integral $(S_A(1)S_A(1)|S_B(2)S_B(2))$ and $\alpha$ is the difference between $\gamma_{AB}{}^{th}$ and the $\gamma_{AA}$ values tabulated in Table III. If A and B are different types of atoms, the arithmetic mean is used.

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# Electronic Structure of Small Organic Free Radicals[1a]

**James M. Howell*[1b] and Poul Jørgensen[1c]**

*Contribution from the Quantum Theory Project, University of Florida, Gainesville, Florida 32601.* *Received August 8, 1972*

**Abstract:** The effects of geometry change and substitution on the electronic structure of some small free radicals are examined using a modified INDO/CI formalism. The nature of the lowest excitation is found to change from being SOMO (singly occupied molecular orbital) → LUMO (lowest unoccupied molecular orbital), for a planar radical site, to HDOMO (highest doubly occupied molecular orbital) → SOMO, for a pyramidal radical site. The effects of $\pi$ donors and acceptors are evaluated and found to be comparable to the effect of geometry. Geometrical preferences are investigated for the model structures. Planar radical sites are preferred.

The electronic structure of small organic radicals has been a subject of continuing interest. While most of the work has been concerned with the calculation of spin properties,[2] there has been effort toward the calculation of ionization potentials[3] and geometry[2b,4] as well as electronic spectra.[5] In this paper we present some simple calculations on radicals, both charged and neutral, which may serve as model structures for large classes of organic radicals.

## Method

The molecular orbitals were calculated by the INDO[6] method. The INDO method has been frequently used to investigate free radicals.[7] The used parameterization was essentially the same as that developed by Jaffé and Del Bene for spectral CNDO investigations of planar systems.[8] However, because we wanted a method which would handle nonplanar structures we modified their approach to $\pi$ orbitals.

Jaffe and Del Bene[8] decreased the $\beta$ matrix elements between orbitals that were perpendicular to the molecular plane (the $\pi$ orbitals) by a factor $K$

$$\beta^{\pi}{}_{ij} = (\beta^0{}_i + \beta^0{}_j)K(S_{ij}/2) \tag{1}$$

Instead, we divide the overlap, $S_{ij}$, between each pair of atomic orbitals into a $\sigma$ ($S^{\sigma}{}_{ij}$) component and a $\pi$ component ($S^{\pi}{}_{ij}$) within a local framework determined by the internuclear axis. The $\pi$ part is then decremented (eq 2) and the $\beta$ matrix element calculated on the basis of the adjusted overlap $S'_{ij}$ (eq 3).

$$S_{ij} = S^{\sigma}{}_{ij} + S^{\pi}{}_{ij}$$

$$S'_{ij} = S^{\sigma}{}_{ij} + KS^{\pi}{}_{ij} \tag{2}$$

$$\beta_{ij} = (\beta^0{}_i + \beta^0{}_j)(S'_{ij}/2) \tag{3}$$

A value of 0.65 for $K$ was found to yield good spectral energies for a variety of closed shell systems and was used in our calculations. The grand canonical Hartree–Fock approximation[9,10] was employed for the calculation of the molecular orbitals and total energies for the radical species. In this method, the unpaired electron in spatial orbital $i$ is assumed, on the average, to be equally distributed between $i\alpha$, the spin up MO, and $i\beta$, the spin down MO, each thus having an occupancy of $^1/_2$ electron. Formally similar approaches have been used before for free radicals[10] and transition metals.[9] Additionally, Slater has used fractional occupation numbers in the Hyper–Hartree–Fock method.[11]

The CI calculation necessary to obtain the excitation spectrum was carried out in a fashion consistent with

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(1) (a) This work was supported in part by the Air Force Office of Scientific Research through Grant AFOSR-71-1714B, and in part by the National Science Foundation through Grant NSF-GP-16666; (b) author to whom correspondence should be addressed at Department of Chemistry, Vanderbilt University, Nashville, Tenn.; (c) Department of Chemistry, University of Aarhus, Aarhus, Denmark.

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**Table I.** Eigenvalues, Configurational Energies Relative to the Ground State, and Singly Excited CI Excitation Energies for the Ethylene System[a]

| | Cation | Neutral | Anion |
|---|---|---|---|
| Eigenvalues, eV | | | |
| LUMO | −5.68 | 2.07 | 11.37 |
| SOMO | −15.46 | | 6.02 |
| HDOMO | −21.42 | −11.51 | −3.76 |
| Configuration Energies, eV | | | |
| SOMO → LUMO | 5.98 | | 1.65 |
| HDOMO → SOMO | 2.23 | | 5.98 |
| HDOMO → LUMO | 8.54 | 8.12 | 8.40 |
| SECI Excitation Energy, eV | | | |
| $\epsilon_1$ | 2.20, HDOMO → SOMO | 7.68, HDOMO → LUMO | 1.64, SOMO → LUMO |

[a] Calculations were done using a modified INDO approximation described in the text. The geometry was the same in all cases and was assumed to be CC = 1.338; CH = 1.086; ∠CCH = 121.3°.

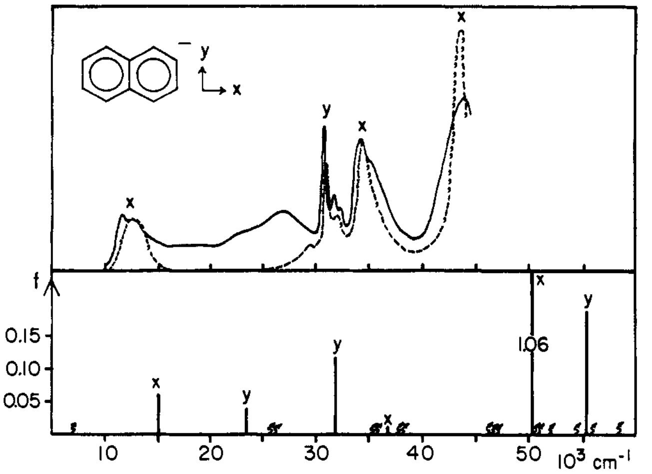


Figure 1. Comparison of the experimental and calculated excitation spectrum of the naphthalene anion. The experimental spectrum, drawn with a heavy line, is taken from ref 15a, while the spectrum drawn with a dashed line is from ref 15b. The experimental moment direction is taken from ref 15c. In the theoretical spectrum the ordinate indicates the calculated oscillator strength $f$ for the transitions. The wavy lines with arrows indicate forbidden transitions.

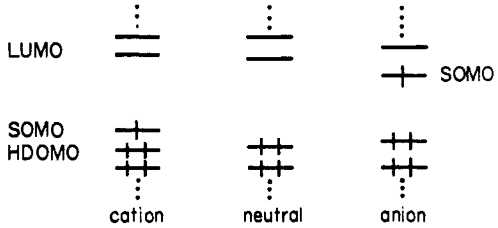
the grand canonical ground state. A detailed description of the grand canonical CI method together with applications on conjugated radicals is given in ref 10.

## Results and Discussion

Radicals may be formed from an electrically neutral closed shell molecule in several ways. We consider two. We can electrically charge the molecule resulting in either a radical anion or a radical cation. Alternatively, we may break a chemical bond within the molecule so that the resulting separated fragments have unpaired electrons.

In a preliminary fashion, let us consider radicals formed by charging a neutral species. The most common examples of this type are the conjugated anions and cations. In Table I we present some results for the ethylene system. "HDOMO" is the highest doubly occupied molecular orbital, "SOMO" refers to the singly occupied molecular orbital, and "LUMO" is the lowest unoccupied molecular orbital.

We see that the excitation of neutral ethylene is well represented. The experimental value for the $\pi \rightarrow \pi^*$ transition is 7.6 eV,[12] which compares well with our calculated lowest excitation energy, $\epsilon_1$, of 7.68 eV. Let us turn to the anion and cation. For the cation the lowest excitation is calculated to be HDOMO → SOMO while for the negative ion it is SOMO → LUMO. This is easily understood on the basis of a molecular orbital diagram.



It is clear that HDOMO → SOMO should be lowest for the cation and the SOMO → LUMO for negative species. This is a well-established theoretical result[13] and has been demonstrated computationally several times.[13,14]

Another test of our parameterization and method is provided by the naphthalene radical anion. Our calculated spectrum is compared with experiment[15] in Figure 1. Once again we note that the lowest (forbidden) excitation is SOMO →LUMO and the lowest allowed transition is SOMO → unoccupied molecular orbitals. We include this result primarily to establish a link with earlier work on $\pi$ systems.

Having seen how the nature of the excitation fundamentally depends on the charge of the ion let us now turn to radicals formed by bond scission. Here the geometry of the radical becomes important. In contrast to the aromatic ions which have a relatively rigid skeleton, the conformational potential of the alkyl radicals is soft. An illustration is given in Figure 2 where the potential curve for the movement of the methyl radical from planar, I, toward the pyramidal structure, II, is displayed using Pople's original INDO parameterization.[6] We predict a relatively flat potential for the motion toward a pyramidal structure but favor

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**Table II.** Eigenvalues, Configurational Energies Relative to the Ground State, and Singly Excited CI Excitation Energies for the Methyl Radical[a]

| | Planar, I | Pyramidal, II[b] |
|---|---|---|
| | Eigenvalues, eV | |
| LUMO | 4.36 | 5.28 |
| SOMO | −4.63 | −5.71 |
| HDOMO | −17.53 | −16.95 |
| | Configuration Energies, eV | |
| HDOMO → SOMO | 8.55 | 6.98 |
| HDOMO → LUMO | 15.67 | 15.60 |
| SOMO → LUMO | 4.88 | 6.88 |
| | SECI Excitation Energies, eV | |
| $\epsilon_1$ | 4.86, SOMO → LUMO | 6.86, SOMO → LUMO |
| $\epsilon_2$ | 7.91 | 6.90, HDOMO → SOMO |
| $\epsilon_3$ | 8.68, HDOMO → SOMO | 8.71 |

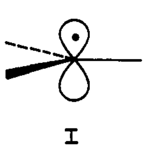
[a] An INDO type formalism described in the text was used. [b] HCH angle is 109.5°.

**Table III.** Eigenvalues, Configurational Energies, and Singly Excited CI Excitation Energies for the Ethyl Radical[a]

| | Planar | Pyramidal |
|---|---|---|
| | Eigenvalues, eV | |
| LUMO | 4.16 | 4.63 |
| SOMO | −4.05 | −5.09 |
| HDOMO | −14.72 | −14.27 |
| | Configurational Energies, eV | |
| SOMO → LUMO | 4.57 | 6.41 |
| HDOMO → SOMO | 7.10 | 5.60 |
| HDOMO → LUMO | 13.13 | 12.99 |
| | SECI Excitation Energies, eV | |
| $\epsilon_1$ | 4.53, SOMO → LUMO | 5.53, HDOMO → SOMO |
| $\epsilon_2$ | 5.92 | 6.03 |
| $\epsilon_3$ | 7.00, HDOMO → SOMO | 6.30, SOMO → LUMO |

[a] An INDO type formalism described in the text was used.

the planar structure, in agreement with previous calculations.[2b,4]



I

II

We will now concentrate on exploring the effect of geometry on the nature of the excited state. As perhaps the simplest case, let us examine the methyl radical.

As shown in Table II the lowest transition for planar methyl radical, I, is calculated to be SOMO → LUMO at 4.86 eV. Experimentally, the lowest transition for the methyl radical is at 5.3 eV.[16,17] The HDOMO → SOMO transition is substantially higher at 8.68 eV. When the radical is forced into the pyramidal configuration, II, the SOMO → LUMO process requires 6.86 eV, but the HDOMO → SOMO has fallen to 6.90 eV. The rationalization of this is simple. The SOMO drops in energy as the pyramidal structure is approached.

For the planar structure, SOMO is antisymmetric with respect to reflection in the molecular plane and therefore will not contain any C 2s component. However, for the pyramidal structure, the SOMO contains considerable C 2s character and is accordingly lower in energy. We also see substantial movement on the part of the HDOMO and LUMO. We must be careful since methyl radical by virtue of its simplicity can be deceptive. For a more highly substituted radical, the bands of doubly occupied and unoccupied orbitals are more stable to the planar ↔ pyramidal change. As will be shown below for a number of different types of radicals formed by bond scission, RH → R· + H·, keeping the R· fragment pyramidal, the HDOMO → SOMO transition is lowest. Geometry optimization "sacrifices" the singly occupied SOMO causing it to rise in energy while allowing the doubly occupied molecular orbitals to drop, yielding the lowest possible total energy. Another example is shown in Table III for

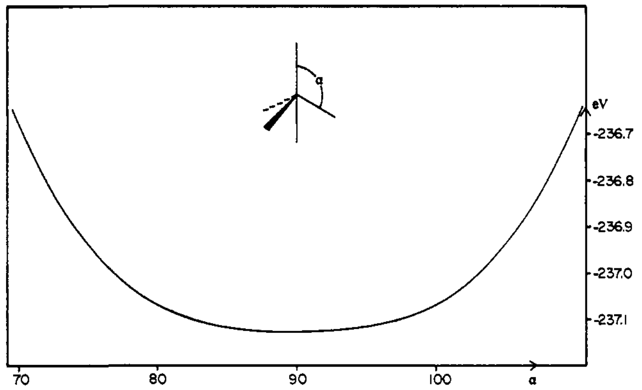


Figure 2. Potential curve obtained for the methyl radical when it is moved from planar (α = 90) toward a pyramidal structure. The modified INDO-type formalism described in the text was used for the calculation of total energies. Pople's parameterization was used.[5]

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**Table IV.** Eigenvalues, Configurational Energies, and Singly Excited CI Excitation Energies for the Isopropyl and *tert*-Butyl Radicals with Planar Radical Centers

| | Isopropyl | *tert*-Butyl |
|---|---|---|
| | Eigenvalues, eV | |
| LUMO | 4.20 | 3.89 |
| SOMO | −3.63 | −3.30 |
| HDOMO | −13.98 | −13.49 |
| | Configurational Energies, eV | |
| SOMO → LUMO | 4.20 | 3.89 |
| HDOMO → SOMO | 6.80 | 6.67 |
| HDOMO → LUMO | 12.57 | 12.13 |
| | SECI Excitation Energies, eV | |
| $\epsilon_1$ | 4.18, SOMO → LUMO | 3.88, SOMO → LUMO |
| $\epsilon_2$ | 5.58 | 5.24 |
| $\epsilon_3$ | 5.99 | 6.28 |
| $\epsilon_4$ | 6.77, HDOMO → SOMO | 6.65, HDOMO → SOMO |

**Table V.** Eigenvalues, Configurational Energies Relative to the Ground State, and Singly Excited CI Excitation Energies for the Amino Methyl Radicals VIa (VIb) and VIIa (VIIb)[a]

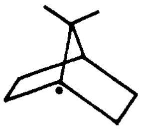
| | Planar $CH_2$– | Pyramidal $CH_2$– |
|---|---|---|
| | Eigenvalues, eV | |
| LUMO | 4.52<br>(4.57) | 4.99<br>(5.72)[b] |
| SOMO | −2.64<br>(−3.19) | −3.79<br>(−4.31) |
| HDOMO | −12.28<br>(−12.39) | −12.13<br>(−12.10) |
| | Configuration Energies, eV | |
| SOMO → LUMO | 3.44<br>(3.89) | 5.21<br>(6.23) |
| HDOMO → SOMO | 5.86<br>(5.47) | 4.64<br>(4.05) |
| HDOMO → LUMO | 10.13<br>(10.43) | 10.27<br>(11.03) |
| | SECI Excitation Energies, eV | |
| $\epsilon_1$ | 3.42, SOMO → LUMO<br>(3.88, SOMO → LUMO) | 4.60, HDOMO → SOMO<br>(3.99, HDOMO → SOMO) |
| $\epsilon_2$ | 5.17<br>(5.44, HDOMO → SOMO) | 5.16, SOMO → LUMO<br>(6.17, SOMO → LUMO) |
| $\epsilon_3$ | 5.85, HDOMO → SOMO<br>(6.13) | 6.41<br>(6.61) |

[a] Values for both planar and pyramidal amino (in parentheses) groups are given. [b] For the calculation with pyramidal $CH_2$– and –$NH_2$ groups the cisoid configuration was used. The results for the transoid form are similar except for a HDOMO at −12.84 eV causing $\epsilon_1$ to be 5.16 eV, HDOMO → SOMO.

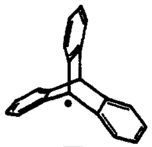
ethyl radicals having planar and pyramidal radical sites. Note that due to the higher degree of substitution, the HDOMO and LUMO orbitals move less in energy when the geometry changes.

Now the energy spacing is such that changing from planar to pyramidal geometry has caused the lowest transition to shift from being SOMO → LUMO to being HDOMO → SOMO. Experimentally,[17] the lowest excitation is 5.1 eV. The experimentally observed shift due to methyl substitution is reproduced in the calculations. Further, the methyl substitution has increased the energy of the SOMO relative to the methyl radical. This is due to the inclusion of some antibonding character between the two carbon atoms in the SOMO.

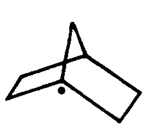
Radicals which are constrained to a pyramidal conformation would be likely to have HDOMO → SOMO as the lowest transition. The point would be difficult to test experimentally. However, bridgehead radicals such as the apocamphoyl[18] (III), the triptycyl[19] (IV), and the norbornyl[20] (V) radicals[21] would be possibilities to investigate. Evidence has been found for pyramidal radical sites in the 1-adamantyl and 1-bicyclo[2.2.2]octyl systems.[22]



III



IV



V

The effect of methyl substitution on the energies of the molecular orbitals is carried further in the isopropyl and *tert*-butyl radicals, the calculated characteristics of which are given in Table IV.

Methyl substitution, for the planar radicals, lowers the excitation energy principally by moving the SOMO

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(21) For further investigations of the effects of geometry on radical sites, see R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3189 (1971), and references therein.

(22) P. J. Krusic, T. A. Rettig, and P. v. R. Schleyer, *ibid.*, **94**, 995 (1972).

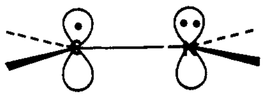
Table VI. Eigenvalues, Configurational Energies Relative to the Ground State, and Singly Excited CI Excitation Energies for the Amino Methyl Radicals VIIIa and VIIIb

| | Planar VIIIa | Pyramidal VIIIb |
|---|---|---|
| | Eigenvalues, eV | |
| LUMO | 4.40 | 5.16 |
| SOMO | −3.87 | −5.13 |
| HDOMO | −9.69 | −9.62 |
| | Configurational Energies, eV | |
| SOMO → LUMO | 4.44 | 6.66 |
| HDOMO → SOMO | 1.99 | 0.75 |
| HDOMO → LUMO | 7.69 | 8.07 |
| | SECI Excitation Energies, eV | |
| $\epsilon_1$ | 1.99, HDOMO → SOMO | 0.74, HDOMO → SOMO |
| $\epsilon_2$ | 4.43, SOMO → LUMO | 6.57, SOMO → LUMO |
| $\epsilon_3$ | 6.77 | 7.76 |

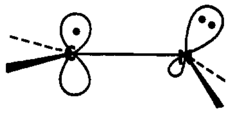
upward toward the LUMO orbital. A second effect is the above-mentioned spreading of the unoccupied and doubly occupied bands and is reflected in our calculation by the decrease in the HDOMO → LUMO excitation energy upon substitution.

We were interested in seeing what may be accomplished by strong substituents. To this end, we employed the amino group, $-NH_2$, and the cyano group, −CN. Amino groups, depending on conformation, are good $\pi$ donors and we expect a strengthening of the trend already seen with methyl groups. Table V presents values for the amino methyl radical with a planar $-CH_2$ group (left) and a pyramidal $-CH_2$ (right).

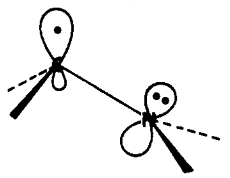
VIa



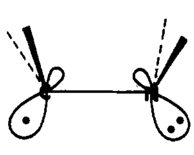
VIb



VIIa



VIIb



Once again the HDOMO has moved to higher energy deceasing the HDOMO → SOMO energy.

What happened as we let the amino and the methyl group become pyramidal? The HDOMO is the bonding combination of the radical orbital and the lone pair, and the SOMO the antibonding. A strong mixing can result in significant destabilization of the SOMO, lessening the SOMO → LUMO gap (see Figure 3). The SOMO → LUMO excitation for the planar species is 3.42 eV in the amino methyl radical but 4.53 eV in the ethyl radical. Any change of geometry which lessens this interaction will tend to stabilize the SOMO and destabilize the HDOMO. This is demonstrated in two ways in Table V, where values in parentheses refer to structures with a pyramidal $-NH_2$ group. We see that causing either the $CH_2$ or the $NH_2$ group to become pyramidal lowers the energy of the SOMO, decreasing the energy of the HDOMO → SOMO transition. A second effect of a pyramidal geometry is mixing of 2s character into the SOMO and HDOMO (rehybridization). This, in our calculations, nearly balances the expected destabilization of the HDOMO. However, it augments the stabilization of the SOMO (Table V). We decided to explore the conjugative interaction of the lone pair and the radical center by calculating the amino methyl radical in a bisected conformation, VIII. Now we will not have any direct interaction of the radical center and the lone pair.

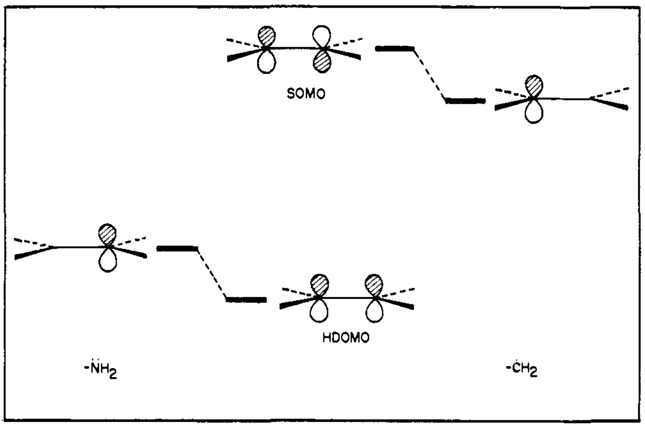
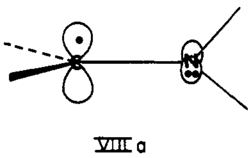
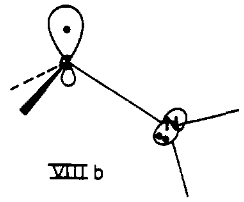


Figure 3. An interaction diagram for the planar radical $NH_2CH_2$. The lone pair of the $NH_2$ group is stabilized while the singly occupied molecular orbital (SOMO) is destabilized.



VIIIa



VIIIb

As expected, the HDOMO, which still may be identified with the amino lone pair, no longer benefits from the bonding interaction and suffers a substantial destabilization. On the other hand, the SOMO is not destabilized by the neighboring lone pair and drops in energy. In concert, these two effects coupled with the high energy of the amino lone pair (HDOMO) lead to very low HDOMO → SOMO energies. It should be noted here that we have kept our $NH_2$ group planar. This accounts for some of the high energy of the amino lone pair. (See Table VI.)

A last effect to be investigated is $\pi$ acceptors. We choose to employ the cyano group which has low lying unoccupied $\pi^*$ orbitals capable of delocalizing the radical function.

Table VII. Eigenvalues, Configurational Energies Relative to the Ground State, and Singly Excited CI Excitation Energies for Planar and Pyramidal Cyano Methyl Radicals

| | Planar | Pyramidal |
|---|---|---|
| | Eigenvalues, eV | |
| LUMO | 2.79 | 2.73 |
| SOMO | −5.40 | −6.17 |
| HDOMO | −12.92 | −12.96 |
| | Configurational Energies, eV | |
| SOMO → LUMO | 4.64 | 5.45 |
| HDOMO → SOMO | 4.18 | 3.53 |
| HDOMO → LUMO | 8.04 | 8.00 |
| | SECI Excitation Energies, eV | |
| $\epsilon_1$ | 4.14, HDOMO → SOMO | 3.48, HDOMO → SOMO |
| $\epsilon_2$ | 4.15 | 3.50 |
| $\epsilon_3$ | 4.63, SOMO → LUMO | 4.81 |
| $\epsilon_4$ | 5.03 | 5.40, SOMO → LUMO |

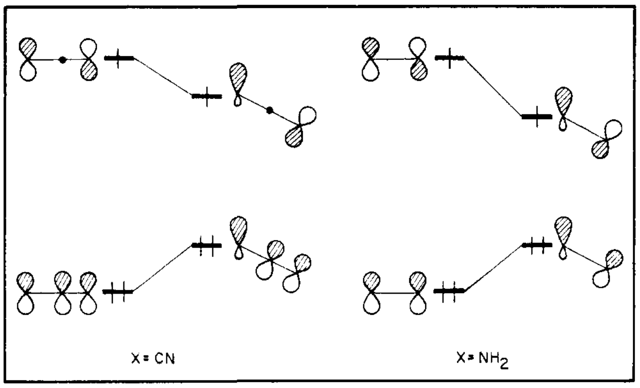
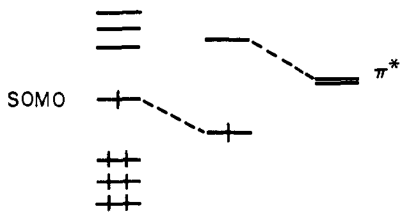


Figure 4. An interaction diagram for the $\pi$ system of $CH_2X$. On the left X = CN and on the right X = $NH_2$.

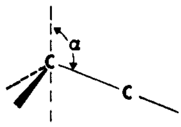


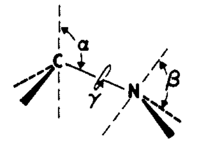
We would expect this delocalization effect to decrease the HDOMO → SOMO energy more for the planar conformation than for the pyramidal radical. Our calculations show this to be the case.

Table VII shows that the HDOMO → SOMO excitation is now the lowest for planar conformation. Although this change in characterization of the lowest energy transition would be difficult to test experimentally, we will note that the SOMO → LUMO excitation is polarized within the reflection plane (pyramidal geometry, $C_s$ symmetry), while the HDOMO → SOMO is polarized perpendicular to the plane.

**Geometry.** The geometrical studies of the amino and cyano methyl radicals were carried out as described earlier. The geometry variations were limited. For the cyano methyl radical we varied only the angle $\alpha$, maintaining a local $C_{3v}$ symmetry about the radical carbon. Three angles were varied for the amino methyl radical. Angle $\alpha$ measures the pyramidality of the radical site while $\beta$ measures the pyramidality of the amino nitrogen. Variation of angle $\gamma$ allows for rotation about the C–N bond. It measures the dihederal angle between the two local $C_{3v}$ axes.

The cyano methyl radical optimizes with $\alpha$ = 90°, a planar radical site. The amino methyl radical site optimizes with $\alpha$ = 90°, a planar radical site, $\beta$ = 106°, a pyramidal amino group, and $\gamma$ = 0°, a maximally interacting $\pi$ system. We wish to look at two aspects of the radicals more closely: the energy cost of forcing a pyramidal radical site and the rotational barriers of the amino methyl radical.





The three radicals we have calculated optimize with planar radical sites. We may order the preference by means of the energy required to produce a pyramid with $\alpha$ = 110°: $CH_2CN$ (0.65 eV) > $CH_3$ (0.45) > $CH_2NH_2$ (0.22). Since we calculated $CH_2NH_2$ to have a very soft planar ↔ pyramidal potential surface and did not perform a complete optimization, we would not unequivocably state that the amino methyl radical is planar. In any event, the ordering is easily rationalized in terms of the $\pi$ system which includes the radical function. In the cyano methyl radical, as for many electron acceptors (-CHO, -NO, etc.,), the lowest lying $\pi$ orbital, $\pi_1$, will involve a strong stabilizing interaction between the cyano carbon and the radical center. The interaction in the next higher $\pi$ orbital, $\pi_2$, the SOMO, will be only slightly antibonding as the wave function tends to be delocalized to the two extreme ends of the system. This resembles the two lowest $\pi$ wave functions for the planar trimethylene radical. When the cyano methyl radical is brought to a pyramidal configuration we weaken the $\pi$ interaction between the radical carbon and the adjacent atom.

While decreasing the $\pi$ interaction costs us substantial energy in the bonding $\pi_1$ orbital, we do not get much energy back in weakening the $\pi$ interaction in the only slightly antibonding $\pi_2$. This causes the high energy of the pyramidal structure for the cyano methyl radical.

The amino group, as many $\pi$ donors, interacts with the radical site by means of a doubly occupied function, the lone pair. As before, $\pi_1$ will be stabilizing, but now $\pi_2$(SOMO) will be strongly antibonding. The pyramidal deformation costs energy in $\pi_1$, but we gain more of it back through lessening the antibonding character in $\pi_2$ than was the case with the cyano substituent. The situation is shown schematically in Figure 4.

The dependence of rotational barrier on the conformation of the amino methyl radical was examined. With $\gamma$ held fixed at 90°, $\alpha$ optimized again to 0°, a planar radical site, and $\beta$ to 112°. The rotational barrier is 0.54 eV. Constraining both the carbon and nitrogen to tetrahedral conformations yields a rotational barrier of 0.62 eV, the transoid structure being lower in energy than the cisoid. The origin of the barrier is displayed in Figure 5 where for simplicity we deal with the $C_{2v}$ geometries, both carbon and nitrogen planar. For $\gamma = 0$ interactions 1, between the radical function and the lone pair, and 2, between the $CH_2$ and $NH_2$ p-like functions, are strong. However, for $\gamma = 90°$, the $NH_2$ function interacts with the energetically well separated radical function, interaction 3, and the $CH_2$ p-like function interacts with the lone pair, 4. Interactions 3 and 4 would be expected to be weaker than 1 and 2. In each conformation we have 4 electrons in bonding orbitals and 3 in antibonding, and the bonding interaction dominates over the antibonding. Consequently, for $\gamma = 0°$, we have stronger interaction and get lower total energy than for $\gamma = 90°$.

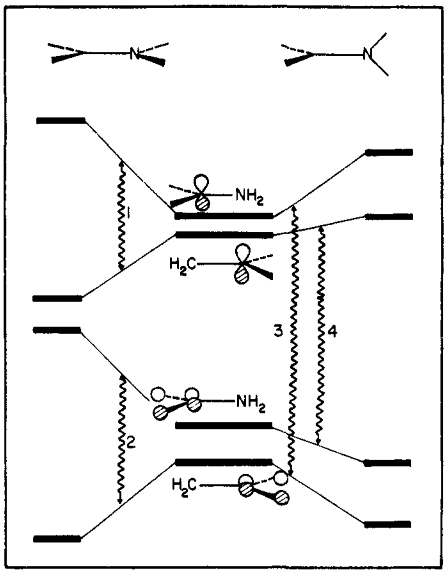


Figure 5. An interaction diagram for the p-like $-CH_2$ and $-NH_2$ localized basis functions, the nitrogen lone pair, and the radical function in the amino methyl radical. On the left the radical is planar and on the right the planes of the $NH_2$ and $CH_2$ are perpendicular to each other.

## Summary

We may ask which has the greater effect on the electronic structure, the geometry changes or the effects of substitution. In the cases we have looked at, it is not clear. Changing the geometry of the radical site can alter the nature of the lowest excitation but so may the nature of a single substituent.

We have seen that a planar radical structure generally favors the lowest excitation being SOMO → LUMO. Pyramidal radical sites on the other hand lead to the HDOMO → SOMO being lowest. We have found that the effects of $\pi$ donors or acceptors may modify these trends.

In our calculations, a planar radical site was preferred for donor, acceptor, and unsubstituted model structures. The strength of the preferences was rationalized.

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# Studies of the Valence Electron Levels of $CrO_4^{2-}$, $Cr_2O_7^{2-}$, $MnO_4^-$, $VO_4^{3-}$, and $FeO_4^{2-}$ by X-Ray Photoelectron Spectroscopy

**Andrew Calabrese and Robert G. Hayes***

*Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556.* *Received November 27, 1972*

**Abstract:** The X-ray photoelectron spectra of the valence regions of the $VO_4^{3-}$, $CrO_4^{2-}$, $Cr_2O_7^{2-}$, $MnO_4^-$, and $FeO_4^{2-}$ ions are presented. Spectral assignments are made using existing MO calculations in conjunction with available X-ray data. Relative atomic cross sections are used in a semiquantitative discussion of line intensities.

In recent years, photoelectron spectroscopy has become a very useful tool in the study of the electronic structure of molecules, particularly in the investigation of the valence regions of gaseous molecules.[1-3] Irradiation of a sample with monochromatic photons of sufficient energy results in the emission of electrons *via* the photoelectric effect. The kinetic energy imparted to the photoelectrons is a direct measure of the binding energy of the level from which they were ejected. Since there are no formal selection rules for electron emission, the process will occur as long as the incident photon energy is greater than or equal to the binding energy of a particular level. Photoelectron spectroscopy thus allows one to study the entire valence region of compounds regardless of orbital symmetry.

X-Ray photoelectron spectroscopy has also been

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(1) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970.

(2) M. B. Robin, N. A. Kuebler, and C. R. Brundle, "Electron Spectroscopy," D. A. Shirley, Ed., North-Holland Publishing Co., Amsterdam, 1972, p 351.

(3) U. Gelius in ref 2, p 311.