

On the Phosphorescence of Benzologues of Furan, Thiophene, Selenophene, and Tellurophene.

A Systematic Study of the Intra-annular Internal Heavy-atom Effect

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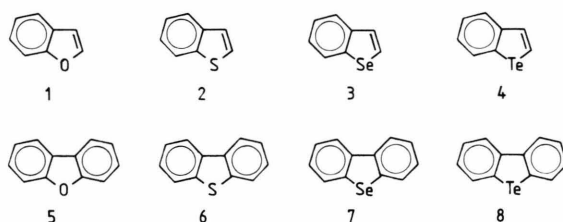
In memory of the late Professor Oskar E. Polansky

Phosphorescence in ethanol and n-pentane at 77 K of the benzologues **1–8** of furan, thiophene, selenophene and tellurophene has been investigated. The rate constants of both the radiative (k_{PT}) and non-radiative (k_{GT}) deactivation of the lowest triplet state correlate linearly with $\sum c_k^2 \zeta^2$ where c_k denotes the Hückel AO coefficients in the HOMO of the carbon atoms bound to the hetero-atom and ζ is the spin-orbit coupling constant of the hetero-atom present. – The linear correlation observed between k_{PT} and k_{GT} is an example for the Orlandi-Siebrand rule. – The influence of an external heavy-atom perturber (methyl iodide) on phosphorescence lifetimes and the vibrational structure of phosphorescence spectra is the more efficient the less efficient is the internal perturbation caused by the intra-annular heavy-atom.

1. Introduction

The intra-annular internal heavy-atom effect [1, 2] determines strongly the photoluminescence properties of many heterocyclic systems. Besides it is well suited for testing important features of the theory of internal heavy-atom effects, particularly if in a series of compounds to be studied the following conditions are met: 1. the hetero-atoms present in the different molecules of the series differ strongly with regard to their spin-orbit coupling constants [3]. 2. The systems are topologically related but the MO coefficients on carbon centres to which the hetero-atom is bound vary within the series of compounds. In this case not only the influence of different spin-orbit coupling constants but also the influence of the strength of interaction between the heavy-atom and the carbocyclic π -electronic system on photoluminescence properties can be examined. 3. Within the series of compounds studied the energy difference between the lowest triplet state T_1 and the electronic ground state S_0 shows little variation, and accordingly the size of the Franck-Condon factor governing the non-radiative $T_1 \rightarrow S_0$ transition can be regarded as being approximately

constant [4]. The compounds are then well suited for studying the electronic effect of the heavy-atom on the rate constants of both the radiative and non-radiative deactivation of the T_1 state. – Though related work has been published [5] no systematic study on the intra-annular internal heavy-atom effect where the compounds investigated meet all these three favourable conditions seems to be available. In the present work the intra-annular internal heavy-atom effect has been studied on the compounds **1–8**.



Very little is known about the influence of external heavy-atom perturbers on photoluminescence properties of substances exhibiting an intra-annular internal heavy-atom effect [6]. Therefore the external heavy-atom effect of methyl iodide on the phosphorescence of compounds **1–8** has also been studied in the present work.

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2. Results and Discussion

2.1 T_1 State Energies

T_1 state energies (phosphorescence 0–0 bands, ethanol, 77 K) as well as energies of the lowest excited singlet state S_1 (taken from fluorescence measurements, ethanol, 77 K) of compounds **1–8** are given in Table 1. As in some cases (compounds **3**, **7** and **8**) phosphorescence 0–0 bands were only poorly resolved in ethanol as the solvent, phosphorescence spectra under Shpol'skii conditions (n-pentane, 77 K) were also measured (0–0 bands see Table 1).

In series **1–4** and **5–8**, respectively, T_1 state energies decrease slightly with increasing Z number of the hetero-atom. T_1 state energies taken from Shpol'skii spectra lie in the range from 25 157 cm^{-1} (compound **1**) to 22 573 cm^{-1} (compound **4**) but for most of the compounds studied the differences between T_1 state energies are much smaller (see Table 1 and Section 2.2).

2.2 Intra-annular Internal Heavy-atom Effect

In Table 1 quantum yields of fluorescence (Φ_f), phosphorescence (Φ_p) and triplet formation (Φ_T) as well as phosphorescence lifetimes (τ_p) and rate constants of the radiative (k_{PT}) and non-radiative (k_{GT}) deactivation of the T_1 state are given (ethanol, 77 K).

A considerably simplified approach to the theory of spin-orbit coupling in molecules [7] leads to

$$k_{PT} = B \left(\sum_k c_k^2 \zeta^2 \right), \quad (1)$$

where c_k denote the Hückel AO coefficients in the HOMO of the parent carbocyclic system (in this work: styrene, biphenyl) on carbon centres k to which the hetero-atom is bound, ζ denotes the spin-orbit coupling constant of the hetero-atom and B is a constant. In the following the term $\sum_k c_k^2 \zeta^2$ will be denoted by K . $\sum_k c_k^2$ amounts to 0.449 for compounds **1–4** and to 0.179 for compounds **5–8** [8]. The following values for spin-orbit coupling constants ζ were used: oxygen ($2p^4$), 146 cm^{-1} (experimental value) [9]; sulphur ($3p^4$), 364 cm^{-1} (calculated value) [9]; selenium ($4p^4$), 1798 cm^{-1} (experimental average) [10]; and tellurium ($5p^4$), 3951 cm^{-1} (experimental value) [11].

In Fig. 1 k_{PT} values are plotted against K values for compounds **1–8** (logarithmic scale). A slope of 45° has been adopted for the straight line drawn in Figure 1. The relation found confirms the validity of (1) and hence the underlying theoretical assumptions.

In the same way, k_{GT} values have been plotted against K values in Fig. 2 adopting again a slope of 45° for the straight line shown. The significant deviation of the value for compound **4** from this straight line may be attributed to a larger Franck-Condon

Table 1. Fluorescence 0–0 band ($\tilde{\nu}_f$), phosphorescence 0–0 band ($\tilde{\nu}_p$), fluorescence quantum yield (Φ_f), phosphorescence quantum yield (Φ_p), phosphorescence lifetime (τ_p), quantum yield (Φ_T) of triplet formation, rate constant of the radiative (k_{PT}) and non-radiative (k_{GT}) $T_1 \rightarrow S_0$ transition (ethanol, 77 K).

Compound		$\tilde{\nu}_f$ [cm^{-1}]	$\tilde{\nu}_p^a$ [cm^{-1}]	Φ_f	Φ_p	τ_p [sec]	Φ_T	k_{PT} [sec^{-1}]	k_{GT} [sec^{-1}]
Benzo[b]furan	(1)	33 110	25 130 (25 157)	0.63	0.24	2.35	0.37	0.28	0.15
Benzo[b]thiophene	(2)	32 895	24 040 (24 010)	0.02	0.42	0.32	0.98	1.34	1.79
Benzo[b]selenophene	(3)	32 360	23 585 (23 585)	$5 \cdot 10^{-4}$	0.27	$7 \cdot 10^{-3}$	≈ 1	38.6	104
Benzo[b]tellurophene	(4)	–	22 730 (22 573)	$< 5 \cdot 10^{-4}$	0.18	$6 \cdot 10^{-4}$	≈ 1	300	1370
Dibenzo[b, d]furan	(5)	33 110	24 450 (24 510)	0.40	0.29	5.6	0.60	0.086	0.092
Dibenzo[b, d]thiophene	(6)	30 395	24 330 (24 272)	0.025	0.47	1.5	0.97	0.32	0.35
Dibenzo[b, d]selenophene	(7)	29 670	23 980 (23 866)	$1 \cdot 10^{-3}$	0.74	0.04	≈ 1	18.5	6.5
Dibenzo[b, d]tellurophene	(8)	–	23 530 (23 585)	$< 5 \cdot 10^{-4}$	0.79	$2.5 \cdot 10^{-3}$	≈ 1	316	84

^a Figures in brackets: phosphorescence 0–0 band in n-pentane, 77 K.

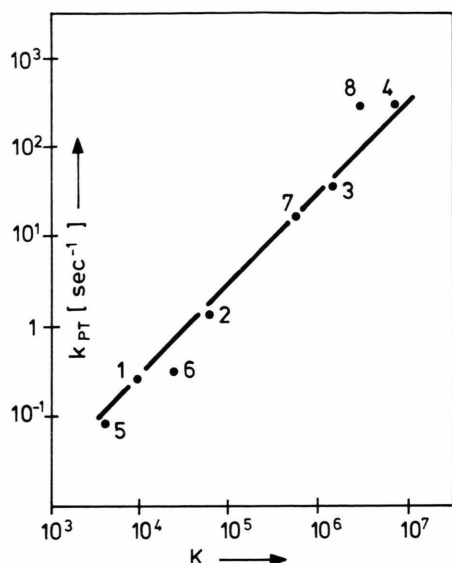


Fig. 1. Plot of the rate constant (k_{PT}) of the radiative $T_1 \rightarrow S_0$ transition vs. K (for definition see Eq. (1) and text) for compounds 1–8.

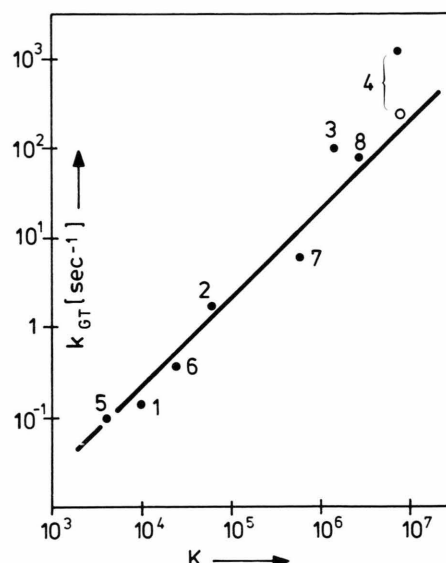


Fig. 2. Plot of the rate constant (k_{GT}) of the non-radiative $T_1 \rightarrow S_0$ transition vs. K (for definition see Eq. (1) and text) for compounds 1–8. (The circle (compound 4) corresponds to the Franck-Condon corrected k_{GT} value).

factor for **4** compared to that for the other compounds. The difference between the T_1 state energies of compounds **1** and **4** equals to 2584 cm^{-1} while the corresponding differences for all other compounds studied is $\lesssim 1600\text{ cm}^{-1}$. Corresponding to Siebrand's plot [4] of k_{GT} values versus T_1 state energies for polycyclic aromatic hydrocarbons, a decrease in T_1 state energy of 2500 cm^{-1} corresponds to an increase of $\Delta \log k_{GT} \approx 0.7\text{ sec}^{-1}$. The circle in Fig. 2 marks the "Franck-Condon corrected" k_{GT} value for compound **4**. It is quite obvious that a relation analogous to (1) also holds for k_{GT} values. This can be rationalized in terms of the theory of non-radiative electronic transitions in molecules [12] by the assumptions that (i) the density of the (vibronic) states factor is approximately constant in the series of compounds studied and (ii) the electronic factor, being determined by the size of the spin-orbit matrix element, is proportional to K .

As both k_{PT} and k_{GT} correlate linearly with K an approximate linear correlation also exists between k_{PT} and k_{GT} (Fig. 3), this being an example for the so-called Orlandi-Siebrand rule [13, 14]. Orlandi and Siebrand [13] have shown by quantum mechanics that in molecules the rate constants of radiative and non-radiative transitions occurring between the same initial and final states are to some degree correlated, i.e.

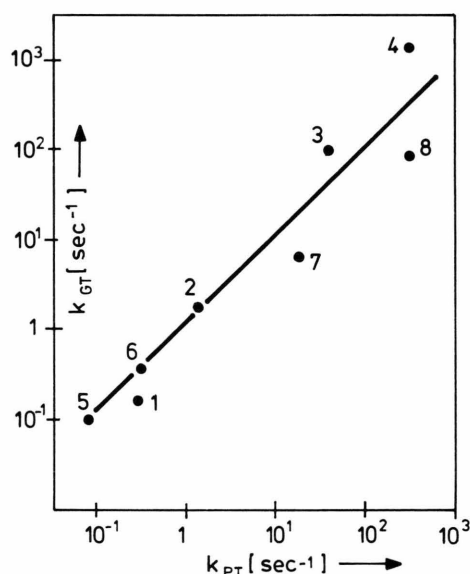
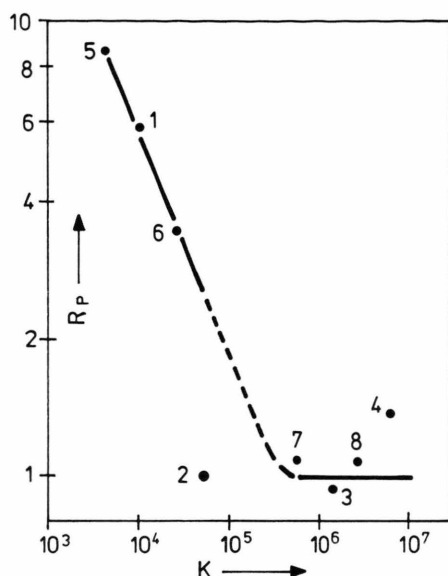


Fig. 3. Plot of the rate constant k_{PT} (radiative $T_1 \rightarrow S_0$ transition) vs. rate constant k_{GT} (non-radiative $T_1 \rightarrow S_0$ transition) for compounds 1–8.

in a series of related molecules higher radiative rate constants should be accompanied by higher rate constants for the competing non-radiative transition. Since the Orlandi-Siebrand rule operates independently of the Franck-Condon principle a relation be-

Table 2. Phosphorescence lifetime in EPA (τ_p^{EPA}), shortest resolvable time constant in JEPA (τ_p^{JEPA}) and $R_p = \tau_p^{\text{EPA}}/\tau_p^{\text{JEPA}}$.

Compound	1	2	3	4	5	6	7	8
τ_p^{EPA} [sec]	2.35	0.35	$6.4 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	5.2	1.4	0.04	$3 \cdot 10^{-3}$
τ_p^{JEPA} [sec]	0.4	0.35	$6.8 \cdot 10^{-3}$	$7 \cdot 10^{-4}$	0.6	0.4	0.036	$2.8 \cdot 10^{-3}$
R_p	5.9	1	0.94	1.4	8.7	3.5	1.1	1.1

Fig. 4. Plot of R_p (for definition see text) vs. K (for definition see Eq. (1) and text) for compounds 1–8.

tween e.g. k_{PT} and k_{GT} can only be observed if the Franck-Condon factors governing the transition, e.g. $T_1 \rightarrow S_0$, are approximately constant in the series of molecules studied. As already mentioned, the molecules studied in the present work meet this condition.

2.3 External Heavy-atom Effects

A mixture, known as JEPA [15], of 10 volumes of EPA (ethanol-isopentane-ether 2:5:5, vol/vol) and 1 volume of methyl iodide was used as an external heavy-atom solvent at 77 K. The well-known observation that phosphorescence decays are multiexponential in the presence of alkyl halides [15, 16] is being confirmed in the present work. However, the ratio R_p of the phosphorescence lifetime in EPA (τ_p^{EPA}) to the shortest resolvable time constant in JEPA (τ_p^{JEPA}) can be regarded as a suitable measure of the external

heavy-atom effect on phosphorescence life-times. τ_p as well as R_p values are given in Table 2. In Fig. 4, R_p is plotted versus K (logarithmic scale). R_p decreases with increasing K and reaches the limit value of ≈ 1 for K values $> 10^5$.

The observed ("saturation") effect as depicted in Fig. 4 indicates that the external perturbation is the more efficient the less efficient is the internal perturbation caused by the intra-annular heavy-atom.

While the phosphorescence spectra (in ethanol or EPA, 77 K) of the furan benzologues 1 and 5 show intense 0–0 bands, these are weak in the spectra of all other compounds studied here. In such cases it has frequently been observed [17, 18] that external heavy-atom perturbors, e.g. methyl iodide strongly enhance the intensity of the 0–0 band. This is due to a second-order mixing of perturber singlet-state character into the T_1 state of the phosphorescent molecule [19]. There is some indication that this "vibrational effect" is the most sensitive external heavy-atom effect known [18].

Phosphorescence spectra of compounds 2, 3, 4, 6, 7, and 8 have been measured under identical conditions in EPA and JEPA. (For a typical example of the vibrational external heavy-atom effect (compound 6) see Fig. 1 in [6]). As a measure of the strength of the vibrational heavy-atom effect the expression

$$\left[\left(\frac{I_{0-0}}{I_{0-1}} \right)_{\text{JEPA}} - \left(\frac{I_{0-0}}{I_{0-1}} \right)_{\text{EPA}} \right] / \left(\frac{I_{0-0}}{I_{0-1}} \right)_{\text{EPA}}$$

was used where I_{0-0} and I_{0-1} denote the intensity of the 0–0 band or the second band respectively observed in the phosphorescence spectra in EPA or JEPA. The V -values were found to be < 0.05 for compounds 3 and 8. The result obtained for 4 ($V = 0.09$) is uncertain because of poor spectral resolution. In the series 6 ($V = 1.30$), 2 (0.425) and 7 (0.17) V -values decrease with increasing K . Thus the vibrational external heavy-atom effect shows the same type of dependence on the strength of the internal perturbation as has been observed with the phosphorescence lifetimes.

Experimental

Substances

Compounds **1**, **2**, **5**, and **6** were highly purified samples from the collection of reference substances of the spectroscopy laboratory of Rütgerswerke AG, Castrop-Rauxel. Compound **8** was a sample obtained from Professor D. Hellwinkel, Heidelberg. Compounds **3**, **4**, and **7** were synthesized according to procedures described in the literature *vic. 3* according to [20], **4** [21], and **7** [22].

The purity of the samples was ascertained by standard instrumental analytical methods. The fluorescence and phosphorescence spectra proved to be independent of the excitation wavelength. The phosphorescence decay curves were monoexponential.

9,10-Diphenylanthracene (99%) was a commercial sample (Aldrich); its purity was ascertained by fluorescence spectroscopy. Methyl iodide was a commercial sample from Merck, Darmstadt.

All solvents used (ethanol, diethylether, isopentane, n-pentane) were of Merck Uvasol quality.

Measurements

Phosphorescence and fluorescence measurements were made on an Aminco-Keirs spectrophosphorimeter and a Perkin-Elmer MPF 44 E spectrofluorimeter.

Phosphorescence lifetimes were determined using the Aminco-Keirs spectrophosphorimeter equipped with a Tektronix 5403 oscillograph.

Phosphorescence and fluorescence quantum yields were derived according to the method described in [23] from the quantum-corrected spectra measured in ethanol at 77 K on the MPF 44 E spectrofluorimeter (reference substance: 9,10-diphenylanthracene, fluorescence quantum yield = 1.00, ethanol, 77 K [24]). The Φ_p value for **2** (0.77 [25]) found previously had to be revised.

Quantum yields (Φ_T) of triplet formation were calculated according to: $\Phi_T = 1 - \Phi_f$, i.e. assuming that the non-radiative deactivation of the S_1 state occurs solely by intersystem crossing into the triplet manifold. For calculating k_{PT} and k_{GT} values from experimental data the following equations were used:

$$k_{PT} = \Phi_p (\Phi_T \tau_p)^{-1} [\text{sec}^{-1}];$$

$$k_{GT} = (\tau_p)^{-1} - k_{PT} [\text{sec}^{-1}].$$

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