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Stilbene-like molecules: sulfur- and selenium-heterosubstituted indolo[3,2-b]indoles

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Abstract

In a series of molecules based on indolo[3,2-b]indole, the sulfur and selenium heteroderivatives exhibit signs of deviation from planarity on excitation. A simple model is proposed to explain the photophysical behavior. For stilbene-like molecules, the distortion can be treated in terms of the torsional motion about the central C–C bond. The torsion may facilitate spin–orbit coupling between states of $\pi\pi^*$ character. Analysis of the electronic matrix elements and Franck–Condon factors responsible for the radiative and non-radiative transitions leads to predictions concerning the correlations between the different rate constants, which are in agreement with the experimental data. © 1997 Elsevier Science S.A.

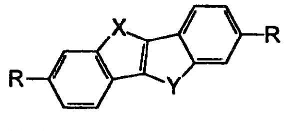
Keywords: Indolo[3,2-b]indoles; Selenium; Stilbene; Sulfur

1. Introduction

Stilbene and its derivatives provide model systems for the investigation of cis–trans photoisomerization [1]. Quite important in this respect are the so-called rigid analogs of stilbene, molecules in which the isomerization process is either blocked or hindered due to bridging. The simplest molecule of this class is indeno[2,1-a]indene [2]. We have recently studied the photophysical properties of a group of 13 indolo[3,2-b]indoles and their sulfur and selenium derivatives (Scheme 1) which, at least formally, can also be regarded as rigid *trans*-stilbene analogs [3]. Our experimental and theoretical results indicate that the excited sulfur and, in particular, selenium derivatives behave similarly to the structurally related *trans*-stilbene chromophore. Of particular interest was the observation that two different channels are responsible for the radiationless deactivation of the sulfur and selenium compounds. Heterosubstitution by these two atoms leads to the parallel acceleration of two processes:

1. $T_1 \leftarrow S_1$ intersystem crossing facilitated by the heavy atom effect;
2. $S_0 \leftarrow S_1$ internal conversion.

A linear correlation between the rates of these two processes was observed pointing to their common origin. On the other hand, the radiative rate of the lowest triplet state depopulation can be correlated with the square root of the non-radiative rate of T_1 depopulation. These findings can be explained by a simple model based on the hypothesis that the matrix elements of the spin–orbit and nuclear kinetic energy operators are dependent on a parameter describing the flexibility of the molecule [3]. No explicit form of this dependence was assumed. In this study, we exploit this concept in more detail, discussing the possible behavior of the electronic and Franck–Condon factors corresponding to transitions between the ground and lowest excited states.



X,Y = NH, NCH$_3$, S, Se

R = H, OCOEt, I

Scheme 1. Formulae of the investigated compounds.

2. Experimental and computational details

The syntheses and purification of the compounds have been described previously [4]. The spectroscopy and photophysics have been studied using stationary and time-resolved

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absorption, luminescence, luminescence polarization and transient absorption techniques, described in detail in Ref. [3]. In order to determine the rate constants of radiative and radiationless depopulation of the S_1 and T_1 excited states, we combined the values of the luminescence quantum yields and decay times recorded in the temperature range 113–293 K with the results of measurements of the triplet formation efficiencies. The latter have been determined at 293 K by two independent methods: thermal lensing [3,5] and studies of the triplet–triplet absorption of anthracene after energy transfer to anthracene from the investigated compound [3,6].

We also performed semiempirical quantum-chemical calculations in order to compare the structure and spectra of *trans*-stilbene with the corresponding properties of the compounds investigated here. For ground state structure calculations, we used the PM3 method. For calculations of the excited state energies, transition intensities and polarizations, the INDO/S algorithm was used to compare *trans*-stilbene with indolo[3,2-b]indole. The results of the calculations confirmed the analogy between heterosubstituted indolo[3,2-b]indoles and *trans*-stilbene with regard to both the shape of the frontier molecular orbitals and the orbital parentage of the excited states. For instance, in the singlet manifold, three electronic transitions were calculated in the low energy range for *trans*-stilbene as well as for indolo[3,2-b]indole. The leading configurations and values of the CI coefficients for these transitions were very similar in both molecules. One of the transitions, described by a HOMO–LUMO $\pi\pi^*$ configuration, was predicted to have a large oscillator strength. The other two transitions, calculated at very similar energies, were described mainly by the HOMO–second LUMO and HOMO–third LUMO configurations, respectively. The former transition was calculated to be very weak and the latter to be forbidden. The analogy between the two molecules was also confirmed by calculations of the triplet levels. The lowest triplet state of B_u symmetry was described in both molecules by a HOMO–LUMO $\pi\pi^*$ electronic configuration.

3. Results and discussion

The results of the spectral and photophysical studies most relevant for the present work may be recapitulated as follows.

1. The absorption spectra of the various indoloindoles are only weakly dependent on the heterosubstituent. Generally, the same pattern, consisting of at least five electronic transitions, is observed in the region below 50 000 cm^{-1}.
2. The radiative constants of S_1 depopulation calculated using the Strickler–Berg formula [7] do not differ greatly for nitrogen, sulfur and selenium derivatives. The values obtained from the fluorescence decay times and quantum yields are the same as those obtained from the integration of the absorption curves for nitrogen compounds, whereas for sulfur- and selenium-containing molecules the former procedure yields values up to twofold higher. This suggests some geometry changes in the excited state.
3. The positions of the fluorescence and phosphorescence bands do not change significantly throughout the series. In contrast, the fluorescence yields decrease and the phosphorescence efficiencies increase on substituting nitrogen by sulfur and selenium. However, even in the selenium derivatives, the phosphorescence quantum yields are quite small and do not exceed 0.06. Such behavior is characteristic of *trans*-stilbene derivatives [1].
4. The rates of $S_0 \leftarrow S_1$ internal conversion and $T_1 \leftarrow S_1$ intersystem crossing change proportionally to each other. Somewhat surprisingly, internal conversion, not intersystem crossing, is the dominant process of S_1 radiationless deactivation, even in selenium-containing compounds. The rate of the latter process is about half that of the former.
5. On passing from nitrogen to sulfur and selenium compounds, the radiative rates of T_1 depopulation increase much more slowly than the non-radiative rates. The radiative rate of the lowest triplet state depopulation correlates with the square root of the rate of non-radiative T_1 depopulation.

These photophysical characteristics of indoloindoles may be understood if we assume that the molecules become stilbene-like on excitation. In other words, the bonds between the central carbon atoms and sulfur and, especially, selenium become weaker. As a result, torsional mobility, corresponding to twisting about the central C–C bond, becomes possible. This may have important photophysical consequences. In particular, spin–orbit coupling matrix elements between the singlet and triplet $\pi\pi^*$ states, which should be very small in a planar structure, may increase significantly.

Evidence for spin–vibronic interactions is provided by inspection of the phosphorescence spectra and their anisotropy. Fig. 1 compares the luminescence of sulfur- and selenium-containing derivatives. The relative intensity of the 0–0 phosphorescence band is stronger in the derivative with two sulfur atoms than in the compound containing two atoms of selenium. The lowest intensity is observed in the compound with one sulfur and one selenium atom. It should be noted that, in the latter, no inversion center is preserved, and therefore a larger number of matrix elements may not be zero due to symmetry.

The anisotropy of phosphorescence varies across the spectrum. It also changes if the excitation is shifted from S_1 to S_2 (cf. Figs. 1 and 2). Since both states are of $\pi\pi^*$ type, no anisotropy change would be expected for a pure spin–orbit coupling involving levels of different orbital character. Thus, phosphorescence contains a component from an in-plane polarized transition. Experiments suggest that it is the S_2 state that contributes. For such a case, simple geometrical considerations show that the angle formed by the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transition moments can be obtained from either the fluorescence or phosphorescence anisotropy values produced on excitation into both S_1 and S_2 bands. Indeed, the anisotropies of fluorescence and phosphorescence yield practically the same value of this angle, 36°.

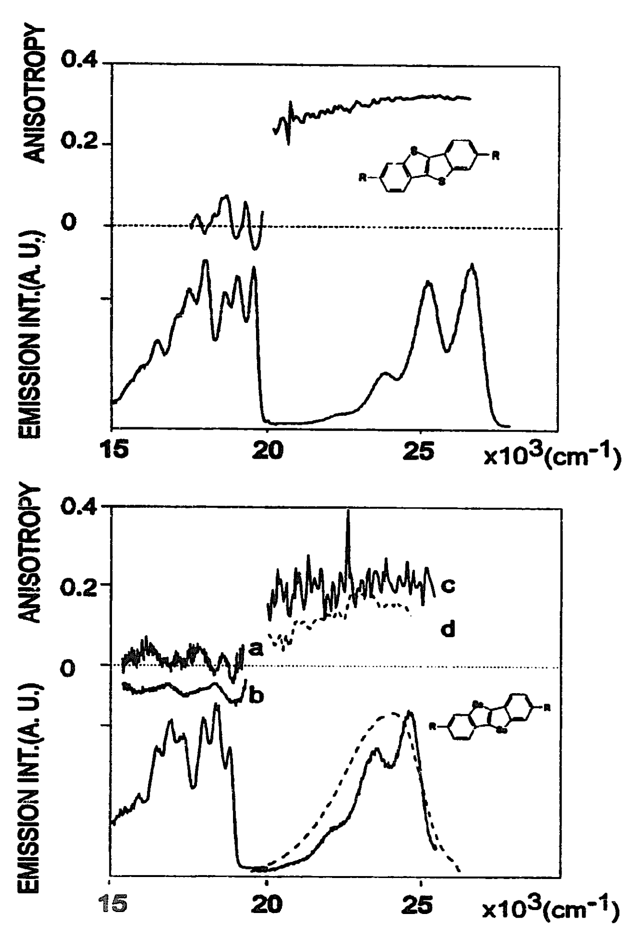

Fig. 1. Top: luminescence of diethyl[1]benzothieno[3,2-b][1]benzothienophene-2,7-dicarboxylate (SS) recorded in *n*-propanol at 113 K; fluorescence anisotropy excited at 27 100 cm^{-1}; phosphorescence anisotropy excited at 31 060 cm^{-1}. Bottom: luminescence of diethyl[1]benzoselenopheno[3,2-b][1]benzoselenophene-2,7-dicarboxylate (SeSe) in *n*-propanol at 113 K (full lines) and 293 K (broken lines) together with the anisotropy curves; phosphorescence anisotropy excited at 29 000 cm^{-1} (a) and 25 000 cm^{-1} (b); fluorescence anisotropy ((c) 113 K; (d) 293 K) excited at 26 000 cm^{-1}. Note the non-zero values of the fluorescence anisotropy at 293 K due to the very short lifetime of fluorescence (less than 20 ps).

We now try to analyze the relations between the different rates of excited state depopulation in terms of one molecular parameter. By analogy with *trans*-stilbene, we consider the torsion about the central C–C bond to be important in the excited state, and denote the torsional angle by α. Since the torsional frequencies are smaller than those corresponding to C–H or C=C vibrations, which are usually considered to act as accepting modes, we may treat α as a parameter in the calculations of the Franck–Condon factors F. The following formula should be valid for the values of the Franck–Condon factors F_{nr} responsible for non-radiative transitions

$$F_{nr}(\alpha)=F_{nr}(0)+B\alpha^2+\dots \qquad (1)$$

Due to the centrosymmetric structure of indoloindoles, positive and negative values of α occur with equal probability, and therefore only even components are possible; $\alpha=0$ corresponds to planar geometry, i.e. the ground state structure. On the other hand, our experimental data suggest a deviation from planarity on electronic excitation. This results in an average absolute value of α different from zero. The analogy between α and Δq, the quantity used in the usual description of the Franck–Condon factors, should be noted. By definition, $\Delta q=q_{e,f}-q_{e,i}$, where q_e describes the equilibrium position of a vibrational coordinate in the initial (i) and final (f) electronic state.

The values of $F_{nr}(0)$ and B should be different for different non-radiative paths. It seems reasonable, however, to assume that, for a particular process, they are similar along the series. The ratio $B/F_{nr}(0)$, and thus the importance of the torsional contribution, should be a strong function of the degree of vibrational excitation of the final state, i.e. its vibrational quantum number. For $S_0 \leftarrow S_1$ and $S_0 \leftarrow T_1$, this ratio may be expected to be much higner than for $T_1 \leftarrow S_1$ in which, due to the smaller energy gap, the lower vibrational levels of the final state are engaged. The $T_1 \leftarrow S_1$ process can also occur via an intermediate triplet state; in this case, the ratio should be even smaller. In addition, for the radiative transitions, the Franck–Condon factors should not be a strong function of α: it is well known that the changes in the molecular properties caused, for example, by deuteration are reflected much more

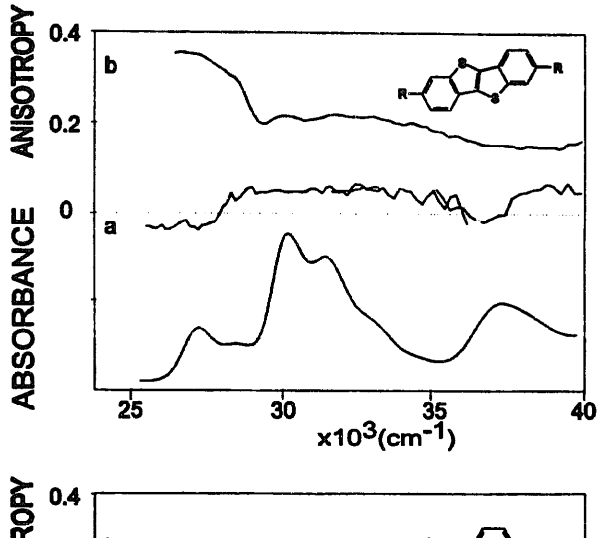

Fig. 2. Anisotropy of phosphorescence (a) and fluorescence (b) excitation of SS (top) and SeSe (bottom) in propanol at 113 K. Fluorescence was monitored at 25 000 cm^{-1} (SS) or 24 500 cm^{-1} (SeSe) and phosphorescence at 18 600 cm^{-1} in both compounds.

in the Franck–Condon factors for non-radiative processes than for radiative processes. We may thus write

$$F_{Fl}, F_{ISC}^{S_1-T_1}, F_{Ph} \approx \text{constant} \qquad (2)$$

$$F_{IC}^{S_1-S_0}, F_{ISC}^{T_1-S_0} \propto \langle \alpha^2 \rangle \qquad (3)$$

where the subscripts Fl and Ph refer to fluorescence and phosphorescence, respectively.

Let us now consider the α dependence of the electronic matrix elements. The transition dipole moments should not change during torsion. A similar behavior is expected for the terms responsible for internal conversion, if we adopt Siebrand's assumption [8]

$$|\langle S_0 | T_N | S_1 \rangle|^2 \rho = \text{constant} \qquad (4)$$

where ρ is the density of states in the final manifold and T_N is the nuclear kinetic energy operator. Since the S_1 state is located at a similar energy in all the indoloindoles, both ρ and the electronic matrix elements should be constant.

In contrast, the matrix elements of the spin–orbit coupling may be expected to depend strongly on α, due to the lack of coupling between the singlet and triplet states of $\pi\pi^*$ character in a planar molecule. We may thus write

$$|\langle S_0 | H_{SO} | T_1 \rangle|^2 \propto \langle \alpha^2 \rangle, \; |\langle T_1 | H_{SO} | S_1 \rangle|^2 \propto \langle \alpha^2 \rangle \qquad (5)$$

Since the rate constants of excited state depopulation can be expressed as products of the electronic elements and Franck–Condon factors [8], the following should be expected

$$k_{Fl} = \text{constant}, \; k_{IC}^{S_0-S_1} \propto \langle \alpha^2 \rangle, \; k_{ISC}^{S_1-T_1} \propto \langle \alpha^2 \rangle,$$
$$k_r^T \propto \langle \alpha^2 \rangle, \; k_{nr}^T \propto \langle \alpha^2 \rangle^2 \qquad (6)$$

Eq. (6) implies that the rate constants of non-radiative S_1 depopulation by internal conversion to S_0 and by intersystem crossing to T_1 should correlate in a linear fashion. A different type of correlation is expected for the radiative and non-radiative rates of T_1 deactivation: the latter should correlate with the square of the former. Both types of correlation have indeed been observed [3].

The above model is quite general and could be tested for other molecules whose photophysical properties are sensitive to distortion from planarity. For instance, diphenylene dioxide derivatives, heterosubstituted by sulfur, selenium and tellurium, seem to behave similarly to indoloindoles [9]. Another class of compounds for which the photophysics could be analyzed according to the above model is the protonated azaaromatics, in which large values of the non-radiative deactivation rate are often observed [10].

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