

THE PHOSPHORESCENCE SPECTRA OF TRIPHENYLENE AND TRUXENE: A COMBINED EXPERIMENTAL AND THEORETICAL INVESTIGATION OF THE VIBRONIC STRUCTURE

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(Received 7 April 1997)

The phosphorescence spectra of triphenylene and truxene, recorded in glassy solvents at 77 K, are presented. Their vibronic structure is interpreted on the basis of intensities computed with the help of quantum-chemical calculations. The agreement between observed and simulated intensities is very satisfactory and contributes to improve and complete the assignment of ground state frequencies of the two disk-like molecules.

Keywords: Phosphorescence spectra; simulations; semi-empirical calculations; spin-orbit interactions; vibronic interactions; truxene; triphenylene

Triphenylene (TPH) and truxene (TN), are two examples of highly symmetric polycyclic aromatic hydrocarbons. Some of their derivatives form discotic liquid crystalline phases, a property which has attracted considerable attention in the field of material science. Indeed, excitation or charge transport phenomena are expected to be quasi

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one-dimensional for these systems which therefore have been suggested as potential 'molecular energy guides' [1]. The elucidation of the electronic transport in columnar phases requires a detailed knowledge of the electronic structure and states of the isolated chromophores. In this study we have investigated the spectroscopy of the lowest triplet state of TPH and TN and we present the phosphorescence spectra of the two molecules, recorded in glassy solvents (methylcyclohexane and ethanol) at 77 K.

The experimental spectra show several vibronic features in the region of fundamentals and combination bands. Similarly to benzene, the phosphorescence of TPH and TN are both symmetry and spin forbidden. Thus, the estimate of vibronic intensities requires the evaluation of spin-orbit along with vibronic perturbations. To analyze the observed vibronic structure we carried out quantum chemical calculations of equilibrium structures, vibrational force fields and T_1-S_0 displacement parameters, with the help of a modified version [2] of the QCFF/PI semiempirical hamiltonian [3]. The displacement parameters B_i , defined as the projection of the geometry change between the two states S_0 and T_1 , onto the S_0 -state normal coordinate $Q_i^{S_0}$, were employed to evaluate the γ_i parameters, $\gamma_i = (1/2)B_i$. These were required to estimate the intensities of totally-symmetric modes in the phosphorescence spectra. Moreover, the vibronically and spin-orbit induced intensities of non totally-symmetric modes were computed with the CNDO/S hamiltonian [4], augmented with Configuration Interaction calculations which included a large number of single excitations (CI space 30×30). This method was recently applied to interpret successfully the phosphorescence spectrum of the fullerene C_{70} [5].

A typical result is shown in Figure 1, where the experimental and simulated phosphorescence spectra of truxene are presented. It is seen that the agreement between observed and computed vibronic structure is very satisfactory. Similarly good results are obtained for triphenylene. In the latter case, the simulated intensities agree very well also with the vibronic structure observed in the high resolution spectrum of Ref. [6]. The encouraging results obtained for these systems suggest that the methods employed can be applied to the derivatives of TPH and TN which are of greater interest in the field of material science.

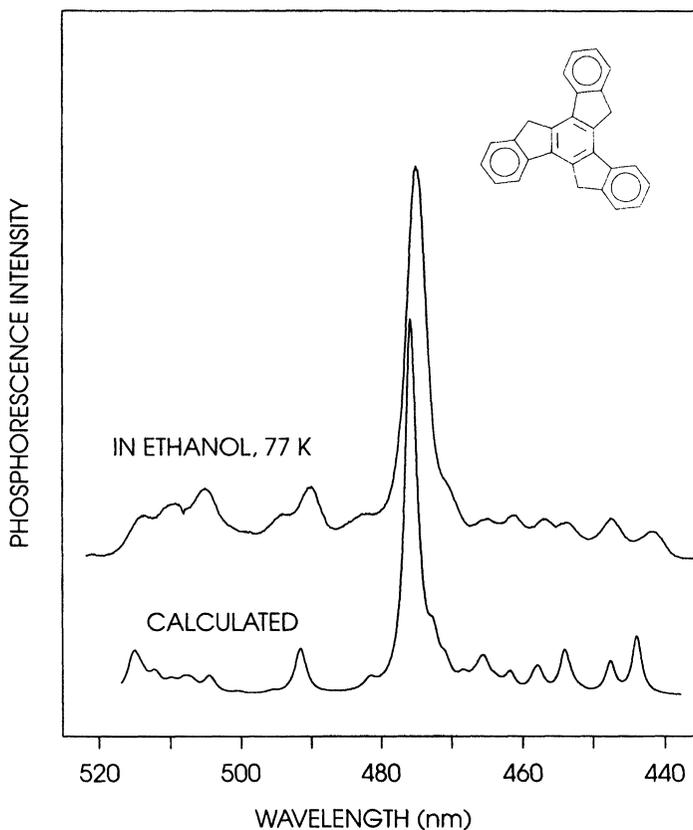


FIGURE 1 The phosphorescence spectrum of truxene: observed (top) and simulated (bottom).

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