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Potential Energies of Rotation of Double Bond in Ethylene Molecule and Ion

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Synopsis. MP3/6-31G** calculations show that the potential barrier of a double-bond rotation in an ethylene ion is 137 kJ mol^{-1} (about half that of the molecular state) and that the orthogonally twisted ion has a C_{2v} symmetry. The geometries are discussed in relation to the total energies.

It is often said that geometrical isomers cannot be distinguished by a mass spectral observation.[1,2] This is dramatically emphasized by the fact that benzene and its linear isomer, 1,3-hexadien-5-yne, give the same mass spectra upon electron-impact ionization.[3] Unsuccessful trials for characterizing geometrical isomers have so far simply suggested that the double bond in an ionized organic molecule easily becomes twisted and changes its geometry. Using the ethylene system, we studied this problem in order to give an answer to the fundamental question regarding organic mass spectrometry. This subject has also drawn some conceptional interests regarding chemical bonding as an example of an isovalent hyperconjugation.[4]

The method for evaluating such rotational energy is straightforward: Simply obtain the energetic difference between the lowest- and highest-energy configurations of the ethylene ion. However, as care must be taken regarding the calculation for determining a twisted geometry, since in an ionic state, the D_2 or D_{2d} (at 90°) symmetry of a molecular state is possibly degraded to C_2 or C_{2v} (or even C_1 or Cs) due to a lack of one of the π electrons. There are some reports regarding Hartree-Fock[5] (HF) MO theoretical calculations for determining the rotational energy of ionized ethylene.[6–8] However, they deal with only the D_{2d} symmetry for a perpendicular structure. In addition, as is often said, a HF calculation regarding a reaction in which the number of bonds changes, is generally unreliable since the energy difference of the electron correlation between the systems becomes non-negligible. Therefore, previous results must be carefully checked. We have performed second- and third-order Møller-Plesset perterbation calculations[9] based on the HF or the UHF (unrestricted Hartree-Fock[10]) 6-31G**[11] (MP3/6-31G**) to obtain the most reliable rotational barrier values presently available.[12]

a. Geometries in an Ethylene Molecule. The various states of an ethylene molecule have been thoroughly studied through experiments[13] and theoretical calculations.[14,15] In order to check the reliability of the present method, we will compare the calculated values with experimental values and previous calculations. The geometries that are obtained by MP3/6-31G** are:

Ground state (D_{2h}):

R_{CC} = 1.333 (exptl 1.339,[13] CIPSI[16] 1.344,[14] CEPA[17] 1.336[15])

R_{CH} = 1.080 (exptl 1.086,[13] CEPA 1.074[15])

∠HCH = 116.6 (exptl 117.6,[13] CEPA 116.3[15])

Twisted triplet state (D_{2d}):

R_{CC} = 1.459 (CIPSI 1.463,[14] CEPA 1.459[15])

R_{CH} = 1.081 (CEPA 1.074[15])

∠HCH = 117.0 (CEPA 117.2[15])

The present method has been shown to be excellent for reproducing experimental values as well as previous calculations, especially regarding the CEPA results.

b. Rotational Barrier of a Ethylene Molecule and Its Ion. The rotational barrier of an ethylene molecule has been observed to be 273 kJ mol^{-1}.[13] The HF/6-31G** result gives a value that is too low (176 kJ mol^{-1}). However, the MP3/6-31G** result as well as previous CIPSI and CEPA calculations give very good experimental values (272, 263, and 280 kJ mol^{-1}, respectively). This shows the necessity for the inclusion of an electron correlation and also demonstrates the appropriateness of MP3/6-31G**.

Table 1 shows the geometries and the total energies of D_{2d} and C_{2v} ethylene ions where a C_1 atom carries an unpaired electron. Figure 1 shows plots of the total energy *vs.* the twist angle (θ). As expected, when θ is 90°, the C_{2v} structure is more stable than D_{2d}.

As can be seen in Figure 1, the rotational barrier in ionic state is found to be about half (137 kJ mol^{-1}) that of the neutral state. The PE of the twisted molecule has been reported to increase steeply as the twist angle (θ) increases.[14] However, that of the ion does not change until θ is 20°. This indicates that the double bond in an ionic state is very flexible regarding rotation in accordance with experience from organic mass spectrometry.

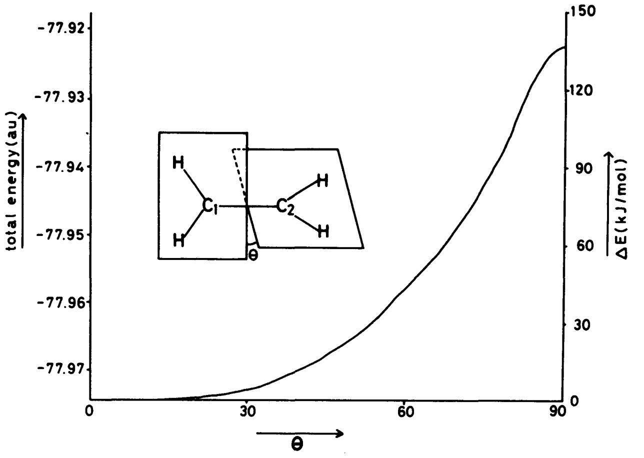

Fig. 1. Total energies *vs.* twist angle (θ) by MP3/6-31G**. All geometrical parameters except the fixed twist angle were optimized with respect to the total energy.

TABLE 1. GEOMETRIES AND TOTAL ENERGIES OF ETHYLENE ION BY MP3/6-31G**[a]

	Planar: D_{2h} θ=0	Perpendicular: D_{2d} θ=90	Perpendicular: C_{2v} θ=90
$R(C_1-C_2)$	1.4167[b]	1.4106	1.4118
$R(C_1-H)$	1.0824	1.0909	1.0891
$R(C_2-H)$			1.0927
HC_1H	118.8[c]	117.6	119.7
HC_2H			116.0
Total energy	−77.974663[d]	−77.922613	−77.922954

a) The geometry optimization was carried out by the Fletcher-Powell method.[22] b) In A. c) In degree. d) au (1 au=2625.5 kJ mol^{-1}).

c. Geometries of the Ethylene Ions. Mulliken and Roothaan proposed that the ethylene ion is an example of isovalent hyperconjugation and predicted a twist angle of 30° from a plane.[4] This is the result of a compromise between normal π bonding (planar structure) and hyperconjugative π bonding (perpendicular structure). This prediction was supported by ultraviolet studies regarding a series of Rydberg states of ethylene, which converge to the ethylene ion.[18] It has been reported that the non-plane structure can be produced by using the ab initio SCF MO CI method.[19] We have tried to reproduce this structure by optimizing all of the geometrical parameters. However, like all other reports regarding reasonably extensive SCF MO CI calculations,[20,21] a planar ion is found to be the most stable and to have a D_{2h} symmetry. It should be noted that the total energy that we have obtained is the lowest (−77.974663 au).

We have tried the Cs, C_{2v}, and D_{2d} structures for the perpendicular ion. The C_{2v} structure was found to be the most stable: The lowering of the order from a D_{2d} symmetry is caused by a configurational difference in which the unpaired electron occupies only one of the methylene groups. Interestingly, the C–C bondlength is maintained at almost the same independance regarding the twist angle (θ), even at 90°.

In summary, an MP3/6-31G** calculation shows that the potential barrier of a double-bond rotation in an ethylene ion is 137 kJ mol^{-1}, about half that of the molecular state. Also, an orthogonally twisted ion has a C_{2v} symmetry.

Refernces

1) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York (1966), Chap. 6.

2) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco (1967), Chap. 1.

3) R. S. Berry, J. Clardy, and M. E. Schafer, *J. Am. Chem. Soc.*, **86**, 2738 (1964); *Tetrahedron Lett.*, **1965**, 1003.

4) R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.*, **41**, 219 (1947).

5) G. G. Hall,*Proc. R. Soc. London, Ser. A*, **205**, 541 (1951); C. C. J. Roothaan, *Rev. Mod. Phys.* **23**, 69 (1951).

6) W. A. Latham, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 808 (1971).

7) D. J. Bellville and N. L. Bauld, *J. Am. Chem. Soc.*,**104**, 294 (1982).

8) J. Kalcher and G. Olbrich, *J. Mol. Struct.*, **104**, 341 (1983).

9) C. Moller and M. S. Plesset, *Phys. Rev.*, **46**, 618 (1934).

10) J. A. Pople and R. K. Nesbet, *J. Chem. Soc.*, **1964**, 571.

11) P. C. Hariharan and J. A. Pople, *Theoret. Chim. Acta*, **28**, 213 (1973).

12) We have used GAUSSIAN 80H program (a Hitac version of GAUSSIAN 80 (QCPE No. 437, Indiana University, IN)) at the computer center of the University of Tokyo.

13) H. O. Kalinowski and H. Kessler, *Topics Stereochim.*, **7**, 295 (1973).

14) M. Said, D. Maynau, J. -P. Malrieu, and M. -A. Barcia Bach, *J. Am. Chem. Soc.*, **106**, 571 (1984).

15) H. J. Kohler and H. Lischka, *J. Am. Chem. Soc.*, **104**, 5884 (1982).

16) B. Huron, J. P. Malrieu, and P. Rancurel, *J. Chem. Phys.*, **58**, 5745 (1973).

17) W. Meyer, *J. Chem. Phys.*, **58**, 1017 (1973).

18) H. Koppel, W. Domcke, L. S. Cederbaum, and W. v. Niessen, *J. Chem. Phys.*, **69**, 4252 (1978).

19) R. J. Buenker, S. D. Peyerimhoff, and H. L. Hsu, *Chem. Phys. Lett.*, **11**, 65 (1971).

20) P. D. Foo and K. K. Innes, *J. Chem. Phys.*, **60**, 4582 (1974).

21) W. R. Rodwell, M. F. Guest, D. T. Clark, and D. Shuttlesworth, *Chem. Phys. Lett.*, **45**, 50 (1977).

22) R. Fletcher and M. J. D. Powell, *Compt. J.*, **6**, 163 (1963).