Heavy Atom- and Deuterium Isotope Effect in Bis-(Phenylethinyl)-Mercury

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The influence of mercury as a heavy atom on the spin orbit coupling is investigated in bis-(phenylethinyl)-mercury and its deuterated derivative. From the experimental results we draw the following conclusions: a) the symmetry of the molecule is D_2, b) the large spin orbit coupling of the mercury atom is introduced via $d_\pi p_\pi$-interaction, c) local $\sigma\pi$-transitions and vibronic coupling are of no importance, d) the weak deuterium effect in the radiationless decay is a consequence of the fact that the triple bonds act as strong energy acceptors.

Introduction

This paper presents a study of the heavy atom- and the deuterium isotope-effect in the lowest triplet state of bis-(phenylethinyl)-mercury (Hg-BPE).

Hg as a heavy atom perturber in an aromatic system provides lone pair orbitals of d-type (5 d) which may couple with the surrounding π-electronic system. The resulting molecular spin orbit coupling at the heavy center can change the dynamic properties of the aromatic triplet state in a drastic manner. To elucidate the influence of molecular vibrations on spin orbit coupling and to investigate the mechanism, by which the mercury atom feeds its strong atomic spin orbit coupling into the ligand frame, we used the method of deuterium substitution [1]. Besides, the deuterium effect reveals some details of distributing the electronic energy among the vibrational degrees of freedom, if the molecule decays nonradiatively to the groundstate [2].

The experimental techniques employed in this study are emission – absorption – lifetime- and quantum yield-measurements. Additionally we used phosphorescence polarization spectroscopy. This method is very useful, because in systems with some symmetry it reflects the radiative properties of the individual triplet sublevels [3].

Experimental

The experiments were carried out at liquid nitrogene temperature in an EtOH glass. The concentrations of the samples were about 10^{-3} m. The setup for measuring the emission and anisotropy spectra is described elsewhere [3]. The optical bandpasses used are shown in the figures. The accuracy of the wavenumber scale is within $\pm 25\ cm^{-1}$.

Lifetime measurements were performed by means of a variable speed light chopper in the exciting beam (PAR 191) and phase detection of the phosphorescence with a PAR 129 vector lock in amplifier. The chopping frequency was 43 cps (for both Hg-$BPE_{h\,10}$ and Hg-$BPE_{d\,10}$). The quantum yield was determined with respect to that of diphenylantracene (EtOH), which is close to unity [4].

Results and Discussion

Figures 1 and 2 show the emission-, absorption- and corresponding anisotropy spectra of Hg-$BPE_{h\,10}$ and Hg-$BPE_{d\,10}$. For comparison the absorbtion spectrum of the parent molecule phenylacetylen (PA) [5] is also drawn. The various rate constants and the quantum yields are listed in Table 1. We want to draw attention to what happens to the spectral and dynamic features on going from PA to Hg-BPE.

Spectra

By comparison of the phosphorescence emission of PA [5] and the spectra given here in Fig. 1, we note that the energy of the lowest triplet and singlet state is little affected. The L_b-transition retains its forbidden character. From this we conclude that the electron distribution in the S_1 and T_1 state is very much the same in PA and Hg-BPE. The L_a-state, on the other hand, shows a strong shift in its energy

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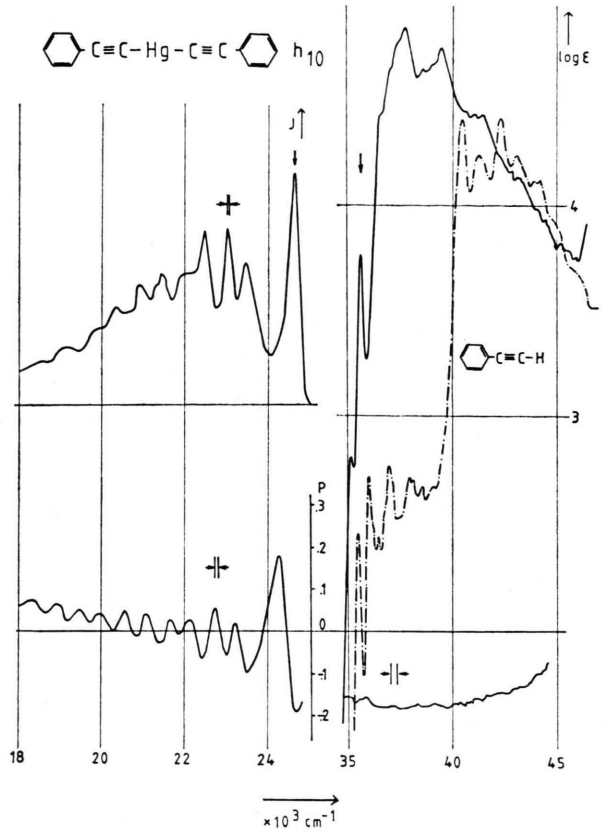

Fig. 1. Spectra of Hg-BPE$_{h10}$: phosphorescence with corresponding polarization spectrum (left) and absorption with polarized phosphorescence excitation spectrum (right). The positions of excitation and observation are marked with arrows. The absorption of phenylacethylene is drawn for purpose of comparison.

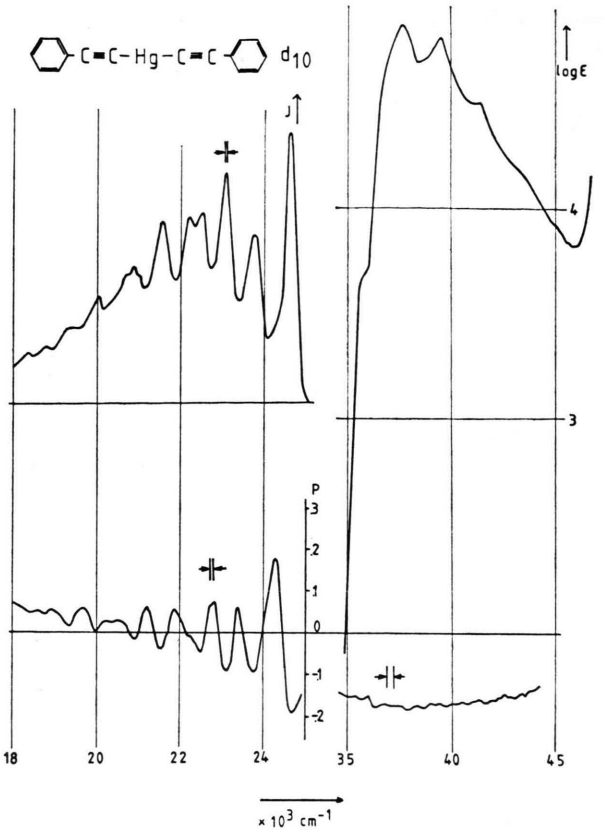

Fig. 2. Spectra of Hg-BPE$_{d10}$: phosphorescence with corresponding polarization spectrum (left) and absorption with phosphorescence excitation spectrum (right). The positions of excitation and observation are the same as in Figure 1.

Table 1. Quantum yields, lifetimes and rate constants of the lowest triplet states of Hg-BPE$_{h10}$ and Hg-BPE$_{d10}$.
Φ_p total quantum yield; Φ_p^0 quantum yield in the 00-transition; P^0 degree of polarization in the 00-transition; k_r total radiative rate; k_r^0 total radiative rate in the 00-transition; $k_{r\tau}^0$ radiative rate in the 00-transition from the τ'th substate; k_{nr} total nonradiative rate.

Hg-BPE	h_{10}	d_{10}	
τ (sec)	$3.39 \cdot 10^{-3}$	$4.11 \cdot 10^{-3}$	(±) 3%
Φ_P	0.24	0.29	(±) 6%
Φ_P^0	0.025	0.03	(±) 7%
k_r (sec^{-1})	71	70.6	(±) 7%
k_r^0 (sec^{-1})	7.4	7.3	(±) 8%
P^0	−0.185	−0.185	(±) 5%
k_{rz}^0 (sec^{-1})	1	1.02	(±) 11%
$k_{rx}^0 + k_{ry}^0$ (sec^{-1})	6.4	6.3	(±) 8%
k_{nr} (sec^{-1})	224	173	(±) 5%

into the immediate neighbourhood of the L_b-state. Additionally it gains an enhancement in intensity. Therefore a strong overlap between the widths of the two bands occurs. As a consequence the degree of polarization P in the absorption region is determined by the L_a-band.

Since the vibrational pattern of the L_a-band is dominated by a progression of the totally symmetric acetylenic stretching mode, no significant structure in the degree of polarization is observed.

The phosphorescence emission also shows only totally symmetric vibrations: all intense vibrational transitions are polarized parallel to the 00-transition. This is contrary to what one observes in the heavy atom effect of halogenated PA [6]. In this case most of the intensity is induced by antisymmetric out of

plane modes. However, the positive deviations from the 00-polarization indicate that there is a very small activity of some antisymmetric vibrations. But their intensity is so weak that they could not be resolved in emission.

The 00-polarization is negative with respect to L_b- and L_a-excitation. It is nearly constant regardless the position of excitation. However, the average value of P (-0.18) indicates that there must be some amount of the phosphorescence intensity, which is polarized parallel to the L_a-band. In the parent molecule excitation into the L_a-band yields a phosphorescence polarization which is near its negative extreme value [5].

Symmetries and molecular structure

We start this discussion with the assumption that the C – Hg – C-bond is colinear [7]. The molecule therefore may have either D_{2h}, D_2 or D_{2d} symmetry. It is reasonable to assume that the L_a-state, which is completely polarized along the z-axis in PA, retains its polarization. (The choice of the axes is shown in Figure 3.) The question arises, what is the symmetry representation of the lowest triplet state T_1 in the symmetry group, the molecule actually belongs to. In PA itself T_1 is of A_1-symmetry and we have already stressed that the electron distribution in T_1 seems not to change by going from PA to Hg-BPE. Table 2 shows the resolution of A_1 into the representations of the point groups D_{2h} and D_{2d} and D_2.

We see that in D_{2h}- or in D_{2d}-symmetry the emission from the lowest triplet state (at the equilibrium position of the molecule) may only have x- or (and) y-polarization. The measured P-value in the region of the L_a-band shows, however, that there is a significant z-polarization. This result fits only with D_2-symmetry of the molecule and A-symmetry of the lowest triplet state. That is, the two phenylrings in Hg-BPE are twisted, but they are not perpendicular to each other (D_{2d}). We see that none of the triplet sublevels is radiatively forbidden.

We want to stress that the z-polarized component could not be induced by a second order HT-coupling, as in the case of halonaphthalenes and halophenylacetylenes, since this mechanism does not change the selection rules. Thus, in a plane Hg-BPE molecule, 2nd order HT-coupling would always produce an y-polarized component and P with respect to L_a would remain at its negative extremum like in PA.

From the photoselection equation [8]

$$\frac{2P}{3-P} = \frac{1}{5}\left(3 \sum_{i=x,y,z} r_i s_i - 1\right),$$

($r_i(s_i)$: relative amount of absorption (emission) in i direction), we obtain for the 00-transition (with $r_z = 1$) $s_z = 0.14$. That is, about 14% of the 00-intensity is z polarized. Because this is a relatively small amount, we conclude that either the deviation from D_{2d}- or from D_{2h}-symmetry is small. The A-orbital symmetry in the D_2-group corresponds to the A_g-symmetry in the D_{2h}-group (Table 2). If the molecule tends to planarity (D_{2h}), each sublevel would become radiatively forbidden.

Therefore, the spectral data suggest that the molecule does not deviate severely from D_{2d}-symmetry, i. e. the planes of the two rings are nearly perpendicular to each other.

Dynamic Features

Clearly, the most striking difference between PA and Hg-BPE occurs in their dynamic behaviour. The heavy atom effect introduced by the central Hg-atom shortens the triplet lifetime by about three orders of magnitude. The enhancement in the intersystem crossing rate reduces the fluorescence below the detection limit of the experimental setup. We attribute the efficient radiative and radiationless processes to and from the lowest triplet state to the very strong spin orbit coupling within the 5 d lone pair electrons of the Hg-center.

In this case the molecular spin orbit coupling integrals are reduced to

$$\langle \pi \,|\, H_{so}^{\tau} \,|\, \pi' \rangle \approx \sum_{m,m'} c_{\pi}^{m}\, c_{\pi'}^{m'} \langle \mathrm{d}, m \,|\, H_{so}^{\tau} \,|\, \mathrm{d}, m' \rangle_{\mathrm{Hg}} .$$

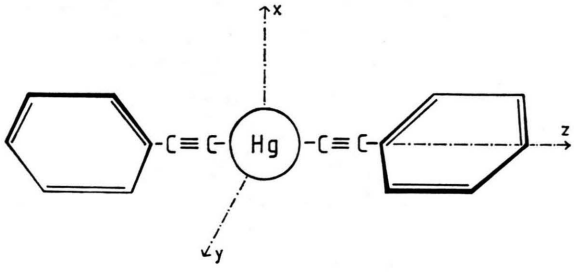

Fig. 3.

Table 2. Symmetry correlation for an A_1-state between the C_{2v}-, D_{2h}-, D_{2d}- and D_2-groups. Ω^τ is the representation of the spin function of substate τ.

C_{2v}		D_{2h}		D_{2d}		D_2	
ΓT_1	$\Gamma T_1 \otimes \Gamma \Omega^\tau$	ΓT_1	$\Gamma T_1 \otimes \Gamma \Omega^\tau$	ΓT_1	$\Gamma T_1 \otimes \Gamma \Omega^\tau$	ΓT_1	$\Gamma T_1 \otimes \Gamma \Omega^\tau$
			B_{1g}		A_2		B_1 (z)
		A_g	B_{2g}	A_1		A	B_2 (x)
	A_2		B_{3g}		E (x, y)		B_3 (y)
A_1	B_1 (x)						
	B_2 (y)		A_u		B_1		A
		B_{1u}	B_{2u} (x)	B_2		B_1	B_3 (x)
			B_{3u} (y)		E (x, y)		B_2 (y)

c_π^m are the corresponding MO-coefficient of the d-electron of type m in the orbital $|\pi\rangle$. Since in a D_2-symmetry all type of d-orbitals may in principle mix with $|\pi\rangle$ and $|\pi'\rangle$, we have to sum over the whole set of d-orbitals. $\langle d, m | H_{SO}^\tau | d, m' \rangle_{Hg}$ is the one center spin orbit coupling term between the d-electrons of type m and m'.

If the electronic charge distribution in the aromatic ligands of Hg-BPE differs not severely from the parent molecule, we may express the equation in terms of the MO-coefficient $C_{\pi\mu}$ of the parent molecule at the carbon center μ and the elements of the reciprocal overlap matrix $S^{-1}_{p\mu,dm}$ between the atomic 2 p orbital at the carbon center μ, and d_m, the d-orbital of type m at the Hg-center.

$$\langle \pi | H_{so}^\tau | \pi' \rangle \approx \sum_{\mu,\nu} C_{\pi\mu} C_{\pi\nu} \sum_{m,m} S^{-1}_{p\mu,dm} S^{-1}_{p\nu,dm} \langle d, m | H_{so}^\tau | d, m' \rangle_{Hg} .$$

The reciprocal overlap integrals represent the $d_\pi p_\pi$-interaction, which (within the approximation used) introduces the strong atomic spinorbit coupling of the heavy center into the ligand system.

Since none of the triplet sublevels is radiatively forbidden, and since there seems to be no symmetry restriction concerning the involvement of the one center contributions at the mercury atom and the overlap integrals of the $d_\pi p_\pi$-interaction, the influence of vibrations may only provide a small contribution. This is exactly what we observe: a very low activity of some antisymmetric modes in the emission (only detectable in P) and no d-effect in the total radiative rate and in the radiative subrates. This observation also indicates that there is no contribution from local $\sigma\pi$-transitions within the aromatic rings * (Table 3).

Table 3. Deuterium effect in the various rate constants of Hg-BPE.

$k_{(H)}/k_{(D)}$	1.21 ± 5%
k_r (H)/k_r (D)	1 ±10%
k_r^0 (H)/k_r^0 (D)	1 ±10%
k_{rz}^0 (H)/k_{rz}^0 (D)	1 ±15%
k_{rx}^0 (H) + k_{ry}^0 (H) /k_{rx}^0 (D) + k_{ry}^0 (D)	1 ±15%
k_{nr} (H)/k_{nr} (D)	1.29 ± 7%
Φ_p (H)/Φ_p (D)	0.83 ± 2%

In the non radiative decay we measured a d-effect of about 30%. This is very small compared to the values one usually observes in aromatic molecules [1]. In an earlier paper [9] we attributed the small d-effect in PA, originally observed by Singh and Laposa [10], to the special ability of the triple bond to act as a strong energy acceptor in the radiationless decay, so that the amount of the energy usually accepted by the CH-vibration is strongly reduced. In PA itself, the proton in ω-position has the largest influence in the d-effect [10]. Since this proton is absent in Hg-BPE its d-effect is further reduced compared to the parent molecule.

Summary

From the analysis of phosphorescence anisotropy spectra it was concluded that Hg-BPE has D_2-symmetry with A-symmetry of the lowest triplet state, but the deviation from D_{2d}-symmetry ist not too severe. The strong spin orbit coupling of the Hg-center is introduced via $d_\pi p_\pi$-interaction. $\sigma\pi$-transitions and vibronic coupling play only a minor role.

* The notation σ and π is used in analogy to the parent molecule phenylacetylen.

This explains the absence of a d-effect in the radiative rates. The strong reduction of the d-effect in the radiationless rate is due to the stretching mode of the triple bonds, which act as a very effective energy sink.

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