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An *ab initio* CI study on the rotational barrier of the allyl anion

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All-electron and pseudopotential non-empirical calculations have been performed on C_{2v} and C_s (syn, anti) allyl anion conformations. Using a double-zeta valence-shell basis set within the Epstein-Nesbet definition of the unperturbed Hamiltonian, a value about 19 kcal/mol is found for the barrier to rotation of the allyl anion. This value is the theoretical value obtained with greater accuracy, and the lowest one for the rotational barrier.

Key words: Rotational barrier — Allyl anion

Introduction

The allyl anion is the simplest π-delocalized carbanion and consequently has been the subject of many theoretical studies, especially concerned with the rotational barrier [1-7], using either semiempirical or ab initio approaches and different basis sets. Allylic resonance is a problem of actual interest owing to its implication in many problems of current chemical significance, and so, very recent work is available [8-12].

When a methyl group of the allyl anion is twisted 90° around a C-C bond in the C_{2v} allyl anion, I, (see Fig. 1), and pyramidalization is allowed, a syn, II, or anti, III, conformation of the allyl anion belonging to the C_s symmetry is formed, and the electronic barrier between a C_s type structure and the C_{2v} form can be related to the π resonance energy.

As far as we know, the MP2/4−31+G value of 22.2 kcal/mol [7] is the lowest theoretical value for the rotational barrier of the allyl anion, and the value of 18 kcal/mol for the allylcesium complex in THF [13] has been experimentally evidenced as the lower limit to the rotational barrier of allyl anion in solution. In this work, we present an ab initio study which includes correlation energy and improved geometries in order to make closer the theoretical and experimental values of the rotational barrier of the allyl anion.

Calculations

Geometry optimization at 6-31G level [14] was performed by using the FORCE program [15] linked to the GAUSSIAN 70 series of programs [16]. Single point 6-31G** [17] and 6-31+G [7] calculations at 6-31G optimum geometries were done with the HONDO program [18]. The PSHONDO algorithm [19], which includes the pseudopotentials of Durand and Barthelat [20, 21] in the HONDO program, was used to carry out valence-shell SCF calculations, with the pseudopotential parameters and properly optimized basis set for carbon atom [22]. The primitive functions were contracted to a double-zeta (DZ) level by a 3+1 procedure, as in [6].

CI calculations were done with the CIPSI formalism [23], where the more important configurations are treated variationally (DIAG.), and the less important perturbationally with the RSPT and either Epstein-Nesbet [24, 25] (EN) or Moller-Plesset [26] (MP) partitions of the unperturbed Hamiltonian. The configurations with a EN coefficient in the first-order wavefunction greater than or equal to 0.015 were included in the variational subspace. Typically, the norm of the first order MP correction to the wavefunction is roughly 0.09 in all the cases.

Results and discussion

The 6-31G optimum geometries of conformations I–III are summarized in Table 1, according to the numbering in Fig. 1, and in Table 2 total and relative energies obtained from the all-electron and valence-shell calculations are shown. All basis sets give the syn more stable than the anti isomer, and therefore, the rotational barrier can be obtained by the energy difference between structures I and II. From Table 2 can be concluded that the inclusion of polarization functions on carbon and hydrogen atoms reduces appreciably the barrier height, however, diffuse functions does not affect it. Also, the DZ valence-shell basis set gives a lower energy barrier than the split-valence 6-31G basis set. Our findings at *SCF* level are in good agreement with previous calculations [5, 7].

Table 3 shows the CI results. As it can be readily seen, a value of about 19 kcal/mol for the rotational barrier of the allyl anion is obtained with the EN partition, in very good agreement with the expected result and the estimated experimental value [13]. Since the EN partition includes all the second order and part of all the higher than second orders of the *MP* partition [25], and since in this case there are not *N*-dependence problems [27, 28], it can be concluded that our EN

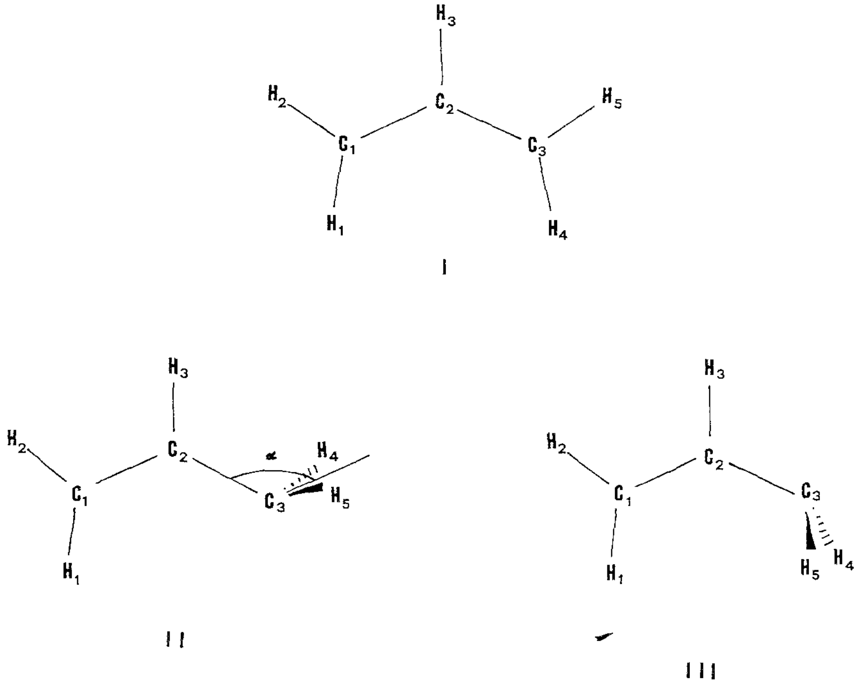

Fig. 1. Allyl anion conformations: C_{2v} allyl anion, I; syn allyl anion, II; and anti allyl anion, III. In the structures II and III, α is the pyramidalization angle between the line bisecting the H(4)C(3)H(5) angle and the C(2)C(3) bond

Table 1. Optimal geometrical parameters for allyl anion structures, (6-31G). Bond length in Ångstroms and angles in degrees

	Conformation		
Parameter	I	II	III
C(1)C(2)	1.385	1.336	1.339
C(2)C(3)	1.385	1.509	1.518
C(1)H(1)	1.080	1.082	1.079
C(1)H(2)	1.079	1.076	1.083
C(2)H(3)	1.091	1.105	1.095
C(3)H(4)	1.080	1.111	1.106
C(3)H(5)	1.079	1.111	1.106
C(1)C(2)C(3)	133.0	125.5	130.6
H(3)C(2)C(1)	113.5	113.3	113.4
H(1)C(1)C(2)	122.0	119.8	121.5
H(2)C(1)C(2)	121.2	122.9	122.6
H(4)C(3)C(2)	122.0	107.4	108.2
H(5)C(3)C(2)	121.2	107.4	108.2
H(4)C(3)C(5)	116.8	104.2	105.6
α[a]		119.2	121.1

[a] Pyramidalization angle (see Fig. 1)

Table 2. Total and relative energies for the optimal structures I–III

Structure	Total energies (a.u.)				Relative energies (kcal/mol)			
	6-31G	6-31G**	6-31+G	DZ	6-31G	6-31G**	6-31+G	DZ
I (C_{2v})	−116.355723	−116.403096	−116.386057	−19.241793	0.0	0.0	0.0	0.0
II (syn)	−116.314638	−116.369344	−116.345389	−19.202962	25.8	21.2	25.5	24.4
III (anti)	−116.312220	−116.365576	−116.343279	−19.199718	27.3	23.5	26.8	26.4

Table 3. CI data for the allyl anion conformation obtained with the DZ basis set

Structure	N_1^a	N_2^b	Total energies (a.u.)			Relative energies (kcal/mol)		
			E(DIAG.)	E(MP)	E(EN)	E(DIAG.)	E(MP)	E(EN)
I (C_{2v})	87	1 495 498	−19.285515	−19.504133	−19.561096	0.0	0.0	0.0
II (syn)	66	2 139 650	−19.250076	−19.469697	−19.530406	22.2	21.6	19.3
III (anti)	64	2 071 236	−19.243192	−19.465335	−19.526803	26.6	24.3	21.5

[a] Number of configurations included in the diagonalized space

[b] Number of configurations which give a contribution to the perturbation correction to the energy

result represents the most accurate theoretical approach to the experimental value of this rotational barrier.

By inspection of Tables 2 and 3 it can be deduced that a large amount of the correlation energy is due to angular correlation. Barrier heights for EN and 6-31G** calculations differ only 1.9 kcal/mol. The inclusion of polarization functions retrieves 4.6 kcal/mol while the inclusion of correlation decreases 5.1 kcal/mol the energy barrier value. Therefore, if the effects of inclusion of polarization functions and correlation were additive, as has been previously found in other systems [29], the computed barrier could well drop to 15-16 kcal/mol. In sum, correlation energy and a more flexible basis set provide the value of 19.3 kcal/mol as the lowest theoretical value of the allyl anion. If a greater accuracy is desired, the geometry optimization of the planar and twisted conformations at CI level might be taken into account, along with the inclusion of polarization functions in the basis set to improve the correlation energy convergence.

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