Empirical Quantitative Relationship between Molecular Structure and Phosphorescence Transition Energy of Polycyclic Aromatic Thiophenes

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Z. Naturforsch. **42 a**, 735–738 (1987); received April 16, 1987

Empirical quantitative models have been studied that relate the phosphorescence transition energies of thiophene benzologs and corresponding aromatic hydrocarbon systems. Phosphorescence 0,0 bands, phosphorescence/fluorescence quantum yield ratios, and phosphorescence lifetimes of 12 thiophene benzologs of which the phosphorescence properties were unknown are reported.

Polycyclic aromatic thiophenes (thiaarenes) exhibit vibronically well-resolved phosphorescence spectra in rigid matrices (e.g. ethanol at 77 K). Although several papers on the properties of the lowest triplet (T_1) states of thiophene benzologs have appeared in the literature [1–5], no systematic study on the relationship between the T_1 state energies (phosphorescence 0,0 bands) of polycyclic aromatic hydrocarbons and their thiophene analogs seems to be available. Such relationships, however, could be of some value in connection with the structure elucidation of unknown thiaarenes. The present study concerns the thiaarenes **1** – **20**. Phosphorescence data of compounds **1**, **4**, **7**, and **12** – **16** were taken from the literature, while to our knowledge, data of the remaining compounds hitherto have not been reported (with the exception of the phosphorescence 0,0 band energies of **5, 9,** and **18** measured in a Shpol'skii matrix at 63 K [4]).

Three different linear models A, B, and C were tested by correlation analysis. The models differ by the variables $k, \ldots, o$ which are defined as follows:

$$k = \tilde{\nu}_p^T, \quad l = \tilde{\nu}_p^{Ar}, \quad m = \tilde{\nu}_p^P, \quad n = \Delta(\tilde{\nu}_p^T - \tilde{\nu}_p^P),$$
$$o = \Delta(\tilde{\nu}_p^{Ar} - \tilde{\nu}_p^P).$$

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$\tilde{\nu}_p$ are the phosphorescence 0,0 bands (cm^{-1}) in ethanol at 77 K of systems T, Ar, and P where T denotes the thiophene benzolog (for example: phenanthro[4,5-bcd]thiophene **17**), Ar represents the corresponding isosteric hydrocarbon (pyrene), and P represents the largest part system present in both T and Ar (phenanthrene). Sample number was 17 for all models tested. Thiophene benzologs **5**, **8**, and **9** were not included because $\tilde{\nu}_p$ values of the corresponding part systems were not available. $\tilde{\nu}_p$ values of the thiophene benzologs are given in Table 1 [6]. The $\tilde{\nu}_p$ values of the corresponding Ar and P systems were taken from the literature [2, 7] or measured in the course of this work and found to agree with published data. In Table 2, the models studied are defined and the results obtained by correlation analysis are summarized.

Application of model A shows that in many cases $\tilde{\nu}_p^T$ is regularly shifted to shorter wavelengths compared to $\tilde{\nu}_p^{Ar}$ (Table 2). However, 5 outliers were identified by statistical tests (thiophene benzologs **3**, **7**, and **12** – **14**). Moreover, there are no structural similarities among these outliers (or their corresponding hydrocarbons), and therefore a uniform structure-based distinction between systems that are expected to fit the linear correlation and those that do not is not possible. Therefore, model A is apparently of little value in structure elucidation of thiaarenes.

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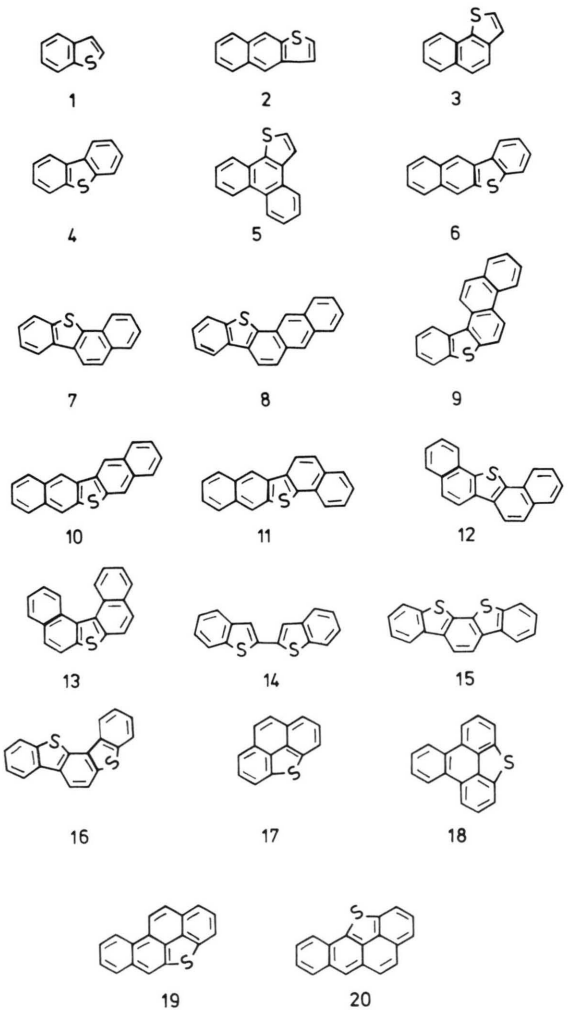
Table 1. Phosphorescence data of thiophene benzologs (Ethanol, 77 K).

Compound No.	$\tilde{\nu}_{phos}$ [cm^{-1}]	Φ_p/Φ_f	τ_{phos} [sec]
1 [a]	24 040	22	0.35
2	17 950	0.035	0.04
3	21 550	>50	1.75
4 [b, c]	24 325	13	1.50
5	21 505	9.8	0.80
6	18 620	3.8	0.25
7 [d]	20 830	–	0.90
8	15 150	–	–
9	20 490	2.6	1.35
10	18 415	0.35	0.55
11	17 270	0.47	0.25
12 [c]	20 660	10.2	1.60
13 [c]	18 350	2.2	0.19
14 [a]	17 600	9.7×10^{-4}	0.008
15 [a]	22 420	1.6	1.00
16 [a]	23 256	16.7	0.60
17	19 570	4.0	0.35
18	21 930	35	1.05
19	17 795	0.20	0.15
20	16 000	–	–

[a] taken from l.c. [5]; [b] taken from l.c. [1];
[c] taken from l.c. [3]; [d] taken from l.c. [2].



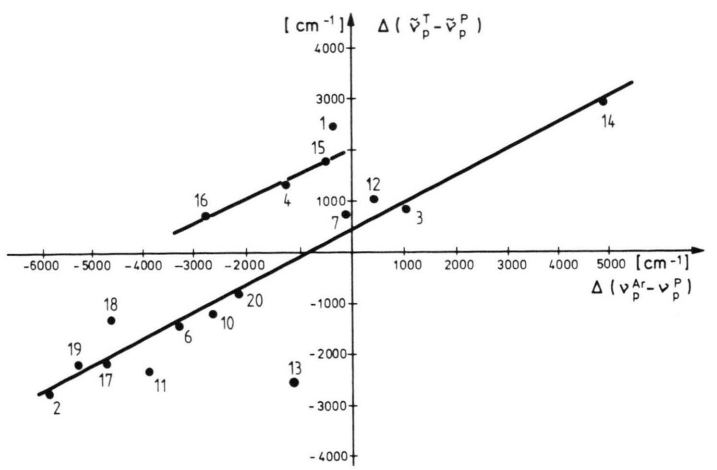


Fig. 1. Relation between phosphorescence shift $\Delta(\tilde{\nu}_p^T - \tilde{\nu}_p^P)$ and $\Delta(\tilde{\nu}_p^{Ar} - \tilde{\nu}_p^P)$ (for details see text).

1 = Benzo[b]thiophene
2 = Naphtho[2,3-b]thiophene
3 = Naphtho[1,2-b]thiophene
4 = Dibenzo[b,d]thiophene
5 = Phenanthro[9,10-b]thiophene
6 = Benzo[b]naphtho[2,3-d]thiophene
7 = Benzo[b]naphtho[2,1-d]thiophene
8 = Anthra[1,2-b]benzo[d]thiophene
9 = Benzo[b]phenanthro[1,2-d]thiophene
10 = Dinaphtho[2,3-b: 2′,3′-d]thiophene
11 = Dinaphtho[1,2-b: 2′,3′-d]thiophene
12 = Dinaphtho[1,2-b: 2′,1′-d]thiophene
13 = Dinaphtho[2,1-b: 1′,2′-d]thiophene
14 = 2,2′-Bis-benzo[b]thiophene
15 = Benzo[2,1-b: 3,4-b′]bis[1]benzothiophene
16 = Benzo[1,2-b: 3,4-b′]bis[1]benzothiophene
17 = Phenanthro[4,5-bcd]thiophene
18 = Triphenyleno[1,12-bcd]thiophene
19 = Chryseno[4,5-bcd]thiophene
20 = Benzo[2,3]phenanthro[4,5-bcd]thiophene

Table 2. Correlations between phosphorescence 0,0 bands [cm^{-1}] of thiophene benzologs and corresponding aromatic hydrocarbons (Ethanol, 77 K).

Model	y	x	Function	[a]	[b]	[c]
A	k	l	$y = 1.139\,x$	12	0.9681	5
B	k	m	$y = 0.908\,x$ ($\sigma_b = \pm 0.0105$) [d]	9	0.9211	–
			$y = 1.069\,x$ ($\sigma_b = \pm 0.016$) [d]	8	0.9517	–
C	n	o	$y = 0.529\,x + 434$	12	0.9779	2
			$y = 0.471\,x + 2006$	3	0.9898	–

[a]: number of points fitting the correlation;
[b]: correlation coefficient;
[c]: number of outliers;
[d]: standard deviation with regard to slope.

Model B has already been recently introduced [5]. In this model, $\tilde{\nu}_p$ of the thiophene benzologs is compared with $\tilde{\nu}_p$ of the part systems. However, it previously has not been recognized that two different correlations actually exist (Table 2). One of them holds for thiophene benzologs with $\tilde{\nu}_p^T$ lying at longer wavelengths compared to the part system (compounds **2**, **6**, **10**, **11**, **13**, and **17** – **20**), and the other for those with $\tilde{\nu}_p^T$ lying at shorter wavelengths (**1**, **3**, **4**, **7**, **12**, and **14** – **16**). Statistical tests reveal that the slopes of the correlations must be regarded as different, so that unification of the correlations to yield one new correlation is not justified. As with model A, no uniform structure-based distinction can be made between the compounds that fit the one or the other correlation, respectively. Although model B governs the whole sample studied (no outliers), its predictive power in structure elucidation of unknown thiophene benzologs suffers from rather low correlation coefficients and the lack of structural criteria that, in a given case, allow a reliable decision to be made as to which of the correlations must be used.

Model C relates the phosphorescence shifts observed between the part system P and the arene Ar or thiaarene T, respectively (Table 2). Thus, it is constructed so as to compare the influence of two different "substituents" (the sulphur atom or the C=C double bond) on the same part system. A good linear correlation is obtained for 12 of the 17 thiaarenes examined (Table 2 and Figure 1). Three additional systems (**4**, **15**, and **16**) fit into another linear correlation (Table 2 and Figure 1). The fitted straight lines have nearly the same slopes but different intercepts. Compounds **4**, **15**, and **16** are topologically clearly related in that the corresponding part systems contain only benzene rings connected by single bonds (biaryl type). On the other hand, no systems of that kind are contained in the group of compounds that fit the other relationship. Thus, unlike as with model B, a straightforward assignment of compounds to the correlations can be made on structural grounds. However, two systems (**1** and **13**) have been identified as outliers with regard to both model C correlations. Perhaps not accidently, thiaarene **13** (and the corresponding Ar system) are the only compounds in the entire sample where nonplanarity is likely to influence the phosphorescence transition energy. It has been observed [8] that the phosphorescence transition of nonplanar aromatic compounds lies at longer wavelengths compared to structurally related but planar compounds, and this effect may be more pronounced in the thiaarene than in the hydrocarbon series. This is supported by the observation that the phosphorescence 0,0 bands of picene and dibenzo[c,g]phenanthrene are different by 280 cm^{-1}, while for the analogous thiaarenes (**12** and **13**) this difference amounts to 2310 cm^{-1}. The structurally most simple member among the systems studied, benzo[b]thiophene (**1**), is the second outlier identified. However, no explanation can be given in this case.

In Table 1 are also included phosphorescence/fluorescence quantum yield ratios (Φ_p/Φ_f) and phosphorescence lifetimes (τ_p) for most of the compounds studied. With few exceptions, the Φ_p/Φ_f values are rather large. This is not unexpected because the sulphur atom exhibiting an intra-annular

heavy-atom effect [3, 9] provides for efficient intersystem crossing from the lowest singlet excited state to the triplet manifold. A dramatic exception from this behavior (compound **14**) has recently been studied in detail [5].

Experimental

Substances: All compounds measured are from M. L. Lee's laboratory or from the spectroscopy laboratory of Rütgerswerke AG, Castrop-Rauxel. The phosphorescence spectra proved to be independent of the excitation wavelength, and phosphorescence decays were monoexponential. Ethanol was of Merck Uvasol quality.

Measurements: Phosphorescence spectra were measured in ethanol at 77 K using an Aminco-Keirs spectrophosphorimeter. Phosphorescence/fluorescence quantum yield ratios were obtained from quantum-corrected spectra taken on a Perkin-Elmer MPF 44 E spectrofluorimeter.

For the measurement of phosphorescence lifetimes, the Aminco-Keirs spectrophosphorimeter equipped with an oscillograph Tektronix 5403 was used.

Acknowledgement

We thank Mr.'s K. Bullik and Th. Preising, Rütgerswerke AG, for valuable assistance with the experiments and regression analyses.

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