inversion occurs for large polyenes. The previously defined n dependence of ΔR and $\Delta E^*_{\mathrm{odd}}$ makes the study of the two extreme cases, namely the rotation around external and most internal double bonds, easy. For the twisting around one external double bond the energy of the singlet excited state is given by eq 10 and 8 and ref 1, if one neglects again the weak effective exchange on the twisted double bond

$$\Delta S^{\perp}{}_{\mathrm{S}_0\rightarrow\mathrm{S}_1}(2n,2n-1) = \Delta E^{2n}{}_{2n-1,2n} + \Delta E^{\mathrm{R}}{}_{\mathrm{D}_0\rightarrow\mathrm{D}_1}(2n-1) = 2.02 + 16.50(2n-1) \text{ (in eV)}$$

For twisting around the most internal double bond, in a $4n + 2$ molecule, one obtains

$$\Delta E^{\perp}{}_{\mathrm{S}_0\rightarrow\mathrm{S}_1}(4n+2,2n+1) = \Delta R^{4n+2}{}_{2n+1,2n+2} + \Delta E^{\mathrm{R}}{}_{\mathrm{D}_0\rightarrow\mathrm{D}_1}(2n-1) = 1.1 + 18.4/2n + 1 - 16.2/(2n+1)^2 \text{ (in eV)}$$

The corresponding curves have been plotted in Figure 11. From these considerations it appears that (i) the cis–trans photoisomerization around double bonds should be impossible from the relaxed planar minima of the covalent S_1 singlet excited states, except for butadiene and hexatriene (for its external double bond only); (ii) the photoisomerization should always remain possible from the *vertically* excited neutral singlet if it occurs around *internal* double bonds; (iii) the singlet photoisomerization around external *double* bonds is *prefered up to 20 carbon* atoms, but for larger compounds it should *become impossible.*

In Figure 11 we have not reported the experimental energy dependence of the allowed vertical singlet excitation toward the ^1B_u (ionic) excited state, for two reasons: (i) our neutral ^1A_g excited states apparently are somewhat too high by 0.5 (octatetraene) to 0.25 eV (decapentene) with respect to experiment; (ii) the relevant experimental X $^1A_g \rightarrow {}^1B_u$ transition energies should concern the gaseous phase, while most experimental data for heavy polyenes concern the liquid phase.[50] The difference is not negligible (0.25 for hexatriene and octatetraene) and the solvent effect may be larger for the ionic excited states (in which important instantaneous dipoles appear, creating larger dispersion forces with the solvant) than for the covalent states. The experimental vertical transition energies (in solvent) to the ^1B_u state would follow in Figure 11 the straight line representing the energy of the singlet excited state twisted around a *terminal* double bond. This proves at least that the vertical absorption energy is always larger than the energy of the twisted covalent excited state, especially for *inner* bonds rotations. A previous paper[8] has shown that the photoisomerization could not occur on the ionic singlet excited surface, and that the molecule had to undergo a conversion into either the neutral ^1A_g covalent excited singlet, the ^3B_u excited state (which would require an intersystem crossing), or the ground ^1A_g state in a high vibrational level. The present results show that the three hypotheses remain valid for large polyenes.

Registry No. Ethylene, 74-85-1; butadiene, 106-99-0; hexatriene, 2235-12-3; octatetraene, 1482-91-3; decapentaene, 2423-91-8; propene, 115-07-1; pentadiene, 504-60-9; heptatriene, 2196-23-8; nonatetraene, 31699-36-2.

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A UV Photoelectron Spectroscopic and Hartree–Fock–Slater MO–LCAO Study of Tetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene and Related Strained Compounds

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Abstract: The UV photoelectron (PE) spectra of tetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene, tetracyclo[3.3.0.0^{2,4}.0^{3,6}]octane, and deltacyclene have been measured. Spectra have been analyzed and assigned by using nonempirical Hartree–Fock–Slater (HFS) calculations. From this analysis and from a comparison with related molecules a remarkable destabilization of the high-lying antisymmetric Walsh orbital (e_A) upon contraction of the molecular cage becomes apparent.

Compounds with the general formula $(CH)_{2n}$ ($n = 1, 2, \ldots$) have generated much interest in organic chemistry for both synthetic and theoretical reasons. Within such families of valence isomers the CH building blocks can be connected in many different ways, often leading to highly strained hydrocarbons. The synthetic challenge posed by such compounds is obvious. One of the most strained molecules of the $(CH)_8$ family is tetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene (**1**; see Figure 1). Since its first successful synthesis in 1977,[1a] the reactivity of this compound has been under active investigation.[1b]

In view of the large amount of strain present in **1**, a study of its molecular orbital structure is of interest. A suitable method for obtaining reliable information about the occupied molecular orbitals in the valence region is UV photoelectron (PE) spectroscopy. Since unambiguous assignment of PE spectra usually requires PE information on a series of related compounds, the saturated analogue of **1**, tetracyclooctane (**2**), and a homologue of **1**, deltacyclene (**3**), have been studied as well. In the literature a large body of PE data is available on related systems containing a cyclopropane ring but lacking the C_4C_5 bridge.[2] Bischof et al.[3]

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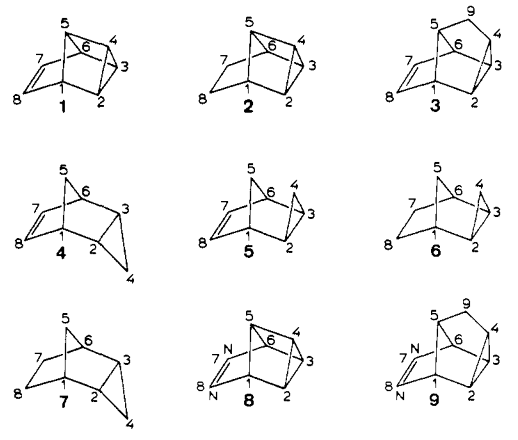

Figure 1. Molecular structures and numbering of atoms in compounds **1**–**9**.

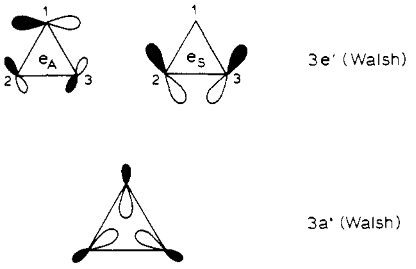

Figure 2. The Walsh orbitals of cyclopropane. The two components of the highest occupied orbital, 3e′, are denoted as e_A and e_S because they are antisymmetric and respectively symmetric with respect to the vertical plane through C_1.

have studied *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**4**), *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**5**), *exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**6**), and *endo*-tricyclo[3.2.1.$0^{2,4}$]octane (**7**). A PE study on a number of related diazo compounds (**8**, **9**) should be mentioned as well.[4]

Special interest has been focused on the position and splitting of the highest occupied level of the cyclopropane ring, derived mainly from the in-plane tangential carbon 2p AOs (3e′ in cyclopropane, see Figure 2) and commonly denoted as Walsh orbitals e_A and e_S.[5] The Walsh orbitals may be approximately written as:

$$e_S = \frac{1}{\sqrt{2}}(P_2 - P_3)$$

$$e_A = \frac{1}{\sqrt{6}}(2P_1 - P_2 - P_3)$$

The difference in amplitudes of these orbitals at C_1 and C_2, C_3, respectively, has played a crucial role in understanding their splitting in substituted cyclopropanes. Observed splitting patterns have been rationalized in terms of "inductive" effects of substituents at the three-membered ring[3] and in terms of "conjugative" interaction with, e.g., the C–C π-bonding orbitals in **4**[3] (or with an N═N π bond as in **8** or **9**[4]). We may summarize the data in ref 2 by noting that in all cases where two alkyl substituents are present (at C_2 and C_3) one finds the e_S level above e_A by 0.6–0.8 eV, whereas with only a single alkyl substituent (at C_1) e_A is above e_S by about 0.8 eV. In the few 1,2,3-trialkylcyclopropanes studied e_S and e_A are either degenerate by symmetry or e_S is above e_A. Our compounds **1** and **2**, however, are found to be unique in having e_A well above e_S. The assignment of the experimental photoelectron spectra is based on nonempirical Hartree–Fock–Slater calculations (see next section), which are also used to show how this unusual behavior of **1** and **2** is related to the cage structure of these molecules.

Computational

The Hartree–Fock–Slater method has been described elsewhere.[6,7] Physically the crucial feature of the method is the use of the Slater $\rho^{1/3}$ (or Xα) exchange (correlation) potential instead of the Hartree–Fock exchange operator:

$$V_{X\alpha} = -3\alpha \left[\frac{3}{8\pi}\rho\right]^{1/3}$$

The resulting one-electron equations are solved by using an expansion in exponential basis functions (Slater-type orbitals or STOs). The computational scheme, involving numerical integration of the Fock matrix elements and fitting of the electron density with a set of auxiliary one-center fitting functions, is designed to yield one-electron energies and ionization energies to a numerical accuracy of ca. 0.01 eV. This is deemed sufficient as errors due to basis set limitations and deficiencies of the Xα one-electron model are at least an order of magnitude larger. From experience on many systems[8-12] we may conclude that the calculated IEs agree in general to within a few tenths of an electron volt with experiment. Sometimes absolute deviations as large as 1 eV have been found, but in those cases the computed spectrum shows a fairly constant shift with respect to the experimental spectrum, the relative band positions being predicted to an accuracy of ca. 0.3 eV. These findings agree with those of De Alti et al.,[13] who also used the Xα method, but Gaussian basis functions instead of STOs (cf. Dunlap et al.[14]). In this paper we employ double ζ STO basis sets, since extended basis sets yield only slight improvements for the calculation of IEs. We stress that the computed ionization energies are obtained from ΔSCF calculations employing the scheme for total energy differences developed by Ziegler and Rauk.[15] Relaxation effects are thus fully incorporated.

Since detailed experimental geometries are not known for these compounds, a geometry optimization procedure has been carried out by using the semiempirical MNDO method.[16] The bond lengths and bond angles obtained in this manner were found to be in accordance with standard values for hydrocarbons and known data for norbornadiene[17] and bicyclopentane.[18] These geometries have been used in the HFS calculations.

The MNDO method can also be employed to calculate IEs from the one-electron energies with Koopmans' theorem.[19] Compared to the HFS results quantitative differences were found, but the ordering of the highest occupied MOs was identical.

Experimental

The PE spectra of compounds **1**,[20] **2**,[20] and **3**[21] were recorded on a modified Vacuum Generators ESCA 3 spectrometer equipped with a hemispherical electrostatic analyzer. A helium dc discharge lamp which produced radiation of 584 Å (21.21 eV) was used as a photoionization source. Spectra were calibrated by using the known ionization energies (IEs) of carbon disulphide, nitrogen, and water. The resolution during

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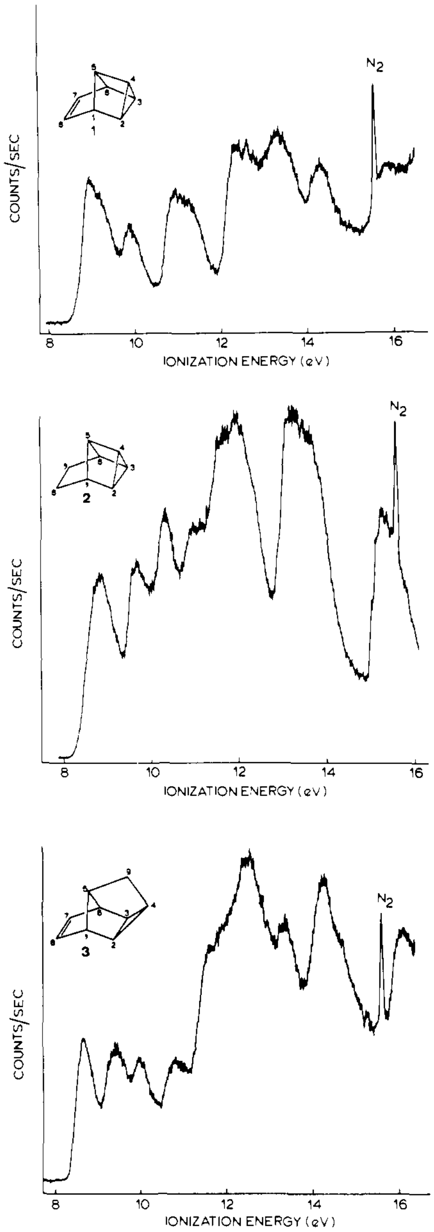


Figure 3. PE spectra of compounds **1**–**3**.

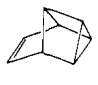
the course of the experiments was approximately 55 meV. From the spectra presented in Figure 3, it is clear that in the region beyond ~12 eV severe overlap of a large number of bands prohibits a detailed analysis. In the lower IE region the situation is more favorable.

Results and Discussion

The PE spectra measured for compounds **1**–**3** are presented in Figure 3. In view of the severe overlap in the high-IE regions, we shall concentrate on the bands with IEs below ~12 eV. For **1** three photoionization signals are observed in this part of the spectrum. The band shapes and relative intensities indicate that two PE bands are hidden under the first and third signals, respectively, leading to a total of five IEs below 12 eV. The spectrum of **2** is more congested. In the region of interest we distinguish three band maxima and a shoulder at the low-IE side of the very strong signal at ~12 eV. Spectral expansions suggest that the signal with a maximum at ~9.70 eV is asymmetric and probably contains two photoionization bands. In the spectrum of **3** the second signal is probably composed of two PE bands. Especially for compounds **2** and **3** the spectral overlap problem is already significant in the low-IE regions. The IEs appearing as separate spectral bands and those estimated from overlapping signals are summarized in Table I. Our supposition that some of the observed signals in the PE spectrum of compounds **1**–**3** contain more than one PE band is supported by our HFS calculations. In Table I we give the HFS calculated IEs together with a characterization of the orbitals. We note that apart from an overall shift by about 1 eV the agreement between the HFS results and experimental band positions is quite reasonable (cf. also Figure 4). We draw attention to the positions of e_A and e_S, the orbitals derived from the 3e′ Walsh orbitals of cyclopropane, e_A being antisymmetric and e_S symmetric with respect to the mirror plane present in **1**–**3** (see also Figure 2). For **1** and **2** the calculations unambiguously

Table I. Calculated and Experimental Ionization Energies and Orbital Characterization of the Low-IE Region of Compounds 1-3

MO	character	calcd (HFS)	exptl
	1		
13a′	π(C=C)	8.0	8.9_5
7a″	60% e_A ($C_2C_3C_4$) – 30% "e_A" ($C_1C_5C_6$)	8.1	9.1_5
12a′	e_S ($C_2C_3C_4$)	8.8	9.9_0
6a″	mainly $C_1C_5C_6$	9.9	10.9_5
11a′	C_4C_5 bridge	10.1	11.2_5
	2		
8a″	65% e_A ($C_2C_3C_4$) – 20% "e_A" ($C_1C_5C_6$)	7.6	8.8_5
13a′	e_S ($C_2C_3C_4$)	8.4	9.7_0
7a″	mainly ($C_1C_5C_6$)	8.4	9.7_0
12a′	C_4C_5 bridge	9.1	10.3_0
11a′	delocalized	9.8	11.0_0
	3		
15a′	π(C=C)	7.3	8.7_5
8a″	e_A ($C_2C_3C_4$)	7.7	9.5_0
14a′	e_S ($C_2C_3C_4$)	8.1	9.6_5
7a″	mainly ($C_1C_5C_6$)	8.5	10.0_0
6a″	mainly ($C_1C_6C_7C_8$)	9.4	10.8_5
13a′	$C_4C_9C_5$ bridge	10.3	11.7



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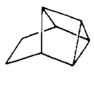

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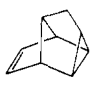

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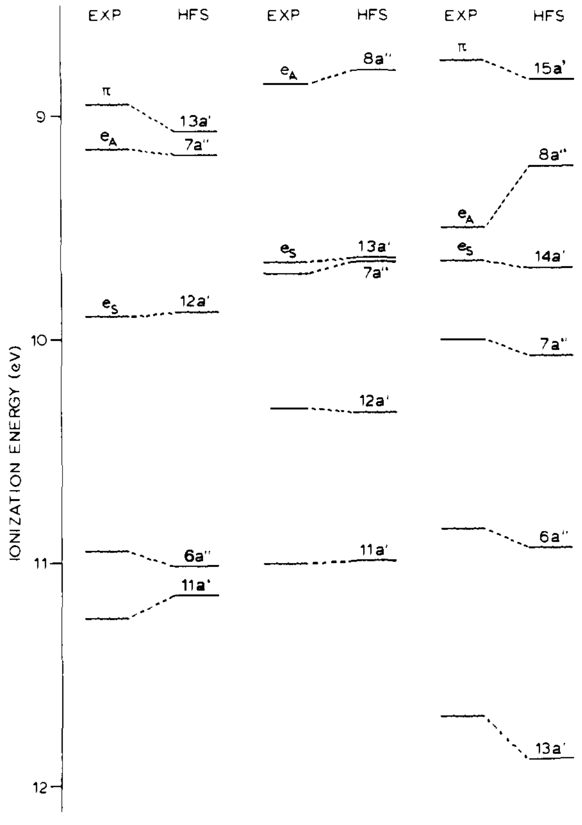

Figure 4. Comparison between experimental band positions and results of HFS calculations (shifted by 1 eV) for compounds **1**–**3**.

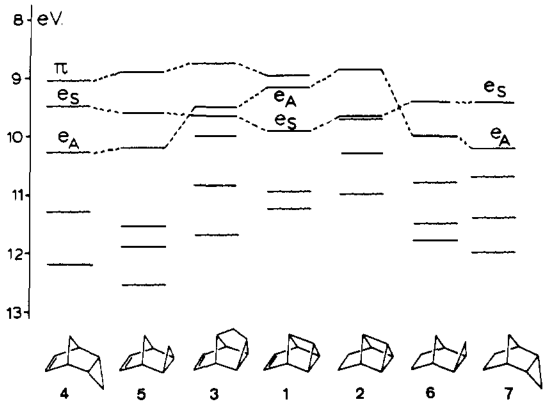

Figure 5. Experimental band positions (from this work and ref 3) and correlations for compounds 1–7.

prove e_A to be above e_S by almost 1 eV. This result is put in perspective by considering the series of molecules **4**–**7** in Figure 5. The experimental band positions of **4**, **5**, **6**, and **7** in this figure have been taken from the literature,[3] and the assignments have been reconfirmed by our present MNDO and HFS calculations. We note the ordering $e_S > e_A$ for the molecules without a C_4–C_5 bridge and the reversed ordering for **1** and **2**.

As a starting point in our discussion of the series depicted in Figure 5 we consider first the moiety C_3H_4, i.e., cyclopropane minus two hydrogens at C_2 and C_3. This moiety has been used as a fragment in building the larger systems **4**–**7**. HFS calculations show that removing two hydrogens at C_2 and C_3 of cyclopropane destabilizes e_S much more than e_A due to the large amplitude of e_S at C_2 and C_3. The calculated $e_S - e_A$ splitting is 2.2 eV in the cyclopropyl fragment. Creating C-alkyl bonds in place of C–H bonds diminishes the $e_S - e_A$ gap to ca. 0.6–0.8 eV, as in **4**, **5**, **6**, and **7**. We note that with two alkyl substituents, complete degeneracy of e_S and e_A is not necessary on symmetry grounds and would indeed be accidental. When we now proceed to **3** we note that introducing a third alkyl substituent at the cyclopropane ring makes e_S and e_A nearly degenerate. This is understandable from the approximate local threefold symmetry at the cyclopropane ring (in systems like nortricyclene and hexahydrobullvalene the threefold axis is conserved, and the Walsh orbitals are therefore exactly degenerate[3]). We also observe that the destabilization of e_A relative to e_S upon alkyl substitution at C_1 of cyclopropane is in agreement with the experimental results for other C_1-substituted cyclopropanes.[2] Moving next to **1** and **2** we observe strong destabilization of e_A, which is apparently related to the contraction of the cage moiety of these molecules. This is substantiated by analysis of the calculations. The e_A orbital has a large amplitude at C_4. When as in **1** and **2** C_4 is brought close to C_5 to form the C_4–C_5 bridge, an antibonding interaction with a "pseudo-e_A" orbital on the $C_1C_5C_6$ triad drives the e_A upwards. This antibonding interaction is illustrated by contour plots of 7a″ of **1** in the $C_4C_2C_3$ and the $C_1C_5C_6$ planes (Figure 6) which demonstrate the large amplitude at the top atoms C_4 and C_5 and the π antibonding character along the C_4C_5 link (note the phase change from one plane to the other). The bonding pseudo-e_A counterpart is calculated to lie below 13 eV, in an extremely crowded region of the spectrum, and cannot be observed separately.

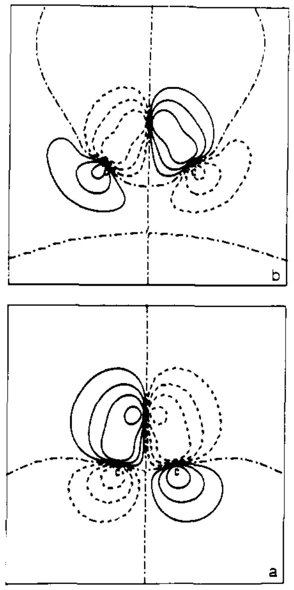

Figure 6. Contour plots of the 7a″ orbital in the $C_2C_3C_4$ plane (a) and the $C_1C_5C_6$ plane (b) in compound **1**.

Conclusion

In summary, we conclude that the strain in compounds **1** and **2** caused by overlap repulsion between $C_2C_3C_4$ and $C_1C_5C_6$, which are forced into a nearly parallel position when the C_4C_5 bridge is formed, shows up quite distinctly in the PE spectrum in an unusual destabilization of the Walsh e_A orbital. It is interesting to note that the HOMO of **2** is e_A, with a″ symmetry, whereas for **6** and **7** the HOMO is e_S, with a′ symmetry. This change in ordering may have implications for the chemical reactivities of these compounds as far as reactions controlled by orbital symmetry are concerned.

The HFS method is found to be a useful and reliable instrument in the assignment of PE spectra of molecules that are of interest in organic chemistry. Often such spectra are analyzed on the basis of empirical considerations alone, using assumptions which may be unwarranted or whose justifiability is difficult to judge. Reliable ab initio calculations avoid these problems. A case in point is the analysis of the PE spectra of **8** and **9**[4] where the basic assumption that e_A in **8** and **9** remains at virtually the same energy is clearly contradicted by the present results.

Acknowledgment. We are grateful to R. Mooyman for experimental assistance. Two of us (G.J. and J.S.) wish to acknowledge the Netherlands Organization for the Advancement of Pure Research for financial support.

Registry No. 1, 35434-64-1; **2**, 29185-91-9; **3**, 7785-10-6.