while II is unstable. The difference between I and II could easily be understood by utilizing the approach presented in this paper.

An additional problem occurs in the case of σ aromaticity. Here, it is assumed that the closely spaced occupied σ MO's of the central bond act collectively as a single symmetric occupied MO and the closely spaced unoccupied σ MO's act collectively as a single antisymmetric unoccupied MO. These assumptions may break down depending upon the inductive nature of substituents, the nature of atoms constituting the central bond, and the type of calculation employed. Thus, σ nonbonded interactions should be discussed for each molecule separately although in most cases expectations based on a mere electron count, i.e., σ Hückel aromaticity, will be met. This is the situation with the molecules discussed in this work.

Finally, the ideas reported here can be used to understand why certain bond angles in molecules are surprisingly small, rotational barriers in molecules which have very high lying unoccupied MO's, and other problems of general interest.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for partial support of this research.

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(6) For a discussion of the MWH method see ref 5.

(7) We have discussed the importance of orbital symmetry in organic structural problems at length in the following papers: (a) N. D. Epiotis, *J. Am. Chem. Soc.*, **95**, 3087 (1973); (b) N. D. Epiotis and W. Cherry, *Chem. Commun.*, 278 (1973); (c) N. D. Epiotis, D. Bjorkquist, L. Bjorkquist, and S. Sarkanen, *J. Am. Chem. Soc.*, **95**, 7558 (1973); (d) N. D. Epiotis, S. Sarkenen, D. Bjorkquist, L. Bjorkquist, and R. Yates, *ibid.*, **96**, 4075 (1974).

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A Molecular Orbital Interpretation of the Static, Dynamic, and Chemical Properties of CH_2X Radicals

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Abstract: The effects of α substituents on the stability of radical centers are rationalized in terms of one-electron molecular orbital (OEMO) theory. The same treatment is used to rationalize the rates of radical reactions and the conformations of CH_2X radicals. Ab initio calculations of the preferred geometries of radicals of the type $CH_2{-}X$, wherein X = O^-, -OH, -SH, -F, -Cl, $-C{\equiv}CH$, $-C{\equiv}CF$, and -CN, are reported which substantiate the qualitative ideas developed on the basis of the OEMO treatment.

I. Introduction

Although the effects of substituents upon the stabilities of carbocations and carbanions are fairly well understood, their effects upon adjacent radical centers cannot be rationalized simply by the assumption that the behavior will be intermediate between that of carbocations and carbanions. Recent kinetic studies of the thermolyses of substituted azopropanes indicate that unsaturated substituents such as $-CH{=}CH_2$,[3a] $-C{\equiv}CH$,[3a] $-C{\equiv}N$,[3b] and Ph[3c,d] stabilize an adjacent radical center to the largest extent. Alkyl groups[4a–c] and first-row heteroatoms such as OR[4a,c,d] have a small stabilizing effect, and second-row heteroatoms such as SR[4a,c] display intermediate effects.[5]

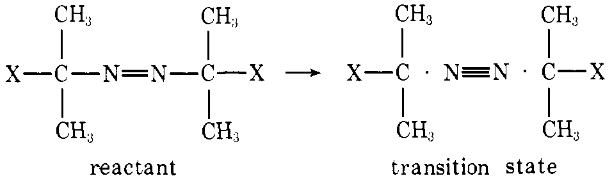
It should be emphasized that since these results have been obtained from kinetic studies, they reflect the effects of substituents on the stability of a radical center as it exists in the transition state of the reaction under study. Typical stabilization energies calculated from the data of ref 3 and 4 for a variety of substituents are collected in Table I. In

Table I. Radical Stabilization Energies (SE) of $\dot{C}H_2$–X

X	SE(I)[a]	SE(II)[b]
H	0	0
CH_3	4.6	6.0
$(CH_3)_3C$	6.5	13.0
F		3.0
HO		12.0
CH_3O	6.4	
C_6H_5O	7.6	
CH_3COO	3.9	
Cl		
CH_3S	12.1	
C_6H_5S	11.2	
CH_3COS	9.6	
CN	14.0	18.0
C_6H_5	15.9	19.0
$CH_2{=}CH$	16.5	19.0
$CH{\equiv}C$	16.6	

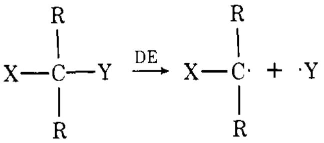
[a] Calculations based on data for thermolysis of azopropanes at 100° collected in ref 4a. [b] Calculations based on best available values of bond dissociation energies compiled in J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

this table, stabilization energy (SE) is taken to be the difference between $\Delta G_H^{\ddagger}$ and $\Delta G_X^{\ddagger}$, the free energies of activation for the unsubstituted and substituted systems.



$$X-\overset{CH_3}{\underset{CH_3}{C}}-N{=}N-\overset{CH_3}{\underset{CH_3}{C}}-X \longrightarrow X-\overset{CH_3}{\underset{CH_3}{C}}\cdot N{\equiv}N\cdot\overset{CH_3}{\underset{CH_3}{C}}-X$$

An alternative way to determine effects of substituents on radical stability employs bond dissociation energies of substituted molecules. Here, the stabilization energy (SE) is taken to be the difference between DE_H, the C–Y bond dissociation energy for X = H, and DE_X, the C–Y bond dissociation energy for X $\neq$ H. Since most bond dissociation



$$X-\overset{R}{\underset{R}{C}}-Y \xrightarrow{DE} X-\overset{R}{\underset{R}{C}}\cdot + \cdot Y$$

energies are obtained from kinetic studies, the calculated stabilization energies again reflect the effect of a substituent on the stability of a radical center as it exists in the transition state. Typical results are included in Table I. It is clear that the trends revealed by the two different sets of data are the same.

A related problem in radical chemistry concerns the effects of substituents upon the structure.[6] For example, in the model system $\dot{C}H_2X$, the degree of planarity at carbon depends upon X. In addition, the singly occupied carbon AO can adopt an eclipsed or staggered conformation with respect to an adjacent σ bond when X = $:\ddot{Y}$-H, where Y is a heteroatom such as O, S, etc.

The principle objective of the present work is to develop a simple MO interpretation of these properties and of the rates of radical reactions. To provide a quantitative theoretical foundation for the analysis, nonempirical SCF-MO computations have been performed on the radicals CH_2O^-, CH_2OH, CH_2SH, CH_2F, CH_2Cl, $CH_2C{\equiv}CH$, $CH_2C{\equiv}CF$, and CH_2CN, using an unrestricted Hartree-Fock procedure[7] and the Gaussian 70 series of programs.[8]

II. Ab Initio Results

1. Computational Method. Since the molecular systems to be investigated are open shell systems, two ab initio methods, the restricted Hartree-Fock[9] (RHF) and the unrestricted Hartree-Fock (UHF), might be employed. The main limitation of the UHF method is that the computed single-determinantal wave function is not an eigenfunction of the spin operator S^2, but contains contaminating terms from higher spin eigenfunctions. Despite this disadvantage, the UHF treatment has been chosen here because of the desire to obtain better spin density values.[10] In any event, with the exceptions of X = $-C{\equiv}CH$ and $-C{\equiv}CF$, contamination from higher spin eigenfunctions was found to be quite small.

Table II. Computed and Experimental Results on the $^3A_1$ State of Formaldehyde

	α, deg	C–O, Å	Inversion barrier, kcal/mol
STO-3G	37.8	1.39	2.009
4-31G	33	1.3586	0.827
Exptl	35	1.31	

The first problem to be solved was the choice of the basis set, which should be simple enough to allow a comparative study to be made but, at the same time, capable of providing reliable values of bond lengths, bond angles, and inversion barriers. Some preliminary computations were therefore performed, in which minimal (STO-3G)[11] and split-valence (4-31G)[12] basis sets were compared. A lack of experimental data on geometrical parameters and inversion barriers of radicals precludes a systematic comparison between the computed results and experimental quantities. Consequently, a study was made of the triplet state of formaldehyde ($^3A_1$) for which some experimental data are available.[13] This system was chosen because of the similarity of its orbital occupancy with that of the radical anion of formaldehyde;[14] in addition, because the system is nonplanar and the degree of nonplanarity is known experimentally, it was possible to check this important geometrical parameter.

The energy and geometrical parameters of the pyramidal conformation at the STO-3G level were obtained from ref 15. To obtain the inversion barrier predicted by this basis set, the planar conformation was optimized with respect to all geometrical parameters. In the computations at the 4-31G level, all geometrical parameters were first optimized for various values of α, the angle between the HCH plane and the C–O bond axis; then the optimum value of α was determined from a parabolic interpolation, and all geometrical parameters were reoptimized at this α value. The results of the computations are summarized in Table II.

It is significant that both computations predict that, in this triplet state, formaldehyde is nonplanar in agreement with experiment; the agreement with the experimental geometrical parameters is slightly better at the 4-31G level. For the inversion barrier, a comparison with experiment is not possible because this result is not available.

In a second test, the C–S bond length of the radical $CH_3S\cdot$ was computed. This system was selected because some of the radicals to be investigated contain a second-row atom (S and Cl) and, in addition, an accurate estimate of the C–S bond length (r(C–S) = 1.8803 Å) was available, computed with a double ζ basis set containing two linearly independent sets of d-type functions on sulfur.[16] In the computations at the STO-3G level, the C–H and C–S bond lengths were optimized with the HCH angles maintained at the tetrahedral value; at the 4-31G level only the C–S bond length was optimized with the remaining parameters the same as in the STO-3G computations. The resulting values are: r(C–H) = 1.0911 and r(C–S) = 2.0376 (STO-3G); r(C–S) = 1.8807 (4-31G). From the comparison it appears

Table III. Computed Energies and Geometrical Parameters for the Planar (α = 0) and Optimum (α = 27) Conformations of $\dot{C}H_2OH$

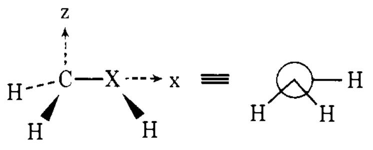
α	E, au	r(CO)	r(OH)	r(CH)	∠COH	$\angle H_1CO$	$\angle H_2CO$
0	−114.24435	1.380	0.954	1.083	114.64	118.79	115.55
27	−114.24525	1.382	0.954[a]	1.083[a]	115.03	123.49	115.91

[a] Not reoptimized for this conformation.

that the C-S bond length of this radical will not be reproduced well by a minimal basis set, but the 4-31G basis set is acceptable.

An additional result of the previous investigation[17a] is that there is negligible participation of d-type functions in the CH_2SH radical. This suggests that the 4-31G basis set, which does not contain d-type functions, will be suitable. All of these considerations have led to the decision to employ the 4-31G basis set to obtain theoretical data at a uniform level.

2. Geometry Optimization of CH_2OH and CH_2SH. For these two radicals, extensive geometry optimization was performed on conformations **1** and **2**, which were found to



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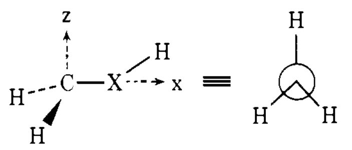

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represent respectively the energy minima and the transition states for rotation about the C-X bonds. The results for CH_2OH are summarized in Table III.[17b]

Several aspects of these results are of interest. (i) The C-O bond length is slightly shorter than that computed for CH_3OH (1.43 Å), but substantially longer than that computed for C^+H_2OH (1.25 Å).[18] It can be concluded, on this basis alone, that conjugative interaction between carbon and oxygen is much less in the radical than in the cation.

(ii) From the C-O bond length optimization, the computed C-O stretching force constant is 6.72 mdyn/Å for CH_2OH, while the value for CH_3OH, computed analogously, is smaller, 5.73 mdyn/Å, in agreement with experimental results (6.25 and 5.22 mdyn/Å, respectively).[19]

(iii) The COH angle (115°) is larger than that in methanol (104°) and reflects the relaxation of the molecule that results when H_1 and H_3 are brought into proximity; the H_1CO angle is, therefore, larger than the H_2CO angle.

(iv) The radical is computed to be nonplanar in its most stable structure, with an out-of-plane angle of 27°.

(v) However, the barrier to pyramidal inversion is only 0.5 kcal/mol. Depending upon the vibrational energy levels associated with the inversion process, the nonplanarity could be reduced.[20]

Table IV summarizes the results for CH_2SH. Points of interest follow.

(i) The C-S bond length in this radical is only slightly shorter than in the tautomer $CH_3S\cdot$.

(ii) The optimum value of the out-of-phase angle α is 10°, so that *in terms of the total energy this radical* is nonplanar.

(iii) However, the barrier to inversion of the radical is only 0.08 kcal/mol, so that it is doubtful whether the nonplanarity could be observed experimentally.[20]

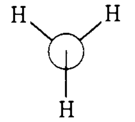
Table IV. Computed Energies and Geometrical Parameters for the Planar (α = 0°) and Optimum (α = 10°) Conformations of $\dot{C}H_2SH$

α	E, au	r(CS)	r(SH)	r(CH)	∠CSH	$\angle H_1CS$	$\angle H_2CS$
0	−436.55264	1.808	1.354	1.068	98.18	121.48	118.2
10	−436.55276	1.812	1.354[a]	1.068[a]	98.45	121.19	116.59

[a] Not reoptimized for this conformation.

(iv) As in the oxygen analogue, the C-S force constant in the radical (3.14 mdyn/Å) is higher than in the parent compound CH_3SH (3.02 mdyn/Å). The latter value compares favorably with experiment (3.26 mdyn/Å).[19b]

Rotation in $\dot{C}H_2OH$ was investigated by computing the energy of **2** (X = O) as a function of α. Positive values of α correspond to the Y conformation **3**, negative values to the W conformation **4**, and zero corresponds to the T conformation **5**. For each value of α, the energy was minimized



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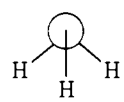

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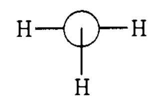

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with respect to the C-O bond length and the HCH and COH angles; the C-H and O-H bond lengths were maintained at the values found in the most stable structure **1**. There is only one minimum in this curve, it corresponds to the Y conformation (α = +24.7°) and it has the following additional geometrical parameters: r(C-O) = 1.3849 Å; ∠HCH = 121.18°; ∠COH = 115.35°. The rotational barrier of $\dot{C}H_2OH$ is the energy difference between the most stable conformation and the Y conformation, and is 2.00 kcal/mol.

Pyramidal inversion in **2**, when X = S, was computed in a similar manner, except that only the C-H bond length was kept fixed at the value optimized for **1**. From this work, it is again evident that only the Y conformation has chemical significance. The value of α is 5.83° and the additional geometrical parameters have the following values: r(C-S) = 1.8314 Å, r(S-H) = 1.3612 Å; ∠HCH = 121.5°; ∠CSH = 98.3°. The rotational barrier is the energy difference between the optimized structure **1** and the corresponding Y conformation, and is 1.66 kcal/mol.

The combined hypersurfaces for rotation and inversion in $\dot{C}H_2OH$ and $\dot{C}H_2SH$ reveal the shallowness of the inversion cross-section as compared to rotation. One also notices that, in the course of a 360° rotation about the C-X bond, two inversions must also occur. To pass over the rotational transition state, the molecule must first invert. After rotating 180°, the molecule must invert again before passing over the second rotational transition state. This final 180° rotation then brings the molecule back to its initial position. The effect is more pronounced in the CH_2OH radical, because the out-of-plane angles in the ground state and transition state are larger. These results agree quite well with the available experimental data on CH_2OH. Line width studies[21] indicate a rotational barrier of ca. 4.8 kcal/mol; furthermore, on the basis of ^{13}C splitting constants, it has been suggested[22] that $\dot{C}H_2OH$ is nonplanar. No experimental data are available for $\dot{C}H_2SH$. However, radicals derived from sulfides (CH_2SR; R = Me, *t*-Bu) are more planar and display higher torsional barriers (1-2 kcal/mol higher) than the corresponding oxygen analogues.[23] While the trend in nonplanarity at carbon is in agreement with the present results, extrapolation of the experimental data leads to a rotational barrier slightly higher than the 1.66 kcal/mol barrier computed for $\dot{C}H_2SH$.

3. Geometry Optimization of CH_2F and CH_2Cl. The computations were performed for various values of α, the angle

Table V. Computed Energies and Geometrical Parameters for the Planar ($\alpha = 0°$) and Optimum ($\alpha = 29°$) Conformations of $\dot{C}H_2F$

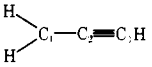
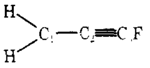
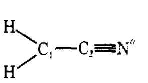
α	E, au	r(CF)	∠HCH
0	−138.22556	1.3698	127.52
29	−138.22639	1.3735	123.04

Table VI. Computed Energies and Geometrical Parameters for the Planar ($\alpha = 0°$) and Optimum ($\alpha = 21°$) Conformations of $\dot{C}H_2Cl$

α	E, au	r(CCl)	∠HCH
0	−497.90699	1.8045	126.68
21	−497.90716	1.8045[a]	125.20

[a] Not reoptimized for this conformation.

Table VII. Total Energies (au) for Various Values of the Angle α

	α, deg	E(STO-3G)	E(4-31G)
	0	−113.82612	−115.09141
	5	−113.82604	−115.09130
	0	−211.27390	−213.78644
	5	−211.27384	−213.78639
	10	−211.27363	
	0	−129.65076	
	4	−129.65070	
	8	−129.65052	

[a] The optimum geometrical parameters at $\alpha = 0$ are: $r(C_1{-}C_2) = 1.3993$ Å; $r(C_2{-}N) = 1.2214$ Å; $r(C_1H) = 1.0835$ Å; $\angle HC_1H = 118.8°$.

Table VIII. π-Overlap Populations between the Methylene Carbon and the Adjacent Atom

	α, deg[a]	O.P. (4-31G)	O.P. (STO-3G)
CH_2O^-	0	−0.0086	
	27[b]	0.0086	
CH_2OH	0	−0.0379	
	28[b]	−0.0267	
CH_2SH	0	−0.0186	
	10[b]	−0.0176	
CH_2F	0	−0.0204	
	29[b]	−0.0144	
CH_2Cl	0	−0.0119	
	21[b]	−0.0140	
$CH_2C{\equiv}CH$	0[b]	0.0727	0.0631
	5	0.0724	0.0628
$CH_2C{\equiv}CF$	0[b]	0.0550	0.0582
	5	0.0548	0.0578
	10		0.0574
$CH_2C{\equiv}N$	0[b]		0.0679
	4		0.0675
	8		0.0373

[a] For a planar CH_2 group, α is assumed to be 0°, and it increases with increasing pyramidalization at carbon (for a tetrahedral angle, $\alpha = 54.8°$). [b] Optimum value.

between the HCH plane and the C-X bond axis. The C-H bond length was kept fixed at 1.07 Å, and the remaining geometrical parameters were optimized for each value of α. The results are summarized in Tables V and VI. Points of interest follow.

(i) Both radicals are computed to be nonplanar in their most stable structure, with out-of-plane angles of 29 and 21° for $\dot{C}H_2F$ and $\dot{C}H_2Cl$, respectively.

(ii) However, the barriers to pyramidal inversion are 0.5 and 0.1 kcal/mol for $\dot{C}H_2F$ and $\dot{C}H_2Cl$, respectively. Again, depending on the vibrational energy levels associated with the inversion process, the nonplanarity could be reduced.[20] The potential energy curves for these two radicals are similar to those of $\dot{C}H_2OH$ and $\dot{C}H_2SH$.

(iii) The STO-3G structure of $\dot{C}H_2F$ has already been published;[15] the comparison shows a good agreement between the geometrical parameters computed at the two different levels, except for the HCH angle.

4. Geometry Optimization of $CH_2C{\equiv}CH$, $CH_2C{\equiv}CF$, and $CH_2C{\equiv}N$. The geometries of the two radicals $CH_2C{\equiv}CH$ and $CH_2C{\equiv}CF$ were examined in previous investigations[24] which considered mainly the reactivities of such radicals. In this section are reported results concerning the optimum conformation of the methylene group. As before, the total energy was computed at various values of α, the angle between the HCH plane and the adjacent C_1-C_2 bond axis. The results are shown in Table VII.

For the $CH_2C{\equiv}N$ radical, convergence in the SCF procedure at the 4-31G level could not be obtained; for this reason the results are reported in this case at the STO-3G level. To check their validity, STO-3G results are also reported for the other two radicals. For these, the angle HC_1H was optimized for each value of α, and the remaining parameters were kept constant at the values computed previously for the planar conformations.

For CH_2-CN, all geometrical parameters were optimized (at the STO-3G level) at α = 0, 4 and 8°. It had already been shown[24] that a radical such as $CH_2C{\equiv}CH$, which contains only first-row elements, shows very similar energy differences and geometrical parameters at the STO-3G and 4-31G levels. This same observation is made in the present investigation of the optimum conformation at the methylene center for the two radicals $CH_2C{\equiv}CH$ and $CH_2C{\equiv}CF$ and suggests that the STO-3G result obtained for the CH_2-CN radical may be reliable.

The result is that these three radicals are planar, but the potential curve around $\alpha = 0$ is very flat.

5. Overlap Population Analysis. All of the radicals investigated in the present paper are π radicals, i.e., the singly occupied radical orbital is of π type. The MO rationalization of stability and conformations presented in the following sections will make use of the π-overlap populations between the methylene carbon and the adjacent atom. These values are listed in Table VIII. In the case of CH_2CN, only the STO-3G results were obtained. For comparison, STO-3G results are also given for the radicals $CH_2C{\equiv}CH$ and $CH_2C{\equiv}CF$.

III. PMO Rationalization

The MO analysis to be employed for the rationalization of the relative stabilities and conformations of CH_2X radicals and of the rates of radical reactions is based upon perturbation theory, utilizes an effective one-electron Hamiltonian operator, and neglects overlap. According to perturbation theory, the magnitude of the interaction between two nondegenerate orbitals is directly proportional to the square of their interaction matrix element H_{ij}, and inversely proportional to their energy separation (ΔE).[25] In most cases it is the ΔE term which dictates a particular trend, and this will, therefore, constitute the principle focus of our attention.

In the discussion which follows, two types of radicals are distinguished: (a) a "free" radical, by which we mean a radical generated and observed in its ground electronic state,[26] and assumed to be minimally perturbed by its environment; (b) an "incipient" radical, by which we mean a species which exists in the transition state of a reaction, and which may interact both with an adjacent substituent and with a second molecular fragment.

It will be clear from these distinctions that azoalkane thermolysis provides experimental data concerning substituent effects upon "incipient" radicals (eq 1), i.e., upon the relative stabilities of various transition states **7**. It is cus-

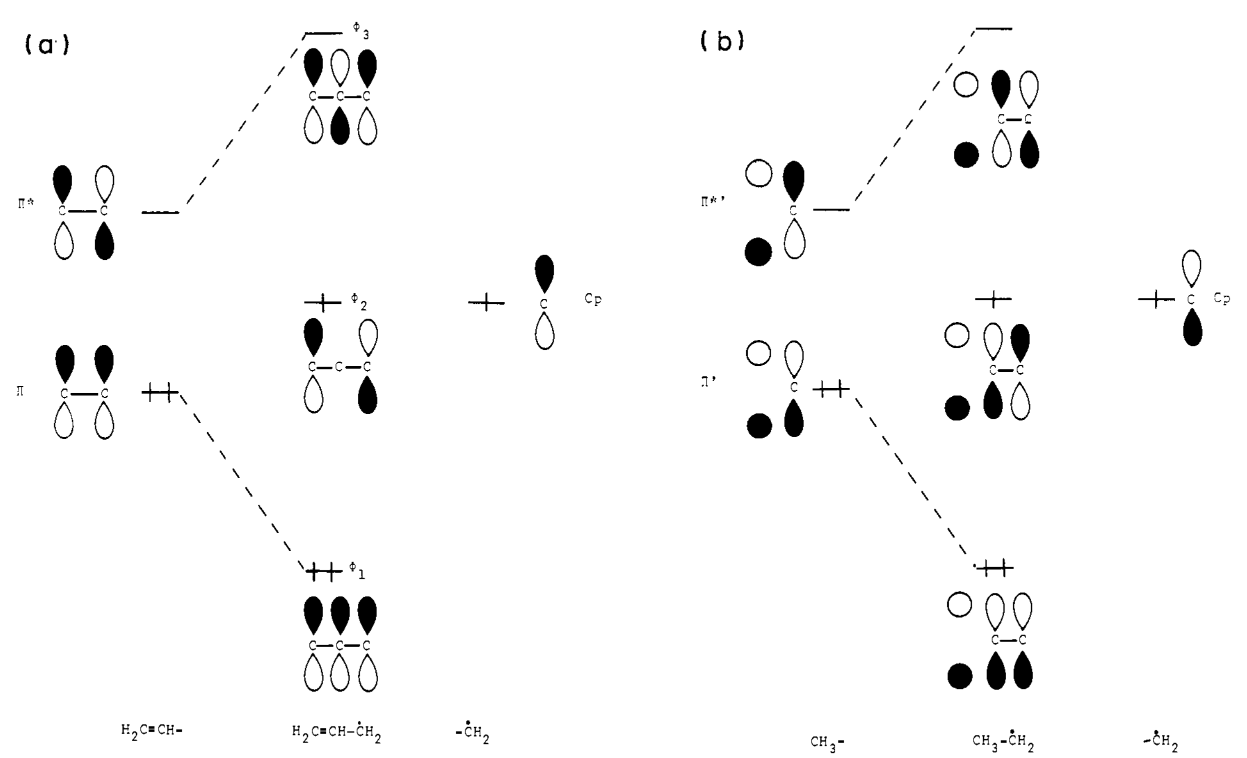


Figure 1. Orbital interactions involved in the stabilization of a radical center by (a) an unsaturated group and by (b) groups such as CH_3 and NH_3^+.

$$\underset{\mathbf{6}}{X—C(Me)_2—N{=}N—C(Me)_2—X} \xrightarrow{\Delta}$$

$$\underset{\mathbf{7}}{[X—C(Me)_2\cdot\cdot N{=}N\cdot\cdot(Me)_2C—X]} \longrightarrow 2Me_2\dot{C}X + N_2 \quad (1)$$

tomary to think of a radical as a species in which a molecular orbital is occupied by a single electron. However, in the transition state **7**, the occupancy may be equal to, greater, or less than one electron depending upon the electronic nature of the extrusion fragment N_2. For example, if the N_2 fragment should behave as an acceptor toward the "free" radical $Me_2\dot{C}X$, the occupancy number of the radical center will be less than 1; conversely, if the fragment behaves as a donor toward $Me_2\dot{C}X$, the occupancy of the radical center will be greater than 1. As will be seen, the sign of the interaction of a radical center with an adjacent group is critically dependent upon the precise MO occupancy when overlap is included in the theoretical analysis. Thus, the interaction of the substituent X with the radical center generated at the transition state may be stabilizing if the occupancy is less than 1 and destabilizing if the occupancy is greater than 1. In general, the *relative effect* of substituents upon the stability of an incipient radical will be shown to be independent of the particular reaction employed. On the other hand, whether this relative effect is to be ascribed to *increasing stabilization* or *decreasing destabilization* will be determined by the nature of the molecule employed in the kinetic study. What this means is that one can rank various substituents in terms of their relative stabilization of an incipient radical, but cannot a priore predict where to place hydrogen in the sequence. There are a number of examples in the literature which indicate that a substituent may have a stabilizing or destabilizing effect upon an incipient radical center depending upon the nature of the reactants.[27]

1. Substituent Effects upon Radical Stability. We begin this discussion with the assumption that we have an "incipient" radical in which the orbital occupation number is one. For unsaturated substituents such as $-CH{=}CH_2$, $-C{\equiv}CH$, $-C{\equiv}CF$, $-C{\equiv}N$, etc., interaction is possible between the singly occupied radical orbital p_c and the π and π^* MO's of the substituent. This is a three-orbital, three-electron interaction, and it leads to net two-electron stabilization (Figure 1a). It is evident that the closer the spacing of the interacting energy levels p_c–π and p_c–π^*, the stronger will be the interaction of the corresponding MO's and, in general, the greater the stabilization energy. This conclusion will be valid provided that the matrix element H_{ij} does not vary appreciably. Also for substituents such as CH_3 or NH_3^+, the interaction diagram has the same form. The orbitals of such groups which can interact with the singly occupied radical orbital are π' and $\pi^{*\prime}$ (Figure 1b). This is also a three-orbital, three-electron interaction, and it again results in a net two-electron stabilization. However, the stabilizing effect is much smaller in this case because the spacing between the interacting energy levels is greater.

The stabilization by an adjacent first-row heteroatom, e.g., OR, can be attributed to the interaction of the singly occupied radical orbital with the doubly occupied nonbonding MO of the heteroatom. This is a two-orbital, three-electron interaction, and it leads to net one-electron stabilization (Figure 2a).

On the other hand, the stabilization of a radical center by an adjacent second-row heteroatom, e.g., SR, can be due to the interaction of p_c with the doubly occupied nonbonding MO (NBMO) of the heteroatom as well as the interaction of p_C with low-lying vacant d orbitals of the heteroatom.[28] However, a recent nonempirical SCF-MO computation on $\dot{C}H_2SH$, employing an extended basis set containing d-type functions on sulfur, has shown that the participation of 3d orbitals in the bonding is negligibly small.[16] Consequently, the stabilizing interaction must be considered to be the two-orbital, three-electron interaction, as in the case of the α-oxy radical. The larger stabilizing effect of the second-row heteroatom is simply a consequence of the greater proximity of the interacting energy levels p_C and X in this case. This arises because the lone-pair ionization potential of a second-row heteroatom (i.e., the energy required to re-

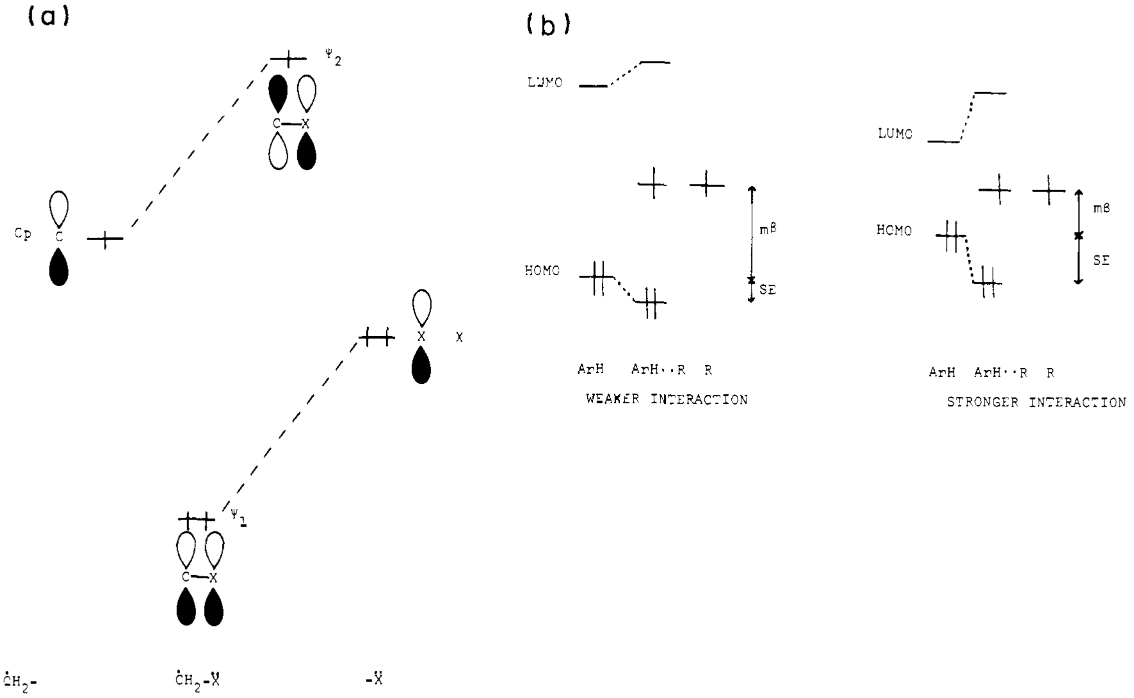


Figure 2. (a) Orbital interactions involved in the stabilization of a radical center by a first- or second-row heteroatom; (b) the dependence of two-electron stabilization on the energy separation of the interacting levels.

Table **IX.** Ionization Potentials of First-Row and Second-Row Hydrides[a]

Molecule	IP, eV
HF	15.77
HCl	12.80
H_2O	12.61
H_2S	10.48
H_3N	10.87
H_3P	10.10

[a] Data taken from *Natl. Bur. Stand.*, No. 26 (1969).

Table **X.** π-Overlap Integrals (S_{CX}) and Optimized C–X Bond Lengths of CH_2–X Radicals

	S_{CX}[a]	Optimized bond length, Å
$2p_C-2p_F$	0.1227	1.3735[b]
$2p_C-3p_{Cl}$	0.1296	1.8045[b]
$2p_C-2p_O$	0.1540	1.3821[b]
$2p_C-3p_S$	0.1540	1.8116[b]
$2p_C-2p_N$	0.1668	1.47[c]
$2p_C-3p_P$	0.1865	1.80[c]

[a] Computed with a CNDO/2[29] program. [b] Present ab initio computations. [c] Estimated.

move an electron from a nonbonding "lone pair" AO) is less than that of the corresponding first-row heteroatom (see Table IX).

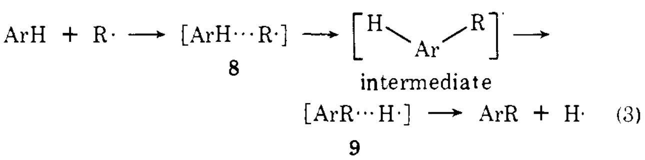
It is extremely important to emphasize that the foregoing analysis of α-oxy and α-thio radicals is based upon the energy separation of the interacting levels. It will lead to the correct prediction if the interaction matrix element between the heteroatom NBMO and the singly occupied orbital of the radical does not vary appreciably. In general, H_{ij} can be assumed to be proportional to the overlap S_{ij}. The matrix element for the π interaction of an atom X with an adjacent carbon radical center will then be given by

$$H_{CX} = KS_{CX} \tag{2}$$

Table X summarizes the values of the $\pi 2p_C$-$2p_X$ overlap integrals of a series of radicals CH_2X at the optimized bond lengths in each case. The trends appear to be clear, viz., that the overlap and, consequently, the matrix element H_{ij} is equal to or greater for the second-row heteroatom, so that this effect operates in the same direction as the (more easily derived) energy separation of the interacting levels.

We may now consider the effect of occupancy of the incipient radical center by more than one or less than one electron. It seems clear that small deviations from unity will not affect the general trends just described. An inspection of Figures 1a and 2a also reveals that changes in the occupancy as a function of the nature of the reactants are expected to affect the stabilizing influence of heteroatom substituents to a greater degree than that of unsaturated groups.

2. The Rates of Radical Reactions. We consider the reaction shown in eq 3. If formation of the intermediate should be rate determining, then the rate of the reaction will depend upon the relative stabilization of the transition state **8**. Alternatively, we may state that the rate of the reaction will depend upon the stabilization of the free radical R by ArH. When the problem is formulated in this way it is seen that this situation is similar to that found in the stabilization of a radical by an adjacent unsaturated group. Thus if Ψ is a carbon $2p_z$ orbital and ArH is an even alternant hydrocarbon, the following relationships hold, where α and β have their usual meanings.[30]



$$\mathrm{ArH} + \mathrm{R}\cdot \longrightarrow \underset{\mathbf{8}}{[\mathrm{ArH}\cdots\mathrm{R}\cdot]} \longrightarrow \underset{\text{intermediate}}{\left[\overset{\mathrm{H}}{}\!\!\searrow_{\mathrm{Ar}}\!\!\nearrow\overset{\mathrm{R}}{}\right]^{\cdot}} \longrightarrow \underset{\mathbf{9}}{[\mathrm{ArR}\cdots\mathrm{H}\cdot]} \longrightarrow \mathrm{ArR} + \mathrm{H}\cdot \tag{3}$$

$$E(\mathrm{HOMO}) = \alpha + m\beta \tag{4}$$

$$E(\mathrm{LUMO}) = \alpha - m\beta \tag{5}$$

$$E(\mathrm{C2p}_z) = \alpha \tag{6}$$

As illustrated in Figure 2b, the magnitude of the two-electron stabilization (SE) is inversely proportional to the energy separation of the interacting orbitals, and is related to

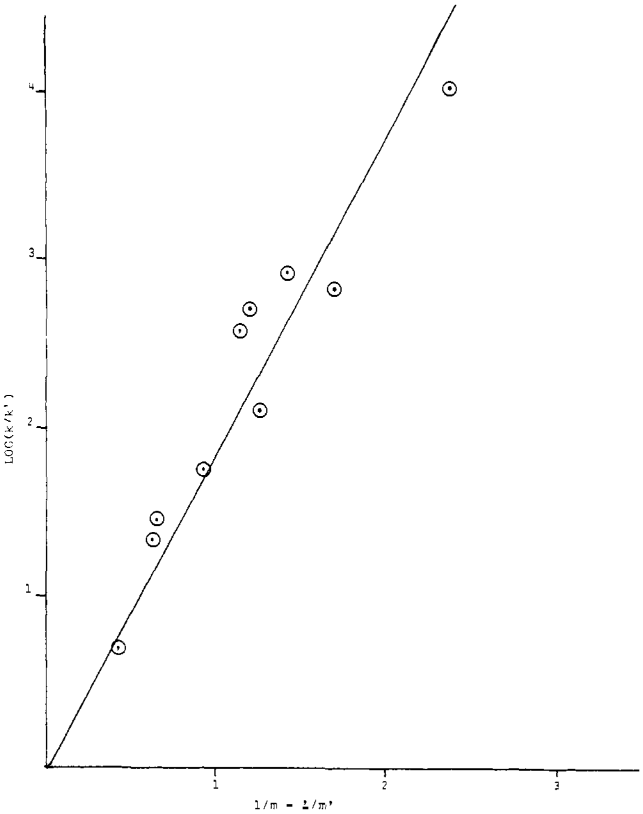


Figure 3. Relative rates of addition of methyl radicals to aromatic even alternant hydrocarbons vs. the inverse of the orbital coefficient *m*.

the coefficient *m* of eq 4 and 5 by

$$\mathrm{SE} \propto 1/m \tag{7}$$

If k_0 and k are the reactivities of benzene and a second aromatic hydrocarbon toward a given free radical, we then arrive at

$$\log (k/k_0) \propto 1/m - 1/m' \tag{8}$$

Figure 3 shows that the data of Levy and Szwarc,[31] on the reactivities of aromatic hydrocarbons toward methyl radicals, are correlated satisfactorily when plotted according to eq 8.

For the case in which the intermediate is formed reversibly, and the formation of transition state **9** is rate determining, relative reactivities will be decided by the relative stabilization of this transition state. No convenient reactivity indices exist to treat this situation and it can be expected that a correlation of the type shown in eq 8 would not exist because it would be necessary to calculate explicitly the stabilization energy for each substrate. Consequently, a finding that theory and experiment are correlated by eq 8 may serve to indicate but, obviously, not prove that the reaction of an even alternant hydrocarbon with a free radical proceeds by rate-determining formation of the radical intermediate.

3 Conformational Preferences of CH_2X Radicals. In the MO interpretation of the stability of substituted methyl radicals presented above, it has been assumed that the geometry at carbon remains constant. This assumption permits a simplification of the discussion and does not affect the qualitative trends revealed by the treatment. We now consider how the stabilization of the radical center by an adjacent substituent can be enhanced by geometric distortion of the methylene group.

It is known that while CH_3 is planar, replacement of hydrogen by a substituent such as fluorine makes the radical center nonplanar,[32] and such observations have been explained using electronegativity arguments.[6] However, it has been found here that, with other types of electronegative substituents such as -C≡CH, -C≡CH, -C≡CF, and -C≡N, the radical center remains planar. For the discussion of these effects, we consider those CH_2X radicals whose substituent X has a lone pair or is an unsaturated group with a HOMO-LUMO system that can interact significantly with the singly occupied radical orbital.

Table XI. π-Orbital Energies (au) of CH_2X Radicals at the Optimized ($\alpha \neq 0$) and Planar ($\alpha = 0$) Conformations[a]

Radical	α, deg	π_α	π_β	π_α*(HOMO)
CH_2O^-	0	−0.2631	−0.0899	+0.0094
	27	−0.2574	−0.0919	+0.0077
CH_2OH	0	−0.5921	−0.5012	−0.3326
	28	−0.5914	−0.5032	−0.3453
CH_2SH	0	−0.4850	−0.3877	−0.3113
	10	−0.4781	−0.3836	−0.3199
CH_2F	0	−0.6916	−0.6261	−0.3915
	29	−0.6953	−0.6247	−0.4056
CH_2Cl	0	−0.5268	−0.4611	−0.3796
	21	−0.5236	−0.4609	−0.3832

[a] 4-31G computations.

The radicals subjected to analysis were CH_2O^-,[33] CH_2OH, CH_2F, CH_2SH, CH_2Cl, $CH_2C{\equiv}CH$, $CH_2C{\equiv}CF$, and $CH_2C{\equiv}N$, for which the results of nonempirical SCF-MO computations have been presented in the previous section.

For the radicals in which the substituent X is a heteroatom, the methylene group is nonplanar, and it can be seen that first-row heteroatoms (O^-, OH, F) cause greater pyramidalization of the adjacent carbon center than second-row heteroatoms (SH, Cl). For the radicals in which the substituent is an unsaturated group, the radical center remains planar.

An important feature of the results is that the π-electron occupancy of the radical is such as to place two electrons in a π bonding orbital and one electron in a π antiboding orbital (X = O^-, OH, F, SH, Cl) or π nonbonding orbital (X = CN, C≡CH, C≡CF).

In addition, the π orbital occupied by a single electron is the HOMO. Typical energy values of the occupied π MO's for planar and pyramidal heteroatom-substituent radicals are given in Table XI.

It is possible to provide a rationalization of these results in terms of two equivalent approaches: (a) an "energy" approach, which examines the variation of the stabilization energy that results from mixing of the singly occupied radical orbital Ψ with the MO's of the adjacent substituent as the geometry at carbon is changed from planar to pyramidal; (b) a "charge transfer" approach, which examines the change in bonding between carbon and the adjacent substituent as the radical center is made nonplanar.

We shall first illustrate the energy approach. The single electron which occupies a p_z carbon AO in the planar structure occupies an sp^3 carbon AO in the pyramidal structure. On the basis of valence state orbital ionization energies,[34] an sp^3 carbon AO is more stable than a p_z carbon AO by 3.23 eV. However, the gain in energy which results from rehybridization at carbon is counterbalanced by a weakening of the CH bonds and an increase in the nuclear-nuclear repulsion,[35] but in those terms the different effects of unsaturated and heteroatom substituents upon the geometry at carbon are not easily rationalized. Therefore, a better approach seems to be to consider that the actual geometry adopted by a CH_2X radical will be that which maximizes the stabilizing interaction between the singly occupied radical AO and the MO's of the substituent. This criterion will,

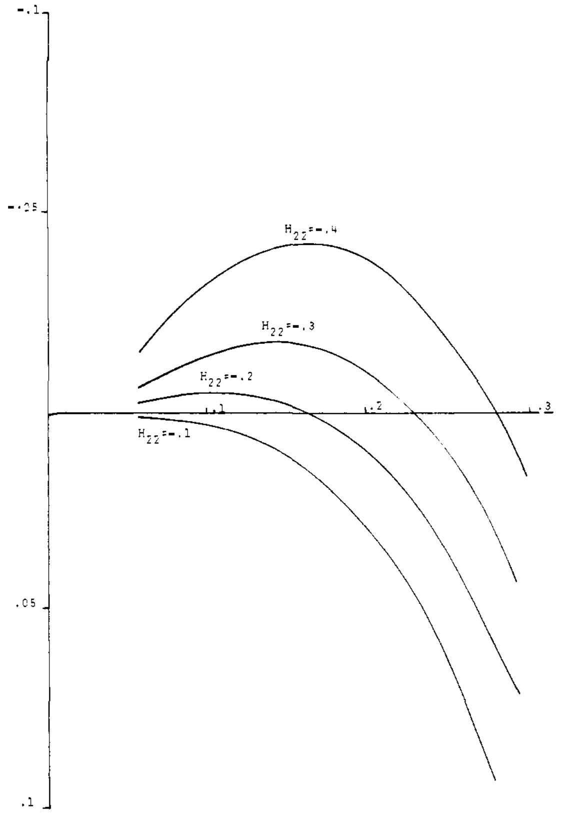


Figure 4. Interaction energy (IE) vs. overlap (S) for a fixed value of H_{11} (−0.5 au) and representative values of H_{22}.

therefore, be used to compare the effects of unsaturated and heteroatom substituents upon the geometry at carbon.

Pyramidalization must result in *decreased* p_C-π and p_C-π^* overlap (in the case of an unsaturated substituent) or *decreased* p_C-X overlap (in the case of a heteroatom substituent). On the other hand, because of the lowering of the energy of the singly occupied radical orbital which accompanies pyramidalization, this process will *strengthen* the p_C-π interaction and *weaken* the p_C-π^* interaction when X is an unsaturated group, but when X is a heteroatom, only one interaction (p_C-X) is involved, and this is strengthened. It follows immediately that the combination of effects is such as to make a radical such as CH_2-X (X = unsaturated substituent) more planar than a radical such as CH_2X (X = heteroatom).

We now adopt the "charge transfer" approach and consider first a CH_2-X radical where X is a first- or second-row heteroatom. According to the interaction diagram of Figure 2a, the radical has in its planar geometry two bonding and one antibonding π electrons. Thus, one can anticipate that a geometric distortion which could reduce the effective number of π electrons will have a beneficial effect by virtue of eliminating part of the antibonding interaction due to the third π electron of the radical CH_2-X. With substituents like O^-, OH, SH, etc., i.e., heteroatoms, the reduction in the antibonding character in Ψ_2 is obtained through a pyramidalization of the methylene group. The pyramidalization lowers the symmetry point group of the radical, permitting different basis functions to mix with the $2p_z$ atomic orbital (AO). For example, in a pyramidal CH_2 radical center, the singly occupied orbital is no longer a pure $2p_z$ AO; it also contains a contribution from the 1s AO's of the two hydrogen atoms as well as the $2p_x$ and 2s AO's of the carbon. In other words, pyramidalization of the methylene group causes a charge shift from the carbon $2p_z$ AO to other carbon AO's of different symmetry (2s, 2p) and also to the two hydrogen atoms. The result of this charge shift is a reduction of the $2p_z$ orbital population and, therefore, a reduction of the antibonding character of Ψ_2.

The effect of pyramidalization on the population of the individual MO's of the system provides additional insights. Here, one expects that the amount of charge transfer from C_{2p_z} to C_{2p_x} and C_{2s} that is contributed by each MO will be proportional to the square of the carbon coefficient of the appropriate MO. Figure 2a illustrates that the bonding MO will contribute to the total charge transfer less than the antibonding MO. For example, the decrease in the bonding character of Ψ_1 will be less than the decrease in the antibonding character of Ψ_2 leading to improved net π bonding. This effect will become increasingly pronounced as the coefficients of C_{2p_z} and X_{2p_z} diverge in magnitude, a situation which obtains as the electronegativity of X increases. Hence, the greater the electronegativity of X, the greater the pyramidalization of the radical center. In other words, the "charge transfer" approach indicates clearly that electronegativity arguments are inexorably connected with the principal orbital interaction which obtains in CH_2-X radicals, viz., that between the odd electron and the heteroatom lone pair. This interpretation is clearly supported by the π-overlap populations between the methylene carbon and the adjacent atom listed in Table X. At this point it should be emphasized that the charge transfer approach supports the idea that the relative effect of substituents upon the stability of a radical center will not be crucially dependent upon conformations. Partly as in the case of the "incipient" radical, the occupancy of the radical center may be one or less than one depending upon the degree of planarity of the radical center and, as long as deviations from unity are not overwhelming, the relative stabilizing effects of substituents can be treated on a uniform basis.

The theoretical analysis that has been presented involves neglect of overlap; this simplifying assumption does not affect qualitative the various trends that have been discussed. On the other hand, inclusion of overlap leads to additional insights and provides for a better theoretical model. The importance of inclusion of overlap in theoretical treatments dealing with three-electron interaction problems has been stressed by Hudson[36] and Salem.[37] In the following section, we illustrate how inclusion of overlap in the theoretical analysis can lead to a better understanding of the nature of three-electron interactions and their control of conformational preferences.

We consider the radical CH_2-X, where X is a heteroatom such as F, Cl, OH, SH, etc., as the prototype system to illustrate the key principles involved. Attention is focussed upon the interaction between the heteroatom lone pair, X, and the singly occupied carbon orbital p_C. The magnitude of this interaction can be computed by solving the secular determinant for the two-orbital problem *including overlap*.

$$\begin{vmatrix} H_{11} - \mathrm{E}S_{11} & H_{12} - \mathrm{E}S_{12} \\ H_{21} - \mathrm{E}S_{21} & H_{22} - \mathrm{E}S_{22} \end{vmatrix} = 0 \qquad (9)$$

The various symbols have their usual meaning with 1 referring to the heteroatom orbital and 2 to the carbon orbital, and with the interaction matrix element H_{12} taken to be proportional to the overlap integral S_{12} ($H_{12} = KS_{12}$). The interaction energy, IE, is then given by the expression

$$\mathrm{IE} = 2E_1 + E_2 - 2H_{11} - H_{22} \qquad (10)$$

A negative IE amounts to stabilization energy and a positive IE to destabilization energy. The quantity IE is plotted as a function of overlap for a fixed H_{11} and representative values of H_{22} in Figure 4. Two important conclusions are reached on the basis of these plots.

(i) For constant energy separation the stabilization energy reaches a maximum at a value of the overlap denoted by S_m, and then declines, eventually becoming destabilization energy as overlap increases. This is a result which can be obtained *only when overlap is included in the analysis*, and it points out that one can increase stabilization (or decrease destabilization) by reducing the overlap between the two interacting orbitals. Specifically, if the overlap between the carbon $2p_z$ orbital and the lone pair of the heteroatom is sufficiently greater than S_m, then pyramidalization of the carbon center can lead to reduced overlap and greater stabilization (or smaller destabilization), assuming that the energy separation of the interacting levels remains constant. In the case of neglect of overlap, the quantity IE for the interaction of a doubly occupied orbital ϕ_i and a singly occupied orbital ϕ_j which are nondegenerate is given simply by the expression[38]

$$\mathrm{IE} = \frac{H_{ij}^2}{E_i - E_j} = \frac{K^2 S_{ij}^2}{E_i - E_j} \tag{11}$$

This quantity is always negative and amounts to a stabilization energy, e.g., the three-electron interaction is predicted to give rise to π bonding between the two centers.

(ii) For constant overlap, the stabilization energy increases if the energy separation between the interacting levels decreases. This result is also obtained when overlap is not included in the analysis. Pyramidalization leads to a decrease in the energy separation of the interacting orbitals, since the energy of an sp^3 orbital is 3.25 eV lower than that of a p_z orbital.[34] For example, upon pyramidalization, the energy of the singly occupied carbon $2p_z$ orbital tends to approach the energy of the heteroatom lone pair. Hence pyramidalization can lead to greater stabilization assuming that overlap remains constant.

The simultaneous variation of the energy of the singly occupied carbon AO and overlap between the carbon AO and the heteroatom lone pair orbital will in most cases lead to better π bonding. Figure 4 clearly shows that, excluding cases where a geometry distortion results in a slight reduction of the energy separation of the energy levels and a very large reduction of the overlap,[39] pyramidalization of the radical center will result in increased stabilization or decreased destabilization. For example, in Figure 4, the change in the stabilization energy upon pyramidalization which changes H_{22} from -0.3 to -0.4 and reduces the overlap from 0.2 to 0.1 will be given by the difference of the ordinates of points A and B. Since point A lies on the curve for $H_{22} = 0.3$ and B lies on the curve for $H_{22} = -0.4$ and always to the left of point A, it will always be true that for overlap of chemical significance, e.g., $S > 0.05$, the stabilization energy will increase upon pyramidalization.

Similar conclusions are reached when H_{11} is fixed at -0.4 or -0.3 au. We conclude that, in radicals of the type CH_2–X, pyramidalization will result in increasing stabilization, converting destabilization to stabilization or decreasing destabilization depending upon where the planar and pyramidal structures lie on the three-dimensional surface of IE as a function of H_{22} and S_{12}. The preferred geometries of CH_2–X radicals as well as the differences in the C_{p_z}–X_{p_z} overlap populations between the planar and the most stable pyramidal forms are shown in Tables III–VIII. The results demonstrate unequivocally that pyramidalization leads to better π bonding by reducing the π antibonding character between the two centers. An INDO calculation, on the same radicals at the *ab initio* optimized geometry, gives quite different results. In this case, neglect of overlap assures that the three-electron interaction will be net bonding as found by the actual INDO calculation. Furthermore, the balance between the numerator and denominator terms in the second-order perturbation (eq 11) leads to increase in bonding upon pyramidalization. In other words, both the overlap and the energy separation of the interacting orbitals decrease but the rate of change of the latter term is faster than that of the former and it is the energy proximity of the interacting levels which ultimately dictates the preferred conformation. Our conclusions concerning the origin of pyramidalization in radicals of the type CH_2–X at the two levels of theory are summarized below: (a) theory excluding overlap, pyramidalization occurs in order to maximize a stabilizing three-electron interaction; (b) theory including overlap, pyramidalization occurs in order to maximize a stabilizing three-electron interaction or minimize a destabilizing three-electron interaction.

The above discussion illustrates a point that may not have been obvious, i.e., that a two-center three-electron bond may not be a bond at all but rather an antibond. The π overlap populations of Table VIII show that this is indeed the case for CH_2OH, CH_2SH, CH_2F, and CH_2Cl in their stable conformations. This could be a basis set dependent result. It should be pointed out that although the one-electron analysis matches the ab initio trends, one cannot definitely exclude the possibility that this agreement is *coincidental* and is due to one particular choice of approximating the interaction matrix element; i.e., H_{ij}. However, on the basis of previous experience, we consider this possibility as unlikely.

The experimental results of Table I which show that all substituents stabilize a radical center might be construed as evidence in favor of the above suggestion. However, it must be noted that the experimental results refer to "incipient" radicals while the calculations refer to "free" radicals. Furthermore the progressive substitution of a methyl radical by fluorine is known to lead to a decreasing stabilization of the radical center and *eventual destabilization in the case of* CF_3. Typical C–H bond dissociation data are shown below.[40]

H_3C–H	104.0 kcal/mol
FH_2C–H	101.0 kcal/mol
F_2HC–H	101.0 kcal/mol
F_3C–H	106.0 kcal/mol

Thus, we suggest that a study of substituent effects upon the stability of *free* radicals may well reveal that certain heteroatomic groups have a destabilizing influence rather than a stabilizing one as is the commonly accepted viewpoint.

Finally, the origin of the rotational barrier of CH_2–XH, in which X = O, S, can also be understood in a simple way in terms of the OEMO theoretical model. In conformation **1**, the interaction between the singly occupied carbon AO with the adjacent Xp_z lone pair is more stabilizing (or less destabilizing) than the interaction between the singly occupied carbon AO with the adjacent HOMO of the XH fragment in conformation **2** due to the lower ionization potential of the Xp_z lone pair as compared with the ionization potential of the HOMO of the XH fragment.

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(1) (a) Universita di Bologna; (b) University of Washington; (c) Queen's University.

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(39) The values of H_{11}, H_{22}, and S_{12} utilized in this study were chosen in such a way as to correspond closely to situations of chemical significance. Thus the values of H_{11} were fixed at −0.5, −0.4, and −0.3 au because the ionization potentials of various heteroatom lone pairs range between 0.579 and 0.371 au. The values of S_{12} for the heteroatoms studied range between 0.1 and 0.2. Finally, the values of H_{22} typically range from −0.36 au (planar radical) to −0.48 au (tetrahedral radical).

(40) See footnote *b* of Table I.

The Temperature Dependence of Carbon-13 Nuclear Magnetic Resonance Shifts. Limiting Factors and Stereochemical Applications[1]

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Abstract: With conformationally homogenous alicyclic hydrocarbons, a linear deshielding of up to 0.006 ppm/K with increasing temperature is observed. In contrast upfield shifts as large as −0.02 ppm/K are found with functionally substituted carbon atoms. These findings are compared with solvent dependences and discussed mainly on the basis of square electrical field effects. In sterically inhomogenous compounds carbon atoms which are involved in gauche/trans equilibria are characterized by upfield shifts nonlinear with temperature. The temperature dependence can be used for stereochemical and ^{13}C NMR spectroscopic assignments, as illustrated with *n*-pentylcyclohexane. The methyl carbon shifts in *n*-butane are computer simulated with gauche/trans differences of 300 to 700 cal/mol (enthalpy) and of 2.5–4.7 ppm (shifts). Other hydrocarbons show shift dependences for which empirical parameters are given, reflecting the number of gauche conformations occurring.

Although chemical shifts are known to be intrinsically temperature dependent,[2] there is a paucity of pertinent data on ^{13}C NMR shieldings.[3] For many molecules carbon shifts can be determined more accurately than proton shifts; knowledge of their temperature dependence is a prerequisite particularly in investigations of equilibria and rates of chemical reactions which are fast on the NMR time scale. Besides holding promise for practical applications including