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PMO THEORY OF n–n, π–π AND n–π ORBITAL INTERACTIONS

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Abstract—Theoretical expressions for orbital interactions were derived based on the PMO theory with simplifications involving use of FMO and "C-approximation". Through-space interaction term was found to be originated from first order perturbation, while through-bond and coupling terms were from second order perturbation. Correct qualitative predictions of level ordering, energy splitting, energy change relative to basis level and splitting ratio were possible using the derived energy expressions for symmetry adapted pair of orbitals.

Both experimental and theoretical aspects of orbital interactions between two nonbonding orbitals, n–n,[1] and between two π orbitals, π–π,[2] have attracted much interest in recent years. These interactions have been conceptually dissected into through-space and through-bond varieties. While level ordering and energy splitting of the symmetry adapted pairs, n_+ and n_-, in the orbital interactions have been accounted for qualitatively, no general theoretical expressions that can accommodate various experimental as well as theoretical results are yet available.

We report[3] theoretical expressions for orbital interactions based on the perturbational molecular orbital (PMO) theory[4] with simplifications involving use of frontier orbitals (FMO)[5] and "C-approximation".[2b,c,6] In the latter approximation, CC sigma MOs are formed as linear combinations of sp^3 hybrids and numerical values are obtained by using the Hückel procedure. General features of the FMOs in this approximation are that: (i) nodes in the highest occupied (HO) σ orbital pass through every intervening C atoms, whereas those in the lowest unoccupied (LU) σ^* orbital pass through centers of all the CC σ bonds, and (ii) magnitudes of hybrid AO coefficients in the HO-σ MO are the same as those of the corresponding hybrid AO coefficients in the LU-σ^* MO. The FMO patterns for systems with 3 and 4 intervening sigma bonds (N = 3 and 4) are illustrated in Fig. 1. Orbital symmetry properties are apparent from the nodal patterns shown in Fig. 1: the FMOs have either a C_2 axis or a σ plane of symmetry depending on whether they belong to N = odd or even system.

PMO Formalism

According to the PMO theory, orbital energy E_i of orbital i in a fragment A of molecular complex AB is given to second order as[7]

$$E_i = E_i^0 + H_{ii} + \sum_{j \neq i}^{A} \frac{H_{ij}^2}{E_i^0 - E_j^0} + \sum_{k}^{B} \frac{H_{ik}^2}{E_i^0 - E_k^0} \qquad (1)$$

where i and j refer to fragment A, while k to fragment B. The first order term H_{ii} originates from the change in potential around A that occurs as a result of complex formation. In terms of environment adjusted levels,[4c,8] E_i' and E_k', eqn (1) is given as

$$E_i = E_i' + \sum_{k}^{B} \frac{H_{ik}^2}{E_i' - E_k'}. \qquad (2)$$

n–n Orbital interaction

Application of eqn (2) to a nonbonding orbital n (energy $e_0 = 0$) in an alkyl radical or an amine with the FMO approximation gives

$$\epsilon_0 = e' - \frac{H_{n\sigma^*}^2}{e_{\sigma^*} - e'} + \frac{H_{n\sigma}^2}{e' - e_\sigma} \qquad (3)$$

where $e' = e_0 + \langle n|H'|n\rangle$, e_σ and e_{σ^*} are the environment adjusted levels for n, framework HO-σ and LU-σ^* MOs. Here the fragment A is an electron(s) in a nonbonding orbital n while the fragment B is a framework alkyl group (or monoamine) which is devoid of a nonbonding electron(s). Thus in the complex AB, A (n) interacts with B (framework) as an electron-donating substituent, whereas B interacts with A as an electron-withdrawing substituent. As a result energy level of A will be lowered, i.e. $e' < e_0$ and hence $e' < 0$, and FMO levels of framework e_{LU} and e_{HO} will be raised to e_{σ^*} and e_σ respectively.[9] For simplicity and without loss of generality, we may assume that the elevation of HO-σ and LU-σ^*, δe, is the same,[10] i.e. $e_\sigma = e_{HO} + \delta e$ and $e_{\sigma^*} = e_{LU} + \delta e$. The second order terms in eqn (3) can then be approximated using $H_{mn} \cong -kS_{mn}$ where k is a positive constant and S_{mn} is an overlap integral between two interacting orbitals m and n. The perturbed n basis level ϵ_0 is finally given as,

$$\epsilon_0 \cong e' + (y - x)(1 + \alpha) - (x + y)\beta \qquad (4)$$

where $y = k^2S_{n\sigma}^2/\Delta e$, $x = k^2S_{n\sigma^*}^2/\Delta e$, $\alpha = |e''/\Delta e|^2 + |e''/\Delta e|^4 + \cdots$, $\beta = |e''/\Delta e| + |e''/\Delta e|^3 + \cdots$, $\Delta e = e_{LU} - e_0 = e_0 - e_{HO}$, and $e'' = e' - \delta e$. The overlap integrals $S_{n\sigma} = \langle n|\Psi_{HO}^0\rangle$ and $S_{n\sigma^*} = \langle n|\Psi_{LU}^0\rangle$ can be taken as those between the n lobe and a vicinal σ and σ^* bonds of the framework respectively.[11] In general a vicinal *trans* overlap is greater than a vicinal *cis*, S(*trans*) > S(*cis*),[12] whereas $S_{n\sigma}$ is greater than $S_{n\sigma^*}$ since in the latter there is some cancellation effect due to a node passing through center of every CC sigma bond in the LU-σ^* orbital. Thus

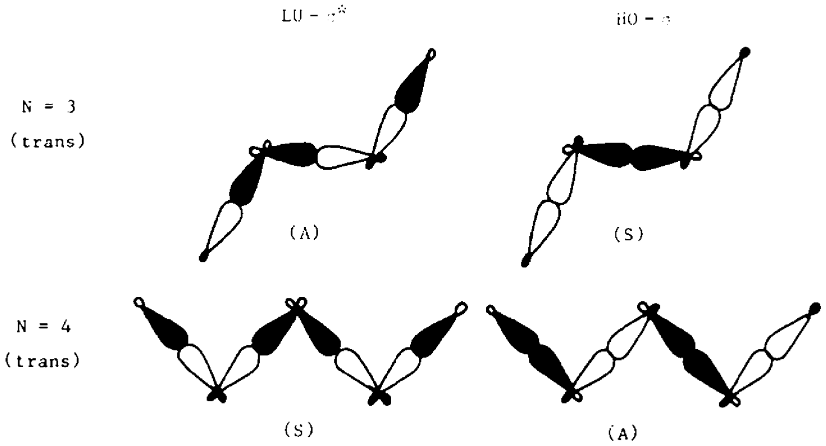


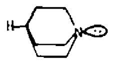
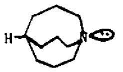
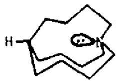
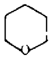
Fig. 1. FMO patterns for $N = 3$ and 4 systems. (S) and (A) refer to symmetric and antisymmetric orbitals, respectively.

it is obvious that x, y, α and β are all positive, and $y > x$ and $\beta > \alpha$.[13] The basis level will be negative, $\epsilon_0 < 0$, since we would expect the first order effect, $e' < 0$, to be greater than the second order effect, $[(y-x)(1+\alpha)+(x+y)\beta] > 0$. The magnitude of second order effect will increase and hence the ϵ_0 level will be raised (i) as the overlaps between n and framework HO-σ and LU-σ^* orbitals $S_{n\sigma}$ and $S_{n\sigma^*}$ (and hence y and x) increase, and (ii) as the number of intervening CC σ bonds (N) increases since an increase in N results in a decrease in Δe, which in turn leads to increases in the α and β values. This prediction of basis level elevation is borne out in the result of our STO-3G calculations as well as in the photoelectron spectroscopy (PES) data presented in Tables 1 and 2. We note that the n basis level ϵ_0 is higher for n-*trans* compared to n-*cis* since a vicinal *trans* overlap is greater than a vicinal *cis* overlap.[12]

Table 1. Nonbonding orbital energies (eV) in some n-alkyl radicals and n-alkyl amines calculated by STO-3G basis set

	N	n-cis	n-trans
Radical	2	-9.48	-9 31
	3	-9 41	-9.12
	4	-9.33	-9.02
Amine	2	-8 50	-8.38
	3	-8.45	-8.31
	4	-8.37	-8.28

Table 2. Some photoelectron spectra data of basis levels

Entry no.	System	n-cis	n-trans	Ref.
1 a	Et_3N	---	-8.08	
b	$n\text{-}Pr_3N$	---	-7 92	1d
c	$n\text{-}Bu_3N$	---	-7.90	
2 a		---	-8.06	
b		---	-7.13	1d
c		-7.84	---	
3 a		---	-9 74	
				14
b		---	-9.57	
4 a	EtOH	-10.64	---	
b	PrOH	-10.49	---	14
c	BuOH	-10.37	---	

In general the effect of basis level elevation due to the change in S, i.e. the effect (i), is greater than that due to the change in N, i.e. the effect (ii). This is clear from comparison of basis levels for entries 2b and 2c in Table 2; the former has n-*trans* form with N = 4 whereas the latter has n-*cis* form with N = 5. In spite of longer chain the latter has lower level due to smaller value of overlap S.

Let us now examine interactions between two nonbonding orbitals n_1 and n_2 which are separated by N sigma bonds in a diradical or a diamine. Linear combinations of the two form two symmetry adapted pairs, n_+ and n_-, with the same energy, $e_0 = 0$,

$$n_+ = \frac{1}{\sqrt{(2+2S)}}(n_1 + n_2)$$
$$n_- = \frac{1}{\sqrt{(2-2S)}}(n_1 - n_2) \qquad (5)$$

where $S = \langle n_1|n_2\rangle$. Since we will be primarily concerned with interaction energies up to second order in overlap, we need to include overlap integral S explicitly in the expressions of symmetry adapted pair of orbitals.[15] In terms of environment adjusted levels e_+ and e_-, the perturbed energies for n_+ and n_- become,

$$\epsilon_+ = e_+ - \frac{H^2_{n\sigma^*}}{e_{\sigma^*} - e_+} + \frac{H^2_{n\sigma}}{e_+ - e_\sigma} \qquad (6a)$$

$$\epsilon_- = e_- - \frac{H^2_{n\sigma^*}}{e_{\sigma^*} - e_-} + \frac{H^2_{n\sigma}}{e_- - e_\sigma} \qquad (6b)$$

where $e_\pm = e_0 + \langle n_\pm|H'|n_\pm\rangle$, e_{σ^*} and e_σ are environment adjusted levels for $n_\pm$, LU-σ^* and HO-σ framework orbitals. The $e_\pm$ levels are evaluated as, $e_+ \cong e' - \delta e_l$ and $e_- \cong e' + \delta e_h$, where $\delta e_l \cong S(k+e')(1-S)$ and $\delta e_h \cong S(k+e')(1+S)$. Since k, which is positive, is greater than e'.[16] $(k+e')$ is always positive and hence δe_l and δe_h are positive. It is also clear that $\delta e_h > \delta e_l$. This shows that as a result of first order perturbation the two orbitals n_+ and n_- split into two different levels; one is destabilized (by δe_h) more than the other is stabilized (by δe_l) relative to the environment adjusted basis level e'. This result is the same as that obtained from a direct or through-space interaction of the degenerate environment adjusted nonbonding orbitals n_1 and n_2.[1a] Thus the result of through-space interaction is to place n_+ level below n_- by an amount ΔE_s,

$$\Delta E_s = e_- - e_+ = \delta e_h + \delta e_l \cong 2S(k + e') \qquad (7)$$

and to destabilize the two degenerate nonbonding orbitals by an amount $\delta\epsilon_s$,

$$\delta\epsilon_s = \delta e_h - \delta e_l \cong 2S^2(k + e') \qquad (8)$$

Equations (7) and (8) demonstrate that energy splitting due to through-space interaction is first order in S, whereas destabilization of nonbonding orbitals is second order in S.

Algebraic manipulations after substitutions of $e_+ = e' - \delta e_l$ and $e_- = e' + \delta e_h$ into second order terms in eqn (6) give the following final expressions for N = odd, eqn (9), and for N = even, eqn (10), systems

$$\epsilon_+ \cong e' - \delta e_l + 2y\left(1 + \alpha + \beta + \frac{\delta e_l}{\Delta e}\right) \qquad (9a)$$

$$\epsilon_- \cong e' + \delta e_h - 2x\left(1 + \alpha - \beta + \frac{\delta e_h}{\Delta e}\right) \qquad (9b)$$

$$\epsilon_+ \cong e' - \delta e_l - 2x\left(1 + \alpha - \beta - \frac{\delta e_l}{\Delta e}\right) \qquad (10a)$$

$$\epsilon_- \cong e' + \delta e_h + 2y\left(1 + \alpha + \beta - \frac{\delta e_h}{\Delta e}\right). \qquad (10b)$$

Considerations of orbital symmetries as well as overlap patterns[3,18] lead us to important simplifications in the calculations of second order terms that n_+ interacts only with HO-σ whereas n_- only with LU-σ^* MO of framework in N = odd systems, and n_+ interacts only with LU-σ^* whereas n_- only with HO-σ in N = even systems.

First order and second order perturbation terms of n_+ and n_- orbitals are summarized in Table 3, and interlevel interactions are schematically presented in Fig. 2.

Equations (9) and (10) reveal that as a result of second order perturbation, n_+ and n_- levels split further by a resultant sum of two contributions: (i) the interaction energy of two nonbonding orbitals n_1 and n_2 through a common σ framework, which is exactly the same as the sum of two separate interactions of n with a (common) σ

Table 3. Interaction energies between symmetry adapted pairs (SAP) and framework FMOs

Effect \ S.A.P. \ Framework FMO		N = odd		N = even	
		HO − σ (S)	LU − σ^* (A)	HO − σ (A)	LU − σ^* (S)
Through Bonds	n_+(S)	$2y(1+\alpha+\beta)$	0	0	$-2x(1+\alpha-\beta)$
	n_-(A)	0	$-2x(1+\alpha-\beta)$	$2y(1+\alpha+\beta)$	0
Coupling	n_+(S)	$2y\,\frac{\delta e_l}{\Delta e}$	0	0	$2x\,\frac{\delta e_l}{\Delta e}$
	n_-(A)	0	$-2x\,\frac{\delta e_h}{\Delta e}$	$-2y\,\frac{\delta e_h}{\Delta e}$	0
Through Space	n_+(S)	$-S(k+e')(1-S)$			
	n_-(A)	$S(k+e')(1+S)$			

(S) and (A) refer to symmetric and antisymmetric orbitals, respectively.

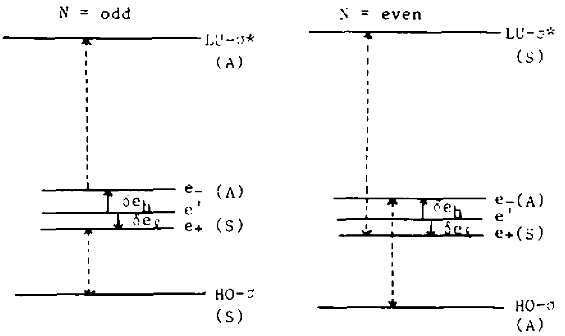


Fig. 2. Schematic presentation of interactions between environment adjusted n_- and n_- levels and framework FMOs. "←----→" refers to inter-level interaction and (S) and (A) to symmetric and antisymmetric orbitals, respectively.

framework given in eqn (4), i.e. $-2x(1+\alpha-\beta)+2y(1+\alpha+\beta)=2\{(y-x)(1+\alpha)+(x+y)\beta\}$. This is none other than the through-bond interaction of two nonbonding orbitals,[18] (ii) through-space-through-bond coupling energies, i.e. terms such as $\delta e_l(2x/\Delta e)$ or $\delta e_h(2y/\Delta e)$, which contains a product of two factors originated from interactions through space (δe_h or δe_l) and through bond (x or y).

In N = odd systems through-bond interaction is seen to depress the n_- level since normally $\beta-\alpha$ is smaller than one,[13] whereas it raises the n_+ level considerably, by $2y(1+\alpha+\beta)$, relative to the environment adjusted n_- and n_+ levels respectively. On the other hand, through-space and through-bond interactions cooperatively depress n_+ and elevate n_- level in N = even systems.

The coupling terms are in line with through-bond effect in N = odd systems while they are in opposition to through-bond effect in N = even systems.

Overall energy splitting between n_+ and n levels for N = odd, ΔE_{odd}, and for N = even, ΔE_{even}, can be obtained from eqns (9) and (10) respectively

$$\begin{aligned}\Delta E_{odd} &= \epsilon_- - \epsilon_+ \cong \Delta E_s - 2\{(x+y)(1+\alpha)+(y-x)\beta\}\\ &\quad -\frac{2}{\Delta e}(x\delta e_h + y\delta e_l)\\ &= \Delta E_s - \Delta E_b - \Delta E_c \qquad (11a)\end{aligned}$$

$$\begin{aligned}\Delta E_{even} &= \epsilon_- - \epsilon_+ \cong \Delta E_s + 2\{(x+y)(1+\alpha)+(y-x)\beta\}\\ &\quad -\frac{2}{\Delta e}(y\delta e_h + x\delta e_l)\\ &= \Delta E_s + \Delta E_b - \Delta E_c. \qquad (11b)\end{aligned}$$

In general, overall splitting ΔE consists of three terms: contributions from through-space, ΔE_s, and through-bond, ΔE_b, interactions and that from a coupling effect of the two, ΔE_c.

Some interesting predictions are possible based on these expressions: (i) Normally through-space effect is sufficiently small ($\Delta E_s \cong 0$)[1b] so that level order is determined by through-bond effect ΔE_b. Normal level order will therefore be n below n_+ level in N = odd system since ΔE_b is negative, and n_+ below n level in N = even system for which $\Delta E_b > 0$. However due to opposing effect of ΔE_c in N = even, $|\Delta E_{even}|$ will be smaller than $|\Delta E_{odd}|$ in through-bond dominated interactions whereas $|\Delta E_{even}|$ will be larger than $|\Delta E_{odd}|$ in through-space dominated interactions, since in the latter ΔE_s and ΔE_b have opposite signs. These are borne out in our STO-3G results in Table 4 and the PES data in Table 5. Entries 3a and 3c in Table 4 are both *through-space* dominated and |ΔE| value of the latter (N = even) is larger than that for the former (N = odd) despite of the longer chain length for the N = even case. Entry 5 (N = even case) in Table 4 shows that ΔE value is the largest for 5c for which through-space interaction is possible. Entries 1, 2, 6 and 7 in Table 5 are all through-bond dominated and |ΔE| values are seen to be larger for the N = odd systems than those for the N = even cases as predicted. (ii) Two anomalies from the normal level ordering may occur: (a) when through-space effect becomes dominant, level order reverses in N = odd system to n_+ below n , (b) when coupling effect becomes dominant, level order reverses in N = even system to n_- below n_-. Examples for these anomalous cases are given in Tables 4 and 5.

Entry number 1a in Table 4 is an example of coupling term dominated N = even case[22] while entry number 3a in Table 4 and entry 5 in Table 5 are examples of through-space dominated N = odd cases. In all of these anomalous cases, |ΔE| values are somewhat smaller compared with the normal cases due to the opposing effects in eqn (11). (iii) Energy splitting in through-bond dominated interaction will decrease as vicinal n-σ and n-σ* overlaps (and hence y and x) decrease. This trend is confirmed with our STO-3G calculations on all *cis*- (entries 1 and 3) vs all *trans*- (entries 2 and 4) triplet polymethylene diradicals and diamines in Table 4. |ΔE| values are smaller for entries 1 and 3 compared with corresponding values in entries 2 and 4, since vicinal *cis* overlaps are smaller than vicinal *trans* overlaps.

Comparison of the average of the two levels $\epsilon_{av} = (\epsilon_+ + \epsilon_-/2)$ with the basis level ϵ_0 will indicate whether interactions of two nonbonding orbitals n_1 and n_2 is stabilizing ($\epsilon_{av}-\epsilon_0<0$) or destabilizing ($\epsilon_{av}-\epsilon_0>0$) provided that occupation numbers of both are the same as in the triplet diradicals and diamines. We already know that the interaction is destabilizing when it is through-space dominated, e.g. entries number 3a and 3c in Table 4 and entries 5 and 8 in Table 5, and hence stabilizing interaction will only result from through-bond dominated interactions. The average of the two levels for N = odd system is given as,

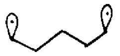
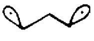
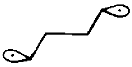
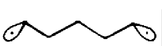
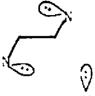
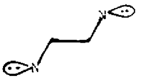
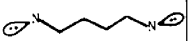
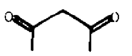
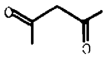
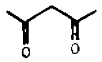
$$\begin{aligned}\epsilon_{av} &= \frac{\epsilon_+ + \epsilon_-}{2} \cong \epsilon_0 + S^2(k+e') - \frac{1}{\Delta e}(x\delta e_h - y\delta e_l)\\ \delta\epsilon &= \epsilon_{av} - \epsilon_0 = \delta\epsilon_s - \delta\epsilon_c. \qquad (12a)\end{aligned}$$

Likewise for N = even system,

$$\begin{aligned}\delta\epsilon &= \epsilon_{av} - \epsilon_0 = S^2(k+e') - \frac{1}{\Delta e}(y\delta e_h - x\delta e_l)\\ &= \delta\epsilon_s - \delta\epsilon_c. \qquad (12b)\end{aligned}$$

In general overall orbital energy change due to orbital interactions, $\delta\epsilon$ can be given as a sum of two opposing interaction energy terms: a destabilizing energy change originated from through-space interaction, $\delta\epsilon_s = S^2(k+e')$, and a stabilizing energy change originated from through-space-through-bond coupling effect, $-\delta\epsilon_c = (1/\Delta e)\ (x\delta e_h - y\delta e_l)$ and $-\delta\epsilon_c = (1/\Delta e)\ (y\delta e_h -$

Table 4. Some STO-3G results of level ordering, energy splitting ΔE(eV), interaction energy change, δε(eV), and splitting ratio (SR)

Entry No.		System	N	Level order[b]	ΔE (eV)	δε (ev)	SR	Remarks[c]	Ref
1	a		2	R	0.65	-0.13	3	C	17
	b		3	N	0.69	-0.09	2		17
	c		4	N	0.43	-0.09	2		17
2	a		2	N	2.17	-0.43	2		17
	b		3	N	1.99	-0.43	3		17
	c		4	N	1.52	-0.30	2		17
3	a		3	R	0.39	+0.43	0.4	TS	19
	b		3	N	0.87	-0.09	1.5		19
	c		4	R	0.52	0.0	0.7	TS	19
4	a		3	N	1.87	-0.48	3.3		19
	b		4	N	1.26	-0.30	3.0		19
	c		5	N	0.87	-0.22	3.0		19
5[a]	a		4	N	0.60	---	--		20
	b		4	N	0.49	---	--		20
	c		4	N	1.05	---	--		20

[a] CNDO/2 results. [b] N and R refer to normal and reversed level orders respectively. [c] C and TS refer to coupling term and through-space dominated interactions respectively.

$x\delta e_l$), for N = odd and N = even systems respectively. It is interesting to note here that a pure through-bond interaction has no contribution to interaction energy change. The coupling terms in eqn (12) are stabilizing, i.e. $x\delta e_h > y\delta e_l$ and $y\delta e_h > x\delta e_l$. That this is so can be confirmed with the experimental and theoretical results on splitting ratios in Tables 4 and 5. Reference to these Tables shows that splitting ratios (SR) for through-bond dominated systems are greater than one irrespective of whether N is odd or even.

$$\mathrm{SR} = \frac{\epsilon_0 - \epsilon_\mp}{\epsilon_\pm - \epsilon_0} \tag{13}$$

where the upper signs refer to N = odd and lower signs to N = even cases.

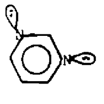
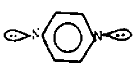
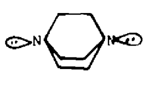
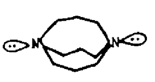
Substitutions of eqns (4) and (9) or (10) into eqn (13) lead to the following expressions:

$$\mathrm{SR(odd)} = \frac{(y-x)\beta + (x-y)(1+\alpha) + \delta e_h\left(\frac{2x}{\Delta e} - 1\right)}{(y-x)\beta + (x+y)(1+\alpha) + \delta e_l\left(\frac{2y}{\Delta e} - 1\right)} \tag{14a}$$

$$\mathrm{SR(even)} = \frac{(y-x)\beta + (x+y)(1+\alpha) + \delta e_l\left(1 - \frac{2x}{\Delta e}\right)}{(y-x)\beta + (x+y)(1+\alpha) + \delta e_h\left(1 - \frac{2y}{\Delta e}\right)}. \tag{14b}$$

Equations (14) require that $x\delta e_h > y\delta e_l$ and $y\delta e_h > x\delta e_l$ in order for SR values to be greater than one as found for through-bond dominated systems in Tables 4 and 5.

Table 5. Some photoelectron spectra data for cyclic diamines, dioxanes, and dithianes

Entry No.	System	N	Level[a] order	ΔE (eV)	δε (eV)	SR	Remarks	Ref
1		2 + 4	N	1.52	-0.91	12		21a
2		3 + 3	N	1.73	-0.91	41		21a
3		3 + 3 + 3	N	2.12	-0.52	3		1d
4		4 + 4 + 4	N	1.05	-0.25	3		1d
5		5 + 5 + 5	R	1.13	+0.52	0.03	TS	1d
6	 X = N	3+3	N	2.58	--	--		(b)
	O			1.22	-0.54	--		21b
	S			0.45	-0.36	--		21b
7	 X = N	2+4	N	1.58	--	--		(b)
	O			0.25	-0.73	--		21b
	S			0.41	-0.30	--		21b
8	 X = N	1+5	R	2.20	+ 0.01	--	TS	(b)
	S			0.95	--	--		21c

[a] N and R refer to normal and reversed level orders respectively.
[b] CNDO/2 results of this work.

π–π Orbital interaction

Two π orbitals separated by Nσ bonds can also interact through space and through bonds. The PMO treatment of π–π interaction will be quite similar to that for n–n interaction. In a single π system (basis level) one fragment will be a pair of electrons with energy zero. Since π electrons participate in bonding, environment adjusted level of π orbital e'_π will be lower than that for nonbonding orbital e'_n.[23] This will increase the energy ratio $|e''/\Delta e|$ in α and β, and the difference between the two values, i.e. $\beta - \alpha$ will become much larger than that for n orbital. This means that in through-bond dominated interactions both π_+ $(\pi_1 + \pi_2)$ and $\pi_-(\pi_1 - \pi_2)$ levels *may* be raised relative to the environment adjusted π basis level, since negative terms with parenthesis in eqns (9b) and (10a) *may* change to positive.

Energy splitting, ΔE, and average energy ϵ_{av} in π–π orbital interactions are still given by eqns (11) and (12), and there will be little change in various aspects of theoretical consequences from these n–n interactions.

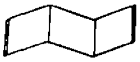
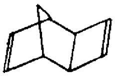
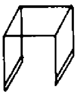
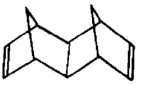
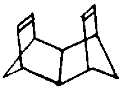
Some PES results are summarized in Table 6. Large decrease in ΔE and δε values for entry no. 3 (N = odd) from those for entry no. 1 is a result of large increase in through-space interaction in the system 3 relative to the system 1. Large increase in ΔE for entry no. 5 (N = even) from that for entry no. 4 is also a result of large increase in through-space interaction. Thus the increase in ΔE_s has opposite effects on $|\Delta E_{odd}|$ and $|\Delta E_{even}|$ as predicted by eqn (11) for through-bond dominated systems.

n–π Orbital interaction

A system which has an n and a π orbital oriented in such a way that the two orbitals can interact through space and through bonds can be treated similarly with the PMO approach. Here the energies of the two levels are different, so that through-space interaction will depress the symmetric combination Ψ_+ level lower than the environment adjusted π basis level and raise the antisymmetric combination Ψ_- higher than the environment adjusted n basis level.[2a]

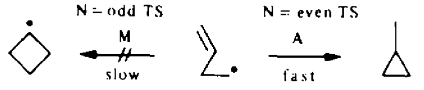
The Ψ_+ level will be somewhat higher than the π_+ level in a π–π orbital interaction. In this type of orbital interaction, however, there is one important difference from the former two, i.e. n–n and π–π interactions. Here when the n is a nonbonding orbital in a radical, the occupation number of the two environment adjusted

Table 6. Some photoelectron spectra data of π–π orbital interactions

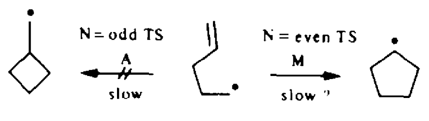
Entry No.	System	N	Level order	ΔE (eV)	δ_ε (eV)	SR	Ref.
1		3 + 3	N	0.97	-0.19	2.3	2a
2		3 + 3	N	1.15	-0.38	6.7	24
3		3 + 3	N	0.36	-0.01	1.1	2d
4		4 + 4	N	0.87	-0.07	1.4	2c
5		4 + 4	N	1.26	---	---	2d

levels, Ψ_+ and Ψ_- are different; two electrons will occupy the lower, Ψ_+, level whereas one electron will go into the higher, Ψ_-, level. Thus unlike in the n–n and π–π interactions where both orbitals are equally occupied, through-space dominated n–π orbital interaction stabilizes while through-bond dominated interaction of *N = odd system* destabilizes the system, since in the latter interaction the lower level, Ψ_+, which is occupied by two electrons interact with HO-σ (Table 3) which is destabilizing, while the higher with single electron interact with LU-σ* which is stabilizing resulting in a net destabilization.

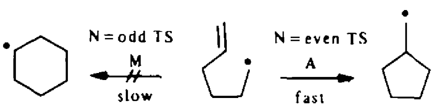
In an N = even system however the Ψ_+ (2 electron level) interacts with LU-σ* which is stabilizing (Table 3), while the Ψ_- (1 electron level) interacts with HO-σ which is destabilizing resulting in a net stabilization purely on account of different occupation numbers of the two levels. This could be the reason for the preference of radical cyclizations of small ω-alkenyl radicals via an even membered transition state (TS)[26,25] as illustrated in eqn (15) where A and M denote anti-Markownikow and Markownikow routes respectively.



(15a)



(15b)

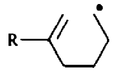


(15c)

In the transition state the radical n and π orbitals may be sufficiently separated so that no through-space dominated interaction may be possible. Bischof[26] has shown that anti-Markownikow cyclization route of 4-pentenyl radical eqn (15b), where an N = odd transition state is involved, has particularly high activation energy, ΔH$^{\neq}$, and activation free energy, ΔG$^{\neq}$. In fact this reaction has not been observed experimentally.

The M route of this reaction involves an N = even TS but this favorable feature is overwhelmed by an unfavourable decoupling effect of the π bond leading to a net destabilized high energy TS. For ω-butenyl, eqn (15a), and ω-hexenyl, eqn (15c), radicals, cyclization proceeds via the A route which has stabilizing N = even TS with no decoupling effect.

Beckwith *et al.*[27] have shown that an alkyl substitution on position 5 reverses regioselectivity of ω-hexenyl (hex-5-enyl) radical from A (1,5-cyclization) to M (1,6-cyclization) route dominance.



R = CH$_3$, i-Pr

They concluded that this is not due to pure steric effects but is mainly controlled by stereoelectronic effects. This reversal of regioselectivity however can be accounted for simply with the polarization of the HOMO of π bond by an electron donating group[5] such as R = Me or i-Pr; in general the lobe size of the HOMO is reduced at the substituted carbon 5 whereas it is enlarged at the unsubstituted position 6.[5] This will result in the decrease in interactions between the nonbonding and π orbitals at the substituted carbon, leading to a reduced reactivity of 1,5-cyclization.

We conclude that the PMO expressions for perturbed levels of n_+ and n_- orbitals, eqns (9) and (10), can accommodate qualitatively most of the experimental as well as MO theoretically calculated results for n–n, π–π orbital interactions.

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[7] The second order perturbation energy terms in eqn (1) should be given properly with explicit dependence on the overlap of the interacting groups as,

$$\sum_{m \neq i} \frac{(H_{im} - E_i^0 S_{im})^2}{E_i^0 - E_m^0}$$

where m = j or k. However it has been found that semiquantitative results may be obtained from the simplified formulas which do not contain overlap explicity.[4a]

[8] $E'_m = E_m^0 + H_{mm} + \Sigma_{n \neq m} H_{mn}^2/E_m^0 - E_n^0$, where m and n refer to a same fragment.

[9] In general an electron-withdrawing (-donating) group lowers (raises) the FMO levels.[5]

[10] This assumption is not essential for our subsequent conclusions derived from general expressions. It can be shown that raising of FMOs to different amount leads to the same conclusions.

[11] A typical value of $S_{n\sigma} = \langle n|\sigma_{cc}\rangle$ in diaminoethane is −0.0915; T. K. Brunck and F. Weinhold, *J. Am. Chem. Soc.* **98**, 4392 (1976).

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[13] Our STO-3G results showed that for n-alkyl radicals and n-alkyl amines with number of intervening sigma bonds $N = 2 \sim 5$, $|e''/\Delta e| \cong |e'/e_\sigma| = 0.75 \sim 0.80$, $\alpha = 1.28 \sim 1.75$ and $\beta = 1.69 \sim 2.21$. Thus $\beta - \alpha = 0.41 \sim 0.46 < 1.0$.

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[15] Inclusion of S in eqn (5) may be considered inconsistent with the neglect of overlap in eqn (1). Neglect of S in eqn (5) may lead to similar semi-quantitative results, but the inclusion of S in eqn (5) is essential to show a net destabilizing energy splitting by direct interaction of two degenerate levels (*vide infra*).

[16] Typical values of e′, Δe and k are −0.4,[3] 0.6,[3] and 0.8 hartrees,[17,4a] respectively.

[17] This k value was estimated from values of H_{ij} and S_{ij} reported by F. Weinhold and T. K. Brunck, *J. Am. Chem. Soc.* **98**, 3745 (1976).

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[22] Coupling term dominated interactions are characterized by (i) a net stabilization, i.e. $\epsilon_{av} < \epsilon_0$ and (ii) a splitting ratio of greater than one, according to eqns (12b) and (14b). These two conditions hold for entry number 1a in Table 4.

[23] The PES results on CH_3CH–NCH_3 gave the following environment adjusted π and n basis levels and the HO-σ level:[2a] $e_{HO\text{-}\sigma} = -12.9$, $e'_n = -9.5$, $e'_\pi = -10.6$ eV.

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