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A Quantitative Analysis of π-Nonbonded and Through-Bond Interactions in n-Butane, n-Butyl Radical and Tetramethylene Diradical[1]

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A quantitative treatment of π-nonbonded and n-σ^* interactions and through-bond coupling effect was attempted using n-butane, n-butyl radical, and tetramethylene diradical. Results of STO-3G level calculations showed that: (1) conformational preferences can be predicted quantitatively based solely on the additive effect of π-nonbonded and n-σ^* interactions, the predominant effect being the π-nonbonded interactions, (2) $(n\text{-}\sigma^*)_{anti}$ is destabilizing whereas $(n\text{-}\sigma^*)_{syn}$ is weakly stabilizing, which are contrary to what we expect from the normal n-σ^* interaction, (3) through-bond coupling of the two radical lobes is destabilizing for the triplet but stabilizing for the singlet tetramethylene diradical.

Introduction

The tetramethylene diradical has been a subject of theoretical interest concerning primarily with two aspects[2]: (1) thermodynamic stability of the species as a possible transitory intermediate in a nonconcerted thermal dissociation of cyclobutane, and (2) effect of through-bond coupling of the two nonbonding atomic orbitals (n AOs) on terminal methylene rotation. Results of various levels of MO calculations appear to agree on: (1) the $(\dot{90}, \dot{90})$ geometry, Figure 1, of the *trans*-tetramethylene diradical is thermodynamically stable and represents an energy well on the potential energy surface of the thermal dissociation of cyclobutane, and (2) as a result of through-bond coupling the two terminal radical lobes the antisymmetric (n_1-n_2) combination falls below the symmetric (n_1+n_2) combination of radiclal lobes. The energetics showed that the $(\dot{90}, \dot{90})$ form is preferred to the $(\dot{90}, \dot{0})$ and $(\dot{0}, \dot{0})$ forms. Borden and Davidson[3] attributed the preference of the $(\dot{90}, \dot{90})$ geometry to the stabilizing effect of through-bond coupling of the two nonbonding AOs on the terminal carbons.

In this work we report the results of *ab initio* studies on *trans*-n-butane, *trans*-n-butyl radical and triplet *trans*-n-tetramethylene diradical with a view to assessing quantitatively effects of π-nonbonded interactions (π-NBI)[4], σ-orbital interactions (n-σ^*),[4,5] and through-bond coupling of the

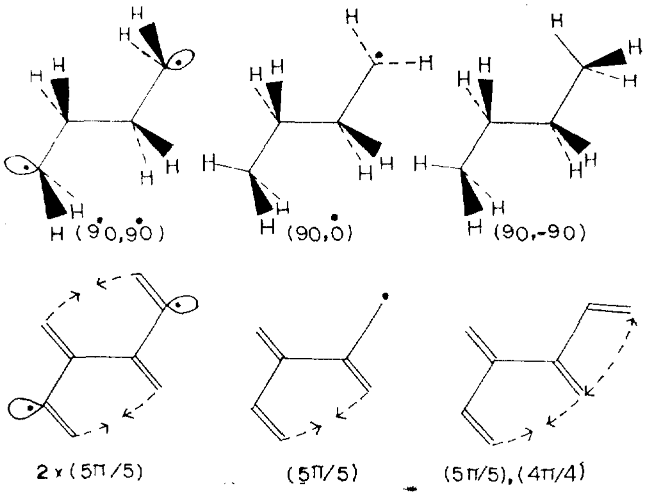


Figure 1. Representative geometries showing notations (a dot indicates the position of terminal radical carbon) and isoconjugate π structures of methylene hydrogens; arrows indicate attractive (→←) and repulsive (←→) π-nonbonded interactions of methylene hydrogens in ($5\pi/5$) and ($4\pi/4$) composite π structures respectively.

two radical lobes[3] on stereochemical preference of the molecule.

Calculations

All calculations were carried out at STO-3G level using the Gaussian 70 series of programs[6]. For the terminal radical carbons we used the HCH angle of 116.4° as given in ref. 3, but we kept the terminal methylenes pyramidalized by 22° during (rigid) rotations. For the central carbons and methyl groups we used the standard values for HCH bond angle (109.5°) and CH bond length (1.095Å)[3].

Results and Discussion

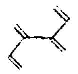
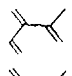
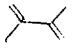
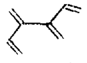
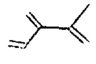
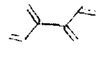
In order to assess effects of through-space π-NBI of methylene hydrogens and n-σ^* interactions, various geometries of *trans-n*-butane and *n*-butyl radical were investigated. Results of calculations on *n*-butane are summarized in Table 1. The (90, 0) and $(-90,0)$conformers are formed from the (0,0) geometry by 90° rotation of a terminal carbon anticlockwise and clockwise respectively, and the others are also formed likewise. Rotation of terminal methyl groups produces two distinct types of π-NBI between methylene hydrogens; an attractive $(5\pi/5)$ and a repulsive $(4\pi/4)$ type. The $(n\,\pi/m)$ notation[7] was introduced to denote a crowded π-conjugate or π-isoconjugate structure[7,8] formed by $n\pi$ electrons over m atoms or centers; thus the π-isoconjugate structure of eclipsed ethane has a $(4\pi/4)$ type π-NBI just as the π-conjugate structure of *cis*-butadiene does. Analyses of π overlap populations between two nonbonded ends i and j, P^{π}_{ij}, in crowded structures have lead us to a simple but useful general rule:[7] a crowded structure with $4n+2$ π electrons is strongly attractive and that with $4n+1$ π electrons is weakly attractive, $P^{\pi}_{ij}>0$, whereas a crowded form with $4n$ π electrons is π-nonbonded repulsive, $P^{\pi}_{ij}<0$, Accordingly a $(5\pi/5)$ system will be weakly π-nonbonded attractive while a $(4\pi/4)$ will be π-nonbonded repulsive, since the former is a $4n+1$ and the latter is a $4n$ π electron system. Composite π-structures within each conformer of *n*-butane are shown in Table 1 using the $(n\pi/m)$ notation. The first important result of the calculation is that the composite π structures $(5\pi/5)$ and $(4\pi/4)$ are truely π-nonbonded attractive, $P^{\pi}_{ij}>0$, and repulsive, $E^{\pi}_{ij}<0$, respectively as expected from the rule. Epiotis *et al.*,[4] have shown that the attractive(repulsive) π-NBI should be accompanied with the increase(decrease) in the total π overlap population, P^{π}_{T}. This requirement is also satisfied as can be seen from Table 1.

Furthermore the data in Table 1 reveal that the relative stabilities of various conformers can be predicted quantitatively to ±0.02kcal/mol based on the additive effect of the composite π-structures[7] by assigning -1.81 ± 0.01 and 1.83 ± 0.01 kcal/mol for the π-NBI of $(5\pi/5)$ and $(4\pi/4)$ structures respectively. An interesting geometry is the (90,-90), in which both a stabilizing $(5\pi/5)$ and a destabilizing $(4\pi/4)$ systems are present with the net effect of near cancellation. The cancellation is however not quite complete since the destabilizing effect of $(4\pi/4)$ is slightly in excess of the stabilizing effect of $(5\pi/5)$. As a result the (90,-90) geometry is less stable by 0.02 kcal/mol $(+1.83-1.81=0.02)$than the (0,0) geometry which has no π-NBI. The order of relative orbital energies, $2\Delta\Sigma\epsilon_i$, which reflects the effect of π-NBI, agrees with the relative stabilities. Table 1 shows that steric effect expected from the internuclear repulsion, V_{nn}, is also consistent with the relative stabilities.

A terminal nonbonding AO is the *n*-butyl radical is expected to introduce σ-orbital interaction of n-σ^* type which can produce a *syn* or *anti* preference[5]. In this type of σ conjugative interaction, charge is transferred from a filled nonbonding orbital (n) of the terminal radical lobe to a vacant antibonding orbital (σ^*) of the central C–C bond. It has been shown that an n-σ^* interaction is much more efficient when the nonbonding lobe and σ^* orbital are oriented in a mutually *anti* (or *trans*) relationship, *i.e.*, an $(n\text{-}\sigma^*)_{anti}$, compared with an $(n\text{-}\sigma^*)_{syn}$.[5]

However there are cases of apparent reversal in stabilizing effects; a conformation in which n lobe is oriented *syn* to the σ^*orbital is actually preferred to that of$(n\text{-}\sigma^*)_{anti}$ orientation. Houk *et al.*[9], have shown that the form which has the nitrogen lone pair of acetaldehyde imine located *syn* with respect to C–C bond is preferred to that of *anti* relation. They rationalized this, somewhat puzzling, preference of the conformation which gives less n-σ^* charge-transfer stabilization by invoking electrostatic domination of the preferred conformation.

TABLE 1: Relative Energies (in kcal/mol) and Overlap Populations for *trans-n*-Butane

Conformer		π-NBI	$\Delta E_T{}^a$	ΔV_{nn}	P^{π}_{ij}	$P_T{}^{\pi}$
(90,90)		$2\times(5\pi/5)$	0.00	0.0	2×0.0003	1.489
(90.0)		$(5\pi/5)$	1.81	10.0	0.0003	1.497
(0.0)		——	3.61	20.0	——	1.497
(90,−90)		$(5\pi/5)$ $(4\pi/4)$	3.63	20.0	0.0003 −0.0071	1.491
(−90,0)		$(4\pi/4)$	5.45	30.0	−0.0071	1.490
(−90,−90)		$2\times(4\pi/4)$	7.29	39.9	$2\times(-0.0071)$	1.483

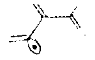
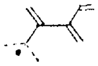
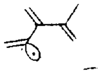
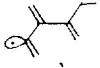
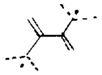
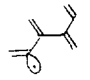
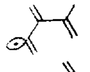
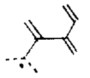
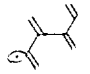
[a] Energies are relative to −155.46466 hartrees.

Composite π structures and n-σ^* type interactions in various forms of the n-butyl radical are listed in Table 2. Using the relative energies of conformers in Tables 1 and 2, the energetic effects (in kcal/mol) of $(n\text{-}\sigma^*)_{anti}$ and $(n\text{-}\sigma^*)_{syn}$ interactions can be estimated from the following equations.

$$(90,\dot{0})+(90,90)=(90,\dot{90})+(90,0),\quad \Delta E=+0.59$$
$$(0,\dot{0})+(0,90)=(0,\dot{90})+(0,0),\quad \Delta E=+0.58$$
$$(-90,\dot{0})+(-90,90)=(-90,\dot{90})+(-90,0),\quad \Delta E=+0.56$$
$$\overline{\Delta E}(n\text{-}\sigma^*)_{anti}=0.58\pm0.01 \text{ kcal/mol}$$
$$(90,\dot{0})+(90-90)=(90,-\dot{90})+(90,0),\quad \Delta E=-0.94$$
$$(0,\dot{0})+(0,-90)=(0,-\dot{90})+(0,0),\quad \Delta E=-0.94$$
$$(-90,\dot{0})+(-90,-90)=(-90,-\dot{90})+(-90,0),\quad \Delta E=-0.98$$
$$\overline{\Delta E}(n\text{-}\sigma^*)_{syn}=-0.95\pm0.02 \text{ kcal/mol}$$

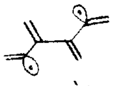
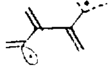
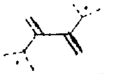
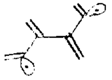
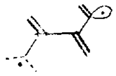
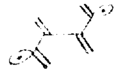
The energetic effects calculated clearly demonstrate that $(n\text{-}\sigma^*)_{anti}$ is actually destabilizing while $(n\text{-}\sigma^*)_{syn}$ is weakly stabilizing. Thus the results for n-butyl radical are is accord with the results obtained for acetaldehyde imine radical and cation. In Table 2 we have shown the relative orbital energies (one electron factor) and the relative interelectronic and internuclear energies (steric factor). It is clear from these data that the three geometries with $(n\text{-}\sigma^*)_{anti}$ have prominently unfavorable Coulombic (nuclear and electronic) repulsion effects although one-electron effects are favorable over the other forms. Inspection of overlap populations between the radical carbon (C_4) and the methylene hydrogens on the adjacent carbon(C_3) indeed revealed large repulsive interactions (large negative overlap

TABLE 2: Relative Energies (in kcal/mol) and Overlap Populations for *trans*-*n*-Butyl Radical

	Conformer	π-NBI	σ-Conj. interaction	$\Delta E_T{}^a$	ΔV_{nn}	ΔV_{ee}	$P_{ij}{}^{\pi}$
$(90,\dot{90})$		$2\times(5\pi/5)$	$(n\text{-}\sigma^*)_{anti}{}^b$	0.00	0.0	0.0	0.0006 0.0005
$(90,\dot{0})$		$((5\pi/5^*)$	——	1.22	−131.9	−114.5	0.0006
$(0,\dot{90})$		$(5\pi/5)$	$(n\text{-}\sigma^*)_{anti}$	1.81	9.9	14.8	0.0005
$(90,-\dot{90})$		$(5\pi/5)$ $(4\pi/4)$	$(n\text{-}\sigma^*)_{syn}{}^b$	2.10	−331.6	−307.2	0.0006 −0.0007
$(0,\dot{0})$		——	——	3.03	−121.8	−99.6	——
$(-90,\dot{90})$		$(5\pi/5)$ $(4\pi/4)$	$(n\text{-}\sigma^*)_{anti}$	3.63	19.8	29.6	0.0005 −0.0011
$(0,-\dot{90})$		$(4\pi/4)$	$(n\text{-}\sigma^*)_{syn}$	3.91	−321.6	−292.3	−0.0070
$(-90,\dot{0})$		$(4\pi/4)$	——	4.89	−111.9	−84.6	−0.0112
$(-90,-\dot{90})$		$2\times(4\pi/4)$	$(n\text{-}\sigma^*)_{syn}$	5.75	−311.7	−277.4	−0.0112 −0.0070

[a] Energies are relative to −154.81384 hartrees. [b] The nonbonding electron(n) is located *syn*- and *anti*-periplanar relation with respect to the central C-C bond(σ^*).

TABLE 3. Relative Energies (in kcal/mol) and Overlap Populations for Triplet *trans*-Tetramethylene Diradical

	Conformer	π-NBI	σ-Conj. interaction	$E_T{}^a$	V_{nn}	P_{ij}
$(\dot{90},\dot{90})$		$2\times(5\pi/5)$	$2\times(n\text{-}\sigma^*)_{anti}$	0.00	0.0	2×0.0006
$(\dot{90},\dot{0})$		$(5\pi/5)$	$(n\text{-}\sigma^*)_{anti}$	0.70	−126.6	0.0006
$(\dot{90},-\dot{90})$		$(5\pi/5)$ $(4\pi/4)$	$(n\text{-}\sigma^*)_{anti}$ $(n\text{-}\sigma^*)_{syn}$	1.65	−319.5	0.0006 −0.0070
$(\dot{0},\dot{0})$		——	——	1,95	−251.5	——
$(\dot{0},-\dot{90})$		$(4\pi/4)$	$(n\text{-}\sigma^*)_{syn}$	2.81	−449.2	−0.0070
$(-\dot{90},-\dot{90})$		$2\times(4\pi/4)$	$2\times(n\text{-}\sigma^*)_{syn}$	3.70	−646.8	$2\times(-0.0069)$

[a] Energies are relative to −154.16206 hartrees.

populations) for the geometries with $(n\text{-}\pi)_{anti}$. These results are in accord with electrostatic domination, or steric domination of the sigma electron interactions[8]. One $(n\text{-}\pi)_{anti}$ gave consistently 0.58 kcal/mol of destabilization to the total energy.

Here again the relative stabilities of conformers can be predicted quantitatively (to ±0.03 kcal/mol) using energetic effects of π-NBI and $n\text{-}\sigma^*$ interactions; $(5\pi/5)=-1.81$, $(4\pi/4)=1.83$, $(n\text{-}\sigma^*)_{anti}=0.58$, and $(n\text{-}\sigma^*)_{syn}=-0.95$ kcal/mol. It is quite clear that π-nonbonded interactions between methylene hydrogens are much stronger than the σ-conjugative interaction of the nonbonding radical electron. In fact the π-NBI is dominant in determining the conformational preference of n-butyl radical; the $(90,\dot{9}0)$ form turns out to be the most preferred simply because of the two stabilizing $(5\pi/5)$ composite π-structures.

In the tetramethylene diradical, there are two radical lobes on the terminal carbons which can interact with the σ^* orbital of the central C-C bond. Thus the $(\dot{9}0, \dot{9}0)$ form has one more stabilizing $(5\pi/5)$ π-NBI and one more destabilizing $(n\text{-}\sigma^*)_{anti}$ interaction as compared with the $(\dot{9}0,\dot{0})$ form, and hence the net stabilizing effect expected over that of the $(\dot{9}0,\dot{0})$ is $-1.81+0.58=-1.23$ kcal/mol. However Table 3 shows that the coupling of the two $(n\text{-}\sigma^*)_{anti}$ results in a net destabilization of 0.53 ± 0.02 kcal/mol. This may be expressed as,

$$(\dot{9}0,\dot{0})+(90,\dot{9}0)=(\dot{9}0,\dot{9}0)+(90,\dot{0}),$$
$$\Delta E=0.52 \text{ kcal/mol})$$

Similar calculations for through-bond coupling in the $(\dot{9}0,-\dot{9}0)$ and $(-\dot{9}0,-\dot{9}0)$ forms gave +0.07 and +0.03 kcal/mol respectively.

With the triplet energies from two-configuration MC SCF calculations[3] through-bond coupling energy in the form $(\dot{9}0,\dot{9}0)$ is +0.28 kcal/mol, which is somewhat smaller but is still clearly destabilizing. With the singlet energies from the same two-configuration MC SCF calculation[3], however, we get stabilizing through-bond coupling effect of -1.54 kcal/mol for the $(\dot{9}0,\dot{9}0)$ form. At present we are unable to account for this stabilizing singlet but destabilizing triplet through-bond coupling phenomena.

If we take these coupling energies into account the relative energies can again be predicted quantitatively with the additive effect of π-NBI and $n\text{-}\sigma^*$ interactions for the tetramethylene diradical. Here also the large Coulombic repulsion (V_{nn}) is seen to be responsible for the destabilizing effect of $(n\text{-}\sigma^*)_{anti}$ interaction.

One important conclusion obtained in this study is that the relative stability of the $(\dot{9}0, \dot{9}0)$ form over the other forms is primarily due to the stabilizing effect of $(5\pi/5)$ π-NBI. Although other effects such as $n\text{-}\sigma^*$ interaction, Coulombic repulsion and through-bond coupling contribute to the relative energies of conformers, it is the effect of π-NBI that is predominant in determining the preferred conformations.

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