871. *Intramolecular Non-bonded Effects involving Hydrogen Atoms.*

By K. E. Howlett.

Use of Hirshfelder and Linnett's potential function for the repulsive state of the hydrogen molecule is described for the purpose of calculating non-bonded energies between hydrogen atoms. When a suitable and intuitively reasonable dependence of this potential on the angle between the bonded and non-bonded direction is introduced, a quantitatively correct answer is computed for the rotational energy barrier in ethane. The same function is then applied to problems related to the diphenyl and *cyclo*hexane skeletons. The results are shown to be in general agreement with the known facts.

A MAJOR difficulty in any quantitative treatment of conformational analysis has proved to be the assignment of a suitable interaction potential function for two hydrogen atoms. Consideration of the apparently simple case of ethane, for example, has led to the unsatisfactory conclusion that, whereas it is not possible to account quantitatively for the potential barrier hindering free rotation in terms of van der Waals forces,[1] yet quadrupole interactions (assuming rather high quadrupole moments [2] or ionicities [3]) give answers of the correct order of magnitude. In other contexts the loose term van der Waals force is usually understood to include multipole interactions. However, by using the principle of the L.C.A.O. approximation, *viz.*, that in the regions of the hydrogen atoms the electron density is similar to that around an isolated hydrogen atom, the unnecessary and artificial assignment of a definite van der Waals radius may be avoided. Hirshfelder and Linnett [4] have given a thorough treatment of the potential of two hydrogen atoms. The mutual potential of two bound hydrogen atoms may be identified with Hirshfelder and Linnett's calculated potential for the repulsive state of the hydrogen molecule because, in each case, the Pauli principle may be invoked to show that the electrons on the two hydrogen atoms cannot occupy the same space. For the repulsive state of H_2 the electron-spin quantum numbers are the same, and for the hydrogen atoms considered in this paper, which are already linked to other atoms, the first quantum level is fully occupied so that the electrons on any other approaching hydrogen atom cannot also enter this level in the same spatial elements. Hirshfelder and Linnett's calculated curve is clearly of the correct form, passing from repulsion to slight attraction at large distances. The reality of the interaction may be gauged from the quantitative agreement of the calculated function with that deduced by Amdur and Mason [5] from collision experiments with hydrogen and helium. Use of the Hirshfelder–Linnett function yields larger repulsive potentials at short internuclear distances than those of earlier calculations [1] which were based on assigned van der Waals radii. This feature is a desirable one.[6] Employment of the function implies an extension in the use of data obtained for a spherically symmetrical electron distribution to cases of cylindrically symmetrical distributions. At present, unfortunately, non-bonded interaction calculations necessarily involve relatively crude assumptions.

Pauling,[7] and more specifically Hughes, Ingold, *et al.*,[8, 9] suggest that the non-bonded interaction between two otherwise bound atoms should be somewhat dependent on the largest positive direction cosine of the non-bonded atom relative to the directly bound

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[1] Barton, *J.*, 1948, 340.
[2] Lassettre and Dean, *J. Chem. Phys.*, 1948, **16**, 151, 553; 1949, **17**, 317.
[3] Oosterhoff, *Discuss. Faraday Soc.*, 1951, **10**, 79.
[4] Hirshfelder and Linnett, *J. Chem. Phys.*, 1950, **18**, 130.
[5] Amdur and Mason, *ibid.*, 1956, **25**, 630.
[6] Cf. Westheimer, " Steric Effects in Organic Chemistry," Ed. Newman, John Wiley, New York, 1956, p. 540.
[7] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, 1939, p. 178.
[8] Dostrovsky, Hughes, and Ingold, *J.*, 1946, 173.
[9] de la Mare, Fowden, Hughes, Ingold, and Mackie, *J.*, 1955, 3200.

atoms (cf. Fig. 1). The form of variation used has effectively been to displace the potential curve laterally to greater separations by an amount $\chi(1 + \cos 2\theta)$ Å per non-bonded atom if $\theta < \pi/2$. For the particular interactions considered [8, 9] χ was assigned the value 0·4 to give agreement with experiment, although this could be an overestimate since from Pauling's illustration [7] it yields virtually zero non-bonded interaction between the chlorine atoms in carbon tetrachloride. From the comparative failure of the simple valency force field (S.V.F.F.) treatment of the vibrational fundamentals for this molecule it seems probable that appreciable non-bonded effects are present.

In the present paper calculations are reported which use the Hirshfelder–Linnett repulsive potential function for non-bonded H–H interactions, and the numerical constant χ, required to allow for angular dependence of the interaction, has been varied from 0 to 0·4. The interaction energy is then summed over every possible pair of non-bonded atoms. The first computations concern the rotational energy barrier in ethane.

For each value of χ taken, the staggered form of ethane is found to be the most stable conformation (in agreement with experiment [10]), and the eclipsed form the least stable.

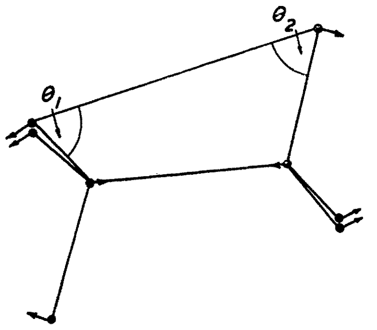

FIG. 1. *The ν_2 normal mode in ethane.*

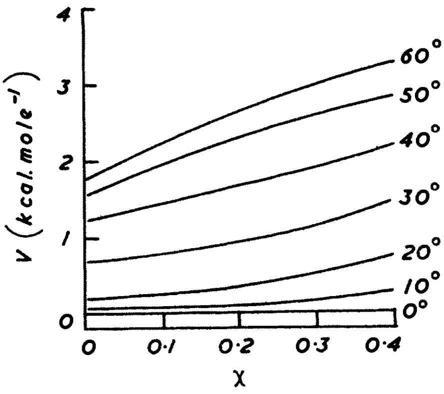

FIG. 2. *Variation of V with rotation in ethane as a function of χ.*

As in earlier calculations on this subject we have assumed that the molecule is rigid except in the rotation co-ordinate. Most of the vibration frequencies are sufficiently high to ensure that the vast majority of ethane molecules are in their ground vibrational states at ordinary temperatures. Therefore the most probable positions of the nuclei are the classical rigid positions. There are, however, appreciable uncertainties (zero-point amplitudes) about these positions. The normal vibrational mode which most affects the relative separation of the hydrogen atoms of the two methyl groups is the ν_2 mode (Fig. 1). Thus, although all the zero-point amplitudes ought to be considered, the ν_2 mode will probably affect the calculated barrier to the greatest extent. A crude assessment of this vibrational effect has been made by considering the motion as that of a 1-dimensional oscillator of frequency 1375 cm.$^{-1}$, with appropriate statistical weighting of configurations of various amplitudes. The vibrational effect in this mode is to raise the calculated barrier height by about 20% over that for the " rigid " model.

Contrary to opinions expressed earlier, the allowance for angular dependence of the effective van der Waals radius raises rather than lowers the barrier because, although it lowers most absolute potentials, it acts rather rapidly in a differential manner with angular rotation about the C–C bond. Most satisfactory, however, is the fact that the calculated barriers are all of the right order, and of the correct magnitude intermediately between the limits considered for the angular dependence function. Table 1 shows the dependence of the height of the barrier (V_0) (neglecting any vibrational effects) upon the assumed value of χ.

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[10] Smith, *J. Chem. Phys.*, 1949, **17**, 139.

Fig. 2 shows the variation of V with rotation (ϕ) about the C–C bond as a function of χ; ϕ is taken as 0 for the staggered conformation. The best value of χ is about 0·2. With this value, $V_0 = 2{\cdot}64$ kcal. mole^{-1} if the hydrogen atoms are always at the rigid positions,

TABLE 1.

χ	0	0·2	0·3	0·4
V_0 (kcal. mole^{-1})	1·77	2·64	2·91	3·25

and $V_0 \approx 3{\cdot}1$ kcal. mole^{-1} when the specified vibrational motion is considered. The angular variation of V (neglecting the vibrational effect) is compared in Fig. 3 with the frequently assumed function, $2V = V_0(1 - \cos 3\phi)$. The cosine barrier shape gives only moderate agreement with the present calculated curve. In fact, the calculated curve corresponds more closely to case C mentioned by Pitzer and Gwinn.[11] Fortunately, as shown by Halford,[12] a difference of this kind from the cosine shape involves minute alterations in the calculated thermodynamic functions of the molecule.

FIG. 3. *Comparison of barrier shapes in ethane*: A, *calculated from non-bonded effects*; B, *cosine shape*.

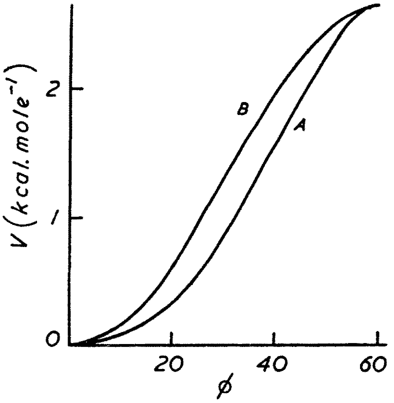


FIG. 4. *The* ν_2 *mode in methane.* (Broken curve shows one ψ contour for sp^3 orbital.)

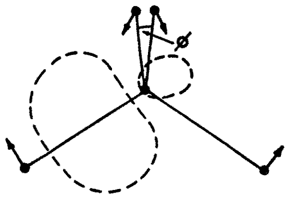
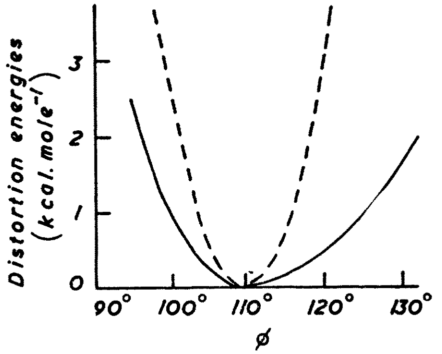


FIG. 5. *Broken curve*: *total distortion energy. Full curve*: *non-bonded energy.*



The present result is frankly obtained to some extent by adjustment of the disposable parameter χ. A real test of the suitability of the potential function with $\chi = 0{\cdot}2$ lies in its applicability to other cases. Beginnings of such applications, together with the attendant difficulties, are discussed below.

(1) As a first illustrative use of the potential function we consider the ν_2 normal vibration in methane (Fig. 4). In the formation of the tetrahedrally spaced bonds, the molecular orbitals may be considered to be formed by overlap of hydrogen 1*s* atomic

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[11] Pitzer and Gwinn, *J. Chem. Phys.*, 1942, **10**, 428.

[12] Halford, *ibid.*, 1947, **15**, 645.

orbitals with carbon sp^3 hybrid atomic orbitals. The density contours of the latter have relatively small curvature in the overlap region so that small vibrations in the ν_2 mode should not greatly affect the overlap. If we make the approximation that the hybridisation of the carbon atomic orbitals changes insignificantly during the vibration, then it is expected that the non-bonding effects should make an appreciable contribution to the rise in potential energy accompanying distortion in this mode. The total distortion energy is known in good approximation from the S.V.F.F. treatment for methane which yields the appropriate force constant of $0{\cdot}5 \times 10^{-11}$ erg radian^{-2} molecule^{-1}. The non-bonded contribution has been calculated by assuming that the C–H bond length is invariant at 1·094 Å throughout the vibration. A comparison of the two energies (summed in each case over the 6 possible interactions) is given in Fig. 5 as a function of one $\mathrm{H\hat{C}H}$ angle (ϕ). It appears that non-bonded effects are appreciable even in methane.

(2) Secondly, we consider the effect of non-bonded interaction on rotation about the 1 : 1′-bond in diphenyl (Fig. 6). The interplanar angle is denoted by ϕ. In order to proceed, the following assumptions are made. The variation of energy with ϕ is regarded as having three components: (*a*) the resonance energy, which has been taken from Guy;[13] (*b*) non-bonded interactions; and (*c*) in-plane bending effects (such as those through the four angles α in Fig. 6). Ring distortion has been neglected.[14] It has also been shown by a subsidiary calculation that energy recovery by bending the four angles β is negligible even in the coplanar conformation. The 1 : 1′-bond length is considered to vary with ϕ. It is taken as 1·54 Å when $\phi = \pi/2$, but shortened to a number of possibilities over the range 1·44—1·50 Å when $\phi = 0°$. In each case the relative shortening from 1·54 Å towards the assumed length when $\phi = 0°$ is taken as proportional to the resonance energy. The aromatic C–C bonds are all taken as 1·4 Å in length, the C–H bonds as 1·1 Å, and the $\mathrm{C\hat{C}H}$ bond bending force constant[15] as $0{\cdot}86 \times 10^{-11}$ erg radian^{-2} molecule^{-1}. Since this force constant is transferred from benzene, it may be assumed that distortion energies calculated with its aid already include non-bonding effects between, for example, H_2 and the $C_{(1')}$, $C_{(1)}$, $C_{(3)}$, and $H_{(3)}$ group. Non-bonding effects between (say) $H_{(2)}$ and $C_{(2')}$ have been neglected in the calculations. These effects are likely to be small. The uncertainty of position effect discussed for ethane has also been neglected.

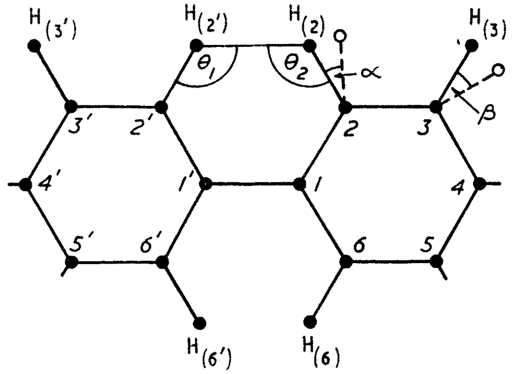

FIG. 6. *Diphenyl.*

For each conformation considered for the molecule, the energy is minimised by summing the effects (*a*), (*b*), and (*c*) over a number of configurations. Table 2 shows the calculated energy barrier (V_0) hindering free rotation of the rings as a function of the length, $d(1:1')$, of the central bond in the coplanar position. Also included in the table is the value of V_0 found if the central bond length is 1·54 Å independently of ϕ, and if there is no resonance energy contribution to the stability of the coplanar state. This figure supplies the

[13] Guy, *J. Chim. phys.*, 1949, **46**, 469.

[14] Cf. Westheimer, *J. Chem. Phys.*, 1947, **15**, 252.

[15] Kohlrausch, *Z. phys. Chem.*, 1935, **30**, *B*, 305.

justification for the inclusion of effect (*a*) in the total energy because delocalisation of the charge distribution can only contribute to the real structure of the coplanar (or any other) state if the lowering of potential energy due to resonance outweighs the rise in non-bonded energy consequent upon the bond shortening.

TABLE 2.

$d(1:1')$ (Å)	1·44	1·46	1·48	1·50	1·54
V_0 (kcal. mole^{-1})	11·5	10·8	10·1	9·5	(15·3)

Table 3 shows the variation in resonance energy,[13] bond shortening, $d(1:1')$, and the computed change in potential energy (V) as a function of ϕ, for the case in which $d(1:1')$ is 1·46 Å at $\phi = 0°$. As in the case of ethane, the shape of the barrier shows maxima only in the eclipsed positions, and it also shows the same type of variation from the cosine form (with two maxima and minima per revolution). A barrier of maximum height 10 kcal. mole^{-1} would give strong preference for conformations well away from coplanarity but would be insufficient to allow of separation of rotational isomers in suitably substituted derivatives. Furthermore, the result may be correlated with experiment. Thus although the variation in resonance energy may be of the form suggested by Guy, the average resonance energy of diphenyl has been calculated[16] to be almost zero. The present calculations support the idea that most free diphenyl molecules will have interplanar angles greater than $\pi/4$. From this result, Guy's estimated average resonance energy would be 0—1 kcal. mole^{-1}. A necessary corollary to this conclusion is that the average central-bond-shortening in diphenyl is only about 0·01 Å. Also it is seen from Table 3 that the variation in V for a change in ϕ near $\phi = \pi/2$ is very small. Thus the restoring force constant for this mode is likewise small. (For the approximately quadratic increase in V as ϕ varies by up to $\pi/8$ from the potential minimum position, $k_\phi = 1 \times 10^{-13}$ erg radian^{-2} molecule^{-1}.) This implies that diphenyl will tend to populate not only the ground vibrational state but also the low-lying excited states in this interannular vibration mode. In fact, the maximum population density probably lies in one of the early excited levels. In such a level the most probable state of the molecule is near the limit of the classical amplitude where the vibrational wave function has its greatest values. Therefore, the instantaneous state of a free diphenyl molecule is most likely to be near that conformation at which the potential curve begins to rise more steeply, *i.e.*, in the region of $\phi \gtrsim 55°$. Bastiansen's electron-diffraction result[17] (which corresponds to a most probable instantaneous state) for ϕ is 45° ± 10°.

TABLE 3.

ϕ	0	$\frac{\pi}{16}$	$\frac{\pi}{8}$	$\frac{3\pi}{16}$	$\frac{\pi}{4}$	$\frac{5\pi}{16}$	$\frac{3\pi}{8}$	$\frac{7\pi}{16}$	$\frac{\pi}{2}$
Resonance energy (kcal. mole^{-1}) ...	6·96	6·32	4·70	2·80	1·29	0·43	0·09	0	0
Central bond shortening (Å)	0·08	0·07	0·055	0·03	0·015	0·005	0	0	0
$d(1:1')$ (Å)	1·46	1·47	1·485	1·51	1·525	1·535	1·54	1·54	1·54
V (kcal. mole^{-1})	10·8	9·1	6·5	3·60	1·57	0·80	0·23	0·06	0

A final correlation with experiment is obtained by the following method. We make the approximation that 3 : 3′-dichlorodiphenyl has the same variation of intramolecular forces with ϕ as diphenyl itself, together with dipolar interactions arising from the 3- and 3′-substituents. The dipolar interaction energies have been computed by assuming two point dipoles of magnitude 1·58 D, situated at the "points of contact" of carbon and chlorine atoms, to be separated by a medium of dielectric constant 2·2. The addition of this electrostatic energy (which is positive for all conformations) to that computed for diphenyl itself yields a resultant potential curve with a minimum at about $\phi = 92°$, *i.e.*, with the chlorine atoms slightly *trans*. The dielectric-constant evidence[18] (obtained by using

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[16] Klages, *Ber.*, 1949, **82**, 358.
[17] Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408.
[18] Littlejohn and Smith, *J.*, 1954, 2552.

radiofrequency and therefore giving an average figure for the dipole moment throughout the molecular vibrations) indicates that $\phi \approx 97°$ with the chlorine atoms *trans*. The agreement is notable and shows that the relative magnitudes of the different effects are about correct.

(3) Some investigation has been made of non-bonding effects between hydrogen atoms in the *cyclo*hexane ring system. In conformity with earlier calculations,[1] the chair form of *cyclo*hexane is found to be more stable than the boat form. All angles are assumed to be tetrahedral. The more interesting isomer in the present calculations is the flexible one, because whilst the extreme boat form is calculated to be 8·0 kcal. mole^{-1} less stable than the chair form, the half-rotated form is only 4·0 kcal. mole^{-1} less stable.[19] Repulsive interactions with the carbon atoms have been neglected—clearly they would have little effect on the result.

In considering the limitations of the present method of computation it will be appreciated that it is impracticable to proceed to more complex molecules unless allowance is made for angular distortion. For example, in the absence of bond bending, *trans*-decalin is calculated to be 16 kcal. mole^{-1} more stable than the *cis*-linked double chair form; whilst the bending of only four C–H bonds by 5° in the *cis*-decalin would lower the overall energy discrepancy to about 11 kcal. mole^{-1}. Since the real strain would be spread over the whole molecule, further lowering would be effected, but, of course, it is impossible to recover the whole of the difference in stability by angular distortion.

Similarly, a direct comparison of equatorial and polar monomethyl*cyclo*hexane yields the correct qualitative result, *viz.*, that the equatorial form is the more stable, but the energy difference (18 kcal. mole^{-1}) calculated by using wholly tetrahedral angles is again too high.

It may be concluded that, although the method of computation is based upon a crude approximation, it yields reasonably quantitative results in simple molecules in which bond bending effects can be estimated with some precision.

BEDFORD COLLEGE, LONDON, N.W.1.

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[19] Cf. Hazebroek and Oosterhoff, *Discuss. Faraday Soc.*, 1951, **10**, 87.