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## Photophysics of Phenylcyclopropanes, Styrenes, and Benzocycloalkadienes<sup>1</sup>

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**Abstract:** The fluorescent and phosphorescent properties of several styrenes, phenylcyclopropanes, and benzoalkadienes were investigated. The effect of the varying orientation of the alkenyl or cyclopropyl group with respect to the  $\pi$  system of the benzene chromophore on the photophysics of the molecules was examined. The photophysics of several phenylcyclopropanes in which the geometry between the cyclopropane ring and the aryl moiety is either not fixed or fixed, in one case, to maximize a conjugative interaction between the two groups, in the other case, to minimize the effect, confirmed a stereoelectronic requirement for an excited state interaction between the aromatic and cyclopropane rings. The phenylcyclopropane with the poorest overlap of the cyclopropane bonds to the adjacent aromatic ring was the most highly phosphorescent of the phenylcyclopropanes studied; presumably the ineffective interaction negates a fast triplet radiationless process, e.g.,  $\alpha,\beta$  C-C bond cleavage, and allows triplet emission to compete more favorably. Alkenylbenzenes, in which the styryl double bond is fixed by steric constraints to be out of plane (at an angle close to 90°) with the phenyl ring, exhibited extremely low fluorescent yields attributable to enhanced internal conversion arising from a closing of the  $S_1$ - $S_0$  energy gap as this highly twisted conformation is reached. A similar mechanism may operate in the triplet states of all the alkenylbenzenes rendering them nonemissive.

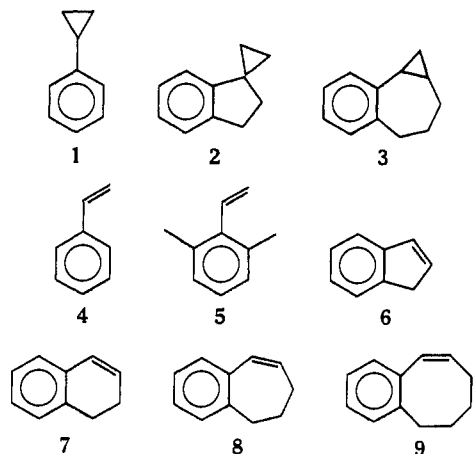
Although the electronic absorption spectra of arylcyclopropanes<sup>2</sup> and arylalkenes<sup>3</sup> have been extensively studied, conclusive information regarding emission characteristics of these molecules<sup>4</sup> is lacking. This is surprising in view of the photochemical interest in these systems. Arylcyclopropane photochemistry has been highly explored, and is known to include many processes, of which cis-trans isomerization and ring opening leading to olefin formation are most important.<sup>5</sup> The photoreactions of conjugated arylalkenes have been investigated to a lesser extent, but dimerization, geometric isomerization, and rearrangements are known to be major pathways of reaction for these molecules.<sup>6</sup>

O'Connell et al.<sup>4a</sup> reported that the luminescence of phenyl and naphthyl chromophores is quenched by adjacent cyclopropyl groups. Specifically, they noted that the phosphorescence quantum yield of phenylcyclopropane was ca. 50 times less than that of a model alkylbenzene. Becker et al.<sup>4c</sup> noted that phenylcyclopropane exhibits a benzenelike fluorescence, but no phosphorescence. Salisbury<sup>4b,d</sup> investigated the fluorescence of several phenylcyclopropanes in conjunction with photochemical studies. Contrary to some of O'Connell's results, these phenylcyclopropanes showed enhanced fluorescence quantum yields over those of model alkylbenzenes.

Reports of studies on the luminescence of alkenylbenzenes are slightly more numerous. Heckmann<sup>4e</sup> reported that indene in EPA solvent at liquid air temperature phosphoresced weakly

in the 400-500-nm spectral region. Recently, however, it has been noted that the emission may be due to an impurity.<sup>4g,i,k</sup> Examination of the recombination luminescence of styrene in a methylcyclohexane glass at 77 K revealed only styrene fluorescence.<sup>4f</sup> The lack of phosphorescence can be attributed to either a negligible triplet population and/or nonradiative triplets. The evidence suggested that styrene triplets, although generated, were deactivated by a radiationless process(es). Recently, Salisbury and Crosby<sup>4m</sup> found through fluorescence studies that nonradiative processes make important contributions to the photophysics and photochemistry of styrenes. Zimmerman et al.<sup>4j,l</sup> observed in a series of 1-phenylalkenes excited state decay processes which correlate with molecular flexibility. Both the Salisbury and Zimmerman studies revealed that the contribution of radiationless decay to the deactivation of the excited states in these systems is strongly structurally dependent.

We undertook a study of the luminescence, fluorescence and phosphorescence, of a series of phenylcyclopropanes, styrenes, and benzocycloalkadienes. The intention was to correlate the radiative and radiationless processes in these molecules with the varying orientation of either a cyclopropyl or alkenyl moiety with respect to the aromatic chromophore. The phenylcyclopropanes included the parent compound **1** as well as the conformationally rigid phenylcyclopropanes **2** and **3**. The alkenylbenzenes included styrene (**4**), 2,5-dimethylstyrene (**5**),



and four ortho-fused conjugated benzocycloalkadienes: indene (6), 1,2-dihydronaphthalene (7), benzocycloheptadiene (8), and benzocyclooctadiene (9).

### Experimental Section

**Materials and Sample Preparation.** Cyclohexane was used as solvent in the room temperature spectroscopic studies. Reagent grade solvent (Matheson Coleman and Bell) was purified by repeated washings with 10% fuming sulfuric acid, followed by washings with sulfuric acid, water, and dilute aqueous sodium hydroxide and drying. Prior to use, it was distilled from KOH, passed through an alumina-silver nitrate column,<sup>7</sup> and redistilled from CaH<sub>2</sub>. Methylcyclohexane (Matheson Coleman and Bell), used as a solvent for low-temperature emission experiments, was purified in the manner employed for cyclohexane. Ethyl ether-ethanol (1:1) was the other solvent system used for emission studies at 77 K. The ethyl ether (Mallinckrodt anhydrous) was used without further purification. Ethanol (95%) was dried over anhydrous K<sub>2</sub>CO<sub>3</sub> and passed through Woelm activity 1 alumina. It was then distilled from CaH<sub>2</sub> prior to use. The cyclohexane, nitrogen bubbled, gave little detectable emission at room temperature. The methylcyclohexane and ethyl ether-ethanol (1:1) as glasses at 77 K were also free of spurious luminescence. Naphthalene and biphenyl were obtained from the Baker Chemical Co. and purified by two recrystallizations from purified ethanol and two recrystallizations from purified cyclohexane, followed by sublimation. Styrene, 2,5-dimethylstyrene, indene, indan, and ethylbenzene were procured from either Aldrich, Matheson Coleman and Bell, or Eastman Kodak. They were purified by preparative gas chromatography (6 ft × 3/8 in., 20% SE-30 on Chromosorb W, base washed) followed by semimicro distillation. The 1,2-dihydronaphthalene, benzocycloheptadiene, and benzocyclooctadiene were prepared from the corresponding benzocycloalkanones which were reduced to the alcohol followed by dehydration.<sup>8</sup> They were also purified by preparative gas chromatography (6 ft × 3/8 in., 20% SE-30 on Chromosorb W, base washed) followed by semimicro distillation. The phenylcyclopropanes were prepared by methods described in the literature.<sup>2a,b,8</sup> These were purified by preparative gas chromatography (6 ft × 3/8 in., 20% SE-30 on Chromosorb W, base washed, and 10 ft × 3/8 in., 20% Carbowax 20M on Chromosorb P, base washed) followed by semimicro distillation.

**Spectroscopic Techniques.** Absorption spectra were recorded on either a Cary Model 14 or a Unicam SP-800A spectrophotometer. Emission spectra were obtained on either a Perkin-Elmer Hitachi MPF-2A or MPF-3L emission spectrophotometer. Room temperature fluorescence quantum yield determinations were done in nitrogen-bubbled cyclohexane solutions. Ethylbenzene ( $\phi_f = 0.11$ )<sup>9</sup> and biphenyl ( $\phi_f = 0.15$ )<sup>10</sup> were used as the quantum yield standards for determining relative fluorescence efficiencies of the phenylcyclopropanes and alkenylbenzenes, respectively. No correction for the emission monochromator-detector response was necessary since sample and reference fluorescence occurred in the same spectral region. The determination of  $\phi_p$  for 3 was performed in an ethyl ether-ethanol glass using naphthalene fluorescence ( $\phi_f = 0.33$ )<sup>11</sup> as a standard. The spectra were corrected in this case. Absorbances at the wavelength of excitation (260 nm) were kept below 0.2 to avoid inner filter effects and were closely matched. They were measured on a Beckman-Gilford spectrophotometer. Fluorescence lifetimes were measured by single photon counting. Excitation was through a

**Table I.** Fluorescent Properties of Several Phenylcyclopropanes and Model Compounds in Cyclohexane Solution<sup>a</sup> at Room Temperature

Compd	$\phi_f^{b,c}$	$\tau_f$ , ns	$k_f$ , s <sup>-1e</sup>	$k_s$ , s <sup>-1f</sup>
1	0.20	31.3	$6.4 \times 10^6$	$2.6 \times 10^7$
2	0.06	20.4	$2.9 \times 10^6$	$4.6 \times 10^7$
3	0.19	39.7	$4.8 \times 10^6$	$2.0 \times 10^7$
10	0.36	29.7	$1.2 \times 10^7$	$2.2 \times 10^7$
11	0.11 <sup>d</sup>	38.8	$2.8 \times 10^6$	$2.2 \times 10^7$
12	0.08 <sup>d</sup>	24.5 <sup>d</sup>	$3.1 \times 10^6$	$3.8 \times 10^7$
13	0.17 <sup>d</sup>	38.2 <sup>d</sup>	$4.5 \times 10^6$	$2.2 \times 10^7$

<sup>a</sup> Deoxygenated by nitrogen bubbling. <sup>b</sup> Relative to ethylbenzene,  $\phi_f = 0.11$ . <sup>c</sup> Error estimated at  $\pm 10\%$ . <sup>d</sup> Reference 9. <sup>e</sup> From  $k_f = \phi_f \tau_f^{-1}$ . <sup>f</sup> From  $k_s = \tau_f^{-1} - k_f$ .

Baird-Atomic interference filter and the emission was isolated by a monochromator. Log  $I_f$  vs. time plots were made from the data obtained from the multichannel analyzer. The solutions were deoxygenated as for the  $\phi_f$  determinations.

### Results and Discussion

**Emission Studies on Phenylcyclopropanes.** Phenylcyclopropane (1), spiro[cyclopropane-1,1'-indan] (2), and 1,1a,2,3,4,8b-hexahydrobenzo[a]cyclopropa[c]cycloheptene (3) have been included in ultraviolet absorption studies of cyclopropylarenes examining geometric factors that may influence cyclopropyl conjugation with a  $\pi$  electron system.<sup>2a,b</sup> Phenylcyclopropane (1) represents the situation where the cyclopropyl group is not in a fixed relationship with respect to the benzene chromophore. Molecules 2 and 3, however, are more rigid systems in which the stereodisposition of the cyclopropane ring with respect to the phenyl group is not only fixed by the cyclic framework, but can be estimated from molecular models with consideration of most stable conformations.<sup>2a,b</sup> The phenylcyclopropane 2 contains the optimum geometry for the cyclopropane ring to enter into a conjugative interaction with the benzene ring. Conversely, the steric relationship in 3 is predicted to totally preclude such an orbital overlap. The ultraviolet absorption studies found no evidence of conformational effects on the perturbation of the cyclopropyl group on the benzene chromophore.<sup>2a,b</sup> The results described below indicate that the photophysical properties of the phenylcyclopropanes included in our study do reflect the consequence of an excited state overlap of the bonds of the cyclopropane ring with the  $\pi$  system of the benzene ring.

The absorption spectra of the three phenylcyclopropanes agree with data previously discussed in the literature.<sup>2a,b</sup> The results of the fluorescence studies are reported in Table I along with data for model and reference compounds indan (10), ethylbenzene (11), isopropylbenzene (12), and *o*-xylene (13). Total emission spectra at 77 K in either methylcyclohexane or ethyl ether-ethanol (1:1) glass revealed that 1 and 2 are nonphosphorescent within the detectable limits of the emission spectrophotometer used.  $\phi_p$  for these two molecules is estimated to be  $\leq 10^{-3}$  on the basis of comparison to the fluorescence intensity and sensitivity of the emission spectrophotometer.<sup>12</sup> The phenylcyclopropane 3, in contrast, was found to be weakly phosphorescent;  $\phi_p$  was measured to be 0.019 in ethyl ether-ethanol (1:1) at 77 K.

The fluorescence quantum yield of phenylcyclopropane (1) is higher than that of model alkylbenzenes, e.g., isopropylbenzene, as seen in Table I. This is the same result obtained by Salisbury,<sup>4b,d</sup> but contrary to the results of O'Connell et al.<sup>4a</sup> The enhancement of the fluorescence efficiency of 1 over that of analogous molecules appears to be the result of an increase in  $k_f$  and a decrease in  $k_s$ , the rate constant for radiationless decay of the singlet which is the sum of internal conversion ( $k_{ic}$ ), intersystem crossing ( $k_{isc}$ ), and photochemistry ( $k_r$ ).

Salisbury noted that the data on gas-phase fluorescence quantum yields of phenylcyclopropane and other monoalkylbenzenes suggested that a decrease in  $k_{isc}$  is responsible for the increase in  $\phi_f$ . The data in Table I show that  $k_s$  for **1** is approximately the same as or slightly lower than that of analogues such as ethyl- or isopropylbenzene. The rise in  $\phi_f$  is primarily due to a 2–3 factor increase in  $k_f$  seen by making the comparison between the molecules **1**, **11**, and **12**. The increase in  $k_f$  finds its origin in the higher absorption strength of the  ${}^1L_b$  band.<sup>2b</sup>

The fluorescence lifetime, quantum yields, and values of  $k_f$  and  $k_s$  for **3** are close to those of an appropriate model compound, e.g., *o*-xylene. The  $k_f$ 's are predicted to be fairly identical as the molar extinction coefficients for the  $S_1 \leftarrow S_0$  transition in **3** resemble those of *o*-xylene or benzosuberone.<sup>2b</sup> One can conclude that the photophysics of the  $S_1$  state of **3** reveal no perturbation peculiar to the presence of the cyclopropane ring.

The phenylcyclopropane **2** exhibits different photophysical behavior than either **1** or **3**. Compared to **10**, a model dialkylbenzene containing the strain perturbations predicted also to be present in **2**, **2** exhibits a fourfold decrease in  $k_f$  and a twofold increase in  $k_s$ . The diminution in  $k_f$  is surprising in view of the absorption strength of the first absorption band, comparable to that of **10**.<sup>2b</sup> The parallel relationship between radiative rate constant and absorption strength is known to break down in instances where the excited state geometry is distorted from that of the ground state.<sup>13</sup> A mechanism by which the molecule could distort its geometry such as to lower  $k_f$  to a value comparable to that of an unstrained monoalkylbenzene, e.g., ethylbenzene, as seen in Table I, cannot be elucidated at this time. Perhaps a weakening of an  $\alpha,\beta$  C–C bond in the cyclane portion of **2** relieves the strain and/or distorts the shape of the  $S_1$  state so as to lower  $k_f$ . The increase in  $k_s$  in **2** may be another example of the general phenomenon noted by Morrison et al.<sup>9,14</sup> whereby alkylbenzenes possessing  $\alpha,\beta$  C–C bonds out of plane with the phenyl group facilitate internal conversion. Although two  $\alpha,\beta$  C–C bonds are locked out of plane in **2**,  $k_s$  is only slightly higher than that of **12**, which has two  $\alpha,\beta$  C–C bonds free to rotate about the aryl,  $\alpha$  C–C bond. *tert*-Butylbenzene was found to have even a higher  $k_s$  value.<sup>15</sup> Either the number of out-of-plane  $\alpha,\beta$  C–C bonds and/or the degree to which the bonds are out of plane is apparently more crucial to this decay mechanism than a rigid conformation with  $\alpha,\beta$  C–C bonds held firmly out of plane. Again, the manner in which the structural characteristics of out-of-plane  $\beta$  C–C bonds facilitates  $S_1 \rightarrow S_0$  decay is not clear.

Low-temperature total emission spectra of **1–3** revealed strong fluorescence, but a low or undetectable phosphorescence yield. The lack of phosphorescence from **1** is in agreement with previous reports,<sup>4a,c</sup> but our report now quantifies the value of  $\phi_p$ . These results contrast with those obtained from alkylbenzenes,<sup>9,16</sup> including benzocycloalkenes,<sup>17</sup> which are strongly phosphorescent as well as fluorescent, with  $\phi_p/\phi_f$  ca. 1.<sup>16</sup> There are two possible reasons for the absence or low yield of phosphorescence in the phenylcyclopropanes. Either  $\phi_{isc}$  has diminished greatly such that a low yield of triplets results and/or the triplets, once generated, are deactivated by a radiationless process(es) before emission can occur. The rate constant of such a radiationless process(es) would not have to be high to quench the phosphorescence as  $k_p$  for alkylbenzenes is low,  $\leq 1$  s<sup>-1</sup>.<sup>16</sup> A rate constant for triplet radiationless decay,  $k_t$ , of  $10^3$  s<sup>-1</sup>, for example, competing with  $k_p \leq 1$  s<sup>-1</sup><sup>16</sup> even after a unit  $\phi_{isc}$  would yield  $\phi_p \leq 10^{-3}$ , a yield approaching or below detectable limits.

A definitive explanation for the poor phosphorescent property of the phenylcyclopropanes is not possible without an independent determination of  $\phi_{isc}$ . Most alkylbenzenes seem

to have  $\phi_{isc}$  greater than 0.1, typically in the range 0.3–0.6.<sup>14,18</sup> A noteworthy exception is *tert*-butylbenzene, whose lack of observable phosphorescence may be due to a low  $\phi_{isc}$ .  $\phi_{isc}$  is 0.09 due to an unusually high  $k_{ic}$  which effectively competes in the decay of the singlet. Assuming that  $\phi_{isc}$  is appreciable in **1–3**, it is intriguing to speculate that phenylcyclopropane **3**, with the poorest geometry between the cyclopropane ring and benzene chromophore for a conjugative interaction, is at least detectably phosphorescent because this interaction is weak. A recent investigation<sup>5f,g</sup> of arylcyclopropane photochemistry has shown that the  $\sigma$  bond of the cyclopropane ring whose orbitals overlap strongly with the  $\pi$  system of the aromatic ring is the bond predominantly weakened and cleaved in an isomerization reaction leading from the triplet state. If photochemistry is a major pathway of triplet decay, it would be expected to be more predominant in **2** and in **1** (in the proper conformation) than in **3**.  $\alpha,\beta$  C–C bond cleavage in the cyclopropane ring of **3** may still be proceeding, but to a lesser extent than in **1** or **2**, and consequently diminishes, but does not extinguish, the phosphorescence. One can conclude from all the spectroscopic data on **3** that photophysically it more closely resembles a model alkylbenzene than either **1** or **2** because of the decreased cyclopropyl conjugation.

**Spectroscopic Studies on Styrenes and Benzocycloalkadienes.** The styrenes, **4** and **5**, and benzocycloalkadienes, **6–9**, are best discussed together as they are both classes of alkenylbenzenes. The ultraviolet absorption spectroscopy of styrenes has been discussed by Suzuki.<sup>3a</sup> The structured weak band in styrene in the 273–291-nm region probably corresponds to the  ${}^1L_b$  band in benzene. The  ${}^1L_a$  band in benzene near 204 nm is extended to 248 nm in styrene. Suzuki refers to this transition as the A band. As the dihedral angle,  $\theta$ , measuring the deviation of the olefinic group from planarity with the phenyl ring is increased by ortho,  $\alpha$ , and cis- $\beta$  substitution, the A band undergoes a hypochromic and hypsochromic shift.<sup>3a,b</sup>

The A band maxima of **4** and **6** both appear at 248 nm in agreement with the planarity of the molecules. Sterically hindered **5** exhibits an A band that has shifted to 238 nm. As the alkenyl group is gradually twisted out of plane as a Drieding model shows occurs in **7**, the structured first absorption band is not discernible and the A band appears at 259 nm. **8** and **9** are characterized by the lack of a distinguishable absorption band in the 270–300-nm region with A bands appearing at 255 and 240 nm, respectively. Literature data show that enlargement of the fused ring to give benzocycloalkadiene results in a weak A band at ca. 240 nm ( $\epsilon \sim 2500$  M<sup>-1</sup> cm<sup>-1</sup>).<sup>19</sup> Drieding models reveal that in **8**, the olefinic group is twisted ca. 45° out of plane while **9** has the double bond almost entirely out of plane,  $\theta$  ca. 90°. The A band of **9** is most hypochromically shifted while **8** has its A band positioned at a longer wavelength in agreement with a smaller  $\theta$ . There seems to be no correlation in this series of benzocycloalkadienes with the position of the A band and the strength of its absorption as is the case with styrenes. Except for benzocycloalkadiene and **8**, the benzocycloalkadienes have A bands of about equal intensity,  $\epsilon \sim 10\,000$  M<sup>-1</sup> cm<sup>-1</sup>.<sup>19,20</sup> Transition wavelength rather than absorptivity seems to be in better correlation with  $\theta$ . A previous study of the benzocycloalkenes series benzocyclobutene through benzocyclooctene revealed the lack of parallel change between the  ${}^1L_b$  0–0 band  $\lambda$  and  $\epsilon$ .<sup>21</sup> Ground-state strain effects<sup>2b</sup> may be responsible for the absence of a common direction and magnitude of change between  $\lambda_{max}$  and  $\epsilon_{max}$  in both the benzocycloalkene<sup>21</sup> and benzocycloalkadiene series.

The luminescence data in Table II reveal that with increasing ring size, the  $\phi_f$ 's of the benzocycloalkadienes increase, then sharply decrease with **9**. The corresponding benzocycloalkenes have been shown to exhibit the opposite effect,<sup>17</sup> a

**Table II.** Fluorescent Properties of Several Styrenes and Benzocycloalkadienes in Cyclohexane Solution<sup>a</sup> at Room Temperature

Compd	$\phi_f^{b,c}$	$\tau_f$ , ns	$k_f$ , s <sup>-1e</sup>	$k_s$ , s <sup>-1f</sup>
4	0.220	21.7	$1.0 \times 10^7$	$3.6 \times 10^7$
5	0.002	<i>d</i>		
6	0.072	23.2	$3.1 \times 10^6$	$4.0 \times 10^7$
7	0.083	16.1	$5.2 \times 10^6$	$5.7 \times 10^7$
8	0.120	24.2	$5.0 \times 10^6$	$3.6 \times 10^7$
9	0.003	<i>d</i>		

<sup>a</sup> Deoxygenated by nitrogen bubbling. <sup>b</sup> Relative to biphenyl,  $\phi_f = 0.15$ . <sup>c</sup> Error estimated at  $\pm 10\%$ . <sup>d</sup> A definitive  $\tau_f$  could not be determined as lifetime was short and fluorescence intensity weak relative to scattered light. <sup>e</sup> From  $k_f = \phi_f \tau_f^{-1}$ . <sup>f</sup> From  $k_s = \tau_f^{-1} - k_f$ .

pattern of decreasing  $\phi_f$  with increasing ring size (decreasing  $S_1 \leftarrow S_0$  absorption strength), with the exception of benzocycloheptene, whose  $\phi_f$  and molar extinction coefficients in the first absorption band<sup>21</sup> are lower than those of the corresponding saturated analogues.<sup>17</sup> For **6** this is due to a decrease in  $k_f$  and an increase in  $k_s$  compared to **10**. **4** shows a greater fluorescence efficiency than **11** while **5** is similar to **9** in being characterized by a low  $\phi_f$ . The  $k_f$  of **4** is higher than that of its analogue **11**, and since the  $k_s$ 's are similar, a higher  $\phi_f$  results.

As was found for phenylcyclopropanes **1** and **2**, **4-9** lack measurable phosphorescence.  $\phi_p$ 's were again estimated to be  $\leq 10^{-3}$  in comparison to the fluorescence intensity.<sup>12</sup> Again, this contrasts with saturated analogues<sup>22</sup> as was noted in the discussion of phenylcyclopropanes.

The ca. 100-fold diminution in the fluorescence efficiency of **5** compared to **4** and the average factor of 30 decrease in  $\phi_f$  of **9** in relation to **6**, **7**, and **8** is a striking result. Zimmerman et al.<sup>4,j</sup> have reported similar results in an investigation of 1-phenylcycloalkenes. The unavailability of lifetime data for **5** and **9** makes it impossible to discern which rate constant(s)  $k_f$  and/or  $k_s$  has changed to bring about such a dramatic  $S_1$  radiationless decay. However, it is worthy to note that Zimmerman's data and calculations indicate that  $k_{ic}$  is greatly enhanced in styryl molecules where the conformation of the  $S_1$  state is such that the styrenelike double bond is twisted about the aryl moiety so that  $\phi$  approaches  $90^\circ$ . Increasing twist was shown by semiquantitative calculations to decrease that splitting between the  $S_1$  and  $S_0$  states, and thus promote radiationless decay. Attainment of a  $90^\circ$  conformation is crucial to rapid internal conversion and the rate constant for this process was shown to be dependent on the ease with which the molecule could reach the twisted conformation. The 2,6-dimethyl groups in **5** provide steric constraints to lock the vinyl group in an out-of-plane conformation. The eight-membered ring in **9** accomplishes the same spatial relation between the phenyl and olefinic moieties through its most stable confirmation. Based on the assumption that the low  $\phi_f$ 's of **5** and **9** have their origin in an enhanced  $k_s$ , i.e., an enhanced  $k_{ic}$  more so than a diminished  $k_f$ , the ease and extent to which the alkenyl group is twisted out of plane correlates with the small values of  $\phi_f$ , and is supportive of Zimmerman's hypothesis. The twisting ability of the singlet excited state with the subsequent minimization of the  $S_1-S_0$  energy gap and enhanced radiationless transition would also explain the low fluorescence efficiency,  $\phi_f = 0.003$ , that Berlman<sup>23</sup> reports for 1,1-diphenylethylene.

The study of Salisbury and Crosby<sup>4m</sup> on the photophysics of styrenes revealed that many styrenes are characterized by high  $k_s$ 's which are primarily responsible for their low  $\phi_f$ 's. It was suggested that radiationless decay from  $S_1$  is due to rotation about the olefinic double bond, and in styrenes with

hydrogen atoms on carbons  $\alpha$  to the double bond, an additional nonradiative process, e.g., photochemistry, is operative. For example, styrene and *trans-tert*-butylstyrene with no  $\alpha$  C-H bonds have  $k_s$ 's much lower than the methylstyrenes,  $\alpha$ -methylstyrene or  $\beta$ -*cis*-methylstyrene. Although these two methylstyrenes have a twisted structure ( $\theta$  ca.  $30-35^\circ$ ),<sup>3a</sup> Salisbury did not attribute the enhanced radiationless decay to the nonplanarity of the conformations. His conclusion is supported by data for (*E*)- $\alpha,\beta$ -dimethylstyrene, whose  $k_s$  is appreciably larger than for the methylstyrenes, but whose conformation is calculated to be no more twisted ( $\theta$  ca.  $32^\circ$ ).<sup>3a</sup>

Comparison of our observation with those of Salisbury shows that a nonradiative relaxation mechanism utilizing  $\alpha$  C-H bonds would not account for the low fluorescence efficiency of **5** compared to **4** nor that of **9** relative to the other members of the benzocycloalkadiene series. However, it is interesting to note that the acyclic analogue of the benzocycloalkadienes, the *cis*- $\beta$ -methylstyrene, is characterized by  $k_f = 1.7 \times 10^6$  s<sup>-1</sup> and  $k_s = 37 \times 10^7$  s<sup>-1</sup> resulting in  $\phi_f = 0.005$ .<sup>4m</sup> Although the  $k_f$ 's of **6**, **7**, and **8** are a factor of 2 or 3 higher, the  $k_s$ 's are ca. 10 times lower. The ring constraint in **6**, **7**, and **8** may preclude a contribution of rotational relaxation to  $k_s$ . Additionally, there are only two C-H bonds  $\alpha$  to the double bond in **6**, **7** and **8**, and this fewer number compared to that of *cis*- $\beta$ -methylstyrene along with any geometric factors which may play a role also could decrease  $k_s$ . The  $k_s$ 's of **6**, **7** and **8** are only slightly higher than those of alkylbenzenes and exhibit no great influence from the olefinic moiety.

Zimmerman's concept of  $S_1$  and  $S_0$  surfaces approaching one another in a  $90^\circ$  conformation, thereby accelerating internal conversion, also demands a minimum in the well of the  $S_1$  surface at ca.  $\theta = 0$ . Consequently, the transitional wavelength and band shape of the fluorescence should reflect this requirement. We found this to be true in our observations as did Zimmerman. The low-temperature fluorescence spectra of **4** and **6** show that the fluorescence is structured, and that the 0-0 band of emission corresponds to those in absorption (291 and 297 nm, respectively). The fluorescence also shows bands corresponding to the first transition submerged in the tail of the A band. **7**, whose absorption 0-0 band appears as a shoulder at 295-296 nm, exhibits a low-temperature fluorescence rich in structure with a 0-0 band at 297 nm. With progressively increasing ring size, the fluorescence emission becomes less resolved indicating a less rigid structure in the molecule. **8** has a broader fluorescence band than **7**, but the 0-0 band is still distinguishable at 300 nm. **9** has a still less resolved fluorescence, but the 0-0 band is still observable as a shoulder at 292 nm. Similarly, **5** exhibits fluorescence with less structure than **4**, at slightly lower energy; the 0-0 band is at 300 nm. Room temperature emission, although less resolved than the spectra obtained at 77 K, shows the same trends. **4** and **6** have narrow fluorescence envelopes with distinguishable 0-0 bands. **5** has a broad, structureless fluorescence, and in the benzocycloalkadienes, there is a progressive loss of resolution of the 0-0 band, and increasing broadness of the emission band is introduced as the fused ring becomes larger.

Berlman<sup>24</sup> has noted that correlations can be made between the fluorescence and absorption characteristics of aromatic compounds and nuclear conformation. 1,1-Diphenylethylene, for example, has a broad, blue-shifted, slightly structured absorption and a diffuse, red-shifted, broad fluorescence. This is taken to be characteristic of a nonplanar excited state. Biphenyl, however, has the same absorption characteristics as 1,1-diphenylethylene, but has a structured, red-shifted, narrow fluorescence. Berlman attributes this to a nonplanar ground state and a (more) planar excited state. This type of correlation is applicable to the styrenes and benzocycloalkadienes included in our study. Despite the variation in the absorption spectra,

the 0-0 bands of fluorescence all fall in the 290-300-nm region. For those molecules nonplanar in the ground state, all except **4** and **6**, the emission is more structured than the absorption which is indicative of the *emissive* excited state being more rigid and closer to planarity than the ground state. This explains the similarity in the 0-0 bands of fluorescence, as noted by Zimmerman, in that the conformation of the radiating molecules is close to a planar one. However, differences in the flexibility and steric constraints in molecules (**4-9**) still play a role as the less rigid benzocycloalkadiene molecules and sterically hindered **5** have broad emission bands.

As previously noted, few reports exist in the literature regarding the phosphorescence of styryllike compounds. From our study, it is apparent that the basis for this lack of information is that they are characteristically nonphosphorescent within the detectable limits of conventional spectrophosphorimeters. In particular, carefully purified indene in our hands exhibited no phosphorescence, confirming previous reports<sup>4g,i,k</sup> that spurious emission from impurities is responsible for an earlier report<sup>4e</sup> of indene phosphorescence. Even Zimmerman's comprehensive study of 1-phenylalkenes makes no mention of the phosphorescence efficiency of these compounds; presumably they are also nonphosphorescent. As in the phenylcyclopropanes, a negligible  $\phi_p$  could arise from a negligible  $\phi_{isc}$  and/or fast radiationless decay of the triplets which competes with a slower radiative deactivation. Triplet parameters on 1-phenylcycloalkenes reveals a combination of low  $\phi_{isc}$ 's as a result of high  $k_{ic}$ 's and high  $k_t$ 's ( $\geq 200 \text{ s}^{-1}$ ) which must result in the lack of phosphorescence. Zimmerman attributed the high values for  $k_t$ 's to the same phenomenon responsible for the enhanced internal conversion, i.e., ability of the triplet state to twist, decrease the  $T_1$ - $S_0$  energy gap, and facilitate radiationless decay. The same mechanism is capable of operating in molecules **4-9**. As mentioned in the discussion of the phenylcyclopropanes,  $k_t$  does not have to be large to compete with the low radiative probability,  $k_p \lesssim 1$ , of alkylbenzenes. For **5** and **9**, a high rate of internal conversion would lead to a small value for  $\phi_{isc}$ , and additionally decrease  $\phi_p$ .

## References and Notes

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