# An INDO-UHF Molecular Orbital Study of the Conformations and Electronic Structures of Some $\sigma$-Type Radicals

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(Received October 4, 1976)

The equilibrium geometric parameters determined for XC=Y radicals (HC=O, $CH_3C$=O, $NH_2C$=O, and HC=$CH_2$) are not characterized by their bond lengths but by their X–C–Y angles, which are wide compared with the angles in their parent molecules (XHC=Y). The %s character of the $\sigma$ orbitals on the C atom in XHC=Y was found to be conserved in the %s character and the s-orbital spin density of the same atom in XC=Y radicals: there are linear relationships between them. Some notable features of the unpaired-electron distribution on the frameworks of XC=Y radicals are also discussed in connection with the electronic properties of the $\sigma$ radicals.

The conformations and electronic structures of paramagnetic species containing an odd electron in their $\sigma$ orbitals (*e.g.*, $\sigma$-type radicals such as vinyl, formyl, and phenyl) have been the object of only limited experimental and MO-theoretical investigations. Concerning the conformations of the $\sigma$ radicals, the equilibrium geometric parameters have hitherto been given only for simple $\sigma$ radicals such as HC=O,[1] even though, in connection with the electronic structures of the $\sigma$ radicals, the nuclear hyperfine constants of several $\sigma$ radicals ($C_6H_5$, $CH_2$=CX, or XC=O, where X=H, $CH_3$, $OCH_3$, *etc.*) have already been obtained by ESR observations.[2]

On the other hand, the distribution of unpaired electrons on the frameworks of $\sigma$ radicals such as vinyl, formyl, and phenyl has been discussed on the basis of their electronic structures obtained by the EHMO,[3] CNDO,[4] or INDO[5] computations with assumed bond lengths and angles; but the first two methods are not capable of giving a proper account of the contribution of spin polarization to the unpaired electron density because they neglect interelectron repulsions (in the EHMO) or about atomic exchange integrals (in the CNDO).

In the present paper, using the semiempirical INDO method,[6] the conformations of some $\sigma$ radicals of XC=Y (HC=O, $CH_3C$=O, $NH_2C$=O, and HC=$CH_2$) are characterized by comparing them with those of the parent molecules of XHC=Y; the unpaired electron distributions are also discussed in connection with their conformations and electronic properties.

## Method of Calculation

The integrations and parametrizations involved in the INDO method, which is relatively reliable for bond angles but less so for bond lengths,[6,7] have been described in detail in Ref. 6, so they will not be repeated here. In the INDO-UHF computations the annihilation procedure was not carried out, because the annihilation has little effect on the electron density distribution[8] and because, in the conventional evaluation of the hyperfine splitting constants ($a_N$), the best fitting proportionality constants to the experimental $a_N$ values have been determined on the basis of the computed spin densities without the annihilation.[5]

The geometric parameters of XC=Y radicals (HC=O, $CH_3C$=O, $NH_2C$=O, and HC=$CH_2$) shown in Fig. 1 were first determined by changing them in turn so as to minimize the total energy until they become identical; then, the optimized conformations of the XC=Y radicals were recalculated by changing all their geometric parameters in the magnitude of $\pm$0.01 Å and $\pm$1° as a check on the reliability of the optimization results. In the above optimizations, some assumed bond lengths ($r_{NH}$=1.0 Å in $NH_2C$=O and $r_{CH}$=1.08 Å in $CH_3C$=O) and angles ($\angle$CNH=120° in $NH_2C$=O and $\angle$HCH=109.5° in $CH_3C$=O) were used to shorten the computation time.

## Results and Discussion

*Optimized Conformations.* The computed equilibrium geometric parameters of the XC=Y radicals (HC=O, $CH_3C$=O, $NH_2C$=O, and HC=$CH_2$) are summarized in Table 1, together with those (obtained by the INDO calculations) of the parent molecules of XHC=Y (HCHO, $CH_3CHO$, $NH_2CHO$, and $H_2C$=$CH_2$). The difference in the bond lengths between XC=Y and XHC=Y was very small (within 0.04 Å) in their respective frameworks, but the computed bond angles ($\theta$) of the former were too large (by 7.42—37.4°) as compared with those of the latter. The optimized bond angle ($\theta$) of XC=Y seems to be overestimated. The experimental $\theta$ value, for example, for HC=O ($\theta$=119.5°[1]) is too small as compared with the calculated one ($\theta$=131°), even though some overestimations of the bond angle ($\theta$) of XHC=Y have been seen, ranging from 2.1° in $NH_2CHO$ (exptl=121.5°[9]) to 3° in

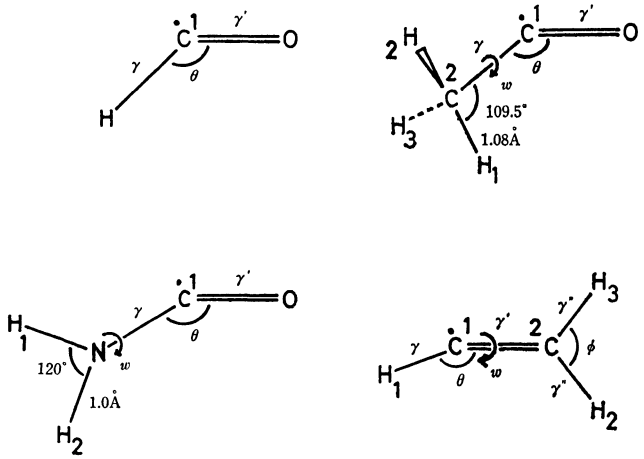


Fig. 1. Geometric parameters for the conformational optimization.

Table 1. Optimized geometric parameters for the XC=Y radicals

| XC=Y | $\gamma$/Å | $\gamma'$/Å | $\theta$/deg | $\omega$/deg | $\gamma''$/Å | $\phi$/deg |
|---|---|---|---|---|---|---|
| HC=O | 1.12 | 1.23 | 131 | | | |
| | (1.12) | (1.25) | (115) | | | |
| $CH_3C$=O | 1.44 | 1.23 | 142 | 0 | | |
| | (1.44) | (1.26) | (124) | (0) | | |
| $NH_2C$=O | 1.35 | 1.26 | 131 | 0 | | |
| | (1.343) | (1.243) | (123.6) | (0) | | |
| $HC$=$CH_2$ | 1.10 | 1.27 | 161.7 | 0 | 1.12 | 107.4 |
| | (1.11) | (1.31) | (124.3) | (0) | (1.11) | (111.4) |

Values in parentheses are those for the parent XHC=Y molecules, and the underlined values are the ones fixed (taken from Ref. 9) for the calculations.

$CH_3CHO$ (exptl=121°[9]) and $H_2C$=$CH_2$ (exptl=121.3°[10]). At any rate, the INDO computations tend to give overestimated bond angles ($\theta$) for the XC=Y radicals, because the widening of the bond angle ($\theta$) unilaterally decreases the electron and nuclear repulsions. For example, the widening of the bond angle in HC=O from $\theta$=115° (corresponding to that in HCHO) to 131° (corresponding to that in HC=O) monotonously decreased the electron and nuclear repulsions ($E_{II}$ and $E_N$ respectively) from 28.827 to 28.724 a. u. in $E_{II}$ and from 13.816 to 13.700 a. u. in $E_N$, with a monotonous decrease in the one-electron attraction ($E_I$) from −67.441 to −67.229 a. u. The balance in the repulsions and the attraction energies, therefore, gave the rather large bond angle ($\theta$=131°) for HC=O. In this sense, it can be said that the underestimation of the electron repulsions, which is the usual trend of the INDO calculations,[5,11] gave bond angles ($\theta$) to the XC=Y radicals which were too large.

Next we discuss the change in the energetical stability of the XC=Y radicals by the internal rotation of the X or Y group around the C–C bond in $CH_3C$=O or $HC$=$CH_2$ and around the C–N bond in $NH_2C$=O. The rotation angle ($\omega$) for the energetically most stable and unstable conformations are given in Fig. 2, together with the rotation barriers. In the most stable or unstable conformations of XHC=Y and XC=Y, the rotation angles ($\omega$) were just the same between the respective parent molecules and the $\sigma$ radicals, but the rotation barriers of the XC=Y radicals were rather low in comparison with those of the XHC=Y molecules (0.345 kcal/mol for $CH_3CHO$, 23.11 kcal/mol for $NH_2CHO$, and 105.22 kcal/mol for $H_2C$=$CH_2$). The INDO computations without polycenter interelectron repulsions usually result in low rotation barriers (for instance, the calculated barrier (0.345 kcal/mol) for $CH_3CHO$ was too low as compared with the experimental value of 1.16 kcal/mol[13]), but the number (105.22 kcal/mol) for $H_2C$=$CH_2$ ($r_{CC}$=1.31 Å at $\omega$=0° was stretched to $r_{CC}$=1.38 Å in the triplet state conformation at $\omega$=90°) was computed to be too high in comparison with the experimental number of 65.0 kcal/mol.[12] The overestimated rotation barrier for $H_2C$=$CH_2$ is probably due to the incomplete optimization of its geometric parameters, such as $r_{CH}$ and ∠CCH, at $\omega$=90°. The decrease in the $E_I$ term by the rotation

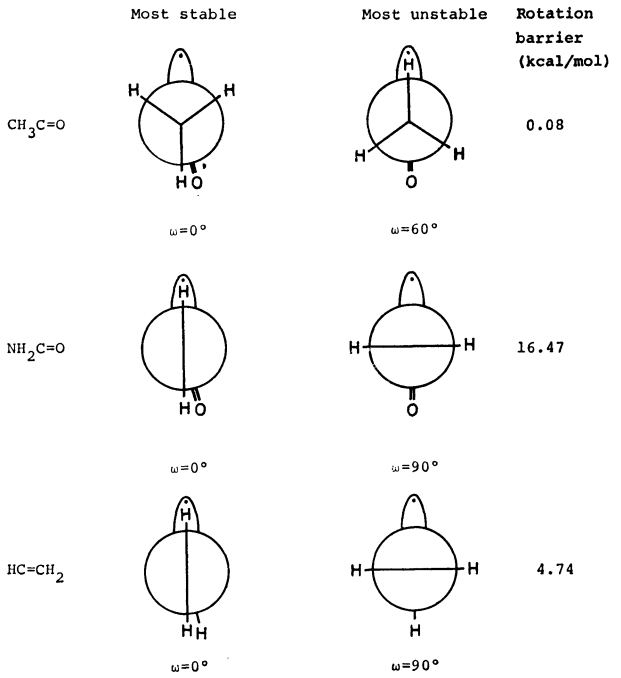


Fig. 2. The most stable and unstable conformers of $CH_3C$=O, $NH_2C$=O, and $HC$=$CH_2$.

from $\omega$=0° to $\omega$=90° (or $\omega$=60° in $CH_3C$=O and $CH_3CHO$) made both species (XC=Y and XHC=Y) more unstable, and this seems to be directly related to the decrease in the contribution of the $\pi$ conjugation (including the pseudo one in $CH_3C$=O or $CH_3$-CHO) between the C–C or C–N bond to the stabilization of XC=Y or XHC=Y (see Table 2).

*Electron Distribution and Spin Density.* The polarization (charge distribution) in the XC=Y radicals was not so markedly different from that in the XHC=Y molecules, as seen from the computed atomic charge densities and dipole moments of XC=Y and XHC=Y in Table 3, but one slight difference is that XC=Y have a less positively charged $C^1$ atom and a less negatively charged O, C, or N atoms attached to the $C^1$, in comparison with XHC=Y. This was mainly caused by the electron shift from the neighboring atoms to the $C^1$ through the $\pi$-bonding orbitals during the widening of the bond angle ($\theta$) in the XC=Y radicals. The hybridizations ($sp^n$) of the $\sigma$ orbitals on the $C^1$ atom, $n$=1.35 (HC=O) —1.75 ($HC$=$CH_2$)

Table 2. Energy contribution terms and overlap populations for the most stable and unstable conformers of the XC=Y radicals

| XC=Y | Conformer | $E_I$/a.u. | $E_{II}$/a.u. | $E_N$/a.u. | Total/a.u. | Overlap population of $\pi$ conjugation | |
|---|---|---|---|---|---|---|---|
| | | | | | | C-C(or C-N) | C=O |
| $CH_3C=O$ | a | −119.781 | 52.270 | 34.228 | $-33.282_5$ | 0.0632 | 0.1866 |
| | | (−130.451) | (57.100) | (39.156) | ($-34.195_4$) | (0.0641) | (0.1851) |
| | b | −119.774 | 52.265 | 34.226 | $-33.282_4$ | 0.0634 | 0.1863 |
| | | (−130.440) | (57.094) | (39.151) | ($-34.194_9$) | (0.0642) | (0.1850) |
| $NH_2C=O$ | a | −127.473 | 56.225 | 34.439 | −36.809 | 0.1204 | 0.1462 |
| | | (−139.746) | (61.780) | (40.247) | (−37.719) | (0.1081) | (0.1706) |
| | b | −127.430 | 56.237 | 34.410 | −36.783 | 0.0571 | 0.1779 |
| | | (−139.558) | (61.683) | (40.194) | (−37.681) | (0.0578) | (0.1899) |
| $HC=CH_2$ | a | −53.617 | 22.122 | 15.891 | −15.604 | 0.3018 | |
| | | (−61.445) | (25.507) | (19.370) | (−16.568) | (0.2835) | |
| | b | −53.612 | 22.125 | 15.891 | −15.596 | 0.2770 | |
| | | (−60.446) | (25.145) | (18.901) | (−16.400) | (0.0978) | |

Values in parentheses are those for the parent XHC=Y molecules.

Table 3. Charge and spin distributions and physicochemical constants for the XC=Y radicals

| HC=Y | Atom | Charge density | Dipole moment (D) | $\rho_s$ | $\rho_p$ | Total | $a_N$(G) | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | calcd | obsd |
| HC=O | $C^1$ | 3.846(3.789) | 1.49(2.10) | 0.1726 | 0.3932 | 0.5658 | 141.58 | 134.5 |
| | O | 6.152(6.188) | | 0.0051 | 0.2742 | 0.2793 | 4.54 | |
| | H | 1.002(1.011) | | 0.1549 | | 0.1549 | 83.63 | 136.5 |
| $HC=CH_2$ | $C^1$ | 4.085(4.003) | 0.33(0.0) | 0.0661 | 0.8171 | 0.8832 | 54.24 | 107.57 |
| | $C^2$ | 3.965(4.003) | | −0.0368 | −0.2059 | −0.2427 | −30.15 | −8.55 |
| | $H^1$ | 0.948(0.999) | | −0.0281 | | −0.0281 | −15.16 | 13.39 |
| | $H^2$ | 1.007(0.999) | | 0.2245 | | 0.2245 | 121.20 | 65.0 |
| | $H^3$ | 0.995(0.999) | | 0.1630 | | 0.1630 | 87.99 | 37.0 |
| $CH_3C=O$ | $C^1$ | 3.861(3.674) | 2.59(2.86) | 0.1276 | 0.4918 | 0.6194 | 104.67 | |
| | $C^2$ | 3.973(4.011) | | 0.0080 | 0.0007 | 0.0087 | 6.56 | 5.3 |
| | O | 6.210(6.286) | | 0.0062 | 0.2747 | 0.2809 | 5.48 | |
| | $H^1$ | 1.002(0.995) | | 0.0796 | | 0.0796 | 42.99 | |
| | $H^2$ | 0.977(0.985) | | 0.0057 | | 0.0057 | 3.05 | |
| | $H^3$ | 0.977(0.985) | | 0.0057 | | 0.0057 | 3.05 | |
| $NH_2C=O$ | $C^1$ | 3.809(3.550) | 3.71(3.90) | 0.1647 | 0.3034 | 0.4681 | 135.06 | |
| | N | 5.163(5.236) | | 0.0308 | 0.0151 | 0.0459 | 11.67 | 21.6 |
| | O | 6.270(6.384) | | 0.0058 | 0.4124 | 0.4182 | 5.18 | |
| | $H^1$ | 0.876(0.876) | | −0.0026 | | −0.0026 | −1.40 | 1.15 |
| | $H^2$ | 0.882(0.871) | | 0.0704 | | 0.0704 | 38.01 | 30.45 |

Values in parentheses are those for the XHC=Y molecules.

in XC=Y and $n$=1.62 (HCHO) —1.80 ($H_2C=CH_2$) in XHC=Y, were also almost the same magnitude in the radicals and the parent molecules. Strictly speaking the order of the %s character of the $C^1$ $\sigma$-orbitals in XC=Y, HC=O(42.50%) > $NH_2C=O$(41.43%) > $CH_3C=O$(38.69%)>$HC=CH_2$(37.62%), was well reflected in that in XHC=Y, HCHO(38.10%)> $NH_2CHO$(37.50%) > $CH_3CHO$(36.76%) > $H_2C=CH_2$ (35.69%), and there is a completely linear correlation between the above %s characters of XC=Y and XHC=Y (Fig. 3). Thus, the %s chracter of the $\sigma$-orbitals on the $C^1$ atom in XHC=Y was conserved in the same $C^1$ atom of XC=Y, and this is in harmony with the fact that the %s character of the C atom in XYZCH molecules (X, Y, or Z=substituent) is conserved in the same atom of XYZC radicals.[14]

In regard to the spin distribution in the XC=Y radicals, the total spin densities (Table 3) chiefly spread over the $C^1$ atom (46.6% in $NH_2C=O$ —61.9% in $CH_3C=O$) and the $C^1$-bound oxygen or carbon ($C^2$) atom (15.7% in $HC=CH_2$ —41.6% in $NH_2C=O$). Such a spin distribution was predominantly recognized on the p orbitals (especially, on the p orbital conjugating with the $C^1$ unpaired-electron orbital) of the O or $C^2$ atom or of the $C^1$ atom *per se*, and the spin densities on the $C^1$ p-orbitals, $\rho_p$, follow the order of $HC=CH_2$ >$CH_3C=O$>HC=O>$NH_2C=O$. The above order is just the same as that in the bond order of the

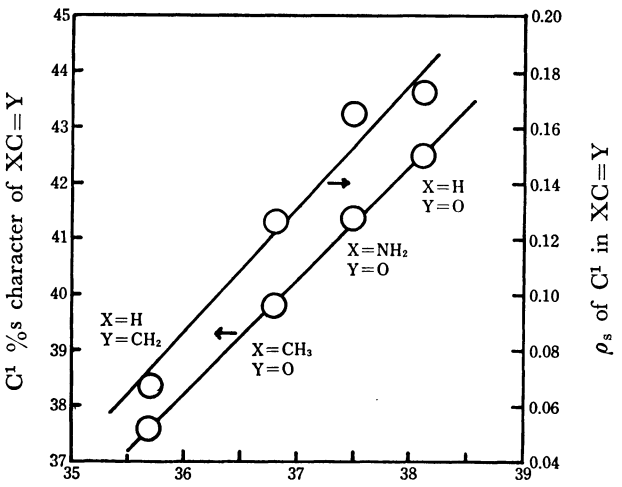


Fig. 3. Linear relationship of the $C^1$ %s character of XHC=Y with the $C^1$ %s character of XC=Y and with the $\rho_s$ of $C^1$ in XC=Y.

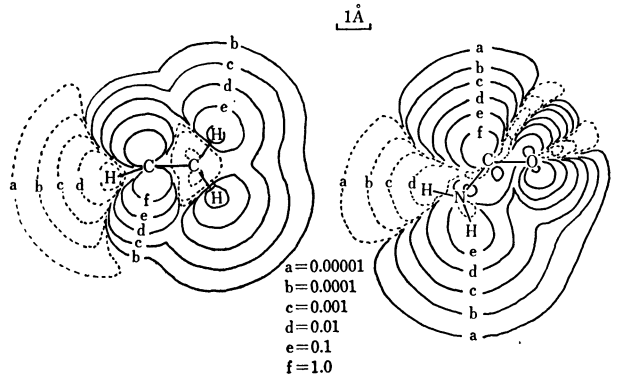


Fig. 4. Spin density contour maps for $HC{=}CH_2$ and $NH_2C{=}O$.

pseudo $\pi$-orbital between the $C^1$ and O (or $C^2$) p-orbitals; that is, $HC{=}CH_2(0.472) > CH_3C{=}O(0.375) > HC{=}O(0.359) > NH_2C{=}O(0.352)$, where the values in parentheses are the bond orders. This suggests that the direct spin polarization from the $C^1$ atom to the neighboring one through the $\pi$-type bonding decreases with increasing the bond order. In this respect, the internal rotation increasing the bond order of the pseudo $\pi$-conjugation in the $C^1$–$C^2$ ($HC{=}CH_2$) or $C^1$–N ($NH_2C{=}O$) bond resulted in the increase of the spin density of the $C^1$ atom (especially, that on the $C^1$ p-orbital).

On the other hand, the spin density of the $C^1$ s-orbital, $\rho_s$, was directly related to the hybridization on the $C^1$ $\sigma$-orbitals. Specifically, the $\rho_s$ values show a linear dipendence on the %s character of the $C^1$ $\sigma$-orbitals (Fig. 3) and follow the order of $HC{=}O > NH_2C{=}O > CH_3C{=}O > HC{=}CH_2$. This is also in harmony with the fact that the hyperfine splitting constant, $a_N$, (reflecting the $\rho_s$ value) of the carbon atom in the XYZC radical correlates linearly with the $J_{C^{13}H}$ coupling constant (reflecting the %s character of the $C^{13}$ atom) of the XYZCH molecule.[14]

It should be noted that the computed spin density of the hydrogen *trans* to the site of the unpaired-electron orbital on the $C^1$ atom in $HC{=}CH_2$, $CH_3C{=}O$, or $NH_2C{=}O$ was considerably larger than that of the hydrogen *cis* to the above orbital. This trend was also seen in the ESR observations: the $a_N$ value of the *trans* hydrogen in $HC{=}CH_2$, $NH_2C{=}O$, or $H_2C{=}CCH_3$ (*trans* H=(+) 57.89 G[15] and *cis* H=(+)32.92 G[15]) is larger than that of the *cis* hydrogen. In view of the fact that the internal rotation from $\omega=0°$ to $\omega=90°$ monotonously decreased the spin density of the *trans* hydrogen in $HC{=}CH_2$ or $NH_2C{=}O$, with equivalent spin densities for $H^2$ and $H^3$ in $HC{=}CH^2H^3$ or for $H^1$ and $H^2$ in $NH^1H^2C{=}O$ at $\omega=90°$, the predominant interaction of the $C^1$ unpaired-electron orbital with the *trans* H s-orbital rather than with the *cis* H s-orbital presumably caused the spin polarization to be stronger for the *trans* H atom. Such circumstances of the spin polarization (or of the spin delocalization) may also be understandable from the contour map of the spin distribution in $HC{=}CH_2$ or $NH_2C{=}O$ (Fig. 4).

Finally, we will briefly point out the hyperfine splitting constants, $a_N$, of the present XC=Y radicals (Table 3). The $a_N$ values computed with the best proportionality constants[5] did not show satisfactorily good coincidence with the observed $a_N$ values, and those for $^1H$, $^{13}C$, $^{14}N$, and $^{17}O$ had almost the same accuracy of agreement with the observed ones. Here, no characteristic feature of the calculated $a_N$ values for the present XC=Y radicals was recognized in terms of a coincidence between the INDO computation results and the ESR observations.

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