A Perturbation Molecular Orbital Study of the Recombination Reactions of Diarylaminyl Radicals

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(Z. Naturforsch. 28a, 1892–1896 [1973] ; received 29 May 1973)

The recombination reactions of arylaminyl radicals are studied on the basis of its order PMO treatment, assuming dimeric intermediates with C — N or C — C bonding modes. In the case of diphenyl aminyl radical the N — N recombination causes an increase in the π-bonding energy and should be most favourable for the low temperature reactions. Due to the low dissociation energy of the N — N bond, the C — N bonding is preferred in the high temperature reactions. It is found that the ortho- and para-additions are energetically more favourable than the meta addition, in agreement with π-SCF MO calculations and experimental results. The recombination of 2,2’-diphenylaminyl radicals proceeds through C — C and C — N bonding, the 1,1’-bonding is most favourable. The PMO-results are parallel to those of the π-SCF MO calculations, providing another demonstration for the utility of this method.

Diarylaminyl radicals are generated through thermolysis of tetraarylhydrazines 1,2 or N, nitroso, diarylamines 3, or through the oxidation of the corresponding diarylamines 4. Their existence was proofed through NO-scavenging 1 and the measurement of their ESR spectra 2. They recombine by the same reaction yielding hydrazines (e.g. by the oxidation of amines), benzidines, semidines and diarylamino derivatives. It was found that the product distribution of the thermal benzidin rearrangement is similar to that of the radical’s recombination reactions. This suggests that the rearrangement proceeds through aminylradicals as intermediates too 5–7.

According to the present available experimental results, the course of the recombination reactions is determined by the relative stabilities of dimeric intermediates formed through the addition of one radical to the arylring of the other 3,4. The relative stabilities of such intermediates can be estimated through the calculation of their relative π-bonding energies on the basis of first order perturbation theory (PMO treatment) 8. The idea behind such a treatment is that the bonding between two odd alternate radicals causes a first order perturbation of their nonbonded orbitals, yielding an increase in the π-bonding energy of the whole system ($\Delta E_\pi$).

$$\Delta E_\pi = 2 a_{\alpha} b_{\alpha} \beta,$$  

(1)

$\alpha_{\alpha}$ = NBMO-coefficient at the atom of connection (r) in the radical II, $\beta_{\alpha}$ = NBMO-coefficient at the atom of connection (s) in the radical I.

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The formation of a dimeric intermediate corresponds to the removal of cyclic conjugation from a
phenyl ring in the radical yielding a system isoconjugate with the anilinyl substituted pentadienyl molecule. The formed substituted pentadienyl system may be thought of as constructed from the anilinyl- and the pentadienyl radical.

\[
\begin{align*}
\text{C} & - \text{N}\text{•} + \text{C} & - \text{C} \\
\text{C} & - \text{C} & - \text{N}\text{•} \\
\end{align*}
\]

The ortho-, meta- and para-intermediates correspond to the bondformation at C atoms 1, 2, and 3 of the pentadienyl radical respectively.

\[
\begin{align*}
\delta E_{\pi-PMO} &= 0.62 \beta, \\
E_{\pi-SCF} &= -16.4 \text{ eV,} \\
\text{ortho-addition} \\
\delta E_{\pi-PMO} &= 0.0 \beta, \\
E_{\pi-SCF} &= -13.66 \text{ eV,} \\
\text{meta-addition} \\
\delta E_{\pi-PMO} &= 0.62 \beta, \\
E_{\pi-SCF} &= -16.37 \text{ eV,} \\
\text{para-addition} \\
\end{align*}
\]

The difference between the \(\pi\)-bonding energies of the aminyl radical and the 2-anilinyl pentadienyl molecule, which may be obtained through a 1st order PMO calculation of the later system, is 2.3 \(\beta\).

Considering this difference, the \(\pi\)-bonding energy of all dimeric intermediates may be calculated, relative to the energy of the aminyl radical. Table 1 shows the relative \(\pi\)-bonding energies of the hydrazine derivative and the C–N as well as the C–C dimeric intermediates.

Except the N–N bonding product, whose relative \(\pi\)-bonding energy is .82 \(\beta\), all the intermediates are signified with a loss in the \(\pi\)-bonding energy. This conclusion explains the experimental fact that, the oxidation of the diphenylamines yields tetra-phenyl hydrazines. Due to the low dissociation energy of the N–N bond (20 – 30 kcal/mol), the hydrazine derivatives redissociate in radicals when heated to higher temperatures,

\[
(Ar)_2 - N - N - (Ar)_2 \xrightarrow{\Delta} 2 X \cdot N(Ar)_2.
\]

The equilibrium may be shifted to the radical side through introduction of an electron donating substituent to the aryl rest, or through the recombination of two radicals forming a C–N bond that dissociates by higher temperatures.

Aromatic resonance is removed from two phenyl rings by the formation of the intermediates 6 – 11. Their relatively small \(\pi\)-bonding energies make them unprobable. In fact no products corresponding to them have been isolated. Intermediates 2 – 5 are more probable, since they correspond to the removal of aromatic resonance in a single phenylring of the whole molecule. Both PMO and \(\pi\)-SCF MO

<table>
<thead>
<tr>
<th>Recombination's mode</th>
<th>Structure of the intermediate</th>
<th>(\Delta E_{\pi-PMO})</th>
<th>(E_{\pi-SCF}) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Free radicals</td>
<td>2 X \cdot N \cdot (Ar)_2</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2. N–N bonding</td>
<td>(Ph)_2 N–N–(Ph)_2</td>
<td>(+0.82 \beta)</td>
<td>–*</td>
</tr>
<tr>
<td>3. N–C ortho</td>
<td>(\text{Ph}^-\text{N}^-\text{Ph})</td>
<td>(-1.68 \beta)</td>
<td>(+1.292)</td>
</tr>
<tr>
<td>4. N–C meta</td>
<td>(\text{Ph}^-\text{N}^-\text{Ph})</td>
<td>(-2.3 \beta)</td>
<td>(4.036)</td>
</tr>
<tr>
<td>5. N–C para</td>
<td>(\text{Ph}^-\text{N}^-\text{Ph})</td>
<td>(-1.68 \beta)</td>
<td>(1.324)</td>
</tr>
<tr>
<td>6. ortho, ortho</td>
<td>(\text{Ph}^-\text{N}^-\text{Ph})</td>
<td>(-3.36 \beta)</td>
<td>(2.584)</td>
</tr>
<tr>
<td>7. ortho, meta</td>
<td>(\text{Ph}^-\text{N}^-\text{Ph})</td>
<td>(-3.98 \beta)</td>
<td>(5.328)</td>
</tr>
<tr>
<td>8. ortho, para</td>
<td>(\text{Ph}^-\text{N}^-\text{Ph})</td>
<td>(-3.36 \beta)</td>
<td>(2.616)</td>
</tr>
<tr>
<td>9. meta, meta</td>
<td>(\text{Ph}^-\text{N}^-\text{Ph})</td>
<td>(-4.6 \beta)</td>
<td>(8.072)</td>
</tr>
<tr>
<td>10. meta, para</td>
<td>(\text{Ph}^-\text{N}^-\text{Ph})</td>
<td>(-3.98 \beta)</td>
<td>(5.360)</td>
</tr>
<tr>
<td>11. para, para</td>
<td>(\text{Ph}^-\text{N}^-\text{Ph})</td>
<td>(-3.36 \beta)</td>
<td>(2.648)</td>
</tr>
</tbody>
</table>

* Since no \(\beta_{N-N}\) parameter is available, no \(\pi\)-SCF calculation could be done for this molecule.
procedures predict equal stabilities for the para and ortho intermediates which should yield ortho and para semidines through hydrogen shifts. In fact both semidines and no meta semidine have been isolated from the recombination reactions of diphenyl aminyl radicals. The higher yield of the p-semidine is most probably caused by the steric hinderance in the ortho substitution.

2,2'-Dinaphthyl aminyl radicals. A similar treatment may be carried out for the recombination of naphthyl aminyl radicals. Consider the dimeric intermediate of the following structure, compelled through an N-C addition:

\[
\begin{align*}
\text{N} & \quad (\text{Ar})_2 \\
\text{C} & \quad \text{C}
\end{align*}
\]

The \(\pi\)-bonding energy of one radical remains constant on addition, that of the second decreases due to the break down of cyclic conjugation in one of its phenyl or naphthyl moieties. This change in the \(\pi\)-bonding energy is significant for the stability of the whole intermediate and varies according to the addition’s position. It can be estimated through the construction of the noncyclic conjugated fragment according to the following scheme;

1. Starting with a heptatrienyl radical a methylene carbon atom is introduced to its middle, unstarrred, carbon atom. The formed bond corresponds to no first order change in the \(\pi\)-bonding energy, i.e. \(\Delta E_{\pi} = 0.0\).

2. The 4-methylene, heptatrienyl diradical has two degenerate NBMO’s, according to the pairing theorem \(\left(\text{N}^*-\text{N}^0=2\right)\). Bonding to another methylene carbon atom and the formation of phenyl derivatives should perturb only one NBMO. This bonding may lead to one of the following two phenyl derivatives, which have the same structure as the dimeric intermediates: a-\(\beta\)-methylene styrene and b-ortho methylene styrene. The PMO treatment shows that, the first derivative is with 0.1 \(\beta\) more stable than the second.

3. The 2-naphthylaminyl radical is then introduced to different positions of the two styrene derivatives and the so caused changes in the \(\pi\)-bonding energies are calculated with the PMO method.

Both changes in \(\pi\)-bonding energy, of step 2 and 3, are added together. The sum is called \(E_{\pi}^n\) \((n=\text{the numbering of the intermediate in Table 2})\).

4. Setting \(E_{\pi}\) of the dinaphthyl aminyl radical \(=0.0\), the relative stabilities of the intermediates may be calculated. For this purpose it is sufficient to calculate the difference between the \(\pi\)-bonding energies of the dinaphthyl aminyl radical and a single intermediate, and between the energies of the same intermediate and all other intermediates. Structure (intermediate) 8 is found arithmetically most suitable for this purpose;

\[
\begin{align*}
\Delta E_{\pi}^8 &= E_{\pi}^\text{rad} - E_{\pi}^8, \quad (2) \\
\Delta E_{\pi}^n &= \Delta E_{\pi}^8 + (E_{\pi}^n - E_{\pi}^8). \quad (3)
\end{align*}
\]

5. The relative stabilities of intermediates 9 and 10, which correspond to additions on C atoms 10 and 9 respectively, are calculated according to the following scheme,
Table 2 shows the relative $\pi$-bonding energies for the possible intermediates.

<table>
<thead>
<tr>
<th>Structure of the intermediate</th>
<th>$\Delta E_\pi$ (PMO)</th>
<th>$\Delta E_\pi$ (SCF), eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 2,2'-Dinaphthylaminyl radical</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2. 2-Naphthyl-</td>
<td>-1.15$\beta$</td>
<td>0.930</td>
</tr>
<tr>
<td>3. 2-Naphthyl-</td>
<td>-1.59$\beta$</td>
<td>1.675</td>
</tr>
<tr>
<td>4. 2-Naphthyl-</td>
<td>-1.57$\beta$</td>
<td>1.654</td>
</tr>
<tr>
<td>5. 2-Naphthyl-</td>
<td>-1.57$\beta$</td>
<td>1.727</td>
</tr>
<tr>
<td>6. 2-Naphthyl-</td>
<td>-2.03$\beta$</td>
<td>3.696</td>
</tr>
<tr>
<td>7. 2-Naphthyl-</td>
<td>-2.03$\beta$</td>
<td>3.822</td>
</tr>
<tr>
<td>8. 2-Naphthyl-</td>
<td>-2.13$\beta$</td>
<td>3.908</td>
</tr>
<tr>
<td>9. 2-Naphthyl-</td>
<td>-1.45$\beta$</td>
<td>2.049</td>
</tr>
<tr>
<td>10. 2-Naphthyl-</td>
<td>-3.13$\beta$</td>
<td>4.653</td>
</tr>
</tbody>
</table>

The order of stability predicted by the PMO treatment is parallel to that of the $\pi$-SCF-MO calculation. Intermediate 9, the relative stability of which is overestimated by the PMO method, forms the only exception. The order of stability is $1 > 2 > 4 = 5 > 3 > 6 > 7 > 8$. Due to the big differences in $\pi$-bonding energies, our treatment predicts that the N–C bonding should proceed mainly at position 1. In fact this is the only kind of C–N bonded derivative which has been isolated experimentally from the reaction media. Our previous data do not seem to agree with the formation of 1,1'-dinaphthyl, 2,2'-diamine, which according to our argumentation, should proceed through a doubly perturbed intermediate, in which the cyclic conjugation of a phenyl ring in two naphthyl segments have been removed.

Such an intermediate should be less stable than that of a C–N coupling or the product of a N–N bond formation (according to the PMO treatment). This contradiction is removed on considering the steric interaction of the dimerization process. Although the N–N bond formation is rather convenient from the $\pi$-bonding energy’s point of view, it is less attractive due to the repulsion between the 1,1' and 8,8' protons of the aromatic rings. Assuming the N–N bond length = 1.47 Å and C–C bond length = 1.39 Å the distance between the atoms $C_1$, $C_1'$ and $C_8$, $C_8'$ is calculated < 2.0 Å. This distance should correspond to a very big repulsion between the protons bonded to them. The molecule may avoid this high repulsion either through twisting of the naphthyl rings out of the molecular plane, or through the nonformation of the N–N bond. In both cases the transition states and products of the reaction are destabilized. However, the N...N approach may constitute the first step toward dimerization through the cyclic $(4n + 2)$ transition state I.

Such a reaction proceeds toward a 1,1'-bonding with a deformation of the local protons out of the plane, followed by two successive hydrogen shifts, which could allow for the formation of the carbazole derivative according to the Shine's postulation. A recombination of two radicals through a pyrazine-type transition state II is also possible. The reaction proceeds to an intermediate, in which the cyclic conjugation of only one annulated phenyl ring has been removed, and which corresponds to a semidine end product. Such semidines have been isolated with good yields from the reactions of such radicals (generated through oxidation of the corresponding amines).

The thermal rearrangement of dinaphthyl hydrazines is an intramolecular reaction that does not yield semidine. If aminyl radicals are formed during this reaction, they don't recombine through transition state II, an exclusion, which confirms the hypothesis that such reactions should proceed through a radical mechanism. The cleavage of
the N–N bond is followed (or accompanied) by a recombination through transition state I. The end-products formed after one or two hydrogen shifts are either 1,1′-dinaphthyl, 2,2′-diamine (exp. yield 80–90%)⁷ or the carbazole derivative (exp. yield 10–20%)⁷. Confirming our previous conclusions, the thermal rearrangement of 1,1′-dinaphthyl hydrazine yield the products; a) 4,4′-diamine-dinaphthyl, b) 1,1′-diamine dinaphthyl or c) carbazole, all of which could be formed through \((4n + 2)\) aromatic transition states.

\[\text{\text{Calculated Spin Densities for the Diphenyl Aminyl Radical}}\]

\(\pi\)-SCF-MO calculations with variable \(\beta\) and applying the half electron approximation gave good spin densities for the benzyl radical¹¹. The \(\pi\)-SCF-MO calculations, which are discussed above, were carried out using a similar SCF-technique¹⁰ and applying the 1/2 electron method for the treatment of radicals too. The calculated spin densities are in good agreement with the experimental spin densities, which were obtained through the application of the McConnell relationship¹³;

\[a^H = -23.7 \ \sigma_C, \quad a^N = 28.6 \ \sigma_N.\]

According to the same calculations the phenyl rings exhibit a slight bond alternation. Table 3 gives the calculated bond distances and spin densities for the completely planar radical.

Table 3. Calculated spin densities and bondlengths for the coplanar diphenyl aminyl radical using the 1/2 electron method.

| Atom | \(\sigma_{\text{calculated}}\) | \(\sigma_{\text{experimental}}\) | Bond- | Bond- |
|------|-------------------------------|-------------------------------| length (Å) | length (Å) |
| N    | .34                           | .31                           | 1.355    |       |
| C₁   | .017                          | .00                           | 1.419    |       |
| C₆,6 | .101                          | .156                          | 1.388    |       |
| C₇,₇ | .00                           | .063                          | 1.401    |       |
| C₄   | .110                          | .183                          |          |       |

* Present address.

⁴ Lecture held on the Chemie Dozenten Tagung, Heidelberg 1972.