Reply to Comment on "Fluorescence of Antiaromatic Systems: An Experimental and Theoretical Study of 1,3,5-Tri-*tert*-butyl-pentalene"

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The Comment on "Fluorescence of Antiaromatic Systems: an Experimental and Theoretical Study of 1,3,5-Tri-*tert*-butyl-pentalene" reports on energy surface crossings between electronic states of pentalene and their role in promoting nonradiative decay. Specifically, it is shown that (i) the S_1/S_0 crossing and the S_1 minimum have almost identical geometries and comparable energies while (ii) the S_2/S_1 crossing is at a much higher energy, ≈40 kcal/mol, than the S_2 minimum and corresponds to a distorted structure with respect to the latter. It is therefrom implied that nonradiative decay dominates over radiative emission in S_1 while no simple deactivation mechanism can be envisaged for S_2, thus favoring fluorescence from this state.

We appreciate the point of view emphasizing surface crossings as the key factor for nonradiative decay in pentalene and we regret our ignorance of the paper dealing with the subject.[1] On the other hand, we were aware of the qualitative basis of our[2,3] and previous[4] understanding on $S_n \rightarrow S_0 (n \geq 2)$ emission in pentalene and indacene derivatives, TTBP and TTBI, respectively. It is definitely positive that the experimental investigation about this antiaromatic property is supported by a more quantitative model of nonradiative decay from S_n.

The second point (ii) of the Comment deserves more attention, being possible a direct comparison with experimental data. It is in fact suggested, on the basis of the S_2/S_1 surface crossing, the assignment of the weak room temperature fluorescence of TTBP when excited at 380 nm to the $S_2 \rightarrow S_0$ transition. There are several indications contrary to this hypothesis. First, no experimental evidence of the $S_2(A_g)$ state was obtained in the energy region 27000−20000 cm^{-1}, below the allowed $S_0 \rightarrow S_3$ transition, though extensive and careful investigations were carried out on glassy samples of TTBP at 77 K and with different concentrations.[3] Second, highly accurate CASPT2 calculations have been reported on vertical $S_0 \rightarrow S_n$, transition energies, locating the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ values of pentalene at 1.69 and 2.91 eV, respectively.[5] The red shift of the transition energies following the butyl substitution has been estimated semiempirically to be 0.3 eV for the former and 0.47 eV for the latter.[5] The final values, 1.39 eV (≈11200 cm^{-1}) and 2.44 eV (≈19700 cm^{-1}), are in good agreement with the broad maxima of the visible absorption spectrum at 15 K, 12100, and 17300 cm^{-1}, shown in Figure 1. The relative intensities of the two bands are also consistent with calculated oscillator strengths.[5] Third, the room temperature $S_0 \rightarrow S_3$ absorption band has non vanishing molar extinction at 380 nm, as seen in Figure 3 of ref 3. These results are a strong evidence that the S_2 state should correspond to the 17300 cm^{-1} band (≈578 nm) of Figure 1 and that the weak fluorescence observed with $\lambda_{exc} = 380$ nm at room temperature is due to the S_3 state. Finally, this interpretation is consistent with preliminary results[6] from transient femtosecond experiments dealing with excited state lifetimes. Combination of these values with the reported fluorescence quantum yield of TTBP[3] suggests that responsible of the observed fluorescence is an allowed state, in agreement with experimental[2] and theoretical[5] estimates of $f_{S_0 \rightarrow S_3}$.

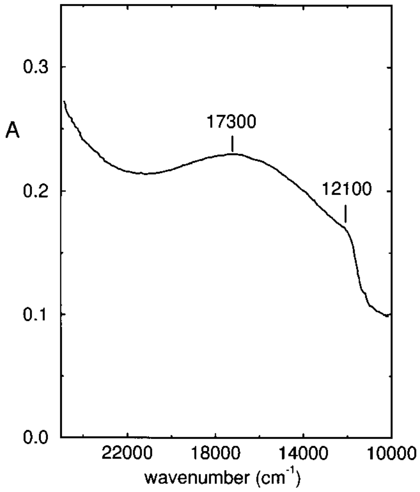

Figure 1. Absorption spectrum of TTBP 10^{-3} M in isopentane/ether solution at 15 K in the energy range 10000−25000 cm^{-1}. The absorption maxima are indicated.

In summary, while point (i) is a strong argument against the occurrence of $S_1 \rightarrow S_0$ fluorescence, point (ii) indicates, to our opinion, only the possibility of observation of $S_2 \rightarrow S_0$ fluorescence. Experimental evidence of this emission is still lacking. In this respect, theoretical calculations on the S_2/S_1 (and possibly S_2/S_0) surface crossing taking into account the ionic nature of the S_2 state would be of great help.

References and Notes

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