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Relationes

The Rotation Barrier of Ethane-Like Molecules

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Based upon the Hellmann-Feynman theorem in its differential form RUEDENBERG [*4*] calculates the barrier of internal rotation in ethane using orthogonal localized one-electron molecular orbitals φ_i. Assuming that ethane consists of the methyl groups a and b, and that b rotates over an angle θ relative to a around the carbon-carbon bond, he obtains:

$$\varDelta E = 3\,\varDelta \sum_{\beta=1}^{3} R_{\beta\alpha}^{-1} - 6\,\varDelta \sum_{\beta=1}^{3} \int \varphi_i^2\, r_{\beta i}^{-1}\, d\tau_i \equiv \varDelta E'_{nn} - \varDelta E'_{ne\,\mathrm{I}}\,. \tag{1}$$

Group a contains electrons i and nuclei α, electrons and nuclei of b are denoted j and β respectively. Only two types of terms — viz. nuclear-nuclear repulsion and nuclear-electron attraction — appear, because differentiation of the hamiltonian to θ removes the contributions not depending explicitly on θ.

With the integral form of the Hellmann-Feynman theorem PARR and WYATT [*2, 3*] derive a similar expression, assuming for group a identical wave functions for the staggered and the eclipsed conformations and a vanishing contribution to the rotation barrier caused by the transition density in the vicinity of group b.

The purpose of this note is to show that the rotation barrier obtained via a first order perturbation treatment of the same model leads to a different result, when the non-bonded interaction of protons and localized charge densities between the two methyl groups is considered as the perturbation. Both conformations have been calculated separately, after which the rotation barrier emerged from the difference in first-order-perturbation energy.

If the wave functions of group a and b are denoted by ψ_a and ψ_b the zero order function to be used in the expression for the first order perturbation term is $\psi_a\,\psi_b$:

$$E' = \int \psi_a\,\psi_b\, H'\, \psi_a\,\psi_b\, d\tau \tag{2}$$

where

$$H' = \sum_{\alpha=1}^{3} \sum_{\beta=1}^{3} R_{\alpha\beta}^{-1} - \sum_{\beta=1}^{3} \sum_{i=1}^{6} r_{\beta i}^{-1} - \sum_{\alpha=1}^{3} \sum_{j=1}^{6} r_{\alpha j}^{-1} + \sum_{i=1}^{6} \sum_{j=1}^{6} r_{ij}^{-1}\,. \tag{3}$$

The four contributions to E' may be written as follows:

$$\int \psi_a \psi_b \left(\sum_{\alpha=1}^{3} \sum_{\beta=1}^{3} R_{\alpha\beta}^{-1} \right) \psi_a \psi_b \, d\tau = \sum_{\alpha=1}^{3} \sum_{\beta=1}^{3} R_{\alpha\beta}^{-1} = 3 \sum_{\beta=1}^{3} R_{\alpha\beta}^{-1} \equiv E'_{nn}$$

$$\int \psi_a \psi_b \left(\sum_{\beta=1}^{3} \sum_{i=1}^{6} r_{\beta i}^{-1} \right) \psi_a \psi_b \, d\tau = \sum_{\beta=1}^{3} \sum_{i=1}^{6} \int \varphi_i^2 r_{\beta i}^{-1} \, d\tau_i = 6 \sum_{\beta=1}^{3} \int \varphi_i^2 r_{\beta i}^{-1} \, d\tau_i \equiv E'_{ne\,\mathrm{I}}$$

$$\int \psi_a \psi_b \left(\sum_{\alpha=1}^{3} \sum_{j=1}^{6} r_{\alpha j}^{-1} \right) \psi_a \psi_b \, d\tau = \sum_{\alpha=1}^{3} \sum_{j=1}^{6} \int \varphi_j^2 r_{\alpha j}^{-1} \, d\tau_j = 6 \sum_{\alpha=1}^{3} \int \varphi_j^2 r_{\alpha j}^{-1} d\tau_j \equiv E'_{ne\,\mathrm{II}}$$

$$\int \psi_a \psi_b \left(\sum_{i=1}^{6} \sum_{j=1}^{6} r_{ij}^{-1} \right) \psi_a \psi_b d\tau = \sum_{i=1}^{6} \sum_{j=1}^{6} \int \varphi_i^2 r_{ij}^{-1} \varphi_j^2 \, d\tau_i \, d\tau_j = 12 \sum_{j=1}^{3} \int \varphi_i^2 r_{ij}^{-1} \varphi_j^2 \, d\tau_i \, d\tau_j \equiv E'_{ee} \, .$$

Apart from the terms given in (1), i.e. contributions from nuclear-nuclear repulsion and attraction between say nuclei β and group a electrons perturbation theory entails also electron-electron repulsion and attraction between nuclei α and group b electrons.

Table

$\Delta E_{nn} = 4.7$ kcal/mol
$\Delta E_{ne\mathrm{I}} = 3.4$ kcal/mol
$\Delta E_{ne\mathrm{II}} = 3.4$ kcal/mol
$\Delta E_{ee} = 2.6$ kcal/mol
$\Delta E_{\mathrm{total}} = 0.5$ kcal/mol

As a simple approximation a perturbation calculation of the rotation barrier using linear localized orbitals introduced by RUEDENBERG [4] has been performed. If L is the C–H bond length these orbitals — giving rise to a constant charge density between the nuclei — are defined by $\varphi_i = L^{-\frac{1}{2}}$. Both terms $E'_{ne\,\mathrm{I}}$ and $E'_{ne\,\mathrm{II}}$ then reduce to integrals of the form

$$\int (x^2 + ax + b)^{-\frac{1}{2}} \, dx = \ln \left[\frac{a}{2} + (x^2 + ax + b)^{\frac{1}{2}} \right] .$$

The contributions to E'_{ee} take the form $\int \ln \left[c + dx + (x^2 + ex + f)^{\frac{1}{2}} \right] dx$, and has been solved numerically*. The constants $a, b \ldots f$ are defined by the molecular configurations [1].

The data summarized in the table show that $\Delta E_{ne\mathrm{II}}$ and ΔE_{ee} are different and of the same magnitude as both other terms. In contrast to a barrier of 1.3 kcal/mol as found by RUEDENBERG via the Hellmann-Feynman theorem the result is now 0.5 kcal/mol. Though the choice of orthogonal localized orbitals prohibits a reliable numerical evaluation of the rotation barrier, it was thought of interest to note the extra terms from this first order perturbation treatment.

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* This calculation is carried out on the X_1-computer of the Rekencentrum of this University.

Literature

[1] Geometrical parameters are taken from DENNISON, D. M., and G. E. HANSEN: J. chem. Physics **20**, 313 (1952).
[2] PARR, P. G., and R. E. WYATT: J. chem. Physics **41**, 3262 (1964).
[3] — — J. chem. Physics **43**, S 217 (1965).
[4] RUEDENBERG, K.: J. chem. Physics **41**, 588 (1964).

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