"hot" ground state levels. Following our analyses of the trifluoro- and trichlorobenzene cations, we expect that these features are to be associated with transitions from the lower levels in the \( j = \frac{3}{2} \) stack which are predicted to be very intense.\textsuperscript{11} We defer detailed discussion of the assignments given in Table I until a future publication\textsuperscript{10} dealing with the theory and calculation of the Jahn–Teller effect.

However, it is appropriate to point out here that the assignment of these combination bands is crucial to the understanding of the Jahn–Teller effect in this compound. We showed\textsuperscript{17} that in the case of \( C_6 H_3 Cl^+ \) and \( C_6 H_3 F^+ \) the simple single mode model of the Jahn–Teller effect used in the earlier work on these compounds\textsuperscript{2,7,11–13} is inadequate and gave misleading results. Not surprisingly, this appears to be the case in \( C_6 H_3 Cl^+ \) also and the assignments given in Table I are based on preliminary calculations using the model involving mode coupling as outlined previously.\textsuperscript{17}

For \( C_6 H_3 F^+ \) and \( C_6 H_3 Cl^+ \), key factors in the reappraisal of their Jahn–Teller effects were the recent availability of laser excited wavelength resolved fluorescence data and the observations of vibrationally unrelaxed emission in the matrix. Similar experiments are planned for \( C_6 H_3 Cl^+ \) to give more information on the ground state vibrational frequencies and Jahn–Teller splittings. Such data together with the more sophisticated analysis should resolve the remaining ambiguities with respect to the Jahn–Teller distortion in this compound.

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**Phosphorescence and Delayed Fluorescence of 1-Chloronaphthalene in Micellar Solutions**

Nicholas J. Turro* and Masayuki Aikawa

*Contribution from the Chemistry Department, Columbia University, New York, New York 10027. Received November 16, 1979*

**Abstract:** Phosphorescence, delayed monomer fluorescence, and delayed excimer fluorescence of 1-chloronaphthalene are readily observable in conventional anionic and cationic micelles. The delayed luminescences are shown to arise predominantly from triplet–triplet annihilation within a single micelle. A kinetic analysis of the data allowed evaluation of the rate constant for intramicellar triplet–triplet annihilation and the rate constant for exit of 1-chloronaphthalene from a micelle.

**Introduction**

The rates of exit and entrance of aromatic compounds into micelles have been investigated recently by phosphorescence decay and by solubility measurements.\textsuperscript{1} The rate constant for triplet energy transfer has been evaluated for aromatic arenes (donor) and rare-earth ions (acceptor). Energy transfer in these systems probably takes place at sites near the micelle–water interface.\textsuperscript{3} The exit rate constants of aromatic hydrocarbons from the micelles are of the order of the cmc lead to the conclusion that DF results predominantly from intramolecular T–T annihilation. An analysis of the triplet decay by P and triplet–triplet absorption allowed evaluation of the rate constant of triplet–triplet (T–T) annihilation in the micelles in addition to the rate constant of the competing exit of triplet CN from the micelles.

**Experimental Section**

1. **Materials.** 1-Chloronaphthalene (Aldrich Chemical Co.) was purified by repeated vacuum distillation. Hexadecyltrimethylammonium bromide (HDTBr), purchased from Sigma Chemicals, was recrystallized twice from methanol after being washed with ethyl ether. Electrophoresis grade sodium dodecyl sulfate (SDS) was used as supplied from Bio-Rad Laboratories. Hexaamminecobalt(III) chloride (Alfa Products) and sodium nitrite were recrystallized twice from water. Spectrograde octane was passed through a silica gel column. Micellar solutions were fully degassed by repeated freeze–thaw cycles (~10⁻⁴ mmHg).

2. **Spectroscopy.** a. **Measurements of Phosphorescence and Delayed Fluorescence Spectra.** Time-resolved spectra of phosphorescence and delayed fluorescence were measured with a high-sensitivity emission spectrophotometer (Spex Fluorolog) whose operation is based on the photon-counting method. The excitation light source used was a xenon flash lamp (EG & G, FX198U) possessing a half-width of ~3 ps, about 5000 mJ of electrical energy dissipating in each flash. The delay time after a flash excitation was determined by the output of the photomultiplier–amplifier–discriminator circuit of the spectrophotometer. The sampling time is defined as the amount of time over which data excited by a single flash are integrated. By changing the delay time and the sampling time appropriately along the phosphorescence decay curve, time-resolved spectra were obtained in time ranges from 10 μs to 1 s.

b. **Measurements of Phosphorescence Decay.** Phosphorescence decay was monitored by two different techniques.

(i) **Photon Counting–Multichannel Digital Boxcar Technique.** In this case, phosphorescence or delayed fluorescence was observed by means of a photon counting based spectrophotometer which was combined with a multichannel analyzer (MCA). The emission signal at fixed observed wavelength was sent to the MCA with a scaling module (Tracer Northern, TN-1710 and 1710-26). The time resolution of the MCA was 10 μs. Decay curves of the emission were measured with a high-sensitivity emission spectrophotometer (Spex Fluorolog) whose operation is based on the photon-counting method. The excitation light source used was a xenon flash lamp (EG & G, FX198U) possessing a half-width of ~3 ps, about 5000 mJ of electrical energy dissipating in each flash. The delay time after a flash excitation was determined by the output of the photomultiplier–amplifier–discriminator circuit of the spectrophotometer. The sampling time is defined as the amount of time over which data excited by a single flash are integrated. By changing the delay time and the sampling time appropriately along the phosphorescence decay curve, time-resolved spectra were obtained in time ranges from 10 μs to 1 s.

---

Phosphorescence of 1-Chloronaphthalene

Figure 1. (a) Conventional steady state photoluminescence spectrum of a degassed aqueous solution of Cl-N with SDS. The emission around 340 nm is assigned to prompt fluorescence. (b) Time-resolved spectrum of an aqueous solution of Cl-N (1 × 10⁻³ M) and SDS (0.25 M) at 22 °C. The emission spectra around 340 nm and 530 nm are assigned to delayed fluorescence and phosphorescence, respectively.

(iii) Phosphorescence measurement have been described elsewhere.7,8

(ii) Triplet-Triplet (T-T) Absorption Measurement. The method used for the measurement of the transient triplet absorption has been described previously.9,10 Samples were excited by a 308-nm emission pulse produced from an excimer laser (Lambda Physik, Excimer EMG 500) employing XeCl as the lasing medium. Transient absorption spectra were observed perpendicular to the direction of the excitation pulse, using a 1000-W Xe lamp as an interrogating source which was passed through a monochromator (Aminco, 1/4 m) and monitored with a five-stage IP28 photomultiplier.10 The signal was displayed on a storage oscilloscope (Tektronix, 7623A) and the trace was photographed on 3000 ASA Polaroid film for analysis. The extinction coefficient of Cl-N at the band maximum around 420 nm has been determined to be 3.0 × 10⁴ L M⁻¹ cm⁻¹.11-13

Results

Figure 1a shows the conventional steady state photoluminescence spectrum of Cl-N in aqueous solutions containing 0.20 M SDS. The spectrum consists totally of prompt fluorescence. Figure 1b shows the time-resolved spectra obtained from 1 × 10⁻³ M Cl-N in 0.25 M SDS solution excited with a microsecond flash. The emission maximizing near 340 nm is assigned by inspection to delayed fluorescence (DF) of Cl-N and the emission maximizing near 530 nm is assigned to Cl-N phosphorescence (P).

Thus, curve a represents the spectrum obtained after a 30-ps delay, curve b, the spectrum obtained after a 200-µs delay, and curve c, the spectrum obtained after a 1500-µs delay. The decay of the intensity of both DF and P is unimolecular and corresponds to lifetimes of ~100 and 400 µs, respectively. It is important to note that DF from Cl-N is not significant in homogeneous isooctane solution in the concentration region studied.

From Figure 1b it is clear that DF dominates the emission spectrum of Cl-N at short delay times and that, as the DF intensity decreases, the phosphorescence intensity increases, relatively. At longer times only phosphorescence remains and it decays exponentially.

In order to obtain information relevant to the mechanism and triplet dynamics which lead to the behavior observed in Figure 1b, and in order to understand the basis for the striking differences in behavior in micellar compared to homogeneous solution, several types of experiments were run. The dependence of the ratio of intensities of DF to P was measured as (a) a function of (Cl-N), the average occupancy number of chloronaphthalene in a micelle; (b) a function of dilution with water at constant (Cl-N); (c) a function of the concentration of quenchers that operated selectively in the bulk aqueous phase.

Variation of I_Df/I_P as a Function of (Cl-N) at Fixed [Cl-N]

The average occupancy number (Cl-N) is defined as

\[
(\text{Cl-N}) = \left( \frac{[\text{Cl-N}]}{[\text{Det}]} \right)^n
\]

where [Cl-N] and [Det] are the bulk concentrations of Cl-N and detergent, respectively, and n is the aggregation number of the detergent. Thus, (Cl-N) may be varied by variation of [Cl-N], [Det], or n. All experiments were performed in concentration ranges of detergent for which n is a known quantity, and for which n is not subject to significant variation (in the absence of Cl-N).

In a series of experiments with [Cl-N] fixed at ~5 × 10⁻⁴ M, the concentration of SDS was varied from 0.025 to 0.25 M. From the literature value of n = 60,13 we find that (Cl-N) varies from ~1.2 to ~0.12 for this variation of [SDS]. The experimentally observed variation of I_Df and I_P as a function of (Cl-N) is shown in Figure 2. The spectrum shown corresponds to a delay time of approximately 50 µs and sampling time of 2000 µs. Similar results were obtained in HDTBr. A new feature appears in the delayed fluorescence spectrum at the highest values of (Cl-N); i.e., a new band, assigned to delayed excimer fluorescence, is observed. From Figure 2 it is apparent that I_Df increases with

Figure 2. Dependence of mean occupancy number on the spectral intensity of DF, DEF, and phosphorescence in SDS solution at 22 °C. Mean occupancy number was varied by changing the concentration of detergent at fixed Cl-N concentration (~5 × 10⁻⁴ M). Sampling time 2000 µs.

the ratio \([\text{Cl-N}] / [\text{Det}]\) remains constant with aqueous dilution, 

if 

should be a specific aqueous phase quencher of \(\text{Cl-N}\) in micellar 

CI-N triplets dissolved in the aqueous phase. Similarly, \(\text{Co}^{3+}\) 

Table I. Dilution Effect of a Micellar System with Water on 

\(I_{DF}/I_p\) at Fixed \(\text{Cl-N}\) 

<table>
<thead>
<tr>
<th>Micelle</th>
<th>[Det], M</th>
<th>[Cl-N], M</th>
<th>[Cl-N] rel (I_{DF}/I_p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDTBr</td>
<td>0.20</td>
<td>1.5 (\times 10^{-3})</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>0.020</td>
<td>1.5 (\times 10^{-4})</td>
<td>0.55</td>
</tr>
<tr>
<td>SDS</td>
<td>0.20</td>
<td>1.5 (\times 10^{-3})</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>0.020</td>
<td>1.5 (\times 10^{-4})</td>
<td>0.82</td>
</tr>
</tbody>
</table>

increasing \((\text{Cl-N})\), whereas \(I_p\) decreases with \((\text{Cl-N})\).

Variation of \(I_{DF}/I_p\) as a Function of Micelle Concentration at 

Fixed \((\text{Cl-N})\). Above the cmc, dilution of a micellar system with 

water does not significantly alter the value of \((\text{Cl-N})\); i.e., since 

the ratio \([\text{Cl-N}] / [\text{Det}]\) remains constant with aqueous dilution, 

if \(n\) remains constant with dilution, then \((\text{Cl-N})\) also remains constant. Figure 3 shows the results of aqueous dilution on the 

ratio \(I_{DF}/I_p\). Data extracted from Figure 3 are summarized in 

Table I. The significant qualitative result is that dilution by a 

factor of 10 results in a variation of \(I_{DF}/I_p\) of less than 

25% for both SDS and HDTBr micellar systems.

Variation of \(I_{DF}/I_p\) as a Function of Quencher in the Bulk 

Aqueous Phase at Fixed \((\text{Cl-N})\) and Fixed \((\text{Cl-N})\). The long 

lifetime of triplet \(\text{Cl-N}\) allows triplet exit into the aqueous phase 

to compete with intramicellar triplet decay. We have determined 

that \(\text{NO}_2^-\) and \(\text{Co}^{3+}\) are excellent quenchers of \(\text{Cl-N}\) in aqueous 

solutions \((k_q = 5.7 \times 10^4\) and \(4.3 \times 10^9\) \(M^{-1}\) \(s^{-1}\), respectively). 

The common charge of the surface of SDS and \(\text{NO}_2^-\) should 

severely inhibit quenching of micellized \(\text{Cl-N}\) triplets relative to 

\(\text{Cl-N}\) triplets dissolved in the aqueous phase. Similarly, \(\text{Co}^{3+}\) 

should be a specific aqueous phase quencher of \(\text{Cl-N}\) in micellar 

HDTBr solutions.

Figure 4 shows the variation of \(I_{DF}/I_p\) \((\text{Cl-N}) = 0.16, \) \([\text{Cl-N}] = 5 \times 10^{-4}\) \(M\) as a function of \([\text{NO}_2^-]\) for 0.20 \(M\) solutions of 

SDS. The phosphorescence intensity decreases dramatically as 

\([\text{NO}_2^-]\) is increased. On the other hand, \(I_{DF}\) suffers an initial drop 

upon addition of a low concentration of \(\text{NO}_2^-\) and then undergoes 

little further change upon further 100-fold increase in the concentration 

of \(\text{NO}_2^-\).

Triple–Triple Absorption of \(\text{Cl-N}\) in Micellar Solutions. The 

decay characteristics of \(\text{Cl-N}\) triplets in micellar solutions were 

monitored by triplet–triplet (T–T) absorption. Figure 5 shows 

a representative decay curve for T–T absorption. The decay curves 

do not fit a simple first-order decay, but conform to a second-order 
decay at short times and a first-order decay at longer times.

Discussion

Mechanisms of Interpretation of the Data and Evaluation of Rate 

Constants. Before selecting a mechanism for the derivation of 

rate constants from our data, we consider several qualitatively 
distinct mechanisms. The major qualitative features of the data 

are (a) the variation in \(I_{DF}\) and \(I_p\) as functions of \((\text{Cl-N})\), micelle 

concentration \([M]\), and quencher concentration \([Q]_w\); (b) the 

observation of DF at high \((\text{Cl-N})\).

Under the assumption that DF is due to intramicellar T–T 

annihilation, three distinct priori mechanisms for production of 

DF may be considered for generating two triplets in one micelle. 

They are given in Scheme I, where circles represent micelles.

In mechanisms I and II individual naphthalenes in singly oc- 
cupied micelles are excited to eventually produce micelles occupied 

by a single triplet, T. In mechanism III, micelles containing two 

(or more) naphthalenes are viewed as eventually producing a 
micelle containing two triplets in the same micelle. In mechanism 

I occupancy of two triplets in a single micelle comes about via 

the interaction of two single occupied micelles. In mechanism 

II occupancy of two triplets in the same micelle comes about via 

escape of a micellized triplet into the aqueous phase followed by 

event of the triplet into a micelle containing a triplet molecule. 

These three mechanisms represent the limiting pathways by which 

the occupancy of two triplets in the same micelle may come about 

after an initial excitation pulse.

From the results discussed earlier, mechanism I (for which 

bimolecular interactions between micelles are rate determining) 

may be ruled out as the main pathway to DF since dilution in 

the concentration of micelles does not lead to a significant change 
in the value of \(I_{DF}/I_p\).
Phosphorescence of 1-Chloronaphthalene

Scheme I. Three Mechanisms for Generation of DF in Micellar Solution

mechanism I

\[
\text{N}^* \xrightarrow{h^+} \text{T} \\
\text{T} + \text{T} \quad \xrightarrow{k_1} \quad \text{T} + \bigcirc \quad \rightarrow \text{DF}
\]

mechanism II

\[
\text{N}^* \xrightarrow{h^+} \text{T} \\
\text{T} \quad \xrightarrow{k_1} \quad \text{T} + \bigcirc \quad \rightarrow \text{DF}
\]

mechanism III

\[
\text{N}^* \xrightarrow{2h^+} \text{T}, \text{T} \quad \rightarrow \text{DF}
\]

\( \text{N} = 1\text{-chloronaphthalene}; \quad \text{T} = 1\text{-chloronaphthalene triplet}; \quad \bigcirc = \text{micelle.} \)

Mechanism II may be ruled out as the major source of DF by the observation that aqueous quenchers of Cl-N triplets fail to significantly influence the value of \( I_{DF} \) while significantly reducing \( I_p \).

Mechanism III, however, is consistent with the results discussed above. The increase in \( I_{DF} \) relative to \( I_p \) with increasing Cl-N is simply a result of the increasing multiple occupancy expected from Poisson statistics. The constancy of the value \( I_{DF}/I_p \) with decreasing micelle concentration at constant (Cl-N) and the specific quenching of \( I_p \) relative to \( I_{DF} \) by aqueous-phase quenchers are also consistent with mechanism III. Thus, the observation of specific quenching of \( I_p \) also suggests that the \( T-T \) annihilation process in micellar phase is faster than the exit rate of Cl-N from the micelle, and consequently is not affected significantly by aqueous-phase quenchers.

In order to evaluate the rate constants for encounter of two triplets in one micelle (\( k_{T-T} \)) and for exit of Cl-N from the micelle (\( k_o \)), we may treat independently two cases of kinetics for micelles which are occupied by one and by two probes (eq 1). The treatment is appropriate if Poisson statistics hold and the intermicellar exchange of solute during the triplet lifetime is negligible.

The kinetic scheme for triplets that are partitioned between aqueous and micelle phase and for which only single occupancy is involved is given by eq 1, where \( T_m, T_w, N_m, \) and \( N_w \) denote the triplet and the ground-state probes in aqueous and water phase, respectively. \( k_t, k_b, k_m, \) and \( k_n \) indicate rate constants for entrance into and exit from micelle and deactivation in the micelle and water phase, respectively.

We assume that the observed transient signal arises only from the micelle phase because of extremely low concentration of the probe in aqueous phase. Under the condition of \( (k_t + k_m[M] + k_q[Q]) \gg (k_m - k_n) \), the kinetic equations for eq 1 give the phosphorescence decay function:

\[
[T_m] = C e^{-\left(\frac{k_mk_t[M] + k_mk_b + (k_m + k_n)k_q[Q]}{k_m + k_t[M] + k_q[Q]} \right) t}
\]

This limitation is safely assumed for the present case: \( k_m - k_n \leq 10^6 \text{s}^{-1} \) and \( k_t[M] \geq 5 \times 10^6 \text{s}^{-1} \). More details of the method for estimation of the order are given in ref 1.

Table II. Unimolecular and Bimolecular Rate Constant of Cl-N in SDS Micelle Solution

<table>
<thead>
<tr>
<th>quencher</th>
<th>unimolecular ( k_{obsd} ) s(^{-1} )</th>
<th>bimolecular ( k_{2-T} ) M(^{-1} ) s(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaN(_2)</td>
<td>5.4 \times 10^3</td>
<td>2.6 \times 10^4</td>
</tr>
<tr>
<td>5 \times 10^{-3}</td>
<td>1.2 \times 10^4</td>
<td>2.7 \times 10^3</td>
</tr>
<tr>
<td>1 \times 10^{-4}</td>
<td>2.6 \times 10^4</td>
<td>2.8 \times 10^4</td>
</tr>
<tr>
<td>5 \times 10^{-4}</td>
<td>2.9 \times 10^4</td>
<td>2.8 \times 10^4</td>
</tr>
<tr>
<td>1 \times 10^{-5}</td>
<td>4.2 \times 10^4</td>
<td>2.9 \times 10^4</td>
</tr>
<tr>
<td>2 \times 10^{-5}</td>
<td>4.8 \times 10^4</td>
<td>3.1 \times 10^4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[SDS]</th>
<th>[Cl-N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20 M</td>
<td>5 \times 10^{-4} M</td>
</tr>
</tbody>
</table>

Here C represents some constant for time \( t \).

Figure 6 shows the plots of the reciprocal of observed first-order rate constant (long component) \( k_{obsd}^{-1} \) as a function of quencher concentration for both SDS and HDTBr solutions, where \( k_{obsd}^{-1} \) is expressed as

\[
[T_m]^{-1} = \frac{k_T-T}{k_{obsd}}
\]

where \( [T_m]^{-1} \) represents the concentration of triplet probe at \( t = 0 \). Thus the overall decay behavior of triplet Cl-N will be represented as the sum of eq 2 and 4.

Table II also shows the observed unimolecular and bimolecular rate constants for SDS solution. \( k_{obsd} \) initially increases, then approaches a limiting value, while \( k_{T-T} \) is constant with increasing quencher concentration, indicating that the \( T-T \) annihilation process is not affected by water-soluble quenchers. This observation is also consistent with the spectral changes shown in Figure 4.
The effect of each double bond on the other is reflected in the molecular rate constant for the T-T annihilation process are of C-C double bonds relative to one another varies with ring size. states arising from electron capture into a

\[ \text{cyclohexadiene} \]

\[ \text{cyclooctadiene} \]

The phosphorescence lifetime at low concentration of C1-N (1 \times 10^{-5} \text{ M}) and high detergent concentration (0.2 M for SDS and 0.5 M HDTBBr) allows evaluation of \( k_m \). Thus, values of \( k_m = 5.0 \times 10^{3} \text{ (SDS)} \) and \( 2.2 \times 10^{3} \text{ s}^{-1} \) (HDTBBr) are obtained. Using these values and \( k_s + k_m \), we can evaluate the exit rates. The exit rate constant and bi-molecular rate constant for the T-T annihilation process are summarized in Table III in comparison with those for 1-bromonaphthalene. The T-T annihilation rate is much greater than the exit rate, leading to the observed enhancement of DF in micellar solution.

### Conclusion

This study reports the first observation of delayed fluorescence of an aromatic compound in micellar solution.\(^7\) Presumably, the combination of a modest fluorescence yield, a good intersystem crossing yield, and a long triplet lifetime is optimal for the occurrence of DF in micelles. The observation of a second-order component in triplet decay of Cl-N in micelles is consistent with T-T annihilation as a significant pathway for DF. The evaluated rate constant for T-T decay \( (\sim 10^{4} \text{ M}^{-1} \text{ s}^{-1}) \) is of the order expected for "diffusion controlled" quenching in micelles such as HDTBBr and SDS.\(^5\)

### Acknowledgments

The authors thank the National Institutes of Health (Grant GM25523) and the National Science Foundation (Grant NSF-CHE78-00692) for their generous support of this research.


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**Table III. Rate Constants for Exit from and the Formation of Delayed Fluorescence in the Micelle**

<table>
<thead>
<tr>
<th>micelle</th>
<th>( k_s )</th>
<th>( k_m )</th>
<th>( k_{T-T} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>4.3 \times 10^{4}</td>
<td>3.3 \times 10^{4}</td>
<td>2.8 \times 10^{4}</td>
</tr>
<tr>
<td>HDTBBr</td>
<td>1.9 \times 10^{4}</td>
<td>4.5 \times 10^{4}</td>
<td>0.8 \times 10^{4}</td>
</tr>
</tbody>
</table>

\( ^a \) Reference 1.

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**Negative Ion States of 1,3-Cycloalkadienes**

Judith C. Giordan,\(^{1a} \) Michael R. McMillan,\(^{1a} \) John H. Moore,*\(^{1a} \) and Stuart W. Staley*\(^{1b} \)

*Contribution from the Chemistry Department, University of Maryland, College Park, Maryland 20742, and the Chemistry Department, University of Nebraska--Lincoln, Lincoln, Nebraska 68588. Received January 22, 1979

**Abstract:**

Attachment energies for 1,3-cyclohexadiene (1), 1,3-cycloheptadiene (2), and 1,3-cyclooctadiene (3) as obtained from electron transmission spectra are presented. The first electron affinity was also obtained for 1,3-cycloheptadiene (1), 1,3-cyclooctadiene (2), and 1,3-cycloheptadiene (3).

The cycloalkadienes provide an excellent opportunity to study the nature of the interaction of semilocalized \( \pi \) orbitals. Geometrical effects on through-space and through-bond interaction can be observed within a series of cycloalkadienes since the orientation of C-C double bonds relative to one another varies with ring size. The effect of each double bond on the other is reflected in the splitting of electronic states. The magnitude of the effect can be assessed from measurements of the energy required to add or remove an electron from a \( \pi \) orbital to create an anion or cation.

We report herein measurements of energies of the negative ion states arising from electron capture into a \( \pi^* \) orbital of 1,3-cyclohexadiene (1), 1,3-cycloheptadiene (2), and 1,3-cyclooctadiene (3).

\[ \text{ZC}_2\text{C}_4 \text{C}_4 \text{C}_5 = 120^\circ. \text{It is now generally agreed that cycloheptadiene (2) has a C}_4 \text{ conformation with the carbon skeleton planar except for C}_4 \text{ whose earlier work has led to suggestions that the double bonds are not coplanar. Electron-diffraction experiments give ZC}_2\text{C}_4\text{C}_4 \text{C}_5 = 129^\circ.} \]

The diene unit of cyclooctadiene (3) is highly twisted. The extent of twist is given as 42\(^\circ\) by electron diffraction, 42–65\(^\circ\) by force-field calculations, and 60–80\(^\circ\) by vibrational spectroscopy.

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\( (4) \) (a) A. Ansmann and B. Scharer, J. Raman Spectrosc., 5, 281 (1976); (b) B. Scharer and A. Ansmann, Angew. Chem., Int. Ed. Engl., 14, 364 (1975).


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**Table III. Rate Constants for Exit from and the Formation of Delayed Fluorescence in the Micelle**

<table>
<thead>
<tr>
<th>micelle</th>
<th>( k_s )</th>
<th>( k_m )</th>
<th>( k_{T-T} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>4.3 \times 10^{4}</td>
<td>3.3 \times 10^{4}</td>
<td>2.8 \times 10^{4}</td>
</tr>
<tr>
<td>HDTBBr</td>
<td>1.9 \times 10^{4}</td>
<td>4.5 \times 10^{4}</td>
<td>0.8 \times 10^{4}</td>
</tr>
</tbody>
</table>

\( ^a \) Reference 1.