DELOCALISATION INTO ANTI ANTIBOND ORBITALS

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A variety of intramolecular interactions have been proposed and recently discussed to account for known conformational and configurational preferences. The need to present rotational phenomena about single bonds in terms of a balance between attractive and repulsive interactions has been emphasised.[1,2] The preference shown by many compounds for the gauche form, e.g., 1,2-difluoro-, 1-chloro-2-fluoro-, 1,2-dicyano- and 1,1,2,2-tetrachloro-ethane, hydrogen peroxide and hydrazine, has led Wolfe et al[1] to propose the rule "When electron pairs or polar bonds are placed on adjacent 'pyramidal' atoms, syn- or anti-periplanar orientations are disfavoured energetically with respect to that structure which contains the maximum number of gauche interactions". The greater preference of an electronegative substituent X for the axial orientation at the anomeric centre of a pyranose ring (1) than in cyclohexane, i.e., the anomeric effect, is diminished by increase in solvent polarity and Eliel[2] has justifiably concluded that dipole-dipole interactions contribute to the effect. In the 1,3-dioxane (2), axial fluorine, which provides maximum dipole repulsion, is preferred; here, C-F is gauche with respect to C_4-O and C_6-O and Wolfe's rule is obeyed. Thus Eliel has been led to write "Our present hypothesis is that the nuclear-electron attraction postulated by Wolfe et al as well as "classical" electrostatic repulsion both contribute to the generalised anomeric effect to a greater or lesser extent". In 1969 Romers et al[3] interpreted the anomeric effect, in so far as it appears in 2-chlorotetrahydropyran (1, X = Cl) and other $\propto$-chloroethers, in terms of double bond-no bond resonance and its molecular orbital equivalent. They pointed out that

this interpretation is compatible with the lengths of the bonds O-C and C-Cl in the group O-C-Cl being abnormally short and long respectively. This apparently important contribution has only once been mentioned and never considered in subsequent discussions of the anomeric effect.

The following is a generalised description of their concept. In each of the pairs of atoms Aa and Bb of the molecule (5), the larger amplitude of bonding orbital character is on the more electronegative atom and the larger amplitude of antibonding character on the less electronegative atom. Consequently, as shown in (6), which represents a system in which a is $\underline{anti}$ to b and the electronegativities of the atoms are in the order a $>$ A and B $>$ b, the best combination for an energy lowering orbital interaction of the Bb bond and the unoccupied Aa antibond orbital appears to involve the most electronegative ligand of A and the most electropositive ligand of B. The magnitude of this second order stabilisation will depend on the difference in energy between these two orbitals and the extent to which they overlap. The interaction will lower the electron density at b, increase the bonding of A to B, partially neutralise the bond A-a and give preference to the configuration or conformation which has the most electropositive ligand (or lone pair of electrons) of B $\underline{anti}$ to the most electronegative ligand of A. Conversely, preference will be given to the most electropositive ligand of A being $\underline{anti}$ to the most electronegative ligand of B. These preferences have the same stereo-chemical implication as though given to placing the most electronegative (or electropositive) ligands of A $\underline{gauche}$ to the most electronegative (or electro-positive) ligands of B and, consequently, accommodate all the examples listed by Wolfe $\underline{et}$ $\underline{al}$ in support of their "$\underline{gauche}$ rule".

Recently, the lowering of the electron density at b in (6) has been cleverly used by Abraham and Rossetti[4]; they write: "In the diaxial conformer of $\underline{trans}$-1,4-dichlorocyclohexane (3), the hydrogen atoms on $C_{2,6}$ in a planar $\underline{trans}$ arrangement with the axial chlorine on C_4, are more positive than usual. These hydrogens are in close proximity to the axial chlorine atom on C_4---- the attractive 1,3-interactions between the negatively charged chlorine atoms and the positive axial hydrogen atoms are the major factor in the extra stabilisation of the diaxial conformer".
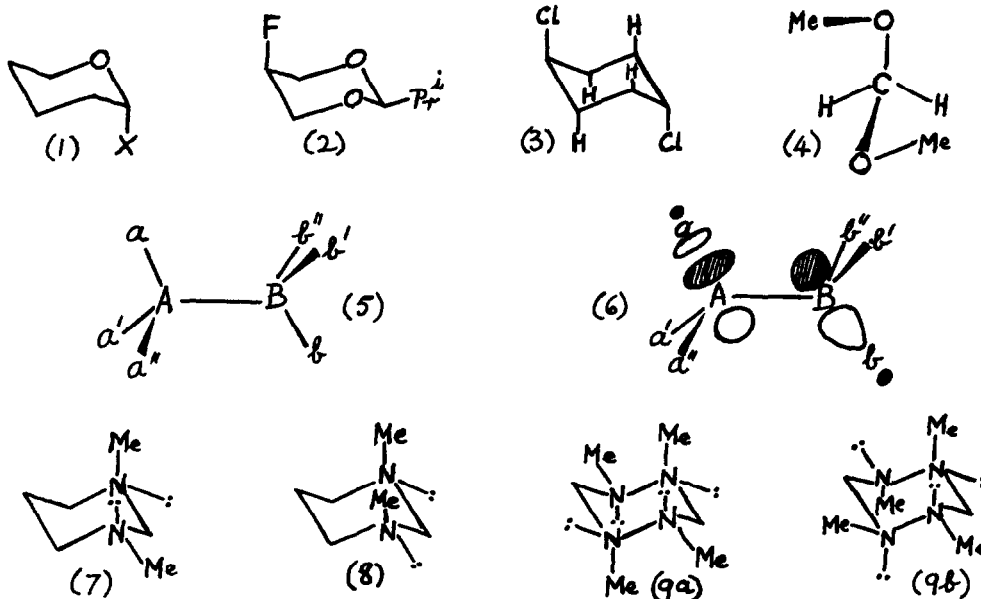
Whereas the interaction of two fluorine atoms through carbon atom, as in methylene fluoride, is symmetrical, that between two oxygen atoms or two nitrogen atoms will be symmetrical only if the conformation or configuration of the molecule allows. For example, it is symmetrical in the 1,3-dioxane (2), in dimethoxymethane when its conformation is that shown in (4) and in 2-alkoxytetrahydropyran (1, X = OR) only when the alkoxyl group is axial. Although this two-way interaction is energetically preferred, the hexahydro-diazine (7) is prevented from having the configuration (8) by steric interaction of axial methyl groups. In (7) the interaction can be only lopsided and results in an electronic delocalisation which tends to place a positive charge on the nitrogen atom with the axial methyl group and a negative charge on the other. These considerations, when applied to the hexahydro-tetrazine (9) which is known to have two axial methyl groups,[5] give preference to the configuration (9a) rather than (9b) since the former is supported and the latter opposed by electrostatic interaction of neighbouring nitrogen atoms. Evidence for lopsided interaction in the systems O-C-O and N-C-N might be provided by anomalous bond lengths, dipole moments and other physical properties.

In molecules and anions of type $\ddot{A}$—B: e.g. N_2H_4 and ROO$^-$, the nucleophilic

reactivity of B is boosted by the unshared pair of electrons on A. This boost, called the α-effect,[6] can be interpreted in terms of <u>anti</u> interaction: the bonding of B to the electrophile in the transition state is developing an antibond orbital into which the lone pair on A, when suitably oriented, can spread. The interaction of <u>anti</u> ligands as in (6) is compatible with the mechanisms of many E2 eliminations and some 1,2-shifts.

References

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