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Studies of Delocalized Electron Bonding

I. Valence Bond Calculation of the Ethane Barrier Using a Six-Electron Model

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A calculation of the ethane barrier is made using a six-electron model in which all single exchange interactions are included. A barrier of 0.6 Kcal. per mole favoring the staggered configuration is calculated. The wave function is used to calculate the NMR proton spin-spin coupling constants, which are found to be at variance with the experimental values. The factors which influence these calculated results are discussed.

Die Potentialschwelle für die innere Rotation des Äthans wird mit einem Sechselektronenmodell unter Einschluß aller Austauschintegrale berechnet. Man erhält eine Schwelle von 0,6 kcal/Mol zugunsten der trans-Konfiguration. Die mit der Eigenfunktion berechneten magnetischen Spin-Spin-Kopplungskonstanten der Protonen weichen von den experimentellen Werten ab. Die die berechneten Werte beeinflussenden Faktoren werden diskutiert.

La barrière de potentiel de la rotation intramoléculaire de l'éthane est calculée à l'aide d'un modèle à 6 électrons et tenant compte de toutes les interactions d'échange. On la calcule à 0,6 kcal/mole en faveur de la configuration trans. Avec la fonction d'onde sont calculées les constantes de couplage magnétique des spins protoniques; elles sont en désaccord avec les valeurs expérimentales. Les facteurs influençant ces résultats sont discutés.

1. Introduction

It is the purpose of this paper, together with others to follow in the series, to investigate the nature of delocalized electron bonding in molecules. Such bonding, which has long been known to exist but not clearly understood, contributes many of the fine structural features which are of interest to the physicist and chemist.

One of the more interesting structural features which has defied a conclusive explanation for some thirty years is that of rotational barriers about single bonds. Recently, considerable interest has been shown in valence bond calculations of the ethane barrier. Harris and Harris [*8*] and Karplus [*12*, *13*] have employed six-electron models. These calculations assumed only nearest neighbor interactions. This valence bond approach has been extended to a ten-electron model, in which all single exchange interactions were considered, by Eyring, Grant, and Hecht [*2*]. Crude estimates were used for some of the exchange integrals involved, however, and these have been re-evaluated in the present work.

Fortunately, we are not required to rely on the energy eigenvalue alone as a criterion for the accuracy of a theoretical calculation. The wave function, which is useful for calculating certain structural parameters determined in magnetic resonance studies, provides an alternative check on the calculations. In particular, the vicinal proton spin-spin coupling constants have been evaluated as a function of the dihedral angle by Karplus [*12*] using the above mentioned model. It has been suggested that certain discrepancies between the calculated and experimental coupling constants might be due to the neglect of all but nearest neighbor interactions [*6, 7*]. The recent evidence that the geminal and vicinal coupling constants are of opposite relative signs [*1, 4, 5, 6, 11, 17, 22*], in contradiction to the theoretical predictions, seems to warrant a calculation of the vicinal coupling constants based upon a similar model in which additional exchange terms are included.

2. Model and Calculations

The model used in the present investigation is the six-electron fragment shown in Fig. 1. a and f represent 1s atomic orbitals centered on the hydrogen atoms, H and H', respectively. b and e are sp^3 hybridized orbitals on carbon atoms directed toward the neighboring hydrogen atoms as indicated in the figure, and c and d are sp^3 orbitals directed toward the adjacent carbon atom.

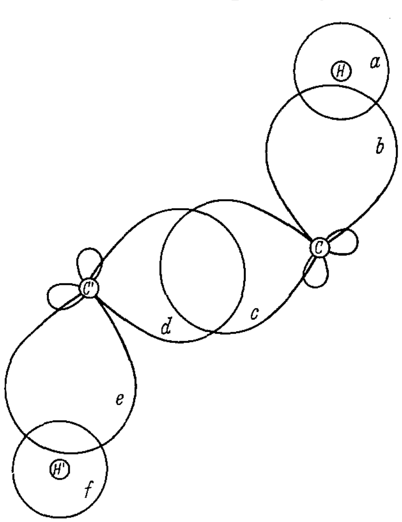

Fig. 1. Six-Electron Model Used for the Calculation of the Ethane Barrier

The wave function is written as a linear combination of the various bond functions:

$$\Psi = \sum_i c_i \psi_i. \qquad (1)$$

There are five canonical valence bond structures arising from this six-electron model, which can easily be found using the Rumer-Pauling [*19, 23*] diagram scheme. These structures are,

$$\begin{aligned} \psi_1 &= (ab)\,(cd)\,(ef) \\ \psi_2 &= (af)\,(be)\,(cd) \\ \psi_3 &= (af)\,(bc)\,(de) \\ \psi_4 &= (ab)\,(cf)\,(de) \\ \psi_5 &= (ad)\,(bc)\,(ef), \end{aligned} \qquad (2)$$

where (ij) represents a bond between the two orbitals, i and j. It will be noted that ψ_1 is the perfect-paired structure, and ψ_4 and ψ_5 are equivalent by symmetry.

The matrix elements between these structures were evaluated by the usual valence bond techniques [*3, 20*]. Retaining only single exchange interactions, these matrix elements can be written as,

$$\begin{aligned} H_{ij} &= \frac{1}{2^{n-x_{ij}}}\Big(Q + \sum_{k\neq l} P_{kl}\, I_{kl}\Big) \\ S_{ij} &= \frac{1}{2^{n-x_{ij}}}, \end{aligned} \qquad (3)$$

where x_{ij} is the number of islands in the superposition diagram for the structures, i and j, and n is the total number of bonds. P_{kl} is the exchange factor between the orbitals, k and l; i. e., $+1$ for orbitals in the same island separated by an odd number of bonds, -2 for orbitals in the same island separated by an even number of bonds, and $-1/2$ for orbitals in different islands. I_{kl} is the single exchange integral between the k and l orbitals,

$$I_{kl} = \int\!\!\int k(1)\, l(2)\, \hat{H}\, k(2)\, l(1)\, d\tau_1\, d\tau_2, \qquad (4)$$

and Q is the Coulomb integral. These matrix elements were constructed at 15° intervals of the dihedral angle, φ.

Using the matrices constructed in this manner, the solution of the secular determinant, $|H_{ij} - E\,S_{ij}|$ was found using an iterative technique with an IBM 1620 computer. The coefficients in the expansion (1) were then found by solving the set of equations, $\sum_j (H_{ij} - E\,S_{ij})\,c_j = 0$, subject to the usual normalization condition, $\int \Psi^* \,\Psi\, d\tau = 1$.

The nuclear spin-spin coupling constant between the two atoms, N and N', has been shown by Karplus and Anderson [*14*] to have the following form in terms of the valence bond formalism (for contact coupling):

$$J_{NN'} = \frac{1}{4\,\Delta E}\left(\frac{2}{3\,h}\right)\left(\frac{16\,\pi\,\beta\,\hbar}{3}\right)^2 \gamma_N\,\gamma_{N'}\,\varphi_N(0)\,\varphi_{N'}(0)\times \\ \times \sum_i \sum_j c_i\,c_j \left(\frac{1}{2^{n - x_{ij}}}\right)(1 + 2\,P_{NN'}). \tag{5}$$

ΔE is the average excitation energy, and $\varphi_N(0)$ is the electron density at the nucleus, N. For proton coupling, $\varphi_H(0)$ can be approximated as the electron density at the nucleus due to a $1s$ atomic orbital. In this case Equation (5) becomes,

$$J_{HH'} = \frac{1.395 \times 10^3}{\Delta E\,(ev)} \sum_i \sum_j c_i\,c_j \left(\frac{1}{2^{n - x_{ij}}}\right)(1 + 2\,P_{HH'}). \tag{6}$$

Equation (6), with an average excitation energy of 9 e. v., was used for the calculation of the vicinal proton spin-spin coupling constants.

3. Evaluation of Molecular Integrals

Of the fifteen single exchange interactions, there are only nine distinct types, due to symmetry. These integrals will be denoted as follows:

$$\begin{array}{ll} \alpha = ab = ef & \varepsilon = af \\ \beta = ac = df & \zeta = bc = de \\ \gamma = ad = cf & \eta = bd = ce \\ \delta = ae = bf & \vartheta = cd \quad \varkappa = be \end{array} \tag{7}$$

Following Karplus and Anderson [*14*], the following empirical values have been used: $\alpha = -87.63$ Kcal. per mole, $\beta = +5.37$ Kcal. per mole, $\zeta = +23.29$ Kcal. per mole. ε has been calculated from a Morse curve for the hydrogen molecule using the distances appropriate for the various values of the dihedral angle.

The remaining integrals can be shown to be of the following form:

$$\gamma = \frac{3}{4}\left(\frac{1}{3}\,N_{hssh} + b^2\,N_{h\pi\pi h} + a^2\,N_{h\sigma\sigma h} + \frac{2}{\sqrt{3}}\,a\,N_{h\sigma sh}\right).$$

$$\delta = \frac{2}{3}\,N_{h\pi\pi h}\sin^2\varphi + \left(\frac{2\,b^2}{3}\,N_{h\sigma\sigma h} + \frac{2\,a^2}{3}\,N_{h\pi\pi h}\right)\cos^2\varphi + \\ + \left(\frac{\sqrt{2}\,b}{\sqrt{3}}\,N_{h\sigma sh} - \frac{\sqrt{2}\,a\,b}{3}\,N_{h\sigma\sigma h} + \frac{\sqrt{2}\,a\,b}{3}\,N_{h\pi\pi h}\right)\cos\varphi + \\ + \frac{1}{4}\,N_{hssh} - \frac{a}{2\sqrt{3}}\,N_{h\sigma sh} + \frac{a^2}{12}\,N_{h\sigma\sigma h} + \frac{b^2}{12}\,N_{h\pi\pi h}.$$

$$\begin{aligned}
\eta = {} & k_1^4\, N_{ssss} + k_2^2\, k_4^2\, N_{\sigma\sigma\sigma\sigma} + (2\, k_1^3\, k_2 - 2\, k_1^3\, k_4)\, N_{sss\sigma} + \\
& + (2\, k_1\, k_2\, k_4^2 - 2\, k_1\, k_2^2\, k_4)\, N_{s\sigma\sigma\sigma} - 2\, k_1^2\, k_2\, k_4\, N_{s\sigma s\sigma} + \\
& + 2\, k_1^2\, k_4^2\, N_{s\sigma\sigma s} - 2\, k_1^2\, k_2\, k_4\, N_{ss\sigma\sigma} + k_1^2\, k_3^2\, N_{s\pi\pi s} + \\
& + 2\, k_1\, k_2\, k_3^2\, N_{s\pi\pi\sigma} + 2\, k_2^2\, k_3^2\, N_{\sigma\pi\pi\sigma}. \\
\vartheta = {} & k_1^4\, N_{ssss} + k_2^4\, N_{\sigma\sigma\sigma\sigma} + 4\, k_1^3\, k_2\, N_{sss\sigma} + 2\, k_1^2\, k_2^2\, N_{s\sigma\sigma s} + \\
& + 2\, k_1^2\, k_2^2\, N_{s\sigma s\sigma} + 2\, k_1^2\, k_2^2\, N_{ss\sigma\sigma} + 4\, k_1\, k_2^3\, N_{s\sigma\sigma\sigma}. \\
\varkappa = {} & k_3^4\, (N_{\pi\pi\pi\pi} - N_{\pi\pi'\pi'\pi}) \cos^2\varphi + [k_1^2\, k_3^2\, (2\, N_{ss\pi\pi} + 2\, N_{s\pi s\pi}) + \\
& + k_3^2\, k_4^2\, (2\, N_{\sigma\sigma\pi\pi} + 2\, N_{\sigma\pi\sigma\pi}) - 2\, k_1\, k_3^2\, k_4\, (2\, N_{s\sigma\pi\pi} + 2\, N_{s\pi\sigma\pi})] \cos\varphi + \\
& + k_3^4\, N_{\pi\pi'\pi'\pi} + 2\, k_3^2\, k_4^2\, N_{\pi\sigma\sigma\pi} + 2\, k_1^2\, k_3^2\, N_{s\pi\pi s} - 4\, k_1\, k_3^2\, k_4\, N_{s\pi\pi\sigma} + \\
& + k_1^4\, N_{ssss} + k_4^4\, N_{\sigma\sigma\sigma\sigma} - 4\, k_1^3\, k_4\, N_{sss\sigma} - 4\, k_1\, k_4^3\, N_{s\sigma\sigma\sigma} + \\
& + k_1^2\, k_4^2\, (2\, N_{ss\sigma\sigma} + 2\, N_{s\sigma s\sigma} + 2\, N_{s\sigma\sigma s}).
\end{aligned} \tag{8}$$

where $a = \cos\,(< CC'H)$, $b = \sin\,(< CC'H)$, $k_1 = \frac{1}{2}$, $k_2 = \frac{\sqrt{3}}{2}$, $k_3 = \sqrt{\frac{2}{3}}$, $k_4 = \frac{1}{2\sqrt{3}}$.

The integrals, $N_{\alpha\beta\gamma\delta}$, are of the form,

$$N_{\alpha\beta\gamma\delta} = \int\!\!\int \alpha_a\,(1)\,\beta_b\,(2)\,\hat{\boldsymbol{H}}\,\gamma_b\,(1)\,\delta_a\,(2)\,d\tau_1\,d\tau_2, \tag{9}$$

and h, s, σ, and π refer to $1s$, $2s$, $2p_\sigma$, and $2p_\pi$ atomic orbitals. It is assumed that the hybridized sp^3 orbitals centered on carbon are tetrahedral.

Using the virial theorem, the $N_{\alpha\beta\gamma\delta}$ integrals can be approximated by,

$$\begin{aligned}
N_{\alpha\beta\gamma\delta} = {} & A_{\alpha\beta\gamma\delta} + Z_a\, Z_b\, \frac{S_{\alpha\gamma}\, S_{\beta\delta}}{R} - \\
& - \frac{1}{2}\, [S_{\beta\delta}\,(Z_a\, J_{\gamma\alpha} + Z_b\, J_{\alpha\gamma}) + S_{\alpha\gamma}\,(Z_a\, J_{\beta\delta} + Z_b\, J_{\delta\beta})],
\end{aligned} \tag{10}$$

where

$$\begin{aligned}
A_{\alpha\beta\gamma\delta} &= \int\!\!\int \alpha_a\,(1)\,\beta_b\,(2)\,\frac{1}{r_{12}}\,\gamma_b\,(1)\,\delta_a\,(2)\,d\tau_1\,d\tau_2 \\
S_{\alpha\beta} &= \int \alpha_a\,(1)\,\beta_b\,(1)\,d\tau_1 \\
J_{\alpha\beta} &= \int \frac{\alpha_a\,(1)\,\beta_b\,(1)}{r_{b_1}}\,d\tau_1 = \int \frac{\beta_a\,(1)\,\alpha_b\,(1)}{r_{a_1}}\,d\tau_1.
\end{aligned} \tag{11}$$

The carbon-hydrogen and carbon-carbon bond lengths used are 1.108 Å and 1.537 Å, respectively [*24*]. Slater-type atomic orbitals have been assumed, and the potential terms in the Hamiltonian have been assigned an effective nuclear charge, $Z_a = Z_b = 1.00$.

Using these assumptions, the exchange integrals involving carbon orbitals necessary for an evaluation of η, ϑ, and $\varkappa$ have been found by interpolation of the tables of KOPINECK [*15*]. Such tables are not available for the exchange integrals between the carbon and hydrogen orbitals at the internuclear separations necessary for the evaluation of γ and δ. These integrals have been calculated from the functions, $A_n\,(\alpha)$, $B_n\,(\alpha)$, and $W_\tau^\nu\,(m, n;\, \alpha)$, using standard molecular integral tables [*16*, *18*]. A table of these integrals is in preparation [*10*].

Table 1. *Molecular Integrals Used in Ethane Barrier Calculation*
(in Kcal/mole)

$\alpha = -87.63$, $\beta = +5.37$, $\gamma = -2.34$, $\zeta = +23.29$, $\eta = +9.53$, $\vartheta = -41.56$

φ	δ	ε	$\varkappa$
0°	+ 4.38	— 9.25	— 1.38
15°	+ 4.43	— 8.97	— 1.26
30°	+ 4.56	— 8.21	— 0.94
45°	+ 4.71	— 7.15	— 0.50
60°	+ 4.77	— 6.00	— 0.06
75°	+ 4.66	— 4.93	+ 0.28
90°	+ 4.33	— 4.03	+ 0.38
105°	+ 4.78	— 3.31	+ 0.28
120°	+ 3.06	— 2.78	— 0.07
135°	+ 2.29	— 2.39	— 0.51
150°	+ 1.60	— 2.14	— 0.96
165°	+ 1.12	— 2.00	— 1.28
180°	+ 0.95	— 1.96	— 1.40

The Coulomb integral occurring in Equation (3) was assumed to be 15 per cent of the total energy of interaction between all of the pairs of orbitals involved. Table 1 summarizes the values of the integrals used.

4. Discussion of Results

The results of the calculations are shown in Table 2. The ethane barrier is the total energy of the staggered configuration, which can be written as $E_{staggered} = \text{constant} + 3\,E_{\varphi=180^\circ} + 6\,E_{\varphi=60^\circ}$ minus the total energy of the eclipsed configuration, $E_{eclipsed} = \text{constant} + 3\,E_{\varphi=0^\circ} + 6\,E_{\varphi=120^\circ}$ [*8*, *9*]. The result is 0.64 Kcal. per mole favoring the staggered configuration.

Table 2
Energy Eigenvalues, normalized eigenvectors, and vicinal proton spin-spin coupling constants

φ	*E(Kcal/mole)*	c_1	c_2	c_3	c_4, c_5	$J_{HH'}$ (c.p.s.)
0°	— 278.6794	0.99007	0.05742	— 0.00309	— 0.02009	26.79
15°	— 278.8170	0.99061	0.05646	— 0.00299	— 0.02012	26.35
30°	— 279.1854	0.99212	0.05379	— 0.00272	— 0.02022	25.11
45°	— 279.6682	0.99430	0.04991	— 0.00234	— 0.02034	23.32
60°	— 280.1158	0.99688	0.04533	— 0.00187	— 0.02051	21.20
75°	— 280.3969	0.99964	0.04037	— 0.00139	— 0.02067	18.90
90°	— 280.4130	1.00240	0.03538	— 0.00088	— 0.02084	16.63
105°	— 280.1680	1.00519	0.03034	— 0.00039	— 0.02101	14.32
120°	— 279.6976	1.00777	0.02559	0.00009	— 0.02117	12.17
135°	— 279.1274	1.01005	0.02127	0.00054	— 0.02132	10.22
150°	— 278.5829	1.01185	0.01782	0.00088	— 0.02144	8.66
165°	— 278.1959	1.01305	0.01554	0.00112	— 0.02153	7.64
180°	— 278.0563	1.01346	0.01476	0.00121	— 0.02156	7.29

As pointed out previously [*2*], the magnitude of the barrier calculated is a sensitive function of the manner in which the integrals are evaluated and consequently its magnitude cannot be considered very meaningful. However, a marked improvement is obtained in this calculation over the result of the ten electron calculation [2], in which a crude extrapolation of empirical integrals was used for the evaluation of γ and δ. It was also suggested [2] that the forty-two valence bond structures involved in the ten electron calculation might cause a weighting of the angular dependent integrals, ε, δ, and $\varkappa$, in such a way that a different barrier would be calculated using a six-electron model. The integrals used in the ten electron calculation were used in the present calculation to check this point. The result is a barrier of 13.36 Kcal. per mole favoring the staggered configuration, which is insignificantly different from the 13.53 Kcal. per mole barrier previously calculated [2].

The vicinal proton spin-spin coupling constants have been calculated using Equation (6) and are also listed in Tab. 2. The major contribution to this coupling arises from the cross term between ψ_1 and ψ_2, which continuously decreases as the dihedral angle increases from 0° to 180°. These results do not correlate with the experimental values, which indicate that the magnitude of the coupling between *trans* protons is about two or three times larger than that between *gauche* protons [21]. The small value of $J_{HH'}$ obtained by KARPLUS [12] for $\varphi \approx 90°$ resulted from an almost exact cancellation of the $\psi_1 \psi_2$ and $\psi_1 \psi_3$ cross terms. When exchange interactions between all the orbitals are considered, however, no such cancellation occurs. An examination of Tab. 1 shows that the angular dependent part of the carbon-carbon exchange interaction ($\varkappa$) is smaller than the angular dependent carbon-hydrogen (δ) and hydrogen-hydrogen (ε) terms. This results from the fact that although the carbon atoms are closer together than the other atoms involved, the sp^3 hybridized orbitals involved are directed away from one another. Thus, the omission of interactions between non-adjacent atoms is not justified. Better agreement between the calculated and observed coupling constants might be obtained using the more complete ten electron model, since, although essentially the same rotational barrier is obtained, there are many more structures involved which can contribute to the delocalized bonding and hence to nuclear spin-spin coupling. A detailed comparison of the wave functions for the six-electron and ten-electron calculations is presently being undertaken to determine the effect of the additional structures on the nature of the bonding.

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