THE EFFECT OF SYMMETRY ON THE STABILITY OF CONFORMERS-GAUCHE EFFECT

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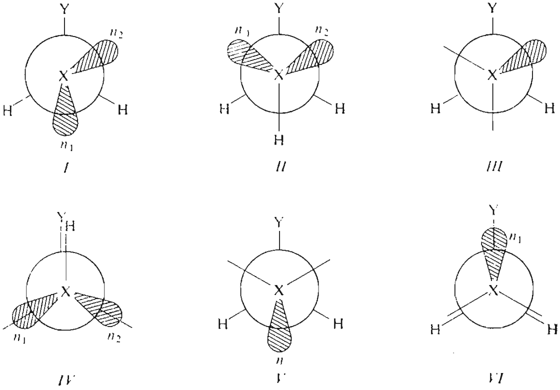
On the basis of Jahn-Teller second-order effect an explanation of anomeric effect was suggested, resulting from analysis of symmetry of corresponding wave functions. The explanation is in harmony with theoretical predictions about the stability of conformers based on EHT, CNDO, and *ab initio* calculations.

Anomeric effect, observed first in the chemistry of saccharides as a preference of axial electronegative substituent on pyranose ring[1], was later generalised as the so called Gauche effect[2], *i.e.* the preference of gauche conformer *I* over conformer *II*. This effect was found to be a general phenomenon occurring in a variety of aliphatic and hetero acyclic compounds.

The above effect was originally explained based on electrostatic dipole-dipole interaction, or on the so called "rabbit ears" effect[3]. Quantum chemical calculations by different methods[4,5]



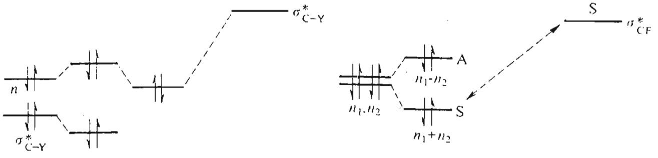
SCHEME 1

show however, that electrostatic interaction of unpaired electrons is not the reason of the anomeric effect[4]. Hoffmann[6] brought to attention the explanation of the anomeric effect suggested by Altona[7] which is based on electron donation from unshaired electron pair of X to the antibonding orbital σ^*_{C-Y} in conformation *I* and suggested to call such an interaction "superjacent orbital interaction". If atom X possesses only one free electron pair and atom Y is more electronegative than hydrogen, then conformation *III* is stabilised by "through space" interaction of n-orbital of atom X with σ^*_{C-Y} orbital[8] (Scheme 1).

Let us suppose that atom X possesses two unshared electron pairs, first in conformation *II*. The corresponding orbital correlation diagram is shown in Scheme 2. Then $n_1 - n_2$ combination differs in symmetry from σ^*_{CY}, and these orbitals cannot therefore interact[9]. Further interaction between $n_1 + n_2$ and σ^*_{CY} is repulsive, as shown by Epiotis[10]. Unsymmetrical gauche conformation *I*, in which both electron pairs of Y are non-equivalent, is then more favoured due to its energy. Furthermore, conformation *I* can be further stabilised by interaction of antiperiplanar free electron pair with two synclinal σ^* CH orbitals[6].

It should be stressed, however, that an equilibrium conformation of a molecule is the result of competition of the two effects, electronic stabilisation and core repulse. Thus, for example, despite of the fact that CNDO/2 calculations[11] on fluoromethanol and ethanol predicted conformation *IV* as that of the lowest energy for both alcohols, the most stable conformation of ethanol is *II* $(Y = CH_3)$ and of fluoromethanol $(Y = F)$ I (ref.[12]). Analogously, the electronic energy of fluoromethylamine and of ethylamine is lowest in conformation *V*, while the most stable conformation of ethylamine is *III* and fluoroamine *V*. For that reason the explanation of anomeric effect based only on analysis of electronic interaction seems incomplete[4].

The effect of core symmetry can be included by means of Jahn-Teller second-order effect[13]. Let us consider conformational conversion of *II* to *I* for fluoromethanol as a chemical reaction. The appropriate reaction coordinate Q is then antisymmetrical with respect to the plane of symmetry σ, and so also $\partial H/\partial Q$. The symmetry and shapes of HOMO and LUMO's calculated by CNDO/2 method are the same as in Scheme 2. Then the respective matrix element of the operator $\partial H/\partial Q$ is $\langle n_1 - n_2 | \partial H/\partial Q | \sigma^*_{CY} \rangle \neq$ $\neq 0$, which means that conformational change connected with this reaction coordinate



SCHEME 2

is favourable by its energy[13]. Wave functions for ethanol, ethylamine, and fluoromethylamine can be analysed similarly. In the case of fluoromethylamine the values of $\langle \mathrm{HOMO}/(\partial H/\partial Q)\, \mathrm{LUMO}\rangle$ indicate that stable conformations are conformation *V* and gauche conformation *VI*. Comparison of electronic energies and core repulse clearly favors conformation *V*. Similarly, for ethylamine conformations *V* and *VI* are not stable, and the most stable conformation is *III*. A somewhat more complicated situation arises with ethanol, since its lowest lying unoccupied orbital, LUMO, is according to CNDO/2 calculation symmetrical with respect to the plane, very close lying LUMO + 1 orbital is, however, antisymmetrical. Interaction with the latter orbital could be the reason why the most stable conformation for ethanol is *II*. In this case a more detailed information about symmetry of LUMO might provide CNDO method with Del Bene and Jaffé parametrisation[14].

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