

THROUGH BOND INTERACTION IN 1,4-DIPOLES

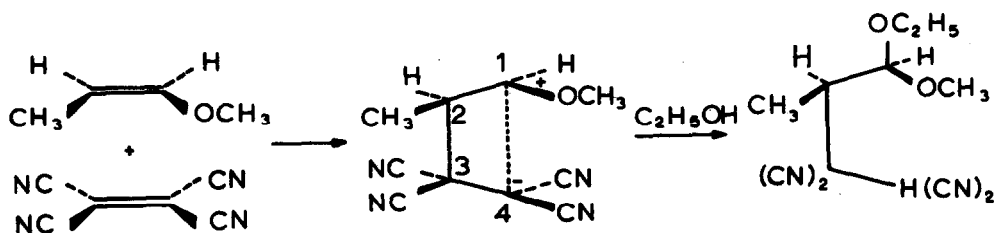
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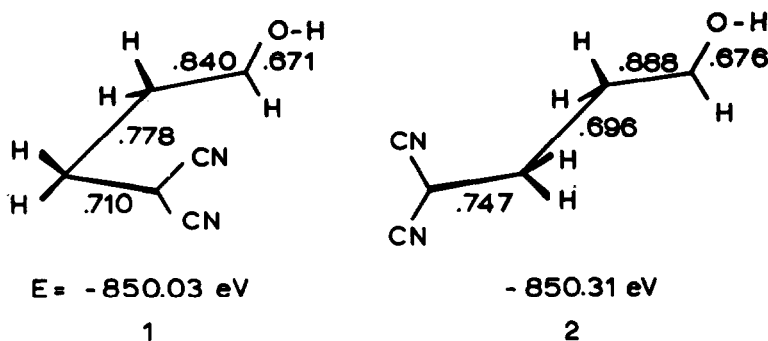
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Recently Huisgen et.al. [1] found that the 1,4 dipoles formed from tetracyanoethylene and enolethers add ethanol stereospecifically in the manner shown below for cis-propenyl-methyl-ether.



Quite the same stereospecificity has been reported for the formation of cyclobutane derivatives in the absence of alcohols [2] and an even higher one for the conversion of these cyclobutanes into the above mentioned acetals [1]. In both reactions the same 1,4-dipolar species with hindered rotation of the carbenium center is involved. This stereospecificity was explained by assuming a U-shaped conformation for the zwitterion, as indicated above. In this conformation a donor-acceptor interaction between the centers 1 and 4 is favoured. We would like to point out that the stereospecificity observed can also be explained by a through bond interaction [3]. Model calculations on tetramethylene [4] and isoelectronic species [5] have shown that the overlap population for the bond C₁-C₂ of the zwitterion hampers free rotation, even in non U-shaped conformations.

To check this qualitative reasoning, based on model calculations [4] [5], we have carried out extended Hückel [6] calculations on the 1,4 dipole arising from the addition of dicyanoethylene to hydroxyethylene for different conformations. The overlap populations of the bonds $O-C_1$, C_1-C_2 , C_2-C_3 and C_3-C_4 for the conformations 1 and 2 are shown below.



For the U-shaped zwitterion 1 with both carbenium - and carbanion-orbitals oriented in the same plane and parallel to the C_2-C_3 -bond, our calculations give a level ordering of "S" below "A" [5]. This indicates dominance of through space interaction between the two centers. As anticipated, there is a considerable rotational barrier for rotation of the OH-group to the outside (compare Fig. 1) due to reduction of C_1-C_4 interaction. This is clearly revealed by the decrease of the frontier orbital splitting in Fig. 1. Rotation of the OH-group to the inside (compare Fig. 1) of course is hindered by steric effects.

Further calculations show that conformation 1 seems to be unfavourable with respect to rotation around the central C_2-C_3 -bond. EH calculations predict that 2 is more stable than the gauche conformations and 1. Going from 1 to 2, through space interaction between the 2p orbitals on C_1 and C_4 vanishes and steric interactions are diminished.

We would like to emphasize here that in those isomers where through space interaction is negligible there still remains a considerable barrier for the rotation around C_1-C_2 due to through bond interaction [2].

The corresponding calculations carried out on 2 show "A" to be below "S". The splitting in energy is again largest in a conformation where the two 2p-orbitals on the centers 1 and 4 are parallel to the C_2-C_3 -bond.

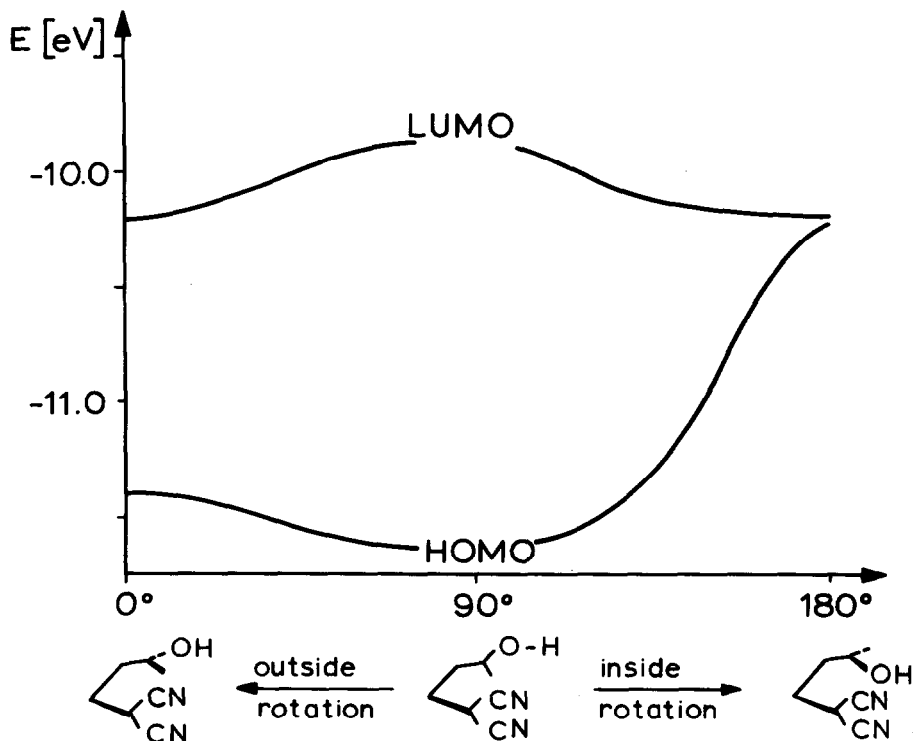


Fig. 1. Orbital energies of HOMO and LUMO of $\underline{1}$ as a function of the dihedral angle between the planes $O-C_1-C_2$ and $C_1-C_2-C_3$.

A comparison of the overlap populations of $\underline{1}$ and $\underline{2}$ shows considerable bond alternation and strengthening of the C_1-C_2 bond in $\underline{2}$ as anticipated from model studies [4] [5].

For the dipoles arising from the formal addition of HNCO and H_2CSO_2 to hydroxyethylene or aminoethylene similar results are obtained. These 1,4-dipoles may be a model for intermediates in cycloaddition reactions discussed recently [7] [8].

In general these calculations suggest that the effect of through bond interaction should not be neglected in discussing cycloaddition reactions with 1,4 dipolar intermediates [9].

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References and Footnotes

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