

ENERGETICAL BASIS OF CONFORMATIONAL ANALYSIS

L. J. OOSTERHOFF

Department of Theoretical Organic Chemistry, University of Leiden, The Netherlands

ABSTRACT

A survey is given of some early and of recent descriptions of the origin of barriers to rotation about single bonds. Special emphasis is given to general theorems (virial theorem, integral Hellmann–Feynman theorem) which are very helpful in analysing interactions between non-bonding atoms. The equivalence of apparently different descriptions of the influence of lone pair electrons is stressed.

If the energy of a molecule is considered as a function of nuclear positions a number of minima can in general be established, corresponding to equilibrium configurations of the nuclei. If the forces opposing the interconversion of these configurations are neither large nor small the equilibrium configurations are called conformations. The vagueness inherent in the words 'large' and 'small' has the advantage of including a large number of investigators (and a large variety of investigations) to their mutual benefit.

The barriers which separate different conformations are often closely related to the barriers restricting rotation around single bonds. Bending forces may be just as important as, for instance, in the pseudorotation in cyclopentane. They are primarily responsible for the inversion phenomena of ammonia and amines.

Steric hindrance is a third factor contributing to the occurrence and relative stability of conformers.

Usually the same forces that are responsible for energy barriers also determine the relative heights of the energy levels of conformers and thereby their equilibrium distributions. Conformational analysis is therefore in several respects served by an insight into the origin of these energetic interactions. What one needs especially is a formulation of the interactions in terms of quantities that appeal to one's chemical or physical intuition, that are easy to employ and can be transferred from one molecule to the other.

There are rules of this kind, which seem to work excellently and suffice for many purposes. They are based on extensive empirical data, but are shaped according to theoretical expectations. Examples are found in the basic work of Westheimer and in the important contributions by von Schleyer. One may wonder whether more is needed by the conformational analyst. But it seems that further insight into the origin of the pertinent forces is needed. This applies especially to the forces of the type opposing free rotation

in ethane. The need for more precise understanding of bending forces and steric hindrance would appear to be of less importance.

I will therefore try to give a survey—necessarily very incomplete within the scope of this paper—of the present ideas about the barriers to internal rotation. A kind of 'state of the union': concealing what I want to hide, because of ignorance, and displaying what appeals to me.

Let us start by considering some simple molecules that exhibit barriers to internal rotation.

The potential barrier in ethane is well described by the function :

$$V = V_0 \frac{1 - \cos 3\phi}{2}$$

V_0 is 2.9 kcal/mole. The same order of magnitude of V_0 is found in many comparable molecules where V mainly depends on the angle of rotation ϕ through $\cos 3\phi$. The barrier in dimethylether is 2.7, in dimethylmethane 3.4 and in trimethylmethane 3.9. These are average values since the energy change by rotating one methyl group is not independent of the position of other methyl groups. In methylcyclopropane the barrier is 2.9. A larger number of more precise data are to be found in the review article by Wilson¹ and in more recent papers by Dale² and by Lowe³.

Comparing the barrier in ethane to the one in methylamine (2.0 kcal/mole) and in methanol (1.1 kcal/mole) (cf. *Figure 1*) the first idea which presents itself

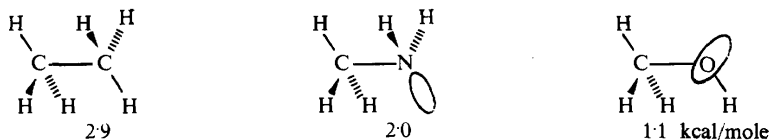


Figure 1

is to regard the barrier as due to repulsions between non-bonded atoms or between bonds. But the question that then arises is what kind of repulsion is operating?

If it is due to long-range interaction between electric charges the extrapolation to other, more complicated, molecules requires a technique which differs from the extrapolation of short-range interactions of the type found between closed shells of noble gases.

1. INTERACTIONS

At this point it may be appropriate to assemble a number of well-known concepts which will serve to illustrate what kind of interactions will come up for discussion. The starting point will be the Kekulé formulae displayed in *Figure 1*. Each line may be thought of as representing an electron pair moving according to a wave function in either valence bond or molecular orbital, or an even more ingenious formulation.

(a) Coulomb and exchange interaction

If two atoms interact to form a chemical bond the binding energy can be attributed—in valence bond terminology—to an exchange integral.

ENERGETICAL BASIS OF CONFORMATIONAL ANALYSIS

In a simplified form, omitting overlap integrals where they are not essential, the formula for the bond energy is:

$$E = C + J \quad (1)$$

where C = coulomb integral and J = exchange integral. The coulomb integral represents an electrostatic interaction between fixed charge distributions as they are present in separate atoms or in separate bonds. As compared to the exchange integral its contribution to the bond energy is usually small. This does not imply that its contribution to the magnitude of the barrier may not be dominant. J has a large negative value. Its appearance is due to the indistinguishability of electrons which implies a delocalization of all the electrons present. According to the Pauli principle the total wave function has to change sign if two numbers identifying the coordinates of two electrons, spin included, are interchanged. For that reason the positive sign in equation (1) is linked up with the presence of antiparallel spins in the electron pair forming a bond. If the spins were parallel, as in a triplet state, the energy expression would read:

$$E = C - J \quad (2)$$

Spins of electrons in different pairs are uncorrelated and since the chance of finding them parallel is $\frac{3}{4}$ (triplet state) whereas the chance of finding them antiparallel is $\frac{1}{4}$ (singlet state), the average interaction between electrons in different pairs is:

$$E = C - \frac{1}{2}J \quad (3)$$

The repulsive interaction of $-\frac{1}{2}J$ is always present between bonds, between bonds and lone pairs, etc.*

(b) Asymmetry induced in the pivot bond

If in ethane the carbon atoms participate in the total wave function with s - and p -orbitals only, the p -orbitals with axes of quantization perpendicular to the C—C bond will, because of symmetry, be equally occupied or working with hybrids: the occupation of the sp^3 -hybrids involved in carbon-hydrogen bonds will be equal. As a result the total coulomb as well as exchange interaction involving these orbitals has cylindrical symmetry and thus does not contribute to the potential barrier.

In principle the participation of d - and f -orbitals should not be excluded. This idea was put forward by Gorin, Walter and Eyring⁶ and has been reconsidered by Pauling⁷. Pauling estimates the amount of d - and f -participation

* Very often this repulsion is named after van der Waals, as a counterpart of the van der Waals attraction. There is good reason for this, because both, repulsion and attraction, were introduced by van der Waals in his famous equation to account for the non-ideal behaviour of gases. The van der Waals attraction, however, has a different origin. It is a second order effect linked with the polarizabilities of atoms and of molecules. Since it is convenient to have a separate name for the repulsive interaction between closed shells one could follow the example of inorganic chemists who use the term Born repulsion. Born⁴ introduced the expression B/r^n to account for the repulsion between closed shell ions in inorganic crystals and later (together with Mayer⁵) investigated the repulsion described by $b \exp(-r/\rho)$.

from the additional strengthening of the C—H bonds which may result, using the concepts of bond strength and promotion energy. The *f*-character of the carbon valence state obtained in this way seems large enough to account for the experimental barrier height. Unfortunately Pauling calls this result 'completely unreliable'. A somewhat related, but otherwise formulated, asymmetry in the C—C bond due to anisotropic polarizability has been discussed in a qualitative way by Dale².

Interaction through the carbon-carbon bond has, just as exchange interaction, the advantage of a short range and could for this reason be considered as a bond property which in one molecule would be the same as in another.

(c) Resonance

Within the scope of localized bond models one might also consider resonance with other Kekulé-like structures:

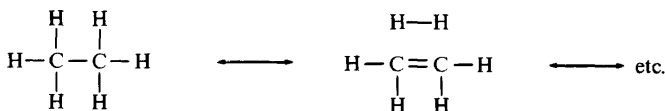


Figure 2

but this would lead to the eclipsed form being the more stable and can presumably be neglected.

2. AB INITIO CALCULATIONS

Another approach, which does not lean on familiar valence bond pictures, makes use of the Hartree-Fock or Self-Consistent Field method.

Starting from atomic orbitals, approximated by Slater functions or Gaussians, molecular orbitals are constructed and the product of molecular orbitals, including spin, is antisymmetrized according to the Pauli principle. The energy is calculated with the complete (non-relativistic) Hamiltonian and all the integrals are determined without invoking empirical parameters.

The first *ab initio* result obtained along these lines is due to Pitzer and Lipscomb⁸. They used the smallest set of basis functions: on each hydrogen atom a *1s*-function, on each carbon atom a *1s*-, a *2s*-, and three *2p*-functions. The value of the energy difference between the staggered and eclipsed configurations was 3.3 kcal/mole. This is quite a satisfactory result, somewhat surprising in view of the error in the total energy of the molecule which appeared to be 160 times as large. Evidently there was a large cancellation of errors in subtracting the total energies of the two configurations.

Other *ab initio* calculations by Clementi and Davis (1966) (3.62 kcal/mole), by Fink and Allen⁹ (2.52 kcal/mole), by Pedersen and Morokuma¹⁰ (2.88 kcal/mole) and by Pitzer¹¹ (3.5 kcal/mole) also gave results close to the experimental value of 2.9. Moreover these values seem neither to depend very much on the extension of the basis set nor on the precise form of the basis functions. Since the correct magnitude of the barrier is calculated with one determinantal wave function only, correlation effects do not seem to be

essential for the explanation of the barrier height. These observations suggest that it should be possible to paraphrase the results in fairly simple terms. This has indeed been tried in several directions, as will be discussed in Part 4 of this paper after various general theorems have been reviewed.

3. GENERAL THEOREMS

(a) Virial theorem

From Schrödinger's equation a very general theorem can be derived, which obtains a very concise form if applied to systems of particles with electrostatic interactions. If in a molecule the total force on each nucleus is zero, i.e. the nuclei are in a stable or metastable equilibrium configuration, the kinetic energy of the electrons is equal to one half of the negative of the potential energy V :

$$T = -\frac{1}{2}V \quad (4)$$

It was pointed out by Clinton¹² that calculations which aim at an explanation of the origin of the barrier from differences in electrostatic interaction between fixed charge clouds, are necessarily at variance with the very fundamental virial theorem. Unfortunately it has turned out that one does not gain much insight from bringing a calculation into line with the virial theorem. The condition imposed by the virial theorem can always be satisfied by multiplying all the coordinates by a common factor. This scaling of the wave function therefore hardly contributes to the understanding of the origin of the barrier.

(b) Variation principle

If ψ' is a wave function, which deviates from a correct solution of Schrödinger's equation ψ by a small but arbitrary function $\varepsilon\chi$ (ε a small number; χ an arbitrary function) then the corresponding energy E' , calculated as the expectation value of the Hamiltonian operator \hat{H} :

$$E = \frac{\langle \psi' | \hat{H} | \psi' \rangle}{\langle \psi' | \psi' \rangle} \quad (5)$$

differs from the true energy E by terms that are at least second order in ε . E is then said to be stationary; conversely, if the difference $E' - E$ is at least second order in ε for arbitrary variations $\psi' = \psi + \varepsilon\chi$, then E and ψ are a solution of the Schrödinger equation.

The variational method uses these statements to determine approximate solutions ψ by requiring that the corresponding E values are stationary for a restricted, appropriately chosen, set of functions χ . This makes it understandable why the total energy is rather insensitive to deviations of the approximate wave function from the correct one, whereas other quantities like the kinetic energy or potential energy separately are not, as is seen when applying the virial theorem.

It is not to be expected that the difference between the energies of two configurations of nuclei will be rather insensitive to changes in wave functions. Nevertheless, when this observation has been made in a number of calculations

it probably means that the origin of the barrier can be formulated in fairly general terms.

On the other hand one may wonder whether rather different wave functions, like those discussed by Pauling, containing non-negligible contributions of d - and f -functions are just as acceptable on the basis of the variation method and will also give the correct value of the barrier. It also makes it somewhat doubtful whether an analysis of the wave functions determined up to now will result in the correct interpretation of the barrier.

(c) Hellmann–Feynman theorem

An important tool in interpreting the wave function has been introduced by Parr¹³ as the integral form of the original differential Hellmann–Feynman theorem. The derivation can be given in a few lines. One writes the Schrödinger equation for both nuclear configurations, staggered (denoted as x) and eclipsed (denoted as y):

$$\begin{aligned} H^x |x\rangle &= E_x |x\rangle \\ H^y |y\rangle &= E_y |y\rangle \end{aligned} \quad (6)$$

In the present problem the wave functions $|x\rangle$ and $|y\rangle$ describe the corresponding ground states. From these equations one derives:

$$\begin{aligned} \langle y | H^x | x \rangle &= E^x \langle y | x \rangle \\ \langle x | H^y | y \rangle &= E^y \langle x | y \rangle \end{aligned} \quad (7)$$

or, because of the hermitean character of H ,

$$\langle y | H^y | x \rangle = E^y \langle y | x \rangle$$

Subtraction yields

$$\langle y | H^y - H^x | x \rangle = (E^y - E^x) \langle y | x \rangle \quad (8)$$

This equation has the advantage that the sought-for energy difference $\Delta E = E^y - E^x$ is expressed with the difference operator $\Delta H = H^y - H^x$ in which only one electron operator occurs. This follows from inspection of the Hamiltonians, which can be written as:

$$H = T + v_{ee} + v_{nn} + v_{ne} \quad (9)$$

where T stands for the kinetic energy operator, v_{ee} for the electron–electron repulsion, v_{nn} for the nuclear–nuclear repulsion and v_{ne} for the electron–nuclear attraction. The difference between the configurations x and y only shows up in v_{nn} and v_{ne} and therefore:

$$\Delta E \langle y | x \rangle = \langle y | \Delta H | x \rangle = \langle y | \Delta v_{nn} + \Delta v_{ne} | x \rangle \quad (10)$$

with $\Delta v_{nn} = v_{nn}^y - v_{nn}^x$ and $\Delta v_{ne} = v_{ne}^y - v_{ne}^x$.

The barrier height ΔE can thus be calculated with the potential energy operators Δv and Δv_{ne} , which either do not contain the electronic coordinates at all or only as one electron operator. This simplifies the calculations provided the wave functions are known. The wave functions should even be known precisely since the derivation of (10) starts from exact solutions of the

Schrödinger equations. If only approximations to the exact wave functions are known, correction terms should be added to (10), since otherwise ΔE calculated with (10) may differ from $E^y - E^x$ calculated with the values obtained with formula (5).

The advantage of this method of analysing the origin of the barrier is the elimination of kinetic energy or electron-electron repulsion operators which are difficult to handle.

The factors determining the barrier height are reduced to electrostatic interactions between nuclei and between nuclei and electronic charge distributions. A disadvantage is the knowledge required of the overlap charge distribution, obtained by multiplying the wave functions $|y\rangle$ and $|x\rangle$, which is often difficult to assess accurately and which is not always easy to visualize.

4. ANALYSIS OF *AB INITIO* RESULTS

The application of the integral Hellmann-Feynman theorem has certainly revealed interesting views on the origin of barriers to rotation about single bonds. Since I do not feel able to give a simple explanation of the results within the limited scope of this paper and an extensive discussion can be found in the review article by Lowe (1968), I would rather restrict the present discussion to two ways of analysing the outcome of *ab initio* calculations, one followed by Allen¹⁴, the other by Sovers, Kern, Pitzer and Karplus¹⁵.

Allen splits up the total Hamiltonian operator (9) into a repulsive component $T + V_{nn} + V_{ee}$ and an attractive component V_{en} and compares the expectation values of each part when the angle of rotation about a single bond changes. It turns out that in ethane the attractive component favours the eclipsed configuration and the repulsive component the staggered one with the repulsive component dominant. This picture is very similar to those which are obtained when analysing in a similar way the interactions between two He atoms or between two H_2 molecules. From this similarity Allen concludes that the barrier can be regarded as strongly influenced by the Pauli principle.

This conclusion is very much in line with the analysis of the results of Pitzer and Lipscomb⁸ by Sovers, Kern, Pitzer and Karplus¹⁵. They have used the atomic orbitals occurring in Pitzer and Lipscomb's calculations to construct bond wave functions for the C—C and the six C—H bonds.

The energy calculations for staggered and eclipsed ethane were carried out once without antisymmetrizing the total wave function (Hartree procedure) and also with complete antisymmetrization (Hartree-Fock procedure). Within the Hartree calculations the barrier is due to electrostatic interactions between fixed charge distributions. The Hartree-Fock treatment introduces a change in the wave function by delocalizing the electrons according to the requirements of the Pauli principle. Since the Hartree-Fock calculations yield a reasonable value for the barrier whereas the Hartree calculation does not, it is concluded that the repulsion due to the Pauli principle—compare equation (3)—can be regarded as responsible for the barrier. It is the same type of repulsion that operates between closed shell atoms or molecules, e.g. between He atoms or between H_2 molecules.

This idea has been put forward several times in the past, but it had to

await the quantification made possible by present-day computing techniques before it could be accepted on firm grounds.

5. RECENT REFINEMENTS

A Hartree-Fock calculation with a much larger basis set which presumably yields energy close to the limit that can be reached with this type of calculation has been carried out by Veillard¹⁶. His barrier value is 3.6 kcal/mole if the nuclei are allowed no other displacement than is implied in rotating one methyl group with respect to the other. If allowance is made of other displacements as well the barrier can be lowered to 3.0 kcal/mole. Then the C—C distance in the eclipsed configuration (1.570 Å) is larger than in the staggered configuration (1.551 Å) and the C—H bonds are displaced slightly away from the other methyl group, the HCH-angle being 107.0° in the eclipsed as compared to 107.3° in the staggered configuration.

This is an important observation in view of a transfer of ethane results to a molecule such as cyclopentane. Here a displacement of the C—H bonds from a neighbouring CH₂ group would be unfavourable with respect to the other neighbour, which could result in a higher barrier value.

6. LONE PAIRS

Although *ab initio* calculations have been carried out for many more molecules than ethane, it seems more difficult to arrive at a clear rationalization of the results in terms similar to those used for ethane. It may nevertheless be opportune to make a few remarks on the way the effects of lone pairs are often illustrated. If one adopts a certain hybridization at the nitrogen atom in methylamine or at the oxygen atom in methanol to account for the observed bond angles, the atomic wave function of the single lone pair in methylamine is fixed. For convenience let us assume sp^3 hybridization. Then the lone pair in methylamine occupies an sp^3 hybrid. In methanol, however, the situation is ambiguous. One could just as well say that of two electron pairs each occupies an sp^3 hybrid (Figure 3a) or that one pair occupies a pure p orbital and the other an sp hybrid (Figure 3b).



Figure 3

For the purpose of calculating coulomb interactions or exchange interactions both descriptions are entirely equivalent. If excitation or ionization of one of the four lone pair electrons or charge transfer to an antibonding orbital of a neighbouring bond has to be considered, then there is a difference and the second representation (Figure 3b) has to be preferred. One must be careful when considering a situation where a neighbouring C—H bond is in a staggered position with respect to the two lone pair orbitals in Figure 3a as representing for this reason a stable configuration, whereas the same bond

would eclipse the *sp* hybrid in *Figure 3b*. It would be better to regard the two lone pairs together as forming one system with a charge distribution such as shown in *Figure 1c*.

7. CONCLUDING REMARKS

It would certainly be helpful to know whether the barrier in ethane can be obtained additively from the repulsive interactions between pairs of CH bonds or if higher order interactions in which three or more bonds are involved are important as well. If the first situation holds it would be desirable to deduce from *ab initio* calculations rules for the computation of the energy of repulsion from the distances between bonds and from their relative orientation.

Moreover, if it is correct to regard the overlap of bond wave functions— together with the Pauli principle— as the origin of the barrier to rotation about single bonds it might be worthwhile to re-evaluate the ideas put forward by Pauling⁷. The introduction of *f*-orbitals into the description of the C—H bonds concentrates the wave functions more in the bond direction. It may be that the diminishing overlap between bonds emanating from neighbouring atoms is replaced by interaction between *f*-orbitals, leading to the same barrier, but capable of a different interpretation. Until further work has been done it will be wise to look at barriers restricting rotation about single bonds as originating from the familiar repulsion between closed shells.

REFERENCES

- ¹ E. B. Wilson. *Advanc. Chem. Phys.* **2**, (1959).
- ² J. Dale. *Tetrahedron*, **22**, 3373 (1966).
- ³ J. P. Lowe. *Progress in Physical Organic Chemistry* **6**, 1 (1968).
- ⁴ M. Born. *Atomtheorie des festen Zustandes*. Teubner, Leipzig (1923).
- ⁵ M. Born and J. E. Mayer. *Z. Phys.* **75**, 1 (1932).
- ⁶ E. Gorin, J. Walter and H. Eyring. *J. Amer. Chem. Soc.* **61**, 1876 (1939).
- ⁷ L. Pauling. *Proc. Nat. Acad. Sci. U.S.A.* **44**, 211 (1958); cf. *The Nature of the Chemical Bond*. 3rd edn. (1960) 130.
- ⁸ R. M. Pitzer and W. N. Lipscomb. *J. Chem. Phys.* **39**, 1995 (1963).
- ⁹ W. H. Fink and L. C. Allen. *J. Chem. Phys.* **46**, 2261 (1967).
- ¹⁰ L. Pedersen and K. Morokuma. *J. Chem. Phys.* **46**, 3941 (1967).
- ¹¹ R. M. Pitzer. *J. Chem. Phys.* **47**, 965 (1967).
- ¹² W. L. Clinton. *J. Chem. Phys.* **33**, 632 (1960).
- ¹³ R. G. Parr. *J. Chem. Phys.* **40**, 3726 (1964). (Also referred to in reference 3.)
- ¹⁴ L. C. Allen. *Chem. Phys. Lett.* **2**, 597 (1968).
- ¹⁵ O. J. Sovers, C. W. Kern, R. M. Pitzer and M. Karplus. *J. Chem. Phys.* **49**, 2592 (1968).
- ¹⁶ A. Veillard. *Chem. Phys. Lett.* **3**, 128 (1969).