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ELECTRONIC SPECTRA AND LUMINESCENCE PROPERTIES OF HELICENES IN CRYSTALLINE MATRICES AT 4.2 K

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Abstract Fluorescence, phosphorescence and excitation spectra of [4]-, [5]-, [6]-,and [7]-helicenes in policrystalline matrices were obtainecl at 4.2 K. Highly-resolved electronic spectra were observed for [4]-, [5]-,and [6]-helicene whereas for [7]-helicene only broad bands were monitored in emission and excitation spectra. Irradiation of [5]-helicene at 4.2 K leads to its photocyclization to dihydrobenzoperylene. The observed concentration effects in [4]-, and [6]-helicene as well as influence of the crystallinity of the medium on the fluorescence-to-phosphorescence intensity ratios are explained assuming the presence of the fluorescent but not phosphorescent preaggregates. The vibronic structures of the site-selected [4]-, and [6]-helicene phosphorescence excitation spectra point to site-dependent distortions of the helicene molecules. Calculations of electronic transitions helicene molecules were performed with the modified Warshel-Karplus method.

INTRODUCTION

It has been accepted that overcrowding and non-planarity of molecules make getting highly resolved electronic spectra difficult, especially for helicoidal π-electron systems [1,2]. Generally, non-planar structures of molecules prevent them from being incorporated into Shpolskii type matrices. However, we obtained at 77 K quasilinear Shpolskii spectra of other strongly overcrowded aromatic molecules[2,3]. On the other hand, we succeeded in obtaining well resolved fluorescence and phosphorescence spectra of [6]-helicene by using chlorobenzene crystalline matrix[4].

The present work reports on results of a investigation of the electronic spectra of [4]-, [5]-, [6]-, and [7]-helicene molecules in Shpolskii matrices at liquid helium temperature.

SYNTHESIS AND PURIFICATION

Details of the synthesis and purification of the helicenes used in this study, and of solvents, have been given in refs. 5-7.

THEORETICAL

Calculation of electronic states for the systems under consideration has been performed within the Warshel and Karplus method[8] starting from experimental geometries. Accordingly, in the core resonance integral, the non-planarity effects have been taken into account.

It has been established that the Warshel and Karplus method overestimates the electronic state energies for large molecular systems. In order to avoid this drawback, we assume the linear dependence of the β_0 parameter on the number N_π electrons: $\beta_0 = 0.021 N_\pi - 2.53$ [eV]. This relationship was found by the least-square method fitting theoretical lowest singlet state energies of cata-condensed aromatic hydrocarbons to experimental data. Allowance for the above relationship leads to an essential improvement in the evaluated π-electron excited state energies of large molecular systems.

RESULTS

[4]-, and [6]-helicene. The best resolved fluorescence spectra were obtained for [4]-helicene in n-alkanes ($C_5 - C_7$) and for [6]-helicene in chlorobenzene, but only at a very low concentration (less than 10^{-5}M). At higher concentrations (e.g. 10^{-4}M), the spectra are poorly structured and red-shifted, in comparison to the 0-0 lines of the $S_{10} \leftrightarrow S_{00}$ transition observed in well resolved spectra, by about 600 cm^{-1} and 250 cm^{-1} for [4]-, and [6]-helicene, respectively.

Highly resolved phosphorescence spectra of [4]-helicene were obtained in C_5 matrices and of [6]-helicene in C_7 for concentrations of helicenes of the order of $10^{-4} - 10^{-6}$ M. The phosphorescence excitation spectra obtained by monitoring selectively two different Shpolskii sites show, in both helicenes, that the vibronic pattern of these spectra are not identical (see fig. 1).

The phosphorescence-to-fluorescence intensity ratio of [4]- and [6]-helicene in crystalline matrices are dramatically lower than that in a glassy ones (see fig. 2).

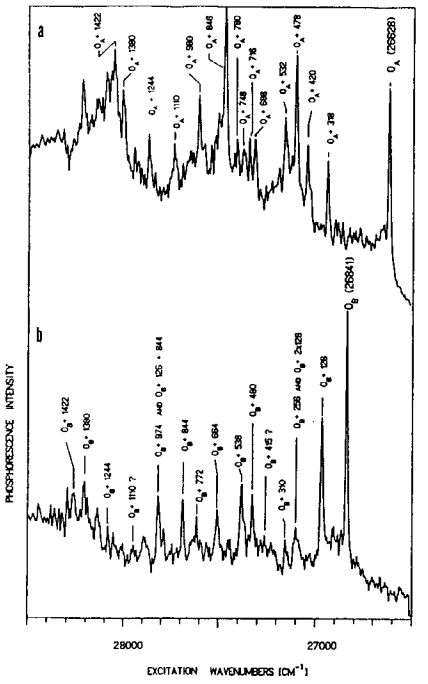

FIGURE 1 Phosphorescence excitation spectra of [4]-helicene in n-pentane matrix, $c = 10^{-5}$M: (a) monitored at the 0_A phosphorescence line, (b) monitored at the 0_B phosphorescence line.

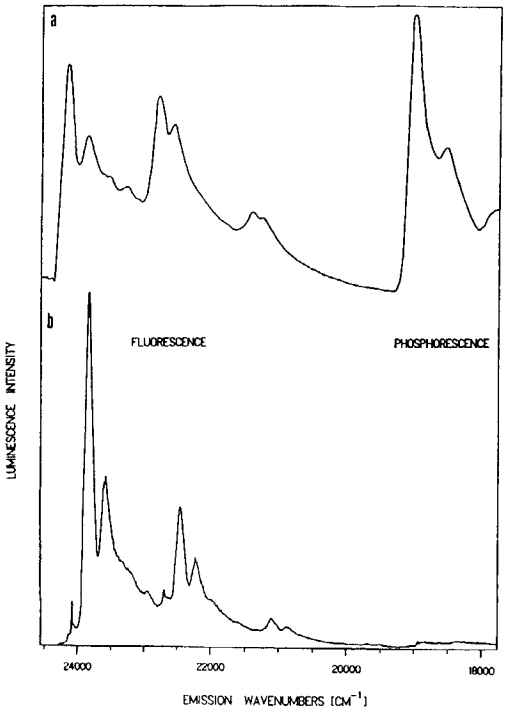

FIGURE 2 Fluorescence and phosphorescence spectra of [6]-helicene, $c = 10^{-4}$M: (a) in a glassy matrix (toluene : diethyl ether – 1:1), (b) in the crystalline matrix (chlorobenzene).

[5]-helicene. The best resolved emission and excitation spectra were observed in n-pentane but, similarly as in other helicenes, sharp lines appear on a strong diffuse background even at concentrations as low as 10^{-6}M. The fluorescence spectrum of [5]-helicene in C_6, measured immediately after cooling of the sample shows only a broad band structure. After irradiation of solutions in both C_5 and C_6 , additional narrow lines appear in the spectrum, their intensities increasing with irradiation time, due to the photochemical reaction of [5]-helicene to dihydrobenzoperylene at 4.2 K [9]. The Shpolskii effect and the photochemical reaction were not observed in C_7 matrix.

[7]-Helicene. Highly resolved electronic spectra of [7]-helicene were not obtained in all used matrices and at all concentrations, and in all cases only the broad band emission and excitation were observed.

DISCUSSION

The fluorescence spectra of helicenes reported in this paper were found to consist predominantly of broad bands whereas the predominant feature of the phosphorescence spectra are sharp peaks. Moreover, broad fluorescence and absorption bands are red-shifted with respect to the corresponding quasi-linear spectra. Such bands have been generally ascribed to aggregates or microcrystals of solutes[10,11]. The guest molecules, which, because of their shape, cannot substitute host molecules, get partly trapped in intercrystalline positions and concentrate there as "preaggregates". Therefore, despite of high freezing rate impending the solute aggregation, fluorescence spectra of the [4]- and [6]-helicene of concentrations of $10^{-4} - 10^{-5}$M are dominated by broad features. At lower concentrations (10^{-6}M) fluorescence quasi-lines emerge from the background, originating from the overlapping fluorescence bands of "preaggregates". The number of phosphorescing species is a small fraction of all solute molecules incorporated and not incorporated in the host crystal lattice but only isolated helicene molecules give rise to the phosphorescence spectra (see fig. 1). This would explain the weakness of the quasi-linear phosphorescence in crystalline matrices and higher phosphorescence–to–fluorescence intensity ratio in glassy solutions containing only dispersed helicene molecules. The phosphorescence excitation spectra of the two sites (A and B) reveal sets of vibration modes in part different, especially in the skeletal and $C-H$ bending modes (see fig. 1). This suggests that the monitored A and B sites are populated by helicene molecules of two different geometries.

It was established by X-ray diffraction [12–15] that [5]-, and [7]-helicene crystallize in two modifications whereas [4]-, and [6]-helicene in only one space group. Moreover, in one of the crystal forms of [5]-, and [7]-helicene two sets of molecules were found, differing in geometry. It seems that helicene molecules with odd number of aromatic rings are more flexible that those with the even ones. This feature seems to explain less structured electronic spectra of the odd-helicenes.

TABLE I Electronic transition energies $(\Delta E, cm^{-1})$ and oscillator strengths (f) of helicene molecules.

[4]-helicene				[5]-helicene			
$State^{(a)}$	ΔE_{calc}	f_{calc}	$\Delta E_{exp}^{(b)}$	$State^{(a)}$	ΔE_{calc}	f_{calc}	ΔE_{exp}
$S_1(B)$	27707	0.0013	26870	$S_1(A)$	26335	0.0013	25250[d]
$S_2(A)$	30732	0.0279	30490	$S_2(B)$	29030	0.1796	29100[d]
$S_3(A)$	33807	0.0108	≈34000	$S_3(B)$	31650	0.0252	32260[d]
$S_4(B)$	34549	1.4352	35380	$S_4(B)$	32765	0.5943	
$S_5(B)$	37870	0.1883	36710	$S_5(A)$	33250	0.0257	33300[e]
$T(A)$	20354		19872[c]	$T(B)$	19335		19750[c]
[6]-helicene				[7]-helicene			
$State^{(a)}$	ΔE_{calc}	f_{calc}	$\Delta E_{exp}^{(f)}$	$State^{(a)}$	ΔE_{calc}	f_{calc}	ΔE_{exp}
$S_1(B)$	24553	0.0160	24390	$S_1(A)$	24109	0.0000	23700[d]
$S_2(A)$	26811	0.0523	28570	$S_2(B)$	26005	0.0756	25900[d]
$S_3(A)$	29264	0.0854	29800	$S_3(B)$	28078	0.0165	28820[h]
$S_4(B)$	29900	0.4478	30640	$S_4(B)$	28489	0.2552	30030[h]
$S_5(B)$	30965	0.0944	31920	$S_5(A)$	29820	0.1012	31450[h]
$T(A)$	17197		18986[g]	$T(B)$	19181		17500[i]

[a]Calculated state symmetry (irreducible representations of the C_2 point group given in parentheses). [b]0,0 band in cooled n-pentane [16]. [c]The main $0-0$ line in n-pentane, 4.2 K. [d] $0-0$ band in toluene, 77 K. [e] Ref. 17. [f] Maxima of the absorption spectrum in isopentane-methylcyclohexane, 78 K [18]. [g] The $0-0$ line, in n-heptane, 4.2 K. [h] $0-0$ band in ethanol, 298 K. [i] $0-0$ band in chlorobenzene, 4.2 K.

Despite of neglecting $\sigma - \pi$ interactions and the assumption that the σ bonds are regarded as a nonpolarisable core, the parametrization used here leads to a reasonable agreement of theoretical results with experiment. In general, the agreement of energies with the experiment for both singlet and triplet electronic states found in our calculations is better than in the previous estimations[19], however, symmetries of higher excitations may differ in some cases from those available in the literature.

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