

The Energy of Substituted Ethanes. Asymmetry Orbitals

(ethane torsion/molecular orbital theory/diastereoisomers)

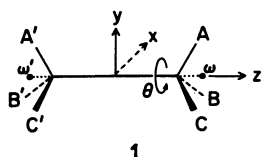
LIONEL SALEM*†, ROALD HOFFMANN‡, AND PETER OTTO§

*Laboratorium für Organische Chemie, ETH, Zürich and Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138; ‡ Department of Chemistry, Cornell University, Ithaca, New York 14850; and § Laboratoire de Chimie Théorique, Université de Paris-Sud, Orsay, France

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ABSTRACT The leading terms in the energy of a general substituted ethane are derived in explicit form as a function of the torsional angle θ , the substituent electronegativities, and their mutual overlaps. The energy is found to be the sum of all four overlaps between pairs of asymmetry orbitals, and satisfies the requisite symmetry properties.

We derive in explicit form the leading terms in an expression for the energy of **1**, a general substituted ethane, as a function of the torsional angle θ , the substituent electronegativities and their mutual overlaps. Our formulation is within the



framework of a one-electron theory and subject to the attendant deficiencies of such a model. We believe, however, that the formula we derive correctly describes, for the first time, the symmetries that any such energy expression, no matter how sophisticated, must possess.

The following assumptions enter our derivation:

(a) We work with a one-electron molecular orbital theory in which the matrix elements of the Hamiltonian are proportional to the overlap and the total energy is taken as the simple sum of orbital energies.

(b) The major contribution to the angular variation of the energy is assumed to come from the two pairs of orbitals in **1** that are descended from the two occupied degenerate e pairs of ethane (1, 2). At the substituent, these pseudo- π orbitals can be written as

$$\begin{cases} X = \frac{1}{\sqrt{2}}(B - C) \\ Y = \sqrt{\frac{2}{3}}\left(A - \frac{1}{2}(B + C)\right) \end{cases} \quad (1)$$

$$\begin{aligned} X' &= \frac{1}{\sqrt{2}}(B' - C') \\ Y' &= \sqrt{\frac{2}{3}}\left(A' - \frac{1}{2}(B' + C')\right) \end{aligned}$$

(c) The substituent orbitals A, B, C, etc. that participate in these pseudo- π orbitals are assumed to have local spherical symmetry. Also a mean bond-length \bar{r}_0 is chosen for all carbon-substituent distances, as well as an idealized tetrahedral geometry at each carbon.

(d) Finally it is assumed that one may expand the interatomic distances between substituents (A, B, C) and substituents (A', B', C') about the centers ω of ABC and ω' of A' B' C'. We call R the distance between ω and ω' along the z axis. Then the distance $R_{ii'}$ between any two centers, which has the general form

$$R_{ii'} = [R^2 + \bar{r}^2 f(\theta)]^{1/2}, \quad \bar{r} = 2\sqrt{\frac{2}{3}}\bar{r}_0 \quad (2)$$

where $f(\theta)$ is some trigonometric function of θ , can be expanded about R in powers or \bar{r}/R . In a similar vein we expand the overlap $S_{ii'}$ ($R_{ii'}$) between substituents i and i' in a Taylor series of increasing powers of $(R - R_{ii'})$. When the 4×4 secular determinant for the interaction of X, Y, X', and Y' is solved, the leading term in the angular variation of the energy is found to be

$$E(\theta) = \text{constant} [\cos \theta (S_{XX'} + S_{YY'}) + \sin \theta (S_{XY'} - S_{YX'})] \quad (3)$$

$$\text{constant} \equiv 12k \frac{\bar{r}^2}{R} \bar{S}'(R).$$

In (3), \bar{S}' is the average value of the first derivative, with respect to the interatomic distance, of the overlap $S'_{ii'}$ over all pairs of substituents ii' , and k is the proportionality factor between Hamiltonian matrix elements and overlaps. The angle $\theta = 0$ in the eclipsed geometry of **1**. The term $S_{XX'}$ is the overlap that would occur between orbitals X and X' if their components A, B, C and A', B', C' were located, respectively, at ω and ω' . Eq. (3) thus leads us to a new concept, the *asymmetry-orbital*. The asymmetry orbitals

$$\begin{aligned} X &= \frac{1}{\sqrt{2}}(B - C)_{\text{centered at } \omega} \\ Y &= \sqrt{\frac{2}{3}}\left[A - \frac{1}{2}(B + C)\right]_{\text{centered at } \omega} \end{aligned} \quad (4)$$

are linear combinations of a number of orbitals placed at the same center. These asymmetry-orbitals are a measure of the orbital asymmetry of a substituted CH_3 group along the x and y directions. They both vanish in CH_3 , one goes to zero in

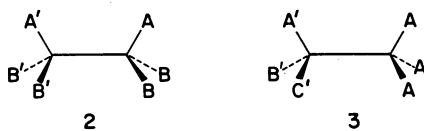
† Address reprint requests to permanent address: Laboratoire de Chimie Théorique, Université de Paris-Sud, Orsay, France.

CH_2X , and both are nonvanishing in CXYZ . The energy of substituted ethanes is then simply the sum of all four overlaps between the two pairs of asymmetry-orbitals, each overlap being multiplied by the angular factor appropriate to the corresponding scalar product. An elegant way of expressing (3) is $E = \text{constant } \mathbf{A}^\dagger \cdot \mathbf{R} \cdot \mathbf{A}'$, where \mathbf{A} and \mathbf{A}' are column matrices with elements (\mathbf{X}, \mathbf{Y}) and $(\mathbf{X}', \mathbf{Y}')$, respectively, and \mathbf{R} is the rotation matrix.

The energy expression (3) has a number of fascinating symmetry properties:

(i) On reflection in a mirror $\mathbf{X} \rightarrow -\mathbf{X}$, $\mathbf{X}' \rightarrow -\mathbf{X}'$, $\mathbf{Y} \rightarrow \mathbf{Y}$, $\mathbf{Y}' \rightarrow \mathbf{Y}'$, and $\theta \rightarrow -\theta$. Therefore, E (molecule) = E (its mirror image).

(ii) For $B = C$, $B' = C'$, $\mathbf{2}$, the asymmetry orbitals \mathbf{X} and \mathbf{X}' vanish, and only $S_{\mathbf{Y}\mathbf{Y}'} \neq 0$. The leading term then goes as $\cos \theta$, as it should. If one overlap, say $S_{\mathbf{A}\mathbf{A}'}$, dominates, then the equilibrium conformation is *trans*, $\theta = 180^\circ$ [The constant in (3) is positive since $k < 0$, $\bar{S}' < 0$].



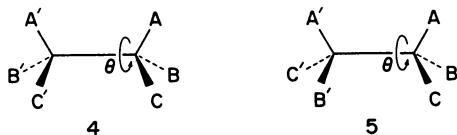
(iii) When $A = B = C$, $\mathbf{3}$, the minimal condition for a three-fold barrier, the leading term (3) vanishes. For the special case of all ligands identical, we can further prove that the leading nonvanishing term in θ is instead a three-fold one

$$E = \text{constant} (\cos 3\theta)$$

$$\text{constant} = 9k \frac{\bar{r}^6}{R^4} S'(R) [RS''(R) - S'(R)] \quad (5)$$

In (5), the ethane barrier is shown to depend only on first (S') and second (S'') differentials of the interatomic overlap, not on the magnitude of the overlap itself.

(iv) In the diastereoisomers $\mathbf{4}$ and $\mathbf{5}$ $S_{\mathbf{X}\mathbf{X}'}$ and $S_{\mathbf{Y}\mathbf{Y}'}$ are identical (3[¶]).



It follows immediately that

$$E_4(\theta) - E_5(\theta) = 2 \times \text{constant} (S_{\mathbf{X}\mathbf{X}'} \cos \theta - S_{\mathbf{Y}\mathbf{Y}'} \sin \theta) \quad (6)$$

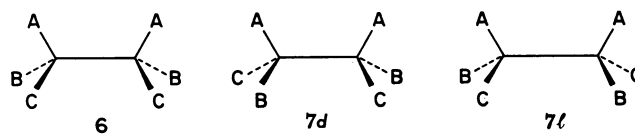
where the asymmetry-orbital overlaps refer to $\mathbf{4}$. It is satisfying that Eq. (6) involves only that asymmetry-orbital \mathbf{X}' of the left-hand group that is parallel to the axis joining the substituents B' and C' whose position distinguishes $\mathbf{4}$ from $\mathbf{5}$. For each value of θ , there is another value ($\theta + 180^\circ$) for which the relative energy of the diastereoisomers is reversed. This is true in particular for a (*threo*, *erythro*) pair.

(v) The asymmetry orbitals in the meso compound $\mathbf{6}$ and in the racemic mixture $\mathbf{7d}$ and $\mathbf{7l}$ are identical, with the exception

that $\mathbf{X}'_{7d} = \mathbf{X}'_6, \mathbf{X}'_{7l} = -\mathbf{X}'_6$. Furthermore $S_{\mathbf{X}\mathbf{Y}'} = S_{\mathbf{Y}\mathbf{X}'}$ in $\mathbf{6}$. Thus

$$E(\text{meso}) - \frac{1}{2} [E(d) + E(l)] = 2 \times \text{constant } S_{\mathbf{X}\mathbf{X}'_6} \cos \theta \quad (7)$$

where the constant has the value given in (3).



We have also derived the next term in the energy expression. This introduces the effects of asymmetric electronegativity changes.

$$E(\theta) = \text{constant} \{ (S_{\mathbf{Y}\mathbf{Y}'} - S_{\mathbf{X}\mathbf{X}'}) (h \cos(\theta + 2\phi) + h' \cos(\theta - 2\phi)) + (S_{\mathbf{Y}\mathbf{X}'} + S_{\mathbf{X}\mathbf{Y}'}) (-h \sin(\theta + 2\phi) + h' \sin(\theta - 2\phi)) \} \quad (8)$$

where the $S_{\mathbf{X}\mathbf{X}'}$, etc., have the same meaning as before, the constant is the same as in (3), and

$$h = \bar{\alpha} - \xi \cos 2\phi - \chi \sin 2\phi$$

$$\bar{\alpha} = \frac{1}{3} (\Delta\alpha_A + \Delta\alpha_B + \Delta\alpha_C) \quad \phi = \frac{1}{2} \arctan \frac{\chi}{\xi} \quad (9)$$

$$\chi = \frac{1}{2\sqrt{3}} (\Delta\alpha_B - \Delta\alpha_C)$$

$$\xi = \frac{1}{3} \Delta\alpha_A - \frac{1}{6} (\Delta\alpha_B + \Delta\alpha_C)$$

$\Delta\alpha_A$ is the electronegativity change for substituent A, $\Delta\alpha_B$ for B, etc. The constants h' and ϕ' are similar functions defined for the left-hand methyl group. The primary symmetry properties are met by this term as well.

In all cases, of course, the detailed comparison with experiment or with full numerical molecular orbital calculations must take into account the still higher-order terms in θ . Such a comparison will be presented in the full account of this work, to be published elsewhere.

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1. The role of these orbitals in the barrier problem is stressed by Lowe, J. P., *J. Amer. Chem. Soc.* **94**, 3799-3800 and Hoffmann, R. (1970) *Pure Appl. Chem.* **24**, 567-583. See however, Epstein, I. R. & Lipscomb, W. N. (1970) *J. Amer. Chem. Soc.* **92**, 6094-6095.
2. The representation of the e orbitals can be traced to Mulliken, R. S. (1933) *J. Chem. Phys.* **1**, 492-503; (1935) **3**, 517-528. They are constructed from methyl orbitals given, *inter alia*, by Gimarc, B. M. (1971) *J. Amer. Chem. Soc.* **93**, 593-599, and Owens, P. H. & Streitwieser, A., Jr. (1971) *Tetrahedron* **27**, 4471-4493.
3. Recent interest in acyclic diastereoisomers has been stimulated by the work of Sicher and collaborators on elimination reactions: Sicher, J. (1971) *Pure Appl. Chem.* **25**, 655-666; (1972) *Angew. Chem.* **84**, 177-191 and references therein.

[¶] In molecules $\mathbf{4}$ and $\mathbf{5}$, like in $\mathbf{1}$, the left-hand group is assumed to be fixed, with A' in the ZY plane. The right-hand group rotates.