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 $C_1$ (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 $\pi$-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 $C_1$ symmetry is formed, and the electronic barrier between a $C_1$ type structure and the $C_{2v}$ form can be related to the $\pi$ 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