# MO Calculation of Some Aromatic Radicals. Geometry and Spin Density of Benzyl Radical

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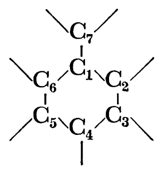
The geometry of benzyl radical, nitrobenzene anion-, benzaldehyde anion-, aniline cation-, and phenol cation-radicals is optimized by means of the energy gradient method in the framework of the CNDO/2 method, and used for the calculation of spin densities by the INDO-UHF method. The geometrical change from a neutral molecule to the ion radical can be understood by considering the shape of particular MO's. It was found that the molecular structure of benzyl radical is not a regular hexagon, the contraction of $C_1$–$C_7$ bond being remarkable. The correct order of the spin densities on ortho($\rho_2$)- and para ($\rho_4$)-positions is obtained by the full geometry optimization. The structure of the deformed ring of benzyl radical is discussed in terms of the orbital mixing rule.

It is difficult to determine the molecular structures of radicals experimentally in most cases, because of their low stability and high reactivity. Thus, it is significant to predict the structure of unstable radicals by means of a quantum chemical method. The spin densities are determined accurately. The spin density distribution in a $\pi$ radical depends considerably on its geometry.[1] Theoretical studies have been made on the spin density of benzyl radical.[2–7] However, the calculated results have not been correlated with the experimental data[8,9] ($\rho_4$ being greater than $\rho_2$) except for a few cases.[10,11] Beveridge and Guth[1] reported that the geometrical change of benzyl radical affects its spin density. Physico-chemical properties of molecules should be calculated on the basis of the most stable structure. Theoretical consideration of the geometrical distortion of benzyl radical from the regular hexagonal geometry would be applicable to the examination of that of other radical species.

In the cases of ion radicals, the structural change by electron removal from or electron attachment to neutral molecule can be explained readily in terms of the shape of the highest occupied or the lowest unoccupied MO's. However, it is difficult to expect a stable molecular structure for a neutral radical. This report describes the semi-empirical MO calculation for benzyl radical, nitrobenzene anion-, benzaldehyde anion-, aniline cation-, and phenol cation-radicals. The geometry is optimized by the energy gradient method in the framework of CNDO scheme.[12–16] Spin desities are calculated by means of the INDO-UHF method.[17]

## Results and Discussion

*Geometries and Spin Densities.* The optimized geometry of benzyl radical is given in Table 1. The numbering of atoms is as follows.



The geometry of benzyl ring differs a great deal from that of benzene. The calculated and experimental spin densities of benzyl radical are given in Table 2. The experimental spin density of ortho-carbon, $\rho_2$, is less than that of para-carbon, $\rho_4$. However, the calculation by means of regular hexagonal geometry shows that $\rho_2$ is greater than $\rho_4$. This problem is solved by calculation with use of optimized geometry. The calculated spin density by means of fully optimized geometry is in good accordance with the experimental data. Calculation with the optimized geometry shows that the spin density of $C_7$ flows somewhat into the ortho-, and para-carbons in comparison with the calculated value by means of the regular hexagonal geometry.

TABLE 1. OPTIMIZED GEOMETRY OF BENZYL RADICAL

| Bond length/Å | | Bond angle/° | |
|---|---|---|---|
| $C_1$–$C_2$, $C_1$–$C_6$ | 1.424 | $\angle C_2C_1C_6$ | 115.8 |
| $C_2$–$C_3$, $C_5$–$C_6$ | 1.371 | $\angle C_1C_2C_3$, $\angle C_1C_6C_5$ | 122.1 |
| $C_3$–$C_4$, $C_4$–$C_5$ | 1.392 | $\angle C_2C_3C_4$, $\angle C_4C_5C_6$ | 120.0 |
| $C_1$–$C_7$ | 1.365 | $\angle C_3C_4C_5$ | 120.0 |
| $C_2$–H, $C_6$–H | 1.118 | $\angle C_1C_2H$, $\angle C_1C_6H$ | 118.0 |
| $C_3$–H, $C_5$–H | 1.117 | $\angle C_2C_3H$, $\angle C_6H_5H$ | 120.0 |
| $C_4$–H | 1.117 | $\angle C_3C_4H$ | 120.0 |
| $C_7$–H | 1.112 | $\angle C_1C_7H$ | 124.0 |
| | | $\angle HC_7H$ | 112.0 |

Since the geometry of ion radicals is not well established experimentally, it is of interest to determine the geometrical changes from their neutral molecules and

TABLE 2. SPIN DENSITIES OF BENZYL RADICAL

| | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_7$ |
|---|---|---|---|---|---|
| With standard geometry[a)] | −0.171 | 0.247 | −0.148 | 0.230 | 0.740 |
| With optimized geometry | −0.188 | 0.275 | −0.156 | 0.283 | 0.667 |
| Expt[b)] | | 0.189 | −0.059 | 0.230 | 0.607 |

a) Calculated by assuming a regular geometry: $l_{C-C}=1.40$ Å, $l_{C-H}=1.08$ Å. b) Ref. 9.

Table 3. Spin densities of the anion radicals of nitrobenzene and benzaldehyde

| Anion radical of nitrobenzene | $C_1$ | $C_2$ | $C_3$ | $C_4$ | N | O |
|---|---|---|---|---|---|---|
| With standard geometry[a] | −0.034 | 0.175 | −0.101 | 0.226 | 0.219 | 0.187 |
| With optimized geometry | −0.018 | 0.151 | −0.088 | 0.197 | 0.287 | 0.204 |
| Expt | | 0.122[b] | −0.041[b] | 0.148[b] | 0.359[c] | 0.326[c] |
| **Anion radical of benzaldehyde** | $C_1$ | $C_2$<br>$C_6$ | $C_3$<br>$C_5$ | $C_4$ | $C_7$ | O |
| With standard geometry[a] | 0.088 | 0.168<br>0.167 | −0.092<br>−0.093 | 0.257 | 0.016 | 0.441 |
| With optimized geometry | 0.068 | 0.158<br>0.168 | −0.086<br>−0.091 | 0.255 | 0.042 | 0.497 |

a) The spin densities of two anion radicals are calculated with use of the standard bond lengths and bond angles obtained by Pople *et al.* b) Ref. 18. c) Ref. 19.

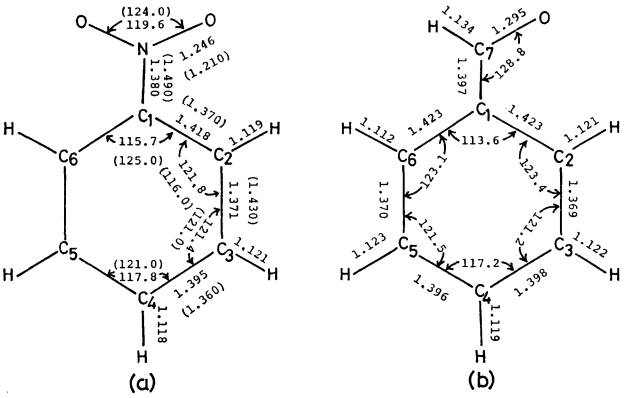


Fig. 1. The optimized geometries of the anion radicals of (a) nitrobenzene and (b) benzaldehyde. The bond lengths and bond angles are in the unit of Å and degree. The experimental values of neutral molecule, nitrobenzene, are also shown in parentheses.[21]

their spin densities theoretically. Figure 1 and Table 3 show the geometry and spin densities of anion radicals of nitrobenzene, and benzaldehyde. The experimental value[18,19] of spin densities of nitrobenzene anion radical is also given in Table 3. By a comparison of these values we see that the spin density calculated by means of optimized geometry is better than that by means of neutral geometry. Since the stabilization owing to the conjugation is maximum in a neutral molecule, the radical center of anion radical tends to localize on the substituent in order to minimize the destabilization due to an extra electron. The calculated results of cation radicals of aniline and phenol are summarized in Fig. 2 and Table 4. In the cation radical its geometrical distortion from that of neutral molecule is small. The spin densities of these cation radicals increase at the ortho- and para-positions.

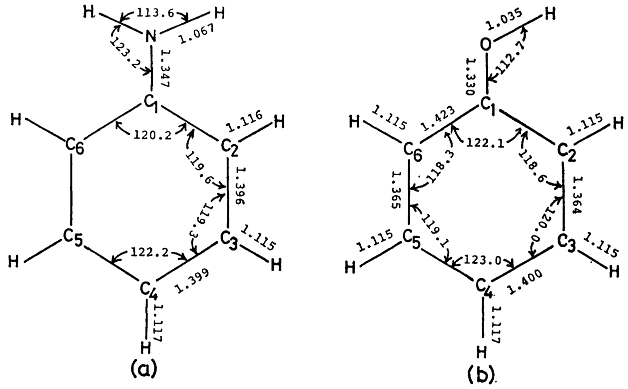


Fig. 2. The optimized geometries of the cation radicals of (a) aniline and (b) phenol. The bond lengths and bond angles are in the unit of Å and dergee.

Table 4. Spin densities of the cation radicals of aniline and phenol

| Cation radical of aniline | $C_1$ | $C_2$ | $C_3$ | $C_4$ | N |
|---|---|---|---|---|---|
| With standard geometry[a] | −0.032 | 0.185 | −0.104 | 0.229 | 0.642 |
| With optimized geometry | −0.021 | 0.195 | −0.105 | 0.279 | 0.562 |
| **Cation radical of phenol** | $C_1$ | $C_2$<br>$C_6$ | $C_3$<br>$C_5$ | $C_4$ | O |
| With standard geometry[b] | 0.048 | 0.162<br>0.172 | −0.083<br>−0.092 | 0.257 | 0.537 |
| With optimized geometry | 0.082 | 0.159<br>0.169 | −0.076<br>−0.087 | 0.307 | 0.440 |
| Expt[c] | | 0.196<br>0.196 | −0.030<br>−0.030 | 0.396 | |

a), b) The spin densities of two cation radicals are calculated with use of the standard bond lengths and bond angles obtained by Pople *et al.* c) Ref. 21.

*Consideration of Geometrical Change.* Since the highest occupied and the lowest unoccupied MO's are responsible for the electron donation and the electron acceptance of the neutral molecule, respectively, the geometrical change in the ion radical may be predicted by consideration of the shape of these particular orbitals. Figure 3 shows the orbitals of neutral molecules. For example, LUMO of nitrobenzene has the bonding character at $C_1$–N, O–O, and $C_2$–$C_3$. The distances between these atoms decrease on accepting an electron. On the other hand, the distances associated with $C_1$–$C_2$ $C_3$–$C_4$ bonds increase.

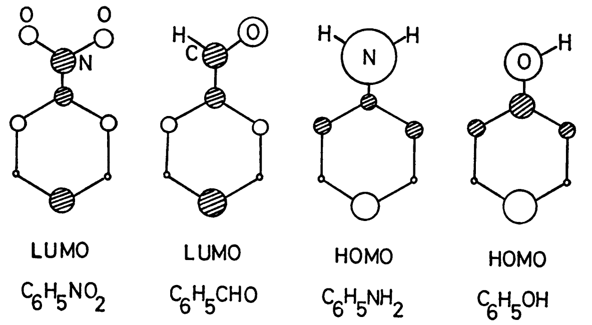
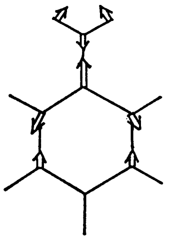


Fig. 3. The shapes of the particular orbitals of nitrobenzene, benzaldehyde, aniline, and phenol.

In cation radical, the distances between atoms being in-phase overlap increase and those in out-of-phase overlap decrease because of a loss of an electron in HOMO. However, the geometrical change is not so remarkable as that in the anion radical.

Let us explain the bond lengths of benzyl radical being neutral in view of the orbital mixing[20)] of phenyl ring with $CH_2$ part. The distortion from one and half bond is visualized as follows.



The π type orbital of benzene and $CH_2$ part and the mode of orbital interaction are shown in Fig. 4. The $p_\pi$ orbital of $C_7$ mixes with the symmetric orbitals about the molecular axis of benzene, $\pi_1$, $\pi_3$, $\pi_5$, and $\pi_6$. Since the energy of p orbital of carbon is located in the middle of those of the HOMO and LUMO of benzene, the singly occupied MO is formed by the following orbital phase combination.

$$\mathrm{SOMO} = p_\pi - \pi_3 + \pi_5.$$

Thus, the amplitude of $C_1$ atom is very small since $\pi_3$ is combined with $\pi_5$ out-of-phase with equal weight, whereas the in-phase orbital, $\phi_2$, formed by $\pi_3$ and $p_\pi$ of $C_7$ contains the large bonding overlap at $C_1$–$C_7$ bond. This is the origin of the shortening of $C_1$–$C_7$ bond length. Since the out-of-phase orbital SOMO formed by $\pi_3$ and $\pi_5$ has the large bonding overlap between $C_2$ and $C_6$, angle $C_2$–$C_1$–$C_6$ becomes smaller. The shortening of $C_2$–$C_3$ bond length and the lengthening of $C_1$–$C_2$ bond length are caused by the decrease in the antibonding overlap at $C_2$–$C_3$ and the decrease in the bonding overlap at $C_1$–$C_2$, respectively. The same consideration can be applied to the expectation of geometrical changes in phenol- and aniline-cations.

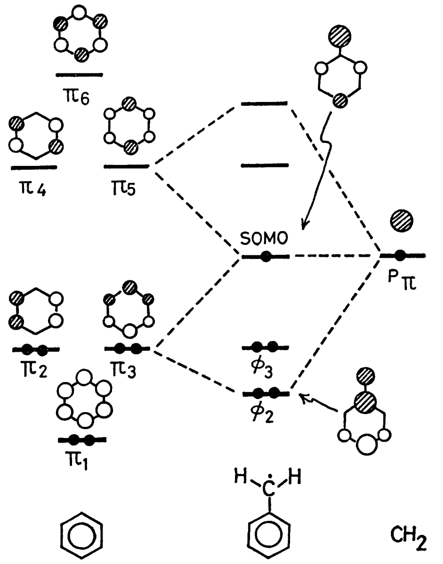


Fig. 4. The mode of the orbital interaction of benzyl radical.

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