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ON THE ROLE PLAYED BY EXCITED ELECTRONIC STATES AND MOLECULAR VIBRATIONS IN ADDITION REACTIONS—II

ADDITION TO THE CARBON-CARBON DOUBLE BOND

L. BURNELLE
Research Institute for Advanced Studies
(Martin Company)
7212 Bellona Avenue
Baltimore, Maryland 21212

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Abstract—A perturbation treatment has been applied to the system formed by a molecule of ethylene and a proton approaching from above the molecular plane toward one of the carbon atoms. According to the calculations the intervention of the V state due to the perturbation induces a twisting of the molecule. This suggests that the electrophilic addition to the double CC bond proceeds through the twisted configuration.

IN a preceding paper,[1] the electrophilic addition to acetylene has been studied by means of perturbation theory, and the intervention of the first excited state of the molecule has been found to produce a *trans* distortion of the latter. The present paper concerns the same reaction with ethylene, which has seemed to us to be another favorable case for the manifestation of a similar feature.

As was established both by experimental[2] and theoretical[3–5] work, ethylene loses its planarity when electronically excited. Figure 1 represents the energies of the low-lying electronic states of the molecule, as a function of the twisting angle θ.[6] Our purpose is to examine if the approach of the reagent, by admixing the wave functions of the distorted states with that of the ground state, may induce the molecule to twist and thus cause the addition reaction to proceed through the twisted configuration.

It is noticed from Fig. 1 that the curves of state N and state T intersect each other, so that if the perturbation mixes both states a radiationless transition is allowed and there is a possibility of some interaction, as in the case of acetylene. However, the two states involved are of different multiplicities, and if the perturbation contains coulombic terms only, no mixing of the two states can actually take place. It is only when the approaching reagent is a radical that such an interaction is possible.[7] As this study is limited to the case where the reagent is a proton, mixing of states of same multiplicity only has been considered, i.e. mixing of states N and V. It was anticipated that since in the twisted configuration the gap between the two levels is much shorter

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[1] L. Burnelle, *Tetrahedron* **11**, 2043 (1964).

[2] P. G. Wilkinson and R. S. Mulliken, *J. Chem. Phys.* **23**, 1895 (1955).

[3] R. S. Mulliken and C. C. J. Roothaan, *Chem. Revs.* **41**, 219 (1947).

[4] H. M. Hulburt, R. A. Harman and H. Eyring, *Ann. N.Y. Acad. Sci.* **44**, 371 (1943).

[5] R. G. Parr and B. L. Crawford, Jr., *J. Chem. Phys.* **16**, 526 (1948).

[6] For a description of the electronic structure of the various states, see Ref. 5.

[7] For the mixing of states of different multiplicity due to the presence of a radical, see H. Tsubomura and R. S. Mulliken, *J. Amer. Chem. Soc.* **82**, 5966 (1960); H. McConnell, *J. Chem. Phys.* **20**, 1043 (1952); Y. Mori, *Bull. Chem. Soc. Japan* **35**, 1584 (1962).

than in the planar case, the twisted N state would be considerably more affected by the perturbation than the corresponding planar configuration.

The CH bonds have been neglected, and the four electrons associated with the CC bond have been included in the wave functions, for which the following expressions have been used:

$$\psi_N = C_1\,|(\sigma\alpha)(\sigma\beta)(\pi_+\alpha)(\pi_+\beta)| + C_2\,|(\sigma\alpha)(\sigma\beta)(\pi_-\alpha)(\pi_-\beta)|$$

$$\psi_V = \frac{1}{\sqrt{2}}\{\,|(\sigma\alpha)(\sigma\beta)(\pi_+\alpha)(\pi_-\beta)| - |(\sigma\alpha)(\sigma\beta)(\pi_+\beta)(\pi_-\alpha)|\,\}$$

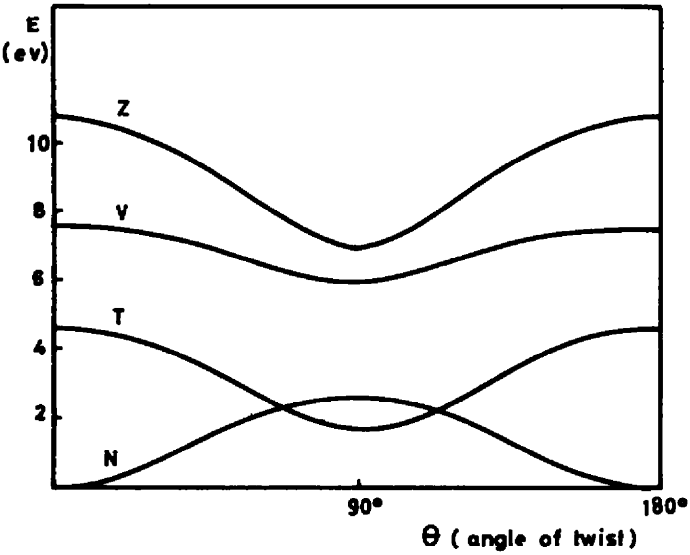

FIG. 1. Energy of the lowest-lying states of ethylene, as a function of the twist angle.

Here σ represents the σ-bond orbital, built up from the superposition of two sp^2 hybrids located on each carbon atoms and pointing toward each other; π_+ and π_- represent the bonding and anti-bonding π-orbitals, respectively:

$$\pi_\pm = 1/(1 \pm S)^{1/2}(2px_A \pm 2px_B).$$

Here, S represents the overlap integral between the two 2p orbitals $2px_A$ and $2px_B$.

The coefficients C_1 and C_2 measure the interaction between the two states where the π_+ orbital and the π_- orbital is doubly occupied, respectively. In the planar molecule, the first coefficient is considerably larger than the second one, and they are equal when the molecule is twisted by 90°. For the planar configuration we have used the values of C_1 and C_2 which result from Parr and Crawford's two-electron treatment.[5]

The proton has been considered to approach toward one carbon atom along the x axis (perpendicular to the molecular plane) relative to this atom. The latter will be designed as carbon 1. In the distorted configuration the $2p\pi$ orbital of the other atom was rotated by 90°. The CC distance was taken equal to 2·551 a.u. (1·35 Å) and to 3·1935 a.u. (1·69 Å)[§] for the planar and for the twisted configuration, respectively.

[§] This is the r_{00} distance obtained by Mulliken and Wilkinson for the V state (Ref. 2). One of the referees has pointed out that this bond length is concerned with the planar geometry of the V state, and that it should become shorter when the molecule is allowed to relax to its favored twisted configuration. It is very likely that the use of a smaller bond length for the twisted molecule would not modify the results significantly.

The following expressions are readily found for the various integrals required in the calculation required in the calculation of the perturbation energy:

$$V_{NN} = -2(H:\sigma\sigma) - 2C_1^2(H:\pi_+\pi_+) - 2C_2^2(H:\pi_-\pi_-)$$
$$V_{VV} = -2(H:\sigma\sigma) - (H:\pi_+\pi_+) - (H:\pi_-\pi_-)$$
$$V_{NV} = -\sqrt{2}(C_1 + C_2)(H:\pi_+\pi_-)$$

For the various energy levels of the isolated molecule we have used the following experimental values, the energy of the planar molecule being taken as reference:

$$E_N(\theta = 90°) = 0{\cdot}0978 \text{ a.u. } (2{\cdot}66 \text{ ev})^9$$
$$E_V(\theta = 0°) = 0{\cdot}279 \text{ a.u. } (7{\cdot}6 \text{ ev}).$$

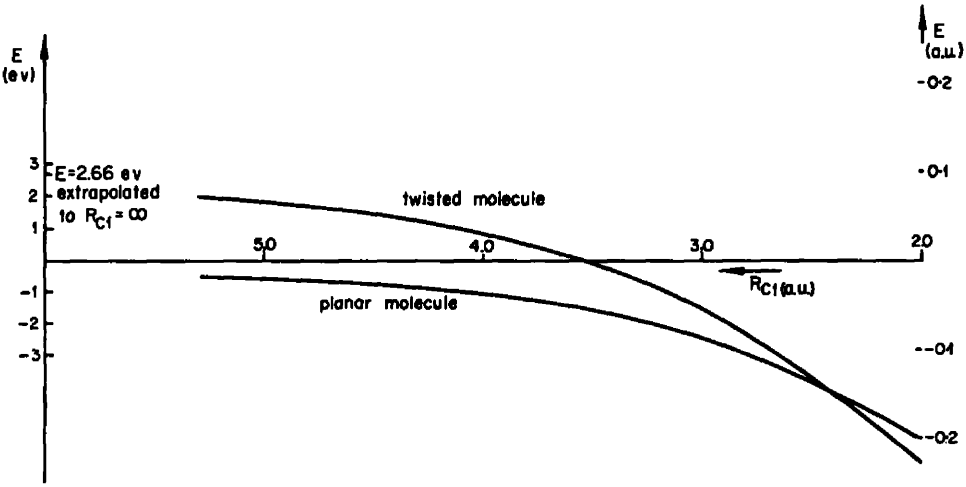

FIG. 2. Energies of the system $C_2H_4^+$ proton vs distance proton-carbon 1.

This corresponds to the intensity maximum in the N → V spectrum[2]

$$E_V(\theta = 90°) = 0{\cdot}182 \text{ a.u. } (4{\cdot}96 \text{ ev}).$$

This is the value of the 0 → 0 transition observed by Mulliken and Wilkinson.[2]

The results of the calculation are illustrated in Fig. 2. In agreement with expectation the energy of the twisted molecule decreases definitely faster than that of the planar one. For a distance proton-carbon 1 smaller than 2·4 a.u. the distorted configuration is actually the most stable. Thus here again, it is found that the reagent causes a distortion of the molecule. So, according to our model, the addition to the ethylenic compounds must proceed through the twisted configuration.

It should be reminded, however, that this reaction is stereospecific, as has been proven for the addition of Br_2 to fumaric and maleic acids[9] and for the addition of HI to the *cis–trans* pair of tiglic and angelic acids[10] as well. Now if these reactions proceed

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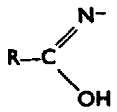
[9] E. S. Gould, *Mechanism and Structure in Organic Chemistry* p. 523. Holt, Rinehart and Winston, New York (1959).

[10] W. C. Young, R. J. Dillon and H. J. Lucas, *J. Amer. Chem. Soc.* **51**, 2528 (1929).

via the route we suggest, they should not be stereospecific, for when the positive ion is fixed and the molecule twisted, the anion may be fixed with the same probability on either one of the two lobes of the π-orbital of the other carbon. A plausible explanation of the stereospecificity would consist in admitting that the molecule becomes twisted, but by an angle of less than 90°. It may very well be that the attack by the negative ion takes place before the twist angle has reached this value. It is then very likely that steric hindrance will prevent fixation of the anion on the same side of the molecule as that where the proton has been attached. The tendency of ions to pair, which would cause the negative ion to come on the same side, may be expected not to manifest itself because the positive charge is certainly distributed among the various atoms of the molecule. But another interpretation of the experimental facts would be that in the V state the molecule is not merely twisted, but that there also appears a change in hybridization such that one has a pyramidal arrangement of the bonds around each carbon atom. Such a structure for this state has actually already been proposed by Walsh.[11] If one assumes that in its V state a molecule like fumaric acid is *trans*- bent and twisted, one may expect that the approach of the positive ion will lead the molecule to adopt such a shape, and the stereospecificity of the addition reaction is then interpreted.

A question which arises is whether the $C_2H_5^+$ system will not tend to reach a more symmetrical configuration before the second step of the reaction takes place. In order to study this point, we have considered the approach of the proton along the binary axis perpendicular to the molecular plane. The calculations indicate that in the range of the proton positions that is covered here, for any given distance of the proton to the CC axis, the energy of the symmetrical configuration lies always higher than that of the non-symmetrical one. The difference between the two energies varies from 0·2 ev to 2 ev, according to the distance of the proton. It is to be mentioned that Hückel-type MO calculations confirm this point. By using his extended Hückel method,[12] Hoffmann has indeed found that for the $C_2H_5^+$ ion the structure $CH_3CH_2^+$ is more stable than the symmetrical conformation.[13] This agreement between results obtained by two different methods is very gratifying. To the extent that one may trust present day quantum chemical calculations, it thus appears that there is no tendency for the system to rearrange and to reach a symmetrical configuration.

The conclusion which emerges from this study is that distorted excited states play a significant role in addition reactions. However crude our treatment is, it points out the importance of molecular distortions in reaction mechanism. It is quite possible that the ideas which have been developed here are not to be restricted only to the addition reactions in which multiple CC bonds are saturated. They probably apply to other reactions as well. For instance, one knows that the hydrolysis of nitriles proceeds through the following intermediate compound:



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[11] A. D. Walsh, *J. Chem. Soc.* 2325 (1953).

[12] R. Hoffman, *J. Chem. Phys.* **39**, 1397 (1963).

[13] R. Hoffman, *J. Chem. Phys.* **40**, 2480 (1964).

This configuration has a definite analogy with the bent excited state of HCN,[14] which suggests a process similar to the one we propose for the addition to CC bonds.

Another example, mentioned by Ingold,[15] is that of the reduction of formaldehyde. This molecule becomes pyramidal in its lowest lying excited state.[16,17] Thus, here again, the excited molecule has a geometry similar to that of the compound it gives rise to, namely, methyl alcohol.

We therefore believe that the method outlined here is susceptible of being usefully extended to various types of chemical reactions.

[14] G. Herzberg and K. K. Innes, *Canad. J. Phys.* **35**, 842 (1957).

[15] C. K. Ingold, *J. Chem. Phys.* **53**, 472 (1956).

[16] J. C. D. Brand, *J. Chem. Soc.* 858 (1956).

[17] G. W. Robinson and V. E. DiGiorigo, *Canad. J. Chem.* **36**, 31 (1958).