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COMMENTS

Comment on “Fluorescence of Antiaromatic Systems: An Experimental and Theoretical Study of 1,3,5-Tri-*tert*-butylpentalene”

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The absorption[1] and emission[2] spectra of 1,3,5-tri-*tert*-butylpentalene (TTBP) have recently been reported in this journal. Fluorescence from an upper excited state was observed, and assigned to the $S_3 \rightarrow S_0$ transition. On the basis of this work and previous studies of 1,3,5,7-tetra-*tert*-butylindacene (TTBI),[3−5] the authors suggest that emission from upper excited states is a common property of such antiaromatic hydrocarbons.[2] We support this suggestion, but offer a different interpretation which emphasizes the importance of crossings between potential energy surfaces for promoting rapid and efficient nonradiative decay.[6−8]

The prototype for upper excited state emission is the azulene molecule,[9−15] for which $\Delta E(S_2-S_1)$ and $\Delta E(S_1-S_0)$ are both ~14000 cm^{-1}. In the original account of Beer and Longuet-Higgins,[9] it was suggested that the large S_2-S_1 energy gap “disfavored” the intersection of these two potential energy surfaces, reducing the probability of radiationless deactivation. Nevertheless, since no emission could be detected from S_1 when exciting with an appropriate wavelength, an intersection of the S_1 and S_0 surfaces (acting as a “funnel”[7] back to the ground state) was proposed. This apparent contradiction was immediately criticized,[10] although it was the suggestion of an S_1/S_0 intersection which was rejected.[16]

In a recent computational study, we have demonstrated that an S_1/S_0 intersection does exist in azulene,[13] and that it is readily accessible (by which we mean that there is a reaction coordinate with a sufficiently low energy barrier that leads from the initial excited state geometry to the crossing region). This result is consistent with femtosecond laser studies[11] and spectroscopic line width measurements[12] which established that complete internal conversion from S_1 to the ground state takes place in less than a picosecond.[14,15] A similar S_1/S_0 crossing has also been located for pentalene,[17] which is consistent with the diffuse S_1 absorption spectrum recorded for TTBP even at 15 K.[1]

It is the electronic character of the S_0 and S_1 states which determines the existence of an accessible S_1/S_0 intersection in azulene[13] and pentalene,[17] rather than the size of the energy gap. Because the transannular bond is almost a double bond on S_1 but a single bond on S_0, relaxation on S_1 raises the corresponding S_0 energy and brings the two states together (as suggested originally for azulene by Ross[18]). Figure 1 shows that, for pentalene, the S_1 minimum (**S_1 M**) and S_1/S_0 crossing (**S_1/S_0 X**) (reoptimized[17] at the CASSCF/6-31G* level of theory) actually occur at almost identical geometries: the transannular bonds differ by only 0.02 Å. Furthermore, Table 1 shows that the S_1-S_0 energy gap at the S_1 minimum is just 2.3 kcal mol^{-1} and that the energy required to reach the crossing to S_0 from this minimum is calculated to be <1 kcal mol^{-1}.

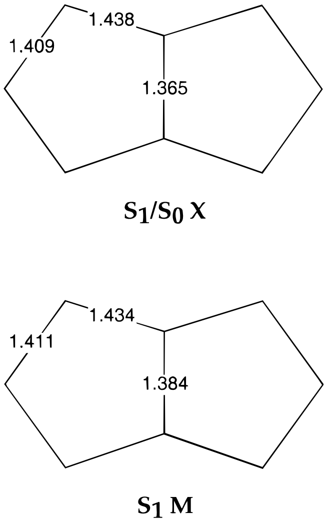

Figure 1. Critical points optimized on the S_1 surface of pentalene using CASSCF/6-31G* and state-averaged orbitals (bondlengths in angstroms): the minimum on S_1 (**S_1 M**) and the adjacent minimum on the S_1/S_0 conical intersection (**S_1/S_0 X**). Both structures have D_{2h} framework symmetry.

In contrast, emission from upper excited states implies that there is no accessible surface crossing between S_n and S_1 promoting fast radiationless decay. Recent CASSCF[2] and CASPT2[19] calculations suggest that the S_2 state of pentalene has A_g electronic symmetry, is dominated by a doubly-excited configuration, and has appreciable ionic character. The vertical excitation energy for the symmetry-forbidden $S_0 \rightarrow S_2$ transition was calculated to be 2.91 eV (~23500 cm^{-1}),[19] a little below an allowed transition to a B_u state at 3.50 eV (~28200 cm^{-1}). Forbidden character and proximity to an allowed ($f = 0.012$[19]) transition account for the fact that the S_2 (A_g) state has not yet been identified in absorption.[1,2,19] However, excitation of room temperature TTBP solutions at ~26300 cm^{-1} (below the 0−0 energy of 27440 cm^{-1} [1] for the allowed B_u band) did lead to weak emission extending to ~18000 cm^{-1},[2] consistent with the existence of an A_g state below B_u which cannot decay efficiently.[20]

Because the S_2 state is dominated by a doubly excited electronic configuration, the MMVB[21−23] method was used to generate approximate starting geometries for the CASSCF optimization of any S_2/S_1 crossing. (Approximate because of the importance of ionic configurations—as indicated by the localized orbital occupations in Figure 2—which are not explicitly treated by MMVB).[21] One S_2/S_1 crossing minimum was found with MMVB (although extensive searching for others was carried out). With CASSCF, this point (**S_2/S_1 X**, Figure 3) lies ~40 kcal mol^{-1} (Table 1) above the C_{2v} minimum (**S_2 M**). The calculated barrier can only be taken as a guide: the ionic

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TABLE 1: CAS (8,8)/6-31G* Energies of Pentalene at the Optimized Geometries shown in Figures 1 and 3[a]

structure	S_0/E_h	S_1/E_h	S_2/E_h	ΔE(lower → upper state)/ kcal mol^{-1}	E relative to **M** on upper state/kcal mol^{-1}
Figure 1					
S_0/S_1 X	−306.42540	−306.42531		0.06	+0.5
S_1 M	−306.42972	−306.42608		2.3	0
Figure 3					
S_1/S_2 X		−306.27019	−306.26990	0.2	+40.5
S_2 M		−306.40251	−306.33451	42.7	0

[a] State-averaged orbitals were used in each case.

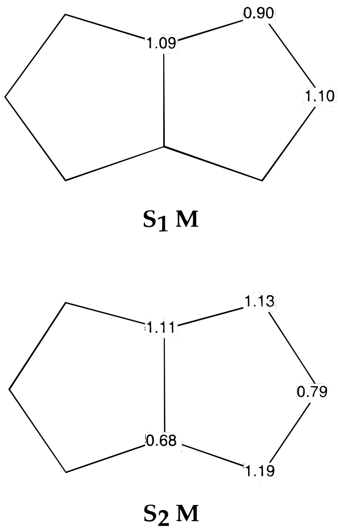

Figure 2. Localized orbital occupations computed using CASSCF/6-31G* at the excited state minimum geometries (same orientation) shown in Figures 1 (**S_1 M**) and 3 (**S_2 M**). Greater deviations from 1.0 for **S_2 M** reflect the importance of ionic configurations in describing the S_2 state.

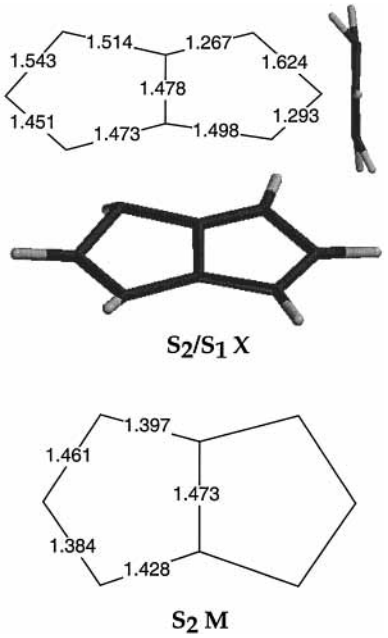

Figure 3. Critical points optimized on the S_2 surface of pentalene using CASSCF/6-31G* and state-averaged orbitals (bondlengths in angstroms): the C_{2v} minimum on S_2 (**S_2 M**) and the C_1 minimum on the S_2/S_1 conical intersection (**S_2/S_1 X**).

character of the S_2 state means that a treatment of dynamic electron correlation (with further geometry reoptimization) would be essential for an accurate result. More important is the nature of the distortion which is required to bring the S_2 and S_1 states of pentalene together, in particular the exaggerated double and single bonds in one ring and the expansion to accommodate four weakly coupled electrons in the other. With S_1/S_0, there is a high probability that the initial motion on S_1 will lead to a crossing at which efficient decay can take place. For S_2, it appears that there is no such coordinate, and consequently there is no special acceleration of nonradiative decay relative to fluorescence.

In summary, our calculations suggest that there is no simple mechanism for efficient nonradiative decay of the S_2 state of pentalene, which is consistent with the fluorescence observed when exciting below the 0−0 transition to S_3. However, an accessible surface crossing[17] between S_1 and S_0 means that nonradiative deactivation of S_1 predominates. The existence (or lack) of a crossing depends on the electronic structure of the two states and is not a simple function of the energy gap. Further calculations would be necessary to generalize these results safely to molecules with analogous electronic states, such as other antiaromatic polycyclic hydrocarbons. With MMVB, the valence excited states of molecules with up to 24 carbon p_π electrons can currently be studied.[22]

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