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Effect of Carbon Atom Pyramidalization on the Bonding in Ethylene

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Abstract: The changes in the bonding that occur on syn and anti carbon atom pyramidalization in ethylene are analyzed from the perspective of the second-order Jahn-Teller effect. Situations in which a pyramidalized geometry might actually be favored over a planar one are discussed, and a preference for anti over syn pyramidalization is predicted. The results of ab initio SCF calculations on planar and pyramidalized geometries are reported. It is found that the energy difference between the lowest singlet and triplet state decreases monotonically with increasing pyramidalization. The C–C bond lengthens and the HCH angle opens on pyramidalization; and, as expected, the anti mode is found to be less energetically costly than the syn. The changes in the bonding that occur on pyramidalization are elucidated by population analyses, which show that orbital following of the motions of the hydrogens is far from complete.

Although bridgehead olefins with torsionally strained double bonds have been studied extensively in recent years,[1] olefins in which the carbon atoms forming the double bonds are pyramidalized have received much less attention. Greene and co-workers have prepared two molecules (**1a** and **1b**) belonging to the latter class of compounds,[2] and recently one of

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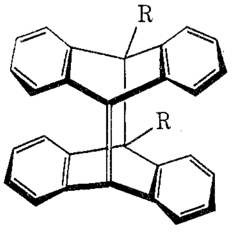
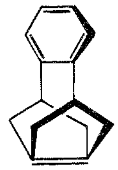
us reported the preparation of a third (**2**).[3] Szeimies has postulated the formation of a fourth such molecule (**3**) as a reactive intermediate.[4]



1a, R = H
b, R-R = —



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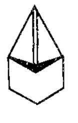

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Our experimental interest in this class of molecules led to the theoretical study reported here. We have carried out ab initio SCF calculations on nonequilibrium geometries of ethylene in order to model the effects of carbon atom pyramidalization in bridgehead olefins. We were interested not only in obtaining estimates of the energetic cost of carbon atom pyramidalization but also in probing qualitatively the effect of pyramidalization on the bonding. In particular, we wanted to ascertain the extent to which the σ orbitals in planar ethylene would follow the motions of the hydrogen nuclei on pyramidalization, concomitantly transforming the p-π orbitals in the planar molecule into hybrids at deformed geometries.

Theoretical Considerations

As in our previous studies of open-shell π systems,[5] the second-order Jahn–Teller effect[6] can be used to predict the consequences of a distortion from the most symmetrical molecular geometry. In this theoretical analysis such distortions are "relaxed" primarily by changes in the wave function that result from the mixing of states which have different symmetries in the most symmetrical molecular geometry. In a closed-shell molecule this is tantamount to the mixing of filled and unfilled orbitals of different symmetry on molecular distortion.[7] Such mixing lowers the energy that would be calculated were the total wave function to remain frozen. In fact, the energy lowering caused by σ–π mixing on carbon pyramidalization in an olefin could, in principle, lead to a nonplanar equilibrium geometry. Whether this actually occurs depends on the magnitude of the energy lowering due to orbital mixing, which, in turn, depends, at least in part, on the proximity of the filled and unfilled orbitals that are mixed.

For example, molecules containing doubly bonded atoms beyond the first row of the periodic table possess high-lying filled and low-lying empty σ orbitals. On pyramidalization of the doubly bonded atoms, mixing can occur between these MOs and the π and π^* orbitals of the double bond. As has been discussed elsewhere,[8] the relatively small energy gap between the filled and unfilled orbitals that are mixed by distortion from planarity in such a molecule indicates that pyramidalization should be much more facile in, for instance, disilaethylene than in ethylene itself. Ab initio SCF calculations show that disilaethylene, in fact, prefers a nonplanar equilibrium geometry.[9] Moreover, the X-ray structure of a derivative of distannaethylene shows the tin atoms to be pyramidalized.[10]

In ethylene itself the energy gaps between filled and unfilled MOs are sufficiently large that the equilibrium geometry is, of course, planar. However, the energies of the filled σ MOs that involve bonding overlaps between the hydrogens and the p_z orbitals, which lie along the line joining the carbons, can be raised by opening up of the H–C–H bond angles. The energies of the corresponding antibonding σ orbitals are concomitantly reduced. Thus, opening of the H–C–H bond angles in ethylene would be anticipated to reduce the barrier to carbon atom pyramidalization. This expectation too is confirmed by the results of recent ab initio calculations.[11]

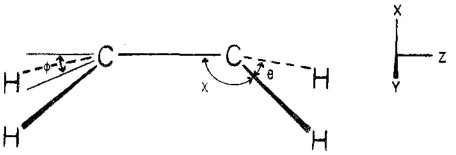

Figure 1. A syn pyramidalized olefin, showing the definition of the angles ϕ, θ, and χ and the choice of coordinate axes.

There are actually two possible modes of pyramidalization of the carbon atoms in ethylene, and the second-order Jahn–Teller effect also can be used to predict which will be the least energetically demanding. If all four hydrogens move in the same direction, the distortion, hereafter referred to as syn pyramidalization, has b_{3u} symmetry in the D_{2h} point group to which the planar molecule belongs. If the hydrogens move pairwise in opposite directions, the resulting anti mode of pyramidalization has b_{2g} symmetry.[12] The symmetry of each distortion can be employed to determine which filled σ MOs will be mixed with π^* and which unfilled σ orbitals will be mixed with π.

For instance, π^* belongs to the b_{2g} representation. The direct product of b_{3u} with b_{2g} is b_{1u}; hence, this is the symmetry of the σ orbitals which mix with π^* on syn pyramidalization. It can similarly be determined that the σ MOs which mix with π^* on anti pyramidalization have a_g symmetry. Since the π orbital has b_{3u} symmetry, the unfilled σ orbitals that mix with it have a_g symmetry for syn pyramidalization and b_{1u} for anti. In planar ethylene there are two filled σ valence orbitals with a_g symmetry and only one with b_{1u}.[13] Thus, there exist two filled σ MOs that can mix with π^* on anti pyramidalization but only one that can mix on syn. Moreover, the upper a_g σ orbital lies above the single filled σ MO of b_{1u} symmetry. Therefore, mixing between π^* and filled σ orbitals is certainly expected to favor anti pyramidalization. This same mode is also favored by the fact that there are two unfilled b_{1u} σ valence orbitals to mix with π on anti pyramidalization but only one unfilled a_g σ orbital to mix on syn. Consequently, we expected that our computational results would show anti pyramidalization of ethylene to be less costly energetically than syn.[14] In fact, calculations on disilaethylene[9] and the X-ray structure of a derivative of distannaethylene[10] reveal a preference for anti pyramidalization in both these molecules. Since the preference for the anti mode is predicted on the basis of greater orbital mixing on this type of distortion, we also anticipated that our calculations would show better following of the hydrogens by the C–H bond orbitals on anti pyramidalization.

Results

Ab initio SCF calculations were carried out on planar and syn and anti pyramidalized ethylene using a basis set of double ζ quality, augmented with one set of uncontracted polarization functions on the carbon atoms. Dunning's (4s/2p) contraction[16] of Huzinaga's (9s/5p) basis[17] was used for carbon and the hydrogens were described by a (5s/3s) set.[18]

Calculations were carried out at 18° intervals of the pyramidalization parameter, ϕ, where ϕ is the angle between the HCH bisector and the line passing through the carbon nuclei. As shown in Figure 1, an angle of $\phi = 0°$ corresponds to planar ethylene, while $\phi = 90°$ can be thought of as representing the ethylene geometry created by joining two methylenes so that the C–C "σ" bond is formed between the π rather than the σ orbitals of the bent CH_2 fragments.

An initial set of calculations was carried out for syn pyramidalization by freezing the HCH angle, θ, and the C–C bond length, r, at the experimental values, $\theta = 117.6°$ and $r = 1.338$ Å.[19] Throughout all the calculations reported in this paper the C–H bond length was kept at its experimental value of 1.086

Table I. Relative Energy (kcal/mol) of the Lowest Singlet and Triplet States of Ethylene as a Function of ϕ^a

ϕ, deg	E_s	E_t	$E_s - E_t$
0	0^b	81.2	81.2
18	5.0	80.1	75.1
36	20.4	81.1	60.7
54	47.6	92.6	45.0
72	86.3	121.1	34.8
90	146.3	181.1	34.8

[a] $r_{C-C} = 1.338$ Å, $r_{C-H} = 1.086$ Å, $\theta = 117.6°$. [b] $E = -78.0369$ hartrees.

Table II. Relative Energies of Optimized^a Syn and Corresponding Anti Geometries for the Lowest Singlet State of Ethylene

	ϕ, deg	r_{C-C}, Å	θ, deg	E, kcal/mol
planar	0	1.32	118	0^b
syn	54	1.37	125	44.9
anti	54	1.37	125	40.5
syn	90	1.45	145	123.4
anti	90	1.45	145	117.1

[a] r_{C-H} fixed at 1.086 Å. [b] $E = -78.0373$ hartrees.

Å.[19] It is easy to show that the relationship between the HCC bond angle, χ, and the other two angles, ϕ and θ, is

$$\cos\chi = -\cos\phi\cos\theta/2 \qquad (1)$$

With $\theta = 117.6$ a value of $\phi = 50°$ gives tetrahedral HCC bond angles.

The results of the frozen geometry SCF calculations are shown in Table I for the lowest singlet and triplet.[20] The initial increase in the energy of the singlet is approximately quadratic in ϕ. The computed quadratic force constant of $k_\phi/r_{CH}^2 = 0.60 \times 10^5$ dyn/cm can be compared with the experimental value of 0.46×10^5 dyn/cm.[21] In contrast, the energy of the triplet initially decreases, reaches a minimum around 18°, and then, starting at about 36°, rises almost quadratically. Throughout, the singlet remains below the triplet, but the singlet–triplet gap decreases from $\phi = 0$ to 90°.

We next examined the effect of optimizing the C–C bond length and the HCH angle at $\phi = 0$, 54, and 90°. The results are shown in Table II. As ϕ is increased r lengthens and θ opens up. The former effect reflects the weakening of bonding between the carbon atoms on pyramidalization; the latter can be viewed as partial movement of the hydrogens back toward coplanarity with the carbons. For any value of ϕ, opening of θ to 180° restores olefin planarity. However, even at $\phi = 90°$ we find a nonplanar structure to be preferred. This result is in accord with the findings of a recent STO-3G study of the effect of closing χ on the preferred geometry of ethylene.[11]

Also shown in Table II are the energies calculated for the same values of ϕ, r, and θ but with the carbons pyramidalized in an anti fashion. As predicted, anti pyramidalization is computed to be more favorable than syn. Because we were most interested in comparing the bonding in the syn and anti structures at the same values of r and θ, these parameters were not optimized for the latter geometries. Therefore, the energy differences between optimum syn and anti structures are probably underestimated by the numbers in Table II.

In order to better understand the bonding in the syn and anti pyramidalized ethylenes, we carried out population analyses on the planar, syn (both unoptimized and optimized), and anti geometries. The method of Davidson was used to project the density matrix onto SCF atomic orbitals of the free atoms.[22] Because of the changes in overlap integrals with geometry, we found it useful to examine these quantities and their associated bond orders separately, instead of considering only their products, the overlap populations. It was found that the changes in the overlap integrals and bond orders were monotonic; therefore, only the values of these quantities at the extrema, 0 and 90°, are reported in Table III.

Discussion

As noted in the introduction, the mixing of π^* with filled σ and π with unfilled σ orbitals is chiefly responsible for the changes in the total wave function that "relax" pyramidalization of the carbons in ethylene. These are by no means the only changes that occur, however. Under the influence of carbon pyramidalization, which allows the hydrogens to interact with the p_x atomic orbitals and decreases their overlap with the p_z, unfilled σ orbitals mix with π^* and filled σ orbitals mix with π. Of course, mixing between two filled or two empty orbitals does not change the energy of the ground state. Nevertheless, the individual orbital energies do change because of these interactions. In fact, because the filled σ orbitals are closer in energy to π than are the unfilled σ orbitals, it is expected that the destabilizing effect of mixing the former set of σ orbitals into π will dominate the stabilizing effect of mixing π with the latter. Similarly, the π^* orbital is expected to undergo net stabilization on pyramidalization, owing to the proximity of the unfilled σ orbitals which lie above it and mix with it more strongly than do the filled σ MOs. Therefore, excitation of an electron from π to π^* should be made less costly energetically by increase of the pyramidalization angle, ϕ. This is precisely what is observed in Table I in the monotonic decrease of the calculated singlet–triplet gap. The energies of the singly filled MOs in the triplet SCF calculations also were found to change in the expected directions.

The rise in the total energy from $\phi = 0$ to 90° is sufficiently

Table III. Overlap Integrals (S) and Bond Orders (ρ) between Atomic Orbitals for Different Ethylene Geometries

	planar^a		syn $\phi = 90°$ unoptimized^b		syn $\phi = 90°$ optimized^c		anti $\phi = 90°^c$	
	S	ρ	S	ρ	S	ρ	S	ρ
2s–2s	0.456	0.040	0.448	−0.051	0.397	−0.098	0.397	−0.256
2s–p_z	0.474	0.257	0.470	0.127	0.443	0.146	0.443	0.246
p_z–p_z	0.221	0.543	0.226	0.818	0.253	0.794	0.253	0.740
p_y–p_y	0.351	−0.093	0.345	−0.212	0.300	−0.161	0.300	−0.103
p_x–p_x	0.351	0.738	0.345	0.546	0.300	0.656	0.300	0.656
2s–H	0.573	0.232	0.573	0.277	0.573	0.301	0.573	0.289
p_z–H	0.263	0.267	0	0.264	0	0.264	0	0.270
p_y–H	0.432	0.486	0.433	0.557	0.484	0.488	0.484	0.476
p_x–H	0	0	0.262	0.141	0.148	0.126	0.148	0.139

[a] $r_{C-C} = 1.33$ Å, $\theta = 116.5°$. [b] $r_{C-C} = 1.338$ Å, $\theta = 117.6°$. [c] $r_{C-C} = 1.45$ Å, $\theta = 146°$.

great for both the singlet and triplet that both are probably unstable with respect to dissociation to two triplet methylenes at the SCF level. We speculate, however, that with sufficient CI the $\phi = 90°$ geometry would probably be found to be bound. Certainly inclusion of CI should reduce the energy of the pyramidalized olefin significantly more than the planar, because of the closer proximity of the filled and unfilled orbitals at distorted geometries. This expectation was confirmed by SCF calculations in which the two highest energy electrons were allowed to occupy nonorthogonal MOs, which is equivalent to 2×2 CI involving the HOMO and LUMO. We found that the planar molecule was stabilized by 17 kcal/mol, relative to the closed-shell SCF result; but the unoptimized $\phi = 90°$ syn geometry was stabilized by 25 kcal/mol, nearly 50% more.

The reason for the sharp rise in energy on going from $\phi =$ 0 to 90° can be discerned in Table III by comparing the results for the planar optimized geometry with those for the 90°, syn pyramidalized, unoptimized one. The overlap integrals between the AOs in the two geometries are essentially identical, except for the p_x–H and p_z–H. The former changes from zero to 0.262 as ϕ varies from 0 to 90°, while the change in the latter is just the reverse. Since at 90° p_z does not overlap the orbitals on the proximate hydrogens, the other carbon atomic orbitals must be used to bond to them. This accounts for the increase in the 2s–H, p_y–H, and p_x–H bond orders shown in Table III. These increases are not without cost, however. They are accompanied by decrease in the bond orders between pairs of AOs on the carbon atoms. Particularly noteworthy is the large decrease in the bond order between the p_x AOs, which form the π bond in the planar molecule. This decrease is consistent with the predicted increase in the occupancy of π^* on pyramidalization, resulting from its mixing with the filled b_{1u} σ orbital in the syn mode. There is also a large drop in the 2s–p_z bond order, but this is accompanied by an increase in p_z–p_z. Note, however, that the p_z–p_z overlap integral is less than half the s–p_z and, moreover, that there are two overlaps of the latter type. Thus, the overlap population in the "σ" bond joining the carbons decreases in going from the planar to the 90° syn pyramidalized geometry.

The diminution of s character in and concomitant weakening of this bond are consistent with the naive picture that, while planar ethylene is formed from σ overlap of the nonbonding σ orbitals of two methylenes, at $\phi = 90°$ the π nonbonding orbitals of the methylenes are used to form the "σ" bond between the carbons. It should be observed, however, that even at $\phi = 90°$ the contribution to the C–C bond involving the 2s orbitals is nonvanishing. In addition, the p_z–H bond order remains essentially unchanged from that in the planar molecule, despite the fact that at $\phi = 90°$ the p_z–H overlap integral is zero. These facts illustrate the shortcomings of the two methylene model for the 90° pyramidalized geometry and show that the C–H bonding orbitals do not follow the motions of the hydrogens perfectly.

Comparison of the overlap populations on going from $\phi =$ 0° to $\phi = 90°$ reveals, somewhat surprisingly, a small increase in C–H bonding (0.413 vs. 0.436). However, there is a large drop in the C–C overlap population (0.598 vs. 0.386). On optimizing the $\phi = 90°$ structure the C–C overlap population is increased to 0.435 with only a small decrease to 0.426 in the C–H. These changes on optimization are the result of many effects, but the single largest is the increase in the p_y–H overlap integral on opening the HCH angle from 117.6 to 146°. This allows a decrease in the p_y–H bond orders with very little net change in the p_y–H overlap population. Associated with the decrease in the p_y–H bond order is a decrease in antibonding between the p_y orbitals. Coupled with the decrease in the p_y–p_y overlap integral on bond lengthening, the resulting reduction in the magnitude of the negative overlap population between p_y AOs makes the most significant contribution to the increase in the C–C overlap population on optimization of the syn 90° structure. The negative H–H overlap population is similarly reduced in magnitude from −0.106 to −0.070 on optimization of the $\phi = 90°$ structure.

Comparison of the syn and anti bond orders at 90° reveals the effect of the fact that π mixes with a_g antibonding σ orbitals in the former mode but with b_{1u} antibonding MOs in the latter. In contrast to a_g orbitals, b_{1u} MOs have a node between the carbons.[13] Consequently, the 2s–2s and p_z–p_z bond orders in the anti geometry are smaller than those in the syn. On the other hand, the pair of 2s–p_z bond orders is larger in the anti. This reflects the fact that the b_{1u} antibonding σ orbital most strongly mixed into π on anti pyramidalization has the 2s AO on one carbon in-phase with the p_z AO on the other. Interestingly, the pair of positive 2s–p_z contributions to the C–C overlap population dominates the negative contributions from 2s–2s and p_z–p_z and acts to stabilize the anti geometry. This has been discussed previously by Hoffmann[23] in connection with his finding that the "π" orbitals in a trans bent acetylene overlap better than those in a cis geometry.

Table III also reveals a greater p_x–H bond order in the anti geometry than in the syn. This difference is even more pronounced at smaller distortion angles (ϕ), where the p_x–p_x bond order is also found to be slightly smaller in the anti than in the corresponding syn geometry. Both these facts point to better orbital following of the motions of the hydrogens along the x axis in anti pyramidalization than in syn. The bond orders indicate that in anti pyramidalization the p_x AOs are used more effectively for C–H bonding than in syn, with a concomitantly greater reduction in the π bond order between the p_x orbitals.

Although the p_x–H bond orders indicate better orbital following along the x axis in the anti than in the syn geometries, as noted above, the electron density does not follow the motions of the hydrogens perfectly in either mode of pyramidalization. This is most evident in the observation that the p_z–H bond orders are essentially the same at both $\phi = 90°$ geometries as in planar ethylene, despite the fact that the corresponding overlap integral is zero at $\phi = 90°$.[24] The degree to which the C–H bonding orbitals follow the motions of the hydrogens can be obtained from the p–H bond orders. These define the components of a vector. The angle between this vector and one joining the C–H nuclei measures the extent of orbital following. The components of the latter vector are easily obtained, since they are proportional to the p–H overlap integrals. In the planar molecule the angle between the two vectors is 2.5°, but at the unoptimized $\phi = 90°$ geometry the angle is 29.6°. Although the components of the two vectors both change on optimization, the angle between the vectors is little affected. It should be noted that, despite the poor orbital following on pyramidalization, the C–H overlap population actually increases. If orbital following were perfect, presumably the C–H overlap population would increase even more. It should be recalled, however, that the increase in C–H overlap populations is achieved at the cost of a substantial decrease in the C–C overlap population. If C–H orbital following were complete, an even larger reduction in the C–C overlap population would be expected. Thus, incomplete C–H orbital following may be seen as a result of a necessary compromise between C–H and C–C bonding, both of which must be simultaneously maintained on olefin pyramidalization.[25]

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(14) The same type of argument can be used to predict that trans bending of acetylene should be favored over cis. After completion of this manuscript, we learned from Professor K. N. Houk that he too had arrived at this argument to explain the preference for trans bending of acetylene that he has calculated.[15] We thank Professor Houk for providing us with a preprint of his manuscript.

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Effect of Protonation of Nitrogen-Containing Organic Molecules on the Reactivity toward Positronium

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Abstract: Positron lifetime parameters in aqueous or methanol solutions of pyrimidine, quinoline, and quinoxaline were determined with and without hydrochloric acid. By analyzing the data, the Ps reaction rate constant k and the Ps inhibition coefficient σ of free molecules and protonated cations were determined. The protonation of these molecules enhances k and σ considerably. The qualitative considerations suggest that the complex formation reaction between Ps and the protonated cations is responsible for the increase of k by protonation.

I. Introduction

The bound state between a positron and an electron, positronium (Ps), can exist in one of the two ground states, i.e., *o*-positronium (*o*-Ps) and *p*-positronium (*p*-Ps). The total angular momentum of *o*-Ps is $\hbar$ and that of *p*-Ps is 0. In free space, *o*-Ps annihilates into three γ quanta with a lifetime of 140 ns and *p*-Ps annihilates into two γ quanta with a lifetime of 0.125 ns. As Ps resembles the hydrogen atom, it can undergo chemical reactions by which its lifetime is shortened. It is well known that Ps is reactive toward inorganic oxidizing agents ($Cr_2O_7^{2-}$, MnO_4^-, IO_4^-, Tl^{3+}, Fe^{3+}, etc.)[1] and organic electron acceptors (nitrobenzene, quinone, tetracyanoquinodimethane, etc.).[2,3]

Up till now, several investigators have studied the effect of complex formation of these inorganic and organic species on their reactivities toward Ps. Lévay et al.[4] and Jansen et al.[5] studied the effect of the charge transfer complex formation of electron acceptors with electron donors. They found that electron acceptors taking part in the complex formation have smaller Ps quenching rate constants and larger Ps inhibition coefficients than those of the uncomplexed electron acceptors. Ache et al.[6,7] and Endo et al.[8] investigated the effect of complex formation of metal ions. They found that the effectiveness of the complexes to quench Ps varies depending on the chemical character of the complexes.

Recently the present authors[9] studied the effect of protonation of "chemically inert" pyridine and observed Ps inhibition by pyridinium ion. This Ps inhibition without Ps quenching was thought to be caused by the change in the local electron distribution in the pyridine ring.

The effect of protonation of nitrogen-containing organic molecules on the reactivity toward Ps was further studied through the positron lifetime measurements in aqueous solutions of pyrimidine and quinoxaline, in methanol solutions of quinoline, and in 1:1 aqueous solutions of pyrimidine, quinoxaline, and quinoline with hydrochloric acid.

II. Experimental Section

Apparatus. Positron lifetime spectra were measured in the usual way by determining the time interval between the detection of a

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