

# Fluorescence, Phosphorescence, and E-Type Delayed Fluorescence of Hexabenzo[bc,ef,hi,kl,no,qr]coronene

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The luminescence of hexabenzob[bc,ef,hi,kl,no,qr]coronene (**I**) has been studied in a perhydrocoronene matrix at temperatures from 77 to 353 K. **I** exhibits phosphorescence and prompt and E-type delayed fluorescence. The phosphorescence transition is symmetry-forbidden. The luminescence behaviour of **I** is closely related to that of coronene (**II**).

Because of its unique electronic structure, the hydrocarbon hexabenzob[bc,ef,hi,kl,no,qr]coronene (**I**) (see Fig. 1) [1] has found much interest among theoretical chemists [2]. On the other hand, very little experimental (chemical or spectroscopic) information on **I** is available [3]. This is mainly due to the extreme low solubility of **I** in organic solvents, which hampers both chemical and spectroscopic studies. In this Note we wish to report on the fluorescence, phosphorescence, and E-type delayed fluorescence properties of **I**, which have been examined in a perhydrocoronene matrix over the temperature range from 77 to 353 K.

The use of perhydrocoronene (PHC) (C<sub>24</sub>H<sub>36</sub>) as a matrix for high temperature luminescence studies of polycyclic aromatic hydrocarbons [4] has several advantages compared to that of other matrix materials normally used for this kind of work, e.g. plastics [5]. Because PHC is an aliphatic hydrocarbon, interferences due to solvent absorption or luminescence do not occur. At low temperature, polycyclic aromatic hydrocarbons dissolved in PHC exhibit fluorescence and phosphorescence spectra with well-resolved vibrational structure and small bandwidths (comparable to the spectra in n-hexane at 77 K). As the melting point of PHC lies above  $\approx 350^\circ\text{C}$ , the matrix can be used up to fairly high temperatures. Thermal band broadening and loss of vibrational structure of the fluorescence and phosphorescence spectra of polycyclic aromatic hydrocarbons is not very extensive in PHC up to  $\approx 370\text{ K}$ . At least for qualitative studies, the preparation of solid solutions of aromatic hydrocarbons in PHC is very simple (see Experimental) and does not require exclusion of air or humidity.

In Fig. 1 the phosphorescence spectra of solid solutions of **I** (curve a) and coronene (**II**) (curve b) in PHC at 77 K are given. Apart from the fact that the spectrum of **I** (phosphorescence 0,0 band:  $17\,700\text{ cm}^{-1}$ ) lies at longer wavelengths than that of **II** (phosphorescence 0,0 band:  $19\,210\text{ cm}^{-1}$ , in EPA:  $19\,410\text{ cm}^{-1}$  [6]) the spectra are very similar. As follows from the very low intensity of the 0,0 band, the radiative transi-

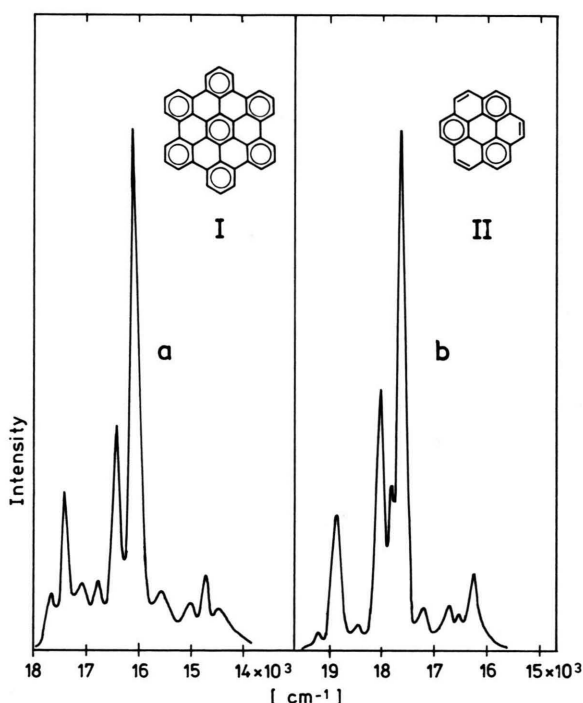


Fig. 1. Phosphorescence spectra in perhydrocoronene at 77 K of hexabenzocoronene (**I**) (curve a, excitation wavelength: 380 nm) and coronene (**II**) (curve b, excitation wavelength: 345 nm). (Spectra have been normalized to the intensity of the most intense band.)

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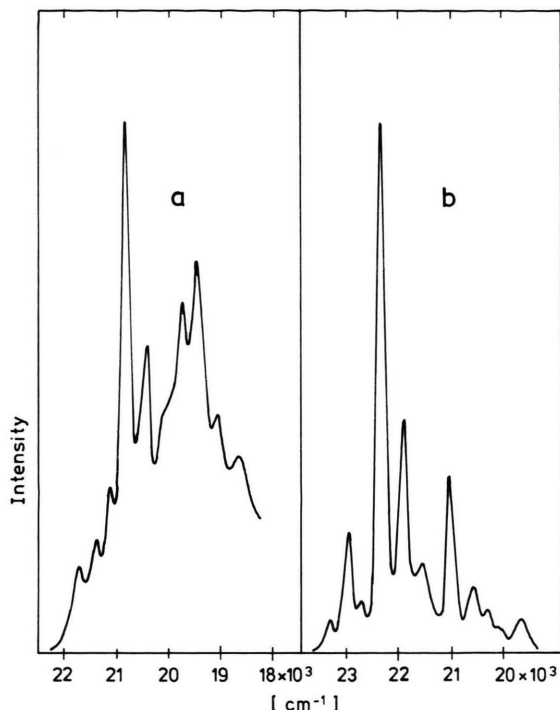


Fig. 2. Prompt fluorescence spectra in perhydrocoronene at 77 K of hexabenzocoronene (**I**) (curve a, excitation wavelength: 380 nm) and coronene (**II**) (curve b, excitation wavelength: 345 nm). (Spectra have been normalized to the intensity of the most intense band.)

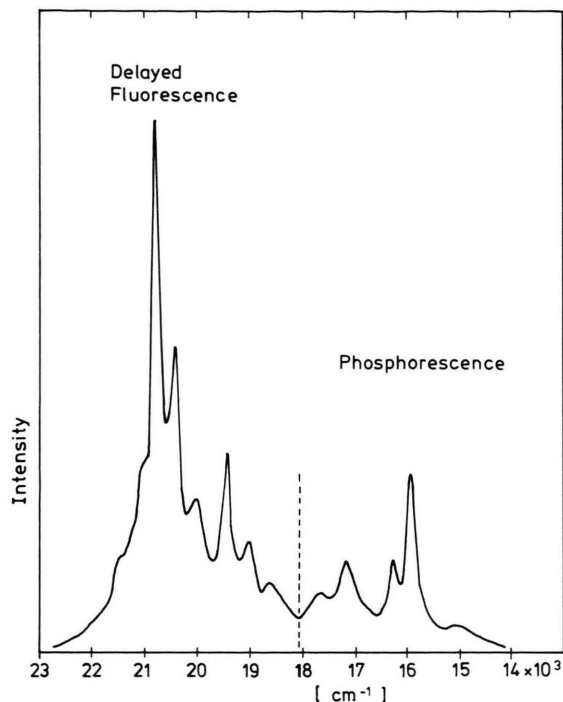


Fig. 3. Delayed luminescence spectrum of hexabenzocoronene (**I**) in perhydrocoronene at 350 K (excitation wavelength: 360 nm).

tion from the lowest triplet ( $T_1$ ) state to the singlet ground state ( $S_0$ ) is symmetry forbidden in both **I** and **II** (note that both hydrocarbons have  $D_{6h}$  symmetry in their electronic ground states). The phosphorescence spectrum of **I** has previously been measured in 1,2,4-trichlorobenzene at 77 K [6]. Due to the "vibronic external heavy-atom effect" [7] the intensity of the 0,0 band increases dramatically and becomes the most intense band in the spectrum. The same observation has been made with coronene [8].

Phosphorescence decay of **I** in PHC at 77 K is mono-exponential with a phosphorescence lifetime  $\tau_p = 6.4$  sec. Accordingly the rate constant  $k_{GT}$  of the non-radiative  $T_1 \rightarrow S_0$  transition must be smaller than  $\approx 0.1 \text{ sec}^{-1}$ . This is an unusually low  $k_{GT}$  value for a  $T_1 \rightarrow S_0$  transition lying at  $\approx 18\,000 \text{ cm}^{-1}$  (vide supra). According to Siebrand's plot [9] a  $T_1 - S_0$  energy gap of  $\approx 18\,000 \text{ cm}^{-1}$  normally corresponds to a  $k_{GT}$  value of  $\approx 1 \text{ sec}^{-1}$ .

In Fig. 2 the rather similar spectra of the prompt fluorescence of **I** (curve a) and **II** (curve b) in PHC at

77 K are shown. For **I** the 0,0 band of fluorescence lies at  $21\,650 \text{ cm}^{-1}$ , for **II** at  $23\,270 \text{ cm}^{-1}$ . The energy difference between the lowest excited singlet ( $S_1$ ) state and the  $T_1$  state is nearly identical for **I** ( $3950 \text{ cm}^{-1}$ ) and **II** ( $4060 \text{ cm}^{-1}$ ). It has previously been shown that due to its rather small  $S_1 - T_1$  interval **II** emits temperature-dependent E-type delayed fluorescence in PHC [4, 10]. This phenomenon has now also been observed with **I**. Figure 3 gives the total luminescence spectrum of **I**, measured through a phosphoroscope in PHC at 350 K; it consists of the spectrum of the delayed fluorescence and the phosphorescence. The lifetimes of the luminescences are equal within experimental error (delayed fluorescence: 3.3 sec, phosphorescence: 3.4 sec). Both lifetimes have been measured in the temperature range 296–353 K. Results are given in Table 1. The lifetimes of delayed fluorescence and simultaneously occurring phosphorescence are equal over the entire temperature range studied and decrease with increasing temperature. That is what has to be expected for an E-type delayed fluorescence [11].

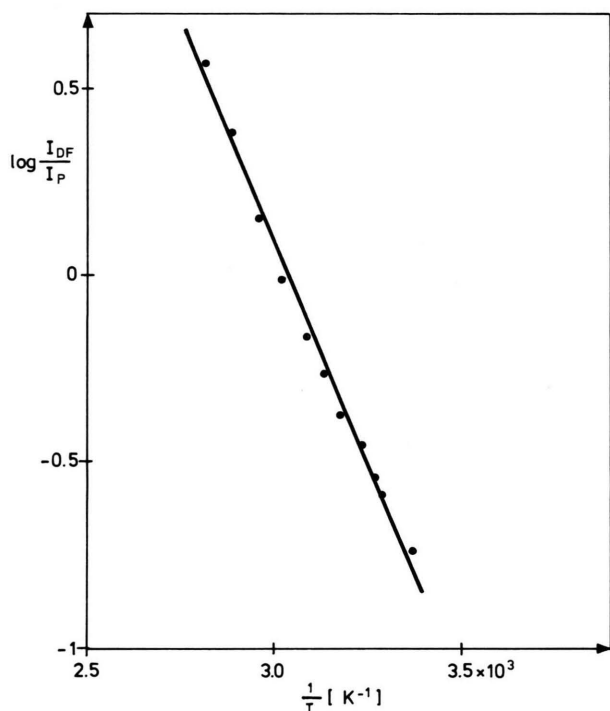


Fig. 4. Arrhenius plot of  $\log$  (intensity of delayed fluorescence/intensity of phosphorescence) versus  $1/T$  ( $K^{-1}$ ) for hexabenzocoronene (I) in perhydrocoronene (excitation wavelength: 375 nm, emission wavelengths: delayed fluorescence 480 nm, phosphorescence 630 nm).

The E-type mechanism of the delayed fluorescence of I has also been confirmed by measurement of the activation energy of the thermally induced fluorescence. In Fig. 4 an Arrhenius plot of  $\log$  (intensity of delayed fluorescence/intensity of phosphorescence) versus  $1/T$  ( $K^{-1}$ ) is shown. An activation energy of  $3700\text{ cm}^{-1}$  is obtained in satisfying agreement with the  $S_1-T_1$  energy gap derived from the spectra ( $3950\text{ cm}^{-1}$ , vide supra).

$T$ ( $^{\circ}\text{C}$ )	$\tau_{\text{DF}}$ (sec)	$\tau_p$ (sec)
23	5.10	5.00
33	4.95	4.95
58	4.25	4.20
74	3.80	3.80
81	3.35	3.50

Table 1. Lifetime of delayed fluorescence ( $\tau_{\text{DF}}$ ) and phosphorescence ( $\tau_p$ ) of hexabenzocoronene (I) in perhydrocoronene at different temperatures.

## Experimental

**Substances:** The **perhydrocoronene** was a sample obtained by purification of an industrial petroleum hydrocracker deposit. The crude material was found by field-ionization mass spectrometry to be approximately 99% pure. This material was purified by extraction with cyclohexane, followed by passing through Woelm activity-grade/neutral alumina. The coronene content determined by uv absorption spectrometry proved to be less than  $3 \cdot 10^{-4}\%$ .

**Hexabenzocoronene (I)** was synthesized according to [1 b]. The luminescence spectra were independent of the excitation wavelength and the phosphorescence decay was mono-exponential.

**Preparation of spectroscopic samples:** Mixtures of perhydrocoronene and hexabenzocoronene (I) were thoroughly grinded, quickly melted in the cylindrical cells used for luminescence measurement and afterwards cooled down to room temperature.

**Measurements:** An Aminco-Bowman spectrofluorimeter equipped with an Aminco-Keirs phosphoroscope was used for the measurements of spectra and lifetimes.

**Excitation source:** Xenon lamp Hanovia 901-C1, multiplier: Hamamatsu type 809. For temperature-dependent measurements the equipment described in [10] was used.

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