactivity of Naphthylalkylamines and Anthrylalkylamines

By D. R. G. BRIMAGE and R. S. DAVIDSON* (Department of Chemistry, The University, Leicester LE1 7RH)

Summary Several NN-diethyl-1-naphthylalkylamines and NN-diethyl-9-anthrylalkylamines exhibit intramolecular exciplex formation and as a result reactions typical of the hydrocarbon singlet states, *e.g.* hydrogen abstraction from tertiary amines and dimerisation, are quenched.

A SERIES of NN-diethyl-I-naphthylalkylamines (1; n = 1, 2, or 3) and NN-diethyl-9-anthrylalkylamines (2; n = 1 or 3) have been prepared by standard reactions. Their u.v. absorption spectra are identical with those of their parent hydrocarbons, 1-methylnaphthalene and 9-methylanthra-

cene respectively. In rigid glass at 77 K, the naphthalene compounds show fluorescence and phosphorescence identical with that of 1-methylnaphthalene, and the anthracene compounds fluorescence like that of 9-methylanthracene.

The position of the maxima of the fluorescence bands exhibited by these compounds in solution at room temperature are shown in the Table. In agreement with Chandross and Thomas,¹ the naphthyl compounds (1; n = 2 or 3) exhibits exciplex formation. The wavelength of exciplex emission is solvent dependent. Compound (1; n = 1) has fluorescence emission typical of 1-methylnaphthalene as well as a structureless band farther to the red. The emission maximum of this band does not alter

TABLE

Position of fluorescence bands exhibited by NN-diethyl-1-naphthylalkylamines (1; n = 1, 2, or 3) and NN-diethyl-9-anthrylalkylamines (2; n = 1 or 3) in solution at 20°

Ami	ine Solvent	Position of f	luorescer	nce bands (nm)
(1) (1) (1) (2)	Methylcyclohexane Benzene Acetonitrile Benzene	n = 1 358 404, 420, 443	n = 2 420 495	n = 3 408 435 516 404, 420, 443
[CH ₂] _n NEt ₂ [CH ₂] _n NEt ₂				NEt ₂

appreciably with change in solvent polarity. Compound (2; n = 3) exhibits fluorescence rather similar to that of the parent hydrocarbon, but the band at 443 nm is much more intense and the tail of the emission extends much farther to the red. Compound (2; n = 1) shows only fluorescence typical of the parent hydrocarbon. The intensity of this emission is about one tenth that of 9-methylanthracene (each at a concentration of ca. 10^{-4} M).

(1)

(2)

From the emission spectra, we expected that the photoreactivity of the aromatic hydrocarbon nucleus in compounds (1; n = 2 or 3) and (2; n = 3) would be strongly affected by intramolecular exciplex formation. On the other hand, we would expect that the photoreactivity of compounds (1; n = 1) and (2; n = 1) would be affected to a lesser degree.

- ¹ E. A. Chandross and H. T. Thomas, Chem. Phys. Letters, 1971, 9, 393.
- ² J. A. Barltrop and R. J. Owers, Chem. Comm., 1970, 1462. ³ R. F. Bartholomew, D. R. G. Brimage, and R. S. Davidson, J. Chem. Soc. (C), 1971, in the press.
- ⁴ D. C. Neckers in "Mechanistic Organic Photochemistry", Reinhold, New York, 1967, p. 98.

1

The first excited singlet state of naphthalene is known to react with tertiary alkylamines in polar solvents to give radical ions which subsequently lead to hydrogen abstraction from the amine.² Reaction in the presence of oxygen leads to oxidation of the amine.³

$$\begin{split} \mathrm{Np}(\mathrm{S}_{1}) &+ (\mathrm{RCH}_{2})_{3}\mathrm{N} \rightarrow \mathrm{Np}^{\perp} + (\mathrm{RCH}_{2})_{3}\mathrm{N} \\ &+ \\ \mathrm{Np}^{\perp} &+ (\mathrm{RCH}_{2})_{3}\mathrm{N} \rightarrow \mathrm{NpH} + (\mathrm{RCH}_{2})_{2}\mathrm{NCHR} \\ &+ \\ \mathrm{NpH} &+ \mathrm{O}_{2} \rightarrow \mathrm{NpH} + \mathrm{HO}_{2} \\ &\cdot \\ (\mathrm{RCH}_{2})_{2}\mathrm{NCHR} + \mathrm{O}_{2} \rightarrow (\mathrm{RCH}_{2})_{2}\mathrm{NCHR} \\ && | \\ && \\ \mathrm{OO} \\ (\mathrm{RCH}_{2})_{2}\mathrm{NCHR} \rightarrow \mathrm{RCHO} + \mathrm{RCH} = \mathrm{NCH}_{2}\mathrm{R} + \\ && | \\ && \\ \mathrm{OO} \\ &(\mathrm{RCH}_{2})_{2}\mathrm{NH} \ etc. \\ && \\ \mathrm{Np} = \mathrm{Naphthalene} \end{split}$$

1-Methylnaphthalene and compound (1; n = 1) sensitised the photo-oxidation of triethylamine in acetonitrile solution with about equal efficiency (as judged by the rate of acetaldehyde formation). In contrast no reaction occurred when compound (1; n = 2 or 3) was used as sensitiser *i.e.* in compound (1; n = 2 or 3) intramolecular quenching of the singlet state of the naphthalene is very efficient.

A well known reaction of the first excited singlet state anthracene is its reaction with ground state anthracene to give a photodimer.⁴ 9-Methylanthracene reacts in a similar way. The efficiency of photodimerisation of compound (2; n = 1) is dependent upon its initial concentration. No dimerisation occurs at 10^{-2} M-(2; n = 1) *i.e.* intermolecular quenching is efficient. In accord with this view, solutions of this concentration do not fluoresce. Photodimerisation does occur with 5×10^{-4} M-(2; n = 1) solutions. It occurs about one eighth as rapidly as that of 9-Methylanthracene $(5 \times 10^{-4} \text{ M})$. Since at $5 \times 10^{-4} \text{ M}$, compound (2; n = 1) exhibits fluorescence of normal wavelength, its slower rate of photodimerisation compared with 9-methylanthracene must be due to some intramolecular quenching. Compound (2; n = 3) was found to be completely stable on irradiation in deoxygenated solutions, i.e. photodimerisation is completely suppressed by intramolecular exciplex formation.

We thank the University of Leicester for a Scholarship (to D.R.G.B.).

(Received, August 11th, 1971; Com. 1403.)