

RADIATIONLESS DEACTIVATION OF THE FLUORESCENT STATE OF 9-METHOXYANTHRACENE

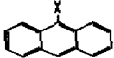
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The sum of the fluorescence quantum yield and the quantum yield for intersystem crossing of 9-methoxyanthracene, 9- OCD_3 -anthracene and 9- OCH_3 -anthracene- d_9 in n-heptane at room temperature is only ≈ 0.60 . While the fluorescence quantum yield in methylmethacrylate monomer has nearly the same value as in n-heptane in the polymer matrix of polymethylmethacrylate, the fluorescence quantum yield is twice as high as in fluid solution.

Table 1

Fluorescence Q_F and triplet quantum yields Q_{ST} of 9-methoxy- and partially deuterated 9-methoxyanthracenes in degassed solution at room temperature

	Solvent	T (°C)	Q_F	Q_{ST}
OCH_3	n-heptane	21	0.34	0.26
OCH_3	glycerol	23	0.56	--
OCH_3	MMA 1)	22	0.23	--
OCH_3	PMMA 2)	22	0.62	--
OCD_3	n-heptane	22	0.31	0.25
$\text{OCH}_3\text{-D}_9$	n-heptane	21	0.33	0.23

1) methylmethacrylate monomer, 2) polymethylmethacrylate

When passing from fluid solution to the polymer matrix, an even more dramatic increase of the fluorescence quantum yield from $Q_F = 0.03$ to $Q_F = 0.53$ can be demonstrated for 9-methoxy-10-cyanoanthracene.

Unlike other substituted meso-anthracenes 9-methoxyanthracene shows an anomalous temperature dependency of the fluorescence quantum yield and fluorescence decay time in oxygen-free n-heptane (1).

An Arrhenius type plot of $\log(1/\tau - 1/\tau_F)$ versus $1/T$ is not linear (fig. 1).

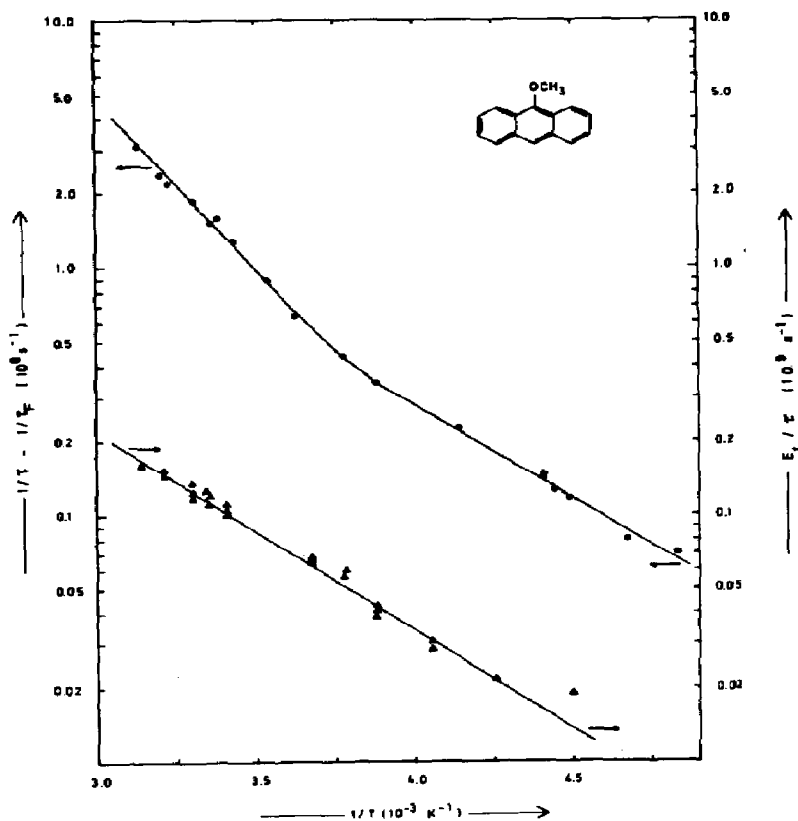


Fig. 1. Temperature dependence of $(1/\tau - 1/\tau_F)$ and triplet extinction E_t/τ in degassed n-heptane.

Since we found no indications of a photochemical process from the S_1 state in 9-methoxyanthracene we conclude that radiationless deactivation by internal conversion must occur to a large extent above -10°C . Computer variations of Eq. 1

$$1/\tau - 1/\tau_F = A_{ST} \cdot \exp\left(-\frac{E_{ST}}{RT}\right) + A_{IC} \cdot \exp\left(-\frac{E_{IC}}{RT}\right) \quad (1)$$

using the least squares method results

$$\begin{aligned} & E_{ST} = 1200 \text{ cm}^{-1}, A_{ST} = 2.75 \times 10^{10} \text{ sec}^{-1}, \\ \text{and } & E_{IC} = 2800 \text{ cm}^{-1}, A_{IC} = 5.0 \times 10^{13} \text{ sec}^{-1} \end{aligned}$$

for the best fit of the measured τ -values with temperature and

$$Q_F = 0.35; Q_{ST} = 0.33 \text{ and } Q_{IC} = 0.32 .$$

The frequency factor calculated for intersystem crossing $A_{ST} \sim 10^{10} \text{ sec}^{-1}$ is similar to those determined for other mesosubstituted anthracenes and is typical for a spin-forbidden process, while the abnormally high frequency factor for $A_{IC} = 5 \times 10^{13} \text{ sec}^{-1}$ might reflect a value for spin-allowed S_1-S_0 transitions. Since the deuterated 9-methoxyanthracenes yield values for Q_F and Q_{ST} which are only slightly different from the perprotonated compound (s. Table 1) the radiationless transition obviously does not proceed via C-H stretch frequencies of the aromatic skeleton as energy acceptors.

A possible mechanism for the radiationless deactivation of the S_1 state of 9-methoxyanthracene will be discussed.

- 1) S. Schoof, H. Güsten and C. von Sonntag,
Ber. Bunsenges. phys. Chem. **81**, 305 (1977)
Die Temperaturabhängigkeit der Fluoreszenzquantenausbeuten von meso-substituierten Anthracenen.