

treated as separable consecutive first-order reactions and treated as above for the simpler case. Because of the fact that  $k_{\text{rearrangement}} \approx 1/20 k_{\text{isomerization}}$  very little error will be introduced by treating the data in this fashion.

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## Molecular Orbital Theory of the Electronic Structure of Molecules. 38. Flexible Olefins Preferring Nonplanar Puckered Structures

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**Abstract:** Ab initio molecular orbital calculations indicate that a number of strained olefins prefer nonplanar structures. These include bicyclobutene- $\Delta^{1,3}$ , bicyclopentene- $\Delta^{1,4}$ , and bicyclohexene- $\Delta^{1,5}$ . In addition, bicyclohexene- $\Delta^{1,4}$ , although planar, is indicated to have a very weak out-of-plane bending force constant. Model calculations from ethylenes distorted to represent these olefins demonstrate the generality of this behavior and provide a theoretical explanation.

Unless dictated by geometrical constraints (e.g., I)<sup>2a,b</sup> or by the lack of the appropriate symmetry,<sup>2c</sup> olefins are planar entities. Remarkably, Hehre and Pople's ab initio calculations on bicyclobutene- $\Delta^{1,3}$  (II)<sup>3</sup> indicated preference for a nonplanar structure even though nothing would seem to preclude

**Table I.** Relative Energies of Distorted Ethylene Models<sup>a</sup> for II and IV (RHF/STO-3G), kcal/mol

$\angle\text{HCC}$ , deg	Planar (VIIA) $D_{2h}$	Nonplanar (VIIB) <sup>c</sup> $C_{2v}$
120	0.0 (-77.071 21) <sup>b</sup>	11.1
110	0.0 (-77.034 59)	7.3
100	0.0 (-76.944 19)	2.1
90	0.0 (-76.786 88)	-5.5
80	0.0 (-76.518 85)	-17.3
70	0.0 (-75.981 37)	-37.9

<sup>a</sup> Assumed geometrical parameters:  $r(\text{C}=\text{C}) = 1.34$ ,  $r(\text{C}-\text{H}) = 1.08$  Å. <sup>b</sup> Total energy (au) of planar form in parentheses. <sup>c</sup>  $\angle\text{H}_a\text{CC} = \angle\text{H}_c\text{CC} = 70^\circ$ ,  $\phi(\text{H}_a\text{CCH}_c) = 0^\circ$ ,  $\angle\text{H}_b\text{CC} = \angle\text{H}_d\text{CC} = \theta$ ,  $\phi(\text{H}_a\text{CCH}_c) = \phi(\text{H}_b\text{CCH}_d) = 0^\circ$ ,  $\phi(\text{H}_a\text{CCH}_d) = 150^\circ$ .

planarity. As possible reasons for this behavior were not analyzed,<sup>3</sup> a more extensive molecular orbital investigation of II and other olefins (III, IV, V, and VI (R = H)) which might also be nonplanar has now been undertaken. IV<sup>4</sup> and VI (R = CH<sub>3</sub>)<sup>5</sup> are known, but no experimental structural studies have been reported. Very recently, a tricyclic derivative of II has been implicated as a reaction intermediate.<sup>6</sup> A platinum

**Table II.** Relative Energies of Distorted Ethylene Models<sup>a</sup> for III, V, and VI (RHF/STO-3G), kcal/mol

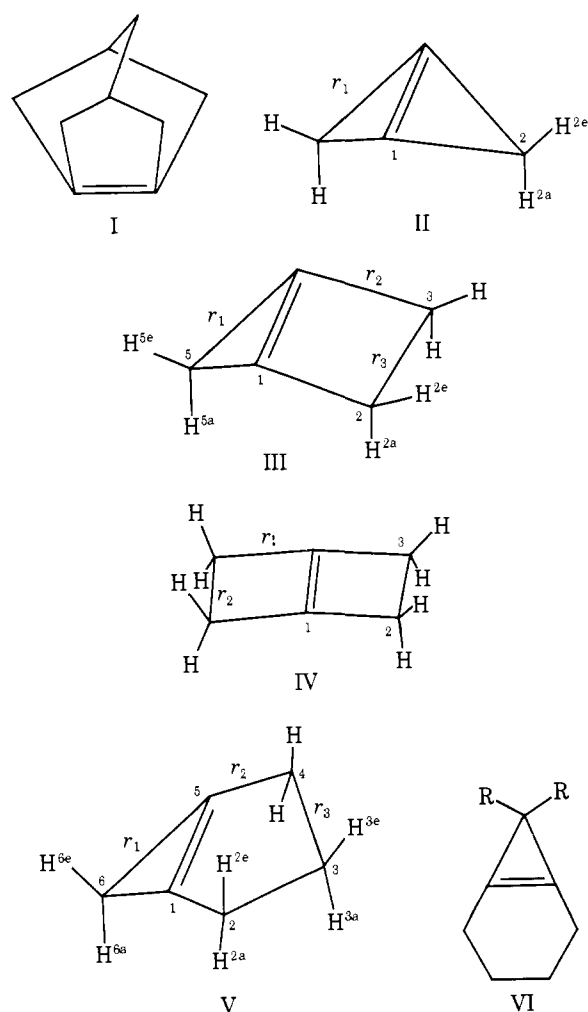
$\theta, ^\circ$ deg	Planar (XIA) $C_{2v}$	Nonplanar (XIB) <sup>c</sup> $C_s$
150	0.0 (-76.608 67) <sup>b</sup>	2.5
120	0.0 (-76.590 17)	-1.1
100	0.0 (-76.501 03)	-6.5

<sup>a</sup> Assumed geometrical parameters:  $r(\text{C}=\text{C}) = 1.34$ ,  $r(\text{C}-\text{H}) = 1.08$  Å. <sup>b</sup> Total energy (au) of planar form in parentheses. <sup>c</sup>  $\angle\text{H}_a\text{CC} = \angle\text{H}_c\text{CC} = 70^\circ$ ,  $\phi(\text{H}_a\text{CCH}_c) = 0^\circ$ ,  $\angle\text{H}_b\text{CC} = \angle\text{H}_d\text{CC} = \theta$ ,  $\phi(\text{H}_a\text{CCH}_d) = 150^\circ$ .

Table III. Total Energies<sup>a</sup> of II-V

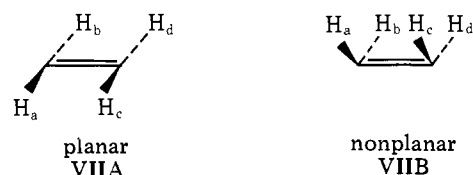
	STO-3G	4-31G	6-31G*	Dipole moment <sup>b</sup>
II planar	-151.602 13	-153.274 28	-153.557 54	0.0
nonplanar	-151.650 18	-153.303 46 <sup>d</sup>	-153.575 70	0.76 <sup>e</sup>
Difference <sup>c</sup>	30.2	18.3	11.4	
III planar	-190.240 57	-192.283 28		0.82
nonplanar	-190.268 30	-192.305 15		1.20
Difference <sup>c</sup>	17.4	13.8		
IV planar	-228.947 61			0.0
V planar	-228.935 02			0.75
nonplanar	-228.936 60			0.86
Difference <sup>c</sup>	1.0			

<sup>a</sup> au. <sup>b</sup> Debye, calculated from the STO-3G wave function. <sup>c</sup> Kcal/mol. <sup>d</sup> Energy of 4-31G optimized structure = -153.305 85 au. <sup>e</sup> 1.18 D at 4-31G, 1.14 D at 6-31G\*. The direction of the dipole is plus (CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub> minus.



complex of IV has a strongly puckered skeletal structure, but this could be due to the effect of coordination.<sup>7</sup>

Before considering such specific cases, it is instructive to study the structural predilections of ethylene distorted in order to simulate II-VI. In one set of *ab initio*<sup>8</sup> RHF/STO-3G<sup>8b</sup> calculations to model II and IV, all HCC angles were reduced symmetrically in increments of 10°. For each value of  $\angle\text{HCC}$ , the energies of the planar  $D_{2h}$  form (VIIA) and a nonplanar  $C_{2v}$  form (VIIB) with the dihedral angle  $\text{H}_a\text{CCH}_d = 150^\circ$  were obtained (Table I). As expected, the planar form is most stable when  $\angle\text{HCC} = 120^\circ$  and the total energy increases sharply as this angle is reduced. However, our concern is the relative energies of VIIA and VIIB, the nonplanar form (VIIB) becomes more stable at lower values of  $\angle\text{HCC}$ , the shift in preference occurring around  $\angle\text{HCC} = 100^\circ$ .<sup>9</sup>



An analysis of the MOs indicates the reason for this startling structural switchover. Consider the ethylene  $3a_g$  orbital VIII composed of carbon  $p_x$  orbitals (Figure 1).<sup>10</sup> When  $\angle\text{HCC}$  is  $>100^\circ$ , favorable overlap with the four hydrogen orbitals is possible (VIIIA). As  $\angle\text{HCC}$  is decreased, such favorable CH overlap diminishes in the planar form as the hydrogens move into the nodal regions (VIIB).

If the symmetry is reduced by making the molecule nonplanar, MO VIII B mixes with the originally pure  $\pi$  MO (IXB). The consequence of this mixing is to produce a new set of MOs (X), one of which (XA) has gained C-H bonding and is considerably more favorable than its counterpart, VIIB. The other MO of this combination (XB) is only marginally less favorable than IXB. The net result is a substantial lowering in energy on going from planar to nonplanar forms when  $\angle\text{HCC} < 100^\circ$ .

This behavior is not seen at large HCC angles. When  $\angle\text{HCC}$  is around  $120^\circ$ , MO VIIIA already has strong C-H bonding as the carbon  $p_x$  lobes are directed toward the hydrogen atoms. Out-of-plane deformation, and consequent mixing with the  $\pi$  orbital (IXA), does not lead (in contrast to VIIB vs. XA) to lowering in the orbital energy. Other orbitals ( $b_{3u}$  and  $b_{2u}$ )<sup>10</sup> of ethylene become destabilized on puckering and ethylenes with  $\angle\text{HCC} < 100^\circ$  prefer to be planar.



Additional calculations were performed on ethylene distorted to simulate III, V, and VI. The  $\text{H}_a\text{CCH}_c$  grouping was held planar with  $\angle\text{H}_a\text{CC} = \angle\text{H}_c\text{CC} = 70^\circ$ . For various values of  $\angle\text{H}_b\text{CC} (= \angle\text{H}_d\text{CC}) = \theta$ ; the relative energies of the planar  $C_{2v}$  form (XIA) and the nonplanar  $C_s$  form (XI B) with dihedral angle  $\text{H}_a\text{CCH}_d = 150^\circ$  (Table II) exhibit similar trends. At  $\theta = 150^\circ$ , a value close to that found in cyclopropane,<sup>11</sup> the planar form is favored, but nonplanar forms are stabilized at lower values of  $\theta$ . The reason for this preference for nonplanarity is analogous to that discussed above.

Thus, the reported behavior of II<sup>3</sup> should not be an isolated case but rather a particular instance of a general structural preference exhibited by olefins suffering these types of dis-

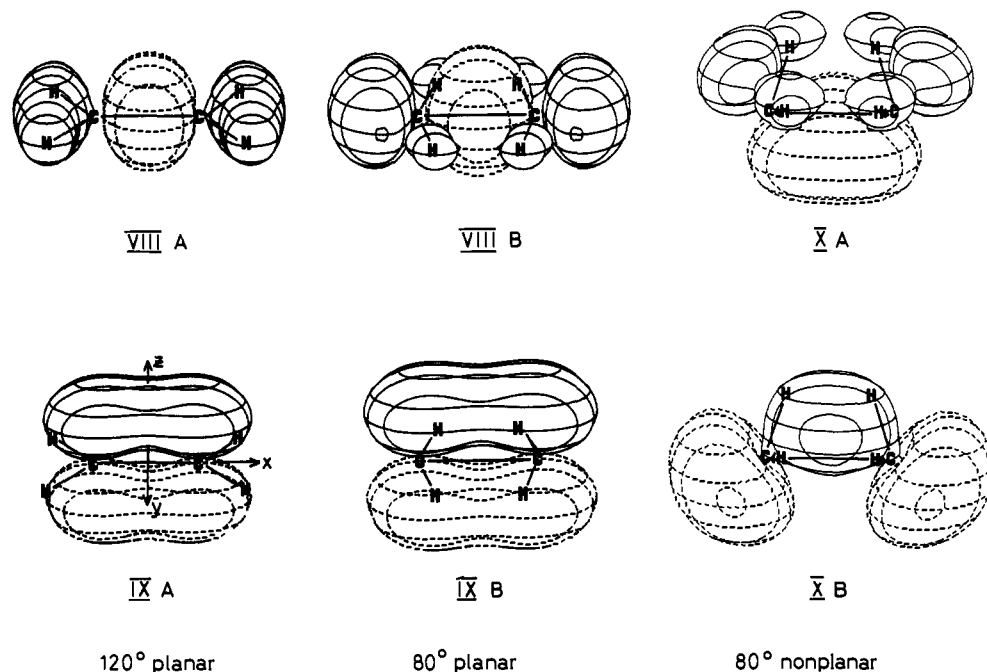


Figure 1. Perspective MO drawings of normal and distorted forms of ethylene. See text for descriptions.

Table IV. Calculated Structural Parameters<sup>a</sup> of II-V (RHF/STO-3G)

	Symmetry	$r(\text{C}=\text{C})$	$r_1^b$	$r_2^b$	$r_3^b$	Angle between rings
II planar	$D_{2h}$	1.407	1.473			180.0
nonplanar	$C_{2v}$	1.381 <sup>d</sup>	1.509 <sup>d</sup>			128.3
		(1.353) <sup>c</sup>	(1.504) <sup>c</sup>			(132.5) <sup>c</sup>
III planar	$C_{2v}$	1.281	1.501	1.536	1.598	180.0
nonplanar	$C_s$	1.347	1.497	1.549	1.557	129.3
IV planar	$D_{2h}$	1.295	1.532	1.596		180.0
V planar	$C_s$	1.270	1.499	1.507	1.588	180.0
nonplanar	$C_s$	1.283	1.508	1.550	1.590	155.0

<sup>a</sup> Distances in Å, angles in degrees. The further parameters to define the full structures are II planar  $r\text{C}^2\text{H} = 1.097$ ,  $\angle\text{HCH} = 111.4$ ; II nonplanar  $r\text{C}^2\text{H}^{2e} = 1.089$ ,  $r\text{C}^2\text{H}^{2a} = 1.092$ ,  $\angle\text{C}^1\text{C}^2\text{H}^{2e} = 114.2$ ,  $\angle\text{HCH} = 113.7$ ; III planar  $r\text{C}^2\text{H} = 1.092$ ,  $r\text{C}^5\text{H} = 1.094$ ,  $\angle\text{HC}^2\text{H} = 109.2$ ,  $\angle\text{C}^1\text{C}^2\text{H} = 114.9$ ,  $\angle\text{HC}^5\text{H} = 111.6$ ; III nonplanar  $r\text{C}^2\text{H}^{2e} = 1.089$ ,  $r\text{C}^2\text{H}^{2a} = 1.089$ ,  $r\text{C}^5\text{H}^{5e} = 1.092$ ,  $r\text{C}^5\text{H}^{5a} = 1.094$ ,  $\angle\text{C}^1\text{C}^2\text{H}^{2e} = 114.3$ ,  $\angle\text{C}^1\text{C}^2\text{H}^{2a} = 114.2$ ,  $\angle\text{C}^1\text{C}^5\text{H}^{5e} = 116.3$ ,  $\angle\text{HC}^2\text{H} = 109.1$ ,  $\angle\text{HC}^5\text{H} = 112.6$ ,  $\angle\text{C}^3\text{C}^2\text{H}^{2e} = 115.9$ ; IV planar  $r\text{C}^2\text{H} = 1.090$ ,  $\angle\text{C}^1\text{C}^2\text{H} = 116.6$ ,  $\angle\text{C}^3\text{C}^2\text{H} = 114.3$ ,  $\angle\text{HCH} = 109.0$ ; V planar  $r\text{C}^2\text{H} = 1.090$ ,  $r\text{C}^3\text{H} = 1.089$ ,  $r\text{C}^6\text{H} = 1.091$ ,  $\angle\text{C}^5\text{C}^1\text{C}^2 = 116.0$ ,  $\angle\text{C}^1\text{C}^2\text{C}^3 = 99.3$ ,  $\angle\text{C}^2\text{C}^3\text{C}^4 = 109.4$ ,  $\angle\text{C}^1\text{C}^2\text{H} = 113.5$ ,  $\angle\text{C}^3\text{C}^2\text{H} = 111.7$ ,  $\angle\text{C}^2\text{C}^3\text{H} = 110.0$ ,  $\angle\text{HC}^6\text{H} = 110.4$ ; V nonplanar  $r\text{C}^2\text{H}^{2e} = r\text{C}^2\text{H}^{2a}$  (assumed) = 1.090,  $r\text{C}^3\text{H}^{3e} = r\text{C}^3\text{H}^{3a}$  (assumed) = 1.089,  $r\text{C}^6\text{H}^{6e} = r\text{C}^6\text{H}^{6a}$  (assumed) = 1.091,  $\angle\text{C}^5\text{C}^1\text{C}^2 = 115.4$ ,  $\angle\text{C}^1\text{C}^2\text{C}^3 = 100.4$ ,  $\angle\text{C}^2\text{C}^3\text{C}^4 = 108.4$ ,  $\angle\text{C}^1\text{C}^2\text{H}^{2e} = \angle\text{C}^1\text{C}^2\text{H}^{2a}$  (assumed) = 112.7,  $\angle\text{C}^3\text{C}^2\text{H}^{2e} = \angle\text{C}^3\text{C}^2\text{H}^{2a}$  (assumed) = 111.7,  $\angle\text{C}^2\text{C}^3\text{H}^{3e} = \angle\text{C}^2\text{C}^3\text{H}^{3a}$  (assumed) = 110.3,  $\angle\text{C}^1\text{C}^6\text{H}^{6e} = \angle\text{C}^1\text{C}^6\text{H}^{6a} = 120.6$ . <sup>b</sup> See II-V for definition. <sup>c</sup> 4-31G optimized values. <sup>d</sup> Values in ref 3 are incorrect owing to transcription errors.

tortions. This conclusion was confirmed by extensive calculations of the planar and nonplanar structures of II-V (Table III).<sup>12</sup>

Fully STO-3G optimized structures of II and III are markedly nonplanar, the angles between the two ring planes being 128.3 and 129.3°, respectively. The energy difference relative to the planar optimized forms are 30 kcal/mol for II and 17 kcal/mol for III. Extended basis 4-31G<sup>8c</sup> and 6-31G\*<sup>8d</sup> calculations on the STO-3G optimized structures of II lead to the same nonplanar preference with reduced but still substantial energy differences of 18 and 11 kcal/mol, respectively. While IV with  $\angle\text{C}=\text{C}-\text{C} = 101.4^\circ$  is calculated to have a planar equilibrium geometry, the potential energy surface is quite flat: for a 20° out-of-plane deformation, the energy changes by only 2.9 kcal/mol (STO-3G). The large puckering (124°) found in the platinum complex of IV<sup>7</sup> may partly be due to this factor.

Important structural parameters calculated at the STO-3G level for II-V are presented in Table IV. The structure of II

does not change significantly when optimization is carried out with the 4-31G basis. At least for II, the calculated dipole moments (Table III) may serve as potential guides for experimental structural determinations. Detailed analyses of the structures and bonding of II-VI and further investigations of ethylene distortions will be presented subsequently.

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## Remote Functionalization Reactions as Conformational Probes for Flexible Alkyl Chains

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**Abstract:** Photolysis of benzophenone carboxylic acid esters of long chain alkanols leads to intramolecular hydrogen atom abstraction and carbon-carbon coupling, resulting in overall insertion of the benzophenone carbonyl into the alkyl chain. An appropriate degradative sequence permits the quantitative determination of the positions functionalized; the distribution of functionalization sites is related to the conformations adopted by the chain in solution. The distribution is affected by the polarity of the solvent, indicating that solvents must be explicitly taken into account in any theory used to account for chain coiling. Another probe of such conformations is the intramolecular halogenation of alkyl chains in a free-radical chain reaction of *p*-dichloriodobenzoate esters of long-chain alkanols, and of corresponding *m*-dichloriodo derivatives. A degradative sequence was devised to locate the site of chlorination, in which one of the steps is a novel and unusual copper-assisted displacement by benzoate ion on a thioether under free-radical conditions. The distribution of functionalization sites with these reactions also depends on the nature of the solvent. There is a general relationship between these chlorination reactions and those with the benzophenone probe which can be understood in terms of simple conformational factors.

Much interest has surrounded attempts to understand the conformational preferences of long alkyl chains.<sup>1</sup> Such chains might be thought to prefer a fully extended conformation with no gauche interactions, and indeed in bilayers this seems to be the conformation adopted.<sup>2</sup> However, except in such special phases alkyl chains are extensively coiled. Each gauche interaction introduces an increased enthalpy of ca. 0.5 kcal/mol,<sup>3</sup> but entropy operates to promote coiling. Thus the Boltzmann factor for the fully extended conformation can be set as unity, but the factor for all possible hexadecyl chains containing exactly one gauche interaction is then  $30e^{-0.5/RT}$ , with a value of 13.04. The inclusion of further gauche interactions introduces additional exponential terms and successively decreasing preexponential terms, but the exponential enthalpy factor does not dominate until the chain is almost completely coiled.

Solvation effects can also influence the relative energies of different conformations, since in the more compact coiled conformations alkyl chains present a smaller surface to the solvent. This means that chain coiling is favored in polar solvents.<sup>4</sup>

Some years ago we reported with Winnick<sup>5</sup> a study of the intramolecular insertion reaction of benzophenone carboxylic esters of octadecanol and similar alkanols. This preliminary study was followed by extensive work using such benzophenone reactions on rigid steroid substrates,<sup>6</sup> in which conformational flexibility is not present. Such studies led to the development

of a number of ways to perform remote functionalization reactions on steroids, and the reactions have been applied to perform some very practical specific steroid transformations.<sup>7</sup>

It was obvious even from our preliminary work<sup>5</sup> that selective reaction did not occur in the functionalization of flexible alkanol substrates, since a distribution of attack sites was observed reflecting the flexible conformation of the substrate. However, such distributions are of considerable interest in their own right as a reflection of the conformational preferences of alkyl chains. Winnick has independently pursued this line in some detail,<sup>8</sup> concentrating on theoretical models to interpret the distributions observed and also on triplet lifetime studies as a function of chain length to furnish an independent parameter related to conformation. Several studies on mass spectral intramolecular reactions are also related to the alkyl chain preferred conformations.<sup>9</sup> Since such studies are performed in the gas phase, they do not reflect the solvation effect on conformational preferences. In that sense gas-phase work is more relevant to any theoretical model in which solvation effects are ignored.

In our original report<sup>5</sup> the benzophenone photolysis product was converted to a keto derivative in the alkyl chain by the sequence shown in Scheme I. This was then submitted to Baeyer-Villiger cleavage and the resulting ester was saponified to produce an alkanol which was analyzed by gas-liquid