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## Photodissociation Spectroscopy of Hexatriene Cations

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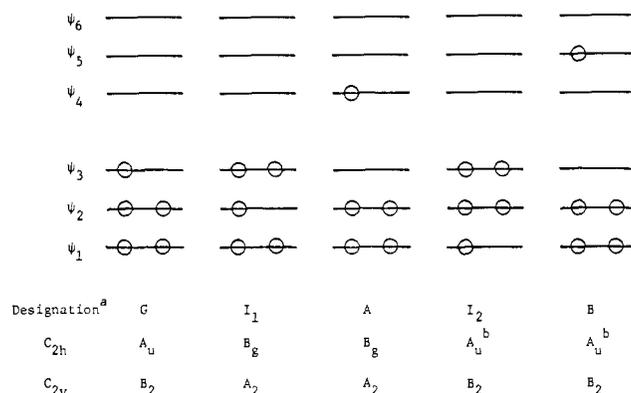
**Abstract:** Photodissociation spectra of 1,3,5-hexatriene radical cations are reported at low resolution across the visible-UV region and at high resolution in the visible. The spectrum is well accounted for in terms of two expected electronic transitions and is in qualitative agreement in both positions and oscillator strengths of the peaks with the predictions of semiempirical calculations. The high-resolution spectrum of the  $\bar{A} \leftarrow \bar{X}$  transition shows resolved vibrational structure attributable to two vibrational progressions at 350 and 1060  $\text{cm}^{-1}$ . By comparison with the cation emission spectra it is concluded that the 0-0 transition at 631.8 nm corresponds to the cis isomer. Photodissociation spectra of cis and trans isomers are identical, indicating interconversion of the isomers on a time scale of seconds. The hot-band intensity suggests several kilocalories of excitation of the ions but does not rule out thermal ions.

The optical spectroscopy of gas-phase ions, while still largely inaccessible to direct study, has recently become an area of considerable interest through the information coming from wavelength-selected ion photodissociation measurements, an approach which has been called photodissociation spectroscopy. Largely using ion cyclotron resonance spectrometers but also other instruments to observe photodissociation of ions, optical spectroscopic information has been obtained and interpreted for a substantial variety of ions.<sup>2-10</sup> It is widely recognized that photodissociation spectra can often usefully be considered as if they were in fact optical absorption spectra. The spectroscopy of 1,3,5-hexatriene radical cation discussed here is of exceptional interest in two respects: first because (as reported in a preliminary communication<sup>11</sup>) it is a polyatomic ion showing the extensive well-resolved vibrational structure which had been expected and sought, but not found, in the photodissociation spectra of other ions; and second because it extends the  $\pi$  system previously investigated in olefins<sup>4</sup> and dienes<sup>4,5</sup> and is thus a further step in systematizing the spectroscopy of conjugated radical ions. Accordingly this paper presents the low-resolution photodissociation spectrum of hexatriene ion and discusses it in terms of electronic transitions in the  $\pi$  system. Also it presents a refined and more accurate version of the high-resolution spectrum previously described<sup>11</sup> and discusses it in terms of possible vibrational modes of the ion, as well as considering the question of cis-trans isomerization of the radical ion.

### Results and Discussion

**The Low-Resolution Spectrum.** The photodissociation spectrum of hexatriene ion at a resolution of  $\sim 150 \text{ \AA}$  is shown in Figure 1. The peak in the visible region is asymmetric, reflecting the vibrational structure described below; the near-UV peak appears to have analogous asymmetry (steeper slope on

Scheme I.  $\pi$  Configurations of Hexatriene Ion



<sup>a</sup> Notation of ref 12. <sup>b</sup> Of the states shown, only these two are optically forbidden.

the long-wavelength side) and might profitably be examined for vibrational structure at high resolution. The data suggest a rise at the extreme UV end of the observed region, but the accuracy of measurement at these wavelengths is too low for any confidence to be placed in this.

The low-lying excited state configurations shown in Scheme I, in which the configurations have been denoted using the terminology of Shida and Iwata,<sup>12</sup> and the symmetry species have been given for both C<sub>2h</sub> (trans) and C<sub>2v</sub> (cis) isomers. Transitions from the ground state to I<sub>2</sub> and B are forbidden in C<sub>2h</sub>, but otherwise all the transitions indicated are optically allowed; since the present experiments yield no polarization information, the polarization of the transitions is irrelevant. Zahradnik and Carsky<sup>13</sup> have made a careful  $\pi$ -electron calculation on this

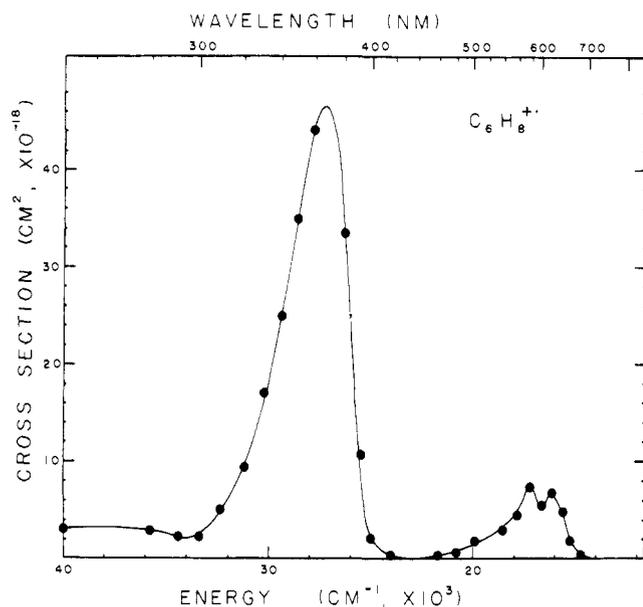


Figure 1. Photodissociation spectrum of hexatriene cations.

ion, using a Pariser-Parr-Pople SCF semiempirical method, with configuration interaction including 40 excited state configurations representing all single-electron excitations from the five highest occupied orbitals to the four lowest empty orbitals. They predict the positions and intensities of the low-lying optical transitions shown in Table I.

The hole in orbital  $\psi_3$  leads to important differences from the neutral molecule: the set of configurations labeled I in Scheme I, corresponding to "hole-promotion" optical transitions, are characteristically ionic and do not exist for the neutral; in addition the changed electron repulsion and configuration interaction effects in the ion lead to a marked energy lowering of the A configuration in the ion relative to the neutral. In aromatic radical-ion systems like toluene the "natural"  $\psi_3$ - $\psi_4$  energy gap (in the terminology of ref 13) is much larger than the "unnatural"  $\psi_2$ - $\psi_3$  gap, and the characteristic ionic  $I_1 \leftarrow G$  optical transition in the visible or infrared is quite free of interaction with other configurations. In the polyenes, however, the "natural" and "unnatural" gaps are of comparable energy, so that the  $I_1 \leftarrow G$  and  $A \leftarrow G$  transitions are close in energy; since they are of the same symmetry, strong configuration interaction and mixing occurs, giving rise to a pair of optically allowed transitions separated by a substantial energy. In hexatriene ion the  $I_1$  and A configurations are predicted by simple HMO calculations<sup>14</sup> to lie  $0.81\beta$  and  $0.89\beta$  respectively above the ground state, which (using  $\beta = 2.8$  eV)<sup>15</sup> would give a pair of transitions near 500 nm. As the calculations of Zahradnik and Carsky<sup>13</sup> indicate, the configuration interaction described separates these by something more than 1 eV; the calculation indicates that the resulting two transitions have almost equal amounts of  $I_1$  and A character. This extensive configuration interaction casts grave doubt on the ability of all-electron calculations like the MINDO and SPINDO calculations, which do not carefully account for these strong interactions, to describe correctly the low-lying  $\pi$  states of polyene ions via Koopmans' theorem.

Table I compares the observations with theory. The qualitative agreement is good, with theory predicting the observed small peak in the red and very intense peak in the blue or near UV. The positions of both peaks are, however, placed about half an electron volt too low by the calculation. As Table I indicates, the calculation of Zahradnik and Carsky also places the peaks for butadiene ion too low, and it appears that there is a systematic shift in the calculations leading to transition

Table I. Electronic Spectra of 1,3,5-Hexatriene and Butadiene Cations

Observed peak <sup>a</sup>	Theory <sup>b</sup>	Assignment <sup>c</sup>
Hexatriene		
2.1 (0.02)	1.6 (0.02)	A + $I_1$
3.4 (0.23)	2.8 (0.7)	$I_1$ + A
	3.1 (0)	$I_2$ (+B)
	4.3 (0)	B (+ $I_2$ )
	5.0 (0.02)	B
Butadiene		
2.3 (0.02)	2.2 (0.01)	
4.0 (0.02)	3.5 (0.4)	
	4.9 (0)	

<sup>a</sup> Energy in eV, oscillator strength in parentheses. <sup>b</sup> Reference 13 (trans isomer). <sup>c</sup> X + Y indicates comparable contributions for the two configurations; X (+Y) indicated predominant contribution from configuration X. From ref 13.

energies below experiment. Although there is some question as to whether the present experimental results refer to the cis or the trans isomer, the near identity of the photoelectron spectra of the two isomers<sup>18</sup> suggests that the electronic structures are similar. The peak positions would then probably be similar; the transition moments might well show some differences between isomers, and this is sufficient reason not to expect quantitative agreement of theory and experiment with respect to peak intensities.

Comparison between calculated transition probabilities and experimental photodissociation cross sections must be done with great caution, because dissociation is not necessarily the only outcome following photon absorption. However, remembering that photodissociation cross sections are always lower limits to the optical absorption cross section, it is of interest to make the comparison. In Table I the photodissociation cross sections have been converted to "apparent" oscillator strengths for comparison, and it is seen that the agreement with calculation is qualitatively good, with both the weak visible peak and the strong UV peak showing order of magnitude agreement with calculation.

**The High-Resolution Spectrum.** The laser photodissociation spectrum of hexatriene ion is shown in Figure 2, and is discussed in terms of accuracy and reliability in the Experimental Section. Since ref 11 reported the preliminary spectrum, the present paper will concentrate on those aspects of interpretation which have been clarified by the observation by Allan and Maier<sup>16</sup> of emission from hexatriene ion and will report subsequent work concerned with establishing more reliable peak positions in the spectrum and with the differences in the spectra of cis and trans isomers. In ref 11 the spectrum was analyzed in terms of a 0-0 transition of the  $\tilde{A} \leftarrow \tilde{X}$  electronic band at about 632.5 nm, with two vibrational progressions corresponding to normal modes of the excited state of frequencies  $\sim 1200$   $\text{cm}^{-1}$  and  $\sim 350$   $\text{cm}^{-1}$ , and a 0-1 hotband in the 350- $\text{cm}^{-1}$  mode. The spectrum in Figure 2 is refined in some details from that in ref 11, but its essential features are unchanged.

Allan and Maier<sup>16</sup> have observed emission from the radical ions of both cis and trans hexatriene immediately following electron impact ionization. On the fluorescence time scale of their observations ( $\approx 10^{-8}$  s) the emission spectra of the two isomers are distinct, with the 0-0 band lying at  $630.2 \pm 0.2$  nm for the trans isomer and  $631.3 \pm 0.2$  nm for the cis isomer. The peak of the 0-0 transition in the photodissociation spectrum definitely lies within the limits 630.8-632.8 nm, which leads to the unexpected but definite conclusion that the major part of the photodissociation spectrum belongs to the cis isomer and not, as previously assigned, to the trans isomer. Since the trans configuration is probably more stable than the cis, it thus ap-

**Table II.** High-Resolution Spectrum in 600-nm Region

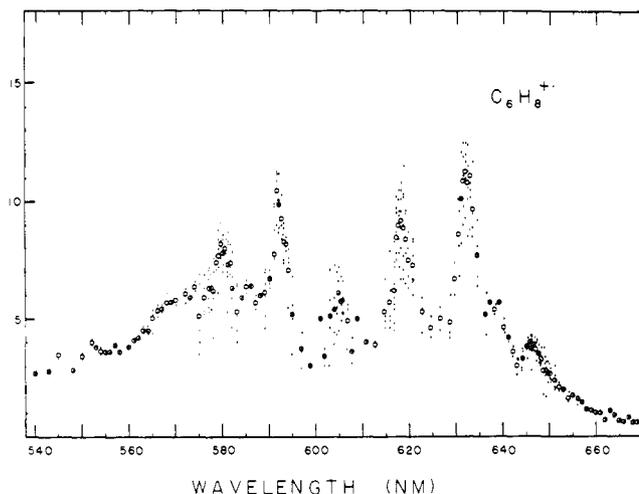
Peak nm <sup>a</sup>	Relative peak area <sup>b</sup>	PES <sup>c</sup> (cis)	Emission <sup>d</sup>
646.0	0.3		
631.8	1.0	636	631.3 (cis), 630.2 (trans)
618.0	0.8		616.7 (trans)
605.0	0.5		
592.0	1.0	589	
580.0	0.9		
569	0.7		

<sup>a</sup> Estimated uncertainty  $\pm 0.5$  nm except for the 646.0-nm peak ( $\pm 1.0$  nm) and the poorly resolved shoulder at 569 nm. <sup>b</sup> From a Lorentzian-peak decomposition of Figure 2, taking the 631.8 peak as unity, and converting intensities to cross sections, wavelengths to energy units. <sup>c</sup> From ref 18, taking the ion ground state to lie at 8.32 eV (converted to wavelength in nm). <sup>d</sup> Reference 16.

pears that the spectrum does not directly reflect an equilibrium mixture of cis and trans. Allan and Maier note that cis is lower than trans by a factor of 20 in its fluorescence yield, and it is attractive to suppose that the trans isomer relaxes from the  $\tilde{A}$  state predominantly by fluorescence emission, while the cis isomer can relax from the same state via dissociation with substantially higher probability. This interpretation, which is consistent with all the available information, would suggest that in the photodissociation experiment photon absorption occurs by both cis and trans ions, but the trans ions reradiate with much higher probability than cis and are thus suppressed in the photodissociation spectrum.

The data of Figure 2 allow assignment of the frequencies of the two vibrational progressions with confidence as  $350 \pm 10$  and  $1060 \pm 15$   $\text{cm}^{-1}$ ; these correspond to vibrational frequencies of the excited  $\tilde{A}$  electronic state of the ion. The frequency of the mode giving rise to the hot band is  $350 \pm 25$   $\text{cm}^{-1}$ , which is the frequency of the mode in the ground  $\tilde{X}$  state of the ion and is seen to be identical, within 30  $\text{cm}^{-1}$ , to that of the corresponding excited state mode. No normal-mode analysis of the cis isomer appears to have been made, but some qualitative conclusions can be carried over from the analysis<sup>17</sup> of the trans isomer. The 350- $\text{cm}^{-1}$  normal mode observed both here and in emission is undoubtedly one of the skeletal bending vibrations which occur in this region. The higher frequency vibration is presumably a skeletal stretching mode of which there are several in the 1100–1700- $\text{cm}^{-1}$  range. The 1060- $\text{cm}^{-1}$  frequency observed for the excited state ion is significantly lower in energy than that observed for the ground state ion in emission,<sup>16</sup> which is not surprising; it is also slightly lower than the  $\sim 1200$   $\text{cm}^{-1}$  reported in the  $\tilde{A}$  state of both cis and trans by photoelectron spectroscopy,<sup>18</sup> but this difference is not more than can be readily attributed to the uncertainty in measuring the poorly resolved vibrational structure of the photoelectron spectra, and the agreement with PES results can be considered acceptable. The mode at 350  $\text{cm}^{-1}$  is in agreement with that observed in emission.

The most significant change that the present larger data set introduced from the spectrum of ref 11 is the reduction in size of the hot band at 646 nm. Clearly the scatter of the data makes accurate measurement of this feature difficult, and quantitative conclusions from it may not be valid, but it is of interest to assess even approximately the apparent temperature of the 350- $\text{cm}^{-1}$  mode in the ground state ion from the intensity of this hot band. The ratio of the 646- and 618-nm peaks gives a direct measure of the relative populations of the  $v = 0$  and 1 levels of the 350- $\text{cm}^{-1}$  mode. Making the reasonable approximation that (for vibrational levels with significant populations) the transition moments  $n \rightarrow n \pm 1$  are all equal (where



**Figure 2.** Laser photodissociation spectrum. The open circles are the mean of the data points.

$n$  and  $n \pm 1$  refer to the 350- $\text{cm}^{-1}$  mode), it is readily shown that

$$I_{10}/I_{01} = 1 - (N_0/N) \quad (1)$$

where  $I_{10}$  and  $I_{01}$  are the intensities observed at the position of the 1-0 (and  $n \rightarrow n - 1$ ) transitions and the 0-1 (and  $n \rightarrow n + 1$ ) transitions, respectively, and  $N_0/N$  is the fraction of molecules in the  $v = 0$  level.

The spectrum of Figure 2 may be reasonably fit by a set of Lorentzian peaks, and from this fit a value of 0.35 is obtained for the ratio of the 646- to 618-nm peak heights (or areas; the value was the same whether peak heights or areas were compared). This corresponds to a vibrational temperature of  $\sim 500$  K in the 350- $\text{cm}^{-1}$  mode of the ion. Since this number is probably uncertain to  $\pm 200$  K, the spectrum does not rule out room temperature ions, although it does suggest that the ions are formed with some excess energy which is retained for at least a few collisions. (Roughly estimating the vibrational heat capacity in this region at 30 cal/deg,<sup>19</sup> the excess energy of the ion is in the range of zero to  $\sim 12$  kcal.)

**Cis-Trans Isomerism.** An extensive attempt was made to observe differences in the spectra of the ions obtained from cis and trans neutral compounds, which were separated by GC and used promptly. The clear differences observed in the PES and emission spectra of the two isomers indicate that isomerization of the neutrals in a vacuum system is not a problem, and it was anticipated that the photodissociation spectra would show similar differences. In fact, no difference was observed: within experimental uncertainty ( $\pm 0.5$ -nm position,  $\pm 20\%$  intensity) the positions and relative intensities of the five major peaks of Table II were identical for the two isomers; furthermore, while absolute cross sections were not precisely determined, they do not differ by as much as a factor of 2 for the two isomers. It would be coincidental to a remarkable degree if the spacing and intensity patterns of the vibrational progressions for the two isomers were identical to the high precision obtained from these spectra, and furthermore the known<sup>16</sup> difference of 1.1 nm in the position of the 0-0 transition would almost certainly have been seen in this comparison. It seems safe to conclude, therefore, that on the time scale of seconds involved in the photodissociation experiment there is no difference in the nature of the ion populations obtained from the two isomeric neutral precursors.

The situation with respect to cis-trans isomerism is then this: in emission, on a time scale of  $\approx 10^{-8}$  s, the two isomers are spectroscopically distinct; however, in photodissociation on a time scale of seconds, a single spectrum, identified with the cis

isomer, is obtained whether the precursor neutral compound is cis, trans, or a 1:4 cis/trans mixture. Several interpretations of these results may be considered.

There is the possibility that a substantial fraction of the ion population has the trans structure and is constantly present in the cell as an inert constituent not dissociated by the light. This was ruled out by determination of the intensity dependence of the observed photodissociation rate. The rate of dissociation should be linear in light intensity if all the ions are being dissociated with the same cross section. Rate versus intensity plots at 630 and 635 nm were found to be linear; it was estimated that as much as 10% of a nondissociating component of the ion population would have given significant curvature to the plots, so that at least 90% of the ions were being dissociated at these wavelengths. A similar conclusion was reached from the extent of dissociation observed using the monochromator at 580 and 370 nm, and the possibility of more than 10% of a stable nondissociating ion component is definitely ruled out.

Two possibilities remain: either the trans isomer isomerizes rapidly and irreversibly to cis or else the cis and trans isomers are in mobile equilibrium, so that by steadily photodissociating the cis ions the entire population is ultimately dissociated. Either of these hypotheses is in accord with observations. In either case, the conclusion is reached that cis-trans isomerization is an accessible pathway on a time scale of seconds for electron-impact-produced ions. That this isomerization would be more facile than in the neutral compound is entirely reasonable, since the electron removed from  $\psi_3$  upon ionization is removed from an orbital having strong  $\pi$ -bonding character between  $C_3$  and  $C_4$ ; removal of this electron would surely decrease the barrier to rotation about this bond. Calculation of this barrier in the radical ion would be of some interest.

## Experimental Section

The methods used to obtain steady-state ICR (ion cyclotron resonance) photodissociation spectra with an arc lamp source and wavelength selection by filters or monochromator have been described.<sup>4</sup> The cross-section measurements were directly referenced to toluene cation at 400 nm.<sup>9</sup>  $C_6H_7^+$  was the only observed product of photodissociation. The ionizing electron energy was kept as low as was consistent with sufficient ion production and was probably within 1 eV of threshold. The pressure was normally in the range  $5-10 \times 10^{-8}$  Torr, and typical ion residence times were of the order of 10 s, so that ions could be expected to undergo 10-100 collisions during their residence in the cell.

The laser photodissociation spectrum was taken in the steady-state ICR mode of operation using a Coherent Radiation laser system consisting of a CR 12 argon ion laser pumping a Model 490 dye laser. Laser dyes used were Rhodamine B, Rhodamine 6G, and sodium fluorescein, all with added cyclooctatetraene. The laser beam was expanded to a larger diameter than the aperture of the ICR cell to give homogeneity to the light beam and thus minimize the possible difficulties with a small diameter light beam irradiating the spatially inhomogeneous distribution of ions in the cell. Although the measured photodissociation rate was determined in several experiments to be linearly proportional to the laser power, so that a correction for varying laser power at different wavelengths would be valid, it was considered more reliable to avoid this correction and to maintain the laser power constant at all wavelengths used in a given sweep; laser powers ranging from 50 to 400 mW were used in various sweeps. Laser power was measured with a Coherent Radiation thermopile.

The laser wavelength read from the readout dial on the dye laser was calibrated on several occasions (with identical results) against a monochromator, which was in turn calibrated on the 632.8 nm line of a helium-neon laser. The wavelength readout of the laser was re-settable within the accuracy of calibration and was stable over a period of months; the uncertainty in absolute wavelengths in the 630-nm region is of the order of  $\pm 0.2$  nm. Since there is some importance to measuring the position of the 0-0 transition near 632 nm, special care was given to this region, which was swept a total of a dozen or more times over a period of months. The peak is quite broad compared with the resolution of the spectrum (0.5 nm spacing of laser wavelengths;

laser line width quoted by manufacturer at  $<0.1$  nm), and this breadth is probably the limiting factor for the measurement of peak position. The peak position is  $631.8 \pm 1.0$  nm, where the quoted limits are in the nature of extreme upper and lower limits.

The local shape of the spectral features in Figure 2 can be quite reliably determined, since the laser operating parameters are stable over modest wavelength changes. We find it difficult, however, to obtain reproducible relative values for cross sections at widely separated wavelengths, such as is necessary to answer the interesting question of the relative peak heights of the five major peaks in Figure 2. It may be seen that the values given in Figure 2 are significantly different from those in ref 11. The values given here reflect considerably more experience in making these measurements as well as a good deal more data and are believed to be more reliable than the earlier ones, but the ratios of peak heights must not be considered accurate to better than perhaps  $\pm 20\%$ .

The sample of hexatriene was obtained from Aldrich and was not further purified; the trans/cis ratio was  $\sim 4:1$ . The isomers were separated by means of a GC column packed with 30-60 mesh Chromosorb containing 30%  $\beta,\beta$ -oxydipropionitrile, as described by Hwa et al.<sup>20</sup> Clean separation was achieved with the column temperature maintained at 25 °C and the carrier (He) pressure at 12 psig. Separated cis or trans isomer was collected over dry ice and transferred to an evacuated glass bulb. Samples were stored in a freezer and used within hours or days of preparation.

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## Appendix

**Nondissociative Component of Ion Population.** The ion population may consist of two components, one dissociating with cross section  $\sigma$ , and the other nondissociative. The most definitive way of showing this to be the case, and of measuring  $\sigma$ , is the "time resolved" photodissociation technique,<sup>2</sup> in which the decay of the ion signal under illumination is monitored as a function of time. However, an upper limit to the fraction of ions which are nondissociative may be obtained in easier ways. For steady-state operation, used in this work, the signal level  $N$  with the light on has been shown<sup>6</sup> to be related to  $I$  by

$$K = I\sigma = K_1 \frac{N_0 - N}{N} \quad (A1)$$

where  $K$  is the dissociation rate,  $K_1$  is the rate of ion loss with no light,  $I$  is the light intensity, and  $N_0$  is the signal level with the light off. Plainly a plot of  $(N_0 - N)/N$  vs.  $I$  is linear. If there is a fraction of nondissociating ions in the population, a part of the ion signal  $N_n$  due to these ions will be constant, giving in effect a change in baseline, and (A1) becomes (assuming  $K_1$  is the same for all the ions)

$$I\sigma = K_1 \frac{N_0 - N}{N - N_n} \quad (A2)$$

A plot of  $(N_0 - N)/(N - N_n)$  vs.  $I$  will be linear. In practice, it is most convenient to plot (A2) for a set of  $N$  vs.  $I$  data, using various trial values of  $N_n$  varying from zero upward. The value of  $N_n$  above which the plot assumes unmistakable curvature represents an upper limit to the nondissociative ion fraction.

A similar analysis holds for pulsed ICR photodissociation.<sup>21</sup> In this case

$$It\sigma = -\ln \frac{N(t)}{N_0(t)} \quad (A3)$$

where  $t$  is the length of the trapping-irradiating period, and  $N_0(t)$  is the no-light signal at time  $t$ .

Again, a population of nondissociative ions effectively shifts the baseline, giving

$$It\sigma = -\ln \frac{N(t) - N_n(t)}{N_0(t) - N_n(t)} \quad (A4)$$

A plot of the right-hand side of (A4) vs.  $I$  at constant  $t$  will be linear only when  $N_n(t)$  is chosen to correspond to the population of nondissociating ions. (With some reworking, this equation also allows analysis of data for  $N(t)$  vs.  $t$  at constant  $I$ .)

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# Photodissociation Spectroscopy and Structural Rearrangements in Ions of Cyclooctatetraene, Styrene, and Related Molecules

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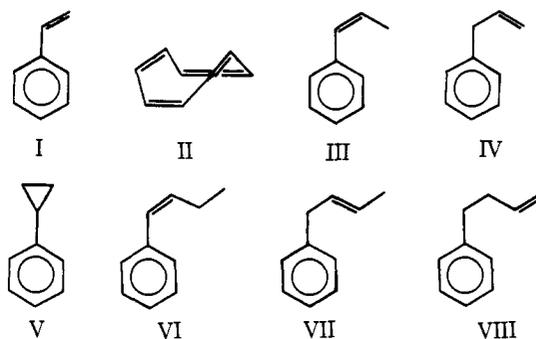
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**Abstract:** Photodissociation spectra of the gas-phase parent ions derived from cyclooctatetraene, styrene, and several hydrocarbons related to styrene have been obtained, along with photoelectron spectra of the neutrals. There is no observable interconversion of styrene and cyclooctatetraene ions. Comparison with the photoelectron spectra and consideration of the likely spectral changes in going from benzene ions to styrene ions suggests that the ions obtained from styrene retain the original structure and account in a satisfactory way for the observed spectrum, while the spectrum obtained for cyclooctatetraene ions is not in accord with expectation and indicates a likely rearrangement or severe distortion of the neutral structure. The spectra of 1-phenylpropene and 3-phenylpropene ions were similar, suggesting migration of the double bond into conjugation, but a similar migration was found to be at most incomplete for 1-phenyl-2-butene and completely absent in 4-phenyl-1-butene. The spectrum of cyclopropylbenzene ion suggests retention of the neutral structure. Positions of a number of the peaks are discussed in terms of interactions of the benzene and ethylene  $\pi$  systems.

Standard methods of mass spectrometry have compiled a large volume of information on the structures and rearrangement processes of fragmenting gas-phase ions.<sup>2</sup> The recent emergence of several techniques having the capacity for characterizing thermalized, nondecomposing ions has given impetus to the reexamination of such questions for many ions of labile geometry. The two new approaches which provide unequivocal information about the nondecomposing ions are photodissociation spectroscopy<sup>3-14</sup> and selective ion-molecular reactions,<sup>15-17</sup> while the collisional activation approach, while nominally a technique characterizing decomposing ions, has also been claimed to provide information about structures of nondecomposing ions.<sup>18</sup> The present study employed the photodissociation-spectroscopic approach in a close examination of rearrangement processes in stable  $C_8H_8^+$  ions<sup>17,19-21</sup> and some related species (I-VIII). The two types of rearrangement of interest were the ring-expansion/ring contraction isomerization of styrene (I) and cyclooctatetraene (COT) (II) and the migration of double bonds into conjugation. The species examined also expand substantially the body of information about spectroscopic properties of highly conjugated and aromatic cations.

## Experimental Section

The experimental arrangement was the same as that used for previous photodissociation studies.<sup>3-14</sup> A standard square ICR cell was



used to trap the ions with a trapping voltage of 2-3 V and near zero drift potentials. An ionization electron energy of about 10 eV was used for most of the compounds. Sample pressures were varied from  $10^{-8}$  to  $10^{-7}$  Torr to keep the trapping times of the ions comparable and the ions were typically trapped for the order of 20 s.

A 2.5 kW Xenon arc lamp and a 2.5 kW Xe-Hg arc lamp have both been used as the light sources. The wavelength selection was provided by using both a monochromator and interference filters. The Baird-Atomic interference filters have a bandwidth of 100 Å, spaced 200 Å apart from 4000 to 7000 Å, and a bandwidth of 150 Å at 7500 and 8000 Å. The Schoeffel monochromator with two 4-mm slits gives a nominal band-pass (FWHM) of 132 Å. An Eppley thermopile was used to measure the relative light intensities and the photodissociation rates at different wavelengths were normalized to the same photon intensity.