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Extended Hückel Calculations of Negative Spin Density

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Extended Hückel molecular orbital calculations have been performed on the vinyl radical ($C_2H_3\cdot$) for a variety of geometries. The net spin densities for the protons have been calculated using a formalism due to McLachlan from the parameters of the Extended Hückel molecular orbital calculations. This calculation includes contributions from the positive spin density at the nucleus and spin polarization contributions, which are weighted by a semi-empirical parameter λ. This is in contrast to the usual Extended Hückel calculation which is incapable of calculating negative spin densities.

The results of our calculations are compared with other calculations on this system and the experimental values for the isotropic hyperfine coupling constants.

Rechnungen im Rahmen der erweiterten Hückeltheorie sind für verschiedene Geometrien des Vinylradikals durchgeführt worden. Die Spindichten am Ort der Protonen sind nach McLachlan's Formalismus bestimmt worden und schließen sowohl Beiträge der positiven Spindichte zum Kern als auch solche infolge Spinpolarisation, die mit einem semiempirischen Faktor behaftet sind, ein – im Gegensatz zur gewöhnlichen Hückeltheorie, die niemals negative Spindichten ergibt.

Die Resultate werden mit denen anderer Rechnungen und experimentellen isotropen HFS-Kopplungskonstanten verglichen.

Des calculs en méthode de Hückel étendue ont été faits sur le radical vinyle pour différentes géométries. Les densités de spin pour les protons ont été calculées en utilisant un formalisme de McLachlan. Les calculs incluent les contributions des densités de spin positives au noyau et les contributions de polarisation de spin, pondérées par un paramètre semi-empirique. Cela contraste avec les calculs Hückel étendus usuels qui ne peuvent pas calculer de densités de spin négatives.

Les résultats sont comparés avec d'autres calculs sur ces systèmes et aux valeurs expérimentales pour les constantes de couplage hyperfins isotropes.

Introduction

The vinyl radical has been the subject of extensive experimental [1a, b, c] and theoretical investigation. The epr hyperfine coupling constants have been calculated by a wide variety of techniques including a modified hyperconjugation method [2], Extended Hückel Calculations [3a, b], and a wide variety of semiempirical SCF-type calculations. An INDO [4] approximation, a ω-technique [5], and a CNDO/2 [6] approximation have been utilized along with other approximate SCF type calculations [7a, b, c, 8]. In addition, both restricted [9] and unrestricted Hartree-Fock [10] methods have been used.

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In view of recent successes [3, 11a, b] in calculating epr hyperfine coupling constants in σ-radicals by means of Extended Hückel Theory and conflicting claims [7b, c, 8, 12] regarding the sign of the α-proton hyperfine coupling constant (see Fig. 1) it was of interest to us to see if the McLachlan method could be extended to σ-radicals using parameters obtained from Extended Hückel Theory calculations. If successful, this would represent an advance since the normal Extended Hückel Theory is incapable of giving negative spin densities.

MacLachlan [13] has been able to fit the experimental spin densities for a variety of alternate hydrocarbon radicals, non-alternate negative ions, and neutral alternate radicals (all π-systems) using Eq. (1) and parameters obtained from simple Hückel theory. He showed that the coefficients calculated from simple Hückel theory agreed well with those calculated from Pariser-Parr theory [14] in these compounds. Although the energies did not compare as well, he was able to obtain satisfactory agreement by adjustment of the variable parameter λ in Eq. (1):

$$\varrho_r = C_{ro}^2 - \lambda \sum_s \pi_{rs} C_{so}^2 , \tag{1}$$

where ϱ_r is the spin density at atom r, C_{ro} is the Hückel coefficient of the orbital containing the odd electron at atom r, λ is the variable parameter, π_{rs} is the mutual polarizability of atoms r and s, and C_{so} is the Hückel coefficient of the orbital containing the odd electron at atom s (the polarizing atom). Thus, McLachlan was able to allow for spin polarization in a semi-empirical manner.

Hence, we have done extensive calculations on the vinyl radical for a wide variety of geometries.

Methods and Parameters

The numbering scheme of the atoms in the vinyl radical, the angle θ, which was varied in this calculation, and the coordinate system used are defined by Fig. 1.

We use the following experimental values [1a] for the proton hyperfine coupling constants: $|A_\alpha| = 13.4\ G$, $|A_\beta| = 65\ G$, $|A_\gamma| = 37\ G$.

The LCAO-MO procedure employed in this study is a modification of the Extended Hückel molecular orbital treatment developed by Hoffmann [15], and has been described elsewhere [16].

The diagonal matrix elements, H_{ii}, were approximated by the valence-orbital ionization potentials (VOIP's) of Basch, Viste, and Gray [17]. The off diagonal elements, H_{ij}, were calculated according to the Mulliken-Wolfsberg-Helmholz approximation [18a, b] with $K = 1.75$.

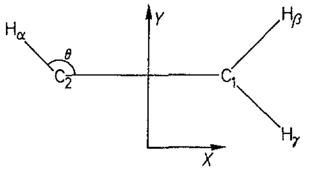


Fig. 1. Coordinate system and variable angle, θ, for the vinyl radical ($C_2H_3\cdot$)

In this study, SCF extended-basis-set atomic orbitals (linear combinations of Slater-type orbitals) were used for carbon. The necessary matrix transformations and molecular orbital calculations were performed by the ILCO 5 program that has been described in detail elsewhere [16].

Clementi double $-\zeta$ functions were used for carbon [19] and an exponent of 1.2 was used for the hydrogen 1*s* Slater type orbital. The charge was iterated to a convergence limit of 0.01. Standard bond distances and bond angles [20] were used except for the angle θ between H_α and C_2 which was varied, *vide infra*. The net spin densities at the hydrogens were then calculated using program NSPIN.

The subroutine NSPIN is appended to ILCO 5 and was written to be compatible with it. This subroutine is used to calculate the net spin density, ϱ_r, at a given nucleus r. The net spin density is calculated according to a formalism due to McLachlan [13], as shown in Eq. (2):

$$\begin{aligned} \varrho_r &= \psi_{or}^2 - \lambda \sum_s \pi_{rs} \sum_m C_{mo}^2 \\ \pi_{rs} &= -4 \sum_i \sum_j \frac{\sum_k C_{ki} \sum_l C_{lj} \sum_n C_{ni} \sum_p C_{pj}}{E_j - E_i}\,. \end{aligned} \tag{2}$$

Here, ψ_{or}^2 represents the positive spin density at nucleus r, the direct contribution from the molecular orbital, containing the unpaired electron. This positive spin density is calculated according to a method described previously [21]. λ is an empirical parameter which will be discussed in more detail later. π_{rs} is a polarization term which represents the polarization of atom r by atom s, where the sum $\sum_S$ runs over all the atomic orbitals of the atom which contributes to the polarization.

C_{mo}^2 is the square of the coefficient of the atomic orbital m in the molecular orbital ψ_o containing the unpaired electron where the sum $\sum_m$ runs over the atomic orbitals. In the polarization term π_{rs}, the double sum $\sum_i \sum_j$ runs over all filled and unfilled molecular orbitals (except molecular orbital o) i and j, respectively. $E_j - E_i$ represents the difference between the orbital energies of the j^{th} and the i^{th} molecular orbitals. Here C_{ki} represents the coefficient of the atomic orbitals of the atom r for the filled molecular orbitals, C_{pj} represents the coefficient of the atomic orbitals of atom r for the unfilled molecular orbitals, and the sums $\sum_k$ and $\sum_p$ run over the atomic orbitals of atom r. C_{lj} represents the coefficient of the atomic orbitals of atom S for the unfilled molecular orbitals, C_{ni} represents the coefficient of the atomic orbitals of atom S for the filled molecular orbitals, and the sums $\sum_l$ and $\sum_n$ runs over the atomic orbitals on atom S.

Thus, depending on the sign and magnitude of π_{rs}, the net spin density ϱ_r, calculated for a given atom may be either positive or negative. This is in contrast to the usual spin density calculation from Extended Hückel Theory where only the calculation of positive spin density is possible.

Results

Our output is divided into two parts: (1) the positive spin density for a given nucleus, known as ψ^2, and (2) the negative (or positive) density from the polarization, known as POLA. Initially, we assumed A_α to be negative, in agreement with recent approximate SCF calculations [7b, c, 8] and an unrestricted Hartree-Fock calculation [10]. Then we solved Eq. (3) for λ at various values of θ.

$$\mp 13.4 = K_\sigma\{\psi_\alpha^2 + \lambda(\mathrm{POLA})_\alpha\}\,. \qquad (3)$$

Here $K_\sigma = 1596$, *vide infra* and λ is a semi-empirical parameter, which is related to the electron repulsion integrals and the effective resonance integral [13]. We note that we are now calculating what might be termed a molecular λ. This quantity may be expected to vary depending on the type of bond involved and should not be generally transferable. Thus λ will differ substantially for the cases

Table 1. *Calculation of vinyl radical hyperfine coupling constants and parameters as a function of* θ

Angle $\theta°$	Proton position	$\Psi^{2\,a}$ ($\times 10^2$)	POLA[b] ($\times 10^2$)	λ	A_H (calcd.) (gauss)	Total energy (eV)
120°	α	1.52	−6.27	0.38		−180.758
	β	5.42	−0.10		85.7	
	γ	0.72	−0.20		10.2	
145°	α	0.64	−5.13	0.29		−181.114
	β	5.24	−0.60		80.9	
	γ	1.95	−0.26		29.8	
150°	α	0.52	−4.44	0.31		−181.124
	β	5.16	−0.71		78.8	
	γ	2.18	−0.35		33.0	
155°	α	0.37	−3.47	0.35		−181.131
	β	5.03	−0.85		75.5	
	γ	2.49	−0.46		37.2	
155° [c]	α	0.37	−6.59	0.18		−181.131
	β	5.03	−0.92		77.6	
	γ	2.49	−0.50		38.3	
160°	α	0.24	−2.43	0.44		−181.131
	β	4.88	−0.97		71.0	
	γ	2.80	−0.59		40.5	
160° [c]	α	0.24	−4.65	0.23		−181.131
	β	4.88	−1.03		74.0	
	γ	2.80	−0.62		42.4	
165°	α	0.14	−1.48	0.66		−181.129
	β	4.69	−1.07		63.5	
	γ	3.11	−0.73		42.0	
165° [c]	α	0.14	−2.81	0.35		−181.129
	β	4.69	−1.10		68.8	
	γ	3.11	−0.75		45.5	
170°	α	0.06	−0.69	1.20		−181.125
	β	4.47	−1.12		50.0	
	γ	3.42	−0.87		38.0	

[a] Positive spin density, corresponding to Ψ^2 in Eq. (3).

[b] Negative spin density with $\lambda = 1.0$, corresponding to POLA in Eq. (3).

[c] All other atoms are used to polarize the given nucleus.

in which all other atoms are used to polarize the nucleus. K is a proportionality constant which may be derived from other fundamental constants [3b]. K_σ for Slater orbitals is:

$$K_\sigma = \frac{8\pi}{6S_{\gamma_e}} g\beta g_n\beta_N \frac{1}{a_o^3} = 1596\ \text{gauss/Å}^3 .$$

Here S represents the total spin ($S=1/2$ for the case of doublets) γ_e is the magnetogyric ratio for the electron, g and g_n the electronic and nuclear g-factors, respectively, β and β_n the electronic and nuclear Bohr magnetons, respectively, and $a_0 = 0.5297$ Å which is the Bohr radius for hydrogen.

The results of our molecular orbital calculations showed a very shallow energy minimum as θ is varied, with a minimum at 155° and 160°. This is in substantial agreement with results reported earlier [3b] for an Extended Hückel Calculation,

Table 2. *Calculation of vinyl radical hyperfine coupling constants and parameters as a function of* θ

Angle θ°	Proton position	$\Psi^{2\,a}$ ($\times 10^2$)	POLA[b] ($\times 10^2$)	λ	A_H (calcd.) (gauss)	Total energy (eV)
120°	α	1.52	−6.27	0.10		−180.758
	β	5.42	−0.10		86.3	
	γ	0.72	−0.20		11.2	
145°	α	0.64	−5.13	−0.04		−181.114
	β	5.24	−0.60		83.9	
	γ	1.95	−0.26		31.3	
150°	α	0.52	−4.44	−0.07		−181.124
	β	5.16	−0.71		83.2	
	γ	2.18	−0.35		35.1	
155°	α	0.37	−3.47	−0.14		−181.131
	β	5.03	−0.85		82.2	
	γ	2.49	−0.46		40.7	
155° [c]	α	0.37	−6.59	−0.07		−181.131
	β	5.03	−0.92		81.2	
	γ	2.49	−0.50		40.4	
160°	α	0.24	−2.43	−0.25		−181.131
	β	4.88	−0.97		8.17	
	γ	2.80	−0.59		47.1	
160° [c]	α	0.24	−4.65	−0.13		−181.131
	β	4.88	−1.03		80.0	
	γ	2.80	−0.62		46.0	
165°	α	0.14	−1.48	−0.47		−181.129
	β	4.69	−1.07		82.8	
	γ	3.11	−0.73		54.7	
165° [c]	α	0.14	−2.81	−0.25		−181.129
	β	4.69	−1.10		79.3	
	γ	3.11	−0.75		52.7	
170°	α	0.06	−0.69	−1.13		−181.125
	β	4.47	−1.12		91.4	
	γ	3.42	−0.87		70.2	

[a] Positive spin density, corresponding to Ψ^2 in Eq. (3).

[b] Negative spin density with $\lambda = 1.0$, corresponding to POLA in Eq. (3).

[c] All other atoms are used to polarize the given nucleus.

but should be contrasted with recent reports [7b, c] of Japanese workers who found an energy minimum at $\theta = 135°$, and a recent [10] *ab initio* unrestricted Hartree-Fock calculation that gave an energy minimum at $\theta = 137°$.

We used the parameter λ from the solution of Eq. (3) to calculate A_β and A_γ for a given angle θ. For $\theta = 155°$, 160°, and 165°, we carried out calculations in which the nucleus in question is polarized by all other atoms and only by the two carbon atoms. The results of these calculations are given in Table 1. The calculated parameters λ, A_β, and A_γ are discussed in the next section along with their implications for future use.

In view of recent experimental results [12] which have shown A_α to be positive in a vinyl-type radical and calculations [2] which have reported A_α as positive, we have also solved Eq. (3) assuming A_α is positive. The results are given in Table 2 along with the calculated parameters λ, A_β, and A_γ.

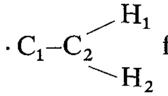
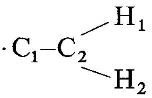
Discussion

By solving Eq. (3) for various geometries, we have attempted to find the "best fit" for the adjustable parameter λ and the calculated coupling constants A_β and A_γ.

An examination of the data reveals that the "best fit" occurs, when A_α is assumed to be negative, at $\theta = 165°$ and $\lambda = 0.66$ if only the carbon atoms are used to polarize the hydrogens. For the case in which all other atoms are used to polarize the hydrogen in question the "best fit" occurs at $\theta = 155°$ and $\lambda = 0.18$ although these fits are poorer. These values of θ correspond well to the very shallow energy minimum and our calculated values of A_β and A_γ are in excellent agreement with experimental values. Reasonable calculated values of A_β and A_γ occur for $\theta = 155°$, 160° and 165°. When A_α is assumed to be positive, the "best fit" occurs at $\theta = 150°$ and $\lambda = -0.07$ when only the carbon atoms are used to polarize the hydrogens. For the case in which all other atoms are used to polarize the hydrogen in question the "best fit" occurs at $\theta = 155°$ and $\lambda = -0.07$. In general, the calculated hyperfine couplings, especially A_β, are in poorer agreement with experiment when A_α is assumed positive than when A_α is assumed negative. Reasonable calculated values of A_β and A_γ occur for $\theta = 150°$ and 155°.

In view of the shallow energy minimum and the good agreement between experimental and calculated values in the range $\theta = 155°$, 160° and 165°, an independent test of these parameters is desirable. Such a check might be provided by the calculation of the ionization potential for the various geometries. The highest filled molecular orbital, containing the unpaired electron, lies at an energy level of -9.56 eV, -9.50 eV, and -9.46 eV for values of $\theta = 155°$, 160°, and 165°, respectively. According to Koopmans' theorem [22] the calculated ionization potentials should be $+9.56$ eV, $+9.50$ eV, and $+9.46$ eV, respectively. All of these values are in excellent agreement with the experimental value of 9.45 eV [23] and do not serve to differentiate between the geometries.

Finally, a discussion of how spin polarization might be expected to affect the various protons of the vinyl radical is in order. Although the unpaired electron is in a σ-orbital, an analysis of the eigenvectors shows that for example at $\theta = 160°$ about 93 % of the electron is in the p_y orbital. Hence, H_α and A_α would be dominated by an atomic exchange coupling mechanism of the type proposed by McConnell [24], and similar to that for the · C–H fragment. Thus, we would expect a negative spin density at H_α and we would estimate a proton hyperfine coupling constant of $A_H = -21.0\ G$ from spin polarization effects alone.

Colpa and De Boer [25] have discussed spin polarization in the $\cdot C_1{-}C_2{-}H_1$ and  $\cdot C_1{-}C_2\genfrac{}{}{0pt}{}{\diagup H_1}{\diagdown H_2}$ fragments. They have shown in the $\cdot C_1{-}C_2{-}H_1$ fragment that there are two opposing spin polarization mechanisms. First, a consecutive polarization whereby the unpaied electron, in a p_y orbital in our system, polarizes the $C_1{-}C_2$ bond which in turn polarizes the $C_2{-}H_1$ bond. This causes a positive spin density to reside on the hydrogen. They estimate its magnitude as $A_H = +0.65\ G$. The second mechanism is a direct polarization of the $C_2{-}H_1$ bond by the unpaired electron and causes a negative spin density to reside on the hydrogen. They estimate the magnitude of the direct mechanism to give $A_H = -1.76\ G$. Hence, the net effect is a negative spin density with an estimated $A_H = -1.16$. They predicted results analogous in magnitude for the  $\cdot C_1{-}C_2\genfrac{}{}{0pt}{}{\diagup H_1}{\diagdown H_2}$ fragment, where the hydrogens no longer lie in the plane. Thus, the much smaller expected magnitudes of spin polarization for H_β and H_γ together with their much larger contribution to the molecular orbital containing the unpaired electron causing a much larger positive spin (density for H_β and H_γ compared to H_α leads us to predict that spin) polarization effects will not be dominant for A_β and A_γ, in agreement with our results.

The usefulness of these parameters and the method employed will depend on its transferability to other σ-radicals, such as cyclopropyl and cyclobutyl. Such calculations are anticipated.

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