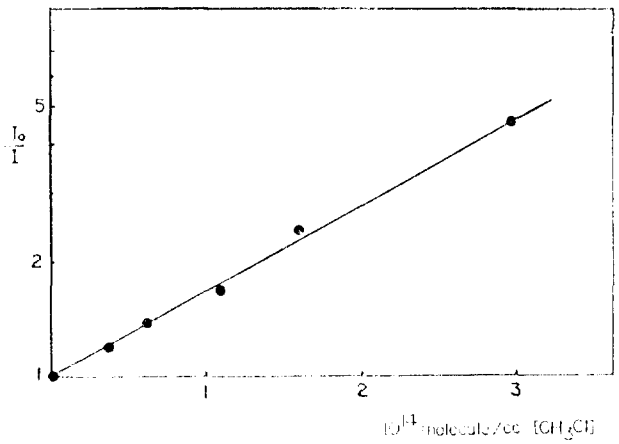

Figure 2. I_{OF}/I_F *vs.* $[CH_3Cl]$ for the 1396 A fluorescence line. $k=4.2\times10^{-13}$ cc/molecule sec.

atoms. If the reactivity of the $Cl(^2P_{1/2})$ atom is more than two orders of magnitude faster than $Cl(^2P_{3/2})$, as reported by Donovan and coworkers, the rate constant obtained by the fluorescence method will be larger than the rate constant obtained by the absorption method since the fluorescence signal intensity is proportional to the mixed concentration of both $Cl(^2P_{1/2})$ and $Cl(^2P_{3/2})$ atoms, and the concentration of $Cl(^2P_{1/2})$ atoms in our experiment is about 5 to 10 % of the $Cl(^2P_{3/2})$ atom concentration.

The fluorescence method is less specific for the study of the individual reactivity of $Cl(^2P_{1/2})$ and $Cl(^2P_{3/2})$ atoms because of the fact that both transitions to $Cl(^2P_{1/2})$ and $Cl(^2P_{3/2})$ are from identical excited energy levels, and also because the fluorescence of Cl atoms apparently involves many unknown interferences. The 1363 A line does not follow the simple assumption that the fluorescence emission is not perturbed by the reaction. We think that the mechanism of atomic fluorescence is much more complicated when the upper (excited) states are very closely stpaced, as in the case of Cl atomic transitions, so great care should be made to get reasonable results.

Acknowledgement. An experimental work was carried out at the Department of Chemistry, Brookhaven National Laboratory. The author wishes to thank Drs. A.P.Wolf and P.P.Gaspar for helpful discussions and support during his stay there.

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MO Studies on Configuration and Conformation (VI). FMO Interpretation of Nonbonded Interactions

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Simple rules for predicting nonbonded interactions have been proposed. It was found that an end-to-end nonbonded interaction is either attractive or repulsive depending on the sign of the product of AO coefficients of two end atoms in the HOMO of a closed shell conjugated system with a crowded structure. The nonbonded attraction becomes the greatest in a 4N+2 electron conjugated system, while it is repulsive in a 4N electron system. For 4N+1 and 4N−1 electron systems, it is attractive but the effect is less than that in 4N+2 system. As a result of the attractive interaction, the overlap population of an atom pair increases (decreases) if the HOMO is antibonding (bonding) for the atom pair. The rules were illustrated with some examples.

Introduction

In the Hartree-Fock SCF method, an orbital energy ϵ_i is an eigenvalue of the effective one-electron operator (Fock operator) $\hat{F}$ associated with eigenfunction Ψ_i.

$$\hat{F}\Psi_i=\epsilon_i\psi_i \tag{1}$$

The total Hartree-Fock energy, E_T, is however not a simple

sum of orbital energies, but is given as,[1]

$$E_T=2\sum_i^{occ}\epsilon_i-V_{ee}+V_{nn} \quad (2)$$

where V_{ee} is the sum of electron-electron repulsions and V_{nn} is the sum of internuclear repulsions.

Each component of the total energy expression (2) may be a function of the dihedral angle θ of internal rotation: $E_T(\theta)$, $\epsilon_i(\theta)$, $V_{ee}(\theta)$ and $V_{nn}(\theta)$. The energy change due to this internal rotation can be decomposed into separate contribution, $\Delta\epsilon_i$, ΔV_{ee} and ΔV_{nn} in the form for closed systems,

$$\Delta E_T=\Delta(2\sum_i^{occ}\epsilon_i)-\Delta V_{ee}+\Delta V_{nn} \quad (3)$$

Thus we can distinguish three important factors which control stereochemical preferences in molecules: (a) a one-electron factor, $\Delta(2\sum\epsilon_i)$, which is responsible for non-bonded interactions and π and/or σ conjugative interactions; (b) a two-electron repulsive factor, ΔV_{nn}; (c) a coulombic internuclear repulsive factor, ΔV_{nn}. The last two factors (b) and (c) can be grouped as "steric effects" and in many cases they tend to cancel approximately each other. Owing to this near cancellation effect, one-electron factor emerges as controlling factor of the conformational preferences in many cases.[2]

Various formulations of the perturbational molecular orbital (PMO) methods[3] are used in the analysis of conformational problems. Recently Epiotis and coworkers[4] have shown using a PMO method that "nonbonded attraction" is an important common denominator in structural problems favoring "crowded" forms. Their approach was to construct an orbital interaction scheme between the different constituent functional groups into which the molecule can be dissected conceptually, and show the stability of "crowded" form by virtue of the nonbonded attractive interactions.

The purpose of this paper is to present simple rules which can be conveniently used in predicting nonbonded interactions. It will be shown that interacting atoms at two ends of a molecule form, in crowded structures, a loose center(or a bond) which acts either as an electron source (donating group) when there is a repulsive interaction, or as an electron sink (withdrawing group) when there is an attractive interaction. The nonbonded interactions are therefore dependent on ability of the system as an electron acceptor or donator respectively: in this sense significant end-to-end interactions are only apparent in conjugated systems.

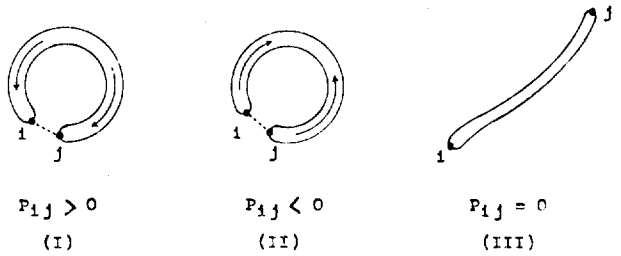
One thing we should bear in mind however is that whenever steric effects dominate over the nonbonded effect preferred conformation of isomer is the sterically favored one.

(A) Attractive and Repulsive Interactions

According to the Mulliken population analysis,[5] the total number of electrons, N_T, in a closed shell system is given by the sum of matrix element $P_{ij}=2\rho_{ij}S_{ij}$

$$N_T=\sum_i\sum_j P_{ij}=2\sum_i\sum_j\rho_{ij}S_{ij} \quad (4)$$

where ρ_{ij} is defined using AO coefficients of μ-th MO, $C_{\mu i}$ and $C_{\mu j}$, as $\rho_{ij}=\sum_\mu^{occ} C_{\mu i}\cdot C_{\mu j}$ and S_{ij} is the overlap integral. The diagonal elements of the population matrix, P_{ii} $(=2\rho_{ii})$ represent the "atomic charge" and the off-diagonal elements P_{ij} are the overlap populations which are related to the population of electrons between atoms i and j. When P_{ij} is positive, i and j is bonding and attractive, whereas if P_{ij} is negative i and j is antibonding and repulsive. When P_{ij} is positive, attraction between i and j has net effect of electron withdrawing from the molecule, while there is a net electron donating effect when P_{ij} is negative. This is obvious from equation (4) since the total



population must be conserved.

(Rule 1)

Nonbonded interactions are significant only in crowded forms, (I) and (II), since the overlap integral between two end atoms is appreciable only in short interatomic distance. The nearer the end atoms approach, the greater the interaction becomes.

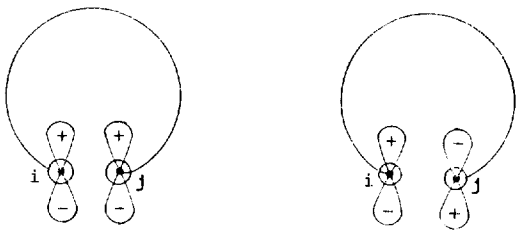
Consequences of this rule are that when there is nonbonded attraction ($P_{ij}>0$), *cis*(or *syn*) form is favored over *trans* (or *anti*) form, and when nonbonded interaction is repulsive ($P_{ij}<0$), *trans*(or *anti*) form is favored over *cis*(or *syn*) form.

(Rule 2)

Nonbonded interactions become appreciable only in crowded conjugated systems; π-conjugated systems have stronger nonbonded interactions than σ-conjugated systems, since conjugative electron donation or withdrawing is much more efficient in π systems owing to more localized nature of σ bonds. In this respect nonbonded effect is just another conjugative effect.

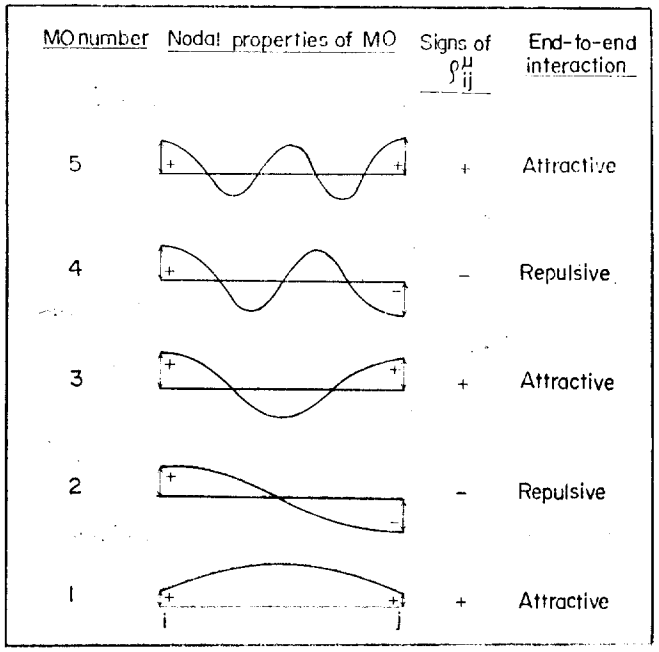
In the rest of this paper, we will therefore restrict our discussion to the π conjugative systems. The σ non-bonded interaction becomes significant when there is exceptionally strong attractive stabilization as in 6 σ electron crowded structure (σ-aromaticity).[6,4d]

One can assume without loss of generality that the signs of all basis orbitals involved are defined so that a positive overlap integral will show bonding character. Since the signs of p_π-p_π overlap integrals are positive,[7] the signs of overlap population of an orbital μ, ρ_{ij}^{μ}, are determined by the product of AO coefficients $C_{\mu i}$ and $C_{\mu j}$, of end atoms i and j, ρ_{ij}^{μ}. Now we know from a one-dimensional particle in a box model that the MOs of a linear conjugated system must have wave patterns with n-1 nodes in the n-th MO as shown in Figure 1. Locations of nodes are however dependent on the number of atoms(or centers) in the conjugated system; the



(IV) (V)

node in MO 2 for 3 atom system is on the center atom while that for 4 atom system it is located in between atoms 2 and 3. According to the frontier orbital (FMO) theory,[8] perturbation caused by a transformation from noncrowded, (III), form to a crowded, (I) or (II), form will have the dominant effect on the highest occupied MO(HOMO), In this respect the simple PMO method of Dewar[3a] is also based on the FMO theory. The "nonbonding" π-orbitals of odd systems on which whole PMO approach of Dewar[3] is based are none other than a FMO. Similar approach was used by Hoffmann and Olofson[9] in explaining the dependence of conformational and isomer stability on the number of electrons in π systems. In a 4N electron closed shell system, the HOMO is not only filled but also repulsive in end-to-end interaction, while the HOMO is filled but attractive in end-to-end interaction in a 4N+2 electron closed shell system.



Fignre 1. Nodal patterns of a one dimensional particle in a box. Only first 5 MO's are shown.

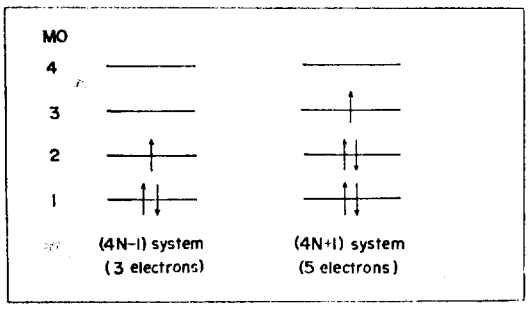


Figure 2. Occupancies of MOs in 4N–1, and 4N+1 system.

Thus a 4N electron system will have repulsive nonbonded interaction in crowded form while a 4N+2 electron closed shell system will have attractive nonbonded interaction in crowded from. This is exactly the same concept as that of antiaromaticity and aromaticity in the Dewar's PMO method.[3a]

Two types of nonaromatic systems(open shell systems) are possible as illustrated with 3 electron (4N−1) system and 5 electron (4N+1) system in Figure 2.

In the former case there are two attractive electrons (in MO 1) and one repulsive electron (in MO 2), so that the system becomes net attractive although the HOMO is a repulsive one. Since this is a net attractive nonbonded system in crowded form, the attractive–HOMO (in actuality, it is the next to the HOMO, an NHOMO) should be considered as the dominant MO.

For the latter case, there is no such complications and the system is net attractive as the HOMO indicates. In this case too, the number of net attractive electron is one. Thus in both cases of nonaromatic systems, the stabilization of crowded from relative to less crowded form will be smaller than that of 4N+2 system. Figure 3 shows the relative changes in stability according to the number of electrons in crowded structure.

(Rule 3)

The nonbonded interactions can be judged by the signs of the products of AO coeffecients of two end atoms in the dominant MO, HOMO, (NHOMO for 4N−1 system). Accordingly the 4N+2 electron system has attractive nonbonded interaction, while 4N electron system has repulsive nonbonded interaction in crowded structures. The 4N+1 and 4N−1 electron systems are attractive but the stabilizing effect is smaller than that for 4N+2 system

Applications

Let us now consider some applications of these rules.

(i) 4π *electron,* $(4N)$, *system.*

In the following, we will adopt the abbreviated notation of $(n\pi/m)$ representing a system of $n\pi$ electrons over m atoms (or centers) in a closed form with a nonbonded atom pair.

$(4\pi/3)$ system: Acetamide with methyl group staggered[3b,10] has a CCNO planar structure. This system contains

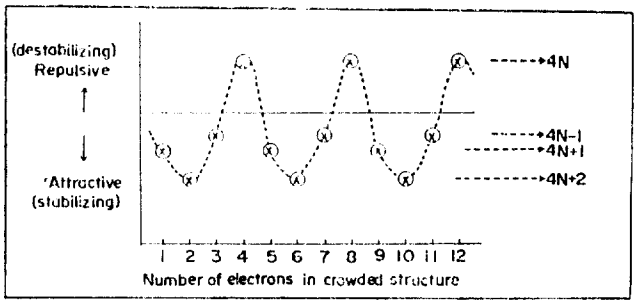
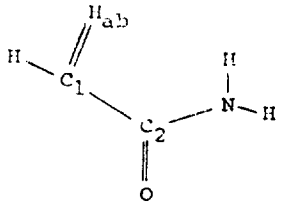


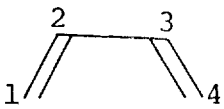
Figure 3. Predicted stabilities of crowded form relative to less crowded form (scale is relative only).

two interesting π–conjugated systems; OC_2N which is repulsive ($4\pi/3$) and $H_{ab}C_1C_2N$ which is attractive ($5\pi/4$) system. Thus in the former there will be an end–to–end repulsion and in the latter an end–to–end attraction. In fact the angles found are $\angle OC_2N = 125 \pm 3°$ while $\angle C_2C_2N = 113 \pm 7°$.[11]



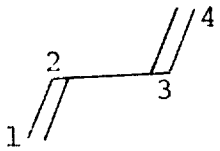
acetamide-S

($4\pi/4$) system: It is well known that the *cis* butadiene and the eclipsed ethane (π isoconjugate to the *cis* butadiene taking the CH_3 group as a double bond)[3b,10] are less stable compared to the *trans* butadiene and the staggered ethane (π isoconjugate to the *trans* butadiene) respectively.



cis

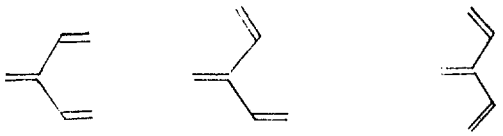
($4\pi/4$)



trans

In the *cis* form, 1, 4–nonbonded interaction is repulsive since the HOMO (MO 2) has $\rho_{14} < 0$, whereas for the *trans* form $P_{14} \cong 0$, since $S_{14} \cong 0$.

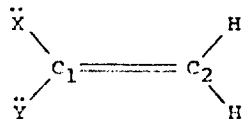
($4\pi/5$) system: 3–methylene–1,4–pentadiene has the stability order of VI>VII>VIII, but the cation has the stability order[19] of VI<VII<VIII as expected from rule 3; examinations of π structures tell us that VI has 4π electron 5–center system, VII has one 3π electron–4–center system and VIII has two 3π electron–4–center system.



VI ($4\pi/5$) VII ($3\pi/4$) VIII two possibilities of ($3\pi/4$)

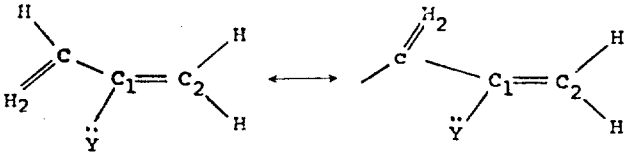
(ii) 5π electron ($4N+1$), system.

($5\pi/3$) system: If both X and Y have π lone pairs, XC_1Y in (IX) forms a 5π electron system. The HOMO for this system is MO 3 (Figure 1) which is end–to–end attractive, and hence X and Y atoms attract each other decreasing the angle $\angle XC_1Y$ compared to $\angle HC_2H$. Such example are known experimentally; *e.g.*, X=Y=F and X=Y=Cl.[4a]



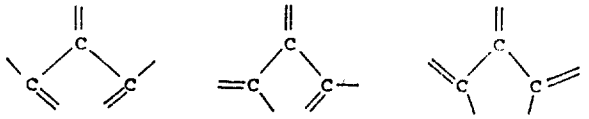
(IX)

($5\pi/4$) system: When X or Y is a methyl group, the staggered arrangement of–CH_3 relative to C_1–Y (or X) will give us 4–center system. Again the preference of staggered over eclipsed form[4] will be the consequence of nonbonded attraction *vs.* nonbonded repulsion;
in the staggered there is a ($5\pi/4$) system (attractive), while there are two repulsive system, ($4\pi/4$) and ($4\pi/3$), in the eclipsed form.



staggered ($5\pi/4$) eclipsed ($4\pi/3$) and ($4\pi/4$)

($5\pi/5$) system: Propane forms a π–isoconjugate system to cyclopentadienyl radical, (X), if the two terminal CH_3 groups are both staggered. The order of stability predicted is X>XI>XII,[6] as (partially) substantiated by experiment.

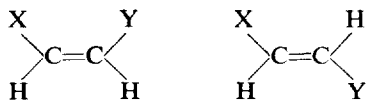


(X) ($5\pi/5$) (XI) $2\times(4\pi/4)$ (XII) $2\times(4\pi/4)$

Another example belonging to this ($5\pi/5$) system is 3–methylene–1, 4–pentadiene molecule discussed above. The order of stability, VI($5\pi/5$)>VII($4\pi/4$)>VIII($2\times(4\pi/4)$) is consistent with the rule 3.

(iii) 6π electron, ($4N+2$), system

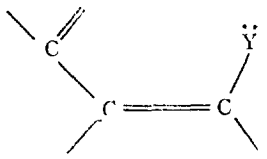
($6\pi/4$) system: 1,2–vicinal–X,Y–ethylene can have two forms; *cis* and *trans*.



cis *trans*

When these two heteroatoms contain π lone pairs, then the *cis* form becomes ($6\pi/4$) system, which should be more stable according to the rule 3. Many examples are known experimentally:[4a] X,Y=F,F; Cl; F,Br; F,I; Cl,Cl.

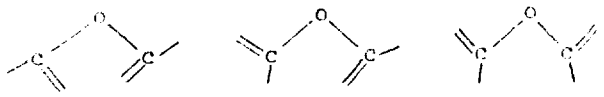
($6\pi/5$) system: If one of the heteroatoms (X,Y) in 1,2–vicinal–X,Y–ethylene is a methyl group, the *cis* staggered form (XIII) will have ($6\pi/5$) system, which will again be more stable than the *trans*: examples are Y=Cl, Br, OPh and OEt.[4a]



(XIII)

(6π/5)

Another well known example is the stability of staggered-staggered form, SS, of dimethylether, (XIV), compared to the staggered-eclipsed(SE) and the eclipsed-eclipsed(EE) forms,[6] the order of stability being SS>SE>EE as the rule predicts.

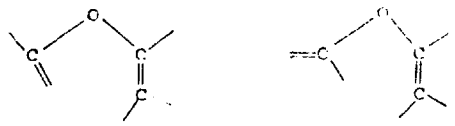


(XIV) (XV) (XVI)

SS SE EE

(6π/5) (5π/4) (4π/3)

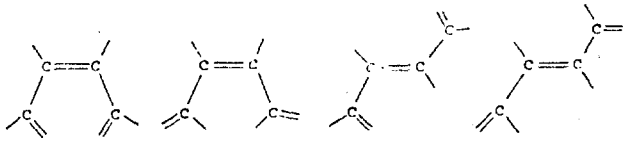
Methylvinylether has the most stable form of *cis*-staggered (cs) arrangement, which constitutes a (6π/5) system; compared to the *cis*-eclipsed CE form, a 5π system, 6π-system(cs) should be the more stable system.



CS CE

(6π/5) (5π/4)

(6π/6) system: 2-butene has 6 conformations among which the two crowded forms C_{ss} and C_{ee} are (6π/6) and (6σ/6) systems.



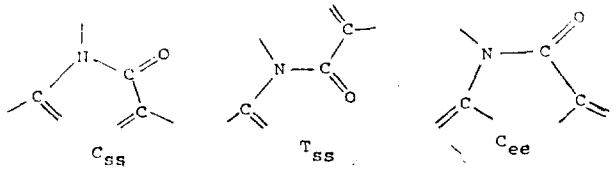
C_{ss} C_{ee} T_{ss} T_{ee}

(6π/6) (6σ/6) 2x(4π/4)

Ab initio calculations showed[4a] that one-electron factors favor the C_{ee} and C_{ss} conformations over the T_{ee} and T_{ss} conformations respectively. The MO calculation also showed that steric effects clearly favored the T_{ss} conformation, but they were dominated by the π aromatic character *i.e.*, (6π/6) system, of the C_{ss} form. That is nonbonded attraction was found to be the key electronic factor which favors the more crowded conformation, C_{ss}, over the less crowded T_{ss}. On the other hand, steric effects seemed to dominate σ aromaticity, *i.e.*, (6σ/6) system, in the case of the C_{ee} *vs.* T_{ee} comparison. These results show that π aromaticity is more important than σ aromaticity (Rule 2). It is also interesting to note that although the T_{ee} and T_{ss} are sterically equivalent, the T_{ee} is the most stable and the T_{ss} was the least stable one among six possible conformers. This is clearly the one-electron effect since the T_{ss} form has two (4π/4) systems.

(iv) 7π electron, (4N-1), system.

(7π/6) system: N-methylacetamide has three interesting forms; C_{ss}, T_{ss}, and C_{ee}. As expected from the rules 2 and 3 the order of stability[12] is $T_{ss}>C_{ss}>C_{ee}$. Here again, π interaction is more important than σ interaction.

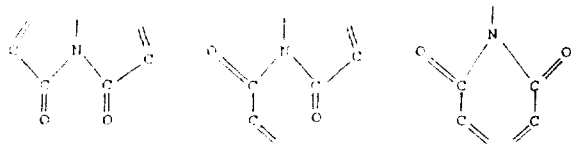


C_{ss} T_{ss} C_{ee}

(7π/6) (6π/5) (6σ/6)
(4π/3) (5π/4) (4π/4)
2x(4π/3)

(v) 8π electron, (4N), system.

Diacetamide has three forms: *trans-trans* (TT), *cis-trans* (CT) and *cis-cis*(CC) form. Arranging methyl groups in the most favorable forms, the three become (6π/5), (7π/6)



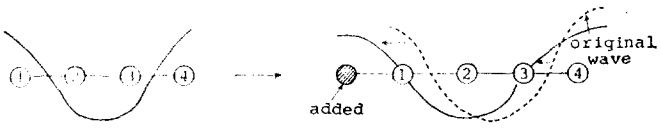
TT CT CC

(6π/5) (7π/6) (8π/7)
2x(5π/4) (5π/4),(4π/3) 2x(4π/3)

and (8π/7) systems. The expected order of stability considering the π-nonbonded interactions alone would be TT>CT>CC. Actually it is in the order CT>TT>CC,[13] and the least stability of CC form is consistent with the prediction based on rule 3. Steric factors seem to dominate the one-electron effect controlling the preference of CT over TT in this system. Steric effect also disfavors the CC form, and hence the CC form is the least preferred on both account.

(B) Variations in Overlap Populations

General nodal patterns for MOs of a linear conjugated system are as shown in Figure 1. Topologically these patterns are independent of the number of atoms (or centers) in between the two end atoms *i* and *j*. If we extend the linear chain by adding atoms (or centers) to either end, the relative positions of nodes must shift without changing the topologies of wave patterns. As an example, let us consider MO 3 of a molecule with 4 atoms (*e.g.* MO 3 of butadiene) XVII. If we add another atom on the left end,



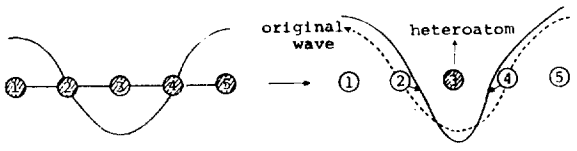
(XVII) (XVIII)

the two nodes will shift toward the left end keeping the topology of wave intact as in XVIII. The same will hold when we add on the right end; nodes will shift toward the right end.

(Rule 4)

Boundary extension of a conjugated chain by adding atoms on either end will shift nodes toward the added end. (Boundary extension shift).

Now if one of the atoms in the conjugated chain is an electron rich center (heteroatom containing perhaps lone pair electrons), then the nodes of HOMO shift normally toward the center(heteroatom).[14] Let us take ($6\pi/5$) system, in which the center atom is a heteroatom.



(IXX) (XX)

By replacing atom No. 3 with *e.g.* oxygen in pentadienyl system, the two nodes of HOMO shift closer toward the oxygen, thereby two nonbonding centers on atoms 2 and 4 now become two antibonding centers between atom pairs 2 and 3, and 3 and 4. On the other hand electron deficient center in a conjugated chain normally attracts nodes of the lowest unoccupied MO (LUMO) toward itself.[14]

(Rule 5)

Electron rich(deficient) center in a conjugated chain attracts nodes of HOMO (LUMO) toward itself. (Heteroatom shrft)

Whenever electron is withdrawn from a bonding orbital (antibonding orbital) of an atom pair, (k, l), bond between the atom pair (k, l) weakens $\Delta P_{kl}<0$, (strengthens $\Delta P_{kl}>0$). These changes in overlap populations resulting from the nonbonded interaction can be used to vindicate the one-electron effect.[15] Of course the changes in overlap populations are relative to the less crowded from where there is no nonbonded interactions.

(Rule 6)

When there is nonbonded attraction (repulsion) between the two end atoms, the overlap population will decrease (increase) in an atom pair where the HOMO is bonding for the atom pair, while the overlap population will increase (decrease) in an atom pair where the HOMO is antibonding for the atom pair (NHOMO for $4N-1$ system). (Population Shift)

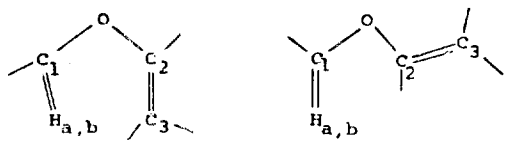
Following are some examples to illustrate the usefulness of the rules 4–6.

Butadiene

The *cis* form of this compound is a ($4\pi/4$) system, and the HOMO of this molecule is MO 2 of Figure 1. The HOMO is bonding between atom pairs 1–2 and 3–4, and antibonding between atom pair 2–3. Thus in the *cis* form the overlap populations between atom pairs 1–2 and 3–4 should increase while the overlap population between atoms 2 and 3 should decrease (Rule 6): the total π-overlap population changes are $\Delta P_{12}>0$, $\Delta P_{34}>0$ and $\Delta P_{23}<0$, since $\rho_{12}^{HO}>0$, $\rho_{34}^{HO}>0$, and $\rho_{23}^{HO}<0$. The CNDO/2 calculations of π-overlap populations for the two forms are consistent with this prediction as shown in Table 1.

Methyl Vinyl Ether

The HOMO for the *cis*-staggered (CS) system is the MO 3 in Figure 1. Due to a heteroatom, O, the nodes are not on C_1

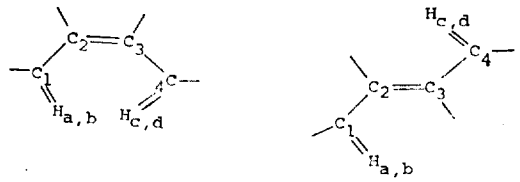


CS TS

($6\pi/5$)

and C_2 but located between atom pairs C_1–O and O–C_2. (Rule 5)

Predictions and results of ab initio calculations are compared in Table 2 for the *cis*-staggered (CS) and *trans*-staggered (TS) forms. Agreements are perfect.



C_{ss} T_{ss}

($6\pi/6$)

The HOMO of the *cis*-staggered-staggered(C_{ss}) form is MO 3, which has two nodes between atom pairs C_1–C_2 and C_3–C_4. The π-overlap populations are compared for the

TABLE 1: π-Overlap Populations for Butadiene

Atom pair (i–j)	ρ_{ij}^{HO}	ΔPredicted P_{ij} (*cis*–*trans*)	CNDO/2 calculated π-overlap population	
			cis	*trans*
C_1–C_2	+	+	0.2581	0.2576
C_2–C_3	−	−	0.0633	0.0645
C_2–C_4	+	+	0.2581	0.2576
C_1–C_4	−	−	−0.0043	−0.0006

TABLE 2: π-Overlap Populations of Methyl Vinyl Ether

Atom pair (i–j)	ρ_{ij}^{HO}	Predicted *Pij* (CS–TS)	Ab initio calculated π-overlap populations	
			CS	TS
$H_{a,b}$–C_1	+	−	0.3667	0.3677
C_1–O	−	+	0.0077	0.0064
O–C_2	−	+	0.0247	0.0211
C_2–C_3	+	−	0.1899	0.1915
$H_{a,b}$–C_3	+	+	0.0014	0.0001

TABLE 3: Comparison of π-Overlap Populations for 2-Butene

Atom Pair (i–j)	ρ_{ij}^{HO}	Predicted Δp_i^f (C_{ss}–T_{ss})	Ab initio calculated –overlap oopulations	
			C_{ss}	T_{ss}
$H_{a,b}$–C_1	+	−	0.3686	0.3694
C_1–C_2	−	+	0.0049	0.0033
C_2–C_3	+	−	0.1996	0.1985
C_3–C_4	−	+	0.0049	0.0033
C_4–$H_{c,d}$	+	−	0.3686	0.3694
$H_{c,d}$–$H_{a,b}$	+	+	0.0004	0.0000

two forms, C_{ss} and T_{ss} in Table . The ab initio results[4d] agree well with the predictions of rule 6. There is one disagreement for atom pair 2-3.

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Properties of Penicillin Amidohydrolase Immobilized on Nylon Fiber

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Penicillin amidohydrolase was partially purified from the fermented broth of *Bacillus megaterium*, and was immobilized on nylon fiber. The surface area of nylon fiber was increased by roughening it with fine sand and activated by acid treatment. The free amino groups on the nylon fiber exposed by such treatment were then utilized to immobilize the penicillin amidase. Enzymatic properties of penicillin amidohydrolase immobilized on the nylon fiber by covalent bonding and cross linking with glutaraldehyde were studied and compared with those of soluble enzyme. The optimal pH and temperature profile of immobilized enzyme showed only slightly broader peaks, and the values of kinetic constants, K_m, K_{ia}, and K_{ip}, of the immobilized enzyme are only slightly greater than those of the soluble enzyme. These rusults suggest that the mass transfer effect on the reaction rate for the penicillin amidase immobilized on nylon fiber is not so significant as the enzyme immobilized on some other support material like bentonite. The experimental results of batch reaction agreed well with the results of computer simulation for both the immobilized and soluble enzyme systems, confirming the validity of the rate equation derived which was based on the combined double inhibition by two reaction products.

Introduction

Penicillin amidohydrolase (or penicillin amidase) is an enzyme that hydrolyzes benzylpenicillin to yield 6-aminopenicillanic acid (6-APA) and phenylacetic acid (PAA). This enzyme is of considerable importance, since many semisynthetic penicillins and cephalosporins are prepared from 6-APA.

Penicillin amidase have been immobilized using various methods including adsorption on bentonite[1], covalent bonding on diethylaminoethyl cellulose[2], and entrapment in fibrous polymer matrices.[3] Nylon polymers have also been