

PHOTOPHYSICS OF PSEUDOAZULENES: 7-AZAINDOLE DERIVATIVES

J. WALUK, B. PAKUŁA and S. J. KOMOROWSKI

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw (Poland)

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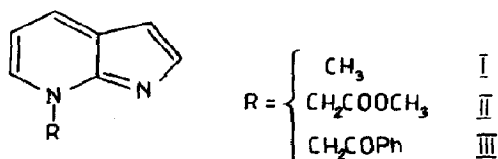
Summary

Three pseudoazulenes derived from 7-azaindole reveal photophysical properties characteristic of this class of compounds: strongly temperature-dependent $S_1 \rightarrow S_0$ fluorescence, weak phosphorescence, very small S_1-T_1 splitting, decrease in dipole moment on excitation to $S_1(\pi\pi^*)$ and $S_2(\pi\pi^*)$ states and dimerization at low temperatures in non-polar solvents. Photoacoustic studies show that internal conversion is the dominant channel for the deactivation of the lowest excited singlet state.

1. Introduction

The unusual spectroscopic features of azulene, such as $S_2 \rightarrow S_0$ and $S_2 \rightarrow S_1$ fluorescence and lack of phosphorescence or large temperature dependence of $S_1 \rightarrow S_0$ emission, make this compound a subject of continuous experimental and theoretical research [1 - 30]. Some of its substituted derivatives [30 - 36] and pseudoazulenes (structures in which one or more $-\text{CH}=\text{CH}-$ groups have been replaced by a heteroatom [37 - 42]) behave similarly to azulene.

In previous work [43] we have measured the dipole moment changes after electronic excitation of three pseudoazulenes derived from the 7-azaindole skeleton: 7-methyl-7*H*-pyrrolo[2,3-*b*]pyridine (I), 7*H*-pyrrolo[2,3-*b*]pyridine-7-acetic acid methyl ester (II) and 1-phenyl-2-(7*H*-pyrrolo[2,3-*b*]pyridin-7-yl)ethanone (III):



It was pointed out, using the solvent shift method, that a decrease in dipole moment occurs in both the $S_1(\pi\pi^*)$ and the $S_2(\pi\pi^*)$ electronic states. Moreover, the direction of the dipole moment is reversed, which is caused by electronic charge flow from the five- to the six-membered ring. No $S_2 \rightarrow S_0$ emission was observed. Except for the lack of emission, this pattern of behaviour is similar to that of azulene [23 - 25]. Looking for further analogies, we have investigated the luminescence properties of I - III. Measurements of luminescence spectra, quantum yields, lifetimes, polarization, temperature dependence, external heavy atom effect and triplet formation efficiency were carried out in order to solve the kinetics and to determine the values of the excited state depopulation rate constants. The results are discussed in comparison with other azulene-like compounds.

2. Experimental details

The pseudoazulenes were synthesized and purified according to ref. 44. All solvents (Merck, spectral grade) were checked for absorption and luminescence before use. Ethyl iodide (POCh, Gliwice) was distilled just prior to measurements and stored in the dark.

The luminescence spectra were recorded on a Jasny spectrofluorometer [45]. Quinine sulphate in 0.1 N H_2SO_4 ($\varphi_{fl} = 0.51$) served as a standard for the quantum yield determination. Fluorescence decay curves were obtained after excitation with an IGT 50 nitrogen laser; the lifetimes were then obtained by reiterative reconvolution [46].

The method of pulsed photoacoustic calorimetry [47 - 48] was applied for the determination of the triplet formation efficiency φ_T . Briefly, the procedure consists of measuring the amounts of "fast" and "slow" heat (occurring on a time scale shorter and longer than 1 μs respectively) released by the sample after excitation by a nitrogen laser (IGL 300/2) pulse. The experiment is performed first in the absence of oxygen and then repeated in aerated solution. The results are compared with those obtained for compounds of known φ_T . Benzanthracene ($\varphi_T = 0.80$) and aminoxyl biradical, bis[2,4,5,5-tetramethylazolidin-1-oxyl]-2-yl]methane ($\varphi_T = 0$), served as standards.

INDO/S calculations [49] were also performed for I in order to obtain singlet and triplet excitation energies, charge densities, dipole moments and transition moment directions. The indole geometry [50] was assumed in the input with the N-C (methyl) distance set to 1.47 Å. All singly excited configurations lying below 10 eV (singlets) or 15 eV (triplets) were included in the CI procedure.

3. Results and discussion

3.1. Absorption and luminescence

It was found that the spectroscopic features of all three compounds under investigation are very similar. Therefore, we restrict ourselves to

showing only the spectra of III, the most stable compound, on which most extensive measurements could be done. Whenever quantitative results are being considered, we shall explicitly refer to each pseudoazulene.

Figures 1 and 2 present the absorption, luminescence and excitation spectra of III in a non-polar solvent, 3-methylpentane (3MP), and in butanol. Only one emission, corresponding to the $S_1 \rightarrow S_0$ transition, is observed, its

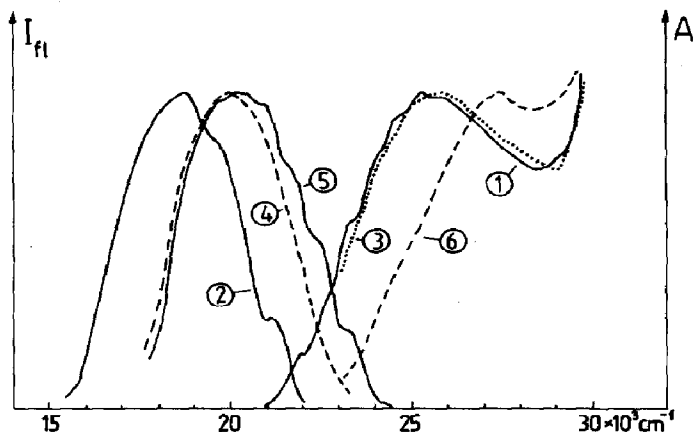


Fig. 1. Luminescence and absorption spectra of III in 3MP: spectrum 1, room temperature absorption; spectrum 2, room temperature fluorescence; spectrum 3, room temperature fluorescence excitation; spectrum 4, fluorescence at 143 K; spectrum 5, fluorescence at 93 K; spectrum 6, fluorescence excitation at 93 K.

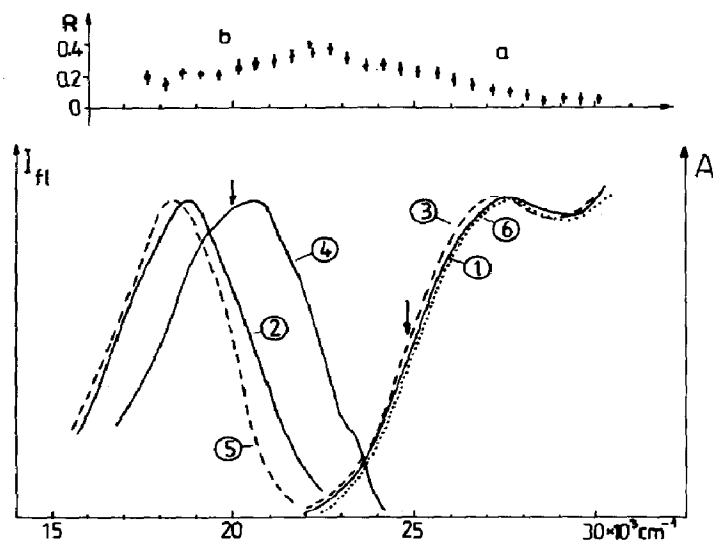


Fig. 2. Absorption and fluorescence of III in butanol: spectrum 1, absorption at 293 K; spectrum 2, fluorescence at 293 K; spectrum 3, fluorescence excitation at 293 K; spectrum 4, fluorescence at 103 K; spectrum 5, phosphorescence at 103 K; spectrum 6, fluorescence excitation at 103 K; curve a, anisotropy of fluorescence excitation at 103 K; curve b, fluorescence anisotropy at 103 K. The regions of excitation and monitoring of the polarization spectra are indicated by arrows.

excitation spectrum coinciding with the first absorption band. Taking into account the sensitivity of our apparatus, we conclude that the possible $S_2 \rightarrow S_0$ fluorescence has a quantum yield lower than 10^{-5} .

The fluorescence spectrum in 3MP, structured at 293 K, becomes blurred as the temperature is lowered, but, at around 110 K, recovers the structure (see Fig. 1). The same behaviour was observed for I and II. The excitation spectra at low temperatures are blue shifted compared with those taken at 293 K and resemble the spectra in alcohols (Fig. 2). This could suggest that some complexes with hydroxylic impurities are responsible for the low temperature emission. However, such a hypothesis can be excluded on noting that the structureless emission begins to appear at lower temperatures in solutions of lower pseudoazulene concentration. This implies that low temperature fluorescence in non-polar solvents is due to dimers or some higher oligomers. It should be recalled that the formation of oligomers and dimers in non-polar solvents has been observed in azulene itself [26].

In the present case, dimerization should be additionally stabilized by much larger dipole moments in the ground state of I, II and III (3.2 debyes, 3.8 debyes and 4.0 debyes respectively [43]), compared with azulene (1.0 debye [25]).

Fluorescence in alcohols does not reveal the peculiarities observed in non-polar solvents. As the temperature is lowered, the emission shifts to the blue: at around 120 K the spectrum becomes weakly structured. Neither the absorption nor the excitation spectra is shifted with temperature and the two match each other very closely.

A weak phosphorescence appears at low temperatures in alcohols. Its low quantum yield, about 10^{-4} , and the spectral overlap with much stronger fluorescence precluded the measurements of excitation and polarization spectra. It is interesting to note a very small energy distance (2500 cm^{-1}) between the maxima of fluorescence and phosphorescence.

3.2. Analysis of the temperature dependence of fluorescence

The fluorescence intensity in alcohols is very strongly temperature dependent: at 100 K its quantum yield is about 40 times larger than that at room temperature ($(8 \pm 3) \times 10^{-3}$ for I and $(4 \pm 2) \times 10^{-3}$ for II and III at 293 K). In order to analyse the kinetics of S_1 depopulation, we assumed that the total radiationless rate constant consists of two terms, of which only one is temperature dependent:

$$k_{nr} = k_1 + k_2 \exp\left(-\frac{\Delta E}{RT}\right) \quad (1)$$

We can thus write for the fluorescence quantum yield

$$\varphi_n(T) = \frac{k_r}{k_r + k_1 + k_2 \exp(-\Delta E/RT)} \quad (2)$$

and after some simple transformations

$$\ln\left(\frac{1}{\varphi_{fl}} - K - 1\right) = \ln k - \frac{\Delta E}{RT} \quad (3)$$

where k_r is the radiative rate constant of S_1 depopulation, $K = k_1/k_r$ and $k = k_2/k_r$.

To optimize the parameters appearing in eqn. (3) it is necessary to use two-step least-squares fitting. First, $\ln k$ and ΔE are calculated while the value of K is held fixed. The procedure is then repeated with different K values until the minimum of the sum of the squares of the differences between computed and experimental values is achieved.

The results are presented in Table 1 and Fig. 3. Upper and lower limits of K , k_1 and k_2 are based on the following considerations [51]: if instead of

TABLE 1

Analysis of the temperature dependence of fluorescence

Compound	ΔE (cm ⁻¹)	k_1 ($\times 10^7$ s ⁻¹)	k_2 ($\times 10^{10}$ s ⁻¹)
I	610 \pm 50 ^a	0.1 - 1.0	0.5 - 1.3
II	550 \pm 50	1.3 - 4.0	1.5 - 3.6
III	650 \pm 50	1.4 - 4.1	1.4 - 3.3

k_1 is the sum of all the temperature-independent radiationless rate constants; k_2 is the pre-exponential factor in the temperature-dependent rate constant.

^aThe confidence limit is equal to three standard deviations.

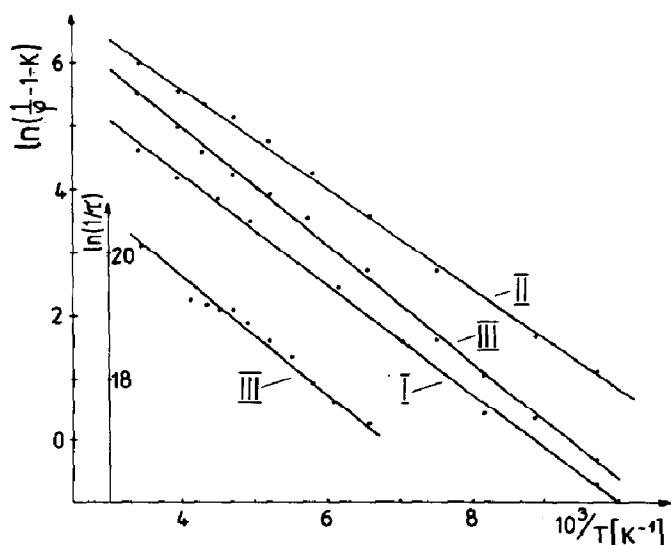


Fig. 3. Plot of $\ln(1/\varphi_{fl} - 1 - K)$ vs. $1/T$ (the fluorescence quantum yields were measured in ethanol:methanol (4:1)). Inset: plot of $\ln(1/\tau_{fl})$ vs. $1/T$ for III (measured in butanol).

using φ , the real value of the quantum yield, we use some $\varphi' = C\varphi$, then distorted results, K' , $\Delta E'$ and k' , are obtained. It is easy to show that

$$\Delta E = \Delta E' \quad (4)$$

$$K = C(K' + 1) - 1 \quad (5)$$

$$k = Ck' \quad (6)$$

where the unprimed symbols denote the true values.

It follows from eqns. (3) - (6) that, when the accuracy in the quantum yield measurement is $\pm 100a\%$ (or, in other words, $C = 1 \pm a$), then K lies between $K' - a(K' + 1)$ and $K' + a(K' + 1)$. The limits of k are $(1 - a)k'$ and $(1 + a)k'$. The activation energy value ΔE is not affected by the error in the quantum yield measurement and, as such, should be treated as the most reliable parameter.

It is frequently assumed in the analysis of the temperature dependence of fluorescence that $K = 0$. This approach is justified only if the temperature-dependent rate constant dominates the depopulation process and thus can be used only over a limited temperature range.

The procedure applied in this paper can only be used when data are taken at both "high" and "low" temperatures, *i.e.* in the regions in which temperature-dependent and temperature-independent rate constants alternately play the major part. In the present case, the "borderline" between these two regions lies at about 140 K. Thus, it would be incorrect to try to find K and k from the data taken only above or below this temperature: the fitted values would be very inaccurate. As an illustration, $\ln(1/\tau)$, but not $\ln(1/\tau - k_r - k_1)$, is plotted against $1/T$ in the inset of Fig. 3 for the temperature dependence of the S_1 lifetime taken down only to 153 K. The slope ($-\Delta E/R$) remains almost unaffected by this simplification, indicating very small contributions of k_r and k_1 in this temperature range, which make them impossible to be extracted from such a plot.

We assumed that our experimental accuracy in quantum yield determination lies within $\pm 30\%$ at 293 K. As the temperature was lowered, a 10% - 20% increase in absorption occurred. It was partially compensated by the increase in n^2 , the square of the refractive index (10%). Thus, we can safely put $a = 0.4$.

From the quantum yield and lifetime measurements at 293 K ($\tau = 1.8$ ns for I; $\tau \approx 1$ ns for II and III) we obtain the value of the radiative rate constant $k_r = 4 \times 10^6 \text{ s}^{-1}$ for all three compounds. This is to be compared with $7 \times 10^6 \text{ s}^{-1}$, a value obtained from the integration of the first absorption band. The latter number, however, is apparently an upper limit, as the $S_0 \rightarrow S_1$ and the stronger $S_0 \rightarrow S_2$ bands overlap.

3.3. The nature of the temperature-dependent radiationless process

A strong temperature dependence of the $S_1 \rightarrow S_0$ fluorescence has already been observed for many azulene derivatives [32 - 34]. The nature of the radiationless transition responsible for the depopulation is not clear;

some researchers [34] claim it is internal conversion, as in azulene itself [9, 10]. In the present case, we first observed that the fluorescence efficiencies did not considerably change when ethyl iodide is added to the solution at room temperature. However, such a lack of heavy atom effect, apparently suggesting that internal conversion is the dominant route for S_1 radiationless deactivation, may not be proof when the initial undisturbed intersystem crossing rate constant is already of the order of 10^9 s^{-1} [52]. Similarly, the very small phosphorescence quantum yield may only reflect the fact that both the $S_1 \xrightarrow{\text{nr}} T_1$ and the $T_1 \xrightarrow{\text{nr}} S_0$ radiationless intersystem crossing processes are very efficient.

The proof that internal conversion is the dominant channel for S_1 depopulation was provided by the results of a photoacoustic study on III. The value of the triplet formation efficiency at 293 K in iso-octane solution was found to be almost zero (less than 0.10, in view of the experimental accuracy).

It should be noted from Table 1 that the temperature-dependent depopulation process has essentially the same activation energy in all three compounds (a slightly smaller pre-exponential factor is observed in I). Also, the phosphorescence properties remain unchanged on passing from I to III, showing that the photophysics is governed by the pseudoazulenic chromophore properties, while the substituent at N(7) acts only as a weak perturbation. This is not a trivial result, as the substituents differ not only in size: the acetophenone group in III has low-lying ($n\pi^*$) singlet ($28\,000 \text{ cm}^{-1}$) and triplet ($26\,500 \text{ cm}^{-1}$) transitions [53] and these states might have been expected *a priori* to influence the photophysical behaviour (e.g. the intersystem crossing rate) of the whole system.

3.4. Discussion

The most spectacular difference between I, II, III and the majority of other pseudoazulenes is the lack of $S_2 \rightarrow S_0$ fluorescence. It is generally believed that the quantum yield of such an emission is determined by the value of the S_2-S_1 energy gap. In the present case $\Delta E(S_2-S_1)$ is about $7\,000 - 8\,000 \text{ cm}^{-1}$ (the first value is the difference in the absorption maxima, the second is the result of calculations (Fig. 4)). A plot of $\ln(k_{\text{nr}})$ against $\Delta E(S_1-S_2)$, obtained for another class of pseudoazulenes, derivatives of cyclopenta[*b*]pyrane [39], would give for the present case $k_{\text{nr}} = 10^{14} \text{ s}^{-1}$. If k_r is assumed to be 10^8 s^{-1} we would expect $\phi_{f1}(S_2 \rightarrow S_0)$ to be of the order of 10^{-6} , a value undetectable under our experimental conditions.

Another spectroscopic feature that deserves mentioning is a very small singlet-triplet separation, a trait characteristic of azulene and its derivatives [19, 20]. The small value of the S_1-T_1 energy gap is also reproduced by calculations (Fig. 4). It is interesting that S_1 and T_1 correspond to the same main configuration: HOMO \rightarrow LUMO, where HOMO is the highest occupied molecular orbital and LUMO is the lowest unoccupied molecular orbital. The same holds for S_2 and T_2 (next-highest MO \rightarrow LUMO). It is seen from Fig. 4 that the electronic density distribution after excitation to singlet states, in particular to S_1 , changes much more than in the corresponding triplets.

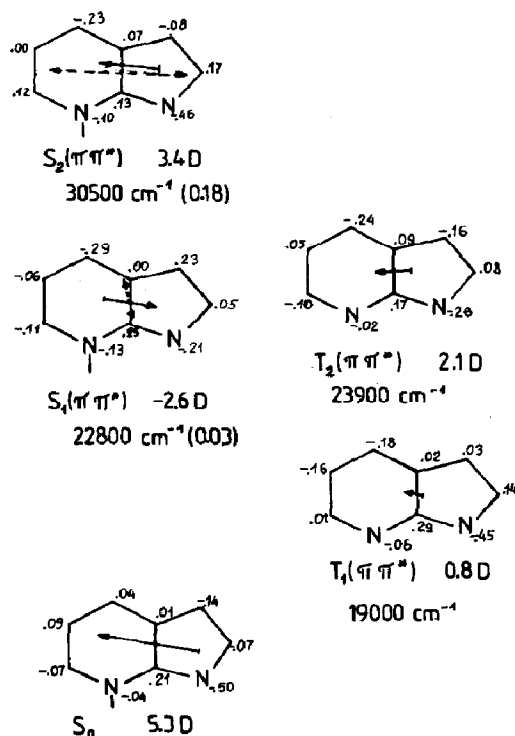


Fig. 4. Results of INDO/S calculations of the lowest excited states: charge densities, dipole moments, energies and oscillator strengths (in parentheses). The directions of the dipole moments and transition moments are shown by arrows.

Experimental evidence of drastic changes in the dipole moments on excitation to S_1 and S_2 was given in ref. 43. The difference in the electronic densities between singlets and triplets arising from the same configuration was also computed for indole, 7-azaindole and 1-azacarbazole and awaits experimental corroboration.

The lowest $n\pi^*$ states were calculated to be considerably higher than S_1 and T_1 : $34\,000\text{ cm}^{-1}$ (singlet) and $32\,100\text{ cm}^{-1}$ (triplet).

In summary, in spite of the lack of $S_2 \rightarrow S_0$ fluorescence, caused by a relatively small (compared with other azulene-like compounds) S_2-S_1 energy gap, the pseudoazulenes derived from 7-azaindole do show other features characteristic of this class of compounds. Of particular interest is the origin of the $S_1 \rightarrow S_0$ internal conversion and its large temperature dependence. Very efficient internal conversion could be due to the large electron density rearrangement on excitation to S_1 . Such a phenomenon should lead to changes in the excited state geometry and, as a consequence, in the vibrational pattern. Indeed, the first absorption band has a large half-width (about 6000 cm^{-1}). Also, a very long progression of about 750 cm^{-1} is observed (this value is close to the activation energy for internal conversion). Interestingly enough, about the same spacing is observed in the low temperature oligomeric fluorescence spectrum (Fig. 1). Further insight into the

vibrational structure of S_0 and S_1 could be gained by measuring absorption and luminescence in Shpol'skii-type matrices or supersonic beams.

Finally, it should be noted that we found internal conversion to be a dominant S_1 deactivation channel in another species having a pseudoazulene structure, 5-methylindolo[2,3-*b*]quinoxaline [54].

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