and isobutyl radical spectra, but no tertiary radical could be produced directly by hydrogen atom abstraction from the neopentyl radical precursor. Furthermore, there is no evidence of such reactions from the many studies that used organic nitrites to cleanly produce specific radicals.[7,26,91] No alternative nitrite decomposition pathways, which would be competitive with reactions 1 and 2 and lead to radical products, can be proposed. It has been reported that 1-butyl radical eliminates molecular hydrogen, presumably to form 1-methylallyl radical.[96] Isobutyl radical undergoing an analogous reaction would form 2-methylallyl radical. These decomposition pathways cannot explain the additional radical bands observed. The adiabatic IPs of these allylic radicals are 7.49 and 7.90 eV, respectively.[90] The band onsets are ~0.1 eV lower but still too high to correspond to those observed for the low-intensity bands appearing near the onset of the 1-butyl and isobutyl radical photoelectron bands.

The primary benefit of these observations may be to suggest new experiments. If these reactions are unimolecular, they provide evidence, at high temperatures, for reactions previously thought not to be competitive with the decomposition reactions. If they are wall catalyzed, they draw attention to possible complications in kinetic experiments involving these radicals.

Conclusion

Photoelectron spectroscopy is unique as an experimental technique for obtaining thermochemical and structural information about high-energy carbonium ion isomers. Analysis of the photoelectron spectra of 1-propyl, 1-butyl, isobutyl, neopentyl, and 2-butyl radicals, combined with the heats of formation of the radicals, yields heats of formation of 1-propyl, 1-butyl, isobutyl, neopentyl, and 2-butyl cations. An examination of the spectra presented here and the spectra of ethyl and 2-propyl radicals reported previously[7] reveals trends in ionization potentials which can be interpreted in terms of inductive and hyperconjugative effects of methyl substituents β to a primary or secondary cation center.

The primary cation heats of formation have been discussed in light of theoretical calculations and energetics of cation rearrangements in solution which may involve primary cations as high-energy transition states or intermediates. The heat of formation of 2-butyl cation derived here is in good agreement with values obtained from appearance potential measurements and equilibrium constants for proton-transfer reactions. This agreement suggests that if classical 2-butyl cation does easily rearrange to a more stable hydrogen-bridged structure, the difference in energy between the classical and rearranged structure is small. NMR experiments support this suggestion. Photoelectron data also yield the difference between the heats of formation of 2-butyl and *tert*-butyl cations. This value is in close agreement with that from solution calorimetric studies. This agreement and the results of comparisons made between relative heats of formation of gas-phase cations and energetics of reactions in stable-ion media support previous studies which indicate that differential solvent effects on cation isomers are small. There is some indication that solvation energies may decrease slightly in the order primary ion > secondary ion > tertiary ion.

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Registry No. $CH_3(CH_2)_3ONO$, 544-16-1; $CH_3(CH_2)_4ONO$, 463-04-7; $(CH_3)_2CH(CH_2)_2ONO$, 110-46-3; $(CH_3)_3C(CH_2)_2ONO$, 24330-48-1; $CH_3CH_2CH(CH_3)CH_2ONO$, 1653-56-1; 1-propyl radical, 2143-61-5; 1-butyl radical, 2492-36-6; isobutyl radical, 4630-45-9; neopentyl radical, 3744-21-6; 2-butyl radical, 16548-59-7; 1-propyl radical, 19252-52-9; 1-butyl cation, 25453-90-1; isobutyl cation, 19252-54-1; neopentyl cation, 14128-47-3; 2-butyl cation, 16548-59-7.

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[96] Gordon, A. S.; Smith, S. R. *J. Chem. Phys.* **1961**, *43*, 331.

Excited States of Polyene Radical Cations: Limitations of Koopmans' Theorem

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Abstract: The electronic absorption spectra of the molecular cations of butadiene, hexatriene, and octatetraene in Ar matrices are presented and compared to earlier related results where possible. From these specta and the accompanying qualitative and quantitative theoretical considerations it must be concluded the Koopmans' theorem breaks down for all excited states of linear conjugated polyene molecular cations (and anions) due to pronounced mixing between Koopmans' and non-Koopmans' configurations. The implications of this breakdown for the widely applied interpretation of linear polyene ultraviolet photoelectron spectra on the basis of orbital energies are discussed.

There has been a long and rich history of experimental and theoretical investigations on the nature of linear polyene excited states.[1] For many years these were thought to be understood quite well within the framework of one-electron theories such as those commonly employed in MO models. Indeed, the position and intensity of the first band in the electronic absorption (EA) spectra of linear polyenes was reproduced with reasonable accuracy by properly parametrized procedures. The puzzling phenomenon of the unusual Stokes shift between the first absorption and fluorescence band onsets[2] was usually explained on the basis of Franck–Condon arguments.[3]

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[1] (a) Hudson, B. S.; Kohler, B. E.; Schulten, K. *Excited States* **1982**, *6*, 1. For very recent work not cited in 1a see: (b) Heimbrook, L. A.; Kenny, J. E.; Kohler, B. E.; Scott, G. W. *J. Chem. Phys.* **1981**, *75*, 4338. (c) Ackermann, J. R.; Kohler, B. E.; Huppert, D.; Rentzepis, P. M. *Ibid.* **1982**, *77*, 3967. (d) Goldbeck, R. A.; Twarowski, A. J.; Russell, E. L.; Rice, J. K.; Birge, R. C.; Switkes, E.; Kliger, D. S. *Ibid* **1982**, *77*, 3319. (e) Mc Diarmid, R.; Doering, J. P. *Chem. Phys. Lett.* **1982**, *88*, 602. (f) Baldo, M.; Pucci, R.; Tomasello, P. *Int. J. Quantum Chem.* **1983**, *23*, 1111.

[2] Hausser, K. W.; Kuhn, R.; Kuhn, E. *Z. Phys. Chem.* **1935**, *B29*, 417. Dalle, J. P.; Rosenberg, B. *Photochem. Photobiol.* **1970**, *12*, 151.

[3] Mulliken, R. S. *J. Chem. Phys.* **1939**, *7*, 364. Thomson, A. J. *Ibid.* **1969**, *51*, 4106.

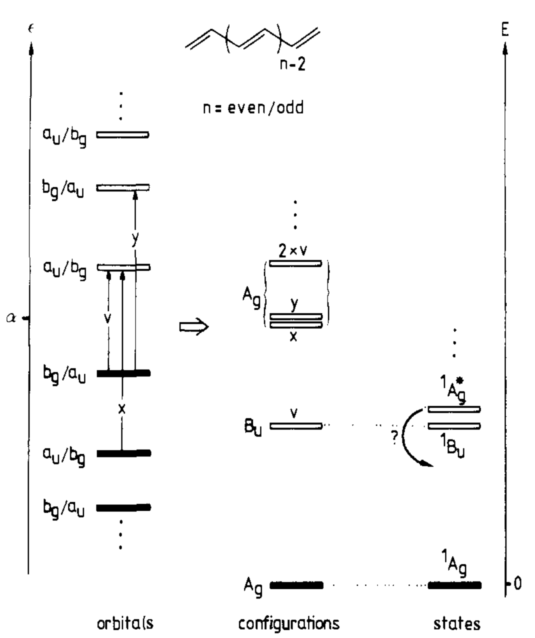

Figure 1. Left: HMO-type π-orbital diagram for neutral linear polyenes with *n* double bonds (solid bars, doubly occupied; open bars, virtual MO's). Symmetry designations to the left and the right side of the slash apply to even and odd *n*'s, respectively. Middle: configurations resulting from electron excitations v, x, and y in the orbital diagram. Right: states arising through configurational mixing.

However, the latter explanations became untenable in the light of observations which indicated that there was a large discrepancy between the measured fluorescence lifetime and the one calculated by integrating the first EA band. In addition, a new weak absorption whose origin coincided with the fluorescence onset was discoverd in diphenyloctatetraene.[4] It was then realized that a simple orbital picture was obviously inadequate for describing the electronic structure of linear polyenes, in agreement with earlier suggestions that configurational mixing such as depicted in Figure 1 may have a profound influence on the ordering of polyene excited states.[5] At that time detailed ab initio CI calculations to support these arguments were, however, unfeasible for systems of this size.

On the basis of semiempirical PPP-CI results it was concluded that the first excited state of polyenes is totally symmetric and has a sizable admixture of the lowest doubly excited configuration ($2 \times v$ in Figure 1).[6] This explained why this state was not detected in conventional one-photon spectroscopy and why the longer polyenes have an unexpectedly long fluorescence lifetime. While this state ordering is in accord with all experimental findings for longer polyenes, it is still a matter of debate,[1e,7] whether the A_g* state is also the lowest one in butadiene and hexatriene and their derivaties.

We presented this brief outline because we believe that we are currently going through a very similar change in the understanding of the excited states of linear polyene *molecular ions*.

The electronic structure of molecular *cations* is most easily probed with the convenient tool of UV-photoelectron (UP) spectroscopy[8] whereas molecular *anion* states can be accessed by the more recently developed tool of electron transmission (ET) spectroscopy.[9] The resulting spectra are usually assigned on the basis of Koopmans' theorem[10] which states that there is a one-to-one correspondence between UP (or ET[10b]) bands and molecular orbital energies as obtained through quantum chemical procedures of the Hartree–Fock SCF type. In the case of π-states of planar conjugated hydrocarbons these can be replaced by simple HMO energies,[11a] and for the case of molecular cations an impressive body of evidence has accumulated showing that properly parametrized Hückel type procedures can be used to predict the position of UP bands in such systems with great accuracy.[11]

However, besides these so-called Koopmans' states there are other ionic excited states that do not arise through simple electron ejection from a doubly occupied or electron addition to a virtual orbital of the neutral but involve electron promotion from the bonding into the virtual manifold of orbitals (most often HOMO to LUMO). These so-called non-Koopmans' states are usually not taken into consideration because they do not manifest themselves in the UP or ET spectra, and they do not interfere with a spectral assignment based on Koopmans' theorem. On the other hand such states are often readily observed in the EA spectra of molecular ions such as obtained in rigid transparent media.[12] In the case of molecular cations Haselbach and his group have encountered a number of cases where non-Koopmans' states are found in an energy region where the UP spectrum is "empty"[13] or where the state observed in the UP spectrum has a symmetry which is incompatible with the occurrence of a strong electronic transition at that energy.[14]

More importantly, mixing can occur between Koopmans' and non-Koopmans' configurations of the same symmetry, and in the case of molecular cations the resulting states should give rise to UP bands of reduced and finite intensity, respectively.[15,16] This phenomenon is quite common in X-ray photoelectron spectroscopy (XPS or ESCA) where one frequently observes small bands (so-called "shake-up satellites") next to the main peaks arising through direct photoejection of an inner-shell electron.[17] Until recently this phenomenon was considered unimportant in UP spectroscopy, and even now only for a handful of small molecules have such "valence electron shake-up" satellites been observed and identified.[18] In particular the UP spectra of planar conjugated hydrocarbons were usually interpreted with neglect of configurational mixing.[11,19,20]

A noteable exception to this rule is 3,7-dimethyl-*p*-quinodimethane (**1**), where a UP band of low intensity was assigned to a strongly mixed π-excited state.[21] This interpretation was re-

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[7] Nascimento, M. A. C.; Goddard, W. A. *Chem. Phys. Lett.* **1979**, *60*, 197. Nascimento, M. A. C.; Goddard, W. A. *Chem. Phys.* **1979**, *36*, 147.

[8] Eland, J. H. D. "Photoelectron Spectroscopy"; John Wiley & Sons: New York, 1974. Rabalais, J. W. "Principles of Ultraviolet Photoelectron Spectroscopy"; John Wiley & Sons: New York, 1977.

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[10] (a) Koopmans, T. *Physica* **1934**, *1*, 104. (b) Koopmans' theorem was originally formulated for molecular cations only, but its extension to molecular anions is straightforward.[9]

[11] (a) Brogli, F.; Heilbronner, E. *Theor. Chim. Acta* **1972**, *26*, 289. (b) Heilbronner, E.; Maier, J. P. In "Electron Spectroscopy. Theory, Techniques and Applications"; Brundle, C. R., Baker, A. D., Eds.; Academic Press: New York, 1977; Vol. 1, pp 205–287.

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[13] Forster, P.; Gschwind, R.; Haselbach, E.; Klemm, U.; Wirz, J. *Nouv. J. Chim.* **1980**, *4*, 365.

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[16] Schulz, R.; Schweig, A.; Zittlau, W. *J. Am. Chem. Soc.* **1983**, *105*, 2980.

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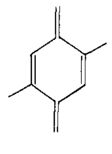
[19] (a) Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1977**, *60*, 2213. (b) Klasinc, L. *Pure Appl. Chem.* **1980**, *52*, 1509.

[20] Note, however, that at least two groups have for many years used CI treatments in the discussion of UP spectra (ref 15 and 16).



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cently queried in a paper concluding "...it would indeed be very suprising if **1**, an apparently normal polyene, showed unique behavior, of a kind that has never been encountered in any of the very many hydrocarbons that have been studied by UP-spectroscopy".[22] Although this statement did not go unchallenged,[16,23,24a,b] it still seems to be representative of the prevailing view among the majority of UP spectroscopists.

This paper describes the use of the tool of molecular cation EA spectroscopy in Ar to probe the electronic structure of linear polyene molecular cations in order to clarify the role of configurational mixing in this important and fundamental class of molecules. Since the following discussion will be limited to the case of molecular *cations*, we wish to note at this point that by virtue of the pairing theorem for alternant π-systems, all qualitative conclusions apply likewise to the corresponding molecular *anions* whose ET[25] and EA[26] spectra have already or will soon be published.

Results and Discussion

1. General. The main features of the electronic structure of linear polyene molecular cations can be derived in a qualitative fashion just as in the case of the neutral parents (see Figure 1) in the way shown in Figure 2.

The crucial feature of their electronic structure is that the first and second excited *configurations* (a and v in Figure 2) are (i) in close energetic proximity (moving closer as the chain length increases), (ii) of different character, the lower one (a) being of Koopmans' and the higher (v) of non-Koopmans' type, and (iii) of the same symmetry. As a consequence, they split into two *states* of the same symmetry (which is furthermore always opposite to the ground-state symmetry) such that the negative combination is lower in energy. It follows also that the electronic transition from the ground state is polarized along the short molecular axis in going to the (a − v) state and along the long axis in going to the (a + v) state. If we neglect for the moment all other excited states (in particular the x/y excited pair), this general picture leads us to expect a weak long-wavelength and a strong short-wavelength electronic absorption band in all linear polyene molecular cations, a prediction which is nicely borne out by experiment as will be shown below.

However, we wish to note that starting with hexatriene, there are further excited Koopmans' configurations (corresponding to lower-lying π-orbitals). For example, b in Figure 2 is of the same symmetry as the degenerate pair of (x/y) excited non-Koopmans' configurations, and so the strong mixing between Koopmans' and non-Koopmans' configurations continues to prevail at higher energies. This fact has interesting implications with regard to the UP spectra of linear polyenes. For example, the Koopmans'-dominated (b + x/y) excited state will end up just above or below the (a + v) excited state, i.e., we expect the second EA band in these ions to (nearly) coincide with the third UP band. In fact, we shall argue that the latter corresponds to *two* states which happen to lie roughly at the same energy and contribute both to the total ionization cross section.

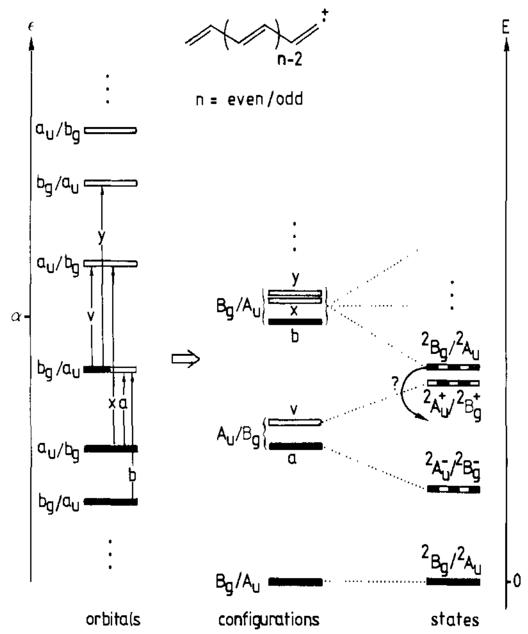

Figure 2. Left: HMO-type orbital diagram for linear polyene molecular ions. Middle: configurations resulting from Koopmans' excitatins a, b... (solid bars) and non-Koopmans' excitations v, x, y... (open bars). Right: Lowest excited states arising through configurational mixing. Shaded bars indicate states of mixed character (see text). For symmetry labels see caption to Figure 1.

Table I. Transition Energies (in eV) for Butadiene$^{+\cdot}$ Obtained by Different Experimental and Theoretical Procedures[a]

	$^2B_g \rightarrow {}^2A_u^-$	$^2B_g \rightarrow {}^2A_u^+$
EA spectrum in Ar[b]	2.32 (0.15)	4.20 (1.0)
EA spectrum in Freon[c]	2.23	4.16
PD spectrum[d] (gas phase)	2.30	4.00
PD spectrum[e] (gas phase)	2.38	4.06
PPP-CI[b,f]	2.22 (0.03)	3.47 (1.0)
Green's fct.[g]	2.60	5.67
6-31G + CI[h]	2.82	5.68
CNDO/S-CI[i]	2.43 (0.13)	4.33 (1.0)
LNDO/S-PERTCI[j]	2.69	4.61

[a] Figures in parentheses denote relative (integrated) intensity of the first and second EA band. [b] Present work. [c] Reference 26b. [d] Reference 31. [e] Reference 32. [f] See also ref 34a. [g] Reference 15. [h] Reference 36. [i] Reference 24c. [j] Reference 37.

2. Butadiene. Several attempts to measure the EA spectrum of butadiene$^{+\cdot}$ in γ-irradiated alkyl halide glasses can be found in the literature. While in the early studies[26a,27] it was mainly dimer cation formation which interfered with the observation of the isolated species, more recent spectra[12a,28] still contain additional bands probably due to secondary products which may arise through interaction with matrix molecules[29] such as observed by Kira et al. in the case of naphtalene$^{+\cdot}$.[30] Only in Freons were spectra observed[26b,29] which resemble that obtained in this work in argon (Figure 3) where dimer cation formation and interaction with other organic molecules can be excluded under the experimental conditions employed. The same spectrum is also obtained after X-ray irradiation of cyclobutene under otherwise identical experimental conditions (see also ref 29). However, there still remain substantial

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(21) Koenig, T.; Southworth, S. *J. Am. Chem. Soc.* **1977**, *99*, 2807.

(22) Dewar, M. J. S. *J. Am. Chem. Soc.* **1982**, *104*, 1447.

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(24) (a) Bigelow, R. W. *Chem. Phys.* **1983**, *80*, 45. (b) Bigelow, R. W. *Chem. Phys. Lett.* **1983**, *100*, 445. (c) Bigelow, R. W., personal communication.

(25) (a) Butadiene: Jordan, K. D.; Burrow, P. D. *Chem Phys. Lett.* **1975**, *36*, 594. (b) Hexatriene: Jordan, K. D.; Burrow, P. D. *J. Am. Chem. Soc.* **1982**, *104*, 5247. (c) Octatetraene: Allan, M.; Neuhaus, L.; Haselbach, E. *Helv. Chim. Acta*, submitted for publication.

(26) (a) Butadiene: Shida, T.; Hamill, W. H. *J. Am. Chem. Soc.* **1966**, *88*, 5371. (b) Hexatriene (and butadiene): Shida, T. *Kagaku no Ryoiki* **1976**, *30*, 31. We thank Professor Shida for pointing out the existence of these data to us. (c) Octatetraene: Shida, T., unpublished results.

(27) Badger, B.; Brocklehurst, B. *Trans. Faraday Soc.* **1969**, *65*, 2576.

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(29) Klemm, U. Dissertation, University of Basel, 1980.

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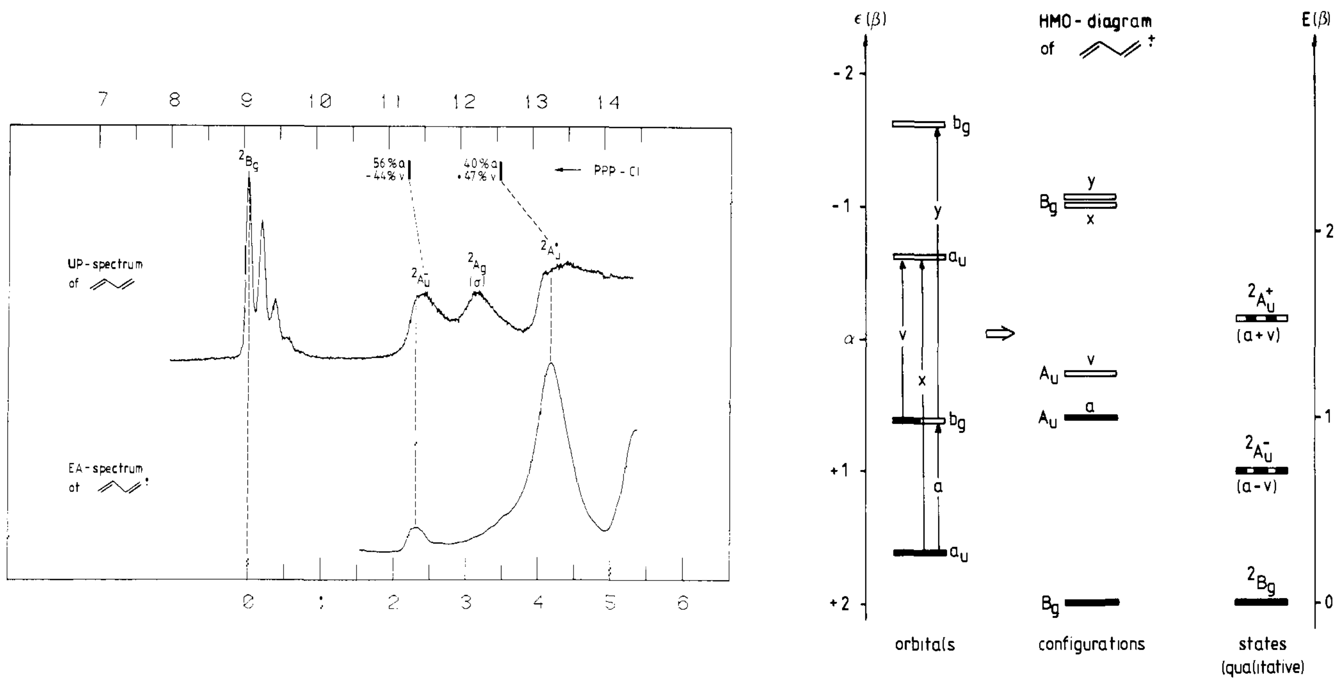

Figure 3. Left: UP spectrum of butadiene and EA spectrum of it's molecular cation in Ar drawn on the same scale (energies in eV). Bars indicate PPP-CI results including amount of configurational mixing. Right: HMO orital (left scale) and configuration (right scale) diagram with expected qualitative splitting into states. For a detailed explanation see the caption for Figure 2.

differences in band positions among the condensed phase spectra[26b,29] and between these and the different gas-phase photodissociation (PD) spectra,[31,32] as can be seen from Table I.

In particular, the marked bathochromic shift of the second band in going from the condensed to the gas phase runs contrary to usually observed trends.[12] We notice that in our spectrum the first EA band coincides with the onset of the second UP band which is in line with our experience of small solvatochromic shifts in Ar matrices.[12a]

The general EAS features are those expected from the qualitative scheme worked out for the case of butadiene$^{+\cdot}$ on the basis of HMO energies in Figure 3 (right side) and borne out well by the open-shell PPP-CI calculations.

The discussion of the UP spectrum of butadiene on the basis of Koopmans' theorem remains a popular exercise[33] even though the occurrence of configurational mixing in this compound has been pointed out repeatedly.[15,16,23,34,35,37] The actual mixing coefficients vary strongly depending on the theoretical method used. In the light of ab initio CI,[36] Green's function[15] or all-valence ZDO-CI calculations1[6,24b,c,37] it seems as though the PPP-CI model[34a] tends to overestimate the degree of mixing between a and v excited configurations (the former procedures give mixing ratios of the order of 4:1). On the other hand, the nonempirical calculations give relatively poor energies (Table I), particularly with regard to the position of the $^2A_u^+$ state.

Table II. Transition Energies (in eV) for Hexatriene$^{+\cdot}$ Obtained by Different Experimental and Theoretical Procedures[a]

	$^2A_u \rightarrow {}^2B_g^-$	$^2A_u \rightarrow {}^2B_g^+$
EA spectrum in Ar[b]	1.92 (0.05)	3.27 (1.0)
EA spectrum in Freon[c]	1.93	3.16
PD spectrum[d] (gas phase)	1.96	3.40
Ne matrix[e]	1.96	–
gas phase[f]	1.96	–
PPP-CI[b]	1.63 (0.03)	2.79 (1.0)
CNDO/S-CI[g]	1.85 (0.11)	3.57 (1.0)
LNDO/S-PERTCI[h]	2.18	3.78

[a] Figures in parentheses denote relative (integrated) intensity of the first and second EA band. [b] Present work. [c] Reference 41. [d] Reference 42. [e] Emission and excitation spectra, ref 47. [f] Emission spectrum, ref 44. [g] Reference 24c. [h] Reference 37.

It is interesting to note that there may actually be evidence based on UP spectroscopy to confirm our results. By virtue of the fluoro effect,[38] the π-ionizations in 1,1,4,4-tetrafluorobutadiene (which is also roughly planar[39] as opposed to the perfluorinated derivative[39,40]) are moved beyond 14 eV, thus uncovering a small shoulder at 13.5 eV.[39] As Herrick suggested recently,[35] this small band may well be due to the $^2A_u^+$ state we observe in our EA spectrum. Herrick's claim has in the meantime received support from different semiempirical CI calculations.[16,23] We note that this state lies 2.3 eV above the ionic ground state, in excellent accord with our second EA band position, which is to be expected if F substitution does indeed leave the relative energies of all π-states unaffected.[38]

3. Hexatriene. The EA spectrum of hexatriene$^{+\cdot}$ has been recorded before in a Freon maxtix.[26b,41] Our spectrum looks very similar apart from a somewhat improved resolution and the usual small shifts in band maxima and also compares well to the gas-phase PD spectrum[42] (Table II).

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

(32) Dunbar, R. C. *Anal. Chem.* **1976**, *48*, 723. Professor Dunbar has informed us that the spectrum displayed in Figure 6 of this paper is *not* that of butadiene. The numbers in Table I refer to Figure 3.

(33) (a) Klessinger, M.; Gunkel, E. *Tetrahedron* **1978**, *34*, 3591. (b) Worley, S. D.; Webb, T. R.; Gibson, D. H.; Ong, T. S. *J. Eltron. Spectrosc. Relat. Phenom.* **1980**, *18*, 189. (c) Chiang, H. J.; Worley, S. D. *Ibid.* **1980**, *21*, 121. (d) Bieri, G.; Asbink, L. *Ibid.* **1980**, *20*, 149. (e) Krishna, B.; Bahuguna, G. P. *Ind. J. Pure Appl. Phys.* **1978**, *16*, 766. In addition, almost every semiempirical scheme developed over the last 15 years has been tested with respect to its ability to reproduce butadiene IP's correctly via orbital energies.

(34) (a) Zahradnik, R.; Carsky, P.; Slanina, Z. *Collect. Czech. Chem. Commun.* **1973**, *32*, 163. (b) Lauer, G.; Schulte, K.; Schweig, A. *Chem. Phys. Lett.* **1975**, *32*, 163. (c) Kluge, G.; Scholz, G. *Int. J. Quantum Chem.* **1981**, *20*, 669.

(35) Herrick, D. R. *J. Chem. Phys.* **1981**, *74*, 1239.

(36) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. "Handbook of He-I Photoelectron Spectra of Fundamental Organic Molecules"; Japan Scientific Societies Press: Tokyo, 1981.

(37) Schultz, R.; Schweig, A.; Zittlau, W., submitted for publication in *Chem. Phys. Lett.*, in press.

(38) Brundle, C. R.; Robin, M. B.; Kuebler, N. A.; Basch, H. *J. Am. Chem. Soc.* **1972**, *94*, 1451, 1466.

(39) Brundle, C. R.; Robin, M. B. *J. Am. Chem. Soc.* **1970**, *92*, 5550.

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(41) Shida, T.; Kato, T.; Nosaka, Y. *J. Phys. Chem.* **1977**, *81*, 1095.

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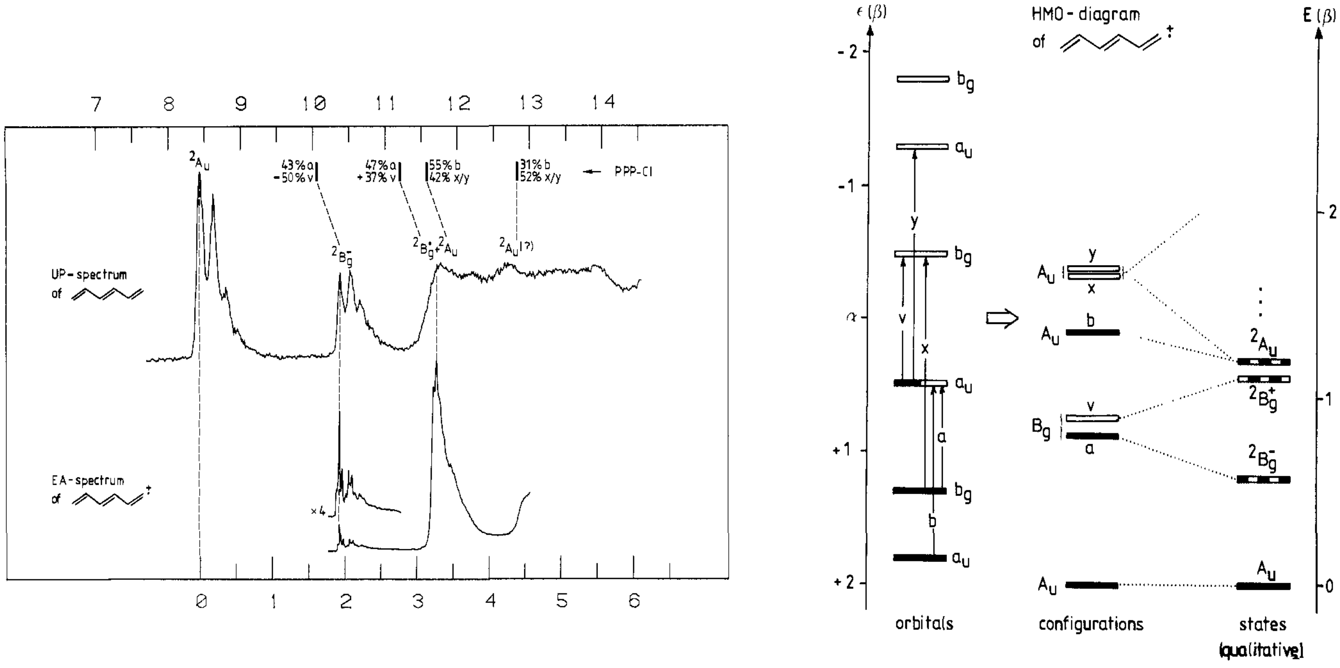

Figure 4. Left: UP spectrum of hexatriene and EA spectrum of it's molecular cation in Ar drawn on the same scale (energies in eV). Right: HMO diagram for hexatriene$^{+\cdot}$. For detailed explanations see the captions for Figures 2 and 3.

There is an interesting ongoing controversy about the nature of the hexatriene$^{+\cdot}$ structure actually observed under different experimental conditions. While the inherently fast methods of UP spectroscopy,[43] PEPICO,[44] and emission spectroscopy from directly formed excited gas-phase hexatriene$^{+\cdot}$[44,45] can clearly differentiate between the ions originating from *trans-* or *cis-*hexatriene, only one isomer is observed in the PD spectrum[42] even if the time span betwen ion formation and photodissociation is reduced to 2 ms.[46] A comparison of the 0–0 peak positions of the first electronic gas-phase emission and high-resolution PD bands led to the conclusion that only the cis cation was present, i.e., that all trans cations had irreversibly isomerized to the cis isomers prior to photodissociation.[42] This suprising conclusion was later challenged by Bondybey,[47] who also observed only a single cation after photoionizing an isomeric mixture of hexatrienes in Ne; his vibronic analysis of the emission spectrum revealed, however, that this ion had the trans structure.

Our first EA band shows the same vibronic progressions as those observed for the excitation spectrum in Ne[47] and for the laser PD spectrum.[42] We therefore conclude that in the latter experiment the trans ion was observed.

Contrary to Shida[41] and Bondybey[47] we obtain mixtures of at least four different hexatriene$^{+\cdot}$ isomers after ionizing either pure *trans-* or *cis-*hexatriene.[48] Selective photobleaching of the bands between 400 and 500 nm results in the EA spectrum displayed in Figure 4 which we believe to represent the all-trans isomer, having the general features predicted by qualitative theory and our PPP-CI calculations. The same spectrum is also obtained by photolyzing cyclohexadiene$^{+\cdot}$[48] in accord with the earlier reports by Shida.[41]

Although the UP spectrum of hexatriene and its derivatives continues to be discussed (with reasonable numerical success) in terms of orbital energies,[19a,33a,e,43,49] the occurrence of configurational mixing in this cation was pointed out before by Dunbar, who was probably the first to expreess concern about the adequacy of one-electron calculations for describing the excited states of linear polyene molecular cations (see last section).

Table III. Transition Energies (in eV) for *all-trans-*Octatetraene$^{+\cdot}$ Obtained by Different Experimental and Theoretical Procedures[a]

	$^2B_g \rightarrow {}^2A_u^-$	$^2B_g \rightarrow {}^2A_u^+$	$^2B_g \rightarrow {}^2B_g^*$
EA spectrum in Ar[b]	1.67 (0.04)	2.77 (1.0)	–
UP spectrum[b]	1.67	?	2.97
gas phase[c]	1.67	–	–
PPP-CI[b]	1.27 (0.02)	2.33 (1.0)	2.54 (0)
CNDO/S-CI[d]	1.48 (0.14)	3.21 (1.0)	2.70 (0)
LNDO/S-PERTCI[e]	1.79	3.28	3.34

[a] Figures in parentheses denote relative (integrated) intensities of the first and second EA band. [b] Present work. [c] Emission spectrum, ref 53. [d] Reference 24c. [e] Reference 37.

With the obvious inadequacy of the simple MO picture in mind we note that the second UP band has roughly 30% less integrated intensity than the first. We propose that this is due to a sizable admixture of non-Koopmans' character to the first excited state, perhaps overestimated by PPP-CI.[50] By the same token, the third UP band (customarily assigned to 2^2A_u[19a,33a,e,43]) most probably borrows intensity from *two* excited π-states, namely $^2B_g^+$, observed in the EA spectrum, and $^2A_u(b + x/y)$, not observable in one-photon absorption.

These same conclusions also emerge from the purely group-theoretical considerations of Herrick,[35] who suggested that more accurate calculations be made to clarify this matter. On the other hand, it is conceivable that a judicious choice of substituents may result in a separation of the two states in question such that they would give distingushable UP bands, thus offering an unambiguous experimental proof of Herrick's and our claim. Finally we note that the remainder of the b-excited configurations is predicted by PPP-CI to end up in a higher excited ^2B_g state at precisely the energy where the UP spectrum shows another peak.

4. Octatetraene. The spectrum of octatetraene$^{+\cdot}$ is presented in Figure 5.[51] As in the case of hexatriene, a mixture of isomers is obtained after ionization of *all-trans-*octatetraene (or photolysis of cyclooctatriene$^{+\cdot}$), which can again be converted to a single

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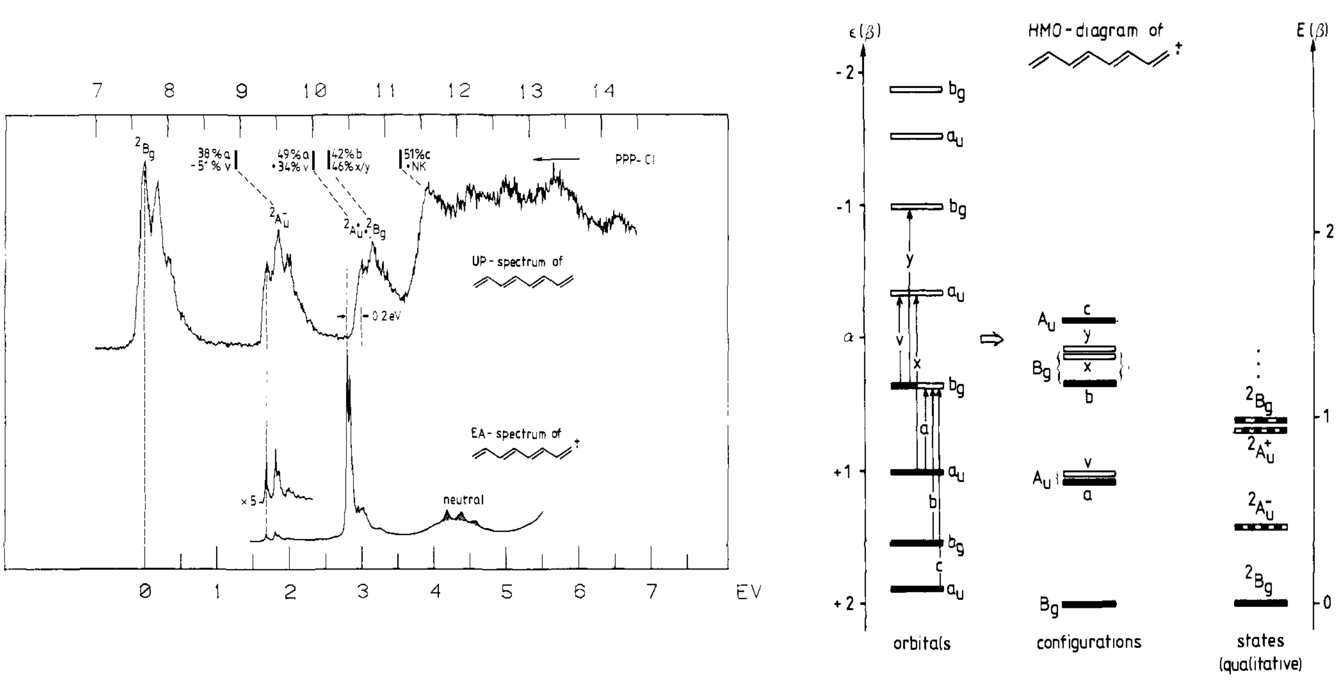

Figure 5. Right: UP spectrum of octatetraene and EA spectrum of it's molecular cation in Ar drawn on the same scale (Energies in eV). Left: HMO diagram for octatetraene$^{+\cdot}$. For detailed explanations see the captions for Figures 2 and 3.

species (the one that dominates the spectrum when one starts from *all-trans*-octatetraene) by selective bleaching.[52]

Again we note the excellent agreement between the first EA band and the second UP band including the vibrational fine structure. Also, the 0–0 transition matches precisely with the 0–0 emission band of octatetraene$^{+\cdot}$ in the gas phase (Table III).[53]

In contrast, the second EA band no longer coincides with the third UP band, a phenomenon which can, however, be rationalized in terms of a medium effect. Already for hexatriene$^{+\cdot}$ we noted a 0.13- and 0.24-eV bathochromic displacement in going from the gas phase (PD spectrum) to Ar[54] or Freon matrices,[41] respectively. A 0.2-eV shift is also observed for the first electronic transition of neutral octatetraene in the gas phase and Ar, respectively.[48] It seems therefore reasonable to conclude that in the gas phase the second EA band would coincide with the third UP band.

In turning to the UP spectrum[53] we note, as for hexatriene, that the integrated area under the second band is only about two-thirds of the first one, reflecting in our view the admixture of the HOMO–LUMO excited non-Koopmans' configuration. The third band is of even smaller intensity and is in our view again composed of two states ($^2A_u^+$ and ^2B_g(b + x/y)). Thus, the assignment given to this band on the basis of Koopmans' theorem[53] is at least *incomplete*.

Since the spectrum of Figure 5 extends to 200 nm we were able to observe another weak broad band peaking at 285 nm (under some residual peaks of neutral octatetraene) which , according to PPP-CI, must be assigned to the next ^2A_u state. Again this state may contribute some intensity to the fourth UP band.

Corollaries

The features outlined above will pertain throughout the series of polyenes, and as the a and v excited configurations move closer in energy their mixing will increase. By the time one comes to longer chains as in carotenoid and visual pigment chromophores, the first two excited states of the moleular ions will each have 50% Koopmans' and 50% non-Koopmans' character. This fact may prove to be of relevance in electron-transfer reactions involving polyenes of biological interests,[55] but it has been ignored in a study of carotenoid polyene molecular ion EA spectra which were simply interpreted on the basis of orbital energy differences.[56] In turning to UP spectroscopy we note that in spite of the great success with which UP spectra have been (and still are) discussed on the basis of Koopmans' theorem using various MO procedures, voices of warning have begun to appear in the literature. One of the clearest recent statements actually comes from the group which had put the greatest efforts into developing and parametrizing single-determinant MO procedures to predict ionization potentials (SPINDO,[57] HAM/3[58]): "Shake-up phenomena are important in UP-spectra in two respects: they cause extra bands which may complicate the interpretation of a spectrum and they cause displacements of the primary ionization bands. This is very disturbing if the ionization energies are used to parametrize a semiempirical quantum chemical method. It is then necessary to correct for these displacements before the UP spectra can be used for parametrization."[59] More specifically, Dunbar has recognized the particular problems associated with polyenes and concludes the following: "This extensive configuration interaction casts grave doubt on the ability of all-electron calculations like MINDO and SPINDO, which do not carefully account for these strong interactions, to describe correctly the low-lying π-states of polyene ions via Koopmans' theorem".[42]

The fact is, however, that the MO procedures alluded to above are fairly successful in predicting UP band positions in a wide variety of compounds, in particular the π-bands in polyenes, and the question arises why this is so. In a noteworthy paper, Heilbronner and Schmelzer have recently pointed out that any calculational procedure which yields a set of numerical values ordered by size within certain boundaries will inevitably give a reasonably looking correlation ($r > 0.9$) with a set of experimentally based values ordered by size within the same boundaries, such as presented in a UP spectrum.[60] This does, however, in no way prove the value of the model behind the calculational

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[52] The rich and interesting photochemistry of this ion will form the subject of a separate publication.

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[54] Incidentally, a similar shift is also observed in neutral hexatriene: Furukawa, Y.; Takeuchi, H.; Harada, I.; Tasumi, M. *J. Mol. Struct.* **1983**, *100*, 341.

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Table IV. Experimental and HMO Calculated Vertical Ionization Energies of Polyenes (in eV)

i	$I_{v,i}$(exptl)	$I_{v,i}$(HMO)[a]	$I_{v,i}$(HMO)[b]
	Butadiene		
1	9.08	8.72	8.92
2	11.47	11.24	11.40
	Hexatriene		
1	8.30	8.29	8.15
2	10.26	10.30	10.29
3	(11.60)	11.70	11.89
	Octatetraene		
1	7.79	8.04	7.67
2	9.61	9.68	9.50
3	10.89	11.02	10.99

[a] Regression line through $I_{v,i}$(exptl) vs. x_i, see text. [b] Modified HMO accounting for first-order double bond fixation; see eq 18 in ref 11a.

procedure as the above authors demonstrated convincingly by choosing a procedure (MORON[61]) with no relation whatsoever to chemistry or quantum mechanics. They also established a set of statistical criteria which can be used to assess whether a given model is significantly better than MORON. Thus, for a set of eight values (the π-IP's of the first three linear polyenes), a correlation coefficient r of 0.990 would allow us to reject the hypothesis that a given MO model is not better than MORON with 99% confidence. How well do the commonly used procedures fare in this respect? Unfortunately we do not have the necessary data at our disposition to carry out a systematic study, but we wish to exemplify the point using HMO.

A plot of eight π-ionization energies of linear polyenes against the HMO energies $x_i = (\alpha - \epsilon_i)/\beta$ yields the linear relationship $I_{v,i}$ (in eV) = 7.17 + (2.52x_i). As shown in Table IV the correlation between experimental and calculated IP's is remarkably good (r = 0.9901), and it can even be improved by accounting for first-order double bond fixation as proposed in ref 11a (third column in Table IV, r = 0.9977). Hence, this slighly improved version of HMO, the simplest and crudest of all possible MO models, is already so much better than MORON that the probability of the latter to give a similarly good correlation is less than 10^{-6}. In particular, HMO predicts equally well the energy for weakly mixed (ground) and highly mixed (excited) states of linear polyene molecular cations (there are no systematic deviations for either group) even though this model neglects all configurational mixing.

Similar conclusions are likely to emerge if all-valence SCF procedures parametrized to give correct IP's (SPINDO, HAM/3) are subjected to the same scrutiny.

On the other hand, CI procedures which certainly give a more realistic picture in terms of wave functions are usually worse when it comes to energies. Again we cannot prove this point by systematic investigations, but the case of butadiene, where a compilation of such results recently appeared,[16] shows that HMO is better in predicting the positions of the two UP bands resulting from π-ionizations than any of the ZDO/CI procedures or the many-body Greens' function calculations, although it must be noted that LNDO/S-PERTCI[16,37] and CNDO/S-CI[24a] come very close to HMO.

We can offer at present no explanation for the amazing success of single-determinant theory even at it's crudest level in a case where it is clearly based on fallacious assumptions.

We wish to conclude by pointing out once more that the conclusions reached in the above discussion of linear polyene molecular *cations* apply qualitatively also to the corresponding *anions*. Indeed a detailed comparison of the ET[25] and EA[26] spectra of these polyenes seems highly warrented.

Experimental Section

Material. Butadiene and cyclohexadiene were purchased from Fluka and used without further purification. Cyclobutene was prepared according to the procedure outlined in ref 62. Pure *all-trans*-hexatriene (95%) was obtained by following the prescriptions of Yamamoto et al.[63] *cis*-Hexatriene was separated from the commercially available mixture (Aldrich) by preparative GC on ODP (se also ref 41). Octatetraene was synthesized according to Gavin et al.[64] avoiding, however, exposure to air after the pyrolysis. Instead of recrystallization or column chromatography the crude material was purified by fractional condensation under high vacuum using a series of traps held at different temperatures. Cyclooctatriene purchased from Organometallics contained only about 60% of the desired product which was extracted by preparative GC on ODP. Ar was 99.995% pure and CH_2Cl_2, which was used as an electron scavenger, was analytical grade.

Sample Preparation and Apparatus. All the UP spectra presented in the figures have been published previously (butadiene in ref 65, hexatriene in ref 43, octatetraene in ref 53); however, they were rerecorded under identical conditions for better comparison and presentation. Several hundred scans were accumulated on a modified PE 16 instrument[66] connected to a multichannel analyzer which was in turn interfaced to a PDP-11/34 computer for data workup. Internal calibraton was done with Ar/Xe. Resolution as measured by the fwhm of the calibration peaks was around 25 mV in all experiments. Samples (polyene: CH_2Cl_2:Ar = 1:2:2000) were deposited from a home-built spray-on line at a rate of ~1 mmol/h for 4–6 h onto a sapphire window mounted on the expander stage of an Air Products CSW-202 displex cryostat. Ionization was effected by a method elaborated earlier in our laboratories for use with Freon matrices.[29] The sample was mounted close to the window of a tungsten anode X-ray tube (Philips PW 2214) operated by a 2-kW generator (Philips PW 1720) at 45 kV/45 mA and irradiated for 90 min. This resulted generally in an ion yield of about 15%. Optical spectra were recorded on a PE-330 spectrometer interfaced to an Apple II+ computer (later: PE 3500) which was also connected to the PDP-11 where the spectra obtained prior to ionization were digitally subtracted before plotting.

Calculations. The PPP-CI calculations were performed by using a program containing the parametric expressions proposed by Zahradnik et al.[50] based on the Longuet-Higgins/Pople formalism.[67] Bond lengths and bond angles were fixed at 140 pm and 120°, respectively. Alternating bond lengths were used in the CNDO/S-CI calculations.[24c]

Acknowledgment. This work is part of project Nr 2.422-0.82 of the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung.* We thank Dipl. chem. Louis Neuhaus (Fribourg) for recording the UP spectra. We are very indebted to R. W. Bigelow (Xerox Webster Research Center) for performing CNDO-S/CI calculations on hexatriene$^{+\cdot}$ and octatetraene$^{+\cdot}$.

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