

because  $\text{Cu}^{2+}$  can interact most favorably with the induced dipole of the methyl group as well as with the molecule dipole. However, the repulsive steric interactions between the ethanols are largest for this trans configuration. In the gauche configuration the electrostatic interaction with the induced dipole of the methyl group is less favorable, but the repulsive steric interactions are minimized. Thus a balance between the trans and gauche configurations is expected for the solvating ethanols. Experimentally, the balance is found to be halfway between the gauche and trans configurations with the OCC plane perpendicular to the HOC plane.

Finally, we compare the solvation structures of  $\text{Cu}^{2+}$  and  $\text{e}_{\text{sol}}^-$  in ethanol.<sup>6</sup> For electrons solvated in ethanol the positive end of

the molecular dipole is oriented toward the electron with the angle between the OCC and HOC planes being 30–60°. For  $\text{Cu}^{2+}$  the negative end of the molecular dipole is oriented toward  $\text{Cu}^{2+}$ , and the angle between the OCC and HOC planes is 90°. The ethanol solvation geometries for the cation and anion are quite similar except for the direction of the molecular dipole. In both cases the solvation structure seems dominated by a charge-molecular dipole interaction.

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**Registry No.**  $\text{Cu}^{2+}$ , 15158-11-9;  $\text{CH}_3\text{CH}_2\text{OD}$ , 925-93-9;  $\text{CD}_3\text{CH}_2\text{OH}$ , 1759-87-1;  $\text{CH}_3\text{CD}_2\text{OH}$ , 1859-09-2;  $\text{CH}_3\text{CH}_2\text{OH}$ , 64-17-5.

## Photodissociation of Stilbene Radical Cation

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Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. Received July 13, 1981

**Abstract:** The fragmentation of stilbene radical cation has been studied with ion cyclotron resonance (ICR) photodissociation spectroscopy. The trans radical cation appears to be formed by electron impact of either the cis or trans neutral based on a comparison of dissociation cross sections with absorption spectra. Dissociation occurred by loss of H,  $\text{H}_2$ , or  $\text{CH}_3$ . The fragmentation via loss of a hydrogen atom or molecule can be explained by photoinitiated trans-cis isomerization and electrocyclic ring closure, processes analogous to those of the neutrals. Reaction pathways are discussed in terms of the Woodward-Hoffmann rules for electrocyclic ring closure in examining the involvement of electronically excited states in ion fragmentation.

Since the advent of mass spectroscopy as an instrumental method for structural characterization, workers have sought to correlate mass spectral fragmentation with photochemical or thermal decomposition of organic compounds.<sup>1-3</sup> By accounting for the effects of available energy range and distribution, electronic states, and charge, some analogies can be found. There is still no master plan which allows one to examine experimentally one mode of decomposition and successfully predict the outcome of another. As an example, we consider the well-studied class of photochemical and mass spectral reactions: those of the stilbenes and other similar 1,2-substituted double-bonded compounds.

The primary photochemistry of stilbene consists of two reactions: cis-trans (trans-cis) isomerization<sup>4,5</sup> and electrocyclic ring closure.<sup>6,7</sup> Photoisomerization occurs efficiently in the gas, liquid, or solid phases. It is of importance in understanding vision,<sup>8</sup> has wide synthetic utility,<sup>9</sup> and is a major focus of processes of com-

mercial interest such as photochromism,<sup>10</sup> photomechanics,<sup>11</sup> and ion transport.<sup>12</sup> However, cis-trans isomerization results in no mass change and is unobservable in conventional mass spectrometers unless one of the isomers can fragment differently from the other.<sup>13</sup> The photocyclization of cis-stilbene to form phenanthrene by loss of hydrogen does have a mass spectral analogue.

Johnstone and Ward<sup>14</sup> proposed that the mass spectral fragmentations of stilbene and some other aromatic compounds occur via electrocyclic pathways which involve excited electronic states of the ions. They concluded that, from the types and extent of the observed fragmentations, one could infer the geometry of the electrocyclic product and the initial electronic state of the reactant. Bishop and Fleming<sup>15</sup> found cases that apparently contradict Johnstone and Ward's suggestion and proposed instead that selection of mode and extent of fragmentation were much more complicated, and depended among other things on whether the reactants were open shell radical cations or closed shell cations.

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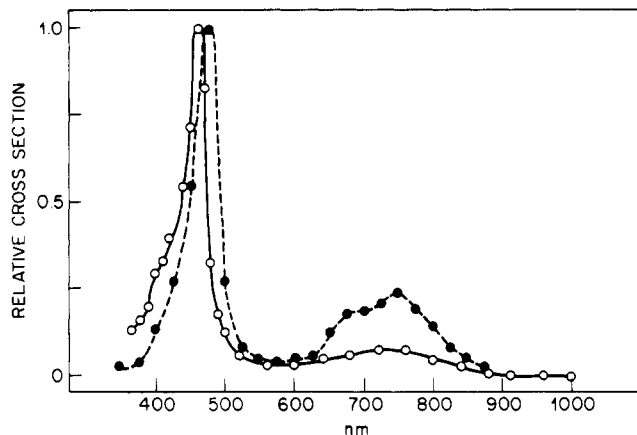
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**Figure 1.** The photodissociation cross section of **1** (○) obtained from *trans*-stilbene and its matrix absorption spectrum (●) from ref 18, wavelength resolution is 9.6 nm (fwhm) for 380 → 500 nm and 39.6 nm above 500 nm. The spectra are normalized relative to their maxima.

We have studied the fragmentation of stilbene radical cation with ion cyclotron resonance (ICR) photodissociation spectroscopy to determine to what extent its light-induced fragmentation is analogous to the photochemical reactions of the neutrals, *cis*-*trans* isomerization, and electrocyclic ring closure. A comparison of the photodissociation spectra with the optical absorption spectra can be made since this cation is formed easily in frozen glasses. The possibility and extent of involvement of electronically excited states in fragmentation is discussed in terms of molecular orbital theory and the Woodward-Hoffmann rules for electrocyclic ring closure.

#### Experimental Section

The experiments were accomplished with use of a Varian V-5900 ICR spectrometer to form, trap, and detect ions. Ions were formed continuously by electron impact at electron energies in the range of 9–20 eV. The ions formed directly from electron impact were usually trapped for 0.5–4 s at  $2\text{--}5 \times 10^{-7}$  torr. Typical cell voltages were in the ranges of 0.3–0.5 V source drift, 0.05–0.1 V analyzer drift, and 2.0–2.5 V trapping potentials.

The light source consisted of a Schoeffel 1000-W xenon arc lamp and power supply with a Schoeffel 0.25-m grating monochromator. A monochromator grating blazed at 300 nm and slit widths of 3.0 and 7.7 nm were used to obtain wavelength resolutions of 9.6 nm (fwhm) and 24.8 nm, respectively, over the range of 300–500 nm, and for 440–1000 nm a grating blazed at 600 nm was used with a monochromator slit width of 3.0 mm for a resolution of 39.6 nm.

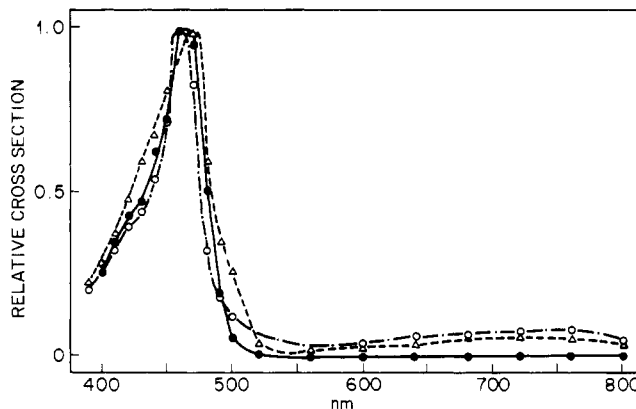
The relative photodissociation and photoformation cross sections were calculated from the measured fractional signal changes due to light irradiation and corrected for variances in photon flux as described previously.<sup>16</sup> The curves represent an average of two determinations at each wavelength for at least four runs with a standard deviation of less than 10% at peak maxima and 20% at the onsets. The maximum signal decreases were in the range of 10–15%.

The photodissociation reactions involving loss of one or two mass units could not be confirmed by double resonance or ion ejection experiments. Owing to the limits of the oscillator frequency and the masses of ions of interest, the overlap of peaks of adjoining masses was observed in some instances.

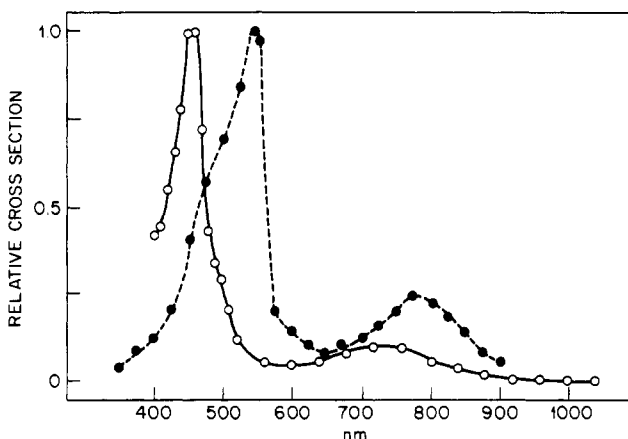
Commercial samples of *trans*-stilbene (M.C.B.) and *cis*-stilbene (Aldrich), were used without further purification. All samples were degassed on the instrument by freeze-pump-thaw cycles prior to introduction. With *trans*-stilbene, the introduction of samples into the cell required heating of the inlet system to 60 °C.

#### Results

The mass spectra of the stilbenes show little fragmentation at low voltages,<sup>14,17</sup> 9–15 eV. For *trans*-stilbene at 11.8 eV, the ions initially present and their relative signal intensities (% total intensity) were 181<sup>+</sup>, 12.2%; 180<sup>+</sup> (M<sup>+</sup>), 78.2%; 179<sup>+</sup>, 4.5%; 178<sup>+</sup>,



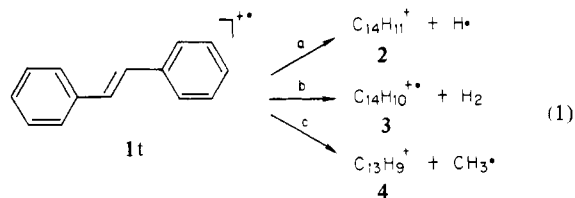
**Figure 2.** The photoformation cross sections of **2** (○), **3** (●), and **4** (Δ). The spectra are normalized relative to their maxima for comparison.



**Figure 3.** The photodissociation cross section of the molecular cation (○) from *cis*-stilbene and the matrix absorption spectrum of *cis*-stilbene radical cation (●).

less than 1%; and 165<sup>+</sup>, 5.1%. Nearly identical signal intensities were observed with *cis*-stilbene.

The molecular ion of *trans*-stilbene, **1**, was found to photodissociate by three pathways; loss of H, loss of H<sub>2</sub>, and loss of CH<sub>3</sub>, eq 1.



The photodissociation spectrum of **1** is shown in Figure 1, compared with its optical absorption spectrum measured in an organic glass matrix.<sup>18</sup> The spectra are similar, with the photodissociation peak at  $\lambda_{\text{max}} = 460$  nm blue shifted by 10 nm from the corresponding peak in the matrix absorption spectrum. The band at  $\lambda_{\text{max}} = 740$  nm is less relatively intense in the photodissociation spectrum.

The photoformation of **2**, **3**, and **4** is shown in Figure 2. Formation of **2** (loss of H) and **4** (loss of CH<sub>3</sub>) occurs over the entire spectral range where **1** dissociates. The product **3** (loss of H<sub>2</sub>) is formed only at wavelengths shorter than 520 nm even with photon fluxes ten times greater than those used to obtain these data. With the arc lamp and filters alone it should have been possible to observe formation of **3** at less than 1% of its maximum formation at 460 nm.

Although the photoformation of **2** and **3** from **1** could not be confirmed by double resonance or ion ejection experiments, as

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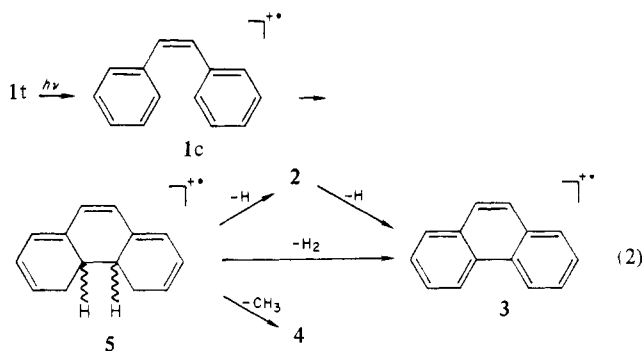
(18) W. H. Hamill in "Radical Ions", E. T. Kaiser and L. Kevan, Eds., Wiley Interscience, New York, 1968, Chapter 9.

with **4**, mass spectral studies show metastable peaks for all of these reactions.<sup>14,17</sup> It is unlikely that light-induced dissociation of **2** or **3** is important because of their low initial concentrations.

The photodissociation spectrum of the molecular ion from *cis*-stilbene compared to its matrix absorption spectrum is shown in Figure 3. Surprisingly, this dissociation spectrum differs greatly from the absorption spectrum but is very similar to the photodissociation spectrum of *trans*-stilbene, **1**. The dissociation spectrum of the *cis*-stilbene molecular ion is nearly constant over an ionizing energy range of 8.6–11.5 eV, strongly suggesting that most of the molecular ion is **1t** and that little if any of the *cis* structure remains after electron impact. In addition, the product distribution is found to be the same as that from *trans*-stilbene. The difference in energy content due to the isomerization is sufficiently small that we would not expect it to have affected our results.

### Discussion

The cationic analogue of the photocyclization of *cis*-stilbene to dihydrophenanthrene which loses hydrogen to form phenanthrene has been proposed to explain the mass spectral fragmentation of stilbene<sup>14,17</sup> (eq 2). If **3** is the phenanthrene radical cation, then



an explanation of our photodissociation results may be made: (a) Electron impact of either *cis*- or *trans*-stilbene produces only **1t**, (b) **1t** photoisomerizes to **1c** which then cyclizes to **5**, and (c) depending on its geometry and excess energy, **5** fragments to **2**, **3**, and **4** at higher energies (>2.4 eV) and to only **2** and **4** at lower energies.

Johnstone and Ward<sup>14</sup> proposed a mechanism based on the symmetry of the upper molecular orbitals to explain the mass spectral fragmentation of stilbene and several other aromatic hydrocarbon cations. By considering the relative intensities of  $(M-1)^+$  and  $(M-2)^+$  peaks, they concluded from their analysis that if the Woodward–Hoffmann rules<sup>19</sup> for concerted electrocyclic cyclization were followed, then the first excited electronic states were responsible for these fragmentation patterns. Their analysis assumed that ring-closed ions which have a *cis* ring juncture will lose these hydrogens concertedly as  $H_2$  and the fragmentation pattern will show a stronger  $(M-2)^+$  than  $(M-1)^+$  peak. Conversely, a *trans* ring juncture will show a pattern of consecutive hydrogen atom loss with a stronger  $(M-1)^+$  peak. Johnstone and Ward's analysis was criticized by Bishop and Fleming,<sup>15</sup> who pointed out a number of problems. They also noted that radical cations tend to lose radicals while closed shell, even electron cations tend to lose molecules.

The behavior of open shell species in electrocyclic reactions remains as an interesting problem.<sup>20,21</sup> As Bishop and Fleming<sup>15</sup> point out, for cyclizations of the type described here (**1c** → **5**, eq 2) the ground state of the starting material does not correlate with the ground state of the product, and neither disrotatory nor conrotatory modes are symmetry allowed. The same problem exists for the cyclopropyl radical → allyl radical reaction.<sup>20,21</sup> A

frontier orbital analysis suggests that the conrotatory mode should be favored over the disrotatory mode, but because of the spin and probably minimal energy constraints, one might reasonably expect to observe appreciable amounts of both pathways. The excited state reactions present an interesting contrast. Here, there is a clear-cut correlation which favors the conrotatory reaction occurring from the first excited state.

The data we have obtained do have some interesting implications. First, loss of  $H_2$  does not occur at wavelengths longer than 520 nm. Second, the 460-nm peak is associated with loss of  $H$ ,  $H_2$ , and  $CH_3$ . Third, across this peak, a range of about 0.6 eV, the ratio of photoproducts remains unchanged. It seems unlikely and very fortuitous that loss of two hydrogens in either stepwise or concerted thermal processes would show an onset at exactly the energy of this band and that the branching ratio for these reactions would then remain constant.<sup>22</sup> Furthermore, the ratio of the loss of methyl to loss of  $H$  remains constant over the entire observed range of over 1.5 eV. All of this suggests that the photoinduced products may be determined by branching from some excited states and not from thermal reactions subsequent to the *trans* → *cis* isomerization. Loss of  $H_2$ , then, may be a concerted process arising from formation of the *cis*-dihydrophenanthrene ion in the 460-nm band. This result is consistent with a Woodward–Hoffmann analysis and photoelectron spectroscopic state assignment for stilbene.<sup>23</sup> The first and third excited states are expected to give *trans* products which cannot eliminate  $H_2$ , while the fourth excited state (the 460-nm band) may do so. We note that this suggestion is not rigorous and is merely the simplest way of accounting for the product ratios as a function of the photon energy.

Photochemical *cis*–*trans* isomerizations of both cations and anions have been observed in solution<sup>25</sup> and organic glass matrices.<sup>18,26</sup> In one study, it was found that in organic glass matrices, isomerization was limited to the *cis*-to-*trans* conversion possibly because the *cis* cation occupies a larger van der Waals volume than the *trans* cation. The quantum yield for isomerization was nearly constant, 0.2–0.4, over the region of 400–600 nm, but dropped off sharply over the region of 650–800 nm.<sup>26</sup>

The neutral photochemical reactions of the stilbenes continue to be subject to wide study both experimentally<sup>27</sup> and theoretically.<sup>28</sup> The geometry of the dihydrophenanthrene formed from *cis*-stilbene has been found to be *trans*, indicating that the reaction occurs directly via the first excited state.<sup>5,29,30</sup> Analogous to our results, the symmetry of this state is expected to yield a *trans* product. Dehydrogenation to phenanthrene occurs only in the presence of oxygen or iodine.<sup>6,7</sup>

It would be of interest to form and to study the photodissociation of **1c** to see if a higher degree of state specificity of dissociation

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(20) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, **87**, 2045 (1965).

(21) G. Boche and G. Szeimies, *Angew. Chem., Int. Ed., Engl.*, **10**, 911, 912 (1971).

is observed due to a simpler reaction pathway than for 1t (eq 2). Formation of 1c would have to be accomplished by energetically milder means than electron impact, such as field ionization<sup>31</sup> or charge transfer.<sup>32</sup> Plans have been made to study the photodissociation of the parent cation of 1,2-diphenylcyclopentene, which cannot undergo cis-trans isomerism.<sup>33</sup>

### Conclusion

The photodissociation of the stilbene radical cation was studied to determine if light-induced fragmentation could be analogous to the neutral photochemical reactions, cis-trans isomerization, and electrocyclic ring closure. The results show that the trans

radical cation is formed predominantly from electron impact of either *cis*- or *trans*-stilbene at low electron energies. The light-induced fragmentation of the trans cation suggests a reaction pathway in which the trans cation isomerizes to the cis cation, which undergoes a ring closure in the excited state prior to fragmentation. The formation of the  $(M - 2)^+$  cation is best explained as occurring via the initially formed excited state rather than after internal conversion to the ground state. The formation of  $(M - 2)^+$  from this state can be rationalized by a Woodward-Hoffmann analysis for electrocyclic ring closure.

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**Registry No.** 1, 59532-48-8; *trans*-stilbene, 103-30-0; *cis*-stilbene, 645-49-8.

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## The Rotational Spectrum, Chlorine Nuclear Quadrupole Coupling Constants, and Molecular Geometry of a Hydrogen-Bonded Dimer of Cyclopropane and Hydrogen Chloride

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**Abstract:** The rotational spectra of several isotopic species of a dimer formed in the gas phase between cyclopropane and hydrogen chloride have been observed by using the technique of Fourier transform microwave spectroscopy conducted in a Fabry-Perot cavity fed by a pulsed nozzle source of molecular dimers. Rotational constants, centrifugal distortion constants, and Cl nuclear quadrupole coupling constants are reported respectively for the three isotopic species ( $\nabla$ ,  $H^{35}Cl$ ), ( $\nabla$ ,  $H^{37}Cl$ ), and ( $\nabla$ ,  $D^{35}Cl$ ) as follows:  $A_0$  (MHz), 20034 (44), 20043 (34), and 20035 (52);  $B_0$  (MHz), 1522.332 (1), 1481.448 (1), and 1521.531 (2);  $C_0$  (MHz), 1454.744 (1), 1417.363 (1), and 1453.978 (1);  $D_J$  (kHz), 1.92 (3), 1.87 (2), and 1.79 (4);  $D_{JK}$  (kHz), 29.8 (2), 28.4 (1), and 29.0 (3);  $\chi_{aa}$  (MHz), -54.41 (2), -42.91 (3), and -56.65 (3); and  $\chi_{bb}$  (MHz), 27.25 (7), 21.49 (8), and 28.47 (5). These spectroscopic constants are interpreted in favor of the edge-on form of the dimer of  $C_{2v}$  symmetry in which the HCl molecule lies in the plane of the ring along the  $C_2$  axis and forms a hydrogen bond to the midpoint of one of the C-C bonds. Some quantitative details of the dimer geometry and the weak binding are determined.

We report the identification and characterization of a dimer formed in the gas phase between cyclopropane and hydrogen chloride. The observation of this weakly bound species through its rotational spectrum<sup>1</sup> has been facilitated by the recently developed technique of Fourier transform microwave spectroscopy conducted in a Fabry-Perot cavity which is fed by a pulsed nozzle source of molecular dimers. A detailed analysis of the rotational spectra of three isotopic species has established that the observed dimer is the edge-on isomer of  $C_{2v}$  symmetry in which the hydrogen chloride molecule lies along the  $C_2$  axis and forms a hydrogen bond to the center of one of the C-C bonds. The spectral analyses lead, moreover, to a diagnosis of the nature of the weak binding.

Cyclopropane is well-known to exhibit certain chemical and physical properties normally associated with unsaturated hydrocarbons. Among the models of the chemical binding in cyclopropane that have been proposed<sup>2,3</sup> to account for these properties a common feature is that, so far as electrons forming C-C bonds are concerned, the lines of maximum electron density do not coincide with C-C internuclear lines. In particular, the Coulson-Moffitt model<sup>2</sup> describes bent bonds in which the line of maximum electron density is displaced from the internuclear line,

the displacement being greatest at the midpoint. The Walsh model<sup>3</sup> predicts, in addition, a region of high electron density at the center of the equilateral triangle formed by the carbon atoms. These predictions are broadly confirmed, experimentally by an electron density difference map from an X-ray diffraction investigation of tricyanocyclopropane<sup>4</sup> and theoretically by an ab initio SCF calculation.<sup>5</sup> The latter study demonstrates that, relative to the central C-C bond of butane in the appropriate conformation, electron density builds up outside the C-C internuclear line and at the center of the ring when cyclopropane is formed.

Given the electron density distributions alluded to and assuming that the hydrogen bond is essentially electrostatic in nature, it is reasonable to expect the electrophilic hydrogen atom in HCl, for example, to seek one or another of the electron-rich regions in forming a complex with cyclopropane. Indeed, the existence of

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