Tetrahedron Vol 41, No 21, pp. 5007 to 5010, 1985
Printed in Great Britain.

0040-4020/85 \$3.00 + .00

n–n ORBITAL INTERACTION INVOLVING σ-AROMATICITY[1]

IKCHOON LEE,* KIYULL YANG and HO SOON KIM
Department of Chemistry, Inha University, Inchon, Korea

(*Received in Japan* 9 *August* 1984)

Abstract—The concept of σ-conjugation has been used to introduce a new type of n–n orbital interaction named the 'sigma aromatic interaction'. This mode of interaction involves both through-space and through-bond interactions simultaneously in a σ-conjugated cyclic structure with σ-aromaticity of Hückel or anti-Hückel type. The introduction of the σ-aromatic interaction proved to be essential in resolving as yet unexplained phenomena such as level order reversal in the trimethylene diradical and the existence of a 'phantom bond' in [1.1.1]-propellane.

Interactions between two non-bonding orbitals, n_1 and n_2, have been conceptually dissected into through-space (TSI) and through-bond (TBI) varieties.[2] The former arises from a direct overlap of the two independent non-bonding orbitals, the interaction energy being first order in the overlap integral S between the two orbitals; the interaction will be stabilising if S is positive and hence the resonance integral β is negative, while it will be destabilising if S is negative, i.e. $\beta > 0$. In the latter type (TBI), non-bonding orbitals interact through framework σ orbitals in two ways: through a σ-conjugative chain involving geminal (1,2-) overlap of n_1 and n_2 with framework σ orbital and through hyperconjugation involving vicinal (1,4-) overlap.[3] The interaction energy in this case is second order in overlap, s, between n and framework σ orbital.[2c] According to a simplified approach, the frontier orbital (FMO) patterns are such that the effect of the two (σ-conjugative and hyperconjugative) interactions are in the same direction so that the relative magnitude of TBI can be estimated qualitatively using only one of them, normally the hyperconjugative (vicinal) interaction.[2c]

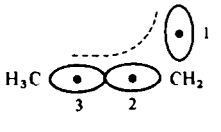
It has been shown that in a system with an even number of intervening σ-bonds between n_1 and n_2 (N = even), both TSI and TBI place n_+ level, the symmetric combination of the two $n_+ = n_1 + n_2$, below n_-, the antisymmetric combination $n_- = n_1 - n_2$.[2] However in an N = odd system the two types of interaction (TSI and TBI) work against each other; in a TSI dominated system n_+ is below n_-, while in a TBI dominated system n_- is below n_+.[2]

There are however cases where the third type of n–n orbital interaction is operative. In this paper we will present the new type of orbital interaction with some important examples, which can only be explained by use of the new interaction mode. In this type of interaction both TSI and TBI are simultaneously involved and the two overlapping n orbitals form terminal AOs within a cyclic structure of a σ-conjugative chain; the cyclic chain may become σ-aromatic or σ-antiaromatic depending on the number of σ electrons and the sign of overlap integral S, giving extra stability or instability to the system.[3,4] We may thus name this as orbital interaction involving σ-aromaticity (SAI).

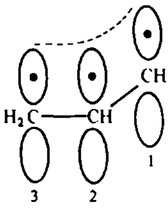
σ-Conjugation and σ-aromaticity

Dewar has shown that the interactions between neighbouring (geminal) CC σ bonds in paraffin are by no means negligible but in fact are greater than those between neighbouring CC π bonds in a conjugated polyene so that the σ bonds in paraffins should form σ-conjugated systems as the π bonds do in conjugated polyenes.[3] Moreover he has argued that CC σ-conjugation is much more effective than CH σ-conjugation;[3] we may therefore safely exclude CH σ bonds from the σ-conjugative chain of paraffin molecules. This simplification is in fact the basis of the 'C-approximation'[5] which was proved adequate in the perturbation molecular orbital (PMO) treatment of n–n orbital interactions.[2c]

In the simple theory of σ-conjugation,[3] the ethyl radical **1** is stabilised by σ-conjugation of the pyramidalised radical centre with the CC bond, just as the allyl radical **2** is stabilised by conjugation. The stabilisation of **1** vanishes if the radical centre is planar, since the unpaired electron then occupies a 2p AO so that the overlap integral and hence the resonance integral between AO 1 and 2 vanishes. This is analogous to the case where the 2p AO 1 is rotated 90° around the C_1—C_2 bond in **2**. Just like the two allyl systems **2** joined together, in such a way that all the AO's in the overlap in phase, form a six π electron conjugative system (benzene) with aromaticity ($4m+2$ π electron system), the two units of **1** when joined together form a six σ electron conjugated system (cyclopropane), which should therefore have σ-aromaticity ($4m+2$ σ electron system).[4] The reality and nature of such σ-aromaticity have been lucidly discussed by Dewar.[3] According to the theory of σ-conjugation, the $4m+2$ σ electron system of cyclic structure should have σ-aromaticity while the $4m$ σ electron system should have σ-antiaromaticity of the Hückel type. On the other hand a system with an odd number of 'abnormal' resonance integrals ($\beta > 0$) should form an anti-Hückel (or Möbius) system,[4,6] and



1



2

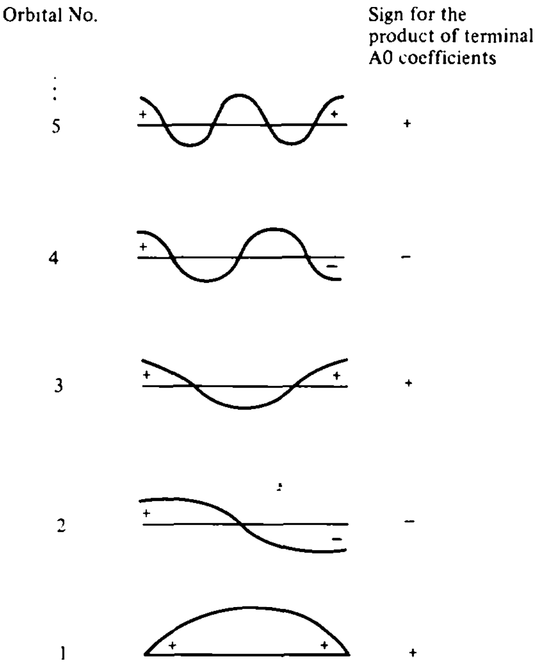
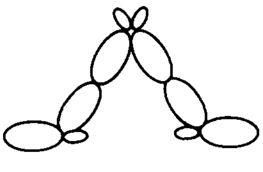


Fig. 1. Orbital patterns and signs for the product of terminal AO coefficients.

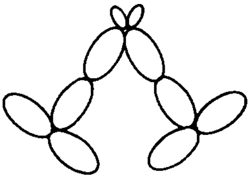
the $4m$ σ electron cyclic structure should have σ-aromaticity while the $4m+2$ σ electron structure should have σ-antiaromaticity. In such anti-Hückel systems, however, signs of the products of terminal AO coefficients for the highest occupied orbital (HOMO) are exactly opposite to those for Hückel systems; $4m$ electron systems have negative signs while $4m+2$ electron systems have positive signs for the product of the terminal AO coefficients of the HOMO as shown in Fig. 1.[7]

Trimethylene diradicals:



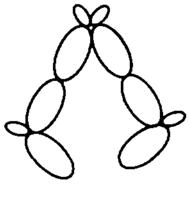
3

TBI (σ-conj + hyperconj)
$S \simeq 0$
n_+ below n_-



4

TBI (hyperconj only)
+ TSI
$S \neq 0$
n_+ below n_-



5

TBI (σ-conj + hyperconj)
+ TSI + SAI
$S \neq 0$
n_- below n_+

This is the smallest N = even system and direct overlap (TSI) of the n lobes may become possible. Being an N = even system, *both TSI and TBI tend to place n_+ below n_-*.[2] In the inward pyramidalised structure,[3] the two n lobes interact through bond (TBI) with negligible TSI. In the structure with the 2p AO radical **4**, σ-conjugation is not possible since the resonance integral between the 2p AO and the hybrid AO used to form the adjacent CC σ bond vanishes.[3] In this structure the two 2p AO's can interact through space (TSI). The level orders for **3** and **4** are normal, i.e. n_+ below n_- as expected for N = even systems.[2] In the outward pyramidalised structure **5**, however, in addition to TBI and TSI, the third type of interaction involving σ-aromaticity becomes possible. This σ-aromatic interaction in **5**, as explained below, is strong enough to reverse the level order to n_- below n_+.[2]

In the frontier orbital theory,[8] the energy change, δE_i, involved in an interaction between the two terminal hybrid AO's, n_1 and n_2, is due mainly to the corresponding perturbation of the HOMO, ψ_i, of the chain.

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

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 diradicals or diamines of the N = even system, the product of terminal AO coefficients of the HOMO has a negative sign, $C_{i1}C_{i2} < 0$, since the HOMO will be that of the $4m$ σ electron system.[9] Thus in **5**, the HOMO will be stabilised, i.e. $\delta E_i < 0$, if β_{12} is positive corresponding to a negative overlap $S_{12} < 0$. Therefore the n_- level which is the HOMO for N = even system, will be stabilised since this level has a positive β_{12}, i.e. $S_{12} < 0$ between two n orbitals. The level order will thus become n_- below n_+, the reverse of the normal order for N = even cases. Since the reversal of the sign of one β at the two overlapping n orbitals to positive brings stabilisation, the system has an anti-Hückel or Möbius type σ-aromaticity.[5,6]

The reversal of level order to n_- below n_+ in structure **5** has been a puzzle and no ready explanation has yet been found.[2,11] It is now clear that the level order reversal in **5** is due to the depression of the n_- level by the stabilising effect of σ-aromaticity. The energy changes of the n_+ and n_- levels accompanied by the change in hybrid of radical carbon centre from sp^2 **4**, to sp^3 **5**, were calculated by the STO-3G method and the results are presented in Fig. 2.[12] It can be seen that the two levels cross at about $sp^{2.5}$.

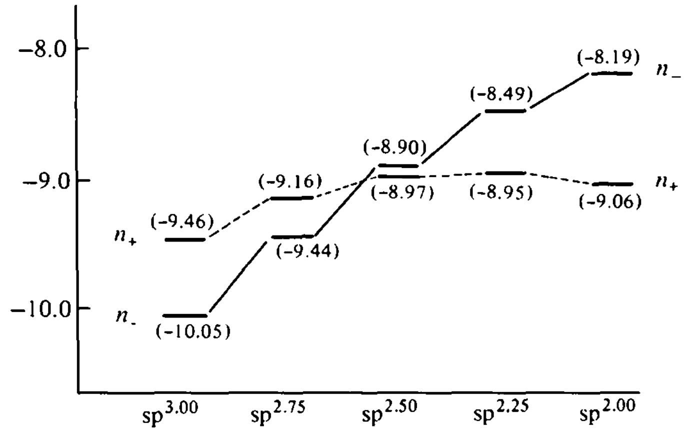
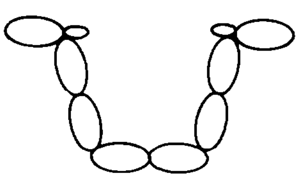


Fig. 2. STO-3G results for level order reversal of outward pyramidalised trimethylene diradical calculated for triplet state with UHF method.

Tetramethylene diradicals:

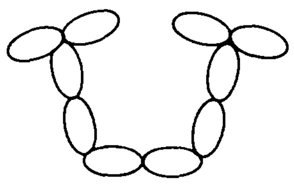


6

TBI (σ-conj + hyperconj)

$S \simeq 0$

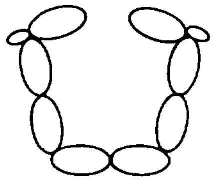
n_- below n_+



7

TBI (hyperconj only)
+ TSI
$S \neq 0$

n_+ below n_-



8

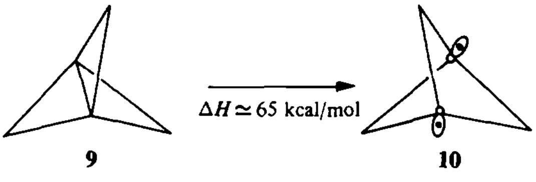
TBI (σ-conj + hyperconj)
+ TSI + SAI
$S \neq 0$

n_+ below n_-

The tetramethylene diradical is an N = odd system; the level order will be n_- below n_+ for the TBI dominated structure **6**, while it will be n_+ below n_- for the TSI dominated structure **7**[2] where only the hyperconjugative type of TBI is possible. In the outward pyramidalised structure **8**, both TSI and TBI with σ-conjugation are possible. Since the tetramethylene diradical will have the HOMO corresponding to the $4m+2\,\sigma$ electron system,[9] structure **8** will have σ-aromaticity of the Hückel type if n_1 and n_2 overlap in phase;[4] the n_+ level will be depressed due to the stabilising effect of σ-aromaticity and n_+ will be below n_- as in structure **7**. However in **8**, both pure TSI and SAI work in the same direction placing n_+ below n_-, whereas in **7** only TSI causes n_+ to be placed below n_-. Thus the energy splitting, $\Delta E = \varepsilon_- - \varepsilon_+$, due to the overall interaction will be greater in **8** than in **7**. We therefore expect that as we change the hybrid of radical centre from sp^2 (2p AO radical lobe) to sp^3 the energy splitting will increase with no level crossing. This was confirmed by our STO-3G results in Fig. 3.

Phantom bond in [1.1.1]*-propellane*

[1.1.1]-Propellane, **9**, having three cyclopropane rings has been of much theoretical interest in recent years as:[13] (i) despite a great deal of strain, results of *ab initio* calculations showed that it will be relatively stable and unreactive, (ii) rupturing the 1,3-bond requires 65 kcal/mol, yet the population analysis, the electron density and hybrid orbitals all suggest a lack of significant bonding and hence may be called a 'phantom bond'. This paradox however can be resolved if we take the outward pyramidalised diradical structure **11** into account in the ground state. Since cyclopropane is stabilised by σ-aromaticity of the Hückel type,[3] structure **9**, which has three cyclopropane rings fused together with a common 1,3-bond, will be stable in spite of its highly strained structure. In structure **11**, there are three outward pyramidalised trimethylene diradicals with a common overlapping pair of n orbitals, which will also be stabilised by threefold σ-aromaticity (of the anti-Hückel type) if the two n orbitals overlap out of phase, i.e. n_-combination (see earlier). Thus energetically **9** and **11** will have



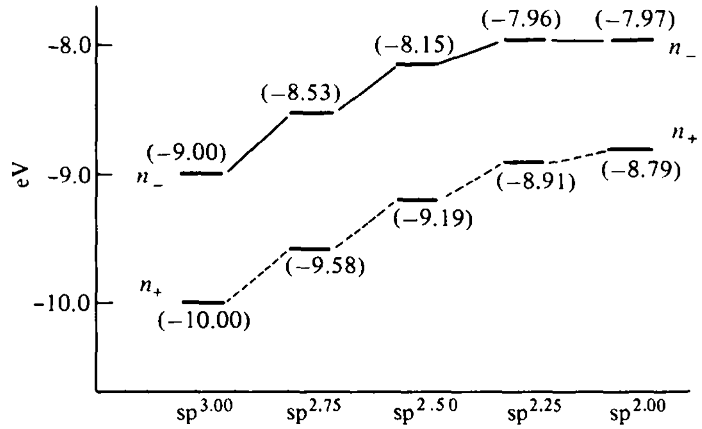
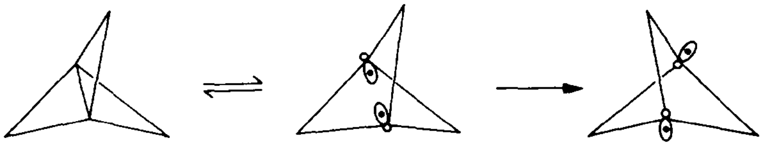


Fig. 3. STO-3G results of level changes with changes in hybrid of radical centre in outward pyramidalised tetramethylene diradical calculated for the triplet state with UHF method.

similar stability since both are equally threefold σ-aromatic. The ground state of [1.1.1]-propellane can therefore be considered to have a resonance hybrid of the two structures **9** and **11** of similar stability. The 1,3-bond in the outward pyramidalised diradical structure **11** should be somewhat longer with release of some strain.[13] On the other hand the bond order (or overlap population) of the 1,3-bond is expected to be quite low[13b] since in the HOMO of each outward pyramidalised trimethylene diradical structure **5** in **11**, the two *n* lobes facing each other overlap in an antibonding manner, i.e. $n_- = n_1 - n_2$.

However once the 1,3-bond ruptures completely into the inward pyramidalised form **10**, the threefold σ-aromaticity is lost and a new threefold σ-antiaromatic structure is formed; thus the conversion of **9** or **11** into **10** should require a great deal of energy as Wiberg and Walker have shown.[13c]



9
3-fold Hückel
σ-aromatic

11
3-fold anti-Hückel
σ-aromatic

10
3-fold Hückel
σ-antiaromatic

We therefore conclude that the new type of *n*–*n* orbital interaction, i.e. the σ-aromatic interaction, can provide us with a satisfactory account of level order reversal phenomenon in **5** and the reality and nature of the 'phantom bond' in [1.1.1]-propellane.

Acknowledgement—This work was supported by the Basic Science Research Institute Programme, Ministry of Education 1984, and by the Korea Research Centre for Theoretical Physics and Chemistry.

REFERENCES AND NOTES

[1] A preliminary report has been submitted for publication.

[2a] R. Hoffmann, A. Imamura and W. J. Hehre, *J. Am. Chem. Soc.* **90**, 1499 (1968); [b]R. Hoffmann, *Acc. Chem. Res.* **4**, 1 (1971); [c]I. Lee, *Tetrahedron* **39**, 2409 (1983).

[3] M. J. S. Dewar, *J. Am. Chem. Soc.* **106**, 669 (1984).

[4] M. J. S. Dewar, *The MO Theory of Organic Chemistry*. McGraw-Hill, New York (1969).

[5a] C. Sandorfy and R. Daudel, *C.R. Hebd. Séances Acad. Sci.* **238**, 93 (1954); [b]M. N. Paddon-Row, H. K. Patney, R. S. Brown and K. N. Houk, *J. Am. Chem. Soc.* **103**, 5575 (1981).

[6] H. E. Zimmerman, *Quantum Mechanics for Organic Chemistry*. Academic Press, New York (1975).

[7] I. Lee, *Bull. Korean Chem. Soc.* **1**, 4 (1980).

[8a] K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.* **20**, 722 (1952); [b]K. Fukui, *Acc. Chem. Res.* **4**, 57 (1971).

[9] 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, or partially occupied in the singlet state[10] so that the HOMO will be the same as that for the diradical anion or dianion; for N = even systems the HOMO corresponds to that for the system with $4m$ σ electrons forming a conjugative chain while for N = odd systems the HOMO corresponds to that for the $4m+2$ σ electron system.

[10] C. Doubleday, Jr., J. W. McIver, Jr. and M. Page, *J. Am. Chem. Soc.* **104**, 6533 (1982).

[11] In ref.[10] the pyramidalised trimethylene diradical had the level order of n_+ below n_- for the outward pyramidalisation angle, γ, of up to 30°. However one can easily recognise a clear trend toward level order reversal to n_- below n_+ for the system at about $\gamma \simeq 40°$ from Fig. 7 of this paper. Thus the level order reversal should occur with the sp^3 type ($\gamma = 60°$) lobes. Moreover, it has been shown that outward pyramidalisation of more than 25° ($\gamma > 25°$) favoured the triplet state.

[12] The hybridisation change of sp^3–sp^2 corresponds to the change of the pyramidalisation angle[10] (angle made by a C—C axis and CH_2 plane) of $\gamma = 60$–$0°$.

[13a] M. D. Newton and J. M. Schulman, *J. Am. Chem. Soc.* **94**, 773 (1972); [b]W.-D. Stohrer and R. Hoffmann, *Ibid.* **94**, 779 (1972); [c]K. B. Wiberg and F. H. Walker, *Ibid.* **104**, 5239 (1982).