

while the 420–1000-nm photolysis failed to alter the band systems. The decrease in stable cation absorbance with UV photolysis is due to photodetachment of electrons from chloride ion traps (340-nm threshold)²¹ and the resulting neutralization of trapped cations. Similar behavior has been observed for CF₃⁺ in a matrix containing Cl⁻ electron traps.²²

1,2,4-Trichlorobenzene. Matrix photoionization experiments with 1,2,4-TCB produced a small but detectable yield of the 1,3,5-TCB radical cation. Visible photolysis did not increase the yield of rearrangement produced, and, as expected, 220–1000-nm photolysis reduced all band systems. The failure to observe significant rearrangement of 1,2,4-TCB⁺ to 1,3,5-TCB⁺ in the matrix may be due to some intrinsic stability of chlorines located para to one another in the cation, since, for instance, both MDCB⁺ and ODCB⁺ rearranged to PDCB⁺. Although the 1,3,5-TCB⁺ yield was low, it could not be due to contamination in the 1,2,4-TCB neutral precursor.

Conclusions

Dichlorobenzene and trichlorobenzene cation isomers have been produced and trapped in matrix photoionization experiments for observation of cation absorption spectra. The matrix absorption

bands are sharp, and the several different isomers can be identified from the spectra. This matrix study shows that the relative absorbances of the dichlorobenzene cation isomers depend on the intensity of vacuum ultraviolet photoionization and visible irradiation of the trapped cation products. It is proposed that *o*- and *m*-dichlorobenzene cations can rearrange to *p*-dichlorobenzene cation after argon resonance photoionization of the precursor molecule or upon filtered high-pressure mercury arc photolysis of the precursor cation. A plausible mechanism for this rearrangement involves a bridged chloronium ion intermediate that is formed from the lone pair hole excited state of the precursor dichlorobenzene cation. This excited state of the cation is accessible either from the argon resonance lamp directly (11.6–11.8 eV) or by visible irradiation of the ground-state cation in the matrix. The matrix cage may aid the formation of the bridged chloronium cation intermediate by quenching excess internal energy. Accordingly, the chlorine lone pair hole excited state provides the necessary conditions for a "chloronium ion walk" around the aromatic ring.

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Registry No. MDCB, 541-73-1; ODCB, 95-50-1; 1,3,5-TCB, 108-70-3; 1,2,4-TCB, 120-82-1.

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Valence Transitions in *cis*- and *trans*-Hexatrienes

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Abstract: In this experimental investigation of the valence states of *cis*- and *trans*-hexatrienes, two triplet and two singlet valence transitions are observed in each isomer. Differences are observed between the *cis*- and *trans*-hexatriene spectra. A comparison of the *trans*-hexatriene results with the best ab initio and semiempirical calculations suggests that the B_u⁺ and A_g⁺ singlet states are observed and that the A_g⁻ state, while not observed, is above the B_u⁺ state. The relation of these results to the polyene problem will be discussed.

We have conducted an experimental investigation of the valence transitions of *cis*- and *trans*-hexatrienes. Various experimental techniques were used in an attempt to locate all singlet–triplet transitions below the first allowed singlet–singlet transitions as well as all other forbidden valence transitions. Previous investigations of hexatrienes include optical absorption,^{1–3} electron energy loss,^{4–8} electron attachment,⁹ photoelectron,¹⁰ resonant multiphoton ionization,¹¹ and excited-state absorption¹² spectroscopies. In most of these investigations, the two geometric isomers were separated and individually investigated, but in several of the electron energy loss investigations, mixed isomer samples were used and assumed to contain predominantly the *trans* isomer. In addition to these experimental investigations, both ab initio¹³ and semiempirical^{3,14,15} calculations have been carried out on the *trans* isomer.

The basic question which underlies the interest in these molecules is whether or not the valence manifold of polyenes can be

described solely in terms of one-electron transitions. It appears that for the longer polyenes ($n > 3$), in condensed phases, at least,

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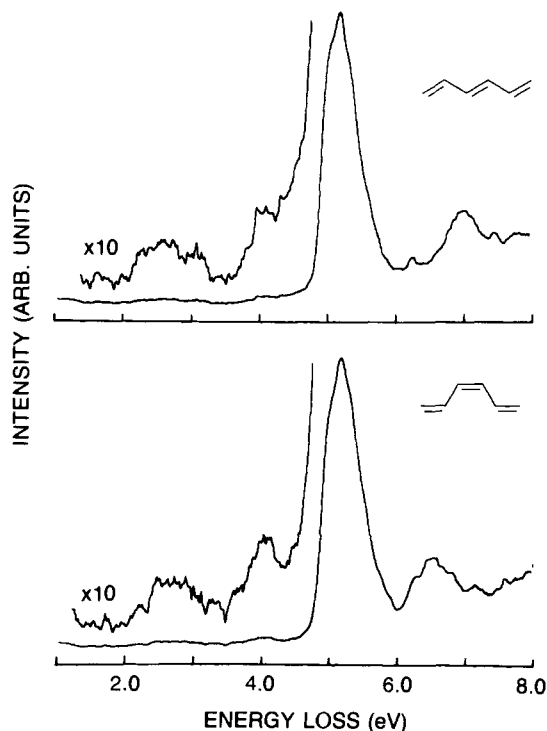


Figure 1. Electron energy loss spectra of *cis*- and *trans*-hexatrienes obtained at 14-eV incident energy and 50° scattering angle. The intensities have been normalized at the peak of the NV_1 transition near 5.15-eV energy loss.

there exists one low-energy transition which cannot be described by single promotion theories.¹⁶ For dienes, ($n = 2$), no evidence exists for transitions below the well-known one-electron allowed transition.^{17,18} Hexatriene is thus the pivotal molecule in the polyene series. Our earlier electron-impact work⁸ suggested that forbidden valence transitions could be observed, but since the scattered intensity in the spectral regions of interest is primarily from Rydberg transitions, the work was not definitive. In the present experiments, we employ techniques which suppress the Rydberg transitions and allow a clearer view of the valence transitions.

In this work we have used both electron energy loss spectroscopy and ultraviolet absorption spectroscopy. Electron energy loss spectroscopy has been shown to be a sensitive technique for distinguishing forbidden from allowed and valence from Rydberg transitions.¹⁸ The electron energy loss spectra have been measured under conditions of very low incident energy and large scattering angles, where optical selection rules do not apply and all transitions appear with their relative intrinsic cross sections.¹⁹ To exclude the possibility that Rydberg states might contribute to the electron impact spectrum, we have compared the electron impact spectra with the optical absorption spectrum of a *n*-hexane solution of each molecule. In condensed phases, Rydberg transitions are suppressed and the remaining absorption bands arise from valence transitions.²⁰ In this way, we hoped to identify the lower valence states of *cis*- and *trans*-hexatrienes, to confirm the assumptions made in the earlier electron energy loss investigations, and to assess the validity of the theoretical calculations.

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Table I. Valence Transitions of *cis*- and *trans*-Hexatrienes (in eV)

molecule	vapor phase				solution	
	T ₁	T ₂	S ₁	S ₂ ^a	S ₁	S ₂ ^a
<i>cis</i>	2.7	4.0	5.15	6.5	4.87 ^b	6.20 ^b
<i>trans</i>	2.7	4.2	5.15	7.0	4.87	

^aThe designation S₂ means the second observed singlet. This enumeration does not include Rydberg states. "S₂" is probably "S₃" (see text). ^b4.87 eV = 255 nm, 6.20 eV = 200 nm.

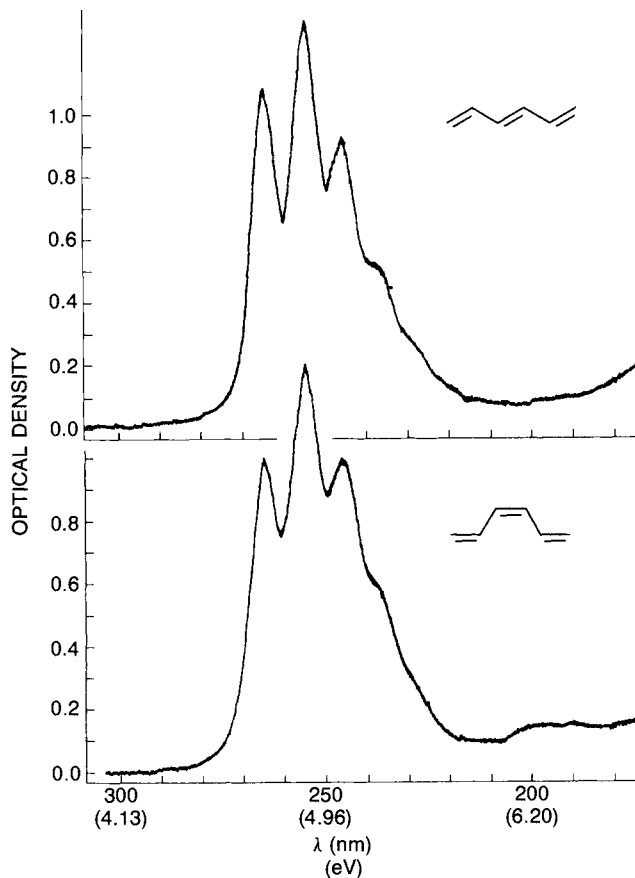


Figure 2. Optical spectra of *cis*- and *trans*-hexatrienes in *n*-hexane. The absorbances have been adjusted to concur with the vapor-phase intensity relations.

Experimental Section

The electron energy loss spectra were measured as before.¹⁸ The scattering angle used was 50°. The incident energies were 9.5 and 14 eV. To maximize the exceedingly weak signals obtained under these conditions, the resolution of the electron spectrometer was reduced to 100 meV (fwhm).

Optical solutions were made by dissolving a small amount of the desired triene in *n*-hexane and diluting this solution until the absorption was small enough to be measured. The absolute solution concentrations are not known. The absorbances were scaled to reproduce the relative vapor-phase absorbances.

Isomerically mixed hexatriene was purchased from Aldrich. The *cis* and *trans* isomers were separated as before.⁸ Each isomer contained approximately 3% of the other and no known chemical impurities.

Results

The electron energy loss spectra of *cis*- and *trans*-hexatrienes obtained at a 50° scattering angle and 14-eV incident energy are presented in Figure 1. The 9.5-eV incident energy spectra are similar, but slightly less well resolved. Two bands are observed below the NV_1 transition in each molecule. The lower energy band occurs around 2.7 eV in each molecule, as previously reported.⁶ The higher energy loss band appears around 4.2 eV in the *trans* isomer and 4.0 eV in the *cis* isomer. Comparison with the previously reported spectrum of the second band⁷ shows clearly that the earlier spectrum was of a mixed isomer sample. In addition to these two bands, several additional bands are observed in each

Table II. Experimental and Theoretical Valence Transition Energies of *trans*-Hexatriene (in eV)

	3B_u	3A_g	${}^1A_g^-$	${}^1B_u^+$	${}^1A_g^+$	${}^1A_g^+$
exptl ^a	2.7	4.2		5.15		7.0
NG ^b	2.71	4.32	5.87			
KGR ^c			4.45	5.26	6.75	7.09

^aThis work. Vertical transition energies are given. The origins are approximately 0.25 eV lower. ^bNascimento, M. A. C.; Goddard, W. A., III. *Chem. Phys.* **1979**, *36*, 147–160. ^cKarplus, M.; Gavin, R. M., Jr.; Rice, S. A. *J. Chem. Phys.* **1975**, *63*, 5507–5508.

molecule. The strongest band is clearly the NV_1 transition, centered around 5.1 eV in each molecule. The next strongest band appears around 6.5 eV in the cis isomer and 7.0 eV in the trans isomer. Several additional weak bands appear in the spectrum of each molecule. The energies of the main bands are presented in Table I.

The solution spectra of *cis*- and *trans*-hexatrienes are presented in Figure 2. Each molecule has an intense NV_1 transition red-shifted relative to the vapor-phase spectrum. In addition, the cis isomer has a second, weak band on the high-energy side of the main transition. These band energies are also presented in Table I.

Discussion

The above data show that each molecule has two singlet–triplet and two singlet–singlet transitions in the vapor phase. The conditions under which these spectra were obtained, 50° scattering angle and 14-eV incident energy, suppress Rydberg transitions and relax the optical selection rules. The relative intensities of the different bands thus reflect their relative intrinsic transition moments. Note that the relative intensities of the first and second triplets and the first and second singlets are comparable in the two molecules. The solution spectra confirm that these are valence transitions. For each isomer, the first singlet transition appears in solution with its peak red-shifted approximately 0.3 eV relative to the vapor-phase spectrum. For the cis isomer, the second transition also appears in solution. It is also red-shifted approximately 0.3 eV. The second transition does not appear in solution for the trans isomer. If it were red-shifted 0.3 eV as are the other three observed valence singlets, it would occur around 185 nm. Whether its absence is due to optical selection rules or to our incomplete understanding of the electronic manifold of the molecule cannot be determined. In any case, the appearance of three of the four singlet transitions in solution indicates that we have correctly located at least some of the valence transitions of *cis*- and *trans*-hexatrienes. The several weak bands that appear in the higher energy loss electron impact spectrum, such as the 6.2 eV-energy loss band in *trans*-hexatriene, are much narrower than the two main bands. While it is possible that they arise from additional valence transitions, it is more probable that they are incompletely suppressed Rydberg transitions known to occur at these energies.⁵ They will not be further considered.

The lower energy triplet and singlet transitions in each molecule appear at essentially the same transition energies as previously reported.^{2,5,6} The higher energy triplet and singlet transitions are 0.2 and 0.5 eV higher in the trans isomer than in the cis isomer, respectively. Although this may appear inconsistent with the essentially identical IP_1 and IP_{11} values reported for each molecule,¹⁰ it is compatible with the respective EA_{11} values of 1.58 and 2.13 eV⁹ and reflects intrinsic electronic differences in the two molecules.

Several theoretical calculations have been carried out on the trans isomer of hexatriene. The best are compared with the experimental results in Table II. We see that the best ab initio calculation¹³ essentially reproduces the two observed triplet transition energies. The higher triplets obtained in this calculation lie within the envelopes of the two singlets and hence cannot be experimentally detected. The NG calculation does not attempt to calculate the transition energy to the B_u valence singlet. The calculated A_g singlet, 5.87 eV, is appreciably lower in energy than our A_g singlet. However, because the calculated state is an A_g^-

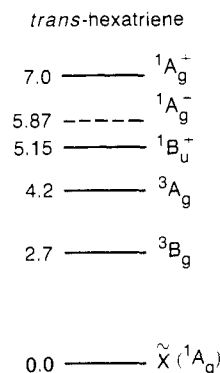


Figure 3. Energy level diagram of *trans*-hexatriene (in eV). The energy of the ${}^1A_g^-$ state is calculated,¹³ the others are experimental (this investigation).

pseudoparity state, the transition to it is predicted to have zero intrinsic intensity and may not be observable even in the absence of selection rule prohibitions. We therefore conclude that we are observing the second excited ${}^1A_g^+$ valence state of the hexatrienes, and the NG calculation of the ${}^1A_g^-$ valence state does not apply.

The comparison of the semiempirical calculations with our experimental spectra is more problematical because these results are strongly dependent on the types of approximations used. The best numerical fit occurs for an all-excitations calculation employing Ohno integrals.¹⁴ The calculated transition energies of the ionic states B_u^+ and A_g^+ essentially reproduce the observed values. However the lowest A_g^- state is calculated appreciably below that of the ab initio calculation (4.45 vs. 5.87 eV). Of these two choices, several factors indicate that the ab initio calculation is more correct. First, there is the experimental observation that *trans*-hexatriene does not fluoresce, in contrast to every other polyene in which the A_g^- state is observed below the B_u valence state.¹⁶ In addition, in the closely related molecule butadiene, the energy manifold of which should be similar to that of hexatriene, ab initio calculations have been shown to correctly determine the location of the experimentally observed A_g^- state, whereas semiempirical calculations underestimate this energy by ~ 1.25 eV.¹⁸ Finally, direct attempts to locate a hexatriene low-lying A_g^- state, either by two-photon thermal blooming¹² or excited-state absorption spectroscopy,²¹ have been unsuccessful. While negative results, like those obtained here, are inconclusive, collectively they indicate that the theory that predicts positive results under these conditions may be incorrect. For these reasons, we question the accuracy of the semiempirical calculations of the A_g^- state of *trans*-hexatriene. Perhaps the parameterization of the repulsion and resonance integrals used in the semiempirical calculation is not quite accurate, resulting in the somewhat (relative) low transition energies calculated for the covalent (–) states. Alternately, perhaps the use of one Hamiltonian to describe both covalent and ionic states is invalid here.²²

What, then, is the correct electronic-state diagram for conjugated polyenes? On the basis of our experimental results and the theoretical results discussed above, we propose the *trans*-hexatriene energy level diagram presented in Figure 3. The locations of the 3B_u , 3A_g , ${}^1B_u^+$, and ${}^1A_g^+$ states are experimentally determined. The ${}^1A_g^-$ state is located at its ab initio calculated level.¹³ (Arguments supporting this calculated energy are given above.) In *trans*-hexatriene, the ${}^1A_g^-$ state is thus deduced to lie above the ${}^1B_u^+$ state. With the aid of previous experimental and theoretical results, we can now extrapolate this energy level diagram to longer polyenes. The A_g^- state, which lies above the B_u^+ state in trienes, is observed to lie below the B_u^+ state in longer polyenes in condensed phases.¹⁶ Although semiempirical calculations place it below the B_u^+ state in all polyenes,¹⁵ in both *trans*-butadiene and *trans*-hexatriene, this calculation underestimates the respective

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A_u^- state energies relative to those of the B_u^+ states and thus erroneously places each A_g^- state below the corresponding B_u^+ state. We propose that in all polyenes, the semiempirical calculations similarly underestimate the A_g^- state energies relative to those of B_u^+ states. But, since the energy of the A_g^- state decreases faster than that of the B_u^+ state as the polyene chain increases,^{15,16} we predict that at some point, the initially higher A_g^- state will fall below the B_u^+ state. This prediction is confirmed by the experimental observations.¹⁶ One should, thus, ask at what chain length does the A_g^- state fall below the B_u^+ state in isolated polyenes? The only vapor phase system in which the A_g^- state is experimentally observed to lie below the B_u^+ state is diphenylbutadiene.²³ Since the chain length equivalent of a phenyl group is estimated to be 1.5 double bonds,²⁴ the diphenylbutadiene result suggests that the A_g^- state falls below the B_u^+ state in isolated polyenes containing 5 or more conjugated double bonds. Thus, we predict that for isolated molecules, decapentaene is the smallest polyene in which the A_g^- state lies below the B_u^+ state. Decapentaene is thus the most propitious candidate for future investigations.

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Conclusion

The main conclusions of this investigation are contained in Table I and Figure 3. The transition energies of the higher valence states of each multiplicity are different in *cis*- and *trans*-hexatrienes, suggesting that the photochemical properties of the two isomers should also differ. The correlation between the experimental transition energies of *trans*-hexatriene and the calculated values suggests that although we are unable to see the A_g^- valence state, it is above the B_u^+ state in this molecule. In addition, our results indicate that current semiempirical calculations of polyenes underestimate the transition energies to covalent states and that the A_g^- state does not descend below the B_u^+ state for polyenes of less than five double bonds.

Note Added in Proof. An analogous investigation of *trans*-octatetraene has recently appeared.²⁵

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Electronegativity Equalization: Application and Parametrization

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Abstract: An analysis is made of three different formalisms which use electronegativity equalization principles for the calculation of partial charges of atoms in molecules. Various scales can be used with each of these formalisms provided that the variation of the (isolated-atom) electronegativity with charge can be evaluated. The Hinze and Jaffé orbital electronegativities, Sanderson's electronegativity scale, or an extension of the electronegativity concepts derived by Iczkowski and Margrave are consistent with these requirements. The geometric average of the compound electronegativity, Sanderson's formalism, may produce valuable correlations with charge-sensitive properties of atoms for homologous compounds. Two formalisms make corrections to the isolated-atom electronegativities by consideration of the effects of the electrostatic potential originating from placing an atom in a molecule. The PEOE (partial equalization of orbital electronegativity) formalism simulates this effect by considering only the connectivities of the atoms. The FEOE (full equalization of orbital electronegativity) formalism explicitly calculates the electrostatic potential, by using interatomic distances and solving a set of simultaneous equations to obtain the atomic charges in a molecular environment. The PEOE and FEOE formalism give results that are highly correlated.

The principal aim of theoretical chemistry is to develop rules to explain chemical reactions and properties of molecules, in a quantitative and predictable way. For years, efforts to attain this goal were based on quantum chemistry, but practical objections soon became apparent because of the drastic increases in computation times with the number of electrons in a system. The formulation of empirical rules based on electronegativity equalization has gained more attention from chemists in recent years. From these rules, it may be expected that, within their proper framework, they approximately predict the outcome of atomic interactions in molecules. A quantitative expression for the atomic electronegativity, and its change during bond formation, should

contain sufficient information to derive the properties of primary interest to chemists: the atomic charges. Sanderson¹ introduced the concept of electronegativity equalization and proposed a formalism to calculate atomic charges, based on the change in electronegativity from the isolated atom value to its value after equalization in the molecule. However, in this way, identical charges are obtained for all atoms of the same elemental type in a molecule.

Sanderson's postulate,¹ that when two or more different atoms combine to form a molecule, their electronegativities change to a common intermediate value, was only recently established by theoretical formulations. Parr et al.^{2,3} investigated the electro-

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