# A Double-well Potential for Olefin Isomerization in Polar Solvents

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*Summary* The potential energy surface for isomerization of unsymmetrical olefins $A_2C=CB_2$ in strongly polar solvents is shown to possess a remarkable double-well form.

AVOIDED surface crossings between an ionic configuration and a covalent configuration, such as occur in alkali halides, have been known for many decades.[1] We show here that a similar avoided crossing can occur in the isomerization of unsymmetrical olefins in polar solvents and that it leads to a remarkable double-well potential for the thermal process. This is accompanied by an inverted double-well potential on the lowest excited singlet surface.

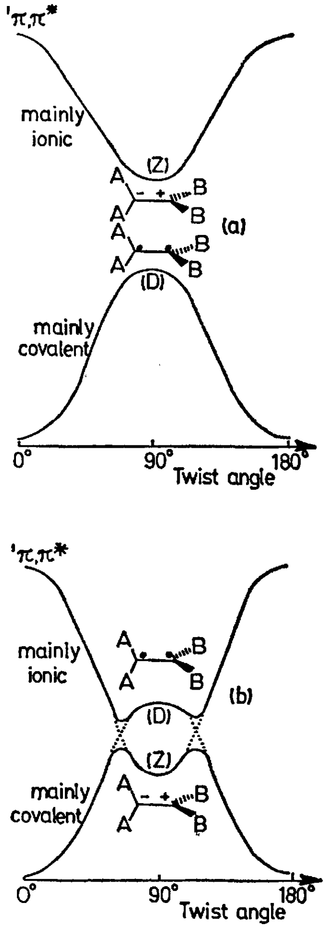

FIGURE. The lowest singlet states of an unsymmetrically substituted ethylene as a function of twist-angle; (a) in non-polar solvent; (b) in strongly polar solvent.

Type-B avoided crossings[2] occur whenever an approximate, purely ionic, surface and an approximate, purely covalent, surface describing two neighbouring states of the same symmetry of a molecular system intersect. The intersection is a direct consequence of the approximate nature of the wave functions of the two states. If the restriction that these wave functions be, respectively purely ionic and purely covalent is lifted, the intersection disappears. There is an 'avoided' or 'intended' crossing.

Consider now the rotation of an unsymmetrically substituted olefin $A_2C{=}CB_2$ from 0 to 90°. The ground state leads to an orthogonal singlet diradical (D), while the singly excited $^1\pi\pi^*$ state leads to an orthogonal zwitterionic singlet (Z).[3] By symmetry, the diradical is purely covalent and the zwitterion purely ionic.† In the intermediate region between 0 and 90°, the lower singlet is mainly covalent while the upper singlet is mainly ionic.‡ The surfaces, which are separated by a significant energy gap,[4] are shown in the Figure (a).

If the unsymmetrical olefin is now introduced into a highly polar solvent, the zwitterionic state should be strongly stabilized, so as to create a situation where (Z) lies below (D). The mainly ionic $^1\pi\pi^*$ state tends to correlate with (Z), while the ground singlet state tends to correlate with (D). In this approximate picture, we obtain the crossing indicated in dotted lines in Figure (b). However, since the states have the same symmetry in the crossing region, their intersection will be avoided, as the ionic and covalent characters mix in the crossing region. A type-B avoided crossing is created, which should be reflected by a potential barrier on the ground surface and by a secondary minimum for (Z) [Figure (b)]. The avoided-crossing region will also be characterized by remarkable changes in physical properties of the two states, in particular a strong increase in the dipole moment of the ground state as the twist angle approaches 90°.

In order to confirm this prediction, we have performed an *ab initio*, minimal basis set, restricted SCF + 3 × 3 CI calculation[5] of the rotation of 1,1-dicyanoethylene in the presence of two water molecules. An 'intermediate' Hamiltonian,[2] equally weighted for ground and excited surface, was used. The reaction co-ordinate corresponds, at 0 and 90°, to an optimized solvent arrangement for the ground state.§ The results confirm the double-well minimum for ground surface and inverted double-well minimum for excited surface, which are schematically shown in Figure (b). The size of the 90° well for the dicyanoethylene in the polar solvent is 6 kcal mol$^{-1}$, while the gap between the two surfaces at their closest approach, in the avoided-crossing region, is 19 kcal mol$^{-1}$. This is an admittedly crude calculation, which suffers from the minimal nature of the basis set (see ref. 6) and sub-optimal geometries in the avoided-crossing region. Hence the 6 kcal mol$^{-1}$ barrier is an upper limit, at least for this two-molecule solvent model, and more sophisticated calculations are certainly called for.

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† The structure adopted here for (Z) implies that (A) is the more electron accepting substituent.

‡ In ethylene itself the $^1\pi\pi^*$ wave function is 100% ionic for all angles.

§ The two water molecules, with standard geometries, are placed symmetrically on either side of the C(1) = C(2) axis with the oxygen atoms defining the C(1)C(2)OO′ reference plane. The olefin $(CN)_2C(1) = C(2)H_2$ is initially perpendicular to this plane; at 90° the cyano groups have rotated into it. The $OH_2$ plane is perpendicular to C(1)C(2)O (intersection Oh). The optimised parameters at 0° (90°) are C(1)C(2) = 1·33(1·53)Å, C(2)O = 3·34(1·84)Å, ∠C(1)C(2)O = 90°(98°), ∠C(2)Oh = 130°(130°) with h *cis* to C(1). Linear interpolation is used at intermediate angles.

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[4] The gap is 88 kcal mol$^{-1}$ in ethylene; R. J. Buenker, S. D. Peyerimhoff, and H. L. Hsu, *Chem. Phys. Letters*, 1971, **11**, 65.

[5] The program is Gaussian 70 (W. J. Hehre, W. A. Latham, R. Dietchfield, M. D. Newton, and J. A. Pople, program No. 236 Q.C.P.E. Univ. of Indiana, Bloomington, Indiana), as amended in our laboratory. The three configurations which are mixed correspond to $^1\pi^2$, $^1\pi\pi^*$ and $^1(\pi^*)^2$ at 0°.

[6] C. F. Bender, T. H. Dunning, H. F. Schaefer, W. A. Goddard, and W. J. Hunt, *Chem. Phys. Letters*, 1972, **15**, 171.