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ON ELECTRONIC AND CONFORMATIONAL EFFECTS IN SIX-MEMBERED RINGS

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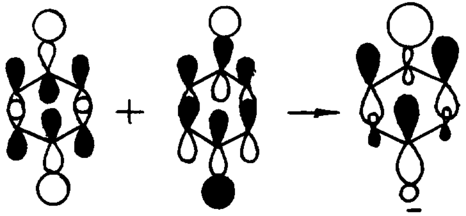
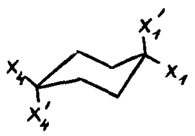
Electronic changes in nonconjugated systems by the substituents are usually discussed in the terms of inductive [1] and hyperconjugative effects. However many examples have been cited which indicate that the polar effects of remote substituents can in some cases be transmitted over very long distances [2]. Here we propose a new general approach to the problem of such "long-range" interaction, which is a generalization of a previously discussed concept for the ethane systems [3,4]. The highest occupied MO's of chair-cyclohexane (D_{3d} symmetry) are a degenerate pair of E_g type. We give a simplified picture of one of them (I) and corresponding LUMO (II), considering X_1 and X_4 positions as equatorial (this picture is given as in [5]; for a better representation see [6]). These "ribbon" orbitals [5] persist in other six-membered rings including boat conformations [5,7].



I II III

Let us consider now a model process of increasing the X_1 electronegativity (IV). The substitution of H_1 by an electronegative (EN) group X_1 we treat as a perturbation. This process mixes together the filled and empty MO's of the unperturbed molecule [8]. The usual perturbation treatment of "frontier orbitals" I and II (taking into account their symmetry and the signs of the AO coefficients) produces polarized MO's wherein the electron density in HOMO is shifted from e-H_4 to C_4 (V). Way of doing this is represented in the schematic drawing I+II → III (for analogous pictures see, for example, [8]). A change of axial H_4 - AO is insignificant in this treatment because the corresponding AO coefficients are zero. Thus, one may draw the following conclusions: (1) the shift of electron density considered must lead to the inhibition of carbenium ion generation at the 4-e-position; (2) e-X_1 EN-group has to favour the introducing of the most electrondonor group (or an electron pair as a limiting case) at the e-X_4 position and vice versa. *)



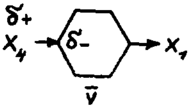
IV X_1 = EN-group
$X_1'=X_4=X_4'$ =H

VI X_1 = EN-group, X_4 =OTs,
$X_4'=X_1'$=H

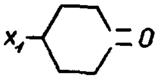
IX X_1,X_4 - EN-groups,
$X_4'=X_1'$=H

X X_1,X_4' - EN-groups,
$X_1'=X_4$=H

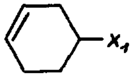
XI X_1',X_4' - EN-groups,
$X_1=X_4$=H



V



VII



VIII

Let us briefly discuss the experimental data, which may summarise as follow : (A). The EN-group at the e-X_1 position creates a great difficulty for developing the positive charge (even partial) on C_4. This conclusion could be supported by the data of solvolysis of tosylates VI [9] (EN-groups decrease the rate) and the data of reduction of ketones VII [10] (EN-group increase the rate). This effect probably operates in boat conformation as it can be seen from the solvolyses data of norbornane and 7-oxabicyclo[2,2,1]-heptane derivatives [11] and from the unusual stability of 2,3-dicarbomethoxy-4-mercuri-5-methoxy-7-oxabicyclo-[2,2,1]-heptane perchlorate [12]. Furthermore, this effect also results in sharp decreasing of the rate of electrophilic addition to the substituted cyclohexenes of type VIII [12, 13]. (B). The following consequences from the conclusion (2) are evident : the factor considered must be included in the stabilization (a) of cis-form of X in

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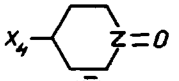
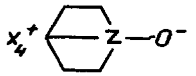
*) A referee kindly informed us that the polarity at C_4-X_4 obtained is a manifestation of a general alternation effect in saturated systems [17].

IX $\rightleftharpoons$ X equilibrium (b) of diaxial form XI in IX $\rightleftharpoons$ XI conformational equilibrium, (c) of axial forms of ketons VII. A large number of experimental facts supports these conclusions [14,15]. An interesting example is connected with the predominance of the diaxial conformer in the conformational equilibrium of trans-XII (Z =S, X_4=Cl). A discrepancy of about 1,5 ccal/mole has been found between the experimental and the calculated ΔG values (the predominance of diaxial conformer is about 1,3 ccal/mole [15]). Novel conformational effects could also be predicted from the conclusion (2).



XII



A preference of the axial conformation for the nonsubstituted compounds of type XII (X_4=H) was also proved [16]. It has been suggested that the axial preference is due to the attractive interactions between the axial substituent and the carbons and the axial protons at the 3 and 5 positions. The Morse-like potential function has an attractive region at these distances [16]. However one may put forward a new alternative explanation. The conformation of XII (X_4=H) with an equatorial Z=O bond should have a relatively large positive charge on e-H_4, as compare with the conformation with an axial Z=O bond. Thus, the destabilization of the equatorial conformation of the compounds XII may be connected with the contribution of non-favourable dipolar structure (the structure XIII in terms of the resonance theory).

In this work we have attempted to suggest novel simple concept drawn from the frontier orbital interactions. The "long-range" electronic effects and some conformational peculiarities may be "build in" into the shape of the delocalized MO embracing the whole molecule of the cyclic compound.

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