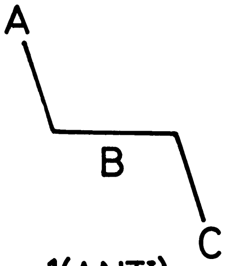
CHEMISTRY LETTERS, pp. 417-420, 1986.

A NEW THEORY FOR THE ANTI-PERIPLANAR EFFECT

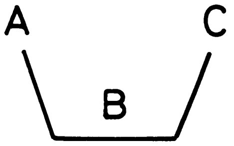
Satoshi INAGAKI,* Koji IWASE, and Yoshio MORI
Department of Chemistry, Faculty of Engineering, Gifu University,
Yanagido, Gifu 501-11

The anti-periplanar effects, including the gauche and anomeric effects, are proposed to be brought about by the continuity of phase of the bonding (nonbonding) and anti-bonding orbitals of the anti-periplanar bonds and the bonding orbital of the intervening bond.

The anti-periplanar effect, including anomeric effect,$^{1)}$ the gauche effect$^{2)}$ and so on, has been widely observed in organic chemistry. That is the effect of the geometrical relation between the periplanar entities on the stabilities of conformers. The anti-form (**1**) is more stable than the syn-form (**2**). This has long been believed to result from greater overlapping between the electron-donating and accepting orbitals in the anti-periplanar form.$^{3)}$ In this letter we will present a new theory for the anti-periplanar effect.

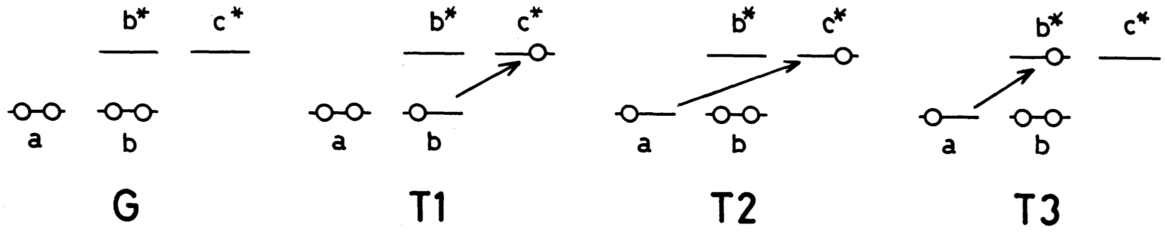


1(ANTI)



2(SYN)

The electron configurations, G, T_1, T_2, and T_3, may be important for the electron delocalization in the three-bond systems with four orbitals, i.e., bonding and anti-bonding orbitals (b and b*) of a σ-bond with an electron-donating orbital (a) at one end and an electron-accepting orbital (c*) at the other.



The off-diagonal matrix element, $I(G,T) = H(G,T)-S(G,T)H(G,G)$, for the interaction between the configurations is approximated in terms of orbitals as follows:

$$I(G,T_1) \simeq 2N_GN_T[h_{bc*}-h_{bb}s_{bc*}-h_{ab}s_{ac*}-h_{ac*}s_{ab}+(h_{aa}+h_{bb})s_{ac*}s_{ab}]$$

where the higher than second-order terms, e.g., $h_{ij}s_{kl}^2$, $h_{ij}^2s_{kl}$, are neglected on the assumption that h_{ij} and s_{ij} are infinitesimals of the first order, relative to h_{ii} and s_{ii}. The overlap integrals between geminal bond orbitals, e.g., s_{ab}, s_{bc*}, are further assumed to be negligibly small since the geminal hybrid orbitals are orthogonal to each other. Neglecting these terms, we obtain:

$$I(G,T_1) \simeq 2N_GN_T[h_{bc*}-h_{ab}s_{ac*}].$$

Similarly, the following equations are obtained for the other electron-transferred configurations:

$$I(G,T_2) \simeq 2N_GN_T[h_{ac*}-h_{aa}s_{ac*}], \quad \text{and} \quad I(G,T_3) \simeq 2N_GN_T[h_{ab*}].$$

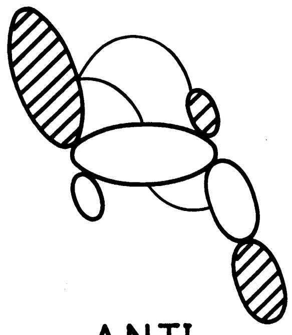
There is an essential difference between the first and latter two equations. The G-T_1 interaction involves the orbitals of a, b, and c*. The magnitude of the interactions depends on the sign relation between the two terms in $I(G,T_1)$. For greater interaction the following condition is required:

$$h_{bc*}h_{ab}s_{ac*} < 0.$$

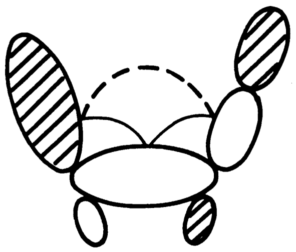
Here we introduce P_{ij}, which is of positive and negative values for in-phase and out-of-phase relation between the orbitals i and j. The h_{ij} is of an opposite sign of P_{ij} while s_{ij} is of the same sign of P_{ij}. Therefore, the condition for the greater interaction is rewritten:

$$P_{bc*}P_{ab}P_{ac*} < 0.$$

This requires an odd number of out-of-phase relation among a, b, and c*. The orbitals, a and b, are electron-donating orbitals, c* being an electron-accepting orbital. The orbital phase requirement is included in those[4)] previously derived for cyclic orbital interaction in a different way: (i) the electron-donating orbitals out of phase; (ii) the accepting orbitals in phase; and (iii) the donating and accepting orbitals in phase. Applying to the orbital interactions of the present interest, the requirements were found to be simultaneously satisfied for the anti-periplanar form but not for the syn form. This means that the delocalization is enhanced in the anti-periplanar relation due to the orbital phase continuity, while depressed in the syn-periplanar relation due to the discontinuity.



ANTI

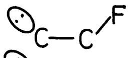
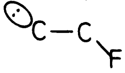
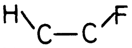
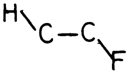


SYN

There is no three-orbital phase restriction on the G-T_2 and G-T_3 interactions. The G-T_2 interaction involves the a-c* interaction, which have been believed to be responsible for the anti-periplanar effect. The G-T_3 interaction is approximated to be the a-b* interaction. This interaction makes no difference between the anti- and syn-periplanar relations.

We carried out the extended Hückel calculations on the four bond orbital (a, b, b*, and c*) systems. The bond orbitals are linear combinations of hybrid orbitals. The single determinant wavefunctions for the ground states were then subjected to the electron configuration analysis for many-system interaction.[5)] Finally, the interaction energies between the electron configurations, $E(G,T)=2C_GC_TI(G,T)$, were calculated, and some results are listed in Table 1. The accepting orbital (c*) is the anti-bonding orbital of C-F σ-bond (σ_{CF}*). The intervening bond orbitals (b and b*) are those of C-C bond (σ_{CC} and $\sigma_{CC}{}^*$). The donating orbital (a) is a nonbonding orbital for lone pair of electrons on carbanion (n_C) or a bonding orbital of C-H bond (σ_{CH}).

Table 1. Matrix Elements (eV) and Interaction Energies (kcal/mol)

		$a = n_C$,	$b = \sigma_{CC}$,	$b^* = \sigma_{CC}{}^*$,	$c^* = \sigma_{CF}{}^*$		
		I(G,T_1)	I(G,T_2)	I(G,T_3)	E(G,T_1)	E(G,T_2)	E(G,T_3)
syn		1.45	1.00	0.97	-4.8	-2.5	-1.9
anti		2.37	0.22	0.97	-13.7	-0.2	-2.0
		$a = \sigma_{CH}$,	$b = \sigma_{CC}$,	$b^* = \sigma_{CC}{}^*$,	$c^* = \sigma_{CF}{}^*$		
syn		1.49	0.20	1.22	-5.7	-0.1	-2.8
anti		2.19	0.33	1.22	-12.2	-0.3	-2.8

The predicted differences between the syn and anti-periplanar forms of both models were found in E(G,T_1) and I(G,T_1), which are associated with the delocalization from the intervening bond to the acceptor bond. The difference in I(G,T_1) comes from the opposite sign relation of $-h_{ab}s_{ac^*}$ (-0.44 and -0.56 for syn, 0.41 and 0.43 for anti) with h_{bc^*} (1.64), as predicted. The direct delocalization from the donor to acceptor, or the G-T_2 interaction, is of a minor factor if it favors the anti-periplanar relation.

References

1) R. U. Lemieux and S. Koto, Tetrahedron, 30, 1933 (1974) and references cited therein.

2) S. Wolfe, Acc. Chem. Res., 5, 102 (1972) and references cited therein.

3) S. David, O. Eisenstein, W. J. Hehre, L. Salem, and R. Hoffmann, J. Am. Chem. Soc., 95, 3806 (1973) and references cited therein.

4) K. Fukui and S. Inagaki, J. Am. Chem. Soc., 97, 4445 (1975); S. Inagaki, H. Fujimoto, and K. Fukui, ibid., 98, 4693 (1976); S. Inagaki and Y. Hirabayashi, ibid., 99, 7418 (1977).

5) S. Inagaki and Y. Hirabayashi, Bull. Chem. Soc. Jpn., 51, 2283 (1978).

(Received December 3, 1985)