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NATURE OF THE HIGHEST OCCUPIED MOLECULAR ORBITALS OF *TRANS*- AND *CIS*-BICYCLO[4.1.0]HEPT-3-ENES

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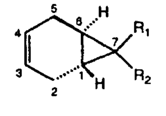
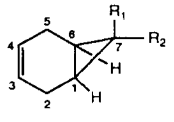
Photoelectron spectra of *trans*-bicyclo[4.1.0]hept-3-ene and two methyl derivatives, 1–3, and *cis*-bicyclo[4.1.0]hept-3-ene and three of its derivatives, 4–7, were measured. *Ab initio* molecular orbital (MO) and density functional theory (DFT) calculations were performed on these compounds. By combining the results of the experimental and computational trends, it was established that the highest occupied molecular orbitals (HOMOs) of 1–3 are the 'twist' bent σ bond at the fusion between the two rings whereas for 4–7 the HOMOs are the π orbital in the six-membered ring. The DFT ordering is the same as that suggested by the photoelectron spectra whereas at the MO level the HOMO always corresponds to the π orbital. The intensities of the photoelectron spectra were calculated at the DFT level and good qualitative agreement with experiment was found.

INTRODUCTION

The chemical and thermal reactivities of derivatives of *trans*-bicyclo[4.1.0]hept-3-ene (**1–3**) have been shown to be dramatically different from those of the corresponding derivatives of *cis*-bicyclo[4.1.0]hept-3-ene (**4–7**).[1] These major changes in reactivity have been attributed to the increased strain energy in **1–3** which results from the *trans*-ring fusion which leads to a 'twist' bent C(1)—C(6) σ bond.[2,3] Whereas chemical evidence from electrochemical oxidation and thermal rearrangement studies indicates that the highest occupied molecular orbital (HOMO) of the *trans*-bicyclo[4.1.0]hept-3-enes is associated with the C(1)—C(6) bond and the HOMO of the *cis*-bicyclo[4.1.0]hept-3-enes is associated with the π bond, we desired more substantial support of this hypothesis. We now report that a combination of photoelectron spectroscopic studies and *ab initio* molecular orbital[4] (MO) and density functional theory[5] (DFT) calculations establishes that the HOMOs of **1–3** are associated with the C(1)—C(6) 'twist' bent σ bonds whereas the HOMOs of **4–7** are associated with the C(3)—C(4) π bonds.



1 $R_1 = R_2 = H$
2 $R_1 = H, R_2 = CH_3$
3 $R_1 = R_2 = CH_3$



4 $R_1 = R_2 = H$
5 $R_1 = H, R_2 = CH_3$
6 $R_1 = CH_3, R_2 = H$
7 $R_1 = R_2 = CH_3$

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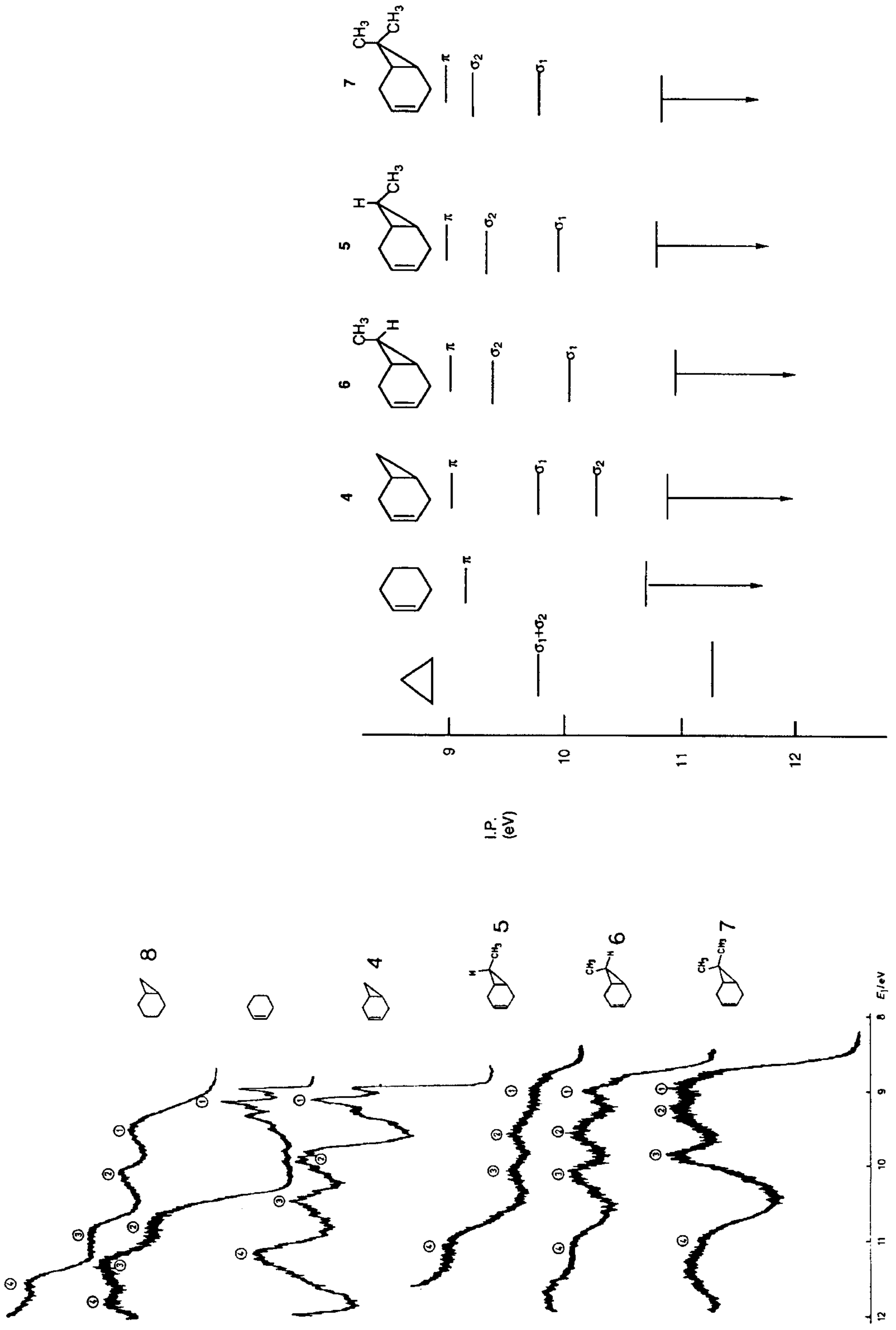
RESULTS

The He(I) photoelectron (PE) spectra of cyclohexene,[6] bicyclo[4.1.0]heptane[7,8] (**8**) and **4–7** below 11·5 eV are shown in Figure 1 and the lowest energy ionization energies are given in Table 1. A schematic diagram of the ionization energies is shown in Figure 1(b). Cyclohexene exhibits a band at 9·11 eV with characteristic vibrational fine structure. *cis*-Bicyclo[4.1.0]hept-3-ene (**4**) has a PE band with similar characteristic vibrational fine structure at 9·05 eV, and additionally two new broad band systems at 9·85 and 10·40 eV. These two additional bands were assigned to the cyclopropyl moiety of **4**. Addition of a methyl group to the 7-position of **4** in the *exo* stereochemistry gave **5** and in the *endo* stereochemistry gave **6**. For **5**, the maximum of the lowest energy band system is shifted to 9·0 eV and the vibrational fine structure had partially disappeared. The two bands assigned to ionization from the cyclopropyl ring are shifted 0·3–0·4 eV to lower energy, which brought them in close proximity to the ionization associated with the π bond. Thus, the methyl group at C(7) shifted the two bands which appeared at 9·85 and 10·40 eV for **4** to 9·55 and 10·05 eV for **5**, but gave only an 0·05 eV shift for the lowest energy system. Since methyl substitution is directly on the cyclopropyl moiety, it is reasonable that a larger shift to lower energy should occur for those PE bands assigned to the cyclopropyl group, but that only a small shift to lower energy should occur for the PE band system assigned to the π bond. The shifts observed in comparing the PE spectra of **6** and **4** were similar to those noted for **5**. Maxima for the two broad bands assigned to the cyclopropyl ring were shifted 0·3 eV to 9·55 and 10·10 eV, whereas the maximum for the π bond associated ionization is approximately the same, 9·0 ± 0·05 eV. For 7,7-dimethyl-*cis*-bicyclo[4.1.0]hept-3-ene (**7**), the second methyl group resulted in additional shifts of the two broad bands assigned to the cyclopropyl ring of 0·3 eV to 9·30 and 9·85 eV. The maximum for the π bond related band is essentially unshifted at 8·95 eV. It is apparent from the PE spectral data that the HOMOs of **4–7** are associated with the π bonds of **4–7**, whereas the NHOMOs of **4–7** are associated with the cyclopropyl σ bonds. It is instructive to compare the PE spectrum of **8** with that of **4**.[8] The PE spectrum of **8** exhibits two broad bands at 9·45 and 10·0 eV. These bands are both shifted to lower energy by 0·4 eV relative to **4**.[9]

Figure 2 shows the He(I) PE spectra of **1–3**. The ionization energies are summarized in Table 1 and a schematic diagram of the energies is given in Figure 2(b). Examination of the PE spectrum of *trans*-bicyclo[4.1.0]hept-3-ene (**1**) shows a band with the same vibrational fine structure that was observed in the first bands of the PE spectra of cyclohexene and **4–7** which were assigned to the π MO of each. However, for **1**, this band with vibrational fine structure overlaps the low-energy broad band associated with the cyclopropyl ring. The band with the characteristic vibrational fine structure has a maximum at 9·30 eV for **1**. This is not the lowest energy band for **1**. Hence the HOMO of **1** is not associated with the π bond. The lowest energy PE band found is a broad band with a maximum at 9·0 eV, which we assign to a localized molecular orbital associated with the C(1)—C(6) 'twist' bent σ bond of **1**. A second, clearly defined, broad band occurred at 10·50 eV in the spectrum of **1**. We believe that this band can be associated with the C(1)—C(7) and C(6)—C(7) σ bonds of **1**. For **2**, the added methyl group at C(7) resulted in the broad bands being significantly shifted to lower energy (as they were in the spectra of **4–7**) with relatively little shift of the π bond ionization energy. Thus, the broad bands at 9·0 and 10·50 eV of **1** were shifted by 0·30 and 0·45 eV respectively, to 8·70 and 10·05 eV, respectively, in the PE spectrum of **2**. By comparison, the π bond associated ionization energy shifts by only 0·10 eV, from 9·30 eV for **1** to 9·20 eV for **2**. Addition of the second methyl to give **3** resulted in additional shifts of 0·10 and 0·35 eV in the ionization energies of the broad bands associated with the cyclopropyl moiety of **3** relative to **2**, to give maxima at 8·60 and 9·70 eV, respectively. The shift in the π bond maximum was 0·02 eV to a value of 9·17 eV for **3**.

Koopmans' theorem[10] was used to calculate the ionization energies at the MO level. At the DFT level, the relationship between the eigenvalue ε_i and the total energy E_{tot} is given by the Janak relation,[11] $\varepsilon_i = \mathrm{d}E_{\text{tot}}/\mathrm{d}n_i$. In order to apply an approximate version of Koopmans' theorem at the DFT level, one has to assume that ε_i is independent of the occupation number n_i. Actually, one does not really need ε_i to be independent of n_i as long as ε_i changes by the same amount for all of the eigenvalues in the region of interest when n_i changes. This constraint is alleviated at the non-local DFT level used here (as opposed to the local DFT level) because the correction to the exchange potential[12] that we used accounts for part of the self-interaction term missing at the local level.[13] It is the self-interaction term that leads to the dependence of ε_i on n_i. Hence we can reasonably approximate the Kohn–Sham eigenvalues as ionization potentials.

The DFT and MO methods predict different results for the molecular ionization potential as shown in Table 1. The MO methods always predict the HOMO to be the π bond. The DFT results, on the other hand, show a clear difference with the *cis* isomers having the HOMO localized in the π bond and the *trans* isomers with the HOMO localized in the 'twist' bent σ bond. At both the DFT and MO levels, the HOMO π bond in the *cis* isomers shows little dependence on methylation.



(a)

(b)

Figure 1. (a) Experimental He(I) PE spectra in the low-energy region of **8**, cyclohexene and **4**–**7**. (b) Schematic diagram of ionization energies

Table 1. Experimental and calculation ionization energies (eV) for bicyclo[4.1.0]hept-3-enes[a]

Orbital	1	2	3	4	5	6	7	8	Cyclohexene	c-C_3H_6
HOMO(expt)	9·00	8·70	8·60	9·05	9·00	9·00	8·95	9·45	9·11	9·86
HOMO(DFT)	5·78 σ_{tb}	5·71 σ_{tb}	5·63 σ_{tb}	5·82 π	5·75 π	5·79 π	5·75 π	6·23 σ_1	5·84 π	7·14(e) $\sigma_1 + \sigma_2$
HOMO(MO)	9·42 π	9·38 π	9·36 π	9·31 π	9·27 π	8·28 π	9·27 π			
SHOMO(expt)	9·30	9·20	9·20	9·85	9·55	9·55	9·30	10·00		
SHOMO(DFT)	6·03 π	5·97 π	5·94 π	6·74 σ_1	6·34 σ_2	6·38 σ_2	6·11 σ_2	6·58 σ_2	7·37	8·78(e)
SHOMO(MO)	9·77 σ_{tb}	9·63 σ_{tb}	9·56 σ_{tb}	10·82 σ_1	10·48 σ_2	10·45 σ_2	10·23 σ_2			
3rd OMO(expt)	10·50	10·05	9·70	10·40	10·05	10·15	9·85			
3rd OMO(DFT)	7·05 σ_2	6·71 σ_2	6·48 σ_2	6·74 σ_2	6·61 σ_1	6·61 σ_1	6·52 σ_1	7·33	7·67	11·43
3rd OMO(MO)	11·15 σ_2	10·80 σ_2	10·57 σ_2	10·85 σ_2	10·67 σ_1	10·65 σ_1	10·54 σ_1			
OMO(DFT)	8·21	8·04	8·01	7·69	7·61	7·68	7·62	7·94	7·86	12·13
OMO(DFT)	8·33	8·22	8·10	8·53	8·36	8·15	8·03	8·19	9·20	14·63(e)
OMO(DFT)	9·23	8·84	8·59	9·13	8·82	9·00	8·75	8·56	9·24	21·13
OMO(DFT)	9·29	9·11	9·03	9·38	9·32	9·28	9·05	9·03	9·49	
OMO(DFT)	9·88	9·49	9·06	10·08	9·43	9·38	9·09	9·19	9·94	
OMO(DFT)	10·18	9·84	9·35	10·23	9·74	9·53	9·26	9·95	10·39	
OMO(DFT)	10·96	9·90	9·76	10·83	10·13	10·12	9·57			

[a] DFT is density functional theory, MO is *ab initio* molecular orbital theory, OMO is occupied molecular orbital.

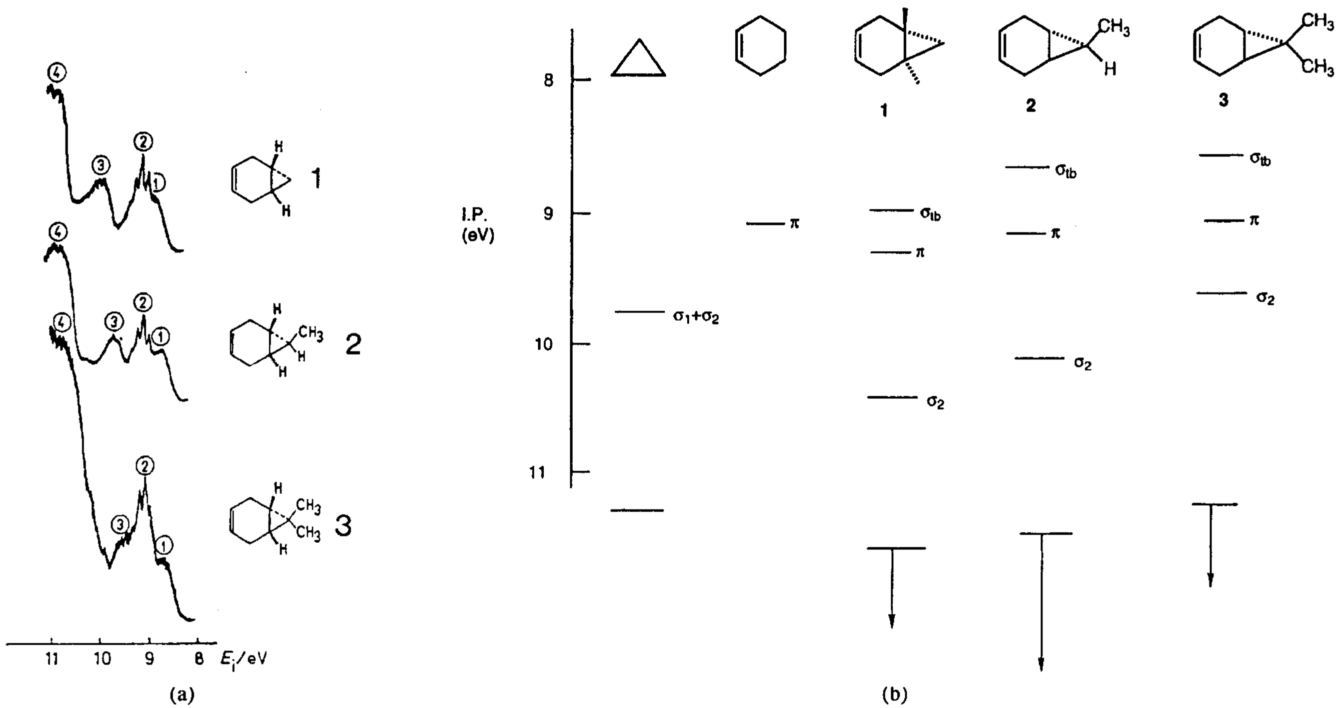
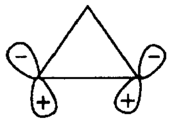


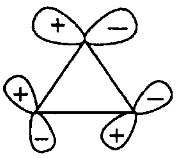
Figure 2. (a) Experimental He(I) PE spectra in the low-energy region of **1**–**3**. (b) Schematic diagram of ionization energies

Similarly for the *trans* isomers, methylation does not strongly affect the SHOMO π bond at the DFT level or the HOMO π bond at the MO level. The HOMO corresponding to the 'twist' bent σ bond in the *trans* isomers at the DFT level shows a larger dependence on methylation, as would be expected, although the differences are smaller than observed experimentally. A similar result is found for the SHOMO of the *trans* isomers at the MO level which corresponds to the 'twist' bent σ bond. The SHOMO of the *cis* isomers which is localized in the cyclopropane moiety shows the largest effect due to methylation. Although the MO calculations do not give the correct ordering of the σ and π orbitals, they do predict the correct magnitudes and directions of the shifts in ionization energies on methylation. In fact, the magnitude of the shifts is treated better at the MO level as compared with the DFT calculations.

In order to understand better the effect of methylation on the cyclopropyl energetics, we calculated the properties of cyclopropane, cyclohexene and the saturated *cis* structure. The HOMO of cyclopropane is a degenerate orbital corresponding to the Walsh-type σ orbitals.[14]



σ_1



σ_2

The energies of these two σ orbitals will split if the threefold degeneracy is lifted. The way in which these orbitals split will determine the influence of methyl substitution and we employ the DFT values in the following discussion. In the saturated *cis* isomer **8**, the HOMO and SHOMO clearly have to be localized in the cyclopropane ring and we find that the orbitals do split with the σ_1 orbital being less stable than the σ_2 orbital by 0·35 eV. Removal of the two hydrogens to generate the unsaturated *cis* compound **4** leads to the two orbitals being essentially degenerate. The methyl group should interact more strongly with the σ_2 orbital as compared with the σ_1 orbital because the σ_2 orbital has more electron density adjacent to the carbon at which the Me is substituted. Indeed, the σ_2 orbital is the NHOMO for the methyl and dimethyl derivatives and shows a significant decrease on methylation from 0·36–0·40 eV for a single methyl group with an additional decrease of 0·23–0·27 eV for a second methyl group. The σ_1 is not as strongly affected, with its energy decreasing by about 0·1 eV per methyl that is added.

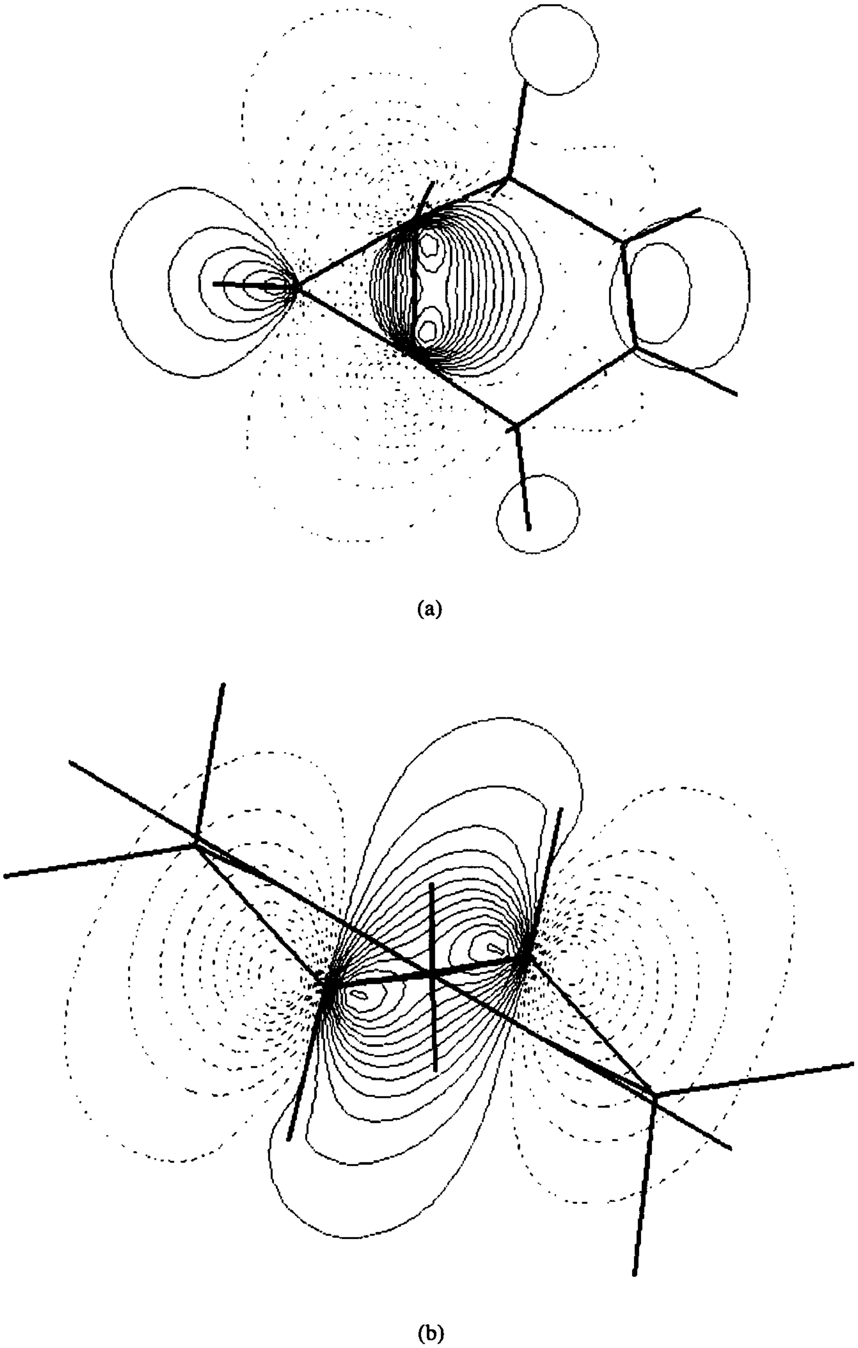
For the *trans* isomers, the σ_1 orbital becomes the 'twist' bent σ bond and localizes away from the site of methylation (see Figure 3). Thus the effect of methyl substitution should be smaller and indeed it is, with a decrease of 0·07 eV for the first methyl group that is added and a decrease of 0·08 eV for addition of the second methyl group. The σ_2 orbital shows a much larger effect on methylation, decreasing by 0·34 eV for addition of the first methyl and 0·23 eV for addition of the second, just as found for the *cis* isomers. The MO calculations on the *cis* and *trans* isomers show similar but smaller effects.

In order to provide more insight into the effect of methylation, we show in Table 2 the σ and π bond distances as compared with the values in the simplest model compounds. For a given series of methyl derivatives, there is very little effect on the π bond distance due to methylation. The *cis* isomers have a π bond distance similar to that of cyclohexene and the bond distances in the *trans* isomers are 0·012–0·014 Å longer. As might be expected, there is a small effect of methylation of the σ bond leading to a slight increase in the bond length on methylation. The value in the parent *trans* compound **1** is closer to the value in cyclopropane and **8** than is that for the parent *cis* compound **4**.

The changes in bond length for the σ bond in the *trans* series as compared with the *cis* series as well as the plots of the 'twist' bent σ bond provide some insight into the difference in the DFT and MO predictions of the ordering of the σ and π orbitals. The MO calculations were done at the closed-shell Hartree–Fock level and, as such, diradical character, if present, cannot be introduced into any orbitals. DFT, on the other hand, is based on the density and diradical character can be incorporated into the final density. The form of the 'twist' bent σ bond (Figure 3) together with the modest lengthening of the C—C 'twist' bent σ bond associated with the *trans* structures suggests that there may be a small amount of diradical character in this bond. The incorporation of such diradical character would destabilize the bond, leading to a lower energy ionization potential. Because the Hartree–Fock method does not account for such character, the ionization energy for the 'twist' bent σ bond is not lowered below that of the π orbital. However, the DFT method can account for such

Table 2. Bridgehead σ and π bond lengths (Å) calculated at the DFT level

Molecule	$r(\sigma)$	$r(\pi)$
1	1·516	1·354
2	1·517	1·355
3	1·522	1·354
4	1·521	1·342
5	1·520	1·343
6	1·523	1·341
7	1·524	1·341
8	1·513	
c-C_3H_6	1·513	
Cyclohexene		1·343



(a)

(b)

Figure 3. Two views of the HOMO for **1** at the DFT level showing the 'twist' bent σ bond. (a) View onto the cyclopropyl plane showing the bent nature; (b) view perpendicular to the cyclopropyl ring showing the 'twist' nature

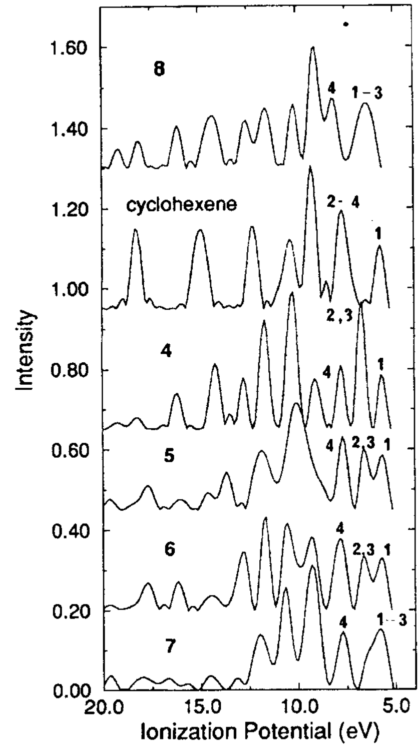


Figure 4. DFT-calculated PE spectra [HE(I) radiation] for **4**–**7**, **8** and cyclohexene

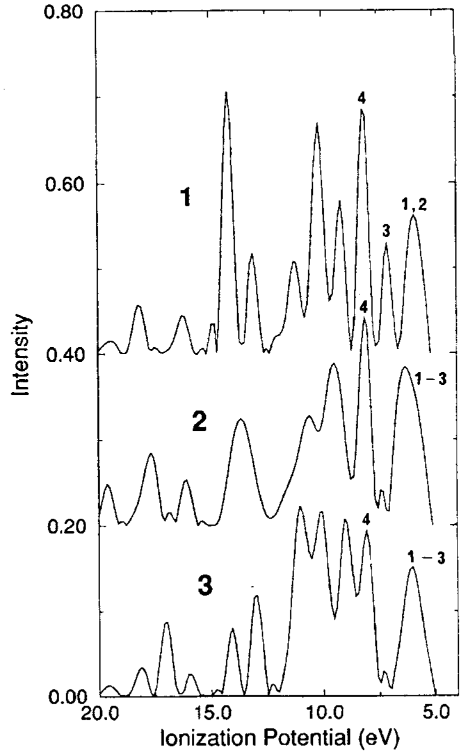


Figure 5. DFT-calculated PE spectra [HE(I) radiation] for **1**–**3**

character and thus it can predict that the 'twist' bent σ bond is less stable than the π bond.

The calculated photoelectron spectra at the DFT level with a line broadening of 0·20 eV are shown in Figures 4 and 5. The calculated intensities[15] are in reasonable agreement with the experimental spectra after accounting for the fact that there is no vibrational motion in our calculation and no structural relaxation.

CONCLUSIONS

The combination of the experimental and theoretical results clearly shows that the HOMO of the *trans*-bicyclo[4.1.0]hept-3-enes is localized in the region of the 'twist' bent σ bond whereas for the *cis*-bicyclo[4.1.0]hept-3-enes the HOMO is localized in the region of the π bond of the six-membered ring. This is in accord with the chemical reactivities of these species that have previously been observed. We note that the DFT method predicts ionization energies that are too low based on our approximate use of Koopmans' theorem by 3·0–3·2 eV. However, this scaling factor based on the difference of the experimental and DFT HOMO energies can be used for the other higher energy ionizations with some reliability in agreement with work on other systems with very different chemical structures.[15] The ability at the DFT level to predict the qualitative intensities of the photoelectron spectrum is an added feature that is useful in analyzing the experimental spectrum.

EXPERIMENTAL

Synthesis. Derivatives of *trans*- and *cis*-bicyclo[4.1.0]hept-3-enes were prepared according to the published procedure.[1] The epimeric *exo*-7-methyl-*cis*-bicyclo[4.1.0]hept-3-ene (**5**) and *endo*-7-methyl-*cis*-bicyclo[4.1.0]hept-3-ene (**6**) were obtained by cyclopropanation of cyclohexa-1,4-diene according to the procedure of Nishimura *et al.*[16] Cyclopropanation of cyclohexa-1,4-diene with 1,1-diiodoethane[17] gave **5** and **6** in the ratio 1 : 2·5. The isomers separated by preparative GLC (SE-30, 110 °C).

Photoelectron spectra. He(I) photoelectron spectra were recorded on a Vacuum Generators Model UVG3 instrument at a resolution of 30 meV with xenon gas as a calibrant.

Calculations. All calculations were done on Cray XMP and YMP computer systems using the program GRADSCF[18] for the *ab initio* molecular orbital (MO) calculations and the program DGauss[19] for the density functional calculations. The geometries were gradient optimized at both levels,[19b,19c,20,21] and these structures were shown to be minima by force field calculations.[22] The basis set for the *ab initio* MO calculations is of double-zeta quality with a set of *d* polarization functions on the carbon atoms (9s5p1d/4s)/[3s2p1d/2s].[23]

The density functional theory calculations were done with the program DGauss,[19] which employs Gaussian basis sets. The basis sets for C and N are triple zeta in the valence space augmented with a set of polarization functions with the form (7111/411/1).[24] For H, a polarized triple-zeta valence basis set was used with the form (311/1). The calculations were done at the self-consistent gradient-corrected (non-local) level (NLDFT) with the non-local exchange potential of Becke[12] together with the non-local correlation functional of Perdew[25] (BP). The local potential of Vosko *et al.*[26] was used. The photoelectron spectra from the DFT wavefunction were calculated by standard first-order time-dependent perturbation theory as described elsewhere.[15]

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