

PHOTOPHYSICAL PROPERTIES OF FLUORANTHENE AND ITS BENZO ANALOGUES

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(Received April 21, 1981)

Summary

The electronic absorption spectra, the absolute fluorescence and phosphorescence spectra, the fluorescence quantum yield and the fluorescence decay time of fluoranthene and its four benzo analogues (benzo(a), benzo(b), benzo(j) and benzo(k)) were measured in *n*-heptane at room temperature with and without oxygen. The photophysical data indicate that only the fluorescence of benzo(k)fluoranthene originates from a $^1L_a \rightarrow ^1A$ transition. In contrast with the other benzofluoranthenes investigated, the first excited singlet state of fluoranthene and of benzo(b)fluoranthene is not quenched by molecular oxygen in a diffusion-controlled process.

1. Introduction

There is considerable theoretical and experimental interest in the excited singlet state behaviour of the non-alternant aromatic hydrocarbon fluoranthene and its benzo analogues [1 - 4]. Fluoranthene exhibits anomalous fluorescence characteristics such as a very large Stokes' shift, a lack of structure in fluorescence as opposed to absorption and an absence of concentration quenching and/or excimer formation; it is relatively resistant to oxygen quenching [5]. Furthermore, in connection with the question whether electronically excited states of polycyclic aromatic hydrocarbons are involved in carcinogenesis [6] there is a need for quantitative luminescence data of the benzofluoranthenes. After all, three of the four benzofluoranthenes (benzo(b), benzo(j) and benzo(k)) are ubiquitous in the environment [7] and among the various analytical techniques for their quantitative determination in the subparts per billion range fluorescence spectroscopy is still the most frequently used method [8].

2. Experimental details

The absolute fluorescence and phosphorescence spectra, the fluorescence quantum yield and the fluorescence decay time were measured using a recording spectrofluorimeter and a fluorimeter relying on the pulse-sampling technique. The spectral sensitivity of the spectrofluorimeter was determined in the spectral range from 320 to 800 nm with a quartz-iodine lamp of known intensity distribution together with a white reflectance standard of MgO replacing the sample. Details about the instrumentation built at this laboratory and about the measurement technique have been published previously [9, 10]. With the exception of the phosphorescence in EPA (diethyl ether:isopentane:ethanol, 5:5:2 by volume), all other photophysical data were measured at room temperature. For the determination of the fluorescence quantum yields according to the method of Parker and Rees [11], quinine bisulphate in 0.1 N H₂SO₄ was used as a reference fluorescence standard, on the assumption of a fluorescence quantum yield of 0.55 at 298 K [12]. The different refractive index of the solvent is taken into account.

The excitation wavelength for measuring the fluorescence quantum yields was 254 nm. To avoid errors due to reabsorption effects, highly diluted solutions ($c < 10^{-6}$ M) were measured.

The natural fluorescence lifetime τ_f was computed by integrating over the first absorption band by the method suggested by Strickler and Berg [13].

Fluoranthene (Fluka AG., Buchs, Switzerland) was purified by column chromatography on neutral Al₂O₃ in benzene followed by two-dimensional thin layer chromatography and final recrystallization from ethanol. Recrystallization was continued until the fluorescence excitation spectrum in the highly diluted solution no longer changed. Benzo(b)fluoranthene (BbF), benzo(j)fluoranthene (BjF) and benzo(k)fluoranthene (BkF) were obtained with 99.5% purity as polycyclic aromatic hydrocarbon reference materials from the Commission of the European Communities (Brussels, Belgium). A pure sample of benzo(a)fluoranthene (BaF) was kindly supplied by Dr. P. Studt. All fluorescence spectroscopy data were measured with and without oxygen in *n*-heptane, fluorescence grade (Merck, Darmstadt), at room temperature. Phosphorescence measurements were carried out with degassed solutions in EPA at 77 K. Degassing of the *n*-heptane and EPA solutions was performed to a pressure of 10⁻⁵ Torr by four freeze-evacuation-thaw cycles. In addition to EPA, room temperature phosphorescence with heavy-atom perturbation of lead acetate was applied according to the method of Vo-Dingh and Hooyma [14] in order to verify the 0-0 band in the phosphorescence spectra.

3. Results and discussion

The absorption and corrected fluorescence spectra of the four benzo-fluoranthenes BaF, BbF, BjF and BkF are shown in Figs. 1 - 4. Both types of

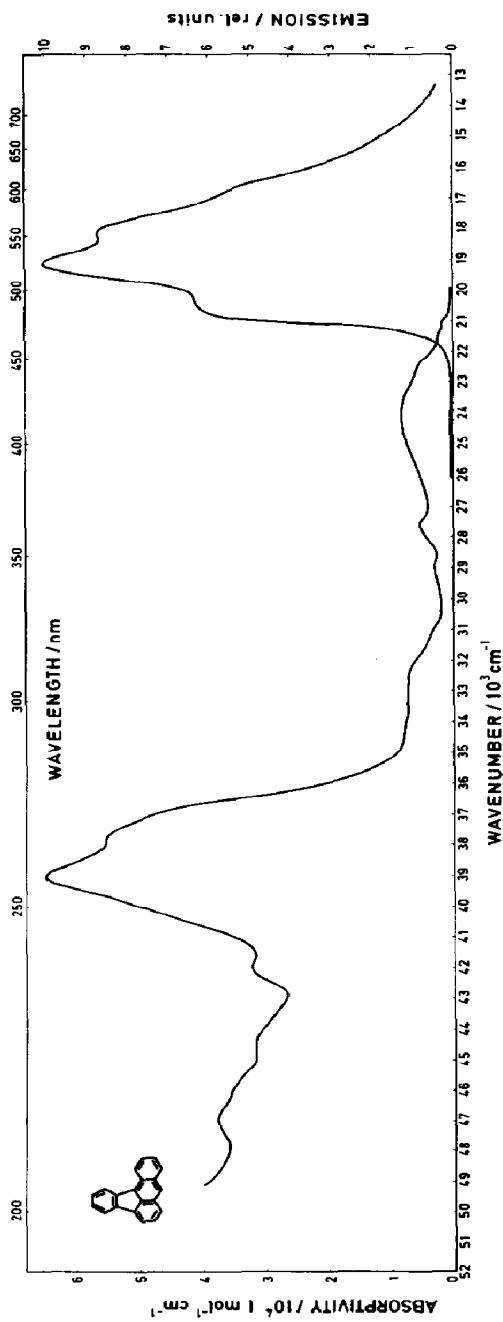


Fig. 1. Electronic absorption and absolute fluorescence spectra of BaF in *n*-heptane at room temperature ($Q_0 = 0.12$; $\tau_0 = 5.5 \text{ ns}$; $L_q = 1.2$).

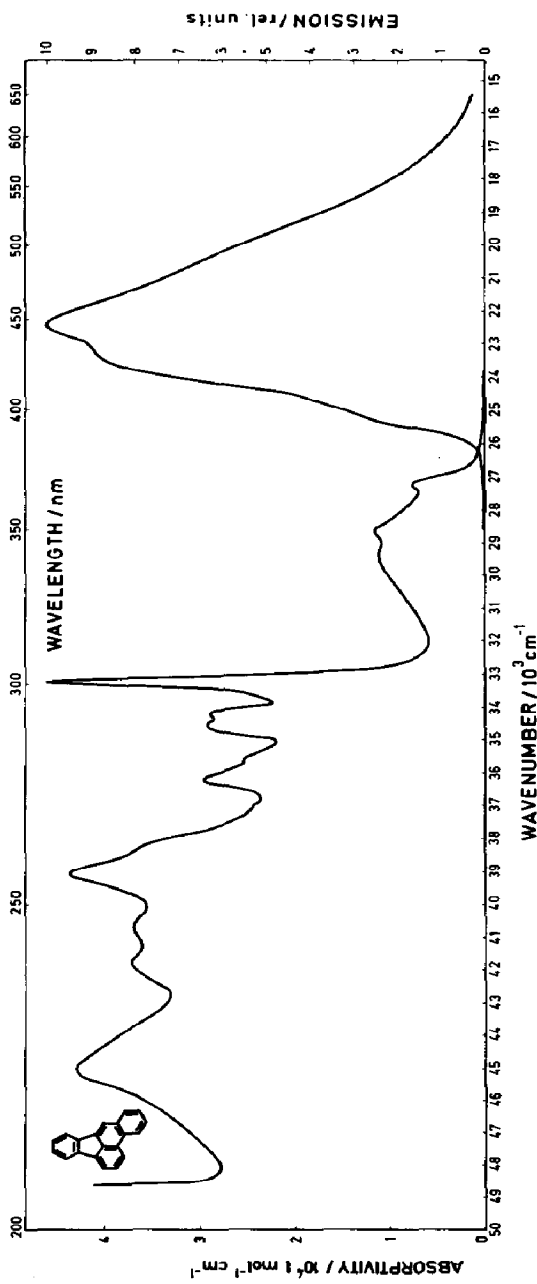


Fig. 2. Electronic absorption and absolute fluorescence spectra of BbF in *n*-heptane at room temperature ($Q_0 = 0.53$; $\tau_0 = 44.3 \text{ ns}$; $L_q = 1.6$).

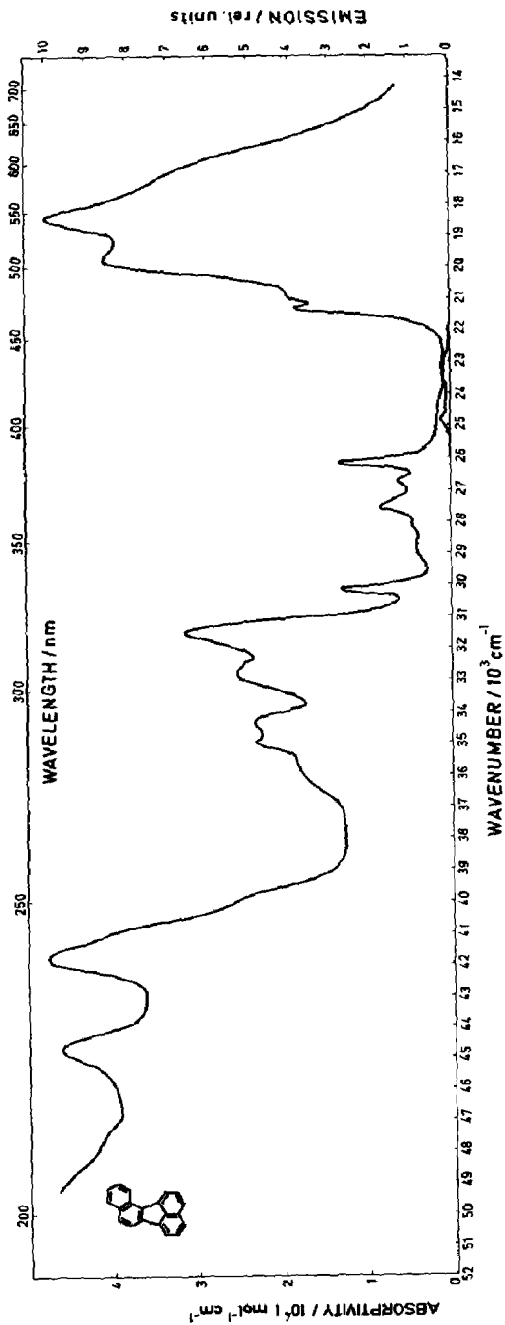


Fig. 3. Electronic absorption and absolute fluorescence spectra of BkF in *n*-heptane at room temperature ($Q_0 = 0.07$; $\tau_0 = 8.0 \text{ ns}$; $L_q = 1.2$).

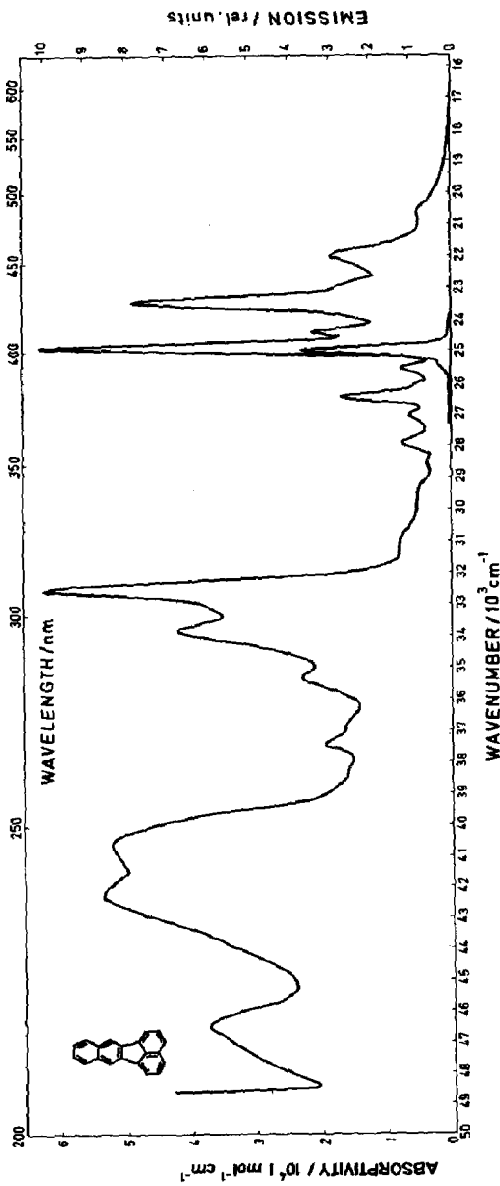


Fig. 4. Electronic absorption and absolute fluorescence spectra of BkF in *n*-heptane at room temperature ($Q_0 = 1.00$; $\tau_0 = 11.3 \text{ ns}$; $L_q = 1.7$).

TABLE 1

Photophysical properties of fluoranthene and its benzo analogues in *n*-heptane at room temperature

Compound	$\Delta\tilde{\nu}_{st}$ (cm^{-1})	$\tilde{\nu}_P^a$ (cm^{-1})	ΔE_{ST} (cm^{-1})	Q_0^b	τ_0^b (ns)	$\tau_{f(\text{exp})}$ (ns)	$\tau_{f(\text{calc})}$ (ns)	L_q	k_q ($\times 10^{10}$ l mol^{-1} s^{-1})
Fluoranthene	6400	18500	6000	0.35	47.0	134	15.9	1.57	0.43
Benzo(a)- fluoranthene	4100	—	—	0.12	5.5	46	17.5	1.38	2.40
Benzo(b)- fluoranthene	4800	19050	5400	0.53	44.3	84	9.7	1.64	0.51
Benzo(j)- fluoranthene	7600	—	—	0.07	8.0	114	30.9	1.29	1.80
Benzo(k)- fluoranthene	1700	17550	6450	1.00	11.3	11.3	12.5	1.71	2.30

^aAt 77 K in EPA in the presence of oxygen and with room temperature phosphorescence.

^bDegassed solutions.

spectra for fluoranthene have been published previously [5]. The left-hand ordinate represents the molar extinction coefficient and the right-hand ordinate the relative emitted photon flux per unit wavenumber. Other photophysical data such as the fluorescence quantum yield Q_0 in the absence of oxygen, the fluorescence decay time τ_0 in the absence of oxygen and the oxygen-quenching constant L_q are likewise given in the legends of Figs. 1 - 4. $L_q = Q_0/Q$ is the quotient of the fluorescence quantum yield without and with oxygen. The absorption spectra and relative intensities of the pure reference compounds BbF, BjF and BkF are in excellent agreement with those of the published absorption curves [2]. In the high energy region above 38 000 cm^{-1} the ordinary absorption curves deviate from those reported nearly 20 years ago [15]. Since the low-lying excited singlet states of fluoranthene [1, 4] and its benzo analogues [2] are understood in fair detail, we shall not discuss the topic further here. It is interesting to note, however, that the characteristic very intense transition in fluoranthene-like hydrocarbons near 33 000 cm^{-1} (see Figs. 2 - 4) exhibits a very low oscillator strength in BaF (Fig. 1). This was theoretically predicted by Souto *et al.* [2].

3.1. Interpretation of the photophysical data

In Table 1 the photophysical properties of fluoranthene and its four benzo analogues are summarized. Since there is little fine structure in the absorption and fluorescence spectra, the 0-0 transition is difficult to determine and the Stokes shift $\Delta\tilde{\nu}_{st}$ is here defined as the energy difference of the wavenumbers between the long wavelength absorption and the emission maximum. With the exception of BkF the fluoranthenes exhibit very large Stokes' shifts, while the singlet-triplet splitting energies ΔE_{ST} are small com-

pared with those of linear alternant conjugated hydrocarbons [16, 17]. The fluorescence quantum yield Q_0 and decay time τ_0 of fluoranthene are in reasonable agreement with those measured by Berlman *et al.* [5]. The fluorescence decay times of fluoranthene and BbF are abnormally long compared with those of the other fluoranthenes investigated. With the exception of BkF there is a large discrepancy between the natural fluorescence lifetime τ_f calculated from the experimental data in the relation $\tau_f = \tau_0/Q_0$ and the value computed by integrating over the long wavelength absorption band with the Strickler–Berg formula [13]. Discordance between the experimental and the computed values has been taken as evidence that fluorescence takes place from a partially forbidden transition [5], *i.e.* that absorption bands not related to the fluorescence transition have been included in the integration. Although BaF, BbF and BkF display a reasonable structure and mirror similarity of the room temperature absorption and fluorescence spectra, there is only a superficial mirror image of each other for fluoranthene and BjF. Thus it is difficult to assess which absorption bands are related to the fluorescence. In fact, theoretical calculations on fluoranthene [1, 4] show that in the integrated absorption range 25 000 - 33 000 cm^{-1} , although the band system looks like one transition with vibrational spacing typical of a planar aromatic hydrocarbon, it actually represents a composite of at least three transitions $S_0 \rightarrow S_3$, $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$. The same conclusion can be drawn for BaF, BbF and BjF [2]. In contrast with these three benzo-fluoranthenes the photophysical data of BkF in Table 1 allow a conclusive prediction. The well-defined structure and mirror similarity of the absorption and fluorescence spectra (see Fig. 4) in conjunction with a small value of the Stokes shift, a high fluorescence quantum yield and the good agreement between the experimental and calculated natural fluorescence lifetimes τ_f indicate that the fluorescence of BkF originates from a ${}^1L_a \rightarrow {}^1A$ transition (Platt notation). This corresponds to the assignment of the 24 000 - 28 500 cm^{-1} energy range of the absorption spectrum with an ϵ_{max} value of $2.3 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and a long axis polarization [18] as a ${}^1A \rightarrow {}^1L_a$ transition [2, 19]. It was inferred by Berlman [20] that a value of $\tau_0/Q_0 > 40 \text{ ns}$ for the natural fluorescence lifetime τ_f is associated with a fluorescence transition corresponding to a ${}^1L_b \rightarrow {}^1A$ transition. This together with the disagreement of the calculated and experimental natural fluorescence lifetimes τ_f and with Vavilov's rule implies that the fluorescence of fluoranthene and three of its benzo analogues (BaF, BbF and BjF) originates from an $S_1 \equiv {}^1L_b$ state which is hidden in the room temperature absorption spectrum by the adjacent stronger absorption to the $S_2 \equiv {}^1L_a$ state. This view is in line with the general empirical rule that for the majority of aromatic hydrocarbons the lowest excited singlet state is 1L_b . Only in "long" rod-shaped π systems such as anthracene and BkF is the S_1 state a 1L_a absorption band system. Furthermore, this argumentation casts doubt on the proposed assignment of the 1L_b transition at 35 100 cm^{-1} and 31 300 cm^{-1} for fluoranthene and BjF respectively [19]. This very intense transition near 33 000 cm^{-1} appears in the absorption spectrum of fluoranthene and the

other benzo analogues (see Figs. 2 - 4) and is more likely to be assigned as a $^1A \rightarrow ^1B_u$ absorption band system.

For all benzofluoranthenes except BkF, rather large Stokes' shifts $\Delta\tilde{\nu}_{st}$, low to medium fluorescence quantum yields Q_0 and discordance between the experimental and computed natural fluorescence lifetimes τ_f have been measured. For fluoranthene the large Stokes shift was interpreted as evidence for a non-planar geometry of the S_1 state [16]. The calculated Stokes shift [4] is in excellent agreement with our experimental value. Theoretical considerations of the excited state geometry of fluoranthene, however, indicate that the large Stokes shift can be understood without the assumption of a non-planar excited singlet state when a substantial bond length change occurs [4]. The rather long bonds connecting the benzene ring to the naphthalene moiety and the bonds in the benzene ring are changed much more in the $S_0 \rightarrow S_1$ transition than in the $S_0 \rightarrow S_2$ transition [4]. Thus, absorption in the 25 000 - 33 000 cm^{-1} energy region of fluoranthene might preferentially lead to higher S_n transitions than S_1 . Since the fluorescence takes place from the S_1 state, large Stokes' shifts are expected because of the larger energy difference with respect to the higher S_n Franck-Condon states.

3.2. Oxygen quenching

The oxygen-quenching constant L_q for all fluoranthenes investigated is lower than the L_q value of many alternant aromatic hydrocarbons [8, 21]. The relative immunity to oxygen quenching of fluoranthene was first pointed out by Berlman *et al.* [5]. Although the L_q values of fluoranthene and BbF are the same, the two fluoranthenes with the long fluorescence decay times (see Table 1) show a marked deviation from the linearity of the Stern-Volmer equation. It can be shown that the quenching constant L_q is related to the fluorescence decay time τ_0 by

$$\frac{Q_0}{Q} = L_q = 1 + \tau_0 k_q [\text{O}_2]$$

when oxygen is the only fluorescence-quenching molecule in the solution. In an $L_q = f(\tau_0)$ plot fluoranthene and BbF deviate from linearity [8]. Taking into account for air-equilibrated *n*-heptane a mean oxygen concentration of 2.8×10^{-3} M at 24 °C, calculated from the oxygen solubility [22], we obtain the bimolecular-oxygen-quenching constant k_q for the quenching of the electronically excited singlet state (see Table 1). Despite the structural similarity of the fluoranthenes, the excited singlet states of the parent compound and of BbF are not quenched by oxygen in a diffusion-controlled process. Since the energy gap between the S_1 and T_1 states of the fluoranthenes is less than the energy difference of 7883 cm^{-1} between the lowest excited singlet oxygen level and the ground state oxygen molecule, oxygen quenching proceeds only through an enhancement of intersystem crossing in the fluoranthenes. We were not able to measure the phosphorescence spectra of BaF and BjF within the resolution limit of our spectrofluorimeter.

Neither in EPA at 77 K, nor in the matrix of polymethylmethacrylate (PMMA), nor by the use of the technique of room temperature phosphorescence with heavy-atom perturbation on filter paper [14] were we able to detect any phosphorescence. The $0 \rightarrow 0$ transition of the phosphorescence of fluoranthene, BbF and BkF obtained in three different environments (EPA, PMMA and filter paper) is in good agreement with published data [6, 23, 24]. Although the fluorescence quantum yield of BkF in the absence of oxygen is equal to unity, we were able to measure its phosphorescence in air. Thus, we have to conclude that the failure to measure the phosphorescence of BaF and BjF is due to a very short phosphorescence decay time. The resolution limit of our instrument is about 1 ms. Nevertheless, we feel that the singlet-triplet splitting energies ΔE_{ST} of BaF and BjF are smaller than 7900 cm^{-1} . Thus, in the non-polar solvent *n*-heptane the population of the lowest excited triplet state of the fluoranthenes is the product of the quenching of fluorescence by molecular oxygen. Because of the small energy splitting ΔE_{ST} for the fluoranthenes it is unlikely that upper triplet states of the fluoranthenes are involved in the oxygen-induced intersystem crossing, as was discussed by Stevens and Algar [25] for the oxygen quenching of alternant aromatic hydrocarbons. To the best of our knowledge, fluoranthene and BbF are the only polynuclear aromatic hydrocarbons whose first excited singlet state is not quenched by molecular oxygen in a diffusion-controlled process. This point adds another mystery to the fluorescence anomaly of the fluoranthenes.

Acknowledgment

We are grateful to Dr. P. Studdt, Bundesanstalt für Materialprüfung, Berlin, for a generous gift of a pure sample of benzo(a)fluoranthene.

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