

The Intra-annular Internal Heavy-atom Effect on the Fluorescence and Phosphorescence Properties of Oxygen, Sulphur or Selenium Containing Heterocyclic Systems Related to Dibenzo[b,n]perylene

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Fluorescence and phosphorescence properties of dibenzo[2,3:10,11]peryl[1,12-bcd]furan (**1**), dibenzo[2,3:10,11]peryl[1,12-bcd]thiophene (**2**), and dibenzo[2,3:10,11]peryl[1,12-bcd]selenophene (**3**) have been studied. Fluorescence quantum yields as well as phosphorescence lifetimes correlate linearly with $\sum_k c_k^2 \zeta^2$ where c_k are the Hückel AO coefficients in the HOMO of the parent carbocyclic system dibenzo[b,n]perylene (**4**) on carbon centres k to which the hetero-atom is bound, and ζ is the spin-orbit coupling constant of the heavy-atom present. The half-value concentration of fluorescence quenching (quencher: methyl iodide) of **1–3** increases with increasing strength of the internal heavy-atom effect present.

In continuation of our work on the intra-annular internal heavy-atom effect in the photophysics of polycyclic hetero-aromatic compounds [1] the photoluminescence properties of dibenzo[2,3:10,11]peryl[1,12-bcd]furan (**1**), dibenzo[2,3:10,11]peryl[1,12-bcd]thiophene (**2**) and dibenzo[2,3:10,11]peryl[1,12-bcd]selenophene (**3**) have been studied. The synthesis of compounds **1** and **2** has been described in the literature before [2, 3] while compound **3** was synthesized for the first time in the course of the present work. **3** was obtained by reacting dibenzo[b,n]perylene (**4**) with selenium at elevated temperature. The constitution of **3** is established by elemental analysis, mass spectrum and infrared spectrum. From the absence of a solo-band [4] in the infrared spectrum of **3** it follows that a reaction with selenium has occurred at the 15,16-positions of **4**. The uv spectra of **2** and **3** are very similar.

As a relative measure of the strength of the intra-annular internal heavy-atom effect the expression

$$K = \sum_k c_k^2 \zeta^2$$

is used, where c_k denote the Hückel AO coefficients in the HOMO of the parent carbocyclic system [dibenzo[b,n]perylene(**4**)] on carbon centers k to which the hetero-atom is bound and ζ denotes the spin-orbit coupling constant of the hetero-atom present [1]. In Fig. 1 the reciprocal of the phosphorescence lifetime at 77 K ($\tau_p^{-1} = k_{PT} + k_{GT}$ [sec⁻¹], where k_{PT} and k_{GT} are

the rate constants of the radiative and non-radiative deactivation of the lowest triplet state, respectively) of compounds **1–3** is plotted against K values (straight line a). Because of the very low solubility of compounds **1–3** in low-temperature glass forming solvents, 1,2,4-trichlorobenzene was used as the solvent for phosphorescence measurements [5]; trichlorobenzene exhibits only a very small external heavy-atom effect on phosphorescence lifetimes. The straight line

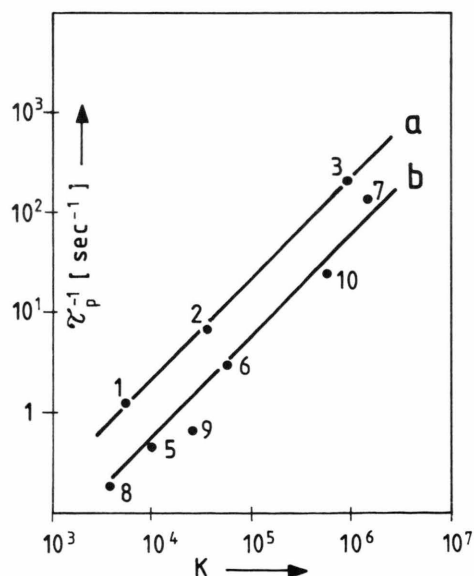


Fig. 1. Plot (logarithmic scale) of the reciprocal of the phosphorescence lifetime (τ_p^{-1} [sec⁻¹]) vs. K (for definition see text) for compounds **1–3** (straight line a) and **5–10** (straight line b).

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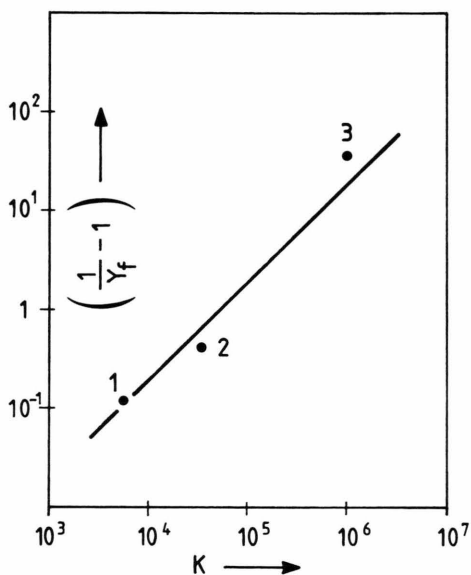
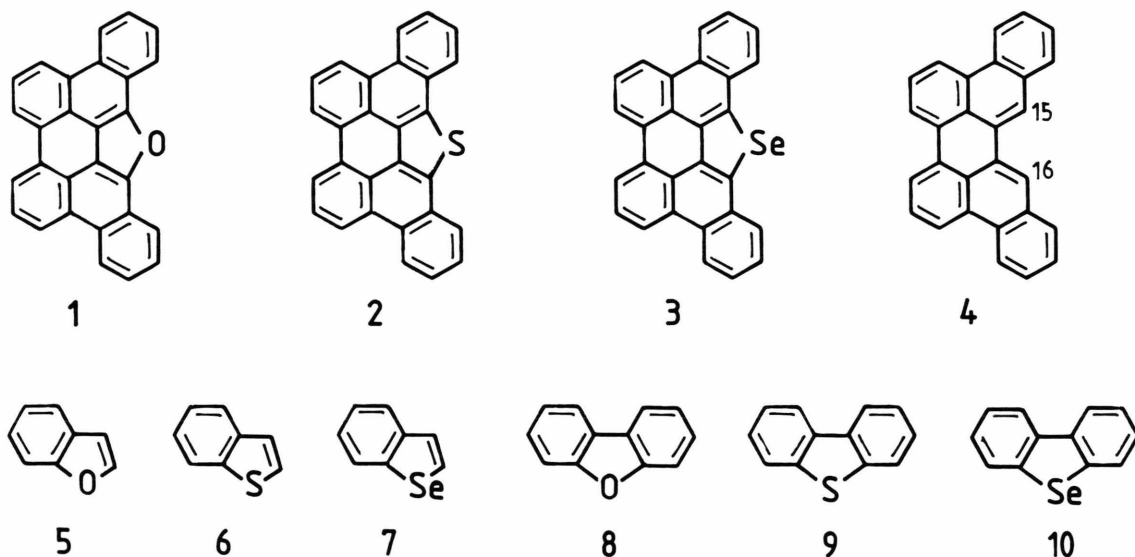


Fig. 2. Plot (logarithmic scale) of $(Y_f^{-1} - 1)$ (Y_f = fluorescence quantum yield) vs. K (for definition see text) for compounds 1–3.

b (Fig. 1) shows the relation between the K and τ_p^{-1} values for the previously studied compounds 5–10 [1]. On the assumption that the rate constant of the non-radiative transition from the lowest excited singlet (S_1) state to the ground state is negligible, one obtains

$$\frac{k_{\text{ISC}}}{k_f} = \frac{1}{Y_f} - 1,$$

Table 1. Fluorescence 0-0 band ($\tilde{\nu}_f$) (1,2,4-trichlorobenzene TCB, room temperature), phosphorescence 0-0 band ($\tilde{\nu}_p$) (TCB, 77 K), fluorescence quantum yield (Y_f) (TCB, room temperature), phosphorescence lifetime (τ_p) (TCB, 77 K) and half-value concentration of fluorescence quenching ($[Q_H]$) (toluene, room temperatures, quencher: CH_3I).

Compound	$\tilde{\nu}_f$ [cm ⁻¹]	$\tilde{\nu}_p$ [cm ⁻¹]	Y_f	τ_p [sec]	$[Q_H]$ [M · L ⁻¹]	$\sum_k c_k^2 \zeta^2$
1	22830	16370	0.90	0.85	1.25	$5.93 \cdot 10^3$
2	23640	16420	0.70	0.16	1.50	$3.68 \cdot 10^4$
3	23360	15900	0.025	0.005	≈ 16	$8.99 \cdot 10^5$
4	22270	—	0.97	—	0.70	—

where k_{ISC} is the rate constant of intersystem crossing from the S_1 state to the triplet manifold, k_f is the rate constant of fluorescence and Y_f the fluorescence quantum yield. The Y_f values of compounds 1–3 were measured in trichlorobenzene at room temperature (Table 1). The relation observed between $(Y_f^{-1} - 1)$ and K is shown in Figure 2.

In the previous paper [1] it has been shown that the influence of an external heavy-atom perturber on phosphorescence lifetimes and the vibrational structure of phosphorescence spectra is the stronger the smaller is the internal perturbation caused by the intra-annular heavy-atom. An analogous observation has now been made with regard to fluorescence quenching by an external heavy-atom perturber (methyl iodide). The half-value concentrations of fluorescence quenching (in toluene at room temperature)

of compounds **1–3** increase with increasing *K* (Table 1). – We are presently exploring an analytical application of this observation, viz. the detection and quantitative determination of small amounts of thiophene benzologues in the presence of large amounts of polycyclic aromatic hydrocarbons by fluorescence measurements in the presence of external heavy-atom perturbers.

Experimental

Substances

Dibenzo[2,3:10,11]perylene[1,12-bcd]selenophene (**3**): A mixture of 0.352 g (10^{-3} mole) dibenzo[b,n]perylene (**4**) and 0.300 g selenium was heated under argon at 380 °C for 14 h. After removing the unreacted selenium by sublimation in vacuo, the crude **3** (0.29 g) was resublimed and crystallized several times from trichlorobenzene until unreacted dibenzo[b,n]perylene was no longer detected in the uv and fluorescence spectra. Yield of pure **3**: 0.05 g (12%). **3** forms light yellow needles; melting point > 400 °C.

UV (trichlorobenzene): $\lambda_{\max}(\log \epsilon) = 418 \text{ nm} (4.26)$, 395 (4.20), 375 (3.94), 331 (4.20).

$\text{C}_{28}\text{H}_{14}\text{Se}(429)$		Calc.(%)	C 78.32	Found(%)	C 77.49
			H 3.26		H 3.46
Molecular weight	429 (mass spectrometry)				

Compounds **1** and **2** were synthesized according to known methods [2, 3].

Measurements

Phosphorescence and fluorescence measurements were made as described in [1].

While Stern-Volmer plots (intensity measurement) for compounds **1** and **2** are linear over the entire range of quencher concentrations used, this does not apply to compound **3**; possibly due to an alkylation reaction of **3** with methyl iodide only the lower part of the Stern-Volmer plot (at quencher concentrations $\leq \text{approx. } 3 \text{ M L}^{-1}$) was found to be linear and sufficiently reproducible. The half-value concentration of **3** (Table 1) was obtained by extrapolation.

Acknowledgement

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