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Sudden Polarization: Pyramidalization of Twisted Ethylene

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Abstract: Nonempirical molecular electronic structure theory has been used to investigate the concept of "sudden polarization". In particular, the departure of twisted ethylene from ideal D_{2d} geometries has been studied. Initially, configuration interaction (CI) studies of all four electronic states (of twisted C_2H_4) arising from the e^2 orbital occupancy were completed. The predicted C–C bond distances and energies relative to the planar ground state follow: $^1B_1$ (N state) 1.49 Å, 2.6 eV; $^3A_2$ (T state) 1.49 Å, 2.7 eV; $^1B_2$ (V state) 1.40 Å, 5.9 eV; $^1A_1$ (Z state) 1.40 Å, 5.8 eV. A major theoretical problem for the zwitterionic Z and V states is to formulate a type of wave function which passes smoothly and correctly from D_{2d} to non-D_{2d} geometries. This problem has been solved and the ensuing calculations predict rather large dipole moments as the Z and V states become pyramidalized. For example, with one of the CH_2 groups bent out of its D_{2d} plane by only 5°, the Z and V state dipole moments μ_z (along the C–C axis) are +1.25 and −1.18 D, respectively. The differing dipole moment signs are meant to imply that for the Z state, the pyramidalized methylene carries the negative charge. The Z state, the lower of the two zwitterionic states, has a pyramidalization angle θ of 31° at its equilibrium geometry.

Background and Development

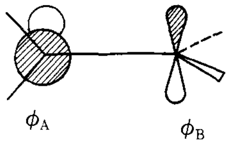
Although the planar ground state of ethylene is stable with respect to the twisting of the double bond, this is not true of the low-lying states. At the perpendicular D_{2d} ($\theta = 90°$) geometry there are four π^2 ($2e^2$) states.[1,2] The two lowest of these states, which are quite close in energy, are the $^1B_1$ (N state) and the $^3A_2$ (T state). The highest two, also quite close to each other in energy, are the $^1B_2$ (V state) and the $^1A_1$ (Z state). Only the lowest of the four states (N state), which correlates with the planar ground state and corresponds to the rotational barrier of ethylene, is unstable with respect to twisting from the D_{2d} geometry. The other low-lying twisted state ($^3A_2$ state) correlates with the planar $^3B_{1u}$ (π,π^*) T state.

The higher pair are known to be ionic[1,3] and highly polarizable[4] and thus are considered to be zwitterionic states. Of these, the $^1B_2$ or V state correlates with the planar $^1B_{1u}$ (π,π^*) V state while the $^1A_1$ or Z state correlates with a much higher planar state where both π electrons have been excited to the π^* orbital. In the absence of an external field, in D_{2d} symmetry, the wave functions of the zwitterionic states may be qualitatively described as

$$\text{Z state} \quad \psi = \phi_A(1)\phi_A(2) + \phi_B(1)\phi_B(2) \qquad (1)$$

$$\text{V state} \quad \psi = \phi_A(1)\phi_A(2) - \phi_B(1)\phi_B(2) \qquad (2)$$

where the atomic carbon p orbitals ϕ_A and ϕ_B are sketched below.



As written neither of these states has a dipole moment. However, when an interaction is introduced by an external field or by a geometry change these states may mix, causing distinct polarity. The requirements for mixing are that first, there must be little or no incipient overlap between radical sites, and second, that there must be a dissymmetry between the sites.[5] In other related systems of interest, substituents other than hydrogen may also result in the necessary dissymmetry between the radical sites.

Bonacic-Koutecky, Bruckmann, Hiberty, Koutecky, Leforestier, and Salem have noted[5] that the charge separation for the related allyl system peaks very sharply about the twisted geometry and drops to practically zero outside a narrow 2° region about $\theta = 90°$. This is the origin of the term "sudden polarization". This zwitterionic polarization can be qualitatively understood by the coupling matrix

$$H = \begin{pmatrix} E_a - E & H_{ab} \\ H_{ab} & E_b - E \end{pmatrix} \qquad (3)$$

where E_a and E_b are the electronic energies of the ionic forms of ϕ_A and ϕ_B, and H_{ab} represents the exchange and overlap terms between the two forms.

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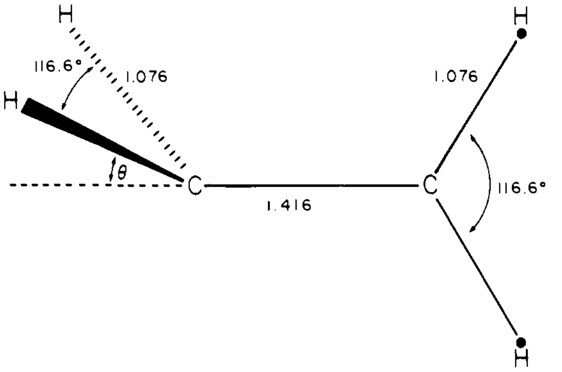

Figure 1. Coordinate system for the pyramidalization of twisted (D_{2d}) ethylene. θ is the angle of pyramidalization, and the other geometrical parameters were constrained as indicated. The C-C bond defines the z axis, while the plane of symmetry is the XZ plane.

If E_a and E_b are identical then the eigenvectors are as expressed in eq 1 and 2; when they differ, the two states will mix. The amount of zwitterionic mixing is roughly proportional to $(E_a - E_b)/H_{ab}$ where infinite mixing corresponds to the two completely ionic species. At $\theta = 90°$ (twisted) H_{ab} is equal to a small exchange term K_{ab}, and only a small dissymmetry is needed for substantial mixing.

For ethylene the simplest method to produce the necessary dissymmetry involves distorting the geometry of the molecule. The most effective distortion is the pyramidalization of one of the methylene groups, keeping the molecule in C_s symmetry. This is illustrated in Figure 1, in which θ is the angle of pyramidalization. Such a distortion allows $|E_a - E_b|$ to increase uniformly and at the same time does not introduce any overlap contribution to H_{ab}.

The above considerations suggest an inherent theoretical interest in the concept of sudden polarization of zwitterionic states. However, much of the motivation for this theoretical activity may be traced to a paper which appeared in 1970 by Dauben and Ritscher.[7] They obtained highly stereospecific products in the photocyclization of *trans*-3-ethylidenecyclooctene. Dauben and Ritscher postulated that their results could be understood in terms of the transient formation of a zwitterionic species, where the charge separation results from rotation around the ring double bond. More recently Dauben and co-workers[8] have extended this proposal to photochemistry of *s-cis,s-trans*-hexatrienes. These experimental findings, as well as the independent theoretical work of Wulfman and Kumei,[4] have motivated a number of continuing theoretical studies by Salem and others.[9-13]

The purpose of the present paper is to report a definitive ab initio theoretical study of the simplest example of sudden polarization. First we examine in detail the four lowest electronic states of twisted ethylene. This is followed by an investigation of the consequences of distortion, specifically pyramidalization of one of the two methylene groups. Perhaps the most critical question to be answered is just how "sudden" the sudden polarization really is. As will be seen in the next section, there are any number of simple (and complicated) wave functions which actually predict the *perfectly* D_{2d} V and Z states to have sizable dipole moments. Since this is physically impossible, one must be very careful to verify the genuineness of any apparently "sudden" polarization.

Theoretical Approach

To examine the concept of sudden polarization one requires a consistent theoretical model which yields an identically zero dipole moment in a natural way for the D_{2d} geometry. Obviously, a zero dipole moment will be guaranteed if one performs restricted self-consistent field (SCF) calculations constraining each molecular orbital to transform according to one of the D_{2d} irreducible representations. The four e^2 wave functions all arise from the electron configuration[2]

$$1a_1^2 1b_2^2 2a_1^2 2b_2^2 3a_1^2 1e^4 2e^2 \qquad (4)$$

and have the analytical forms

$$\mathrm{N}\ ^1\mathrm{B}_1\ \frac{1}{\sqrt{2}}[2e_x\alpha\, 2e_y\beta - 2e_x\beta\, 2e_y\alpha] \qquad (5)$$

$$\mathrm{T}\ ^3\mathrm{A}_2 \quad 2e_x\alpha\, 2e_y\alpha \qquad (6)$$

$$\mathrm{V}\ ^1\mathrm{B}_2\ \frac{1}{\sqrt{2}}[2e_x\alpha\, 2e_x\beta - 2e_y\alpha\, 2e_y\beta] \qquad (7)$$

$$\mathrm{Z}\ ^1\mathrm{A}_1\ \frac{1}{\sqrt{2}}[2e_x\alpha\, 2e_x\beta + 2e_y\alpha\, 2e_y\beta] \qquad (8)$$

Although each of these SCF wave functions will yield an identically zero dipole moment, it should be apparent that they are not applicable to the distortions from D_{2d} symmetry required to examine sudden polarization.

Since pyramidalized, twisted ethylene (see Figure 1) maintains only a plane of symmetry, it is helpful to recast (5-8) in terms of this lower symmetry. In C_s symmetry all four states share the inner electron orbital occupancy

$$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 6a'^2\ 1a''^2 \qquad (9)$$

and have the precise forms

$$\mathrm{N}\ ^1\mathrm{B}_1\ \frac{1}{\sqrt{2}}[7a'\alpha\, 2a''\beta - 7a'\beta\, 2a''\alpha] \qquad (10)$$

$$\mathrm{T}\ ^3\mathrm{A}_2 \quad 7a'\alpha\, 2a''\alpha \qquad (11)$$

$$\mathrm{V}\ ^1\mathrm{B}_2\ \frac{1}{\sqrt{2}}[7a'\alpha\, 7a'\beta - 2a''\alpha\, 2a''\beta] \qquad (12)$$

$$\mathrm{Z}\ ^1\mathrm{A}_1\ \frac{1}{\sqrt{2}}[7a'\alpha\, 7a'\beta + 2a''\alpha\, 2a''\beta] \qquad (13)$$

It is noteworthy that restricted SCF calculations of the forms (10-13) also maintain perfect D_{2d} symmetry if the nuclei belong to the D_{2d} point group. Thus SCF wave functions (10-13) all yield identically zero dipole moments for twisted ethylene.

However, as twisted ethylene is pyramidalized, the point group is lowered to C_s, and the coefficients of the two determinants in (12) and (13) need no longer be equal. That is, for both the V and Z states (which now are of ^{1}A$'$ symmetry) the optimum combination of the . . . 7a$'^2$ and . . . 2a$''^2$ configurations should be determined by a multiconfiguration (MC) SCF procedure.[14] However, there is a fatal flaw associated with this strategy. Namely, the MCSCF procedure does not[17] yield

$$C_1 = C_2 = \frac{1}{\sqrt{2}} \qquad (14)$$

as the pyramidalized form returns to twisted D_{2d}. In other words, this two-configuration (TC) SCF "breaks" the D_{2d} symmetry and yields polar TCSCF wave functions for both the ^{1}B$_2$ and ^{1}A$_1$ states. Since it is not possible for any D_{2d} twisted ethylene state to have a nonzero dipole moment, it is clear that a nonphysical solution of the TCSCF equations has been obtained. This illustrates in a dramatic manner the point made at the conclusion of our introductory section. Namely, there is a severe danger of associating the term "sudden polarization" with a nonphysical symmetry breaking due to the inadequacy of simple wave functions.

What is required is a description of the V and Z states which properly yields a zero dipole moment for D_{2d} geometries and is equally meaningful for pyramidalized C_s geometries. The most obvious wave function which satisfies this requirement is a full configuration interaction (CI). Unfortunately, full CI is not practical using basis of the type considered desirable,

Table I. Carbon-Carbon Bond Distances and Energies for D_{2d} Twisted Ethylene[a]

		DZ SCF			DZ two-electron CI			DZ 12-electron CI			DZ + d SCF			DZ + d two-electron CI		
		r_e (CC)	E, hartrees	E, eV	r_e (CC)	E, hartrees	E, eV	r_e (CC)	E, hartrees	E, eV	r_e (CC)	E, hartrees	E, eV	r_e (CC)	E, hartrees	E, eV
N	$^1B_1$	1.481	−77.9416	1.91	1.481	−77.9419	2.79	1.494	−78.1048	2.44	1.476	−77.9658	2.05	1.474	−77.9667	2.95
T	$^3A_2$	1.478	−77.9435	1.86	1.478	−77.9438	2.74	1.496	−78.1013	2.53	1.472	−77.9680	1.99	1.470	−77.9690	2.89
Z	$^1A_1$	1.383	−77.7781	6.36	1.380	−77.7920	6.87	1.413	−77.9784	5.88	1.369	−77.8101	6.29	1.367	−77.8294	6.69
V	$^1B_2$	1.380	−77.7842	6.20	1.379	−77.7933	6.84	1.416	−77.9735	6.04	1.363	−77.8164	6.12	1.364	−77.8300	6.67

[a] Energies in eV are given relative to ground-state planar ethylene at its experimental equilibrium geometry.

namely, of double ζ or better quality. A very simple approach which goes smoothly from D_{2d} to C_s geometries is the use of a constrained SCF procedure. For example, for the V state, the coefficients of the $7a'^2$ and $2a''^2$ configurations are constrained to be $\pm 1/\sqrt{2}$, even though we know that these coefficients will be less than optimum for severely distorted geometries. The latter problem can be corrected most simply by carrying out a full CI for the outer two electrons only. In retrospect, this constrained SCF followed by full two-electron CI appears to be the simplest model capable of yielding qualitatively plausible results. Larger CIs, involving many more of the valence electrons, can actually lead to nonphysical results. For example, if the iterative natural orbital procedure is applied to a 12-electron CI including all single and double excitations, we obtain nonzero dipole moments for the perfectly D_{2d} V and Z states.

Four States of Twisted Ethylene

Our first calculations were carried out to determine the equilibrium C-C separations for the N, T, V, and Z states of twisted ethylene. The standard Dunning-Huzinaga[15] contracted Gaussian double ζ (DZ) basis set, designated C(9s 5p/4s 2p), H(4s/2s), was adopted. The C-H distance, 1.076 Å, and HCH angles, 116.6°, were restricted to be those determined experimentally[16] for the planar ethylene $^1A_{1g}$ ground state. CI was carried out including all single and double excitations (except that the two core orbitals were always doubly occupied) relative to the respective SCF reference configuration (5), (6), (7), or (8). The results of these calculations are summarized in Table I.

Table I shows that the CC bond distances of the twisted N and T states are ~1.49 Å, while those of the higher lying Z and V states are ~1.40 Å. These two distinct bond distances were synthesized by adding to the DZ 12-electron CI values a correction for the shortening of these bond distances due to carbon d functions. Note for the N $^1B_1$ state, for example, that the DZ + d SCF bond distance is 0.005 Å shorter than the DZ SCF result, while the DZ + d 2e⁻ CI value of r_e (CC) is 0.007 Å shorter than the DZ 2e⁻ CI result. Thus our primary result is that the N and T C-C bond distances are about equal, as are the Z and V distances.

The only previous comparable ab initio studies of D_{2d} twisted ethylene are those of Buenker and Peyerimhoff (BP).[17] BP used a somewhat larger basis set, but a less complete CI procedure (involving selection of configurations), and find the same difference in bond distances. They predict the N and T states to have a slightly shorter (1.48 Å) bond distance, and the Z (1.41) and V (1.43) CC separations to be slightly longer than in the present research.

In good qualitative agreement with the previous work of BP,[17] we predict the order of D_{2d} ethylene states to be N, T, Z, V. At the DZ CI level, Table I shows that the predicted excitation energies are 2.44, 2.53, 5.88, and 6.04 eV, compared with the BP results 2.71, 2.79, 6.14, and 6.22 eV. From our results (columns 2 and 4 of Table I) including carbon d functions, we can make "final" theoretical predictions of 2.59, 2.67, 5.76, and 5,92 eV.

Both BP and this research predict, in violation of Hund's rules, that the $^1B_1$ state lies below the $^3A_2$ state. Since the two states have nearly identical D_{2d} geometries, the violation of Hund's rules is not a geometrical effect. Perhaps one should not be too surprised by this behavior since Hund's rules are only rigorously valid when the single-configuration approximation is applied to both states using the *same* set of molecular orbitals.

A perhaps even more interesting result is that the order of the Z and V states is not independent of the level of theory applied. Namely, the 12e⁻ CI is the only level to predict that the Z $^1A_1$ state lies below the V $^1B_2$ state. However, we are reasonably confident about this prediction since (a) it holds up when we correct for the effect of d functions in an additive way and (b) BP make the same prediction.[17] As we shall see, however, the electronic structure of the pyramidalized Z and V states changes rather drastically in going from the 2e⁻ CI to the 12e⁻ CI.

Pyramidalization of Twisted Ethylene

Levels of theory comparable to those applied to D_{2d} C_2H_4 were used to examine the sudden polarization problem. However, for these C_s geometries we must include in the CI all single and double excitations relative to the two (now independent) configurations .... $7a'^2$ and .... $2a''^2$. With the double ζ basis set,[15] this means that a total of 6238 configurations were included in the 12-electron CI calculations.

Tables II and III summarize the application of five levels of theory to the pyramidalization of the V and Z states. By "DZ SCF" in these tables, we mean the *constrained* SCF procedure discussed above in which the coefficients of the $7a'^2$ and $2a''^2$ configurations are required to be $\pm 1/\sqrt{2}$. As is evident from Tables II and III these V and Z state wave functions are effectively prevented from having a significant dipole moment component along the z(C-C) axis.

The most important conclusion of this paper is that both the V and Z states develop sizable dipole moments, ~1.2 D, for pyramidalization angles as small as 5°. For a C-C separation of 1.416 Å, this corresponds to having opposite partial charges of 0.18 e. Thus the term "sudden" polarization seems reasonably appropriate.

Our second most important conclusion is that simpler CI methods may substantially overestimate the "suddenness" of the sudden polarization. This is readily seen by comparing columns 2 and 3 of Table II at a pyramidalization angle of 5°. The 2e⁻ CI predicts a V state dipole moment $\mu_z = +2.89$ D, while the much more complete 12e⁻ CI yields −1.18 D for μ_z. We shall return to the change in sign shortly, but here restrict consideration to the 1.71-D difference in $|\mu_z|$. This difference can only be ascribed to the neglect of correlation effects involving the ten other valence electrons. It is encouraging that as one goes to larger pyramidalization angles, this difference between the two levels of theory fades away. For example, at $\theta = 10°$ the 12e⁻ CI value of μ_z has increased to 2.71 D, now only 0,7 D less in magnitude than the 2e⁻ CI result.

The difference in sign of the 2e⁻ CI and 12e⁻ CI μ_z values is a simple consequence of the fact that the order of the V and Z states switches between these two levels of theory. That is, for pyramidalized geometries the V and Z states are both of

Table II. Pyramidalization of the V $^1B_2$ State of Twisted Ethylene[a]

pyramidalization angle, deg	DZ SCF			DZ two-electron CI			DZ 12-electron CI			DZ + d SCF			DZ + d two-electron CI		
	E, kcal	μ_x, D	μ_z, D	*E*, kcal	μ_x, D	μ_z, D	*E*, kcal	μ_x, D	μ_z, D	*E*, kcal	μ_x, D	μ_z, D	*E*, kcal	μ_x, D	μ_z, D
0	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00
0.25	0.000	−0.01	−0.00	0.000	−0.01	0.01	0.001	−0.01	−0.00	0.001	−0.01	0.00	0.001	−0.01	0.02
0.5	0.004	−0.03	−0.00	0.004	−0.03	0.06	0.004	−0.03	−0.01	0.003	−0.02	0.00	0.004	−0.02	0.07
1.0	0.014	−0.06	−0.00	0.015	−0.06	0.22	0.014	−0.05	−0.05	0.011	−0.05	0.00	0.012	−0.05	0.33
1.5	0.033	−0.09	−0.00	0.032	−0.09	0.50	0.031	−0.08	−0.11	0.026	−0.07	0.00	0.024	−0.08	0.72
2.0	0.058	−0.12	−0.00	0.053	−0.13	0.86	0.055	−0.11	−0.20	0.046	−0.10	0.00	0.034	−0.12	1.21
3.0	0.131	−0.17	−0.00	0.089	−0.23	1.72	0.131	−0.15	−0.45	0.103	−0.15	0.00	0.032	−0.21	2.20
4.0	0.232	−0.23	−0.00	0.104	−0.34	2.44	0.254	−0.18	−0.78	0.184	−0.19	0.00	−0.012	−0.31	2.83
5.0	0.364	−0.29	−0.01	0.090	−0.45	2.89	0.438	−0.20	−1.18	0.289	−0.24	0.01	−0.095	−0.40	3.13
10	1.482	−0.56	−0.03	−0.275	−0.96	3.41	2.658	−0.22	−2.71						

[a] Pyramidalization angles refer to the angle between the tilted methylene plane and the original methylene plane of twisted ethylene. The C-C separation was fixed at 1.416 Å, and the C-C bond is the *z* axis.

Table III. Pyramidalization of the Z $^1A_1$ State of Twisted Ethylene[a]

pyramidalization angle, deg	DZ SCF			DZ two-electron CI			DZ 12-electron CI			DZ + d SCF			DZ + d two-electron CI		
	E, kcal	μ_x, D	μ_z, D	*E*, kcal	μ_x, D	μ_z, D	*E*, kcal	μ_x, D	μ_z, D	*E*, kcal	μ_x, D	μ_z, D	*E*, kcal	μ_x, D	μ_z, D
0	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00
0.25	0.001	−0.01	0.00	0.001	−0.01	−0.03				0.001	−0.01	0.00	0.001	+0.01	−0.04
0.5	0.004	−0.03	0.00	0.004	−0.03	−0.12				0.004	−0.02	0.00	0.004	−0.02	−0.14
1.0	0.017	−0.05	0.00	0.019	−0.05	−0.47	+0.014	−0.05	+0.05	0.014	−0.05	0.00	0.017	−0.05	−0.56
1.5	0.039	−0.08	0.00	0.047	−0.06	−1.02				0.032	−0.07	0.00	0.044	−0.05	−1.19
2.0	0.069	−0.11	0.00	0.094	−0.07	−1.67	+0.057	−0.11	+0.20	0.057	−0.09	0.00	0.091	−0.05	−1.90
3.0	0.155	−0.16	0.00	0.254	−0.06	−2.74				0.130	−0.13	0.00	0.257	−0.04	−2.90
4.0	0.275	−0.22	0.00	0.512	−0.06	−3.25				0.231	−0.18	0.00	0.523	−0.04	−3.31
5.0	0.431	−0.27	0.01	0.860	−0.07	−3.46	+0.270	−0.31	+1.25	0.362	−0.23	0.01	0.880	−0.04	−3.46
10.0	1.746	−0.53	0.02	3.876	−0.11	−3.62	0.231	−0.83	+2.77						
15.0	4.022	−0.78	0.05				−0.504	−1.28	+3.19						
20.0	7.400	−1.01	0.08				−1.490	−1.67	+3.30						
25.0	12.103	−1.23	0.10				−2.351	−2.03	+3.34						
30.0	18.399	−1.44	0.12				−2.760	−2.35	+3.35						
35.0	26.579	−1.64	0.12				−2.506	−2.62	+3.33						

[a] Pyramidalization angles refer to the angle between the tilted methylene plane and the original methylene plane of twisted ethylene. The C-C separation was fixed at 1.416 Å, and the C-C bond is the *z* axis.

$^1A'$ symmetry, and for the lower of the two the nonplanar methylene group carries the "minus" charge. This is of course consistent with the fact that CH_3^- is slightly pyramidal,[18] while CH_3^+ is planar.[19] More specifically, our definition of the sign of μ_z is meant to associate a positive value of μ_z with a negatively charged pyramidalized CH_2 group. Thus positive μ_z values are always predicted for the energetically *lower* of the Z and V states.

Equilibrium Geometry of the Z State

Among the geometries considered for the V state of C_2H_4, the twisted or D_{2d} structure lies lowest. This is not surprising, since placing a positive charge on the pyramidalized CH_2 moiety is unfavorable, in analogy with the known planar structure[19] of CH_3^+.

However, one might expect the lower lying Z state to actually favor pyramidalized geometries. This expectation is fulfilled in Table III, where it is seen that the relative energy of pyramidalization becomes negative at $\theta = 15°$. The minimum computed energy occurs at $\theta = 30°$ and further analysis considering in addition several adjacent angles suggests an equilibrium angle $\theta = 30.7°$. This geometry yields an energy 2.8 kcal below the reference energy of D_{2d} twisted ethylene and 5.76 eV above that of the C_2H_4 $^1A_{1g}$ electronic ground state.

We should note explicitly that the results of Table III do *not* imply that there is a maximum in the potential energy curve for pyramidalization. To establish the existence of such a maximum (or saddle point), a full optimization of all other geometrical parameters would be required. We suspect that the minimum energy pathway for the pyramidalization goes down monotonically from $\theta = 0°$ to $\theta = 30°$.

Table IV. Coefficients of the Two Leading Configurations in Two Different CI Wave Functions for the Z State of Ethylene

pyramidalization angle, deg	two-electron CI			12-electron CI		
	$c_1(7a'^2)$	$c_2(2a''^2)$	μ_z, D	$c_1(7a'^2)$	$c_2(2a''^2)$	μ_z, D
0	0.703	0.703	0.00	0.672	0.672	0.00
1.0	0.656	0.747	−0.47	0.677	0.667	+0.05
2.0	0.517	0.849	−1.67	0.692	0.651	+0.20
5.0	0.161	0.981	−3.46	0.784	0.536	+1.25

Concluding Discussion

To examine in more detail the differences between the π CI and large CI dipole moments μ_z, we show in Table IV the weights of the two leading configurations in the Z state wave functions for several slightly pyramidalized geometries. This was done after it was established that no individual configuration included in the 12e⁻ CI but not considered in the 2e⁻ CI is unusually important.

As expected from the immediately preceding observation, the contributions of the $7a'^2$ and $2a''^2$ states are radically different in the two Z state wave functions. As anticipated from previous sections, the structure of the V state 2e⁻ CI wave function is actually much more similar to that of the 12e⁻ CI Z state. The main difference is that the weightings of the $7a'^2$ and $2a''^2$ configurations are nearly equal in the large CI, whereas they become very different even for $\theta = 2°$ with the π-electron CI.

The above comments notwithstanding, it has been shown that the pyramidalization of twisted ethylene does indeed lead to strong changes in electronic structure as a function of conformation. The present paper, then, provides a firm foundation for the continuing research of Salem and colleagues[6] on the subject of sudden polarizations.

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Conformations, Stabilities, and Charge Distributions in 2- and 3-Monosubstituted Thiophenes. An ab Initio Molecular Orbital Study

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Abstract: Ab initio molecular orbital theory with the STO-3G basis set is used to determine the equilibrium geometry for thiophene and to study the conformations, stabilities, and charge distributions of several monosubstituted thiophenes. The conformational preferences are rationalized in terms of orbital interactions and electrostatic interactions. The stabilizing effect of substituents attached to thiophene, furan, and benzene rings is compared. As with the furyl group, the thienyl group usually prefers to act relative to phenyl as a π-electron donor and σ-electron acceptor and it is stabilized by substituents characterized as being π-electron acceptors and σ-electron donors. These effects are greater at the 2 than at the 3 position. Differences between the thiophene and furan derivatives are discussed.

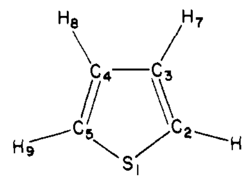
Introduction

The conformational problem which arises when an asymmetric planar substituent is attached to an unsaturated five-membered ring has attracted continued theoretical and experimental interest.[1-7] The preference between the two possible planar conformations of the resulting monosubstituted heterocycles is often strongly medium dependent because of their differing polarities. In these circumstances, the conformational preference in the absence of solvent is of some importance. Ab initio molecular orbital theory provides a means of determining such intrinsic conformational preferences. Detailed ab initio studies have previously been reported for monosubstituted furans[1,2] and pyrroles.[2,3] In this paper, we present the results of a similar though less extensive study for 2- and 3-substituted thiophenes, Th–Z, with Z = H, CHO, OH, $CHCH_2$, CH_3, CN, NO_2, F, and Li. In addition to the conformational preferences that are of interest for some of these molecules, we examine in all cases the effect of the substitutent on stability and charge distribution. Extensive comparison is made with the previously reported results for monosubstituted furans[1] and monosubstituted benzenes.[8]

Computational Aspects and Results

Standard LCAO SCF molecular orbital theory was employed using a modified version of the GAUSSIAN 70 system of programs.[9,10] Unless otherwise specified, calculations were carried out at the STO-3G minimal basis set level of theory.[11,12] Some calculations were carried out with the split-valence 44-31G set.[13] Although there is some debate in the literature as to the importance of inclusion in the basis set of d-type functions on sulfur, we note that both STO-3G and 44-31G basis sets have been successfully employed in previous studies[14-16] of the structures and energies of sulfur-containing molecules.

As a first step in the present study, the geometry of thiophene (**1**) was fully optimized subject only to a C_{2v} symmetry constraint. The optimized structure and comparative experimental data[17-19] are shown in Table I.



1

For the substituted thiophenes, the geometry of the thiophene nucleus was taken from the STO-3G fully optimized structure while standard bond lengths and angles[20] were used for the substituent groups. Only cis and trans conformations were considered in this work; the cis form is defined as having the heaviest (i.e., generally nonhydrogen) atom of a substituent group cis to the ring sulfur atom (cf. **2** and **3**). For a methyl

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