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

	exit rate, s^{-1}		
micelle	1-chloronaphthalene (this work)	1-bromonaphthalene (lit.)[a]	k_{T-T}, M^{-1} s^{-1}
SDS	4.3×10^4	3.3×10^4	2.8×10^8
HDTBr	1.9×10^3	4.5×10^3	0.8×10^8

[a] Reference 1.

Equation 2 shows that the limiting values at [Q] → ∞ gives $k_b + k_m$ which corresponds to the constant values of k_{obsd} at high quencher concentration (Figure 6). The phosphorescence lifetime at low concentration of Cl-N (1×10^{-5} M) and high detergent concentration (0.2 M for SDS and 0.5 M HDTBr) allows evaluation of k_m. Thus, values of $k_m = 5.0 \times 10^3$ (SDS) and 2.2×10^3 s^{-1} (HDTBr) are obtained. Using these values and $k_b + k_m$, we can evaluate the exit rates. The exit rate constant and bimolecular 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.[17] 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 (~10^8 M^{-1} s^{-1}) is of the order expected for "diffusion controlled" quenching in micelles such as HDTBr 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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Negative Ion States of 1,3-Cycloalkadienes

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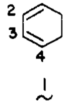
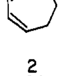
Abstract: Attachment energies for 1,3-cyclohexadiene (**1**), 1,3-cycloheptadiene (**2**), and 1,3-cyclooctadiene (**3**) as obtained from electron transmission spectra are presented. The first electron affinity was also obtained for **1** and **2**. Changes in the experimentally measured attachment energies are correlated with changes in the energies of the unoccupied molecular orbitals. The trends in the orbital energies are analyzed by INDO molecular orbital calculations in terms of $\angle C_1C_2C_3$ and the degree of twist about C_2–C_3. The data indicated the importance of through-space C_1–C_3 and C_1–C_4 interactions and reconcile the first ionization potentials of **1** and **2** with a nonplanar π system in **1** and a planar π system in **2**.

The cycloalkadienes provide an excellent opportunity to study the nature of the interaction of semilocalized π orbitals. Geometrical effects on through-space and through-bond interaction can be observed within a series of cyclodienes 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 π orbital to create an anion or cation. We report herein measurements of energies of the negative ion states arising from electron capture into a π^* orbital of 1,3-cyclohexadiene (**1**), 1,3-cycloheptadiene (**2**), and 1,3-cyclooctadiene (**3**).



$\underset{\sim}{1}$



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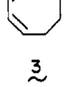

$\underset{\sim}{3}$

The series 1–3 provides an interesting range of orientation of the double bonds relative to one another. The conformation of cyclohexadiene (**1**) is a semichair with the diene moiety twisted approximately 18° about the C_2–C_3 bond and with $\angle C_1C_2C_3$ and $\angle C_2C_3C_4 = 120°$. It is now generally agreed that cycloheptadiene (**2**) has a C_s conformation with the carbon skeleton planar except for C_6,[2-4] although earlier work[5,6] led to suggestions that the double bonds are not coplanar. Electron-diffraction experiments[3] give $\angle C_1C_2C_3 = 129°$. The diene unit of cyclooctadiene (**3**) is highly twisted. The extent of twist is given as 42° by electron diffraction,[7] 42–65° by force-field calculations,[8-10] and 60° by vibrational spectroscopy.[4]

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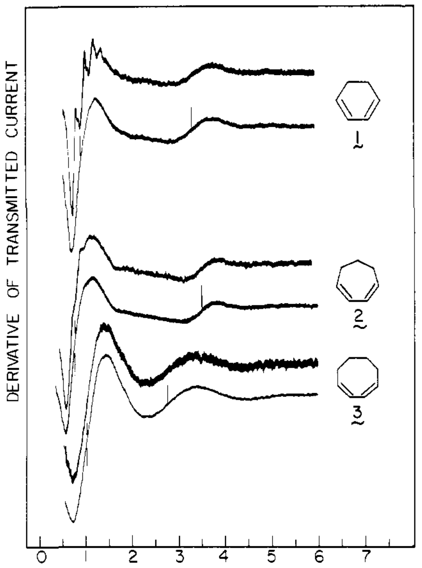
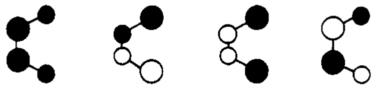


Figure 1. Spectra of **1–3** presented as the derivative of transmitted electron current vs. electron energy. For each compound the upper trace is the high-resolution spectrum (modulation amplitude = 22 meV) and the lower is the low-resolution spectrum (modulation amplitude = 440 meV).

The 1,3–dienes are conjugated systems. The π orbital, as well as the π* orbital, associated with each double bond interacts with its neighbor giving rise to four orbitals: $b_2(\pi_1)$, $a_2(\pi_2)$, $b_2(\pi_3^*)$, and $a_2(\pi_4^*)$ in order of increasing energy and with reference to the symmetry of *cis*-1,3-butadiene. Only the π orbitals are occupied in the molecule in its ground state. The π* orbitals may be occupied if the molecule is electronically excited or if an electron is added to produce an anion. For the molecules of interest these anions are transients with lifetimes of the order of 10^{-13} s. The formation of these negative ions can be observed as sharp variations in the cross sections as a function of energy for scattering of electrons from the corresponding neutrals. The electron energy at which such behavior is observed corresponds to an electron affinity. We make these measurements by electron transmission spectrometry (ETS)[11] in the format devised by Sanche and Schulz.[12] The energies of the occupied π orbitals can be related to the energy required to remove an electron from one of these orbitals. This measurement is conveniently performed by means of ultraviolet photoelectron spectroscopy (PES). The cyclic dienes have been well characterized by this technique.



Experimental Section

In electron transmission spectroscopy the transparency of a sample gas to an electron beam is measured as a function of electron energy.[11,12] The transmission is related in some inverse fashion to the electron scattering cross section. The process of interest here, temporary negative ion formation, occurs with large cross sections only over a narrow energy range. Since the negative ion decays promptly by giving up the trapped electron, the formation and decay process appear as a rapid fluctuation in the electron scattering cross section. The process as well as the feature in the cross-section curve is referred to as a "resonance". Experimentally the first derivative of the transmitted current as a function of energy is examined since the derivative is sensitive to a rapid change of current.

The electron transmission spectrometer consists of an electron source followed by a trochoidal monochromator, a sample gas cell, a retarding potential analyzer, and an electron collector. The device is similar to that developed by Stamatovic and Schulz[12] with modifications described elsewhere.[13] Our spectrometer is constructed of molybdenum and is baked daily to 350 °C to assure stable operation after exposure to hydrocarbon samples. The derivative of the transmitted current is obtained by modulating the energy of the electrons passing through the sample cell and recording the amplitude of the modulation of the transmitted current.[14]

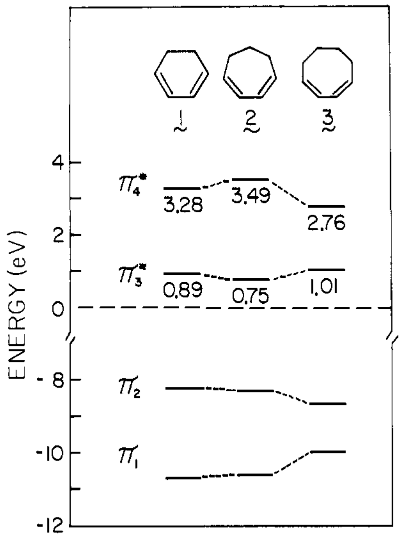


Figure 2. Correlation diagram for the π and π* orbitals of **1–3**. π_1 and π_2 correspond to the ionization potentials (ref 15) and π_3^* and π_4^* to the attachment energies.

In ETS as in all other forms of spectroscopy a problem exists in defining the characteristic energy of an asymmetric feature of finite energy width. Thus concepts such as "adiabatic energy" and "Franck–Condon energy" or "vertical energy" have arisen to specify the energy characteristic of a spectroscopic transition. A resonance in the derivative electron transmission spectrum appears as a minimum followed by a maximum as the electron energy is increased through the region of the resonance (see, for example, Figure 1, bottom trace). If the resonance peak in the scattering cross section were symmetric, the point in the electron transmission spectrum midway between this minimum and maximum would correspond to the maximum of the cross section. Although these peaks may not be symmetric, it is nevertheless general practice to take as characteristic the energy at the point vertically midway between the minimum and maximum of a resonance in the derivative spectrum. We refer to this energy as the "attachment energy" (AE) associated with the insertion of an electron into an unfilled orbital.

If the temporary negative ion survives for a time comparable to a vibrational period, sharp structure indicating progressions of anionic vibrational levels may appear (see, for example, Figure 1, top trace). In this event an adiabatic electron affinity (EA) corresponding to the lowest vibrational level can be obtained. We take the EA as the point vertically midway between the first minimum and the first maximum of the resonance feature.

A problem arises in comparing a resonance with vibrational structure to one without structure. To make such comparisons we increase the modulation amplitude and thus decrease the experimental resolution until the vibrational structure is washed out. An AE can then be defined in the usual manner.

Results and Discussion

Electron transmission spectra of **1–3** are given in Figure 1. For each compound, spectra were obtained with modulation amplitudes of 22 and 440 mV. In the former the resolution is about 50 meV while in the latter the vibrational structure is washed out. The energy scale was calibrated with reference to the first maximum in the derivative spectrum of N_2.[15] The two resonances in each spectrum correspond to negative ion states associated with capture of electron in π_3^* and π_4^*, respectively. The attachment energies associated with π_3^* and π_4^* have been determined with precisions of ± 0.05 and ± 0.10 eV, respectively, from measurements on at least five spectra of each compound. These data complement

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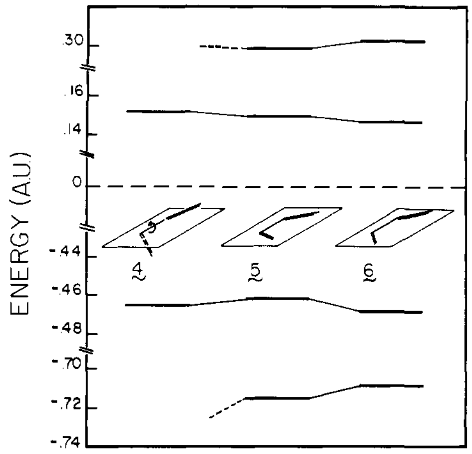

Figure 3. INDO orbital energies for various 1,3-butadienes. Structures: **4**, same as in ref 20 except dihedral $\angle C_1C_2C_3C_4$ = 18°; **5**, same as **4** except dihedral $\angle C_1C_2C_3C_4$ = 0°; **6**, same as **5** except $\angle C_1C_2C_3$ = $\angle C_2C_3C_4$ = 129°.

photoelectron data on the ionization potentials from the two highest filled orbitals (π_1 and π_2).[16] The ETS and PES data are presented as a correlation diagram in Figure 2.

Attachment energies and ionization potentials can be only approximately equated with the corresponding molecular orbital energies. However, for a series of structurally similar compounds, variations in measured energies may reasonably be analyzed in terms of changes in orbital energies.[17] This sort of analysis is implied in Figure 2. The trends illustrated in this correlation diagram are in large part consistent with established ideas of the π electron interactions involved in the phenomenon of conjugation. As suggested by the Hückel model,[18] rotation about the C_2–C_3 bond on going from 1 to 3 causes a decrease in π overlap leading to destabilization of π_1 and π_3* and stabilization of π_2 and π_4*. Thus an increase in the dihedral angle about the C_2–C_3 bond reduces the extent of conjugation with a concomitant decrease in the π_1–π_2 and π_3*–π_4* splittings. The greater changes in π_1 and π_4* reflect the larger atomic orbital coefficient at C_2 and C_3 in these molecular orbitals compared to π_2 and π_4*.

On going from cyclohexadiene (**1**) to cycloheptadiene (**2**) the ETS data imply an increase in the π_3*–π_4* splitting as expected since **2** is planar. On the other hand, the PES data are anomalous in that a decrease in the π_1–π_2 splitting is observed. This result led previous workers to suggest that the π system of cycloheptadiene (**2**) is twisted.[6]

As an aid in understanding the apparent anomaly in the experimental observations, we have performed INDO molecular orbital calculations[19] on cyclohexadiene (**1**) and cycloheptadiene (**2**) and their radical cations and anions. Additionally, a number of models based on *s-cis*-1,3-butadiene were treated in an effort to segregate the main geometrical differences between **1** and **2**. The models are the following: **4**, *s-cis*-1,3-butadiene with the C_2–C_3 twist angle = 18° and $\angle C_1C_2C_3$ = 120°; **5**, planar *s-cis*-1,3-butadiene with $\angle C_1C_2C_3$ = 120°; **6**, planar *s-cis*-1,3-butadiene with $\angle C_1C_2C_3$ = 129°. Fragment **4** is analogous to **1**, while **6** is analogous to **2**. The calculations on **1** and **2** are consistent with experiment, but the calculated orbital energies of the model compounds **4**–**6**, presented as a correlation diagram in Figure 3, are perhaps more useful in understanding the experimental observations. The values for π_1 and π_4* or **4** are not included because of unrealistic σ–π mixing caused by the inaccurate representation of σ levels in the INDO calculations.[21]

Increasing $\angle C_1C_2C_3$ (and $\angle C_2C_3C_4$) on going from **5** to **6** affects both the C_1–C_3 (C_2–C_4) and the C_1–C_4 through-space interactions. We evaluated these specific interactions by the "inverse perturbation technique" of setting equal to zero the p_z resonance integrals between C_1 and C_3 (C_2 and C_4) and between C_1 and C_4 in the core Hamiltonian matrices of **5** and **6**. The effect on the orbital energies of deleting the C_1–C_3 (C_2–C_4) interactions was of the same magnitude as the effect of deleting the C_1–C_4 interaction. Thus the change on going from **4** to **6** can be dissected into three parts: (a) the effect of flattening the π system on going from **4** to **5** as illustrated in Figure 3, (b) changes in the C_1–C_3 π interactions due to an increase in $\angle C_1C_2C_3$ on going from **5** to **6** and (c) changes in the C_1–C_4 π interactions due to the increase in $\angle C_1C_2C_3$ on going from **5** to **6**. With respect to the frontier orbitals, π_2 and π_3*, it can be seen that (a) and (b) oppose and dominate (c) in π_3* whereas the through-space effects, (b) and (c), oppose and dominate (a) in π_2.

The variation in the extent of vibrational development in the first resonance in the electron transmission spectra also deserves some comment. As discussed by Jordan and Burrow[11] and Birtwistle and Herzenberg,[22] the sharpness of vibrational structure is related to the lifetime of the negative ion. Well-developed vibrational structure is associated with a relatively long-lived anion while broad resonant peaks are characteristic of anions which survive for less than a vibrational period. Generally speaking, when comparing two anions, the species with the lower electron affinity tends to be longer lived and, all other things being equal, the more symmetric anion will have the longer life. Thus in the present case the vibrational structure in cyclohexadiene (**1**) is more strongly developed than for cycloheptadiene (**2**).

Two vibrational modes are apparent in cyclohexadiene (**1**). Jordan et al.[23] have suggested that the higher frequency mode is the C–C symmetric stretch and the lower frequency vibration is a ring-breathing mode. In any event, the presence of vibrational structure permits a measurement of the electron affinity. The EAs for **1** and **2** are −0.73 ± 0.05 and −0.63 ± 0.05 eV, respectively.

Summary

The measurement of attachment energies involving the unfilled π* orbitals of unsaturated hydrocarbons provides information complementary to ionization-potential data on the filled π orbitals. The results of electron transmission experiments on a homologous series of 1,3-cyclodienes can be interpreted in terms of the orbital picture. Interactions between atomic centers that are not nearest neighbors in the π system–that is, C_1–C_3 and C_1–C_4 through-space interactions–must be taken into consideration to reconcile the ETS and PES data on the cyclodienes.

Acknowledgments. We thank the National Science Foundation (Grant CHE 77-14930 A01) for support of this work, the craftsmen of the University of Maryland Space Science Shop for fabrication and Michael Peck for assembly of the apparatus, Mark Bjorke for performing some of the computations, and the Nebraska Computer Center and Maryland Computer Science Center for computer support.

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