spectral data of the hydrogenolyzed product were exactly matched with those of authentic L-proline methyl ester (7), unambiguously prepared from L-proline and methanol. Optical rotation of the hydrogenolized product ($[\alpha]_D^{24} = -32.6°$) was also in full agreement with that of L-proline methyl ester (7) ($[\alpha]_D^{24} = -32.9°$, methanol, lit[8]., $[\alpha]_D^{24} = -34°$).

From the above results, it was confirmed that diborane reduction of N-benzyloxycarbonyl-L-glutamic acid α-methyl ester (4) undoubtedly afforded N-benzyloxycarbonyl-L-proline methyl ester (6), although its mechanism could not be clearly understood.

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n-n Orbital Interaction Involving *anti*-Hückel σ-Aromaticity

Ikchoon Lee

Department of Chemistry, Inha University, Inchon 161, Korea (Received October 6, 1984)

Interactions between two nonbonding orbitals, n_1 and n_2, are normally dissected into two varieties, *i.e.*, through-space (TSI) and through-bond (TBI) interactions.

We wish here to report the third kind of interaction which becomes important only in cases where the two orbitals can overlap significantly. In this type of interaction both TSI and TBI are involved and the two overlapping nonbonding orbitals are considered to constitute terminal hybrid AOs within a cyclic form of σ conjugative chain. In the frontier orbital approach,[2] the energy change, δE_i, involved in an interaction between the two terminal hybrid AOs, n_1 and n_2, is due mainly to the corresponding perturbation of the HOMO, ψ_i, of the chain.[3]

$$\delta E_i = \nu_i \int \psi_i P \psi_i d\tau = \nu_i c_{i1} c_{i2} \beta_{12} \qquad (1)$$

where ν_i is the number of electrons occupying the HOMO, c_{i1} and c_{i2} the AO coefficients of n_1 and n_2 in the HOMO, and β_{12} is the resonance integral between the two orbitals. In the simple theory of σ conjugation[4] (C-approximation),[1c,5] the AO coefficients are determined by an HMO calculation, while the sign of β_{12} depends on the symmetry adapted orbitals; β_{12} will be negative (overlap integral S_{12} will be positive) for $n_+ (= n_1 + n_2)$ and β_{12} will be positive ($S_{12} < 0$) for $n_- (= n_1 - n_2)$ level.

In the diradicals or diamines with even number of intervening sigma bonds between n_1 and n_2 (N = even),[1c] the product of terminal AO coefficients of the HOMO has a negative sign,[6,8] $c_{i1} \cdot c_{i2} < 0$. Thus for an N = even system having a crowded structure with significant overlap between two terminal nonbonding lobes, δE_i will be negative, *i.e.*, stabilizing, if β_{12} is positive corresponding to a negative overlap, $S_{12} < 0$. Therefore the *anti*-symmetric combination of orbitals, n_-, having positive β_{12} will be stabilizing and symmetric combination, n_+, will be destabiliz-

ing. The level order will thus become n_- below n_+ level which is the reverse of the normal level order for N = even cases.[1c,9] Since the reversal of the sign of one β to positive ($S < 0$) brings stabilization, the system has an *anti*-Hückel or Möbius type σ aromaticity[3,10]; an N = even system with a crowded a structure having significantly overlapping terminal nonbonding lobes forms an *anti*-Hückel or Möbius system[6] so than n_- level has

(I)   (II)   (III)

(IV)   (V)
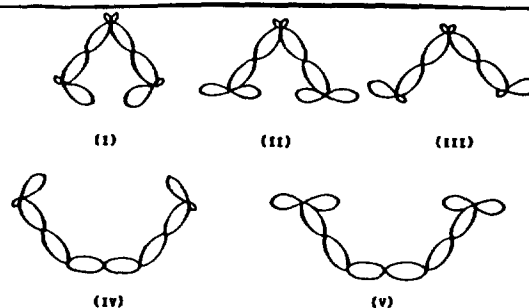
σ-aromatic whereas n_+ level has σ-antiaromatic[3] structure.

Various levels of MO calculations[1,7] gave in fact the level order of n_- below n_+ for outward pyramidalized trimethylene diradicals, (I).[7]

This reversal of level order has been a puzzle[1] and no ready explanation has yet been found. It is clear that this level order reversal in (I) is due to the third type of n-n orbital interaction, in which both the direct overlap between the two nonbonding orbitals (TSI) and the σ-conjugative and hyperconjugative interactions of the nonbonding orbitals with the CC bonds forming framework σ orbitals (TBI)[1c] are involved. This type of coupling term involving both contributions has been known to exist,[1c,7] but the nature of the interaction was not explicitly
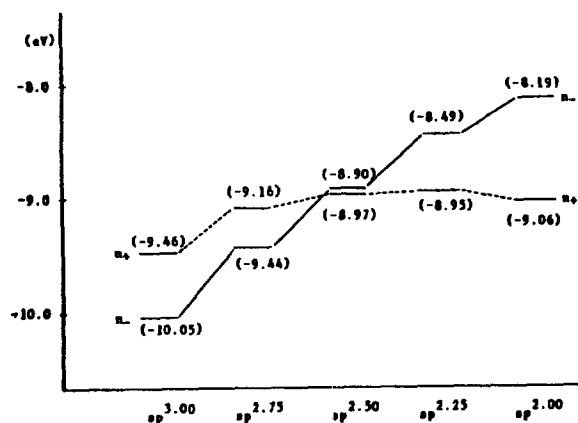
Figure 1. STO–3G results for level order reversal of outward pyramidalized trimethylene diradical.

understood.

That the reversal of level order in (I) is due to the σ-conjugation of nonbonding orbitals with the framework σ orbital was confirmed by the change of level order to normal, i. e., n_+ below n_+ below n_, when we changed the pyramidalized lobes to sp² (or p-AO) type, (II), as shown is Figure 1; the overlap integral and hence the resonance integral between the sp² lobe and the hybrid AO used to form the adjacent CC σ bond vanishes[4] and the nonbonding lobe no longer forms a part of the σ conjugative chain. In the inward pyramidalized structure (III), the overlap between the two nonbonding lobes will be neglibgible so that σ aromatic stabilization will no longer be possible and the level order will become normal to n_+ below n_-.

Analogus argument leads us to the σ aromaticity of the Hückel type for an N = odd system with a crowded structure having significant overlap between two terminal nonbonding lobes[6]; the n_+ level will be σ aromatic whereas n_- will be σ antiaromatic giving level order of n_+ below n_-. In this type (N = odd) of system, however, TSI is in line with the σ-conjugative (the third kind) orbital interaction, both placing n_+ below n_-.[1c,11] Hence the change of nonbonding lobes to sp² type will cause no level order reversal but will only result in decrease in the overall interaction. Our STO–3G calculations on tetramethylene diradical system (IV) in fact showed no level order reversal but only showed a decrease in energy splitting, $\Delta E = e_- - e_+$, when we changed the lobes to sp² type (V).[12] Full details will be reported elsewhere.

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(6) In diradicals, both of the symmetry adapted orbitals, $n_+ = n_1 + n_2$ (S) and $n_- = n_1 - n_2$ (A), are singly occupied in the triplet state, be the same as that for diradical anion or dianion; for N = even σ electrons forming a conjugative chain while for N = odd systems the HOMO corresponds to that for the 4m + 2σ electron system.

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(9) Both TSI and TBI place n_+ below n_- level in N = even systems.

(10) Aromaticity will be of the *anti*–Hückel or Möbius type for 4m electron cyclic system, while it will be the Hückel type for 4m + 2 electron cyclic system.

(11) For N = odd systems, however, TBI is in opposition to TSI, and hence the level order becomes n_- below n_+ level in the through-bond dominated system, where direct overlap of the two nonbonding lobes is negligible.

(12) Our STO–3G computations gave energy levels (of n_- and n_-) for sp³ (IV) and sp² (V) type lobes in tetramethylene diradical as $\varepsilon_+ = -10.004$, $\varepsilon_- = -8.998$ and $\varepsilon_+ = -8.786$, $\varepsilon_- = -7.972$ eV, respectively.