unstirred reaction.

Relative Absorption. Each of polymers 1–4 (0.10 g) was added to separate 50-ml culture tubes containing 5.0 mL of aqueous saturated sodium chloride plus 5.0 mL of a toluene solution which was 0.125 M in *n*-decyl methanesulfonate and 0.0625 M in *n*-hexadecane (internal standard). After the resulting mixtures were stirred at room temperature for 2 h, 1-μL aliquots were withdrawn from each organic phase and analyzed by GLC. In all cases, the concentration of mesylate was identical with that found in the absence of polymer.

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Structure of 1,2-Difluorocyclopropane and the "Cis Effect"

Anne Skancke[1] and James E. Boggs*

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. Received July 28, 1978

Abstract: The geometries of *cis*- and *trans*-1,2-difluorocyclopropane have been obtained by single determinant ab initio geometry optimization at the 4-21 level, using the gradient method in which all internal coordinates are optimized simultaneously. The corresponding 1,2-difluoroethylenes have been reexamined for comparison. Analysis of the geometries and Mulliken population analysis support the explanation given by Bingham for the "cis effect", the general greater stability of the cis isomer of haloethylenes. The same mechanism is shown to interpret the greater stability of the trans isomer of 1,2-difluorocyclopropane. Delocalization is greater in the isomer having the straighter path connecting the substituents and leads to destabilization of that form.

Introduction

Disubstituted ethylenes are generally more stable in the trans than in the cis form, as illustrated by 2-butene, for example. Eyring and co-workers[2] have suggested that a principle of minimum bending of localized and delocalized orbitals plays a major role in determining the fine structure of molecules. Electrons seek the smoothest paths. In quantum mechanical terms, the effect can be interpreted in terms of electron kinetic energy. The principle is, for instance, applied in explaining the so-called "trans effect" in the dissociation of certain metal complexes. For those molecules, the dissociation constants for the trans forms are higher, a fact which is explained by a more favorable pathway in the dissociation of this form. Eyring and co-workers believe that this principle is also responsible for "the usually greater stability of trans over cis disubstituted ethylenes".

There is, however a substantial amount of experimental evidence that, for a number of 1,2-dihaloethylenes, the cis form is more energetically favorable than the trans form. Typically, *cis*-1,2-difluoroethylene is more stable than than the trans form by 1080 ± 120 cal/mol.[3] Even more striking is the difference in electronic energies between *cis*- and *trans*-difluorodiazine, the cis form being in this case more stable by 3050 ± 400 cal/mol.[3]

Several authors have commented on this "cis effect", and it seems clear that one has to take a combination of different effects into account. As pointed out by Craig and co-workers,[3] the F···F distance for *cis*-1,2-difluoroethylene lies on the repulsive side of the van der Waals potential curve, and Binkley and Pople[4] estimate the Coulomb repulsion to be 1.2 kcal/mol lower in *trans*-1,2-diethylene than in the cis form, suggesting that the extra stabilization of the cis form must amount to about 2 kcal/mol.

There are two fundamentally different sources to the possible factors leading to this so-called "cis effect". One is the various factors leading to an extra stabilization of the cis form, the other the possible sources leading to a destabilization of the trans form. We will list the possible sources and refer to previous articles in the field for a more extended discussion.

Three different types of attractive forces have been proposed: contribution of resonance structures, a $p\pi$ attraction, and a $p\sigma$ attraction. The first has been proposed by Pitzer and Hollenberg[5] and is based on contributions of resonance structures of the kind $X^-;CHCH=X^+$. This type of structure would lead to a net attraction between the halogens and should cause a relatively long C–C bond. The other cis stabilizing effects are based upon overlap between fluorine–fluorine lone pairs. Hoffmann and Olofson[6] have rationalized the stability of *s*-
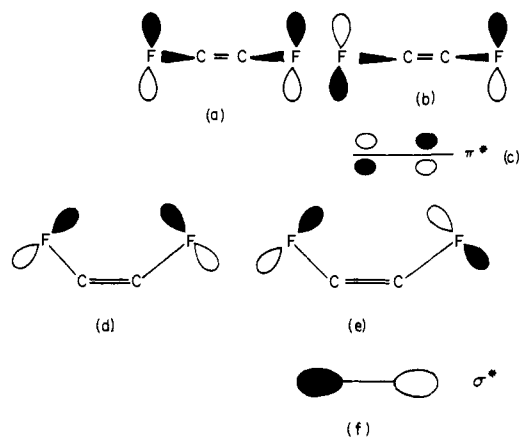
Figure 1. Fluorine lone pair orbitals in 1,2-difluoroethylene.

cis-butadiene dianion by a positive overlap between lone pairs. Epiotis[7a] used a similar argument for explaining the stability of *cis*-1,2-difluoroethylene. Considering only the π set of lone pairs, he argued that the system can then be considered isoelectronic with butadiene dianion. The forms a and b in Figure 1 represent the symmetric and antisymmetric combination of the π lone pairs as viewed from the side. It is seen that the symmetry of b permits interaction with the antibonding π* orbital (c) so that form a becomes more important than b, leading to a positive pπ overlap. In a similar way, form e of the σ lone pair is seen to interact with σ* (f) increasing the relative weight of form d which gives an overlap between these σ type orbitals. These views have recently been extended and modified.[7b] Support for the original qualitative idea based on one-electron molecular orbital treatment has come from ab initio SCF calculations indicating a dominating π type attraction in the cis form.[7c]

In a recent paper Bingham[8] proposes that the main effect responsible for the "cis effect" of ethylenes is an effect which tends to destabilize the trans form rather than provide extra stabilization for the cis form. In short, this is an unfavorable conjugation effect which stems from the fact that the conjugation in these cases is between two *filled* orbitals (halogen lone pair and π bond). The interaction gives rise to two new orbitals, one bonding and one antibonding, the latter being more antibonding than the former is bonding. Consequently, the total interaction is energetically unfavorable, in contrast to interaction in hydrocarbon polyenes. This would be equally true for both the cis and trans forms but, following Eyring's argument,[2] the delocalization is greater in the trans form. Consequently this form will be the less stable one.

A confirmation of the greater delocalization of the trans form is given by photoelectron spectra.[9] The NMR ^{13}C chemical shifts reported[10] for the difluoroethylenes may also reasonably be interpreted as being due to larger delocaization of the trans species. Force constants,[11] calculated on the basis of vibrational frequencies[12] and electron diffraction structures,[13] give a good all-over consistency between the values for the cis and trans species, but a much larger $f_{CF,CF}$ is interpreted as being due to more delocalization of the trans molecule.

As a final point in this connection we would mention one point in the electron diffraction data[13] which appears to be relevant for our discussion. The structural data are given in Table I. The CCF angle is determined to be 122.5° for the cis form and 119.8° for the trans form. This difference should be outside the limits of error, and the trend should have been in the opposite direction if a noticeable stabilization due to attractive potentials in the cis form were the main explanation for the "cis effect". Analysis of the rotational structure of an infrared band has also indicated that the CCF angle is larger in the cis isomer.[12]

Although the "cis effect" was first recognized for ethylene derivatives, similar phenomena have been observed for saturated molecules which are ethane derivatives. Realizing the resemblance of selected orbitals of these systems to true π orbitals, it has been suggested that the same mechanisms may be operative also for these systems.[8] In this connection, we should remember the conformational preference for cisoid rather than transoid forms of 2,2'-dihalobiphenyls.[14,15] It has been proposed by Bastiansen[15] that London-type dispersion forces[16] are responsible for the structural preferences for this series of molecules. In view of the similarities of the molecules and the fact that the prevailing forms in all cases have halogen–halogen distances on the repulsive side of the van der Waals potential function, we propose that the 2,2'-dihalobiphenyls also belong to the class of molecules displaying the "cis effect" and believe that the factors responsible for the structural preferences should be the same in all cases.

Calculation of the energy difference between *cis*- and *trans*-difluoroethylene has proved to be singularly difficult, but Binkley and Pople,[4] using an extended basis set and geometry optimization, have managed to reproduce correctly the sign of the energy difference within the Hartree–Fock approximation. The magnitude of the difference was not nearly large enough, being only 0.26 kcal/mol for their most extensive basis set compared with the experimental value of 1.08 kcal/mol.[3] They have also carried out correlation corrections using second-order Møller–Plesset perturbation method for two smaller basis sets (4-31G and 6-31G). Since the correlation contribution remained nearly independent of basis, an estimated correction for the largest basis set would give a total cis–trans difference of 0.63 kcal/mol.

An anomaly in the picture of the "cis effect" is found in recent work on 1,2-difluorocyclopropane. In view of the well-known unsaturated properties of the cyclopropane ring, this compound would be expected to be very similar to 1,2-difluoroethylene. However, a recent experimental determination[17] based on thermodynamic measurements[3] and vibrational spectra[17] shows the trans form of 1,2-difluorocyclopropane to be more stable by 2.8 ± 0.2 kcal/mol, a result which contrasts sharply with the previously mentioned examples. We have therefore investigated the isomeric forms of this molecule, hoping that information about the sources of the energy difference in this "abnormal" example may also shed more light on the general question. We have carried out complete geometry optimizations, since consistent geometrical models are essential in discussing small energy differences, and, furthermore, any difference in the structures of these isomers may give a clue to the solution of our problem. In addition, we have carried out some calculations on the 1,2-difluoroethylenes where the cis form is found experimentally to be more stable. Although these molecules have been extensively studied by Binkley and Pople,[4] we found it worthwhile to see what effect a simultaneous variation of geometric parameters might have on the relative energies and the fine details of the structures.

Method of Calculation

We have used the computer program TEXAS written by Péter Pulay.[18] This is a gradient program[19] which enables simultaneous optimization of all internal coordinates. Most of the calculations have been carried out using a 4-21 basis set,[20] which is considerably less time consuming than the widely used 4-31G set and which has been shown in a number of previously reported cases to predict geometries with equal accuracy. It is to be noted, however, that the 4-21 basis set does not describe energies as well as the 4-31G, and in some of the calculations we therefore used the latter set. Also, the 4-31G basis set is thought to describe overlap interactions between distant fluorine lone pairs better, the smaller set being quite "tight" on

Table I. Experimental and Theoretical Geometries of the 1,2-Difluoroethylenes[a]

	cis-1,2-difluoroethylene					*trans*-1,2-difluoroethylene			
	exptl			present work		exptl		present work	
	E.D.[b]	M.W.[c]	4-31G[d]	4-21	4-31G	E.D.[b]	4-31G[d]	4-21	4-31G
C_1-C_2	1.311	1.324	1.302	1.301	1.303	1.320	1.304	1.301	1.300
C—F	1.332	1.337	1.362	1.365	1.361	1.338	1.366	1.369	1.370
C–H	1.100		1.063	1.064	1.069	1.088	1.066	1.064	1.062
<CCF	122.5	122.9	122.6	122.6	122.4	119.8	119.5	119.6	120.0
<CCH	127.0	121.16	123.7	122.8	123.7	125.0	126.0	125.6	125.2

[a] Distances in ångstroms, angles in degrees. [b] Reference 14. [c] Reference 21. [d] Reference 4.

the fluorine atoms. For all of the calculations, we have carried out geometry optimization until the displacements were less than 0.002 Å or 0.35°. This should not be regarded as an upper limit on the absolute error, but rather a measure of the relative consistency of the results.

Results and Discussion

1. 1,2-Difluoroethylenes. The data obtained by simultaneous optimization of all geometric parameters are shown in Table I. In this case, the difference between the results of this procedure and the results obtained previously[4] using the same basis set but with serial optimization are not large, although several of the differences are slightly outside the convergence limits and may be significant. The agreement between the data from the 4-31G and the 4-21 basis sets is extremely good and illustrates again the quality of the 4-21 set for geometry optimization.

The relative energy $E_{trans} - E_{cis}$ obtained from the 4-21 basis set is −1.4 kcal/mol compared to the experimental value of +1.08 kcal/mol. As mentioned previously, double ζ basis sets have not been able to reproduce even the correct sign of this energy difference. Using the 4-31G basis set, we calculate an energy difference of −1.16 kcal/mol. Compared with the value of −1.32 kcal/mol reported by Binkley and Pople[4] using serial rather than simultaneous optimization, there is a slight improvement accompanying the almost negligible difference in structure obtained by our method. This might be a slight indication that an even larger fraction of the observed energy difference is to be found within the Hartree–Fock approximation than the values reported by Binkley and Pople.

It is seen that the optimized C–F distances are consistently too large as compared to the experimental ones. It is well-known that these relatively modest basis sets describe polar bonds rather poorly, and it is to be expected that an increase in the basis set would decrease the C–F bond lengths. It is important to note, however, that the overestimation is consistent so that comparisons between molecules may still be valid.

Angles are known to be more accurately determined than are polar bond lengths by calculations such as these. The agreement shown in Table I for the CCF angles is excellent throughout. There is, however, a considerable discrepancy between the 4-31G values of 123.7° and the electron diffraction value of 127° for the CCH angle. Fortunately, there is a microwave investigation[18] of the cis form which has determined that angle to be in the range of 121–122° depending on other assumptions made in the analysis. The value of 121.16° shown in Table I is that preferred by Laurie.[21] These values are in agreement with our calculated angles and, more important for the main question behind our present investigation, give us additional reason to believe that the larger CCF angle reported for the cis form than the trans form is real. This difference does not seem to be compatible with an extra attraction between the cis halogens, as any such attraction, particularly the resonance type suggested by Pitzer and Hollenberg[5] mentioned in the Introduction, should tend to decrease this angle. It seems that

Table II. Gross Atomic Charges of the 1,2-Difluoroethylenes (4-31G Basis Set)

atom	*cis*-	*trans*-
C	0.2577	0.2572
F	−0.4241	−0.4323
H	0.1664	0.1757

Table III. Distortion Coordinates for the 1,2-Difluorocyclopropanes (deg)[a]

	cis-	*trans*-
ϕ_{rock}FCH	−1.94	2.2
ϕ_{rock}HCH	−3.8	0
ϕ_{wag}FCH	0.62	1.05
ϕ_{wag}HCH	0	0
ϕ_{twist}FCH	−1.04	1.15
ϕ_{twist}HCH	0	−1.54

[a] Definition of distortion angles: $\phi_{twist} = (\alpha_{73} - \alpha_{71}) + (\alpha_{51} - \alpha_{53})$; $\phi_{wag} = (\alpha_{73} + \alpha_{53}) - (\alpha_{71} + \alpha_{51})$; $\phi_{rock} = (\alpha_{73} + \alpha_{71}) - (\alpha_{53} + \alpha_{51})$. For definition of α_{ij} see Figure 3.

any contribution from this type resonance structure must be very small. Also, the Pitzer and Hollenberg type resonance structure should produce a slightly longer C–C bond for the cis form. If any trend concerning the C–C bond in the cis and trans forms can be read from the material in Table I, it is, however, rather in the opposite direction.

The gross atomic populations shown in Table II give an indication of a somewhat more polar bonding in the trans than in the cis molecule. This picture is, however, modified and complicated when the total charge is split into spatial components. The charges in the z direction are identical in the two species, indicating identical π systems.

2. 1,2-Difluorocyclopropanes. The main geometrical features resulting from our calculations are shown in Figure 2. Table III gives the deviations from symmetry of the methylene and FCH groups. Since no experimental determination of molecular structure has been done for either of these two molecules, we find that the optimization has some value in itself apart from the discussion of the energy differences. In view of the findings for the ethylene derivatives, we believe that the C–F bonds are too long by about 0.03 Å, but the relative magnitudes of the various parameters should be determined with a precision comparable to that which can be expected from good experiments. It is these relative values and differences which are of importance here.

In our previous studies[22] of cyclopropyl fluoride and 1,1-difluorocyclopropane we found the C–C bond adjacent to the substituent shorter than the cyclopropane C–C bond length, while a lengthening was found for the C–C bond opposite the substituent. The effect seemed to be additive within the range of our investigation. The calculated C–C bond length for cyclopropane using the 4-21 basis set is 1.514 Å, and, as is seen in Figure 2, both types of C–C bonds are shortened somewhat
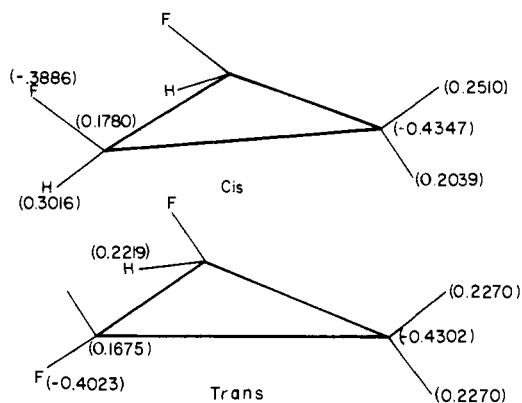
Figure 2. Gross atomic charges for (a) *cis-* and (b) *trans-*1,2-difluorocyclopropane.
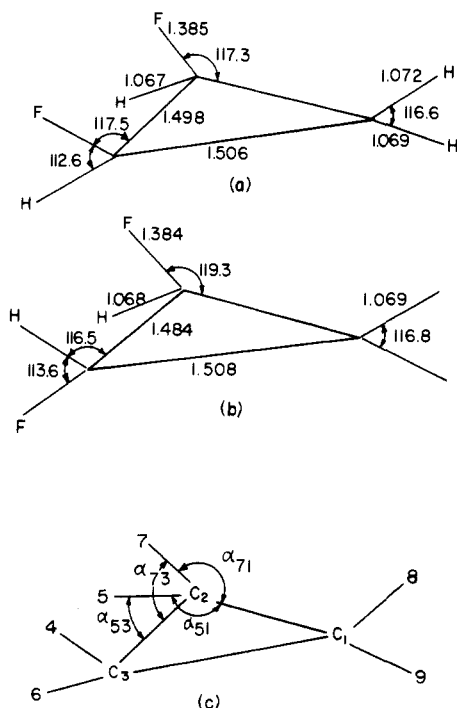

Figure 3. Computed geometries for (a) *cis-* and (b) *trans-*1,2-difluorocyclopropane. (c) Definition of angles as used in Table III.

compared to the parent compound, but C_2-C_3 more than C_1-C_2 (C_1-C_3). This would be expected simply from the assumed additivity of the effect, since the C_2-C_3 bond is between two substituted carbon atoms and the C_1-C_2 (C_1-C_3) bond adjacent to only one substituted carbon atom. This general trend in the structures has been predicted in an ab initio study by Allen and co-workers.[23]

Inspection of Figure 2 reveals that, whereas the C_1-C_2 (C_1-C_3) bond is practically identical for the two molecules, there is a marked difference in the C_2-C_3 bond, the longer being in the cis form. Most other geometrical parameters seem to be nearly identical for the two molecules. If it is remembered that the basis set used seems to overestimate C–F bond lengths by about 0.03 Å, as demonstrated with the difluoroethylenes, the computed C–F distance is quite reasonable compared with the value of 1.354 Å found for *cis-*1,2,3-trifluorocyclopropane in a recent microwave investigation.[24]

For those cyclopropane derivatives where angular distortions have been calculated, we have for all substituents containing lone pairs observed a tendency for the methylene groups to bend toward the lone pair. This also seems to be the case for

these molecules. For instance, the rocking motions for the cis form (given in Table III) tend to bend the fluorines toward the H_8 atom. The total energies are found to be -313.9687 and -313.9625 au for the trans and cis forms, respectively.

The computed energy differences are 3.9 kcal/mol (the trans form being more stable), a result we consider to be in fair agreement with the experimental value of 2.8 ± 0.2 kcal/mol, and the very fact that the energy difference is reproduced that well within the Hartree–Fock limit suggests that interactions involving unoccupied antibonding orbitals as illustrated in Figure 1 are not of primary importance as the cause of the energy difference for this system.

The shorter C_2-C_3 bond of the trans form could be an indication of a greater double bond character for that bond, or, in other words, a more delocalized cis form. A delocalization of the cis form would imply some positive charge (or, more correctly, less negative charge) on the fluorine atoms. This is indeed in accordance with the longer C_2-C_3 bond and with opening of the angle $C_3C_2F_4$ for the cis form. The identity of the C–F bonds lengths in the two molecules certainly seems quite puzzling, but the overlap populations for the cis and trans forms are 0.42 and 0.39, respectively, and this might be an indication of somewhat greater partial double bond character of the C–F bond in the cis form.

Conclusions

The main contribution to the energy differences between cis and trans forms of 1,2-difluoroethylene and 1,2-difluorocyclopropane is reproduced within the Hartree–Fock limit. In the former case, the cis form is more stable, while the trans form is the more stable in the latter system. Nevertheless, we believe that both of these systems are illustrations of the same effects and can be interpreted on a common basis.

For the 1,2-difluorocyclopropanes, both calculated optimized geometries and results from Mulliken population analysis point to a larger delocalization of the charges of the cis isomer. This effect is an example of the unfavorable delocalization suggested by Bingham.[8] In the example at hand, this leads to a more stable trans form. We believe that the higher degree of delocalization in the cis isomer is due to the possibility of a straighter electron pathway in that form in accordance with the suggestions of Eyring.[2]

The fine details of the picture are somewhat more complicated for the 1,2-difluoroethylenes, but the basic explanation is similar. Existing structure data, both from electron diffraction and from the optimized theoretical geometries, point to a larger delocalization of the trans form, again the isomer displaying the straighter electron pathway. This leads to a prediction that the cis form would be the more stable, in complete agreement with observation. However, the rather complicated picture furnished by the population analysis of this system, as well as the larger correlation energy of the cis form, seems to indicate that some form of steric attraction may be present in this isomer, thus providing some additional degree of stabilization compared to the trans form.

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Photoelectron Spectroscopy of Methyl, Ethyl, Isopropyl, and *tert*-Butyl Radicals. Implications for the Thermochemistry and Structures of the Radicals and Their Corresponding Carbonium Ions

F. A. Houle and J. L. Beauchamp*

Contribution No. 5927 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125. Received December 8, 1978

Abstract: The first photoelectron bands of the series of simple alkyl free radicals CH_3, CH_3CH_2, CH_3CD_2, CH_3CHCH_3, and $C(CH_3)_3$ have been obtained. The adiabatic and vertical ionization potentials, respectively, are 9.84 ± 0.02 eV for methyl radical, 8.39 ± 0.02 and 8.51 ± 0.02 eV for ethyl radical, 8.38 ± 0.02 and 8.50 ± 0.02 eV for ethyl-*1,1-d_2* radical, 7.36 ± 0.02 and 7.69 ± 0.02 eV for isopropyl radical, and 6.70 ± 0.03 and 6.92 ± 0.03 eV for *tert*-butyl radical. The heats of formation of the corresponding carbonium ions are calculated to be 261.8 ± 0.5 kcal/mol for methyl cation, 219.2 ± 1.1 kcal/mol for ethyl cation, 187.3 ± 1.1 kcal/mol for isopropyl cation, and 162.9 ± 1.2 kcal/mol for *tert*-butyl cation. The implications of these data for the gas-phase proton affinity scale are explored. Band structure is resolved, and possible assignments are presented. The results are discussed in terms of the interactions of methyl groups with trigonal carbon radical and ion centers.

Introduction

Methyl groups bonded to a radical or positive ion center exert a profound influence on both structure and stability of the trigonal site. However, the nature and magnitude of the interactions involved differ markedly in the neutral and charged species. Photoelectron spectroscopy offers a means of probing these substituent effects in a direct way. The extent to which nuclear coordinates and force constants of the equilibrium ion and radical structures differ is reflected in the Franck–Condon envelope of the first photoelectron band. For example, consider the case of CH_3, the simplest alkyl radical. Removal of the unpaired electron to form CH_3^+ primarily affects the force constant of the out-of-plane bending coordinate,[1,2] as shown schematically in Figure 1. Both radical and ion are planar, and the first photoelectron band[3,4] reflects this by mainly consisting of a single sharp peak. The force-constant change produces small Franck–Condon factors for transitions to higher vibrational levels, with the selection rule restriction that $\Delta v = 2$. This rather simple situation changes markedly when methyl groups are substituted to form CH_3CH_2, CH_3CHCH_3, and $C(CH_3)_3$, and the first photoelectron bands of these radicals reflect these changes. In addition, ionization potentials taken together with heats of formation provide quantitative information on relative stabilities. When considered along with results of other experimental and theoretical studies, the photoelectron data allow a better understanding of the effects of methyl substitution in alkyl radicals and ions.

Previous studies utilizing electron spin resonance (ESR)

have probed the interaction of methyl groups with the unpaired electron on a carbon-centered radical. Electron spin densities can be derived from observed hyperfine splitting constants. The spin density on the radical center is found[5] to decrease in the order $CH_3 > CH_3CH_2 > CH(CH_3)_2 > C(CH_3)_3$. This trend is explained by the constraints on the unpaired electron to be orthogonal to the C–H orbitals of the same symmetry.

Extensive ESR studies have considered the effect of substituents on the conformations of radical centers. Electronegative substituents such as F and O are known to induce bending toward a pyramidal geometry. The mechanism for this is debated, however, and probably involves a combination of inductive and conjugative interactions.[6-8] The question remains as to whether CH_3 substituents also induce nonplanarity in radicals, and to what extent.[9-14]

Optical[15] and electron spectroscopy[3,4,16] have established that methyl radical is essentially planar. These results are supported by large basis set, configuration interaction calculations, which indicate that the out-of-plane bending coordinate has a single minimum.[1,2] Substitution of CH_3 for H to form CH_3CH_2 does not appear to change this situation appreciably. ESR data reveal essentially free rotation about the C–C bond,[5] consistent with a nearly planar trigonal carbon.[17] A Hartree–Fock geometry optimization using a large basis set[18] showed the radical center to be bent $6°$ out of plane. The two methyl groups in isopropyl radical are also freely rotating.[5]

The center of controversy rests on *tert*-butyl radical. Studies of the temperature dependence of the ^{13}C hyperfine splittings[12,13] indicate that the radical is nearly tetrahedral, with