On the Fluorescence Quenching of Polycyclic Aromatic Hydrocarbons by Nitromethane

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Fluorescence quenching of 22 polycyclic aromatic hydrocarbons by nitromethane in toluene and acetonitrile solutions has been studied. Contrary to Sawicki's observations that the fluorescence of hydrocarbons with the fluoranthene skeleton is not quenched that of 11.12- and 3.4-benzofluoranthene and fluoranthene itself is quenched. These compounds have a high energy of the fluorescence transition. The fluorescence quenching of the compounds investigated follows a dynamic quenching mechanism. The bimolecular rate constant of fluorescence quenching increases exponentially with the energy of the fluorescing state of alternant hydrocarbons.

Fluorescence quenching of polycyclic aromatic hydrocarbons in fluid solution by nitromethane has found analytical applications. The underlying photophysical processes, however, are still basically unknown. The analytical applications – e.g. in the investigation of air dust samples – are based on an observation made by Sawicki[1]: According to this author the fluorescence quenching of aromatic hydrocarbons in nitromethane solution is characteristically different for compounds with exclusively six-membered rings and for those containing the fluoranthene skeleton. According to Sawicki, fluorescence of the first group is quenched while it is not quenched in the second group.

To prepare the basis for a mechanistic model of the quenching properties of nitromethane, this paper reports on quantitative fluorescence quenching experiments of 22 aromatic hydrocarbons (Table 1).

Exceptions to Sawicki's rule[1] are readily apparent: Of 10 hydrocarbons with a fluoranthene skeleton investigated, 7 showed no measurable reduction of fluorescence intensities nor reduction in fluorescence life times in toluene and acetonitrile solutions at room temperature even at high concentrations of nitromethane (14.8 mole/l). However, 11.12- and 3.4-benzofluoranthene showed significant fluorescence quenching, while fluoranthene itself is slightly quenched as investigated by life time measurements to circumvent the inner filter effect. All non-fluoranthenic systems investigated, on the other hand, (12 compounds with fluorescence transitions between 26,100 cm^{-1} and 18,000 cm^{-1}, see Tab. 1) showed measurable fluorescence quenching in toluene and acetonitrile solutions at room temperature.

In all systems with measurable quenching of fluorescence the intensities and life times of fluorescence decreased in a parallel fashion with increasing quencher concentration as required by a dynamic quenching mechanism. In toluene as a solvent, however, the intensities and life times did not decrease according to a hyperbolic Stern-Volmer law for high concentrations ($>$ quenching constant $[Q]_{\mathrm{H}}$), since in these cases the highly polar quencher changed the polarity of the solvent. In agreement with this interpretation hyperbolic quenching laws were observed when acetonitrile was used as a solvent since in this case the quencher did not drastically change the polarity of the solvent. To illustrate this observation Fig. 1 gives the Stern-Volmer plots of the fluorescence of perylene in toluene (curve a) and in acetonitrile (curve b) with nitromethane as a quencher.

The mechanism of fluorescence quenching by nitromethane might be either (i) energy transfer to and dissociation of the quencher, (ii) formation of an exciplex which does not fluoresce or (iii) electron transfer between excited aromatic molecule and quencher to produce aromatic and nitromethane radical ions.

The presently available data do not allow to discriminate definitively between these possibilities. In case of the electron transfer mechanism (iii) a cor-

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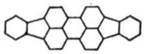
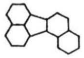
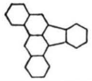
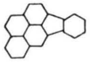
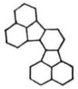
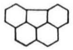
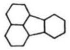
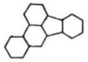
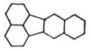
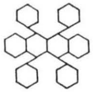
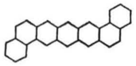
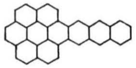
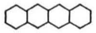
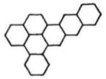
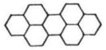
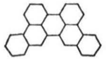
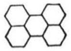
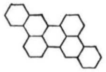
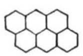
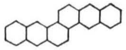
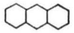
Table 1. Experimental fluorescence parameters. $\tilde{\nu}_{0-0}(F)$ = O—O band of the fluorescence, $[Q]_H$ = quenching constant (quencher: nitromethane), τ^0_F = fluorescence, life time, k_q = bimolecular rate constant of fluorescence quenching (quencher: nitromethane). All measurements at room temperature.

	hydrocarbon		$\tilde{\nu}_{0-0}(F)$	$[Q]_H$	τ^0_F	k_q
No.	formula	name	[cm^{-1}]	[mole/l]	[ns]	[l·mole^{-1}·s^{-1}]
1		peri-flanthene	T [a]: 17680 A [a]: —	> 14.8 —	— —	— —
2		rubicene	18150 18180	> 14.8 > 14.8	6.1 —	— —
3		10.11-benzo-fluoranthene	20650 —	> 14.8 —	7.8 —	— —
4		2.3;5.6-dibenzo-fluoranthene	20700 20700	> 14.8 > 14.8	9.9 —	— —
5		2.3-o-phenylene-pyrene	21000 21000	> 14.8 > 14.8	8.0 8.0	— —
6		10.11-(peri-naphthylene)-fluoranthene	21920 —	> 14.8 —	13.4 —	— —
7		2.13-benzo-fluoranthene	23500 —	> 14.8 —	ca. 22 —	— —
8		fluoranthene	23920 —	ca. 47 [b] —	49 —	ca. $4.3 \cdot 10^5$ —
9		3.4-benzo-fluoranthene	24200 24200	12.0 11.5	27 25	$3.09 \cdot 10^6$ $3.48 \cdot 10^6$
10		11.12-benzo-fluoranthene	24390 24400	4.0 3.4	7.5 7.4	$3.33 \cdot 10^7$ $3.97 \cdot 10^7$
11		rubrene	18020 18020	15.5 ca. 23 [b]	11.3 6.2	$5.71 \cdot 10^6$ ca. $7.0 \cdot 10^6$
12		1.2;8.9-di-benzo-pentacene	18950 —	8.2 —	6.5 —	$1.87 \cdot 10^7$ —
13		anthraceno-(2′.3′;1.2)-coronene	20230 —	2.4 —	9.8 —	$4.25 \cdot 10^7$ —
14		tetracene	20830 21040	2.6 1.1	4.0 4.1	$9.62 \cdot 10^7$ $2.22 \cdot 10^8$
15		1.2-benzo-naphtho-(2″.3″;4.5)-pyrene	22100 22340	0.60 0.24	5.8 6.1	$2.87 \cdot 10^8$ $6.85 \cdot 10^8$
16		peropyrene	22180 22470	0.40 0.075	3.1 —	$8.06 \cdot 10^8$ —
17		2.3;10.11-dibenzo-perylene	22260 22370	0.22 0.14	3.0 —	$1.51 \cdot 10^9$ —
18		perylene	22350 22610	0.39 0.11	4.5 4.6	$5.70 \cdot 10^8$ $1.98 \cdot 10^9$
19		2.3;8.9-dibenzo-perylene	22660 22750	0.40 0.16	2.9 3.1	$8.62 \cdot 10^8$ $2.02 \cdot 10^9$
20		anthan-threne	22800 22880	0.20 0.045	3.8 —	$1.32 \cdot 10^9$ —
21		anthraceno-(2′.1′;1.2)-anthracene	23250 —	0.37 —	6.9 —	$3.92 \cdot 10^8$ —
22		anthracene	26100 —	0.035 —	3.5 —	$8.16 \cdot 10^9$ —

a) T = fluorescence data in toluene; A = fluorescence data in acetonitrile. b) extrapol.

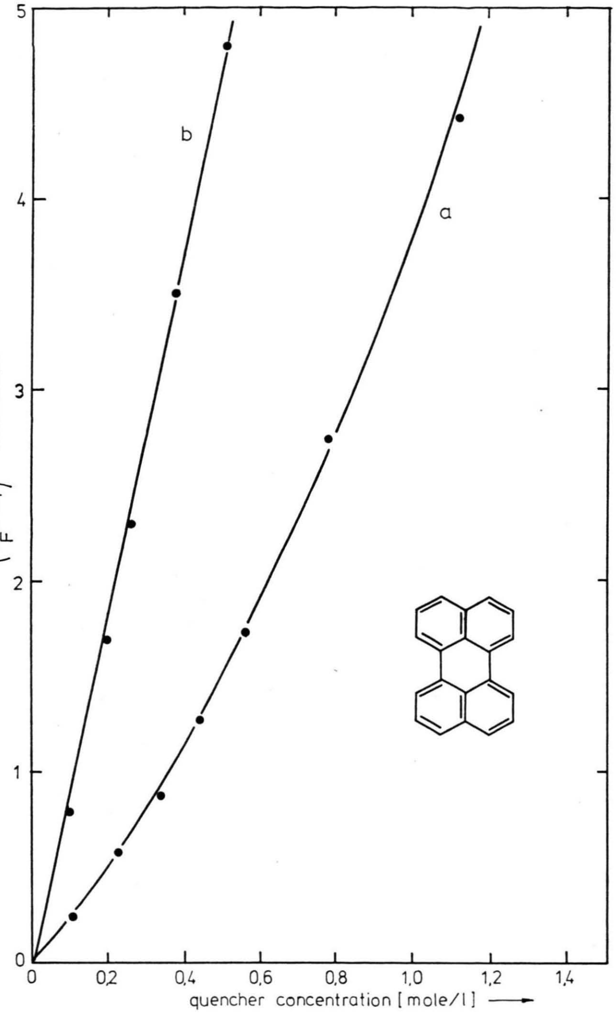


Fig. 1. Stern-Volmer plot of fluorescence intensities of perylene quenched by nitromethane at room temperature (22 °C), a) in toluene, b) in acetonitrile.

relation should exist between the energy of the fluorescing state S_1 of the aromatic and the bimolecular rate constant of fluorescence quenching by nitromethane. Therefore, the energy of the S_1-state was computed from ionization potentials as published by Clar et al.[2] or measured in these laboratories by photo-electron-spectroscopy and the energy of the first absorption band. No such correlation was found, arguing against the electron transfer mechanism (iii).

For the non-fluoranthenic systems the bimolecular rate constant of fluorescence quenching k_q by nitromethane is correlated to the energy of the fluorescence O – O transitions (see Fig. 2), increasing exponentially with the excitation energy of the aromatic compounds. The strong dependence of the rate constant of quenching k_q as a function of the energy of the fluorescence transition points to a dissociation mechanism (i). This mechanism was proposed by Lippert[3] to explain the absence of fluorescence in NO_2-substituted aromatics, where the fluorescence transition energy would be expected to be greater than 18,000 $\text{cm}^{-1} \cong 51$ kcal/mole which corresponds closely to the energy of a $C-NO_2$-bond. The fluorescence energy in rubrene of 18,000 $\text{cm}^{-1} \cong 51$ kcal/mole agrees closely to the dissociation energy of nitromethane. Accordingly the fluorescence of rubrene is quenched by nitromethane only at high concentrations (quenching constant 15.5 mole/l).

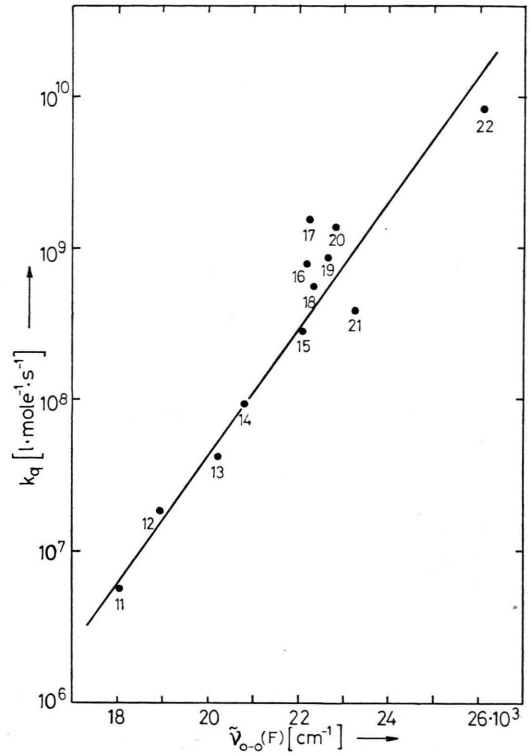


Fig. 2. Dependence of the bimolecular rate constant of fluorescence quenching by nitromethane on the energy of the O – O band of the fluorescence (at room temperature: 22 °C in toluene) of non-fluoranthenic systems.

For the fluoranthenic systems there appears to exist a similar correlation, which is, however, shifted by some 5000 cm^{-1} to higher energy values. At the present, it remains an open problem why fluoranthenic systems require an excitation energy some

$5000\,\mathrm{cm}^{-1}$ higher than non-fluoranthenic hydrocarbons to be quenched by nitromethane. Here it is proposed, however, that the different quenching properties are based on the different molecular properties of alternant and non-alternant aromatic systems.

Experimental

Compounds: The hydrocarbons investigated were taken from the spectroscopic laboratory of the Rütgerswerke AG, Castrop-Rauxel. They were purified by repeated crystallisation, chromatography and sublimation in vacuo until the optical properties reached constant values. Nitromethane, toluene and acetonitrile were purified by destillation and chromatography until the long wave length part of the absorption spectrum was constant.

Measurement: The concentration of the samples were $2 \cdot 10^{-5}$ mole/l throughout. They were degassed by repeated freeze-pump-thaw cycles and measured at room temperature (22 °C).

Fluorescence intensities were measured on an Aminco-Bowman spectrofluorimeter or a Hitachi-Perkin-Elmer spectrofluorimeter MPF-2A. Fluorescence life times were measured on a modified TRW instrument with data storage on a VARIAN C-1024 using a TEKTRONIX 7704 oscilloscope.

Particular attention was paid to conduct experiments in such a way as to exclude the inner filter effect. Generally the fluorescence quenching was investigated by fluorescence intensity and life time measurements and it was independent of the excitation wavelength. Therefore, discrepancies may exist to publications [1] which have an analytical application as main objective.

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[1] E. Sawicki, T. W. Stanley, and W. C. Elbert, Talanta **11**, 1433 [1964].

[2] R. Boschi, E. Clar, and W. Schmidt, J. Chem. Physics **60**, 4406 [1974].

[3] E. Lippert, Z. physik. Chem. N. F. **2**, 328 [1954].