Additive Through Space and Through Bond Orbital Interactions

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Orbital interactions through space and through bond can be additive rather than counteractive as previously shown by Hoffmann. An application to the nonbonding MOs in alternant hydrocarbons is shown.

As Hoffmann [1] pointed out in a pioneering discussion on the trimethylene system, an antisymmetric (A) π-type MO is lower in energy than its symmetric (S) counterpart. This is summarized in Figure 1. The combination $p_1 - p_2$ (A) cannot mix by symmetry with σ and σ*. For the interaction of $p_1 + p_2$ (S) with σ and σ* the former dominates, due to the inclusion of overlap in one-electron perturbation theory.[2]

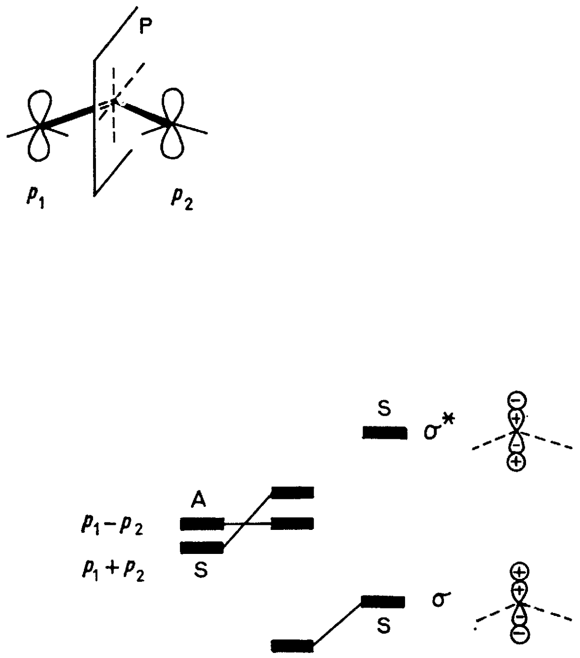


FIGURE 1 Interaction diagram for the π-type orbital interactions in the trimethylene system according to Hoffmann.[1] The symmetry classifications are with respect to the plane P

In this paper, I present theoretical evidence that orbital interactions through space and through bond can be *constructive* rather than *destructive*.

Consider the higher homologue of the trimethylene system, the tetramethylene system in its analogous π-conformation. A corresponding interaction diagram for the π-type orbitals is given in Figure 2. The methylene groups adjacent to the p orbitals possess a π-component which splits into a set of MOs symmetric (S) and antisymmetric (A) with respect to the symmetry plane P. The system of MOs is then analogous to that of *cis*-butadiene.

According to one-electron perturbation theory [2] the combination of p orbitals symmetric (S) with respect to the symmetry plane P interacts with σ_1 and σ_3*; the former raises while the latter lowers the energy of $p_1 + p_2$. Similar arguments apply to the interaction of $p_1 - p_2$ (A) with σ_2 and σ_4*.

Because the antisymmetric orbitals σ_2 and $p_1 - p_2$ are closer to each other than the symmetric orbitals σ_1 and $p_1 + p_2$. according to perturbation theory the antisymmetric levels will perturb each other more strongly than the symmetric levels. The result is to *enhance* the splitting between $p_1 + p_2$ and $p_1 - p_2$ from through space interactions.

This is in contrast with the results on the trimethylene system [1] where *only one symmetric* orbital interacts with the $p_1 + p_2$ pair.

A quantitative assessment of these types of orbital interactions (which are additive) can be made by comparing the following model geometries, with the MO system computed with EH theory.[3] In (1) the methylene groups at C(2) and (3) are omitted, without changing the orientation of the methylene groups at C(1) and C(4). On this basis (1) merely reflects orbital interactions through space while (2) accounts for orbitals interactions through space plus through bond.

Dependence of Valence Angle Deformation.—Because

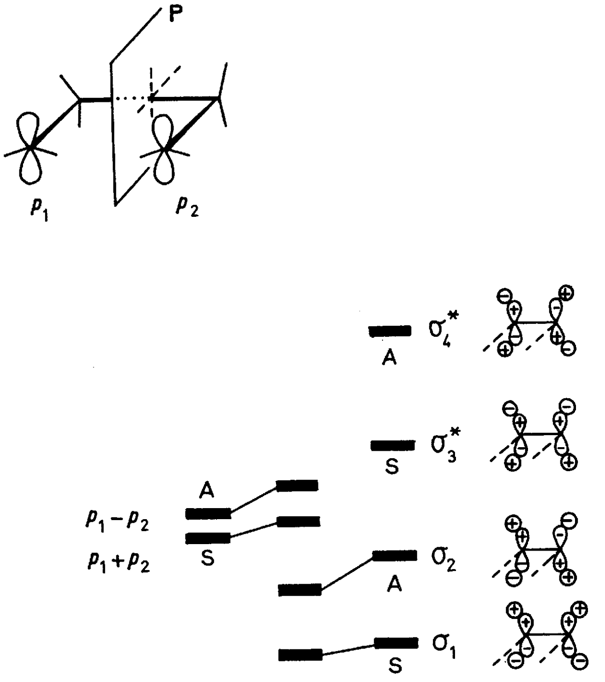
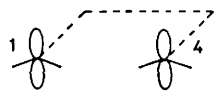


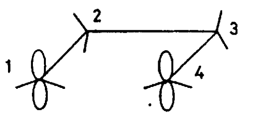
FIGURE 2 Interaction diagram for the π-type orbitals in the tetramethylene system. The symmetry classifications are with reference to the plane P

the energies and shapes of the MOs of methane change considerably under distortion[4] of the tetrahedral geometry, I have explored the angular dependence of the two effects, orbital interaction through space *versus* orbital interaction through bond for the tetramethylene system in its *cis*- and *trans*-conformations. The results are summarized in Figure 3. The dotted lines in Figure 3 reflect only through space interaction. Here the methylene groups at C(2) and (3) are removed.



(1)

S −11·628
A −11·160



(2)

−10·949 (eV)
−10·174

C(1)-C(4) = 2·526 Å

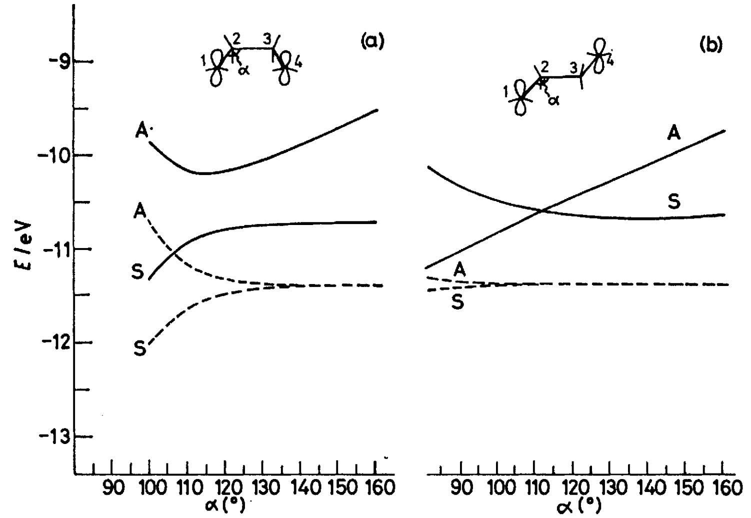


FIGURE 3 Plot of energies (in eV) of HOMO and LUMO as a function of valence angle α [C(1)$\widehat{C}$(2)C(3) = C(2)$\widehat{C}$(3)C(4)] in the tetramethylene system [C–C = 1.50 Å; H$\widehat{C}$(1)H = 120, H$\widehat{C}$(2)H = H$\widehat{C}$(3)H = 110°]: (a) *cis*-; (b) *trans*-conformation. The energies are derived from EH calculations

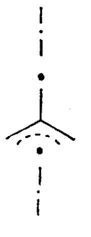
In the *cis*-conformation the A level is raised in energy more than the S level. This tendency is reinforced by extending the valence angle α. The energy splitting between HOMO and LUMO reaches a maximum at small *and* large values of α. In the *trans*-conformation at values of α below 112° the A level becomes the HOMO. This is a consequence of two effects: (a) through space orbital interaction between the *p* orbitals at C(1) and (4) is very small; (b) with decreasing valence angle α orbital overlap between the π-components at C(4) and (2) makes itself felt. Since the orbital overlap is positive (see Figure 2) the A level slips below the S level.

The above considerations are derived from EH calculations. Although this procedure is known to yield bad energies, it gives a correct picture of the timing of orbital changes as functions of geometrical parameters.

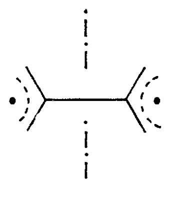
In the next step we have varied the HCH angle at C(2) and (3). Here it turned out that a change of these parameters has no significant influence on the extent of HOMO — LUMO energy splitting.*

Our theoretical findings are of crucial importance for a discussion of the effects of cyclic substitution[5] on the electronic properties and states of alternant hydrocarbons such as (3)—(5) which possess a set of two non-bonding MOs within the Hückel approximation.[6] These two NBOs are always symmetric (S) or antisymmetric (A) with respect to a symmetry plane P (dashed line) perpendicular to the π-system and bisecting the molecular plane.

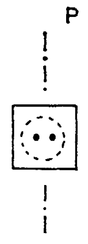
For example, in case (4) the two NBOs are[6] symmetric (S) or antisymmetric (A) according to the symmetry plane P. Similar considerations hold for the NBOs in the other π-systems (3) and (5).



(3)



(4)



(5)

As in the case of (2), the NBOs interact with the set of σ-orbitals in the cyclic structures (6)—(8) (see Figure 2). The cyclic substitution then removes the degeneracy of the NBOs by through bond interaction as follows. For $n = 1$, the A level will be placed below the S level as a consequence of *counteractive* through bond and through

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* Angle variations for H$\widehat{C}$H at C(2) and (3) by 10° changes the energy difference between HOMO and LUMO by <0.01 eV.

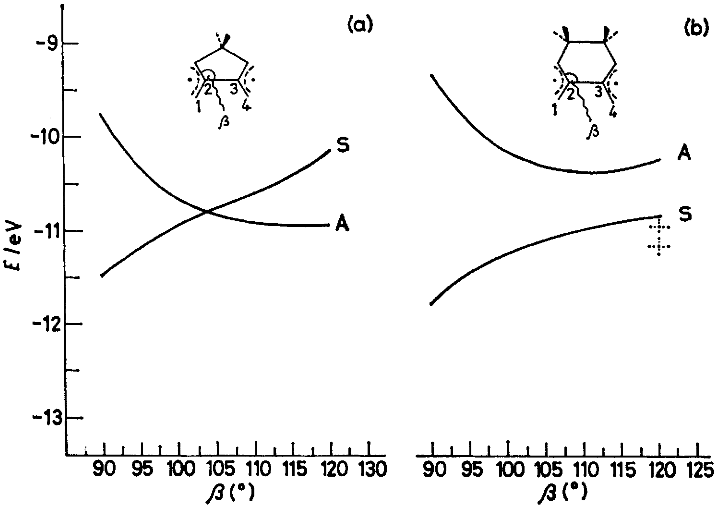
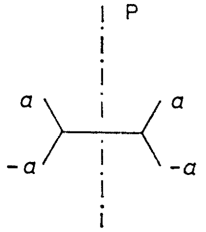
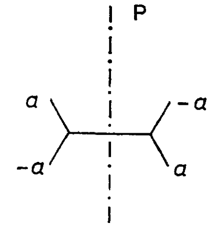


FIGURE 4 HOMO and LUMO energies (in eV) for (7) [(a) $n = 1$; (b) $n = 2$] as a function of the valence angle β [$C(1)\widehat{C}(2)C(3) = C(2)\widehat{C}(3)C(4)$] and derived from EH calculations. The dotted lines correspond to the parent compound (4) (β 120°). The bonding parameters were chosen from ref. 7 and with C–C = 1.50 Å, $H\widehat{C}(1)H$ = 120°, and $H\widehat{C}(2)H = H\widehat{C}(3)H$ = 110°

space interactions. For $n = 2$, the S level will lie below the A level, due to *additive* through bond and through space interactions.



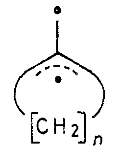
(S)



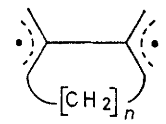
(A)

$a = 0{\cdot}5$

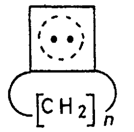
In case (7) this is further illustrated by the EH calculations depicted in Figure 4. These results support the above outlined arguments.



(6)



(7)



(8)

n = 1 or 2

Clearly our observations are qualitative but correct in principle, because they are derived from symmetry arguments about the wavefunction. The lifting of orbital degeneracy in (6)—(8) should be energetically favourable to a singlet ground state,[5,7] over a triplet state in these systems. However, the magnitude of the energy splitting remains to be established by SCF-calculations including configurational interaction.[7]

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[8/641 *Received, 11th April,* 1978]

REFERENCES

[1] R. Hoffmann, *J. Amer. Chem. Soc.*, 1968, **90**, 1475. An elegant experimental verification of the double rotation process in the reaction of cyclopropane has been reported, J. A. Berson, L. D. Pedersen, and B. K. Carpenter, *J. Amer. Chem. Soc.*, 1976, **98**, 122.

[2] (*a*) L. Salem, *J. Amer. Chem. Soc.*, 1968, **90**, 543; (*b*) R. Hoffmann, *Accounts Chem. Res.*, 1971, **4**, 1.

[3] R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397 and subsequent papers.

[4] B. M. Gimarc, *J. Amer. Chem. Soc.*, 1971, **93**, 593.

[5] (*a*) W. W. Schoeller, *J.C.S. Perkin II*, 1978, 525; (*b*) see also W. W. Schoeller, *J. Amer. Chem. Soc.*, 1977, **99**, 5919.

[6] H. C. Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265 and subsequent papers.

[7] *E.g.* for the parent (4) the most accurate calculations at an *ab initio* level including CI have been reported recently, W. T. Borden and E. R. Davidson, *J. Amer. Chem. Soc.* 1977, **99**, 4587.