between the two nearly parallel MEI^+ ions. A similar structure with the central Cl^- replaced by an $AlCl_4^-$ was also optimized so that frequencies of the C–H stretches could be compared. The frequency of the C-2–hydrogen stretch for this model was 3111 cm^{-1} compared to the 3107 cm^{-1} for the Figure 7 system with Cl^- thus reproducing the direction (but not the magnitude) of the shift observed to form the Cl^- interaction band. However, the C-4– and C-5–hydrogen stretches shifted from 3225 and 3238 cm^{-1} with no Cl^- present to 3239 and 3251 cm^{-1} in the Figure 7 structure. Thus the calculated shift is in the opposite direction from that observed and leads us to conclude that the AM1 method is not capable of reproducing the experimentally observed Cl^- interaction band frequencies using this model. Nonetheless, two important results were obtained from the AM1 calculations. First is the confirmation of the assignments of the C-2–, C-4–, and C-5–hydrogen stretching frequencies. Second is the identification of Cl^- centered between two adjacent MEI^+'s (Figure 7) as a stable configuration for this system.

Conclusion

In basic melts of MEICl and $AlCl_3$, our IR spectral analysis showed that Cl^- interacts with MEI^+ to cause similar shifts in the frequencies of the C-2–, C-4–, and C-5–hydrogen stretches. Thus the description of the interaction of MEI^+ with Cl^- cannot be restricted to ion pair formation solely by hydrogen bonding of Cl^- through the C-2 hydrogen. Our experimental results are consistent with a stack model for the interaction of MEI^+ with the anions in the melt, although the inability to theoretically predict the experimental shifts in ring C–H frequencies leaves the exact nature of the interactions an open question.

Acknowledgment. Support for this work by the National Research Council is gratefully acknowledged by one of the coauthors (J.W.R.). We also thank Dr. Jimmy Stewart for many helpful discussions on the MOPAC calculations. Finally, we thank Missy Landess for her expert word processing and assistance in editing this manuscript.

Photodissociation of Conjugated Diene Radical Cations: Methyl Substituent Band Shifts

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44118. *Received September 18, 1987*

Abstract: Photodissociation spectroscopy (PDS) in an ion cyclotron resonance (ICR) spectrometer was used to investigate the methyl substituent effects on the observed PDS bands of nine gas-phase methyl-substituted butadiene radical cations. The lower energy PDS bands, the I bands, are located between 1.61 and 2.56 eV, depending on the position and number of methyl groups. Methyl substitution on an inner-carbon atom gives a red shift of the I band compared with butadiene cation, while outer-carbon substitution results in a blue shift. The higher energy PDS bands, the A bands, were located between 3.5 and 4.2 eV. Inner-carbon substitution gave no significant shift of the A bands relative to butadiene cation, while outer-carbon substitution gave a red shift increasing with the number of methyl groups. The observed trends in the PDS I band shifts are compared with energy shifts measured by photoelectron spectroscopy (PES). The prior assignment of the PES band near 11 eV as a π orbital is strongly confirmed. Shifts in the PDS A band are compared with results from electron transmission spectra and optical spectra of the corresponding neutrals, and the results are found to be correlated but with considerable scatter. Theoretical calculations using the CNDO/S-CI program clarify the nature of the electronic transitions involved in these open-shell cations. The CNDO/S method is somewhat successful in predicting the substituent effects in both of the spectroscopic bands of butadiene ion, confirming the utility of the method for open-shell ion transitions.

Systematic study of substituent perturbations of a spectroscopic transition has been a central theme in developing theoretical understanding and practical applications of electronic spectroscopy of polyatomics. While such ideas have been extensively worked out for neutral closed-shell molecules, much less understanding exists of the spectroscopy of radical cation chromophores. This is mainly due to the intrinsic difficulty in building up a sufficient density of gas-phase ions to permit direct absorption-spectroscopic measurements, while the extreme reactivity of these species often precludes condensed phase spectroscopy. Much useful spectroscopic information about gas-phase ions has come from the indirect approach of photodissociation spectroscopy (PDS). We describe here the use of the PDS technique in a systematic study of the methyl group substituent effects on the spectroscopy of the butadiene radical cation chromophore.

Besides PDS, other sources of information on the energy levels and optical transitions of radical cations include absorption spectroscopy in low-temperature glassy matrices, gas-phase emission spectroscopy, photoelectron spectroscopy (PES), and theoretical calculations. The butadiene radical-ion chromophore is not among the few systems (mostly halobenzenes and acetylenes) from which fluorescence emission has been observed, so this is not a useful avenue. Some glassy matrix spectra of butadiene-ion derivatives have been reported, as noted below, but their interpretation is not straightforward, and they are of limited interest for comparison with our results. Electron transmission spectroscopy (ETS) and optical absorption spectroscopy of the neutrals both give some information about the empty excited orbitals of the system, and the correlation with the cation results will be explored, although the correlation is not found to be very close. We will try to build up understanding of the spectroscopy of this system principally by correlating PDS results, PES results, and theoretical calculations by using the method, CNDO/S, which currently seems most useful for this purpose.

PDS results for several conjugated diene radical cations have been reported previously. Butadiene cation, the first conjugated diene radical cation system studied by the PDS technique, was considered in a correlation of PDS spectra with optical absorption spectra, PES, and theoretical calculations, elucidating the nature of the two observed dissociation bands in the UV-vis region.[1] 2,4-Hexadiene and its isomers were also studied by PDS to determine the structure of the ions and to investigate the rearrangement involving migration of a double bond into conjugation.[2] PDS results for pentadiene, octadiene, cyclohexadiene, and cyclooctadiene radical cations were reported more recently from the

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(1) Dunbar, R. C. *Chem. Phys. Lett.* **1975**, *32*, 508.

(2) Benz, R. C.; Dunbar, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 1799.

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Table I. Photodissociation Band Energies of Methyl-Substituted Butadiene Radical Cations, Along with the Comparison of the Lower Energy Band with the Difference between Their First and Second PES Ionization Potentials (eV)

	visible band		UV band
cations	PDS	PES[a]	PDS
1	2.30[b]	2.37	4.0[b]
2	2.14	1.99	4.2
3	1.61	1.57	4.0
4	2.43*c*	2.46	3.75[c]
5	2.17	2.05	3.9
6	2.26	2.19	
7	2.48	2.50	
8	2.18	*e*	
9	2.50[d]	2.49	3.75[d]
10	2.65[d]	2.47	3.5[d]

[a] Average of the values from ref 7a and 7b. [b] Reference 1. [c] Reference 3. [d] Reference 2. [e] Not available.

point of view of further characterizing this facile rearrangement process.[3]

As discussed previously,[1-4] the PDS spectra of these ions have two typical peaks, one in the UV region and the other in the visible. The UV band, denoted the A transition, reflects an electron transition from the half-filled highest occupied orbital (HOMO), π_2, to the lowest unoccupied molecular orbital (LUMO), $\pi_3{}^*$, which is the transition also observed in neutral diene molecules. The lower energy band, denoted the I transition, which cannot occur in the neutral molecules, is considered to be a "hole excitation" of an inner π-electron (π_1) into the vacancy in the singly occupied HOMO, π_2.

Experimental Section

ICR Photodissociation Measurements. Photodissociation spectra were obtained in the UV and visible regions by using a Varian ICR-9 spectrometer operated in pulsed mode with a rectangular cell. A typical experimental procedure consisted of ion formation with a 100-ms electron beam pulse at 11 eV nominal electron energy, 2 s of ion trapping, and optical irradiation time, followed by detection of the remaining parent ions by ICR bridge-mode detection. The UV region was studied by using light from a 2.5 KW Hanovia Hg–Xe arc lamp with wavelengths selected by a Schoeffel grating monochromator with two 2-mm slits giving nominal band pass (fwhm) of 6.6 nm. The wavelengths in the visible region were selected by using Baird-Atomic interference filters spaced 20 nm apart. The relative light flux of the arc lamp after wavelength selection was calibrated with Eppley thermopile measurements. Sample pressure (indicated at the ion gauge or ion pump) was kept lower than 2×10^{-8} Torr in all cases. All of the samples were obtained from Aldrich and Chemical Samples Co. and used without further purification.

Theoretical Calculations. The MO calculations were done by using the CNDO/S-CI program parametrized by Del Bene and Jaffe.[5] This method uses semiempirical values for most integrals, calculates the wave function of the ground state, and develops excited configurations by using the virtual orbitals of the ground state. It then invokes limited configuration interaction (CI) with singly excited configurations to obtain excited state energies, transition moments, and polarizations for the transitions. In the open-shell CNDO/S-CI calculation used here for the radical cations, all the adjustable parameters as well as all systematic parameters were carried over unchanged from the closed-shell CNDO/S method. In our calculation, two-center repulsion integrals were calculated by the Pariser-Parr method. The CI calculations were carried out with 60 configurations. The geometries of the radical cations were taken to be the same as those of corresponding neutral molecules, which were taken from literature experimental values.[6] In cases where an experimental geometry was not found, geometry optimization was carried out by the program.

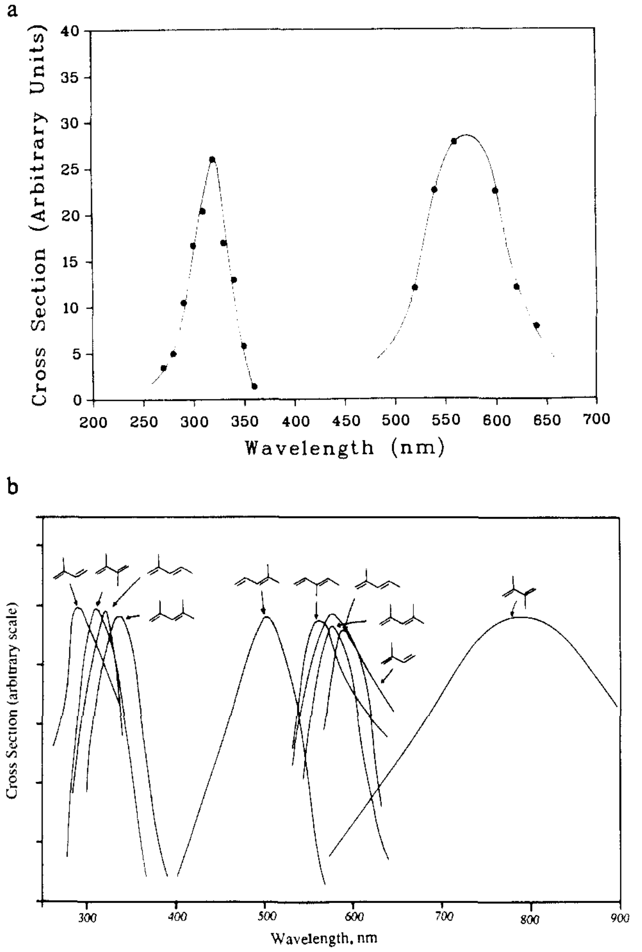
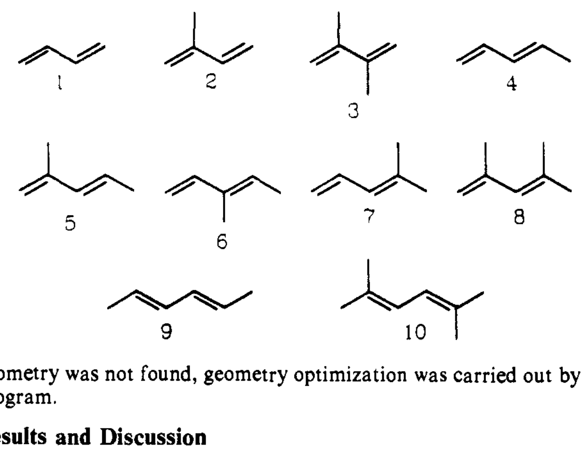


Figure 1. (a) Representative photodissociation spectrum of the cation of compound **5**. (b) Photodissociation spectra of several of the gas-phase radical cations studied here.

Chart I



Results and Discussion

Figure 1 shows several of the photodissociation spectra from this work. The experimental PDS results for 1,3-butadiene cation and its methyl-substituted radical cations are listed in Table I, giving the energies of the photodissociation maxima. Some previously reported photodissociation results are included with the present data for comparison. Chart I shows the set of ten compounds considered here.

The band maxima for the two PDS bands are plotted in Figure 2. It can be readily seen, for instance by comparing **2** with **4** and **3** with **9**, that the position of methyl substitution determines whether the I band energy increases or decreases relative to butadiene cation. An increase of the I band energy is observed with the cations having methyl groups on the terminal carbons of butadiene (outer methyls) and a decrease for methyls on the

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(3) Dunbar, R. C.; Fitzgerald, G. B.; Hays, J. D. *Int. J. Mass Spectrom. Ion Phys.* **1985**, *66*, 313.

(4) (a) Shida, T.; Iwata, S. *J. Am. Chem. Soc.* **1973**, *95*, 3473. (b) Zahradnik, R.; Carsky, P. *J. Phys. Chem.* **1970**, *74*, 1235.

(5) Chang, H. M.; Jaffe, H. H.; Masmanidis, C. A. *J. Phys. Chem.* **1975**, *79*, 1118, and references therein.

(6) (a) Kuchitsu, K.; Fukuyama, T.; Marino, Y. *J. Mol. Struct.* **1967–1968**, *1*, 463. (b) Vilkov, L. V.; Sadova, N. I. *Zh. Strukt. Khim.* **1967**, *8*, 398. (c) Aten, C. F.; Hedberg, L. *J. Am. Chem. Soc.* **1968**, *90*, 2463. (d) Traetteberg, M.; Paullen, G.; Cyvin, J.; Panchenko, Yu. N.; Mochalov, J. *J. Mol. Struct.* **1975**, *116*, 141.

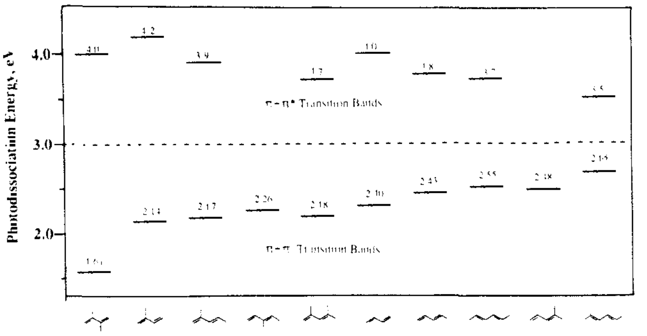

Figure 2. Plot of the photon energy of the two PDS band maxima observed for each of the ions. The ions are ordered according to increasing energy of the I band predicted by the simple empirical linear additivity scheme described in the text.

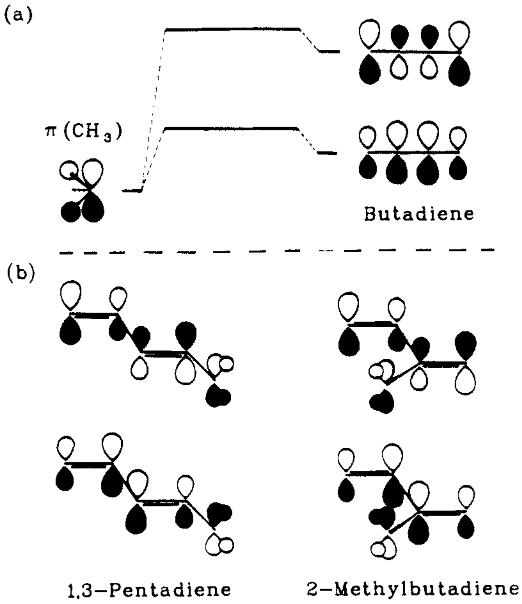

Figure 3. (a) Linear combination of the butadiene molecular orbitals and pseudo-$\pi(CH_3)$ molecular orbital to construct the two high-lying occupied π molecular orbitals of the butadiene methyl derivatives. (b) Molecular orbital picture of the two occupied π orbitals of 2-methylbutadiene and 1,3-pentadiene, showing the possibility of through-space interaction in the 2-methylbutadiene case (see ref 7a).

interior carbons of butadiene (inner methyls). Shifts in the A band are smaller and appear to be induced by outer methyls.

The methyl substituent effects appear to be additive to a good approximation: By using the additive rule that each outer methyl shifts the peak 0.1 eV higher and each inner methyl shifts it 0.25 eV lower, the positions of the I transitions are predicted for nine ions (relative to butadiene ion) with an average error of less than 0.06 eV. Similarly, by using the rule that each outer methyl shifts 0.15 eV lower while inner methyls have no effect, the positions of the A transitions are predicted for seven ions with an average error of less than 0.08 eV. Figure 2 clearly shows the progressive band shifts for increasing inner or outer methyl substitution and the opposite trends in the substituent effects for the I band and the A band.

Beez et al.[7a] proposed an explanation for the differing substituent effects for inner and outer methyls in their interpretation of the ionization potential shifts in the PES spectra. Figure 3 shows the two π m olecular orbitals involved in the hole-promotion process corresponding to the optical I band. These orbitals are constructed by an antisymmetric linear combination of two butadiene bonding orbitals with the pseudo-π-orbital of a methyl

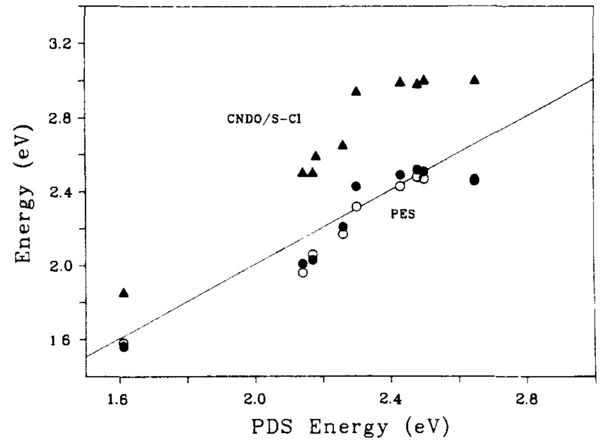

Figure 4. Correlation of PDS I band positions with the calculated values from CNDO/S (▲) and with the PES peak difference using PES data from ref 7a (●) and ref 7b (○). The solid line represents perfect agreement with the PDS values.

group. The proposal of Beez et al. is that the methyl substituent effects on these orbitals are equal for inner and outer methyls, except that the inner methyl case is distinguished by a through-space interaction between the pseudo-π-orbital on the methyl and the π orbital of the opposite (but spatially nearby) double bond. This interaction can be seen in Figure 3b for 2-methylbutadiene, while for 1,3-pentadiene the outer methyl group is clearly too far from the butadiene π framework for significant through-space interaction. The interaction is stabilizing (bonding) for π_2 but destabilizing (antibonding) for π_1, with the result that the I band transition energy is reduced relative to what it would be in the absence of the through-space interaction. This proposal was supported by molecular orbital calculations and was in accord with the methyl substituent effects seen in the PES spectra of several methyl-substituted butadienes.

I Band Comparison with PES Spectra. The energies of the ground electronic state and the hole-promotion excited states of the ion give rise to peaks in the PES spectrum. Beez et al.[7a] and later Masclet et al.[7b] published PES data for this series of molecules. Because the photodissociation I band corresponds to an optical transition between the ground state and a hole-promotion excited state, it is reasonable to compare the lower energy PDS band with the difference between the adiabatic first ionization potential (IP) and the vertical second IP of the PES spectrum. The difference between the first and second IP's from PES are listed along with the I band energies from PDS in Table I and are plotted in Figure 4. It can be seen that the agreement is quite good, with an average deviation for nine compounds of 0.08 eV. (The average deviation between the two sets of literature PES values is itself 0.04 eV for the nine compounds.) The PDS energies are on the average 0.05 eV higher than the PES energies, a difference which may not be experimentally significant but might be ascribed to different Franck–Condon envelopes for the peaks: PES peaks reflect the Franck–Condon envelope of the neutral-to-ion transition, while PDS peaks reflect that of the ion-to-ion transition. Since in both cases the energies are measured for envelope maxima, this can give small differences between the band positions from these different techniques.

The present results give an unambiguous confirmation of the assignment of the ~11-eV peak in the PES spectra of these molecules.[7] The excellent agreement between PES and PDS results for the nine molecules means that the same electronic excited state of the cation is observed in both cases. The fact that PDS shows this state to be strongly optically allowed, and therefore a state of π symmetry, absolutely confirms Beez et al.'s assignment[7a] of this peak as belonging to the first excited π state.

A Band Comparison with Neutral UV Spectra and ETS Spectra. As the A bands of PDS arise from electronic transitions between π_2 and π_3^*, comparison with PES is no longer meaningful. Probably the most direct comparison of the A band of a PDS of a radical cation can be made with absorption spectra acquired

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[7] (a) Beez, M.; Biere, G.; Bock, H.; Heilbronner, E. *Helv. Chim. Acta* **1973**, *56*, 1028; **1977**, *60*, 2213. (b) Masclet, P.; Mouvier, G.; Bocquet, J. F. *J. Chim. Phys.* **1980**, *78*, 99.

Table II. Substituent Effects on the $\psi_2 \rightarrow \psi_3^*$ Electron Promotion Energy in Butadiene Ion (eV)

cations	ΔPDS[a]	ΔUV[a]	ΔETS[b]
1	(4.0)[c]	(5.9)[c]	(9.79)[d]
4	−0.2	−0.1	−0.23
9	−0.3	−0.2	−0.57
10	−0.5	−0.7	−0.95
2	+0.2	−0.1	−0.22
3	0	−0.25	−0.57

[a] Energy of UV peak relative to butadiene. [b] Energy of the ψ_3^* ETS peak (ref 13 and 14) plus the ionization energy of the neutral molecule, relative to the value for butadiene. [c] Energy of UV peak in unsubstituted butadiene. [d] Energy of ETS peak plus ionization energy of butadiene.

from the radical cation formed in a low-temperature matrix. Although optical spectra of some diene radical cations in an irradiated glass environment have been reported,[8] their interpretation is not straightforward because of the presence of impurity bands, polymer bands, and matrix bands and the complication of unknown matrix shifts. Badger and Brocklehurst[8b] report cation monomer maxima at 2.19 eV for **1** and 2.29 eV for **4**, which in comparison with the PDS results suggest a matrix red shift of ~0.1 eV.

The A band of the radical-ion spectrum and the UV peak commonly observed in the neutral molecule involve the same electron promotion from π to π^* molecular orbitals, but there is a large transition-energy difference between the two. The reported neutral optical absorption maxima for six of the molecules[9] are compared with the A band energies from the cation PDS spectra in Table II. For the ions with outer-carbon methyl substituents, a reasonable linear correlation with unit slope is seen but with the neutral peaks about 1.9 eV higher in energy than the ions. The neutrals show similar red shifts for inner-carbon substituents, but no consistent substituent shifts are observed for the corresponding ions.

Just as in the present case of the butadiene derivatives, it has in general been observed that the π–π^* transition energies from the doublet ground states to the π^* excited doublet states of radical cations are lower than those corresponding to the singlet–singlet π–π^* transitions of neutral molecules.[10] A substantial red shift (1.2 eV) for butadiene ion compared with the neutral is also predicted by the CNDO/S calculations.

The lowest energy peak in the ETS spectra of substituted butadienes is believed to reflect the energy of the lowest unoccupied molecular orbital (LUMO) (ψ_3^* orbital).[11] Since the species characterized in this experiment is a transient anion state, the energy is not directly comparable to the cation or neutral spectroscopy, but it is still interesting to see if similar substituent patterns are exhibited. With a bit of care in analyzing the situation, an expression (eq 5 below) can be written which has some hope of affording a useful comparison between the spectroscopic results and the ETS results.

ETS data give the energy of the LUMO (relative to the neutral plus a free electron)

$$E(\mathrm{ETS}) = E(\mathrm{LUMO}) \tag{1}$$

We are going to compare this with spectroscopic peaks, which give an energy difference between the LUMO and the HOMO (highest occupied molecular orbital)

$$E(\mathrm{UV}) = E(\mathrm{LUMO}) - E(\mathrm{HOMO}) \tag{2}$$

In order to make a comparison, we must use a value for the

Table III. Comparison of PDS Values with Theoretically Calculated Values Using the CNDO/S-CI Program (eV)

	π–π transition		π–π* transition	
cations	PDS	CNDO/S-CI	PDS	CNDO/S-CI
1	2.30	2.94	4.0	4.41
2	2.14	2.50	4.2	4.19
3	1.61	1.85	4.0	4.19
4	2.43	2.99	3.76	4.33
5	2.17	2.50	3.9	4.03
6	2.26	2.65		4.09
7	2.48	2.98		4.26
8	2.18	2.59		3.95
9	2.55	3.00	3.75	4.13
10	2.65	3.00	3.5	3.95

HOMO energy, which we can take from the ionization energy of the neutral molecule

$$E(\mathrm{HOMO}) = -\mathrm{IE} \tag{3}$$

Thus

$$E(\mathrm{LUMO}) - E(\mathrm{HOMO}) = E(\mathrm{ETS}) + \mathrm{IE} \tag{4}$$

In practice this equation is poorly obeyed, because the energy cost of separating the electron from the cation upon ionization and the energy gain in bringing the electron to the neutral in forming the anion have not been correctly accounted for, and values from eq 4 agree poorly with the spectroscopic energies.[12] However, we can hope that these effects will cancel out in looking at substituent effects. If we use the symbol Δ to represent the change in a quantity upon substitution, relative to its value for butadiene, we can write

$$\Delta E(\mathrm{LUMO}) - \Delta E(\mathrm{HOMO}) = \Delta(\mathrm{UV}) = \Delta(\mathrm{ETS}) + \Delta(\mathrm{IE}) \tag{5}$$

Table II shows this quantity derived from the ETS spectra of several representative members of the series.[13,14] It can be seen that the substituent shifts from ETS are in the expected direction and with the expected order of magnitude but are somewhat larger than the corresponding neutral UV results. Agreement with the PDS values for the cation is poorer. The only substituent effect large enough to be clear above the scatter among the three techniques compared in Table II is the consistent shift to lower energy upon methylation of the outer carbons of butadiene.

Comparison with CNDO/S-CI Calculations. The CNDO/S predictions for the hole transition energies of the diene radical cations, using CI with 60 configurations, are listed in Table III, and are plotted in Figure 4 for the I band. The absolute values calculated for the transition energies are all too high by ~0.4 eV, but, as Figure 4 shows, the calculation does a good job of reproducing the substituent band shifts. Even better, as seen by comparing the CNDO/S points with the PES points in Figure 4, is the agreement between the CNDO/S transition energy and the orbital difference energy from PES. The fact that such good agreement is obtained between CNDO/S and PES may be due to the fact that both of these techniques are based on the neutral-molecule geometry, whereas PDS refers to the ion geometry, and small discrepancies may arise from the differing Franck–

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[8] (a) Shida, T.; Hamill, W. H. *J. Am. Chem. Soc.* **1966**, *88*, 5371. (b) Badger, B.; Bocklehurst, B. *Trans. Faraday Soc.* **1969**, *65*, 2576.

[9] (a) Carr, E. P.; Pickett, L. W.; Stucklen, H. *Rev. Modern Phys.* **1942**, *14*, 260. (b) Mulliken, R. S. *Ibid.* **1942**, *14*, 265. (c) Jones, L. C.; Taylor, L. W. *Anal. Chem.* **1955**, *27*, 228.

[10] Leach, S.; Dujardin, G.; Taieb, G. *J. Chim. Phys.* **1980**, *77*, 705.

[11] Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341.

[12] A somewhat fuller analysis can be given if we separate conceptually the process of bringing an electron into the vicinity of the neutral (or the cation) from the process of inserting it into the appropriate molecular orbital. Call E^- the electrostatic energy released in bringing an electron from infinity into the vicinity of the neutral and E^+ the energy released in bringing an electron from infinity to the vicinity of the cation. Call E(HOMO) and E(LUMO) the energies required to insert a nearby electron into the HOMO and the LUMO, respectively. (E(HOMO) will be negative, since the HOMO lies below zero.) With these terms, $E(\mathrm{ETS}) = E(\mathrm{LUMO}) - E^-$ and $-\mathrm{IE} = E(\mathrm{HOMO}) - E^+$. The more correct counterpart of eq 4 is then $E(\mathrm{ETS}) + \mathrm{IE} = E(\mathrm{LUMO}) - E(\mathrm{HOMO}) + (E^+ - E^-)$. Thus the simple expression of eq 4 is in error by the electrostatic term $(E^+ - E^-)$, which is substantially positive. The hope embodied in writing the relative expression of eq 5 is that $(E^+ - E^-)$ will be independent of substituents to a useful degree of approximation.

[13] Burrow, P. D.; Jordan, K. D *Chem. Phys. Lett.* **1975**, *36*, 594. Staley, S. W.; Giordan, J. C.; Moore, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 3638.

[14] Giordan, J. C. Ph.D. Thesis, University of Maryland, 1980.

Condon envelopes. While the PDS bands arise directly from electronic transitions of cations, PES measurements are made on neutral molecules, and the CNDO/S method was originally parametrized to study the singlet–singlet or singlet–triplet transitions of neutral molecules.

In the case of the A band, the CNDO/S transition energies, shown in Table III, are again predicted about 0.4 eV higher than observed. The calculations account fairly well for the substituent effects. Two chief predictions from the calculation are, first, that the substituent effects should be much smaller than for the I band, with a total range of about 0.5 eV, and, second, that the largest perturbation, a red shift, is expected with several outer-carbon substituents. These two theoretical expectations are seen to be borne out in the PDS results.

Conclusion

The two photodissociation bands observed in the conjugated diene radical cations show band shifts depending on the number and position of the methyl group substituents. The hole-transition bands show a blue shift with inner-carbon substitutions and a red shift with outer-carbon substitutions: These trends can be interpreted in terms of a nonbonding through-space interaction between the molecular orbitals of butadiene and the methyl groups. For the π–π^* transition bands, methyl group substitutions on the outer carbons give a red shift, while substitution on the inner carbons gives no clear band shifts. A comparison of PDS results, neutral spectroscopy, and ETS results for the UV transition shows considerable scatter, but a clear shift of 0.15 or 0.2 eV per methyl group can be discerned for substituents on the outer carbons. Calculational results for the two transitions using the CNDO/S-CI program show a good correlation with the experimental results.

Acknowledgment. We are most grateful to Professor Hans Jaffe for providing the CNDO/S program and for help in its use. We thank a referee for bringing ref 14 to our attention. The support of the National Science Foundation and of the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Ethenylphosphine. Synthesis by Flash-Vacuum Thermolysis and Characterization by Photoelectron Spectroscopy[1]

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Abstract: Ethenylphosphine and prop-1-en-2-ylphosphine, obtained by flash-vacuum thermolysis of the corresponding Diels–Alder adducts, have been characterized by their photoelectron spectra. In both cases, the broad shape of the first two bands respectively at 9.65 and 10.85 eV for ethenylphosphine and at 9.50 and 10.3 eV for prop-1-en-2-ylphosphine can only be accounted for if we assume a free-rotating P–C bond. This conclusion was inferred from a complete theoretical study of the rotation process of the PH_2 group around the P–C bond. Two privileged forms were found: a syn form ($\phi = 0$, the lone pair of the phosphorus eclipsing the P–C bond) and a gauche form 3.5 kJ·mol^{-1} less stable ($\phi = 127°$), separated by low rotation barriers (8.19 and 10.74 kJ·mol^{-1}). Evaluation of the accurate ionization potentials according to a configuration interaction formalism has been achieved for ethenylphosphine in different conformations. The results of these calculations clearly indicate that during the rotation process the energy of the first two ionic states extends over a 0.4 eV interval.

1. Introduction

Although many spectroscopic and theoretical studies have been carried out on ethenylamine,[2] ethenol,[3] and ethenethiol,[4] ethenylphosphine has, to our knowledge, only recently been synthesized by flash thermolysis (FVT) of the corresponding Diels–Alder adduct.[5]

It was thus of interest to define the electronic and structural characteristics of these ethenylphosphines, by using flash thermolysis–UV photoelectron spectrometry coupling, as reported by our laboratory.[3i,6] These experimental data were compared to a complete quantum mechanical study of the internal rotation process and the ionic state energies of energetically favoured rotamers.

2. Photoelectron Spectra

Ethenylphosphine (**1**) and prop-1-en-2-ylphosphine (**2**) were obtained by the retro-Diels–Alder reaction of 9,10-dihydro-9,10-ethanoanthracen-11-ylphosphine and 11-methyl-9,10-dihydro-9,10-ethanoanthracen-11-ylphosphine (**3**) and (**4**), respectively, prepared by the reduction of the corresponding phosphonates[5] (Figure 1).

The photoelectron spectra of alkenylphosphines **1** and **2**, obtained by the flash thermolysis of **3** and **4**, respectively, are shown in Figures 2 and 3. In contrast to observations with ethenylamine, the nitrogen analogue of **1**,[3i] no change in the phosphine spectrum is observed, even after several minutes. Alkenylphosphines **1** and

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[1] "Application of Photoelectron Spectroscopy to Molecular Properties" Part 32. Part. 31: Guimon, C.; Pfister-Guillouzo, G. *Organometallics* **1987**, *6*, 1387.

[2] (a) Lovas, F. J.; Clark, F. O.; Thieman, E. *J. Chem. Phys.* **1975**, *62*, 1925. (b) Eades, R. A.; Weil, D. A.; Ellenberger, M. R.; Farneth, W. E.; Dixon, D. A.; Douglass, C. H. *J. Am. Chem. Soc.* **1981**, *103*, 5372. (c) Saebo, S.; Radom, L. *J. Mol. Struct.* **1982**, *89*, 227. (d) Ripoll, J. L.; Lebrun, H.; Thuillier, A. *Tetrahedron* **1980**, *36*, 2497. (e) Albrecht, B.; Allan, M.; Haselbach, E.; Neuhaus, L.; Carrupt, P. A. *Helv. Chim. Acta* **1984**, *67*, 220.

[3] (a) Saito, S. *Chem. Phys. Lett.* **1976**, *42*, 399. (b) Nobes, R. H.; Radom, L.; Allinger, N. L. *J. Mol. Struct.* **1981**, *85*, 185 and references therein. (c) Ripoll, J. L. *Nouv. J. Chim.* **1979**, *3*, 195. (d) Albrecht, B.; Allan, M.; Haselbach, E.; Neuhaus, L.; Carrup, P. A. *Helv. Chim. Acta* **1984**, *67*, 220. (e) Capon, B.; Siddhanta, A. K. *J. Org. Chem.* **1984**, *49*, 255. (f) Capon, B.; Siddhanta, A. K.; Zucco, C. *J. Org. Chem.* **1985**, *50*, 3580. (g) Rodler, M.; Bauder, A. *J. Am. Chem. Soc.* **1984**, *106*, 4025. (h) Rodler, M. *J. Mol. Spectrosc.* **1985**, *114*, 23. (i) Lafon, C.; Gonbeau, D.; Pfister-Guillouzo, G.; Lasne, M. C.; Ripoll, J. L.; Denis, J. M. *Nouv. J. Chim.* **1986**, *10*, 69.

[4] Plant, C.; Mac Donald, J. N.; Boggs, J. E. *J. Mol. Struct.* **1985**, *128*, 353 and references therein.

[5] Lasnes, M. C.; Ripoll, J. L.; Thuillier, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1428.

[6] Lafon, C. Thèse de 3ème Cycle, Université de Pau, 1987.

0002-7863/88/1510-2730$01.50/0