

**A Quantitative Analysis of  $\pi$ -Nonbonded and Through-Bond Interactions in *n*-Butane, *n*-Butyl Radical and Tetramethylene Diradical<sup>1</sup>**

Ikchoon Lee and Young Gu Cheun

Department of Chemistry, Inha University Incheon 160, Korea (Received June 24, 1981)

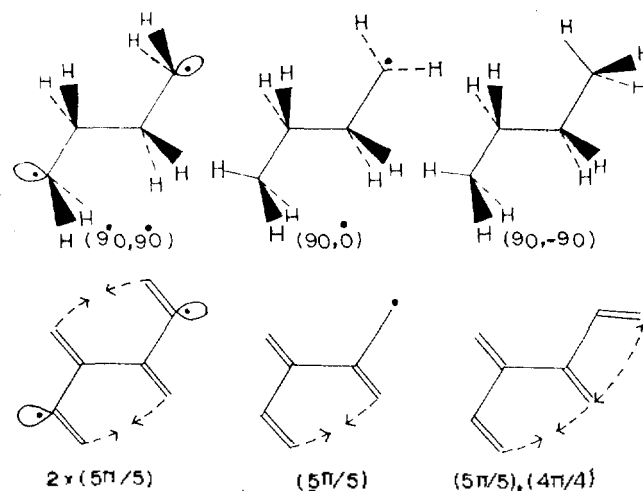
A quantitative treatment of  $\pi$ -nonbonded and  $n-\sigma^*$  interactions and through-bond coupling effect was attempted using *n*-butane, *n*-butyl radical, and tetramethylene diradical. Results of STO-3G level calculations showed that: (1) conformational preferences can be predicted quantitatively based solely on the additive effect of  $\pi$ -nonbonded and  $n-\sigma^*$  interactions, the predominant effect being the  $\pi$ -nonbonded interactions, (2)  $(n-\sigma^*)_{anti}$  is destabilizing whereas  $(n-\sigma^*)_{syn}$  is weakly stabilizing, which are contrary to what we expect from the normal  $n-\sigma^*$  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<sup>2</sup>: (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  $(90, 90)$  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 radical lobes. The energetics showed that the  $(90, 90)$  form is preferred to the  $(90, 0)$  and  $(0, 0)$  forms. Borden and Davidson<sup>3</sup> attributed the preference of the  $(90, 90)$  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  $\pi$ -nonbonded interactions ( $\pi$ -NBI)<sup>4</sup>,  $\sigma$ -orbital interactions ( $n-\sigma^*$ ),<sup>4,5</sup> and through-bond coupling of the



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

two radical lobes<sup>3</sup> on stereochemical preference of the molecule.

### Calculations

All calculations were carried out at STO-3G level using the Gaussian 70 series of programs<sup>6</sup>. 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)<sup>3</sup>.

### Results and Discussion

In order to assess effects of through-space  $\pi$ -NBI of methylene hydrogens and  $n$ - $\sigma^*$  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  $\pi$ -NBI between methylene hydrogens; an attractive (5 $\pi$ /5) and a repulsive (4 $\pi$ /4) type. The ( $n\pi/m$ ) notation<sup>7</sup> was introduced to denote a crowded  $\pi$ -conjugate or  $\pi$ -isoconjugate structure<sup>7,8</sup> formed by  $n\pi$  electrons over  $m$  atoms or centers; thus the  $\pi$ -isoconjugate structure of eclipsed ethane has a (4 $\pi$ /4) type  $\pi$ -NBI just as the  $\pi$ -conjugate structure of *cis*-butadiene does. Analyses of  $\pi$  overlap populations between two nonbonded ends  $i$  and  $j$ ,  $P_{ij}^\pi$ , in crowded structures have lead us to a simple but useful general rule:<sup>7</sup> a crowded structure with  $4n+2$   $\pi$  electrons is strongly attractive and that with  $4n+1$   $\pi$  electrons is weakly attractive,  $P_{ij}^\pi > 0$ , whereas a crowded form with  $4n$   $\pi$  electrons is  $\pi$ -nonbonded repulsive,  $P_{ij}^\pi < 0$ . Accordingly a (5 $\pi$ /5) system will be weakly  $\pi$ -nonbonded attractive while a (4 $\pi$ /4) will be  $\pi$ -nonbonded repulsive, since the former is a  $4n+1$  and the latter is a  $4n$   $\pi$  electron system. Composite  $\pi$ -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  $\pi$  structures (5 $\pi$ /5) and (4 $\pi$ /4) are truly  $\pi$ -nonbonded attractive,  $P_{ij}^\pi > 0$ , and







repulsive,  $E_{ij}^\pi < 0$ , respectively as expected from the rule. Epitotis *et al.*,<sup>4</sup> have shown that the attractive(repulsive)  $\pi$ -NBI should be accompanied with the increase(decrease) in the total  $\pi$  overlap population,  $P_T^\pi$ . 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  $\pm 0.02$  kcal/mol based on the additive effect of the composite  $\pi$ -structures<sup>7</sup> by assigning  $-1.81 \pm 0.01$  and  $1.83 \pm 0.01$  kcal/mol for the  $\pi$ -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  $\pi$ -NBI. The order of relative orbital energies,  $2\Delta\epsilon_i$ , which reflects the effect of  $\pi$ -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 in the *n*-butyl radical is expected to introduce  $\sigma$ -orbital interaction of  $n$ - $\sigma^*$  type which can produce a *syn* or *anti* preference<sup>5</sup>. In this type of  $\sigma$  conjugative interaction, charge is transferred from a filled nonbonding orbital ( $n$ ) of the terminal radical lobe to a vacant antibonding orbital ( $\sigma^*$ ) of the central C-C bond. It has been shown that an  $n$ - $\sigma^*$  interaction is much more efficient when the nonbonding lobe and  $\sigma^*$  orbital are oriented in a mutually *anti* (or *trans*) relationship, *i.e.*, an ( $n$ - $\sigma^*$ )<sub>anti</sub>, compared with an ( $n$ - $\sigma^*$ )<sub>syn</sub>.<sup>5</sup>

However there are cases of apparent reversal in stabilizing effects; a conformation in which  $n$  lobe is oriented *syn* to the  $\sigma^*$  orbital is actually preferred to that of ( $n$ - $\sigma^*$ )<sub>anti</sub> orientation. Houk *et al.*,<sup>9</sup> 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  $n$ - $\sigma^*$  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	$\pi$ -NBI	$\Delta E_T^a$	$\Delta V_{nn}$	$P_{ij}^\pi$	$P_T^\pi$
(90,90)	 2×(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×(4 $\pi$ /4)	7.29	39.9	2×(-0.0071)	1.483










<sup>a</sup> Energies are relative to -155.46466 hartrees.

Composite  $\pi$  structures and  $n$ - $\sigma^*$  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  $(n-\sigma^*)_{anti}$  and  $(n-\sigma^*)_{syn}$  interactions can be estimated from the following equations.

$$\begin{aligned} (90, \dot{0}) + (90, 90) &= (90, \dot{90}) + (90, 0), & \Delta E &= +0.59 \\ (0, \dot{0}) + (0, 90) &= (0, \dot{90}) + (0, 0), & \Delta E &= +0.58 \\ (-90, \dot{0}) + (-90, 90) &= (-90, \dot{90}) + (-90, 0), & \Delta E &= +0.56 \\ \Delta \bar{E}(n-\sigma^*)_{anti} &= 0.58 \pm 0.01 \text{ kcal/mol} \\ (90, \dot{0}) + (90, -90) &= (90, -\dot{90}) + (90, 0), & \Delta E &= -0.94 \\ (0, \dot{0}) + (0, -90) &= (0, -\dot{90}) + (0, 0), & \Delta E &= -0.94 \\ (-90, \dot{0}) + (-90, -90) &= (-90, -\dot{90}) + (-90, 0), & \Delta E &= -0.98 \\ \Delta \bar{E}(n-\sigma^*)_{syn} &= -0.95 \pm 0.02 \text{ kcal/mol} \end{aligned}$$

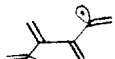
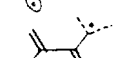


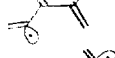
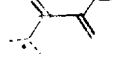
The energetic effects calculated clearly demonstrate that  $(n-\sigma^*)_{anti}$  is actually destabilizing while  $(n-\sigma^*)_{syn}$  is weakly stabilizing. Thus the results for  $n$ -butyl radical are in accord with the results obtained for acetaldehyde imine radical and cation. In Table 2 we have 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  $(n-\sigma^*)_{anti}$  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	$\pi$ -NBI	$\sigma$ -Conj. interaction	$\Delta E_T^a$	$\Delta V_{nn}$	$\Delta V_{ee}$	$P_{ij}^d$
(90, $\dot{90}$ )	 $2 \times (5\pi/5)$	$(n-\sigma^*)_{anti}^b$	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, $\dot{90}$ )	 $(5\pi/5)$	$(n-\sigma^*)_{anti}$	1.81	9.9	14.8	0.0005
(90, $-\dot{90}$ )	 $(5\pi/5)$ $(4\pi/4)$	$(n-\sigma^*)_{syn}^b$	2.10	-331.6	-307.2	0.0006 -0.0007
(0, $\dot{0}$ )	 —	—	3.03	-121.8	-99.6	—
(-90, $\dot{90}$ )	 $(5\pi/5)$ $(4\pi/4)$	$(n-\sigma^*)_{anti}$	3.63	19.8	29.6	0.0005 -0.0011
(0, $-\dot{90}$ )	 $(4\pi/4)$	$(n-\sigma^*)_{syn}$	3.91	-321.6	-292.3	-0.0070
(-90, $\dot{0}$ )	 $(4\pi/4)$	—	4.89	-111.9	-84.6	-0.0112
(-90, $-\dot{90}$ )	 $2 \times (4\pi/4)$	$(n-\sigma^*)_{syn}$	5.75	-311.7	-277.4	-0.0112 -0.0070

<sup>a</sup> Energies are relative to -154.81384 hartrees. <sup>b</sup> The nonbonding electron(n) is located *syn*- and *anti*-periplanar relation with respect to the central C-C bond( $\sigma^*$ ).

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

Conformer	$\pi$ -NBI	$\sigma$ -Conj. interaction	$E_T^a$	$V_{nn}$	$P_{ij}$
( $\dot{90}, \dot{90}$ )	 $2 \times (5\pi/5)$	$2 \times (n-\sigma^*)_{anti}$	0.00	0.0	$2 \times 0.0006$
( $\dot{90}, \dot{0}$ )	 $(5\pi/5)$	$(n-\sigma^*)_{anti}$	0.70	-126.6	0.0006
( $\dot{90}, -\dot{90}$ )	 $(5\pi/5)$ $(4\pi/4)$	$(n-\sigma^*)_{anti}$ $(n-\sigma^*)_{syn}$	1.65	-319.5	0.0006 -0.0070
( $\dot{0}, \dot{0}$ )	 —	—	1.95	-251.5	—
( $\dot{0}, -\dot{90}$ )	 $(4\pi/4)$	$(n-\sigma^*)_{syn}$	2.81	-449.2	-0.0070
( $-\dot{90}, -\dot{90}$ )	 $2 \times (4\pi/4)$	$2 \times (n-\sigma^*)_{syn}$	3.70	-646.8	$2 \times (-0.0069)$

<sup>a</sup> Energies are relative to -154.16206 hartrees.

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

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

In the tetramethylene diradical, there are two radical lobes on the terminal carbons which can interact with the  $\sigma^*$  orbital of the central C-C bond. Thus the  $(\dot{9}0, \dot{9}0)$  form has one more stabilizing  $(5\pi/5)$   $\pi$ -NBI and one more destabilizing  $(n-\sigma^*)_{anti}$  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  $(n-\sigma^*)_{anti}$  results in a net destabilization of  $0.53 \pm 0.02$  kcal/mol. This may be expressed as,

$$(\dot{0}, \dot{0}) + (90, 90) = (\dot{9}0, \dot{9}0) + (90, \dot{0}),$$

$$\Delta E = 0.52 \text{ kcal/mol}$$

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<sup>3</sup> through-bond coupling energy in the form (90,90) 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<sup>3</sup>, 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  $\pi$ -NBI and  $n-\sigma^*$  interactions for the tetramethylene diradical. Here also the large Coulombic repulsion ( $V_{nn}$ ) is seen to be responsible for the destabilizing effect of  $(n-\sigma^*)_{anti}$  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  $(5\pi/5)$   $\pi$ -NBI. Although other effects such as  $n-\sigma^*$  interaction, Coulombic repulsion and through-bond coupling contribute to the relative energies of conformers, it is the effect of  $\pi$ -NBI that is predominant in determining the preferred conformations.

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## Reference

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