APPLICATIONS OF MOLECULAR ORBITAL-VALENCE BOND THEORY
IN CHEMISTRY

Nicolaos D. Epiotis

Department of Chemistry, University of Washington, Seattle, Washington
98195, USA.

Abstract--According to Molecular Orbital-Valence Bond (MOVB) theory,
ground state organic molecules can be viewed as the result of "forbidden"
union of two fragments.  Consequently, the stability of a molecule is a
function of the fragment excitation requirement for its formation and
chemical stereoselection a manifestation of fragment excitation reduction.
The pi electronic structure of benzene and the conformational isomerism of
$N_2H_4$ and its derivatives are two simple illustrators of how and why MOVB
theory has revolutionized our own thinking about the structure and
reactivity of molecules.

MOVB Theory is the qualitative theory which stands at the same level of sophistication as
the "best" ab initio  polydeterminantal VB or MO computation, which has unparalleled concept-
ual clarity, and which can be equally well taught to chemistry beginners and to theoretical
experts.  The formal development and illustrative applications of MOVB theory were presented
in a recent work.[1]  This lecture is an introduction to a second volume which contains appli-
cations of MOVB theory to different types of problems:  organic and inorganic, ground state
and excited state, thermodynamic and kinetic, etc.[2]  This yet unpublished volume defines
what I call the "nightmare scenario of chemistry", i.e., it argues that our present under-
standing of chemistry at the electronic level is to a large extent illusory.  In support of
this proposition, I will discuss two entirely different problems with the first illustrating
the conceptual advantage of MOVB theory over any MO-type theory and with the second illus-
trating the formal advantage of MOVB theory over the popular Hückel (HMO) theory (and any
monodeterminantal MO or constrained VB theory).  The conceptual clarity of MOVB theory is
illustrated by reference to the problem of $N_2X_4$ and the formal "correctness" of MOVB theory
by reference to the problem of benzene pi "aromaticity".  In both cases, the emerging con-
clusions are nowhere to be found in the existing scientific literature.  Thus, I argue that
the fact that $N_2H_4$ is gauche rather than trans has nothing to do with the nitrogen lone
pairs and that benzene is pi destabilized rather than pi stabilized!  Both of these

conclusions are the indirect result of a fundamental realization:  most ground state mole-
cules can be thought of as the products of "forbidden" unions of core and ligand fragments.


## A.  $N_2X_4$ CONFORMATIONAL ISOMERISM

Like "aromaticity", hyperconjugation is nearly a half-century old idea.  It refers to the

"mechanism" by which the interaction of an electron pair bond with a vicinal doubly occupied,

singly occupied, or vacant AO, or, with a vicinal electron pair bond confers stabilization to

the total system in question.  The original concept of hyperconjugation was founded on intu-

itive VB theory.  Mulliken placed the idea of hyperconjugation on an MO theoretical basis in

1941.  In recent times, the hyperconjugation argument has been enunciated in the language of

Frontier Orbital (FO) Perturbation MO (PMO) theory.  A number of investigators have made

imaginative use of the concept of hyperconjugation in rationalizing and predicting chemical

phenomena.[3]  After some time of intense fascination with these ideas and extensive explora-

tion of their applicability, we began to realize that the successes of hyperconjugation were

rivaled by failures for which no easy rationalization could be offered.  A typical example

is provided by the comparative study of conformational isomerism of $H_2O_2$ and $N_2H_4$.  As first

pointed out by Bauer and Yokozeki,[4] the gauche preference of $H_2O_2$ seems to be augmented

while the same preference of $N_2H_4$ is diminished upon replacement of the hydrogens by fluo-

rines despite the fact that hyperconjugation ascribes the gauche preference of both $H_2O_2$ and

$N_2H_4$ to the same stabilization "mechanism" and, thus, forecasts an identical response to

substitution of the ligands or the core.  In this section, I will demonstrate that $H_2O_2$ and

$N_2H_4$ are qualitatively unrelated systems, the gauche preferences of which are due to entirely

different factors.  As a result, the effect of substituents on conformational isomerism is

entirely different in the two systems.  In other words, hyperconjugation works by accident

in rationalizing the preferred conformation of $H_2O_2$ and $N_2H_4$ and it fails naturally in

rationalizing the effects of substituents upon conformational preferences.  Since $H_2O_2$ is

gauche for the same reason that $H_2O$ and singlet $CH_2$ are bent,[1] our discussion is confined

to $N_2H_4$ and derivatives.

The preferred geometry of $N_2H_4$ can be predicted (or, better, anticipated) by MOVB theory in

a very simple and straightforward manner.  Thus, one may consider three likely geometries,

planar (P), trans (T), and gauche (G) and compare their electronic structure by reference to

the corresponding bond diagrams.  These can be constructed by assuming a core-ligand dis-

section in which $N_2$ plays the role of the core and $H_4$ the role of the ligand fragment,

developing the core and fragment symmetry orbitals according to well known perturbation the-

oretical procedures, and identifying the core-ligand bonds dictated by orbital symmetry. Now,

as we have emphasized before,[1] one cannot understand molecular stereochemistry unless the

role of nonbonded interaction is properly appreciated.  With this in mind, the symmetry

orbitals of $H_4$, $\sigma_1$-$\sigma_4$, of $N_2H_4$ are constructed recognizing that:

a)  Geminal nonbonded overlap of the hydrogen 1s AO's is very large.  For example, using

$r_{NN}$ = 1.47Å and $r_{NH}$ = 1.42Å, it is computed to be 0.1542 in P $N_2H_4$.

b)  Vicinal nonbonded overlap of the hydrogen 1s AO's is much smaller but far from neg-

ligible.  For example, it is computed to be 0.0338 in P $N_2H_4$.

Statements (a) and (b) are strictly valid whenever the core is made up of first row atoms.

When the core is made up of second, third, etc., row atoms, the increasing core atom-ligand

atom bond lengths cause the ligands to move further away from each other and nonbonded ligand

AO overlap tends to become negligible.  These above considerations lead to the conclusion

that the final symmetry MO's of $H_4$ will separate into two bands so that electron excitation

from $\sigma_1$ or $\sigma_2$ to $\sigma_3$ or $\sigma_4$ will always be costly and the corresponding deexcitation benefi-

cial regardless of geometry.  The qualitative energy levels of $H_4$ appropriate to P, T and G

$N_2H_4$ would be radically different had we assumed that nonbonded overlap of the hydrogen 1s

AO's is zero.  In such an event, excitation or deexcitation could no longer be defined

simply because all four MO's would be degenerate.  We will see that assumption of one or the

other $H_4$ MO patterns makes a "night-day" difference insofar as the final prediction of the

preferred geometry of $N_2H_4$ is concerned.

The bond diagrams for P, T, and G $N_2H_4$ are shown in Figure 1.  We note the following:



Fig.1
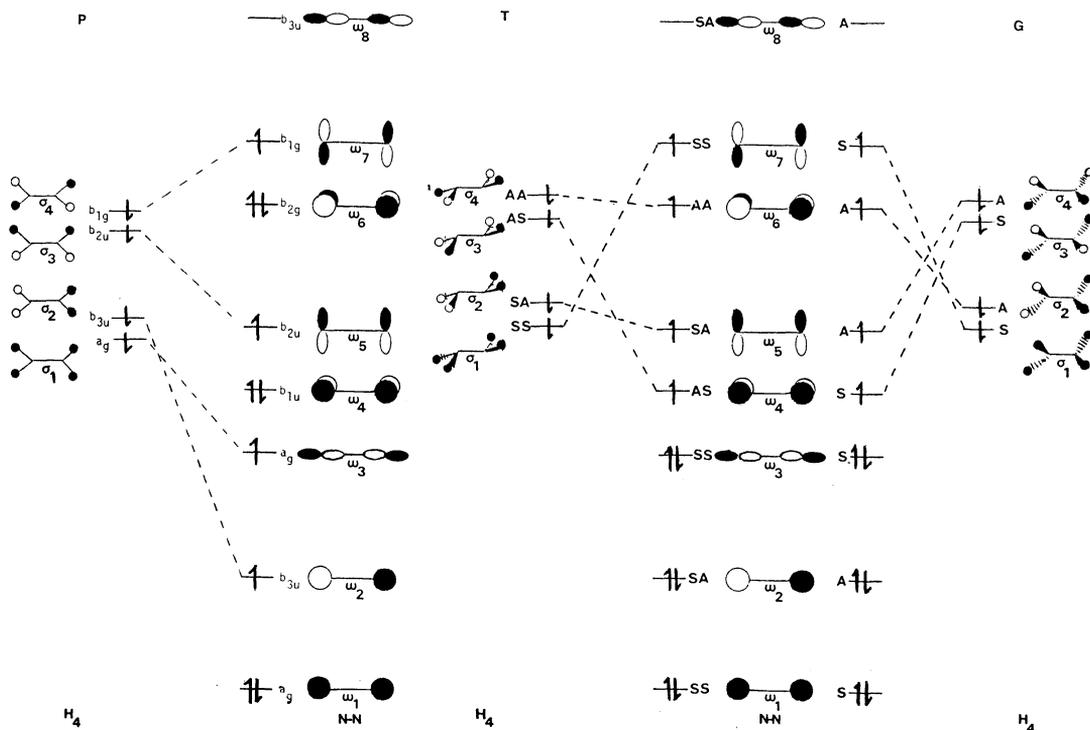
a) In comparing P and T, we first recognize that the former is the maximum overlap form. Hence, a dagger must be affixed to whatever label is appropriate for T. The transition P → T is accompanied by $U \to H^{\dagger}$ rebonding. In more descriptive language, we can say that it is accompanied by core deexcitation of the $\omega_6 \to \omega_2$ type. Since the energy separation of the $\omega_2$ and $\omega_6$ orbitals is very large, we expect that deexcitation will dominate loss of spatial overlap and T will attain lower energy than P.

b) In comparing T and G, we recognize that the former is the maximum overlap form. The transition T → G is again accompanied by $U \to H^{\dagger}$ rebonding. In more descriptive terms, we can say that it is accompanied by core plus ligand deexcitation of the $\sigma_4 \to \sigma_2$ and $\omega_6 \to \omega_5$ type. Since the energy separation of $\sigma_4$ and $\sigma_2$ as well as the energy separation of $\omega_6$ and $\omega_5$ are large we expect again that deexcitation will dominate the loss of spatial overlap and G will attain lower energy than T. Note that, if $\sigma_1$ to $\sigma_4$ were degenerate, the rebonding would be simply of the N → N' type, i.e., rebonding accompanied by bond weakening due to loss of spatial overlap without any deexcitation benefit. In this case, T would end up being energetically more favorable than G. Since whether $\sigma_2$ and $\sigma_4$ are degenerate or not depends on the strength of geminal nonbonded interaction, we can see that two different predictions can be arrived at depending on whether geminal nonbonded overlap is deemed important or not: If geminal nonbonded interaction is appreciable, $\sigma_2$ and $\sigma_4$ will be substantially split in energy, the T → G transformation will be accompanied by $U \to H^{\dagger}$ rebonding, and G will be the lowest energy form. By contrast, if geminal nonbonded interaction is negligible, $\sigma_1$ to $\sigma_4$ will be degenerate, the T → G transformation will be accompanied by N → N' rebonding and T will be the lowest energy form. Since geminal nonbonded overlap is actually very large, the first prediction is the correct one.

Once we have properly understood why $N_2H_4$ is gauche, the reason for the fact that $N_2F_4$ shows no comparable preference for the gauche geometry becomes self evident. Specifically, because of the smaller spatial extension of the fluorine valence AO's, geminal nonbonded overlap between F and F in $N_2F_4$ is much smaller than between H and H in $N_2H_4$. As a result, the motivation for the T → G transformation largely ceases to exist and $N_2F_4$ tends to adopt a T, rather than a G, geometry for reasons explained above.

Finally, consider the molecule $AH_n$ in which A is a first row atom. Replacement of A by a second row atom of the same column of the Periodic Table will cause an increase of the H---H distance, $r_{HH}$, and a very significant reduction of nonbonded AO overlap. This suggests that, upon replacing N by P in $N_2X_4$, we must observe a dramatic reduction of the energy difference between the G and the T form and even a reversal of its sign. That is to say, we expect that the diminution of the geminal nonbonded interaction will tend to convert the rebonding accompanying the T → G transformation from $U \to H^{\dagger}$ to N → N' and, thus, reverse the order of relative stability of T and G. The trend will become even more pronounced as P

is replaced by As.  The available experimental results leave no doubt that, as the covalent

radius of A increases, the trans becomes increasingly more stable relative to the gauche

conformer.  This trend is exactly opposite to the one encountered in ethane-like $A_2X_6$ mole-

cules and it has been noted by several authors.[5]


B.  WHY PI BENZENE IS NOT WHAT CHEMISTS THINK IT IS.

Hückel MO (HMO) theory predicts that pi benzene is more stable than three pi ethylenes.

This conclusion seems to be compatible with the fact that the heat of hydrogenation of ben-

zene is much less than the heat of hydrogenation of three cyclohexenes and the known unwill-

ingness of benzene to undergo addition reactions, opting for aromatic substitution instead.

These data have prompted an on-going preoccupation with "resonance energies", "aromaticity",

and the like.  In this section, we suggest that, while the experimental facts are indisput-

able, the concepts which chemists have devised over more than a century are most likely

erroneous and that benzene is pi destabilized yet "aromatic".



**Fig. 2**

**Fig. 3**
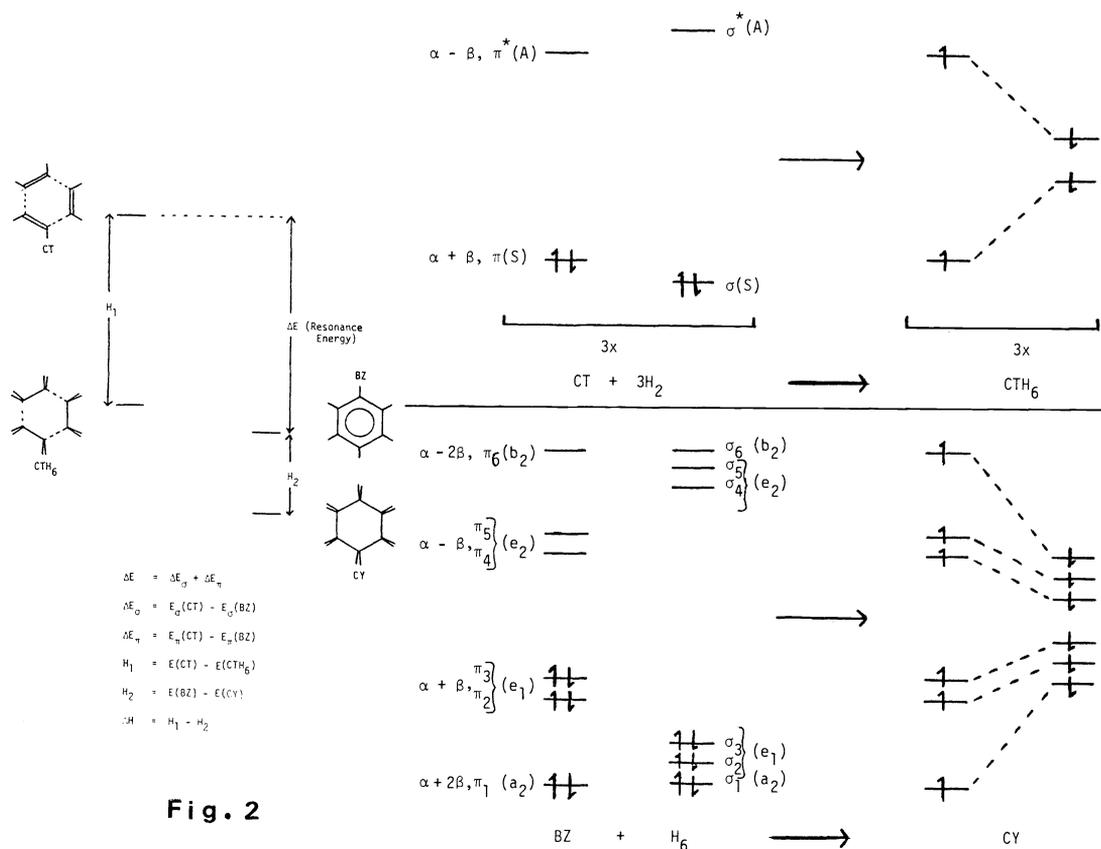
There are two equivalent ways of explaining why the heat of hydrogenation of benzene (BZ) is much less negative than that of 1,3,5-cyclohexatriene (CT): One is to compare CT and BZ _directly_ and another is to examine the difference between the CT → CTH$_6$ → CY and the BZ → CY transformations depicted in Figure 2. That is to say, we can describe a clockwise (CT → BZ) and counterclockwise (CT → CTH$_6$ → CY → BZ) thermochemical cycle realizing that the end result is always the same but the associated explanations are not necessarily identical. In one case, in travelling from CT to BZ, there is sigma bond formation accompanied by "aromatic" pi delocalization. Now, such delocalization lowers the one-electron energy of a system, because of the interaction of "covalent" and "ionic" CW's, at the expense of strong interelectronic repulsion, the characteristic attribute of "ionic" CW's. Hence, in comparing CT and BZ, one must consider one-electron and two-electron effects while recognizing that HMO theory describes _overdelocalization_ because of the neglect of electron-electron interaction. By contrast, in travelling from CT to CTH$_6$ to CY to BZ, one no longer has to deal with "aromatic" pi delocalization. Rather, attention is now focused exclusively on the energy for converting C-C pi to C-H sigma bonds, i.e., the CT → CHT$_6$ and BZ → CY transformations, as well as the energetics of sigma bond formation between saturated fragments having doubly occupied orbitals which can only engender strong interfragmental overlap repulsion, i.e., the CTH$_6$ → CY transformation. Now, addition of 3 H$_2$ to CT and BZ requires intrafragmental excitations which cause similar readjustments of the relative weights of the "ionic" and "covalent" CW's. Furthermore, the transformation of CTH$_6$ to CY involves formation of relatively localized sigma bonds. As a result, one may assume that the CT → CTH$_6$ → CY → BZ thermochemistry is determined, in a qualitative sense, by only one-electron effects because the change of interelectronic repulsion accompanying the CT → CTH$_6$ tends to cancel that accompanying the CY → BZ transformation while the CTH$_6$ → CY conversion involves no appreciable change of electron repulsion due to bond localization. Recognizing that the CT → BZ will be a more exothermic process than the CTH$_6$ → CY transformation, it is immediately evident that the problem of benzene "aromaticity" can be considered solved if one can explain why ΔH is positive, assuming that interelectronic repulsion effects are unimportant, and determine whether $\Delta E_\pi$ is indeed positive, as predicted by HMO theory, or actually negative as a result of bielectronic destabilization dominating monoelectronic stabilization of the cyclic pi system of benzene. We now show that ΔH and ΔE have opposite signs and that $\Delta E_\pi$ has probably the same sign as ΔE. In other words, we argue that the correct interpretation of benzene "aromaticity" is tantamount to a proper rationalization of the sign of either ΔH or ΔE and that $\Delta E_\pi$ actually leads to the prediction that benzene is _pi_ _destabilized_. Thus, the fact that benzene resists addition, while an olefin readily undergoes such a reaction, can be explained in two different, yet equivalent ways, with the ΔH explanation being the more physically meaningful one as it directly links the pi

electronic structure of two reactants to their differing ability to form "new" sigma bonds to replace the "old" pi bonds.  In what follows, we make consistent usage of the definitions spelled out in Figure 2.

In general, $H_i$ reflects two factors:

a.  The energy required for preparation of the reactants for bonding, i.e., the requisite reactant excitation energies.

b.  The energy payback due to bond formation.

Since we make C-H bonds in both CT and BZ, the AO resonance integrals describing bond formation are kept constant.  Thus, the only difference between CT and BZ with respect to reaction with $H_6$ is due to the differing excitation energies.  The bond diagrams which show explicitly how $CTH_6$ is formed by adding CT and $H_6$ and how CY arises from the union of BZ and $H_6$ are shown in Figure 3.  Both $CTH_6$ and CY can be regarded as the products of the "forbidden" unions of CT plus $3H_2$ and BZ plus $3H_2$, respectively.  It is immediately evident that there is a greater excitation requirement in the case of BZ than in the case of CT.  Hence, $\Delta H$ is predicted to be positive.  Since $\Delta H$ is a measure of relative reaction exothermicity, we say that CT is a _hyperdesmic_ and BZ is a _hypodesmic_ molecule, in a relative sense.

Why does HMO theory predict that pi benzene is stable with respect to three pi ethylenes?  We immediately recognize that, if we view each of CT and BZ as a composite of three HC = CH fragments $(F_1, F_2, F_3)$, there exists a set of purely "ionic" charge transfer MOVB CW's which "contain" VB CW's that can contribute to the VB wavefunction of BZ but not to that of CT, e.g., $\Phi_1$ and $\Phi_2$ shown below.  "Excusing" interelectronic repulsion at the level of HMO theory makes $\Phi_1$ and $\Phi_2$ unduly important and causes BZ to be more stable than CT.
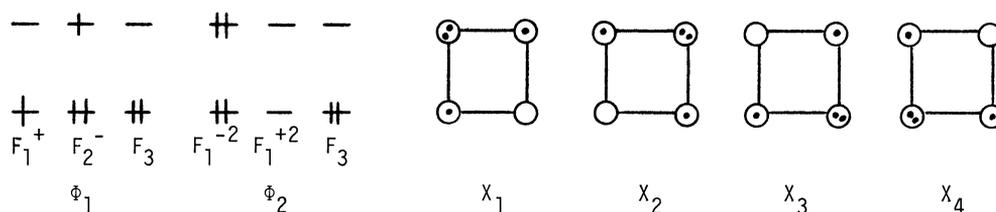


A related example drawn from our previous work[1] is the constitution of the VB wavefunctions of pi cyclobutadiene with noninteracting pi bonds (CB*) and Möbius pi cyclobutadiene (MCB), two hypothetical systems analogous to CT and BZ.  According to VB theory, and in complete analogy to MOVB theory, the advantage of MCB over CB* lies in four unique "ionic" VB CW's, $X_1$-$X_4$, which contribute to the wavefunction of the former but not the latter system.  Once again, neglect of interelectronic repulsion at the level of HMO theory causes these unique "ionic" CW's to achieve undue prominence and stabilize the "allowed" or "aromatic" MCB

complex relative to the "nonaromatic" CB* more than it "deserves".

It is then evident that we cannot neglect interelectronic repulsion because we deal with interbond excitations (charge transfer) in the case of BZ which can only occur at the expense of severe interelectronic repulsions and which, if neglected, would lead one to believe that BZ is more stable than CT while, if included, they can lead to exactly the opposite conclusion, i.e., that $\Delta E_\pi$ is negative. That pi CT is more stable than pi BZ has been implicitly suggested more than a half century ago when Eyring used the Diatomics In Molecules method[6] to show that $3A_2$ is more stable than hexagonal $A_6$ provided that A is a strong overlap binder.[2] $A_6$ can become more stable than $3A_2$ only when A is a weak overlap binder (e.g., Li) in which case the greater stability of hexagonal $A_6$ is due to the fact that such atoms bind to a large extent via "classical" coulomb interactions in the absence of interatomic charge transfer.[7]

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7. Of course, in order to explain why $\Delta H$ is positive, we had to first recognize that the CT→BZ is more exothermic than the $CTH_6$ → CY transformation because the former engenders less interfragmental overlap repulsion than the latter as the pi electrons of CT are delocalized more than the C-H sigma electrons of $CTH_6$. If the energy changes accompanying these two transformations are symbolized by $\Delta E$ and $\Delta E'$, respectively, the $\Delta H$ explanation is entirely equivalent to the $\Delta E-\Delta E'$ explanation but more appealing as it directly illuminates the source of the reactivity differences between olefinic and "aromatic" systems.