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Molecular Orbital Theory of the Electronic Structure of Molecules. 37. Transition States for Internal Rotation in Allene

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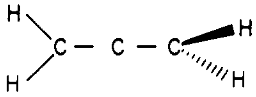
Abstract: The transition state for internal rotation in allene is studied by ab initio molecular orbital methods which include correlation energy corrections. It is concluded that the ^1A_g state of D_{2h} planar allene with four π-electrons lies about 76 kcal/mol above the D_{2d} ground state, in good agreement with previous calculations. It is found that the lowest energy form of planar allene is a bent C_{2v} structure in a $^3A_2$ state with three π-electrons. This has an energy about 48 kcal/mol above the ground state. The lowest planar singlet state is $^1A_2$ and is 2 kcal/mol higher, in good agreement with estimates of the barrier from experimental data on 1,3-dialkyl allenes. It is concluded that deformation of the CCC angle during rotation lowers the barrier by about 6 kcal/mol.

Introduction

The internal rotation barrier in allene (**1**) is usually discussed in terms of a planar D_{2h} transition state (**2**). The electronic structure and energies of low-lying states of **2** have been the subject of several molecular orbital studies[2-6] leading to a wide range of calculated barriers.[7] The three most significant orbitals of **2** (apart from those corresponding to inner shells and σ-bonds) are illustrated schematically in Figure 1. $1b_{3u}$ is π-bonding and has the lowest energy of these. $1b_{2g}$ and $2b_{2u}$ are nonbonding and of comparable energy. Assignment of four electrons to these orbitals gives rise to the states:



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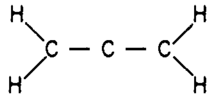

2

2a	$(1b_{3u})^2(1b_{2g})^2$	^1A_g
2b	$(1b_{3u})^2(1b_{2g})(2b_{2u})$	^3A_u
2c	$(1b_{3u})^2(1b_{2g})(2b_{2u})$	^1A_u
2d	$(1b_{3u})^2(2b_{2u})^2$	^1A_g

Buenker[2] carried out closed shell Hartree-Fock calculations on the singlet states **2a** and **2d** and established that **2a** was lower in energy. The corresponding rotation barrier was found to be 82 kcal/mol, substantially larger than the recently established experimental values of 46-47 kcal/mol for 1,3-dialkyl-substituted allenes[7] and an estimate of 50 kcal/mol for unsubstituted allene.[8] However, Buenker gave qualitative arguments that the ground state of **2** is really the triplet **2b** with the corresponding singlet state **2c** only slightly above. More recently, Staemmler[5] has undertaken open-shell restricted Hartree-Fock calculations on the singlet state **2c** and has obtained a theoretical barrier of 50 kcal/mol. Dykstra[6] found a similar value (49 kcal/mol). Staemmler predicted only a small increase due to electron correlation, but Dykstra suggested that such a correction might raise the barrier to as much as 70 kcal/mol.

Roth et al.[7] pointed out that, in view of the nonlinearity of the vinyl radical C═C—H sequence, the possibility of a bent C_{2v} planar transition state (**3**) can not be ruled out. In terms of electronic structure, this is because the nonbonding orbital $2b_{2u}$ (Figure 1) acquires s-character becoming a hybrid in C_{2v} symmetry (Figure 2). Hence, if this orbital is occupied, the energy may be lower with the bent C-C-C geometry. The states **2a–2d** then become (in C_{2v} notation):

3

3a	$(1b_1)^2(1a_2)^2$	$^1A_1$
3b	$(1b_1)^2(1a_2)6a_1)$	$^3A_2$
3c	$(1b_1)^2(1a_2)(6a_1)$	$^1A_2$
3d	$(1b_1)^2(6a_1)^2$	$^1A_1$

Evidently **3b, 3c,** and **3d** may have minima with nonlinear CCC geometries. The aim of this paper is to investigate the struc-

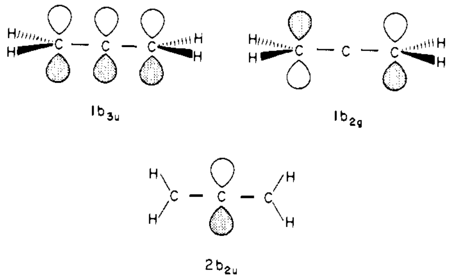

Figure 1. Molecular orbitals of D_{2h} planar allene.

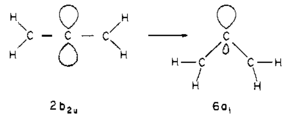

Figure 2. Acquisition of s-character by the in-plane nonbonding molecular orbital under C–C–C bending.

Table I. Hartree-Fock/STO-3G Geometries Constrained to D_{2h} Symmetry[a]

Parameter	2a	2b	2d
R(C-C)	1.322	1.359	1.313
R(C-H)	1.072	1.086	1.120
∠(CCH)	111.48	122.09	126.35

[a] Distances in angstroms and angles in degrees.

Table II. Hartree-Fock/STO-3G Geometries Contrained to C_{2v} Symmetry[a]

Parameter	3b	3d
$R(C_1-C_2)$	1.381	1.402
$R(C_1-H_1)$	1.083	1.096
$R(C_1-H_2)$	1.082	1.099
$\angle(C_1C_2C_3)$	135.4	102.8
$\angle(H_1C_1C_2)$	121.5	121.8
$\angle(H_2C_1C_2)$	121.5	126.5

[a] Distances in angstroms and angles in degrees.

tures of these states and to assess the consequences of CCC bonding on the rotational barrier of allene.

Method

Initially, geometry optimizations on **a**, **b**, and **d** were carried out using Hartree-Fock theory and the minimal STO-3G basis set.[9] For the closed-shell singlet states **a** and **d**, restricted theory (RHF) was used. For the triplet states **b**, we applied the spin-unrestricted version (UHF). These studies were followed by single calculations at higher levels of theory using these geometries. To test the effects of larger basis sets, the HF/4-31G and HF/6-31G* methods were applied.[10,11] To evaluate the role of correlation, second-order Møller-Plesset theory[12] was used with the 4-31G basis (UMP2/4-31G). For the structures **2a**, **2b**, and **3b**, these calculations were refined to configuration interaction with single and double substitutions of spin orbitals in the Hartree-Fock reference determinant (apart from substitutions involving carbon inner shells). This technique (UHFCISD/4-31G) was further corrected for size-consistency errors by a method described elsewhere.[13]

The open-shell singlet state **c** cannot be studied directly using these techniques. The energy of this state relative to the triplet **b** was estimated by (1) applying restricted Hartree-Fock (RHF) theory to the triplet and (2) estimating the elevation of the open-shell singlet **c** above the triplet **b** as twice the exchange integral between the singly occupied orbitals. No geometry optimization was done on the singlet. As the exchange integral is quite small, it is reasonable to suppose that the structure optimized for the triplet is also sufficient for the singlet.

Results and Discussion

The RHF/STO-3G equilibrium geometry for the allene structure **1** has been published previously.[14] For the states **2a**, **2b**, **2d**, **3b**, and **3d**, the corresponding parameters (UHF/STO-3G for triplets) are given in Tables I and II. The closed shell singlet **3a** with four π-electrons was found to return to the more symmetrical form **2a**, consistent with absence of electrons in the in-plane nonbonding orbital $2b_{2u} \leftrightarrow 6a_1$ (Figure 2). The triplet state **3b** is bent with a CCC angle of 135.4°. The singlet state **3d** is more strongly bent (CCC angle of 102.8°) as expected since it has two electrons in the $6a_1$ orbital. These angles are close to triplet and singlet values in CH_2. Total energies for the closed-shell singlet and triplet states are given in Table III. Table IV gives the energies relative to that of the D_{2d} equilibrium ground state.

Let us first consider rotation through the 4π ^1A_g closed shell singlet state of the planar form **2a**. As noted above, this state has a linear CCC structure. Our best Hartree-Fock barrier for ^1A_g (with the 6-31G* basis) is 70.8 kcal/mol. This may be compared with previous estimates of 82 by Buenker,[2] 73 by Schaad et al.,[3] and 68 by Dykstra.[6] The correlation correction (using MP2/4-31G) actually increases the barrier by 5.1 kcal/mol. Adding this to the 6-31G* Hartree-Fock value gives 75.9 kcal/mol as our best estimate of the energy of **2a** relative to **1**. This is close to the best value of Dykstra (76.2 kcal/mol) using similar methods. These values are substantially higher than the experimental estimate (50 kcal/mol) and indicate that the lowest energy isomerization path does not go through the planar closed-shell ^1A_g state.

The results for the 2π ^1A_g closed shell state (**2d**) give an even higher barrier of 126.9 kcal/mol in the D_{2h} form (at RHF/6-31G*). This was also found by Buenker.[2] As noted above, this state does bend to **3d** (Figure 2), significantly lowering the barrier to 78.1 kcal/mol. Correlation does not change this significantly. However, this value is still substantially higher than that obtained for the 4π ^1A_g closed shell state. We conclude that bending does not lower the energy of this state sufficiently to make it a possible route for the lowest energy rotation path.

As with previous studies, our results suggest that the lowest energy state of planar D_{2h} allene is the triplet ^3A_u state **2b**. At our best Hartree-Fock level (UHF/6-31G*), this is 36.4 kcal/mol above the ground state. A previous (restricted) Hartree-Fock value for this difference is 49 kcal/mol by Dykstra.[6] However, these values are expected to be low as correlation energy correction is generally greater in closed shell singlet states than in triplets. According to the HFCISD/4-31G results reported in Table III, the correlation energy lowering (frozen core + size-consistency correction) is 0.29649 hartrees in the ground state and 0.26777 hartrees in the planar ^3A_u state. The difference would increase the energy of **2b** relative to **1** by 18.0 kcal/mol. Combining with the Hartree-Fock value of 36.4 kcal/mol gives our final estimate of 54.4 kcal/mol for **2b**.

As noted previously, a lower energy triplet state **3b** can be obtained by lowering the symmetry to C_{2v}. Our best Hartree-Fock (UHF/6-31G*) energy is lowered thereby to 28.5 kcal/mol above the ground state. Again, this must be too small. At the UHFCISD/4-31G (corrected) level, the correlation energy lowering is 0.26582 hartrees in the $^3A_2$ state, indicating that

$$E_{\text{correlation}}(\mathbf{3b}) - E_{\text{correlation}}(\mathbf{1}) = 19.2 \text{ kcal/mol}$$

If this is added to our best Hartree-Fock (UHF/6-31G*)

Table III. Total Energies (hartrees)

State				UHF/STO-3G	UHF/4-31G	UHF/6-31G*	UMP2/4-31G	UHFCISD/4-31G[a]	UHFCISD/4-31G[a] (corr)
D_{2d}	**1**	Perpendicular	$^1A_1$	−114.42172	−115.69835	−115.86070	−115.96480	−115.96351	−115.99484
D_{2h}	**2a**	Planar (4π)	^1A_g	−114.27359	−115.58369	−115.74785	−115.84201		
	2b	Planar (3π)	^3A_u	−114.37197	−115.63938	−115.80277	−115.86475	−115.87874	−115.90715
	2d	Planar (2π)	^1A_g	−114.17663	−115.48817	−115.65854	−115.75842		
C_{2v}	**3b**	Planar (3π)	$^3A_2$	−114.38715	−115.65126	−115.81530	−115.87461	−115.88881	−115.91708
	3d	Planar (2π)	$^1A_1$	−114.45930	−115.55501	−115.73620	−115.82414		

[a] Frozen inner shell core approximation used.

Table IV. Energies Relative to Ground State (kcal/mol)

State				UHF/STO-3G	UHF/4-31G	UHF/6-31G*	UMP2/4-31G	UHFCISD/4-31G (corrected)	Final
D_{2h}	**2a**	Planar (4π)	^1A_g	93.0	72.0	70.8	77.1		75.9[a]
	2b	Planar (3π)	^3A_u	31.2	37.0	36.4	62.8	55.0	54.4[b]
	2c	Planar (3π)	^1A_u						55.8[c]
	2d	Planar (2π)	^1A_g	153.8	131.9	126.9	129.5		124.5[a]
C_{2v}	**3b**	Planar (3π)	$^3A_2$	21.7	29.6	28.5	56.6	48.8	47.7[b]
	3c	Planar (3π)	$^1A_2$						50.1[c]
	3d	Planar (2π)	$^1A_1$	101.9	90.0	78.1	88.3		76.4[a]

[a] Final estimate obtained by combining UMP2/4-31G correlation energy with UHF/6-31G* value. [b] Final estimate obtained by combining UHFCISD/4-31G (corrected) correlation estimate with UHF/6-31G* value. [c] Final estimate obtained from triplet value by adding twice the relevant exchange integral (see text).

value, our final estimate of the triplet barrier is 47.7 kcal/mol.

Finally, we discuss the open shell singlet states **2c** and **3c.** These have the same orbital occupancies as the triplets **2b** and **3b.** They cannot be handled by the unrestricted Hartree–Fock methods used elsewhere in this paper. However, the geometries are not likely to differ much from the corresponding triplets (Dykstra[6] found almost no change for D_{2h}). To estimate the energies of **2c** and **3c,** we have performed RHF/4-31G calculations on the triplet states (using the geometries of Tables I and II together with a partitioning technique described previously[15]). The energies are −115.62139 hartrees for **2c** and −115.63431 hartrees for **3c.** In the RHF scheme, the energies of the corresponding open shell singlets lie above the triplet energies by twice the exchange integral between the singly occupied orbitals. The values of these exchange integrals are 0.00109 hartrees for **2b** and 0.00187 hartrees for **3b.** If these corrections are added to final estimates of the triplet energies, we conclude that the ^1A_u state **2c** lies 55.8 kcal/mol above the ground state. For the bent system, the $^1A_2$ state **3c,** the corresponding energy is 50.1 kcal/mol. **3c** appears to be the lowest singlet state of planar allene. Since no spin change from the ground state is involved, this is likely to be the effective transition state for internal rotation; 50.1 kcal/mol is therefore our final value of the barrier, in good agreement with the experimental estimate.[7,8] Had we restricted ourselves to the linear CCC form **2c,** the corresponding barrier would have been about 6 kcal/mol higher.

Our results may be compared with those of Staemmler,[5] who has carried out open-shell SCF calculations on the singlet state **2c.** He found a barrier of 50 kcal/mol for this D_{2h} state without correlation and without allowing for bending. He made a partial estimate of the change due to correlation effects, treating only the π-electrons. Assuming equal correlation energies in the singlet and triplet open-shell states (as we have done) he found an increase in the barrier of only 5 kcal/mol. This is below our predicted correlation difference of 19 kcal/mol between ground (**1**) and triplet (**3b**) states. However, part of this arises because we have used UHF theory for the triplet which gives an energy 11 kcal/mol below the RHF value. It appears, therefore, that Staemmler underestimated the correlation effect by an amount comparable to the barrier lowering due to CCC angle bending.

Conclusion

The principal conclusion from this work is that the transition state for (singlet) internal rotation in allene is a planar C_{2v} structure with a nonlinear CCC sequence. CCC bending during the rotation lowers the barrier by about 6 kcal/mol.

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