Comparison of Calculated Electron Densities and Electron Paramagnetic Resonance Coupling Constants for σ Radicals

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Abstract: In an earlier paper we discussed procedures for correlating the output from extended Hückel theory (EHT) calculations with results from epr measurements.[2] In this article data are presented which illustrate the utility of these procedures when applied to hydrocarbon radicals in which the unpaired electron is in an essentially σ molecular orbital, *i.e.*, the unpaired electron is in direct contact with hydrogen nuclei. Excellent results are obtained for the correlation of calculated electron densities and electron–nuclear spin coupling constants for vinyl, cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexadienyl σ radicals. The effect of several variables in the EHT calculation on the correlations obtained were investigated, leading to a set of parameters which are best suited for the systems studied. In several calculations the geometry of the radical was varied and was found to have a profound influence on the results. Several predictions regarding the geometries of these radicals are suggested by these calculations.

Simple Hückel theory has been very successful in the correlation of calculated unpaired electron density on a carbon atom of a π system with the attached proton–electron spin coupling constant observed in the epr spectrum. The unpaired electron density on a given carbon is estimated by squaring this carbon p_z coefficient in the MO containing the unpaired electron, *i.e.*, by employing the net atomic population. McConnell has proposed[3,4] a mechanism whereby the unpaired spin in the π system can be transmitted to the protons which are orthogonal to the π system.

A brief attempt to extend these correlations to σ systems by carrying out extended Hückel-type (EHT) calculations on phenyl radical has not been successful and has led some authors[5] to conclude that this is a shortcoming in the extended Hückel calculation. In a previous article we pointed out that although the square of the coefficient of the p_z orbital could be used as an indication of unpaired electron density on a carbon in the π system, the square of the proton coefficient in a σ molecular orbital containing an unpaired electron could not be used as a reliable indication of the unpaired electron density on the proton. Instead, the total value of the wave function at the proton, $\Psi^2(0)$, must be used. A procedure for evaluating $\Psi^2(0)$ was reported. Even employing this procedure, we have been unsuccessful in attempting to fit the epr coupling constants of phenyl radical, but we have been successful in calculating the reported epr coupling constants of all other hydrocarbon σ radicals attempted.

Since the geometries of many of these radicals are not known, the calculations were made for a number of assumed geometries. The spin density and total energy results lead to consistent predictions of the geometries of several of these radicals. Several of our conclusions concerning geometry are contrary to those previously reported by Dixon,[6] who employed a molecular orbital approach based on a modified theory of hyperconjugation in his calculations. These discrepancies are discussed. Subsequent to the completion of this research Petersson and McLachlan reported[7] the results of noniterative EHT calculations on several σ radicals. Excellent agreement between these results and ours is obtained for the systems studied by both groups.

Calculations

$\Psi^2(0)$ Evaluation. The procedure employed for the $\Psi^2(0)$ evaluation has been reported previously.[2]

Extended Hückel Calculations. Hoffman-type EHT calculations[8] were carried out with essentially the previously described modifications.[9] Coulomb integrals, H_{ii}, are approximated by charge-adjusted valence-state ionization potentials.[10] The VSIP's were corrected for charge using

$$H_{ii} = H_{ii}^0 - Bq_i \qquad (1)$$

where H_{ii} is the adjusted Coulomb integral, q_i the charge, and B a constant particular to each element.[11] The Wolfsberg–Helmholz arithmetic mean[12] with $K = 1.75$ was used to estimate H_{ij}. Slater-type exponents have also been corrected for charge in this investigation.[13] An exponent of 1.2 was used for hydrogen. In the course of settling upon these parameters, several variations were attempted. Instead of the variable B described in eq 1, a constant value of 2.0 was also tried for all elements. Burns' exponents[14] were also employed and hydrogen exponents of 1.0 and 1.2 were both studied.

The calculated electron densities are multiplied by a scaling factor to convert them to coupling constants. This scaling factor, K_σ for σ radicals and K_π for π

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(1) Abstracted in part from the Ph.D. thesis of H. Petersen, Jr., University of Illinois, Urbana, Ill., 1966.

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radicals, can be determined by fitting the electron density Ψ_H^2 at one proton (or at a carbon for π systems) in the molecule to the measured proton coupling constant, A_H, *i.e.*, $K_\sigma\Psi_H^2 = A_H$ or $K_\pi\Psi_C^2 = A_H$. The reasonableness of the parameters used in the MO calculation is then assessed by the internal agreement of the calculated coupling constants (using a given value for K_σ or K_π) in a molecule containing more than one kind of proton. In addition to internal consistency, the transferability of a given value of K from one molecule to the next is an additional criterion. Of all the parameters we tried in the MO calculation, those described above as best met these requirements most satisfactorily.

Results and Discussion

Vinyl Radical. The numbering system and assumed geometry employed for the calculations on the vinyl radical are indicated in Figure 1. Except for the angle θ (see Figure 1) all bond distances and angles are assumed to be the same as those for comparable atoms in ethylene. Fessenden and Schuler[15] have reported a determination of the spectrum of this species in a 35:65 ethylene–ethane mixture at −180° (liquid). Based on the assumed geometry in Figure 1, one would expect eight lines from the three supposedly nonequivalent protons. Four lines split by 102.44 and 13.39 gauss are observed (if two of the protons were equivalent ($\theta = 180°$) six lines would be expected). This spectrum is rationalized[15] by assuming that the radical exists in two interconverting forms in which the α-proton flips between the position shown in Figure 1 and the form produced by a mirror image reflection in the xz plane. As a result of an intermediate rate for the inversion process, the central lines are broadened such that they are not detectable. An estimate of 2 kcal mole^{-1} is set as a minimum energy for the inversion barrier. This assumption is supported by the spectrum of 1-methylvinyl radical, which is locked in one configuration, and by a comparison of the spectra of C_2D_3 and C_2H_3. To obtain approximate magnitudes of the β and γ vinyl coupling constants, a further assumption is made that their magnitudes are in the same ratio as those of 1-methylvinyl radical, leading to 65 and 37 gauss for the β and γ positions. The α position is assigned the 13.39-gauss value. Values of 68, 34, and 16 have also been reported[16] for the β, γ, and α positions, respectively.

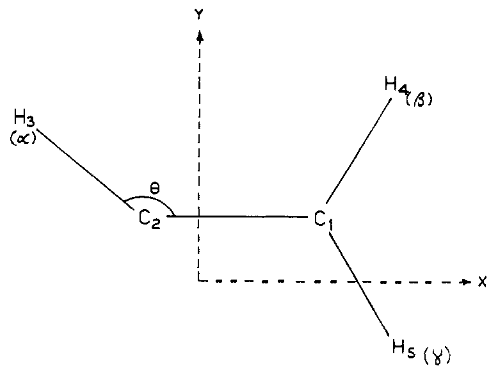

Figure 1. Assumed geometry and labeling of the vinyl radical (z axis perpendicular to page).

Table I. Vinyl Radical Ψ^2 Evaluation of Hyperfine Coupling Constants

Angle θ,[a] deg	Proton position	Ψ^2 [c]	a_H(calcd)[b,d]	Total energy, ev
125	α	17.53	33.1	−188.744
	β	40.31	76.1	
	γ	9.32	17.6	
144	α	8.93	16.9	−188.956
	β	38.60	72.8	
	γ	15.91	30.0	
155	α	4.66	8.8	−188.988
	β	36.94	69.7	
	γ	20.39	38.5	
165	α	1.765	3.3	−188.990
	β	34.70	65.5	
	γ	24.56	46.3	
180	α[e]	2.626	28.0	−188.940
	β			
	γ			

[a] The $H_3C_2C_1$ angle in Figure 1. [b] Experimental values[16] are $\alpha = 13.39$, $\beta = 65$, $\gamma = 37$ gauss. [c] $\times 10^3$. This is the square of the value of the MO containing the unpaired electron evaluated at each indicated proton. [d] Scaling factor equals 1887, our transferable value for K_σ. [e] The electron density on the adjacent carbon is scaled with K_π because this proton is orthogonal to the orbital containing the unpaired electron.

The results of our $\Psi^2(0)$ evaluation on the vinyl radical as a function of the angle θ are reported in Table I. These results were obtained using the set of parameters described under Calculations as best. The scaling factor 1887, for K_σ, was empirically found best for scaling the Ψ^2 value from the MO calculation to the value of the electron–nuclear spin coupling constant, a_H. This scaling factor, K_σ, is used for all protons which make a direct contribution to the MO containing the unpaired electron, and with our best set of EHT parameters we obtain the required intramolecular and intermolecular consistency discussed under Calculations. The theoretical scaling factor calculated from

$$A(\text{gauss}) = \left[\frac{\pi 8}{3\hbar\gamma_e} g\beta g_N\beta_N \frac{1}{(a^\circ)^3}\right] |\Psi(0)|^2$$

is 1596, in very good agreement with the empirically derived quantity. Better agreement could be obtained by varying the parameters in our calculation, *e.g.*, the Slater exponent for hydrogen. However, in view of the approximate level of this treatment this was not deemed meaningful. Upon examination of the 120, 136, 144, and 150° results, it is found that the $\Psi^2(0)$ values for the β position remain fairly independent of this wide variation in angle θ. The α and γ values, on the other hand, are quite sensitive to the angle. A value of $\theta = 155°$ is found to fit *all three* values quite well and also occurs near a minimum in a plot of total energy[17] *vs.* θ. In the case of this radical, a very shallow minimum is obtained and an energy barrier to inversion of about 1.4 kcal mole^{-1} is predicted. The calculated coupling constants are insensitive to small angle variations near the minimum. At $\theta = 180°$, the α proton is orthogonal to the MO containing the unpaired electron. The $\Psi^2(0)$ value on carbon is scaled with K_π (equal to 1066) to produce a_H at the α-hydrogen position. This procedure is employed for all orthogonal hydro-

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(15) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(16) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *ibid.*, **40**, 213 (1964).

(17) The total energy is defined as the product of orbital energy and orbital occupation number summed over all molecular orbitals.

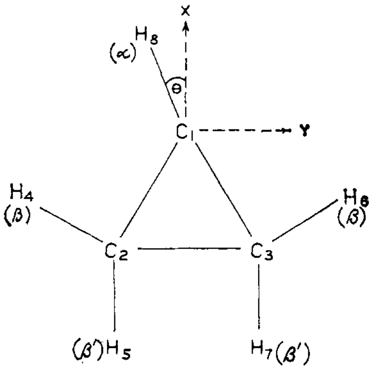

Figure 2. Assumed geometry and labeling of the cyclopropyl radical (z axis perpendicular to page).

gens bonded to carbons. This is referred to as the indirect contact interaction, in contrast to the direct mechanism which places unpaired spin directly on the proton. The value of 1066 to scale Ψ^2 is that previously reported[2] for the cyclohexadienyl radical and benzonitrile negative ion radical.

The eigenvector for the MO containing the unpaired electron and $\Psi^2(0)$ values for the unpaired electron obtained from the extended Hückel calculation using our best set of parameters are listed in Table II. Note in the comparison of H_3, H_4, and H_5 1s orbital contributions to the respective $\Psi^2(0)$ values at the hydrogen nuclei that the H_3 term contributes only about 78% of the total electron density at the α position (the H_3 nucleus), the remaining amount consisting of contributions from other atoms. Similar changes are observed in other radical systems. This illustrates the necessity for a complete evaluation of $\Psi^2(0)$ for the molecular orbital containing the unpaired electron in σ systems. Use of the squares of hydrogen 1s orbital coefficients would lead to the incorrect result.

Table II. Vinyl Radical Unpaired Electron Density Calculation[a] $\theta = 155°$

		Ψ term		
Atom[b]	Coefficient	α	β	γ
C_1	+0.0299	+0.0001	+0.0024	+0.0024
	+0.0000	+0.0000	+0.0000	+0.0000
	−0.0567	+0.0003	−0.0039	−0.0039
	−0.0861	−0.0001	−0.0103	+0.0103
C_2	−0.1319	−0.0105	−0.0009	−0.0009
	+0.0000	+0.0000	+0.0000	+0.0000
	+0.2358	−0.0295	+0.0025	+0.0025
	+0.9431	+0.0551	+0.0050	−0.0050
H_3	+0.0715	+0.0530	+0.0001	+0.0000
H_4	−0.2548	−0.0003	−0.1890	−0.0026
H_5	+0.1888	+0.0001	+0.0019	+0.1400
	Ψ total =	−0.0682	−0.1922	+0.1428
	$\Psi^2 \times 10^3$ =	4.655	36.94	20.39

[a] These are calculated using our best parameters (see under Calculations). [b] The carbon orbital coefficients are listed in the order 2s, $2p_z$, $2p_x$, and $2p_y$. Hydrogen coefficients are for 1s orbitals. The z direction is perpendicular to the plane of the molecule.

Cyclopropyl Radical. The cyclopropyl radical represents an interesting test of the use of EHT in the prediction of hyperfine coupling constants. In particular, the ability of our calculation to reproduce the experimentally found abnormally low α-position coupling constant should indicate if a good reflection of unpaired electron density can be obtained from our wave functions.

Fessenden and Schuler[15] have observed the esr spectra of the cyclopropyl radical. The reported coupling constants are 6.51 gauss for the α position and 23.42 gauss for the β and β' positions. As the α coupling constant is so much smaller than that for the equivalent position in other systems (see the discussion of cyclobutyl and cyclopentyl), the authors[15] conclude that the α-proton is displaced from the plane of the carbon skeleton. According to their arguments, if the hydrogen is in the plane, a large coupling constant will result. Since the β- and β'-position coupling constants are equivalent, they also conclude that H_8 is oscillating from a position above the ring to an equivalent position below the ring at a high frequency.

The geometry of the radical used in the calculation is illustrated in Figure 2. The angle, θ, which the α-hydrogen makes with the ring plane was varied in the calculations. The geometry of cyclopropane[18] consists of a symmetrical carbon ring skeleton with 1.524-A C–C bond lengths, 1.07-A C–H bonds, and 120° H–C–H bond angles. Except for variation in the angle θ, these bond distances and angles were used in the calculation.

The MO containing the unpaired electron takes on one of two general forms, depending on the angle θ. At θ greater than 0°, that is, when the C_1–H_8 bond makes an angle with the ring plane, contributions from all orbitals of the basis set except the C_1 p_y orbital are observed. In these cases, the H_4 and H_5 1s orbital coefficients are not equal, nor are the $\Psi^2(0)$ values calculated at the nucleus of each hydrogen. Different coupling constants are predicted in this case for the β and β' positions in the absence of oscillation of H_3 to an equivalent position below the ring. Table III lists the Ψ term values for orbitals of the basis set in the molecular orbital containing the unpaired electron for the case when the C_1–H_3 bond makes a 20° angle with the ring. This serves to illustrate both the general form of the MO containing the unpaired electron and the relative magnitudes of terms making up Ψ_{total} at each of the hydrogen nuclear positions. Note that when θ is greater than 0°, a *direct* contact interaction is observed at *each* hydrogen nucleus.

When θ = 0°, the general form of the MO containing the unpaired electron differs. Only the carbon p_z and β and β' position hydrogen 1s orbital coefficients are different from zero in this orbital. Since the H_8 1s orbital coefficient is zero (H_8 is in the ring plane in this configuration), interaction of the unpaired electron density with the H_8 nucleus must originate through the indirect π-type mechanism found in conjugated π systems. As the coefficient of the C_1 p_z orbital in this molecular orbital is 1.0008, the predicted coupling constant for the α (H_8) position *in this configuration* is 28.5 gauss (using the π-system scaling factor of 28.5 for the square of the orbital coefficient, c_z^2, as in the benzonitrile negative ion radical and cyclohexadienyl radical cases).[2] The calculated coupling constants evaluated from the $\Psi^2(0)$ value for this configuration as

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(18) "Table of Interatomic Distances" and "Configurations in Molecules and Ions," Special Publications No. 11 and 18, The Chemical Society, London, 1958.

Table III. Cyclopropyl Radical Total Unpaired Electron Density Calculation ($\theta = 20°$)

Atom[a]	Coefficient	Ψ term α[b]	Ψ term β[b]	Ψ term β'[b]
C_1	−0.1032	−0.0086	−0.0005	−0.0005
	+0.9687	+0.0477	+0.0037	−0.0037
	−0.1928	−0.0095	−0.0007	+0.0007
	−0.0000	−0.0000	−0.0000	−0.0000
C_2	+0.0080	+0.0000	+0.0007	+0.0007
	−0.0611	−0.0000	−0.0076	+0.0076
	+0.0629	+0.0003	−0.0023	−0.0023
	+0.0345	−0.0000	+0.0021	+0.0021
C_3	+0.0080	+0.0000	+0.0000	+0.0000
	−0.0611	−0.0000	−0.0002	+0.0002
	+0.0629	+0.0003	−0.0001	−0.0001
	+0.0345	+0.0000	+0.0003	+0.0003
H_4	−0.1410	−0.0001	−0.1046	−0.0016
H_5	+0.1300	+0.0001	+0.0014	+0.0964
H_6	−0.1410	−0.0001	−0.0004	−0.0001
H_7	+0.1300	+0.0001	+0.0001	+0.0004
H_8	+0.0448	+0.0332	+0.0000	+0.0000
	Ψ_{total} =	+0.0633	−0.1080	+0.1003
	$\Psi^2_{total} \times 10^3$ =	4.004	11.66	10.05
	a_H(calcd)[c] =	7.56	22.00	18.96
	a_H(exptl) =	6.51	23.42	

[a] The carbon orbital coefficients are listed in the order 2s, $2p_z$ $2p_x$, and $2p_y$. Hydrogen coefficients are for 1s orbitals. See Figure 2 for numbering system. [b] The positions α, β, and β' refer to the H_8, H_4 (H_6), and H_5 (H_7) nuclei, respectively. [c] a_H is calculated using the scaling factor 1887.

well as for three configurations where θ differs from zero are listed in Table IV. Note that, as θ is decreased toward zero (but not equal to zero), a decreasing α-position coupling constant is predicted by the $\Psi^2(0)$ evaluation for the direct interaction. This results from the decrease in the H_8 1s orbital coefficients and a decrease in the sum of other orbital Ψ terms at the H_α nucleus. However, the problem is very difficult for a small θ since both the direct and indirect mechanism should contribute to a_H.

Table IV. Cyclopropyl Radical Ψ^2 Evaluation of Hyperfine Coupling Constants as a Function of θ[a]

Angle θ,[a] deg	Position[a]	Ψ^2[b]	SF[c]	a_H(calcd)	E, ev
60	α	1.319	1887	24.89	−292.180
	β	0.8332	1887	15.72	
	β'	0.5741	1887	10.83	
30					−292.327
20	α	0.4004	1887	7.56	−292.401
	β	1.166	1887	22.00	
	β'	1.005	1887	18.96	
10	α	5.657×10^{-2}	1887	1.07	−292.387
	β	1.151	1887	21.72	
	β'	1.082	1887	20.42	
0	α	2.719	1066	28.99	−292.381
	β (β')[d]	1.132	1887	21.36	

[a] The angle the C_1–H_8 bond makes with the ring; see Figure 3 for labeling of atoms. [b] $\times 10^2$. This is the square of the value of the MO containing the unpaired electron evaluated at each indicated position. [c] Scaling factors; these are the direct contact (1887) and indirect contact (1066) interaction scaling constants found in our investigations for the best Hückel parameters. [d] The positions β and β' are equivalent in this configuration.

As both H_4 and H_5 coupling constants are observed to be equivalent in the esr spectrum,[15] either the C_1–H_8 bond makes a 0° angle with the carbon ring skeleton or it makes an angle with the ring but is flipping at a frequency fast enough to avoid detection in the spectral observation. Based on the calculations listed in Table IV, a large α-position coupling constant would be expected if the system were planar ($\theta = 0°$). This is in poor agreement with the experimentally observed value, but the β- and β'-position coupling constants are equal in this case and in good agreement with the experimentally observed value. If $\theta \sim 20°$, however, an excellent fit of calculated and experimental values is observed for the α-position coupling constant. Both the up and down position of the flipping hydrogen (H_8) are equally probable (they are simply related by a plane of symmetry parallel to and in the carbon ring). An average of the calculated value for the β- and β'-position constants is 20.48 gauss, also in good agreement with the experimentally determined value.

When a hydrogen atom is removed from tetrahedral methane to produce the planar methyl radical, the HCH angles increase from 109 to 120°. This can be thought of as due in part to less repulsion between an unpaired electron and a C–H bonded pair of electrons than between two pairs of C–H bonded electrons. The removal of a hydrogen atom from cyclopropane might be expected to produce similar results. However, it seems unreasonable to expect that planarity ($\theta = 0°$) could be obtained in this case for this would require sp^2 hybridization and a C–C–C angle of 120°. "Ring strain" would prevent the angle θ from being 0°. The predicted angle for θ of approximately 20° seems to be a reasonable estimate of the change in geometry from that in cyclopropane realizing that strain prevents θ from being 0°.

Dixon[6] has calculated the average of the β- and β'-position coupling constants on the basis of $\theta = 54.75°$, and has obtained good agreement between the calculated value of 24.1 and the experimental value. The α position which is the critical one was not evaluated. If θ were approximately 60° and the C_1H_8 hydrogen *were* oscillating rapidly enough, according to our calculation, the β- and β'-position average would be 20.3 gauss, which is also in good agreement with the experimental value, however, the α-position coupling constant would then be predicted by this calculation to be 24.89 gauss, in poor agreement with the observed value of 6.51 gauss.

The energy minimum as a function of angle is more sharply defined in this system than in vinyl radical. The inversion barrier for flipping H_8 is calculated to be approximately 0.5 kcal $mole^{-1}$, in good agreement with that estimated[15] from the epr work.

Cyclobutyl Radical. The geometry of cyclobutane[17] consists of a four-carbon skeleton with C–C bond lengths of $1.56_8 \pm 0.02$ A, C–H distance $1.09_8 \pm 0.04$, and angle H–C–H 114 ± 8°. The ring appears to be nonplanar but it is not possible, based on the electron diffraction data from which these values were obtained, to differentiate between static nonplanarity (bent ring with D_{2d} symmetry) and dynamic nonplanarity (planar ring of D_{4h} symmetry with out of plane ring bending mode). The esr spectrum,[15] obtained from the radical derived from this molecule at −80°, indicates that the *radical* is planar, because the coupling constants for the β and β' positions (and γ and γ' positions) are equal. At −80°, vibrations could conceivably be

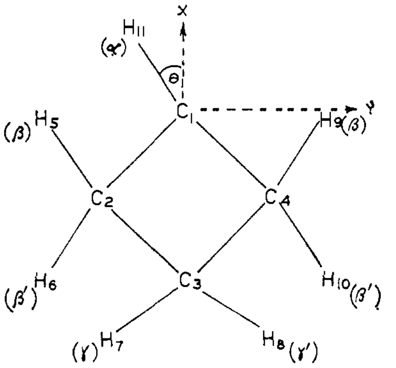

Figure 3. Assumed geometry and labeling of the cyclobutyl radical (z axis perpendicular to page).

damped to such an extent that the ring is essentially planar.

In view of the discussion above involving the geometry of the methyl radical, it is expected that, in this radical, the C_2–C_1–C_4 angle would be greater than the 90° symmetrical ring value but certainly not 120° because of ring strain. In the present calculation, a C_2–C_1–C_4 angle of 95°, a C_1–C_2–C_3 (C_1–C_4–C_3) angle of 88°, a C_1–C_2 (C_1–C_4) bond length of 1.46 A, and a C–H bond length of 1.09 A were employed. The labeling of the atoms is indicated in Figure 3.

The spectrum of the cyclobutyl radical consists of 30 lines, ten main lines each split into a triplet. This is consistent with splittings of 21.20 gauss for the α position, 36.66 gauss for the β and β' positions, and 1.12 gauss for the γ and γ' positions. The authors[15] conclude that C_1H_{11} lies in the ring plane (*i.e.*, $\theta = 0°$) based on these equivalences (and magnitudes).

The results of the $\Psi^2(0)$ evaluation of the MO containing the unpaired electron are given in Table V. At angle $\theta = 0°$, both β-position coupling constants and both γ-position coupling constants are equal. The scaled $\Psi^2(0)$ values from this evaluation are also listed in Table V. The agreement between these calculated values and the experimentally determined values is seen to be very good. The scaling factors used here again illustrate the transferability of these values in the systems we have studied. These calculated values are in complete agreement in every way with the experimental observation of the equivalence of the β and β' positions, small and equivalent coupling constants at the γ and γ' positions, and a large α-position coupling constant value. Note that this latter value is a consequence of the indirect π-type interaction between the unpaired electron density in the C_1 p_z orbital and the α-position hydrogen atom nucleus. The carbon p_z term in the $\Psi^2(0)$ evaluation for this coupling constant is actually *reduced* to a small extent by other orbital contributions to this position. This is an exception to the more generally observed phenomenon of other orbital contributions canceling as found in phenyl π-type systems. The reason for the net decrease in this case can be seen in Table V. For example, p_z orbitals C_2 and C_4 are equivalent with respect to C_1 and are both antibonding with respect to C_1 (the coefficient of C_1 p_z is positive, these are negative), hence both make an equivalent *negative* contribution to the value of γ at the C_1 p_z orbital. Similar arguments apply with other pairs of equivalent orbitals. If the position at which $\Psi_2(0)$ were evaluated were not on the molecular plane of symmetry (σ_v), unequal contributions would be encountered from the other orbitals, and the net result from other orbitals could be zero or a negligibly small value. The net result including the C_1 p_z term at C_1 is, however, very large, hence the large a_H(calcd) for the α-position coupling constant.

Table V. Cyclobutyl Radical Total Unpaired Electron Density Calculation ($\theta = 0°$)

		Ψ term		
Atom[a]	Coefficient	α[b]	β (β')[b]	γ (γ')[b]
C_1	+0.0000	+0.0000	+0.0000	+0.0000
	+1.0030	+0.1674	+0.0066	+0.0009
	−0.0000	−0.0000	+0.0000	+0.0000
	−0.0000	−0.0000	−0.0000	−0.0000
C_2	+0.0000	+0.0000	+0.0000	+0.0000
	−0.1030	−0.0016	−0.0131	−0.0006
	+0.0000	+0.0000	−0.0000	−0.0000
	+0.0000	−0.0000	+0.0000	−0.0000
C_3	−0.0000	−0.0000	−0.0000	−0.0000
	+0.0459	+0.0001	+0.0003	+0.0058
	−0.0000	−0.0000	−0.0000	+0.0000
	−0.0000	−0.0000	−0.0000	−0.0000
C_4	−0.0000	−0.0000	−0.0000	−0.0000
	−0.1030	−0.0016	−0.0001	−0.0006
	−0.0000	−0.0000	+0.0000	+0.0000
	+0.0000	+0.0000	+0.0000	+0.0000
H_5	−0.1748	−0.0022	−0.1296	−0.0010
H_6	+0.1748	+0.0003	+0.0014	+0.0002
H_7	+0.0270	+0.0001	+0.0002	+0.0200
H_8	−0.0270	−0.0000	−0.0000	−0.0002
H_9	−0.1748	−0.0022	−0.0001	−0.0010
H_{10}	+0.1748	+0.0003	+0.0000	+0.0002
H_{11}	−0.0000	−0.0000	−0.0000	−0.0000
	Ψ_{total} =	+0.1606	−0.1346	+0.0238
	$\Psi^2_{total} \times 10^3$ =	25.80	18.11	0.5646
	a_H(calcd)[c] =	27.50	34.17	1.07

[a] The carbon orbital coefficients are listed in the order 2s, $2p_z$, $2p_x$, and $2p_y$. Hydrogen coefficients are for 1s orbitals. The z direction is perpendicular to the ring. [b] See Figure 3 for labeling. [c] The scaling factor 1066 was used for the indirect interaction at the α-hydrogen and 1887 for the direct interaction at the bond γ-hydrogens.

Dixon[6] has also calculated the average of the β and β' positions and the average of the γ and γ' positions, but assumes that $\theta = 54.75°$ as in the cyclopropyl case.

Cyclopentyl Radical. The cyclopentyl radical geometry was assumed to be symmetrically planar, with C–C bond lengths of 1.54 A, C–H bond lengths of 1.09 A, and H–C–H angles of 109° symmetrically dispersed about the carbon framework as illustrated in Figure 4. The angle θ was again varied from 54.5 to 0°, producing the same trend of results found in the cyclopropyl radical. In addition, based on arguments previously presented for ring distortions, the calculation was repeated at $\theta = 0°$ with the following changes in the geometry: the C_2–C_1–C_5 angle was increased to 114°, the C_1–C_5–C_4 (C_1–C_2–C_3) angle reduced to 106°, the C_2–C_3–C_4 (C_3–C_4–C_5) angle reduced to 107°, the C_1–C_5 (C_1–C_2) distance reduced to 1.46 A, and the other distances maintained at 1.54 A. The results of the $\Psi^2(0)$ evaluation of the unpaired electron density in each case are given in Table VI.

Irradiation of liquid cyclopentane produces a solution whose esr spectrum is extremely simple in that it

Table VI. Cyclopentyl Radical Ψ^2 Evaluation of Hyperfine Coupling Constants as a Function of θ and Molecular Geometry[a,e]

Angle θ,[a] deg	Position[b]	Ψ^2 [c]	SF[d]	a_H(calcd)	Total energy, ev
54.5	α	0.7689	1887	14.51	−500.543
	β	0.9909	1887	18.70	
	β'	1.383	1887	26.10	
	γ	4.372×10^{-2}	1887	0.83	
	γ'	3.682×10^{-5}	1887	7.0×10^{-4}	
15	α	7.932×10^{-2}	1887	1.50	−501.010
	β	1.643	1887	31.00	
	β'	1.794	1887	33.85	
	γ	1.810×10^{-2}	1887	0.34	
	γ'	6.793×10^{-3}	1887	0.13	
0 (sym geometry)[e]	α	2.583	1066	27.54	−501.036
	β (β')[f]	1.771	1887	33.42	
	γ (γ')[f]	1.172×10^{-2}	1887	0.22	
0 (altered geometry)[e]	α	2.505	1066	26.70	−497.992
	β (β')[f]	2.037	1887	38.44	
	γ (γ')[f]	2.095×10^{-2}	1887	0.40	

[a] The angle the C_1–H_{14} bond makes with the ring. [b] The positions α, β (β'), and γ (γ') refer to the H_{14}, H_6 (H_7) or H_{12} (H_{13}), and H_8 (H_9) or H_{10} (H_{11}) nuclei, respectively. [c] $\times 10^2$. This is the square of the value of the MO containing the unpaired electron evaluated at each indicated position. [d] Scaling factor; these are the direct contact (1887) and indirect contact (1066) interaction scaling constants. [e] These two geometries are described and discussed in the text. [f] The positions β and β' and γ and γ' are equivalent in this configuration.

can be entirely ascribed to the cyclopentyl radical. At −40°, the protons which can be related by the two-fold rotation axis appear to be equivalent. At this temperature, the spectrum indicates a splitting of 21.48 gauss for the α position, 35.16 gauss for the β and β' positions, and 0.53 gauss for the γ and γ' positions. At lower temperature (while the system is still liquid), some of the lines broaden. At −120°, the solution is frozen, and the spectrum shows still more broadening. The fact that some of the lines are wider than others is consistent with nonequivalence of H_6 and H_7, according to the authors.[15] The same conclusion applies to the H_8 and H_9 pair, implying that the ring is nonplanar and that at −40° the flipping is rapid enough to make the four β protons appear equivalent. Based on references given in the paper, the authors[15] state that at liquid nitrogen temperature the spectrum is consistent with two sets of equivalent protons (no splitting from the γ protons is apparent at this temperature). The splitting of one pair of protons is approximately equal to one-half that of the remaining triad.

That our results are consistent with these observations can be shown as follows. The geometry of cyclopentane has been reported to be[19] a pseudo-rotating puckered ring, with maximum displacement of carbon atoms about 0.3 A from a planar ring. This displacement is said to be due to a torsional force about carbon–carbon bond axes resulting from hydrogen–hydrogen interactions. By analogy with the changes in geometry of the parent hydrocarbons upon formation of the methyl and cyclopropyl radicals, we have calculated a_H values at several values of θ equal to and less than the corresponding value in the parent hydrocarbon. From ring geometry arguments, as above, we predict $\theta = 0°$ for the cyclopentyl radical. As a consequence of this geometry variation, several of the hydrogen–hydrogen interactions are reduced in magnitude and, therefore, instead of using a puckered ring geometry we have used a planar ring. These assumptions are supported by the very good agreement between the calculated a_H values for $\theta = 0°$, altered ring geometry, and the observed a_H values at −40°. However, as indicated above, some of the lines in the spectrum broaden at lower temperatures, implying a non-planar ring.[15] As the α,β hydrogen–hydrogen interactions have been considerably lessened by the use of $\theta = 0°$, it is expected that the source of the ring distortion is by β,γ hydrogen–hydrogen interaction. As the sum of all such interactions has been significantly reduced by the use of $\theta = 0°$, and as this implies essentially sp^2 hybridization about C_1, atoms H_{14}, C_1, C_2, and C_5 should all lie in a plane. This leaves C_3 and C_4, which if symmetrically displaced above and below the plane, and oscillating, would produce the observed spectral behavior. As much of the hydrogen–hydrogen interaction has been significantly reduced by the use of the geometry variation described above, their displacement from the plane is expected to be only about 0.1–0.2 A. This small displacement of C_3 and C_4 from a planar configuration will produce a small change in the calculated a_H values for H_6 and H_7 when compared with the planar configuration. Only an average of these is seen when oscillations are rapid (*i.e.*, very nearly that calculated from the planar configuration), but their difference becomes apparent when the oscillations are damped, *i.e.*, at −120° and lower.

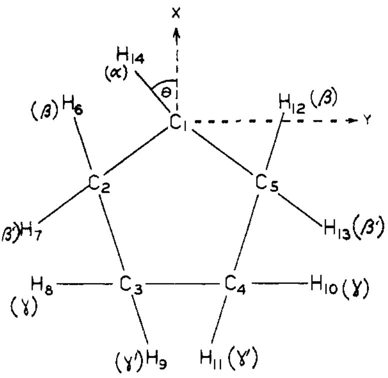

Figure 4. Assumed geometry and labeling of the cyclopentyl radical (z axis perpendicular to page).

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Conclusions

We have shown that constant values of K_σ and K_π can be employed to scale predicted values of $\Psi^2(0)$ from extended Hückel calculations to experimental values of the epr coupling constants. The results lend quantitative support to the qualitative predictions of geometry made directly from epr spectral interpretations.[15] The agreement between calculated and experimental values of a_H is excellent considering the approximations made. We have assumed that when $\theta = 20°$ or more there is no contribution to the measured coupling constant from an indirect type interaction. We have also assumed that all coupling constants treated by the direct interaction are positive. This is a good assumption for large values of a_H, but the small values of a_H could be negative with significant contributions from exchange-type interactions. Consequently, we are satisfied with the degree of correlation obtained and question the wisdom of trying further to improve the agreement by variation of the parameters in the MO calculation at this level of sophistication, *i.e.*, without taking explicit account of higher state mixing.

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Reactions of Coordinated Ligands. XIV. Reactions of Tris(diamine)nickel(II) Ions with Various Carbonyl Compounds, Especially β-Hydroxy Ketones and Aldehydes

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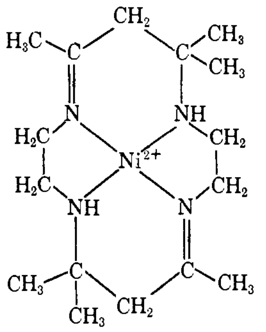
Abstract: Under various conditions, mesityl oxide, diacetone alcohol, and acetone all react with tris(ethylenediamine)nickel(II) salts to yield either the macrocyclic complex 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,7-dienenickel(II) or the complex of a long-chain tetradentate, 1,9-diamino-4,6,6-trimethyl-3,7-diazanona-3-enenickel(II). The reaction also occurs for a β-hydroxyaldehyde and various β-hydroxy ketones containing primary, secondary, and tertiary alcohol groups. The same product (1,9-diamino-6-methyl-3,7-diazanona-3-enenickel(II) tetrachlorozincate) is obtained by reaction of tris(ethylenediamine)nickel(II) salts with acetaldehyde, aldol, and crotonaldehyde. The corresponding compounds from tris(1-propylenediamine)nickel(II) tetrachlorozincate are also described. This general reaction provides a very useful route to the synthesis of chelate rings containing desired arrangements of substituents. The β-hydroxy ketone route is probably preferable to the reactions based on the condensations of simple carbonyl compounds.

The use of the reactions of coordinated ligands for the synthesis of useful and unusual ligands has seldom been exploited. One of the more fully developed examples of this controlled approach to ligand synthesis is contained in the work of Curtis and his co-workers. These researchers have shown that tris(ethylenediamine)nickel(II) perchlorate will dissolve in acetone and then react with the solvent to form the macrocyclic complex I (isolated as the perchlorate).[1]



I

Most recently it has been shown that the free ligand may be prepared either from the analogous iron(II) system[2] or by reaction of en·$HClO_4$ with mesityl oxide under mild conditions.[3] The latter represents an application of a reaction first reported from this laboratory.[4] The isomers of the nickel(II) complex have been fully characterized.[5–7]

Reduction of I and separation of the reduced ligand yields a second interesting macrocycle II.[8] House and Curtis[9] have also demonstrated that, under different conditions, tris(ethylenediamine)nickel(II) ion reacts with acetone to give the cation III. Since these and related reactions may hold for the preparation of aliphatic tetramines in general and because of the unusual nature of the products, we[4] have studied new synthetic routes to I and III using diacetone alcohol

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