The Mechanism of Intersystem Crossing for Some Substituted Aromatic Hydrocarbons

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THE MECHANISM OF INTERSYSTEM CROSSING FOR
SOME SUBSTITUTED AROMATIC HYDROCARBONS

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ABSTRACT

In view of the experimentally observed energy levels, the mechanism of intersystem crossing for 9,10-diphenylanthracene, 9,10-dimethylanthracene, and 1,3,6,8-tetraphenylpyrene is discussed and compared with that for parent hydrocarbons. The proposed mechanism explains the drastic changes in the photophysical properties upon phenyl or methyl substitution at the most active centers of anthracene and pyrene rings.

INTRODUCTION

Certain types of perturbations result in significant changes in the photophysical properties of molecular systems. These changes have been explained in terms of concurrent alterations in the location of triplet levels with respect to that of the first excited singlet state of these molecules.

The heterocyclic compound, quinoline, exhibits a greater ratio of phosphorescence to fluorescence than the parent hydrocarbon, naphthalene.

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The (n,π^*) triplet level, which is absent in naphthalene and lies between the lowest (π,π^*) singlet and (π,π^*) triplet levels, enhances the inter-system crossing process in quinoline.[1]

Aromatic aldehydes and ketones like benzaldehyde and benzophenone show strong phosphorescence and almost no fluorescence whereas the corresponding aliphatic carbonyl compounds exhibit both. In aromatic carbonyl compounds, a (π,π^*) triplet level lies between the (n,π^*) singlet and (n,π^*) triplet levels. This intermediate triplet level again enhances the yield of triplet population. In the carbonyl compounds of aliphatic character, no such intermediate triplet level is extant so that fluorescence can easily compete with phosphorescence.[1]

The high quantum yield of triplet state formation (Q_T) in anthracene, which is 0.70 in ethanolic solutions, drops abruptly to almost zero if the anthracene crystal is examined. The fluorescence quantum yield (Q_F) becomes 0.99 in the crystalline state. The high Q_F value for crystalline anthracene was interpreted as being due to the red shift in the position of the first excited singlet state in crystalline state which now lies 1260 cm.$^{-1}$ below the second triplet state[2] (see Figure 1).

Phenyl or methyl substitution at the most active centers of anthracene and pyrene rings also causes some significant changes in the photophysical properties. Close examination of the values[3,4,5] for the quantum yields of fluorescence and triplet state formation of anthracene, 9,10-diphenyl-anthracene, 9,10-dimethylanthracene, pyrene, and 1,3,6,8-tetraphenylpyrene revealed some rather drastic changes in the photophysical properties accompanying substitution at the most active centers of the parent hydrocarbons. The fluorescence quantum yield (Q_F) increases from about 0.30 for anthracene to 0.89 for 9,10-diphenylanthracene and 9,10-dimethylanthracene, all for ethanolic solutions. The quantum yield for triplet state formation (Q_T)

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in the same solvent decreases accordingly to a value of 0.03. Q_F of pyrene in ethanol is 0.72 and Q_T is 0.28 at 21°C. If the most active centers in a pyrene ring are substituted to give 1,3,6,8-tetraphenylpyrene, the fluorescence quantum yield again approaches unity. These observations suggested the present work on the relative position of the first excited singlet state vs. various triplet levels.

The experimental observation[2,6,7] of the T_2 state in anthracene provided valuable insight toward understanding of the high intersystem crossing yield of this hydrocarbon in solution. The energy of this state, in solution, closely matches that of the first excited singlet state so that an efficient intersystem crossing can occur to populate the lowest triplet level.

Windsor and Novak,[6] utilizing a double-beam near-infrared detection technique, have revealed the existence of a theoretically predicted[8] second triplet state for pyrene which lies 1300 cm.$^{-1}$ above the first excited singlet. This level is responsible for the promotion of inter-system crossing as in anthracene, but this time with some activation energy associated with it. (The activation energy for intersystem crossing in pyrene has been found to be 3 kcal/mole,[9] corresponding to 1150 cm.$^{-1}$.)

Ting,[10] using Pariser-Parr calculations, has offered an explanation for the difference in the fluorescence quantum yields of anthracene and 9,10-diphenylanthracene. In the latter hydrocarbon, the calculated triplet state energies are shifted upward, with respect to the position of the first excited singlet, to an extent such as to preclude an easy intersystem crossing pathway. The calculated ΔE ($S_1 \longleftrightarrow T_1$) was found to be less than that of anthracene because of the apparent conjugation with two phenyl rings (which were assumed to be planar with the anthracene ring) and thus lessening exchange interaction which determines ($S_1 \longleftrightarrow T_1$) energy gap.

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The experimental energy levels for the above substituted anthracenes and for 1,3,6,8-tetraphenylpyrene were not known. It is the purpose of this communication to present the experimentally observed energy levels of such substituted hydrocarbons and compare them with that of the corresponding parent hydrocarbon and to discuss their influence on the efficiency of crossover from the singlet to triplet manifolds.

EXPERIMENTAL RESULTS

The positions of the first triplet levels of the substituted compounds were estimated from the maximum of the shortest wavelength band of the phosphorescence spectrum in EPA at 77°K., and from the induced singlet ⟶ triplet direct absorption spectrum at 25°C. in EtBr as a heavy-atom solvent and $(CH_3COCHCOCH_3)_2Cu$ as paramagnetic perturbing species. Triplet-triplet absorption spectra (in acetonitrile at 25°C.) were obtained with a kinetic spectrophotometer.[11] The unimolecular lifetimes of triplets in acetonitrile at 25°C. under an argon atmosphere were found to be 1.11, 0.91, and 1.05 msec. for 9,10-diphenylanthracene, 9,10-dimethylanthracene, and 1,3,6,8-tetraphenylpyrene, respectively. Figure 1 and Figure 2 summarize the energy levels of the anthracenes and of the pyrenes.

DISCUSSION

The results obtained in this study of 9,10-diphenylanthracene and 9,10-dimethylanthracene show that, upon substitution of the most active centers in the anthracene ring with either phenyl or methyl groups, ΔE $(S_1 \longleftrightarrow T_1)$ splitting is greatly decreased with respect to the same splitting of the parent hydrocarbon. Ting[10] has attributed the splitting to the exchange interaction. It is clear from the experimental value of
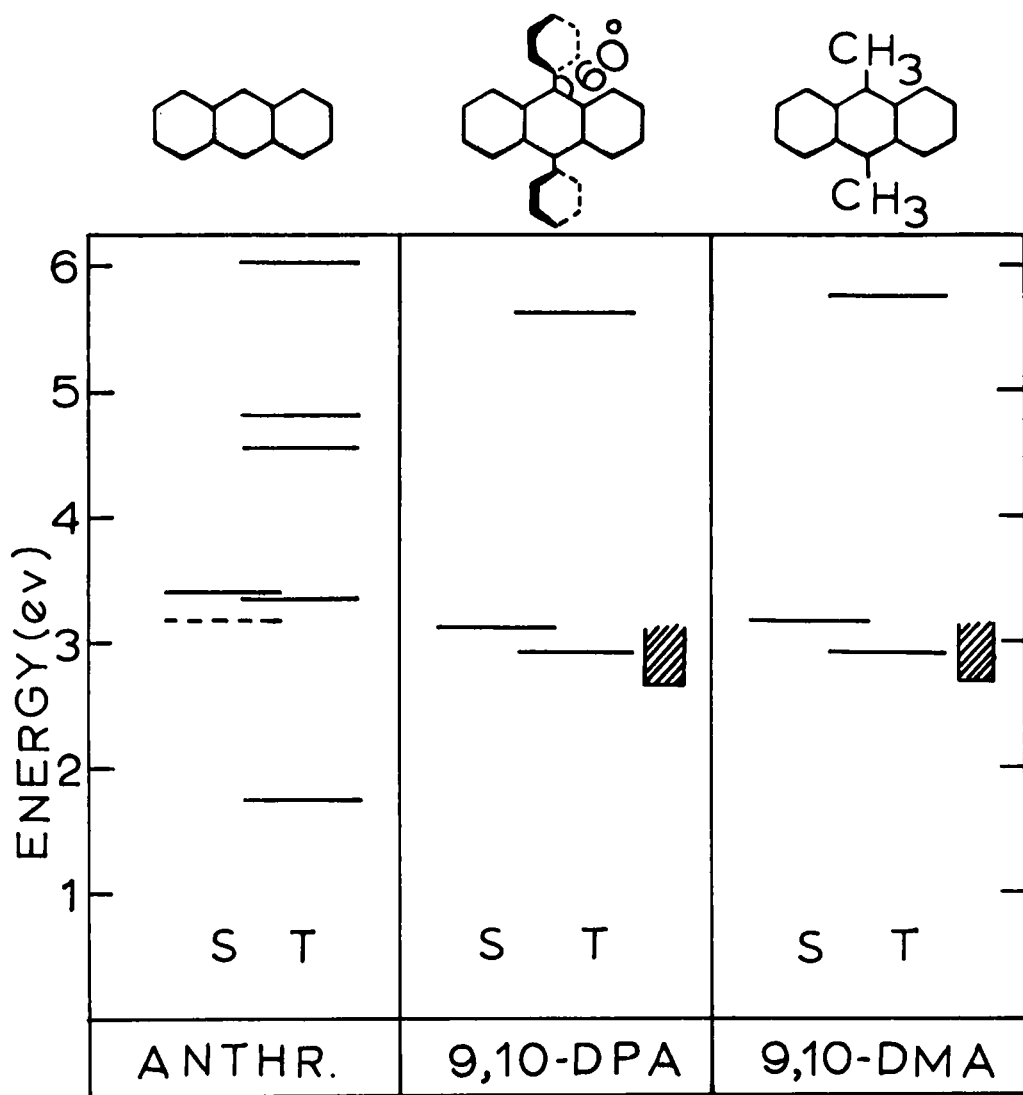
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Figure 1.   Estimated energy levels of anthracene, 9,10-diphenylanthracene, and 9,10-dimethylanthracene.

Energy levels of anthracene are taken from the literature (2,6,7,16)

$S_0 \longrightarrow T_1$ induced absorption bands

- - - - First singlet level of crystalline anthracene
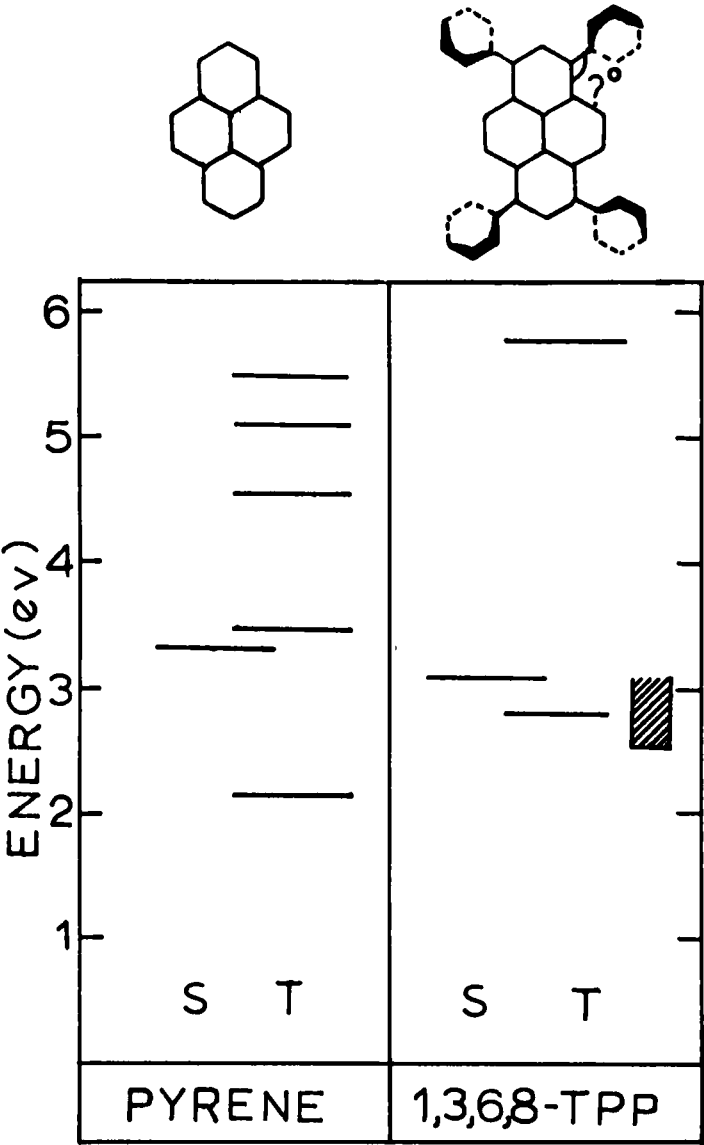
Figure 2. Estimated energy levels of pyrene and
1,3,6,8-tetraphenylpyrene. Energy levels
of pyrene are taken from the literature (6,16).

$S_0 \longrightarrow T_1$ induced absorption bands

ΔE ($S_1 \longleftrightarrow T_1$) that the exchange interaction is less than his calculations indicate.

The reactivities of the cation radical ions[12] and the esr hyperfine splitting constants[13,14] of the cation and anion radical ions of these two substituted anthracenes are quite similar. It is also established that, in 9,10-diphenylanthracene, the phenyl substituents are twisted (by about 60°) from the plane of the anthracene ring both in the ground state[13] and in the excited singlet state[15] due to steric hindrance by the α hydrogens. The similarities noticed in the values of Q_F/Q_T and in the observed optical energy levels of the two substituted anthracenes also indicate that contrary to the assumption of the theoretical work,[10] the redistribution of the electron density upon substitution occurs primarily within the anthracene ring.

The examination of these energy level diagrams for the substituted hydrocarbons further implies that, for an effective intersystem crossing and triplet state population, not only is the existence of the higher lying (whose energies closely match with that of S_1 level) triplet levels required but also needed is a low lying triplet states which can take energy from intermediate triplets (after crossover has occurred) via a very fast internal conversion process. For parent hydrocarbons (anthracene and pyrene) the presence of a close lying T_2, coupled with the rapid internal conversion within the triplet manifold, results in a much more significant loss of singlet excitation energy via intersystem crossing. Owing to the shift in the position of the triplet levels in the substituted hydro-carbons such as 9,10-dimethylanthracene, 9,10-diphenylanthracene, and 1,3,6,8-tetraphenylpyrene, one important pathway[17] for the intersystem crossing processes (i. e., from S_1 to T_2) is now removed, reducing the efficiency of triplet population.

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The importance of the position of the higher lying triplet levels in populating the first triplet state of aromatic hydrocarbons via intersystem crossing appears to be far greater than that of so-called density-of-states argument. This can be illustrated by comparing the photophysical properties of two planar molecules whose ΔE ($S_1 \longleftrightarrow T_1$) splittings are identical (phenanthrene[18]: $Q_F \simeq 0.15$, $Q_T = 0.80$ vs. perylene[19]: $Q_F \simeq 0.89$, $Q_T \simeq 0.06$). If the density-of-states argument were operative (which is the same for the two molecules), Q_F and Q_T values of these would also be almost identical. The theoretically predicted,[20] but experimentally as yet unobserved,[6] T_2 state which lies close in energy to the S_1 of phenanthrene is probably responsible for this efficient intersystem crossing. It should be noted that this T_2 level has been detected[21] for 4,5-dihydropyrene (which is a substituted phenanthrene ring where the substitution is not at the most active sites).

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