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A Simple Model of Short-Range Interactions

II. The Orientation Dependence of the Interaction between Non-Bonded Hydrogen Atoms

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The simple model of short-range interactions described in the preceding paper has been applied to the study of the orientation dependence of the interaction between the non-bonded hydrogen atoms of two CH fragments. Calculation shows that for *the same* interatomic distance the interaction energy between non-bonded hydrogen atoms is strongly dependent on the relative orientation of the two bonds even for large values of R.

Das einfache Modell für Wechselwirkungen kurzer Reichweite, das in der vorhergehenden Arbeit beschrieben wurde, wird auf die Orientierungsabhängigkeit der Wechselwirkung der untereinander nicht gebundenen Wasserstoffatome zweier CH-Fragmente angewendet. Die Berechnungen zeigen, daß bei *gleichbleibendem* Atomabstand die Wechselwirkungsenergie zwischen untereinander nicht gebundenen Wasserstoffatomen stark von der relativen Orientierung der beiden Bindungen abhängt; dies gilt selbst noch für große Werte von R.

Le simple modèle des interactions à courtes distances décrit dans le précedent travail a été applié à l'étude de la dépendence de l'orientation entre les atomes d'hydrogène non-liés de deux fragments CH. Le calcule montre que pour la *même* distance intératomique, l'énergie d'interaction entre les atomes d'hydrogène non-liés est fortement dépendente de l'orientation relative des deux liaisons même pour des grandes valeurs de R.

1. Introduction

In the present paper we apply the simple model of short-range interactions previously described [1] to the study of the orientation dependence of the interaction between the non-bonded hydrogen atoms of two CH fragments. This problem has recently received some attention [2].

On physical grounds it seems likely that the conformational properties of small polyatomic molecules and simple polymers can be obtained in a first approximation from the knowledge of the interaction forces existing between *vicinal bonds* within the molecule. The short-range part of this interaction is essentially due to the repulsive interpenetration of the electron density belonging to pairs of localized chemical bonds and ultimately to the Pauli exclusion principle.

The simplest approximation to these interactions is given by an expression containing one [3] or more [4] exponential terms for the repulsive part of the potential (sometimes a R^{-n} term with $n > 6$) [5, 6] and an attractive term in R^{-6} as functions of the distance between pairs of *non-bonded atoms* in the molecule. In other words according to this model the conformational potential energy is given by

$$E = \sum_{\mu, \nu} E_{\mu\nu}, \qquad (1)$$

where $E_{\mu\nu}$ is assumed to depend only upon the nature and the reciprocal distance of the *two* centres of force μ and ν. While such a simple model can be worked to reproduce the barriers to internal rotation for ethane-like molecules [3, 4] and the absolute stability of some helical conformations for simple polymer chains [6–8] it entirely fails in predicting the *relative* stability of different conformers in higher saturated hydrocarbons [9] or in polymer chains [7], and, in general, in molecules containing multiple bonds or lone pairs of electrons.

Empirical calculations [10] on systems of biological interest have also shown the inadequacy of this approach, thus forcing the introduction of an additional "torsional" term, essentially empirical in origin, which turns out to be responsible for the largest part of the interaction.

According to our opinion the physical reason for this failure has to be found in the oversimplification inherent to that model and precisely in the fact that in a chemical bond the electron density around the atoms is not spherical, as it would be in the case of free atoms, but is usually "pear-shaped" around the bond direction (see Fig. 1). The interaction should therefore exhibit as an essential feature the dependence on the relative orientation of the two bonds. In order to construct a more realistic model we must take into account the interaction between *pairs of electrons* whose densities are suitably directed in space.

This is accomplished by the quantum mechanical model described in I, within the limits of the validity of the model itself. Accordingly, the study of the interaction between two CH fragments was undertaken in order to gain a feeling about the magnitude of the error inherent to the model of "non-bonded" atoms. After a short sketch of the underlying theory we shall outline some important remarks which result from the partitioning of the interaction energy into atomic components.

More details about the theory can be found elsewhere [1].

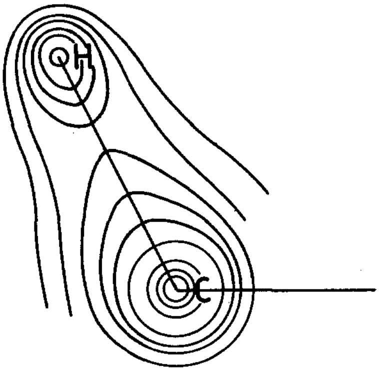

Fig. 1. Contour lines of equal electron density in the region of a C–H bond for the ${}^1A_1$ ground state of CH_4 (schematic, density decreasing outwards). The non-spherical character of the density around the proton and the polarization of the electronic charge towards the C atom yielding a "pear-shaped" density are apparent

2. Theoretical Background

A one-electron Hückel-type Hamiltonian $H(1)$ is chosen and the total wave function written as an antisymmetrized product of two nonorthogonal bond orbitals Φ^A, Φ^B built up from a linear combination of suitable directed hybrid atomic orbitals ϕ's. The coefficients of the linear combination are determined by the variation theorem through the iterative solution of a coupled pseudo-eigenvalue problem until self-consistency [11]. The intramolecular interaction between two localized bonds or, more generally, two localized electron groups results then from three contributions [12]:

i) The repulsive interpenetration of the static charge distributions of the two bonds.

ii) The energy lowering associated to the extra-charge pushed onto each bond as a consequence of the Pauli exclusion principle.

iii) The lowering of the total intramolecular energy resulting from the charge-transfer within each bond from interatomic regions of larger repulsion towards regions where the repulsion is smaller.

The last term being small for vicinal bonds [13], the intramolecular interaction energy results essentially from (i) + (ii), both contributions being strongly dependent on the orientation.

For two bonds A, B the partitioning of the interaction energy into atomic components yields

$$\Delta E^{(1)} = \sum_{\mu,\nu} E_{\mu\nu}, \tag{2}$$

where

$$E_{\mu\nu} = \tilde{P}_{\mu\nu}(H_{\nu\mu} - H^A S_{\nu\mu}) + \tilde{P}_{\nu\mu}(H_{\mu\nu} - H^B S_{\mu\nu}) \tag{3}$$

represents the contribution to $\Delta E^{(1)}$ arising from ϕ_μ (an atomic orbital belonging to A) and ϕ_ν (an atomic orbital belonging to B), $P_{\mu\nu}$ being the charge distributed according to the overlap density $\phi_\mu(1)\,\phi_\nu(1)$, H^A the orbital energy for bond A, and $H_{\nu\mu}$ and $S_{\nu\mu}$ the matrix elements:

$$H_{\nu\mu} = \langle \phi_\nu | H | \phi_\mu \rangle, \quad S_{\nu\mu} = \langle \phi_\nu | \phi_\mu \rangle .$$

In the case of two carbon-hydrogen bonds C–H and C′–H′ the interaction between the non-bonded hydrogen atoms H, H′ may then be written as (see the orbital labelling in Sect. 3 and Fig. 2)

$$E(\mathrm{H}, \mathrm{H}') \equiv E_{hh'} = 2\tilde{P}_{h'h}(H_{hh'} - H^{\mathrm{CH}} S_{hh'}), \tag{4}$$

where the charge $\tilde{P}_{h'h}$ may be expressed in terms of coefficients and overlap integrals between atomic orbitals as follows:

$$\begin{aligned} \tilde{P}_{h'h} = -2(1-S^2)^{-1}[&C_1^B C_2^B S_{t't} C_1^A C_2^A + (C_2^B)^2 S_{h't} C_1^A C_2^A \\ &+ C_1^B C_2^B S_{t'h} (C_2^A)^2 + (C_2^B)^2 S_{h'h} (C_2^A)^2] . \end{aligned} \tag{5}$$

S is the nonorthogonality integral between the bond orbitals, namely

$$S = \langle \Phi^A | \Phi^B \rangle = C_1^A S_{tt'} C_1^B + C_2^A S_{ht'} C_1^B + C_1^A S_{th'} C_2^B + C_2^A S_{hh'} C_2^B , \tag{6}$$

and the orbital energy for bond A is given by

$$H^{\mathrm{A}} \equiv H^{\mathrm{CH}} = (C_1^{\mathrm{A}})^2 H_{tt} + (C_2^{\mathrm{A}})^2 H_{hh} + C_1^{\mathrm{A}} C_2^{\mathrm{A}} (H_{th} + H_{ht}) . \tag{7}$$

According to this model the interaction between the "nonbonded" hydrogen atoms H, H′ depends upon all the 4 centres at a time through the dependence of the charge in (5) on the coefficients of both groups and the overlap integrals between all orbital pairs. Each interatomic contribution to the short-range interaction depends now upon the nature and the relative position of *four* centres of force, $E_{\mu\nu}$ in (2) assuming an entirely different meaning from the corresponding quantity in (1).

A similar partitioning holds for the other atomic pairs.

3. Details of Calculation, Results and Discussion

The geometry of the model is shown in Fig. 2.

The CH bond length was taken $R_0 = 1.09$ Å. Five different orientations of the two bonds were defined in terms of the two angles θ_1, θ_2:

I $\theta_1 = \theta_2 = 90°$

II $\theta_1 = \theta_2 = 109.5°$

III $\theta_1 = 75°, \theta_2 = 195°$

IV $\theta_1 = \theta_2 = 180°$

V $\theta_1 = 180°, \theta_2 = 45°$.

Each relative orientation of the two bonds was then studied as a function of R, the distance between the *non-bonded* atoms H, H′.

Valence C(2*s*), C(2*pσ*), C(2*pπ*), H(1*s*) atomic orbitals were chosen in the usual Slater form [14], with orbital exponents $\zeta_{\mathrm{C}} = 1.625$ for carbon and $\zeta_{\mathrm{H}} = 1.2$ for hydrogen. The orbital exponent for hydrogen was chosen in order to represent more closely the contraction of the density around the proton as it should be in the bonding situation [15]. Experimental evidence that the effective nuclear charge of the bonded hydrogen atom in CH bonds is larger than that in the free atom has also been obtained by analysis of X-ray diffraction data on hydrocarbons [16]. Suitable directed sp^3 hybrids were constructed from the basis set

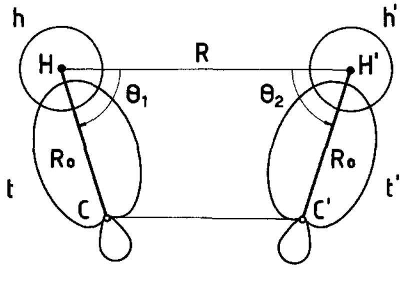

Fig. 2. Geometry of the model and schematic picture of the orbitals involved in the two CH bonds

in the form

$$t = \frac{1}{2}\,\mathrm{C}(2s) + \frac{\sqrt{3}}{2}\,\mathrm{C}(2p)\,,$$

where $\mathrm{C}(2p)$ is a $2p$ AO of carbon pointing in a given direction and which can be resolved into components of σ and π character.

One-electron localized bond orbitals were written as

$$\Phi^{\mathrm{CH}} = C_1^{\mathrm{CH}} t + C_2^{\mathrm{CH}} h\,,$$

where $h = \mathrm{H}(1s)$ and t is the appropriate sp^3 hybrid on carbon (Fig. 2). A corresponding expression holds for $\Phi^{\mathrm{C'H'}}$. The coefficients which determine the mixing of the atomic orbitals in each bond orbital were obtained by setting the effective Hamiltonian for each bond and by solving the resulting set of coupled pseudo-eigenvalue equations.

The overlap matrices were set up in terms of elementary overlap integrals of the type $S_{ss}, S_{s\sigma}, S_{\sigma\sigma}, S_{\pi\pi}, S_{hh}, S_{sh}, S_{\sigma h}$.

The elements of the Hamiltonian matrices over the hybrid basis were chosen in terms of coulomb and exchange integrals α's and β's as in the familiar extended Hückel theory [17]. The basic Hamiltonian matrices are:

$$\mathscr{H}^{\mathrm{CH}} = \begin{pmatrix} \alpha_t & \beta_{th} \\ \beta_{th} & \alpha_h \end{pmatrix}, \qquad \mathscr{H}^{\mathrm{CH,C'H'}} = \begin{pmatrix} \beta_{tt'} & \beta_{th'} \\ \beta_{ht'} & \beta_{hh'} \end{pmatrix}.$$

The α values were chosen as the Pritchard and Skinner [18] valence state ionization potentials for hydrogen and for $\mathrm{C}(sp^3)$:

$$\alpha_h = -13.6\ \mathrm{eV}, \quad \alpha_s = -21.34, \quad \alpha_p = -11.5.$$

The β's were roughly approximated with a modified Mulliken approximation over the basic atomic orbitals:

$$\beta_{\mu\nu} = \frac{K}{2}(\alpha_\mu + \alpha_\nu) S_{\mu\nu} \qquad \text{direct (bonded) interactions}$$

$$\beta_{\mu\nu} = \frac{K'}{2}(\alpha_\mu + \alpha_\nu) S_{\mu\nu} \qquad \text{indirect (non bonded) interactions.}$$

For $K = K' = 1$ we get the usual Mulliken approximation [19]; $K = K'$ gives the Wolfsberg-Helmholtz formula [20].

The distinction between direct (bonded) and indirect (non bonded) interactions in evaluating the β's is a new feature of the present approach and seems reasonable in view of the need of keeping the exchange integrals smaller than the corresponding coulomb integrals, as they should be. The two parameters were given the value $K = 1.3$ and $K' = 1.95$ in order to get reasonable values for the bond energy of a single CH fragment and for the energy difference between conformational isomers in hydrocarbons [13].

A program written in FORTRAN coded language for the electronic computer of the University of Genoa [13]. After the best bond orbitals have been obtained (in the usual sense of variation theory) the results are subjected to a population analysis and to the breakdown of the energy into components referred to in the preceding Section.

Table. *Short-range interaction energy (kcal/mole) between non-bonded hydrogen atoms as a function of the interatomic distance R*(Å) *between hydrogens for the 5 relative orientations of the two coplanar* CH *bonds*

R	I	II	III	IV	V
1.8	14.33	10.25	9.34	7.21	6.03
2.0	8.87	6.72		4.78	5.69
2.2	5.35	4.20	4.74	3.02	4.73
2.4	3.16	2.54		1.84	3.54
2.6	1.83	1.49	1.88	1.09	2.44
2.8	1.04	0.86		0.64	1.58
3.0	0.58	0.49	0.65	0.37	0.98

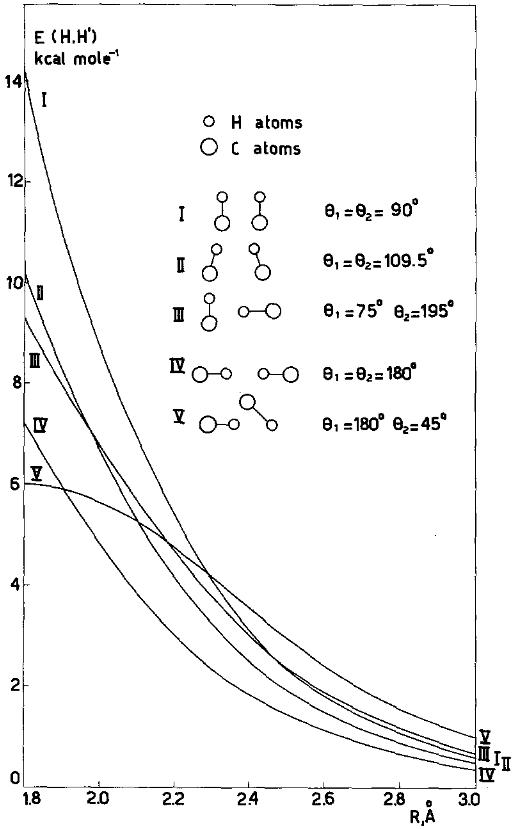

Fig. 3. Short-range interaction energy between "non-bonded" hydrogen atoms for the 5 different relative orientations of two coplanar C–H bonds as a function of the interatomic distance *R* between hydrogens

The resulting *E*(H, H′) are given in the Table and plotted against *R* in Fig. 3. Not too much confidence should be attached to the *absolute* values of the interaction energies given in the Table. We again emphasize that the parameters used in this work were fitted to reproduce values of energy *differences* between different conformers in saturated hydrocarbons [13]. Hence, only *differences* in behaviour between the various cases examined should be considered as significant.

It is apparent that for the *same* interatomic distance the interaction energy between "non-bonded" hydrogen atoms is strongly dependent on the relative orientation of the two bonds even for large values of R. The orientation dependence of the short-range interaction decreases with increasing R, because the density becomes more and more uniform at larger distances. We notice, however, that even for the largest values of R the percentage difference among the cases examined is still very important. Despite the crudeness of the present approximations we may therefore safely conclude that the orientation dependence of the interaction between non-bonded atoms is numerically relevant.

In a forthcoming paper [13] the present approach will be applied to the study of the conformational energies of the first terms in the series of saturated hydrocarbons.

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