Preliminary Note

Quantum yield of triplet state formation of 9-cyanoanthracene in three solvents

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Various values of the quantum yield of fluorescence (Φ_F) of 9-cyanoanthracene (9-CNA) have been reported. According to Bowen and Sahu[1] Φ_F of 9-CNA is independent of temperature and solvent and nearly equal to unity. Melhuish[2] measured a Φ_F value of 0.88 in benzene and of approximately 0.85 in 99% ethanol and petroleum ether at infinite dilution and room temperature. Taking into account the difficulties inherent in fluorescence quantum yield measurements these discrepancies are not surprising. Moreover, it has been shown that the quantum yields of triplet state formation (Φ_T) of 9- and 9,10-substituted anthracenes are often strongly solvent dependent. This effect has been ascribed to variations of the rate constant of intersystem crossing (k_T) as a function of the solvent-dependent energy difference between the fluorescent state (S_1) and a triplet state (T_x) of higher energy than S_1.[3,4] Since Φ_F of 9-CNA is in any case very large, small variations of k_T in different solvents should have a vanishing effect on Φ_F, whereas Φ_T values should vary approximately linearly with k_T (eqn. (1))

$$\Phi_T = k_T/(k_F + k_T) \cong k_T/k_F \qquad (1)$$

It was checked that the integration ($\int_0^\infty \varepsilon_\nu \, d\nu$) carried out on the whole of the $^1L_a \leftarrow {}^1A$ band is, within experimental uncertainties, independent of the medium. Therefore, k_F may be considered as constant in the three solvents used during this work. Application of Strickler and Berg's expression[5] to the absorption and emission spectra of 9-CNA in cyclohexane leads to the S_1 radiative lifetime:

$$\tau^0{}_{S_1} = 8.3 \times 10^{-9} \text{ sec}$$

Using the Φ_T value obtained in this work, the fluorescence lifetime in cyclohexane can be evaluated:

$$\tau_F = \tau^0{}_F (1 - \Phi_T) = 8.0 \times 10^{-9} \text{ sec}$$

With the aim of searching for a possible correlation between the rate constants of $S_1 \rightarrow T$ radiationless deactivation and medium properties, the Φ_T values of 9-CNA were determined in cyclohexane, benzene and acetonitrile as solvents.

The method based on the modifications of fluorescence intensities $(F^0/F)^*$ and optical densities of triplet to triplet absorption (D_T/D^0_T) observed by flash photolysis in the absence and in the presence of heavy-atom quenchers was used[4] (eqn. (2)):

$$F^0/F = (D_T F^0/D^0_T F - 1)\Phi_T \tag{2}$$

Dimethylmercury was employed as the heavy atom molecule[6]. As it was shown previously for bromobenzene[1] and during this work for tetramethyllead and tetramethyltin, these heavy-atom species have at room temperature, virtually no effect on the fluorescence intensity of 9-CNA.

All our attempts to observe the T–T absorption spectrum of 9-CNA by spectrographic flash photolysis were unsuccessful. As it appeared later on, the strongest T–T band is located around 430 nm which corresponds to the middle of the intense fluorescence emission of the molecule. This has the effect to blacken the photographic plates in the region of the T–T band which is difficult to detect under these conditions. On the other hand, the transient spectrum could be observed by kinetic flash spectroscopy. The maxima of absorption are given in Table 1 and compared to those obtained by pulse radiolysis.

TABLE 1

T_1-T_n ABSORPTION OF 9-CYANOANTHRACENE

Solvent	Flash photolysis		(Pulse radiolysis[7])
	λ_{max} (nm)	τ_T (sec$^{-1} \times 10^3$)	λ_{max} (nm)
Cyclohexane	433	0.6	425
Benzene	440	1.9	445
Acetonitrile	433	1.8	–

A plot according to eqn. (2) is given in Fig. 1. The O–O transition energy of the $^1L_A \leftarrow {}^1A$ band of 9-CNA measured on the absorption and fluorescence spectra and the Φ_T values are joined together in Table 2.

TABLE 2

9-CYANOANTHRACENE Φ_T VALUE AND $^1L_a \leftarrow {}^1A$ TRANSITION ENERGY IN THREE SOLVENTS

Solvent	v^a_{00} ($\pm$ 60 cm^{-1}) Absorption	v^f_{00} ($\pm$ 60 cm^{-1}) Fluorescence	$\dfrac{v^a_{00} + v^f_{00}}{2}$	Φ_T
Cyclohexane	25,040	24,820	24,930	0.040 $\pm$ 0.005
Benzene	24,770	24,170	24,470	0.042 $\pm$ 0.003
Acetonitrile	24,925	23,970	24,447	0.021 $\pm$ 0.003

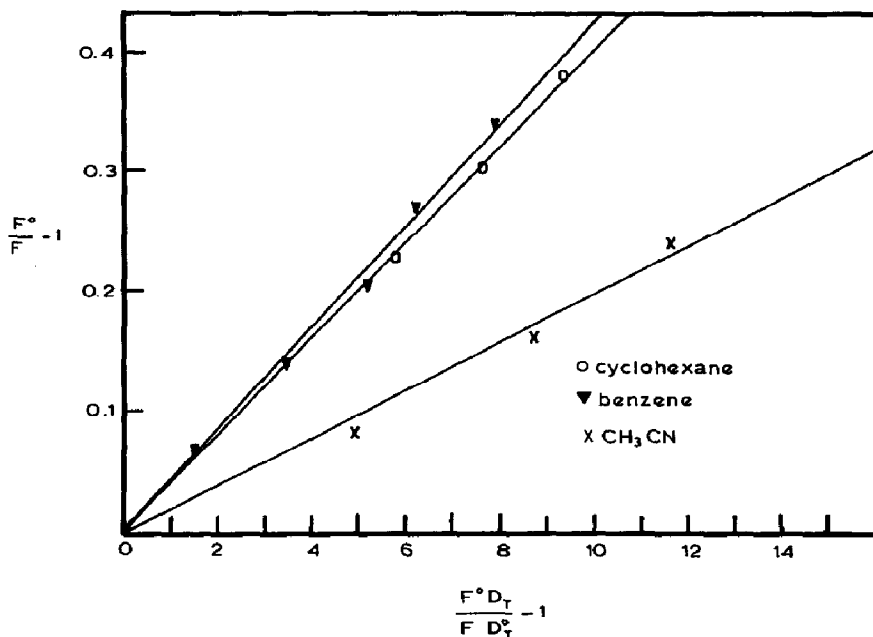* The superscript ^{0} indicates "in the absence of quencher".

Fig. 1. Triplet yield plot of 9-cyanoanthracene according to eqn. (2).

Using literature data[2], the quantum yields of fluorescence and $S_1 \to T$ intersystem crossing of 9-CNA add up to about 0.90. Remembering normal errors in measuring Φ_F absolute values, our result does not indicate that $S_1 \to S_0$ radiationless decay takes place (eqn. (1)).

Since Φ_F is large, a 50% decrease of Φ_T when going from benzene to acetonitrile corresponds here to a $\sim 2\%$ increase of the quantum yield of fluorescence. Yet, this effect is too small to be displayed unambiguously by the fluorescence intensities measured in the different solvents. The decrease of the $^1L_A{-}^1A$ energy interval when going from cyclohexane to acetonitrile is accompanied by a decrease of a factor 2 in the k_T value (Table 2 and eqn. (1)). This is, qualitatively, a phenomenon similar to the one observed for other meso- substituted anthracene derivatives. However, the rate constant for intersystem crossing appears to be equal in the two non-polar solvents, independent of the fact that the $^1L_A{-}^1A$ energy difference is smaller in benzene than in cyclohexane. The lack of information concerning the energy of the T_x state, which appears to play an important role in the $S_1{-}T$ radiationless deactivation of 9-substituted anthracenes, makes two independent interpretations of this result possible in the case of 9-CNA; either the k_T frequency factor may be larger in benzene than in cyclohexane or, if this factor is not appreciably solvent dependent, the energy interval between the S_1 and the T_x state should also be kept constant. The examination of the temperature effect on k_T should remove this ambiguity. Work is now going on along this line.

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