# The Determination of the Energies Associated with Internal Rotation

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## 1 Introduction

The rotation of one part of a molecule with respect to another about a chemical bond is accompanied, in general, by a change in the internal potential energy of the molecule. The concepts associated with rotation of this kind are now well understood[1–7] and have many applications, for example, conformational analysis in organic stereochemistry, and theories concerning the structure of macromolecules. The most fundamental property associated with a molecule undergoing a conformational change is the change in internal energy. The purpose of this Review is to examine the different experimental methods with which the energies associated with conformational changes can be measured; in addition some of the theoretical models proposed to account for the experimental facts will be discussed.

The energy changes are usually depicted in the form of a potential energy diagram. As an illustration we choose the 'classical' example of internal rotation in 1,2-dichloroethane. The potential energy curve as one of the $-CH_2Cl$ groups rotates with respect to the other about the central $C-C$ bond is shown in Figure 1. The azimuthal angle $\phi$ is defined as zero in the conformation where the two Cl atoms are in a *trans* position with respect to one another. As a rule intramolecular non-bonded interactions are mainly repulsive in character and depend on some inverse power of the non-bonded distance. This means that the eclipsed (or *cis*) forms of the molecule will have the higher energy. Conversely the minima of the potential energy curve correspond to the stable staggered conformers in which the repulsive intramolecular forces are minimised. The three conformations having minimum energy represent the stable rotational isomers; the energetically equivalent pair are optically active isomers ($\phi = -120°, +120°$). These isomers are generally regarded as having more energy than the *trans*-isomer ($\phi = 0°$) which therefore has greater stability. It is fairly obvious that any molecule

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[1] S. Mizushima, 'Structure of Molecules and Internal Rotation', Academic Press, New York, 1954.

[2] N. Sheppard, *Adv. Spectroscopy*, 1959, **1**, 288.

[3] E. L. Eliel, N. L. Allinger, S. J. Angyal, and S. A. Morrison, 'Conformational Analysis', Interscience, New York, 1965.

[4] M. Hanak, 'Conformation Theory', Academic Press, New York, 1965.

[5] M. V. Volkenstein, 'High Polymers, vol. 17, Configurational Statistics of Polymer Chains', Interscience, New York, 1963.

[6] J. E. Anderson, *Quart. Rev.*, 1965, **19**, 426.

[7] F. G. Ridell, *Quart. Rev.*, 1967, **21**, 375.

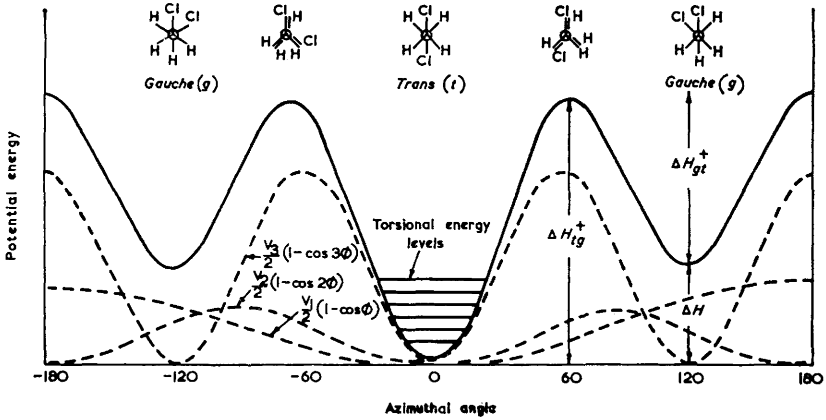

**Figure 1** *Potential energy function for* 1,2-*dichloroethane*

having momentarily an eclipsed or any other intermediate form will tend to lose energy in order to obtain the staggered conformation corresponding to the nearest potential minimum.

The energies associated with internal rotation in these systems are the enthalpy difference, $\Delta H$, between the stable isomers (difference in energy between non-equivalent neighbouring minima) and the potential energy barrier hindering rotation $\Delta H^+$ which is the difference in energy between neighbouring maxima and minima as shown in Figure 1. One stable isomer can be converted into the other by supplying the system with enough energy such that the barrier to internal rotation can be surmounted. The rates of interconversion of the *trans*- to the *gauche*-isomers and *vice versa* will be governed by the magnitude of the potential energy barrier hindering rotation between the two forms. If this barrier is very small compared to $kT$ then rapid isomeric change will occur where one part of the molecule will rotate 'freely' with respect to the other. As the barrier is increased the rate of interconversion (or isomerisation) becomes slower until an extreme case is reached where the barrier is greater than $kT$. In this situation the rates are so slow that physical separation of stable isomeric forms is possible, for example *cis–trans* isomerism in substituted ethylenes. This Review discusses internal rotation in molecules where the potential barriers are of the same order of magnitude as $kT$, *i.e.*, in the range *ca.* 3—28 kcal./mole. In these systems there is a dynamic equilibrium between the various stable isomers; this also means that they cannot be separated physically.

In 1,2-dichloroethane the equilibrium between the *trans*, *t*, and *gauche*, *g*, can be treated as a two-state process

$$t \rightleftharpoons g \tag{1}$$

with the state *g* being degenerate owing to the optical activity of the *guache*-isomers. The equilibrium constant, *K* is given by

$$c_g/c_t = K = \exp(-\Delta G/RT) \tag{2}$$

where the $c_g$ and $c_t$ refer to the relative populations of the *guache-* and *trans-*isomers respectively; actually $c_g = c'_g + c''_g$ where $c'_g$ ($= c''_g$) is the population of any one of the individual optical *gauche*-isomers, $\Delta G$ is the Gibbs free energy difference related to the enthalpy, $\Delta H$, and the entropy, $\Delta S$, difference by the relation,

$$\Delta G = \Delta H - T\Delta S \tag{3}$$

In many publications equation (2) is treated from a statistical-mechanics approach, leading to

$$c_g/c_t = 2(\Pi_{ft}/\Pi_{fg}) \exp(-\Delta E/RT) \tag{4}$$

where $\Delta E$ is the internal energy difference between the isomers and $\Pi_{fg}$ and $\Pi_{ft}$ are the usual products of the partition functions for the *gauche-* and *trans-*isomers. The factor 2 is introduced to account for the statistical weight of the *gauche*-isomer. To a first approximation $\Delta E \approx \Delta H$ ($\Delta H = \Delta E + P\Delta V$) where $P$ is pressure and $\Delta V$ is the volume change between the isomers and is normally considered to be negligible. It follows that

$$\Delta S = R \ln 2 + R \ln(\Pi_{fg}/\Pi_{ft}) \tag{5}$$

The translational partition function for the two isomers are equal in magnitude and it is also usual to assume that the partition functions for the overall rotation and vibration are approximately the same which thus gives $\Delta S = R \ln 2$. There is some recent experimental evidence to justify this approximation.[8] In equilibrium (1), if $\Delta G$ is greater than 2 kcal./mole, the *gauche*-isomer exists only to the extent of *ca.* 3% of the molecules at 300°K. In the system where $\Delta G > 2$ kcal./mole the equilibrium is sometimes termed anancomeric,[9] this term defining the rather extreme conformational equilibrium.

The magnitude of the rate of isomeric exchange in equation (1) will be a function of the energy barrier hindering rotation. To a first approximation the temperature dependence of the forward and reverse rates of isomerisation can be described by the Arrhenius rate equation

$$k_{ij} = A \exp(-E/RT) \tag{6}$$

where $k_{ij}$ represents the rate constant and $A$ and $E$ are respectively the Arrhenius '$A$' factor and activation energy. For the unimolecular isomerisation (1) it is safe to assume that the '$A$' factor will lie in the range $10^{11}$—$10^{14}$ sec.$^{-1}$. In those conformational equilibria where the barrier is in the range 3—28 kcal./mole the extreme limits for the rate constants are $7 \times 10^{11}$ and $9 \times 10^{-4}$ sec.$^{-1}$; this corresponds to actual isomeric lifetimes of $1{\cdot}5 \times 10^{-12}$ and $1 \times 10^{+3}$ sec.

The shape of the potential energy diagram for 1,2-dichloroethane shown in Figure 1 can be represented in terms of a cosine function,[1] *viz.*,

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[8] P. J. D. Park and E. Wyn-Jones, *J. Chem. Soc.* (*A*), 1969, 646.

[9] M. Antenius, D. Tavernier, and F. Borremans, *Bull. Soc. chim. belges*, 1966, **75**, 396.

$$V(\phi) = \sum_{n=1}^{n=i} (V_n/2)\,(1 - \cos n\phi) \tag{7}$$

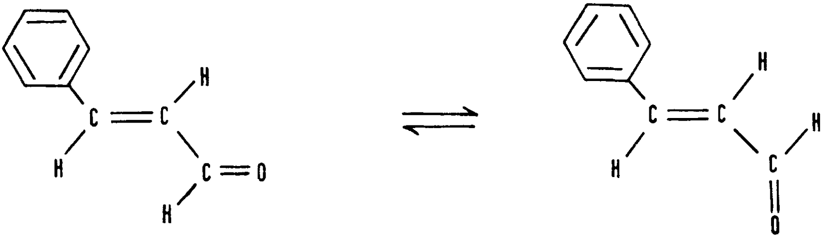
where $V(\phi)$ represents the potential energy corresponding to an azimuthal angle $\phi$. For 1,2-dichloroethane, only the first three terms are necessary:

$$V(\phi) = (V_1/2)\,(1 - \cos\phi) + (V_2/2)\,(1 - \cos 2\phi) + (V_3/2)\,(1 - \cos 3\phi) \tag{8}$$

The broken lines in Figure 1 represent the contributions from each of these three terms.

The main type of conformational changes which have been studied, in addition to substituted ethanes, are:

axial–equatorial isomerism in cyclic and heterocyclic systems; and internal rotation in unsaturated systems.



*s-trans* *s-cis*

## 2 The Determination of Potential Barriers to Rotation

The potential barrier hindering internal rotation in any conformational equilibrium may be determined either by measuring the rates of isomerisation followed by the application of the Arrhenius or Eyring rate equations, or by calculation of the potential function from the information provided by the torsional oscillation as observed by such techniques as i.r. spectroscopy.

**A. Kinetic Methods.**—(i) *Ultrasonic absorption.* The rates of isomerisation for systems with barriers in the range 3—14 kcal./mole can be measured by means of the acoustic absorption method, which is a relaxation method[10] for the study of the kinetics of fast chemical equilibria in the liquid phase. The principle involved in relaxation studies of fast reactions is to impose a sudden change in the external conditions (*e.g.* temperature, pressure) of the system. This sudden impulse will obviously affect the equilibrium which in turn will respond to this change according to Le Chatelier's principle. In relaxation studies there is a time constant, known as the relaxation time $\tau$, which measures the response of the equilibrium after the application of a sudden change in external parameters.

[10] M. Eigen and L. de Maeyer, in 'Techniques of Organic Chemistry', ed. A. Weissberger, Interscience, New York, 1963, 2nd edn. vol. 8.

The relaxation time is defined as the time it takes for the concentration of one of the reactants to change to $1/e$th of its original value; this time constant is obviously related to the kinetics of the equilibrium and for the two-state conformational equilibrium (1) it can easily be shown that[10]

$$\tau = (k_{tg} + k_{gt})^{-1} \tag{9}$$

where the $k$'s are the forward and reverse rate constants.

When a sound wave passes through a liquid, successive compressions and decompressions are produced in the liquid. In most liquids the ratio of the specific heats, $\gamma$, is greater than unity and the passage of a sound wave is adiabatic; this means that periodic temperature changes also accompany the passage of a sound wave. These periodic temperature changes will perturb the conformational equilibrium (1) in such a way that the equilibrium will alternate periodically about an ambient value. When conditions are such that the relaxation time of the equilibrium is comparable to the time of one cycle of the sound wave an ultrasonic relaxation, centred around a frequency corresponding to $1/2\pi\tau$, will occur. In this situation the periodic disturbances in the equilibrium are out of phase with those of the sound wave; this means that the equilibrium takes up enthalpy during the crest (compression cycle) of the sound wave and part of this enthalpy is returned to the trough (decompression cycle) with an inevitable attenuation of the sound wave as it goes through the system. The maximum loss in sound energy per cycle occurs when the phase difference between the sound wave and the equilibrium disturbance is 45°; this corresponds to an acoustic frequency, $f_c$, given by

$$f_c = 1/2\pi\tau \tag{10}$$

In practice an ultrasonic relaxation is detected by a decrease in the quantity $\alpha/f^2$ with increasing frequency $f$; $\alpha$ is the sound absorption at frequency $f$. For a single relaxation it can be shown that[11]

$$\alpha/f^2 = [A\,/\,(1 + (f/f_c)^2)\,] + B \tag{11}$$

where $A$ is a relaxation parameter and $B$ represents contributions to $\alpha/f^2$ that are not related to the relaxation process in question. From equations (2), (9), and (10) it follows that

$$k_{gt} = 2\pi f_c/(1 + K) \tag{12}$$

where $K$ is the equilibrium constant. The temperature dependence of the rate constant can be described by the Eyring rate equation:

$$k_{gt} = \kappa(kT/\mathbf{h})\exp(-\Delta H^{+}{}_{gt}/RT)\exp(\Delta S^{+}{}_{gt}/R) \tag{13}$$

where $\kappa$ is the transition probability, $\Delta H^{+}{}_{gt}$ the potential energy barrier hindering rotation, $\Delta S^{+}{}_{gt}$ the activation entropy, and $k$ and $\mathbf{h}$ have their usual meanings. It can be shown from a combination of equations (12) and (13) that the

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[11] R. O. Davies and J. Lamb, *Quart. Rev.*, 1957, **11**, 134.

slope of a plot of $\log(f_c/T)$ *vs.* $1/T$ will give an accurate value for $\Delta H^{+}{}_{gt}$.[12]

This technique has been extensively applied to the determination of the potential barriers in a number of conformational equilibria including the *trans–gauche* isomerisation in substituted ethanes, *cis–trans* isomerisation in unsaturated aldehydes, ketones, ethers, and esters as well as axial–equatorial ring inversion in asymmetric acyclic and heterocyclic molecules.[13,14] An advantage of this method is that the potential barrier can be evaluated directly from experimental data. In practice acoustic measurements may be made over the frequency range 100 kHz—500 MHz. Temperature variation from $-100°$ to $+100°$c enables equilibria with relaxation times in the range *ca.* $10^{-6}$—$10^{-9}$ sec., and thus barriers to internal rotation in the range 3—14 kcal./mole, to be determined. In the analysis of the experimental data the *a priori* assumption that the observed relaxation can be attributed to a conformational equilibria has to be made. Although several other molecular processes can give rise to an acoustic relaxation,[14] that due to the perturbation of a conformational equilibria is the only one known involving an intramolecular process. This means that the relaxation frequency is sensibly independent of solvent effects. In practice this method is not suitable for systems where three or more isomers are in equilibria with each other, because a spectrum of relaxation times is then expected. This technique has the advantage, however, of being sensitive to as little as 1% of the higher isomer and can be applied to the study of anancomeric equilibria.

(ii) *Nuclear magnetic resonance.* In theory the two conformers *t* and *g* in equilibrium (1) will both have their own independent chemical shifts and, when coupling between sites exists, coupling constants. However, because the isomeric exchange in equilibrium (1) is fast the conformers cannot be separated and the shape of the n.m.r. spectrum depends on the relative magnitude of the rates of isomerisation compared to the n.m.r. time scale. The overall lifetime, $\tau$, in equation (1) given by equation (9) can also be denoted by[15]

$$\tau = \tau_t\tau_g/(\tau_t + \tau_g) \tag{14}$$

where $\tau_t = 1/k_{tg}$ and $\tau_g = 1/k_{gt}$, the $\tau$ with subscripts denoting the actual isomeric lifetimes. In the simplest situation, *i.e.* when each isomer gives a single resonance line, the n.m.r. spectrum of the isomeric system can be described in relation to the relaxation time for the natural relaxation processes (n.m.r. processes) as follows:[6]

(*a*) $\tau_t\tau_g$ greater than the n.m.r. process.

In this situation the n.m.r. spectrum will consist of two resonance peaks, one belonging to each of the isomers.

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[12] E. Wyn-Jones and W. J. Orville-Thomas, 'Molecular Relaxation Processes', *Chem. Soc. Special Publ. No.* 20, 1966, 209.

[13] J. Lamb, 'Physical Acoustics', ed. W. P. Mason, Academic Press, New York and London, vol. 2, Part A, 203.

[14] E. Wyn-Jones, *Roy. Inst. Chem. Rev.*, 1969, **2**, 59.

[15] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution NMR Spectroscopy', Pergamon Press, Oxford, 1965, vol. 1.

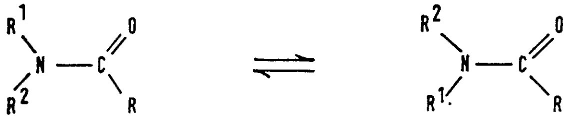
(*b*) $\tau_t\tau_g$ less than the n.m.r. process.

In this case the nucleus sees an average environment because of the rapid isomeric exchange that is taking place resulting in one peak which is an average of the two isomers.

(*c*) $\tau_t\tau_g \approx$ n.m.r. process.

When the magnitude of the above times are comparable it is possible, by careful temperature control, to observe experimentally the change-over in the spectrum from the two extreme cases (*a*) and (*b*). When the temperature is decreased the single collapsed peak starts to broaden and is eventually resolved into a doublet. The temperature at which this occurs is known as the 'coalescence temperature'.

At the coalescence temperature the phenomenological Bloch and density matrix equations which describe the shape of the n.m.r. spectrum are considerably simplified and in favourable cases it is possible to calculate the average lifetime $\tau$. From the rate equation (13) the barrier to internal rotation can then be derived. This method has been applied widely to the amide system:



especially when $R^1 = R^2$, thus further simplifying the problem by making the population of the two states equivalent. In such an equally populated isomeric equilibrium with no coupling the mean lifetime of each conformer is given by

$$\tau_t = \tau_g = 2^{\frac{1}{2}}\,(\pi\delta\omega)^{-1} \tag{15}$$

where $\delta\omega$ is the chemical shift difference between the two forms in Hz. It must be emphasised that the barriers obtained from coalescence temperature measurements alone are only approximate. In order to get more accurate data for conformational equilibria in which $R^1 \neq R^2$, a more precise approach involving the calculation of lineshapes using the density matrix or Bloch equations is required. In order to calculate the rate constants, a knowledge of the n.m.r. parameters (chemical shifts and coupling constants) of the individual isomers is necessary. These parameters can be obtained in a number of ways. If the isomeric equilibrium is cooled to *ca.* 20°C below the coalescence temperature, and provided the molecules do not associate, accurate n.m.r. parameters can be measured directly. In systems where ring inversion occurs, Eliel and his collaborators[16] have shown that the introduction of a bulky substituent, such as the tertiary butyl group, will lock the ring in a rigid chair conformation, thus enabling the n.m.r. parameters of that form to be evaluated. This method does not however take into account the effects of any ring distortion. Another indirect way of

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[16] E. L. Eliel and R. J. L. Martin, *J. Amer. Chem. Soc.*, 1968, **90**, 689.

deriving the individual n.m.r. parameters is that by Abraham *et al.*[17] for substituted ethanes. This method involves taking into account polar and dipolar effects of the solvent on the enthalpy difference between isomers. It is also possible to derive individual n.m.r. parameters from the spin echo technique;[18] this method has not been widely applied to the study of site exchange although in theory it can provide the most accurate measurements of exchange lifetimes.

From a knowledge of the n.m.r. spectrum at different temperatures and the individual n.m.r. parameters it is possible to use the density matrix or Bloch equations to calculate the isomeric exchange rates. This procedure involves calculating the n.m.r. spectrum by adjusting the exchange lifetimes, *i.e.* the rates of isomerisation, in the theoretical equations until a best fit between experiment and theory is obtained. This technique has been elegantly applied by Newmark and Sederholm[19] who have calculated the exchange rates for the

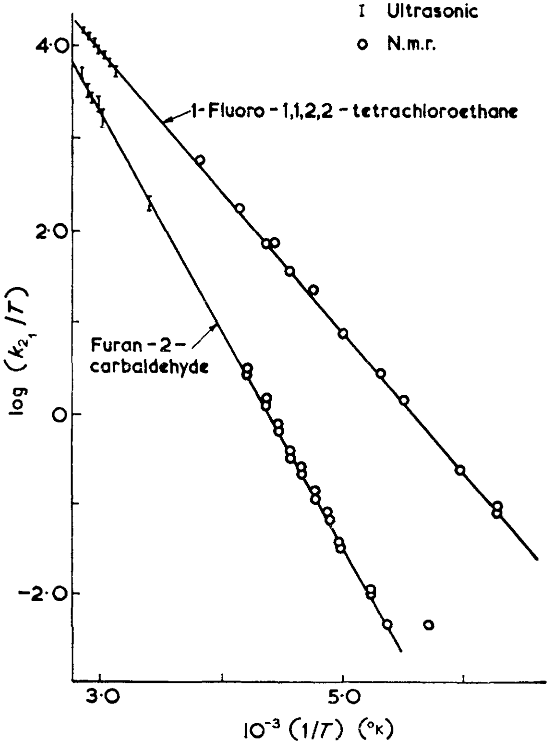

**Figure 2** *Eyring rate plot for isomerisation*

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[17] R. J. Abraham and M. A. Cooper, *J. Chem. Soc.* (*B*), 1967, 202.

[18] A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Amer. Chem. Soc.*, 1966, **88**, 3185.

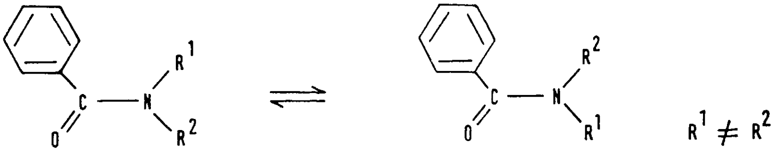
[19] R. A. Newmark and C. H. Sederholm, *J. Chem. Phys.*, 1965, **43**, 602.

rotational isomers of the diastereoisomers, *meso* and the (±) forms of ClFBrC·CBrFCl.

Both the n.m.r. and ultrasonic techniques give kinetic data on isomerisation and thus provide complementary information. In a recent study of the rates of isomerisation in furan-2-carbaldehyde and 1-fluoro-1,1,2,2,-tetrachloroethane in which both techniques have been used, the rates are compared in the form of an Eyring plot, in Figure 2, and there is good correspondence between the two sets of data.[20]

(iii) *Electron spin resonance.* The electron spin resonance technique gives the same information on conformational equilibria as the n.m.r. method. In practice if the e.s.r. relaxation times are taken into account it is possible to construct phenomenological equations which describe the e.s.r. spectrum of the system. However, only molecules which possess unpaired electron spin can be studied, which means that they are usually free radicals or ions. These studies have been reviewed in recent articles.[21]

(iv) *Determination of rates of isomerisation using n.m.r. as probe.* In those conformational equilibria which are very slow compared with the n.m.r. time scale, *e.g.* in substituted benzamides:



the rate constants will be of the order of $\min^{-1}$ the n.m.r. spectrum will possess resonances arising from each of the stable conformers. If this equilibrium is disturbed, either physically or chemically, then at any given temperature the rate at which the system returns to equilibrium can be measured directly by using the n.m.r. technique as a probe to follow the equilibrium. This is done by observing the change in the intensity of the n.m.r. resonance peaks since the intensity of a peak is proportional to the number of molecules with that conformation. This method has been successfully applied to study internal rotation in a series of benzamides and the barriers were found to agree with those derived from conventional lineshape analysis.[22]

(v) *Determination of rates of isomerisation using infrared as probe.* The infrared method has been used as a probe to study the rates of isomerisation in a number of rotational isomers. The limiting maximum value of the rates of isomerisation in fast conformational equilibria is *ca.* $10^{11}$—$10^{12}$ sec.$^{-1}$. The time constant for the interaction of electromagnetic radiation with the molecular dipole which

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[20] R. A. Pethrick and E. Wyn-Jones, *J. Chem. Phys.*, 1968, **49**, 5349; *J. Chem. Soc. (A)*, 1969, 713.

[21] D. H. Geske, *Progr. Phys. Org. Chem.*, 1967, **4**, 125; R. O. C. Norman and B. C. Gilbert, *Adv. Phys. Org. Chem.*, 1967, 53.

[22] A. Mannshreck, A. Matthers, and G. Rissman, *J. Mol. Spectroscopy*, 1967, **23**, 15.

gives rise to i.r. absorption is *ca.* $10^{13}$ sec.$^{-1}$ and thus the lifetime of each of the stable isomers is long enough for their i.r. spectrum to be observed. Provided the population of the stable isomer in the equilibrium is greater than *ca.* 4%, then in theory, the vibrational frequency of each separate isomer can be observed. In practice it is found that many vibrational modes of the individual isomers occur in similar environments and their frequencies will be coincident. If an isomeric equilibrium system is cooled, the population of the more stable conformers increases until at the melting point all the molecules are in this form. This process can be followed spectroscopically by observing absorption bands belonging to each of the stable isomers. Due to the normal thermodynamic distribution of energy and also the stabilising influences of the intermolecular forces of the crystal packing, only the stable form normally exists in the solid crystalline phase.[1,2] Pentin and his collaborators[23] have shown that certain rotational isomers *e.g.* 1,2-dichloroethane and chlorocyclohexane, when supercooled below their melting points form a glassy solid in which all the stable isomers are present. At certain temperatures the glassy solid changes phase from a glass to crystalline. During this phase change the isomeric equilibrium is also adjusted until only one stable form is present. The rate of disappearance of the less stable isomer in the solid phase can be measured spectroscopically at this temperature by observing the rate at which one of the *gauche*-bands decreases. The potential barrier can then be derived from the rate equation. The method however suffers in that the temperature range of study is limited (*ca.* 10°c) and also that the kinetics are measured during a phase change in the solid. Piercy[24] has pointed out that for 1,2-dichloroethane the frequency factor in the Arrhenius equation for the *gauche–trans* isomerisation is as low as $10^5$ sec.$^{-1}$.

(vi) *Dielectric absorption.* For molecules with a permanent dipole moment the rates of overall molecular rotation in the solid and liquid phase can be measured using the dielectric relaxation technique. This method involves measuring the complex and real dielectric constants (permittivity) over a range of electromagnetic frequencies up to *ca.* $10^{12}$ sec.$^{-1}$. In theory when a molecule can exist as different conformers both molecular rotation and internal rotation should give rise to anomalous dielectric absorption.[25] In most cases the rates of both processes are very close and the resulting data cannot be resolved. In some molecules the rates of internal rotation and overall molecular rotation are so different that two dielectric loss curves, one for each process, can be observed experimentally. In this situation the rates of internal rotation can be measured from the dielectric data and the energy barriers found by application of the rate equations. An illustrative example is the work of Meakins and Davies[26] on the internal rotation of the $-$OH group in substituted phenols.

**B. Indirect Methods of Determining Barriers.**—For the conversion of a *gauche*-

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[23] Yu. A. Pentin, Z. Shavipon, S. S. Katova, A. V. Kamormitaka, and A. A. A'khrem, *Zhur. struct. Khim.*, 1963, **4**, 194.

[24] J. E. Piercy, *J. Chem. Phys.*, 1965, **43**, 4066.

[25] C. P. Smyth, 'Molecular Relaxation Processes', *Chem. Soc. Special Publ. No.* 20, 1966, 1.

[26] M. Davies and R. J. Meakins, *J. Chem. Phys.*, 1957, **26**, 1584.

isomer of 1,2-dichloroethane to a *trans*-form the pertinent internal motion is clearly the torsional mode of vibration about the C–C bond. For each isomer the torsional oscillation is, of course, one of the fundamental vibrational modes. The potential energy diagram for the torsional oscillation of the *trans* and *gauche*-isomers is shown in Figure 1; for the *trans*-isomer the horizontal lines represent the torsional energy levels. In practice the torsional wavenumber is of the order of 100 cm.$^{-1}$ (290 cal./deg/mole). Consider the torsional oscillation of the *trans*-isomer in a molecule such as 1,2-dichloroethane where the *trans–gauche* isomerisation takes place and the barrier is at *ca.* 5·8 kcal./mole. Neglecting tunnelling effects and assuming that the torsional oscillations are simple harmonic it is clear that for interconversion to occur the *trans*-isomer must have enough energy to be excited to the 20th vibrational mode (1 cm.$^{-1}$ $\equiv$ 2·9 cal./mole). It is of interest to point out that the potential energy curve for any conformer which can undergo internal rotation is analogous to the Morse curve for a diatomic vibrator. In the former case enough energy to reach the top of the potential energy curve results in internal rotation, and in the latter dissociation. The potential energy diagram for the internal rotation in 1,2-dichloroethane can be represented by the general cosine function given by equation (8). The problem is to derive the constants $V_1$, $V_2$, and $V_3$ of this function from spectral information on torsional frequencies.[27] If the torsional motion in, say, the *trans*-isomer of 1,2-dichloroethane is assumed to be simple harmonic, the torsional frequency $\nu$ is given by the expression,

$$\nu = (1/2\pi c)\ (f/I_r)^{\frac{1}{2}} \tag{16}$$

where $I_r$ is the reduced moment of inertia and $f$ is the force constant for the torsional oscillation. By definition

$$f = \partial^2 V(\phi)/\partial\phi^2 \tag{17}$$

where $V(\phi)$ is given by equation (8). For the *trans*-isomer $\phi = 0$ and if the amplitudes of the torsional oscillations are very small equation (8) reduces to

$$V(\phi) = [(V_1 + 4V_2 + 9V_3)/4]\phi^2 \tag{18}$$

and by use of equations (16) and (17)

$$\nu = (1/2\pi c)\ [(V_1 + 4V_2 + 9V_3)/2\, I_r]^{\frac{1}{2}} \tag{19}$$

This equation relates the torsional frequency of the *trans*-isomer to the potential energy parameters $V_1$, $V_2$, and $V_3$.

(i) *Infrared and Raman spectroscopy.* In practice the torsional frequencies can be measured using far-i.r. or Raman spectroscopy provided the relevant selection rules are obeyed. This simple procedure of determining potential energy terms directly from torsional frequency contains several approximations. These include the assumption that the torsional oscillations are simple harmonic, the

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[27] F. B. Brown, A. D. H. Clague, N. D. Heitkamp, D. F. Koster, and A. Danti, *J. Mol. Spectroscopy*, 1967, **24**, 1963.

torsional mode is a pure mode, and the potential energy curve is a cosine function; also in many cases the molecular geometry has to be assumed.

(ii) *Microwave spectroscopy.* The rotational spectrum of a molecule can be observed in the microwave region provided the molecule is light enough and also that it has a dipole moment. In general there are two ways in which barriers to internal rotation can be found from microwave spectroscopy:[28] (*a*) line splitting. In theory the pure rotational spectrum of any molecule can be derived from a solution of the wave equation provided that the relevant energetic terms are substituted in the Hamiltonian. The microwave spectrum of a flexible molecule will be different from that for a rigid molecule because in the former, terms such as interaction of pure rotation with torsional motion, tunnelling effects through the potential barrier, as well as the orientation of the part of the molecule that is undergoing internal rotation with respect to the molecular framework have to be introduced in the Hamiltonian. These terms lead to a splitting of the rotational energy levels; the magnitude of this splitting being a function of the potential barrier. The procedure to derive potential barriers from splitting of rotational lines and the approximations therein, have been discussed by Lin and Swalen;[29] (*b*) intensity. Vibrational transitions between torsional energy levels correspond to far-i.r. frequencies in the region 50—200 cm.$^{-1}$. These low frequencies mean that the number of molecules with energies corresponding to the first few torsional levels may be substantial and in turn the rotational spectrum of the molecule can be determined in both the ground torsional level as well as in some of the excited torsional states. The resulting microwave spectrum will contain a series of intense lines from the ground-state spectrum and weaker satellite lines in the different torsional states; the ratio of the number of molecules and hence the energy difference between the torsional states can be determined. The assignment of the corresponding rotational lines in the different torsional states is facilitated by Stark modulation. From these data the shape of the potential energy curve and hence the potential barrier can be derived. Although the determination of the intensity of the lines can be difficult, this method has been applied successfully to the study of several symmetric top molecules.[28,29]

Microwave studies are limited to systems which have an appreciable vapour pressure and also a significant dipole moment. In some systems *e.g.* ethyl formate[30] and acrolein[31] where one of the isomers has a low dipole moment and is present in small amounts, the rotational spectra were not detected.

(iii) *Neutron scattering.* A recent innovation is the determination of torsional frequencies from the time-resolved neutron scattering method.[32] This has the great advantage that it is not restricted by optical selection rules which in certain cases preclude the observation of the torsional transition by i.r. and

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[28] W. H. Flygare, *Adv. Phys. Chem.*, 1967, 331.

[29] C. C. Lin and J. D. Swalen, *Rev. Mod. Phys.*, 1959, **31**, 841.

[30] J. M. Riveros and E. Bright Wilson jun., *J. Chem. Phys.*, 1967, **40**, 4605.

[31] E. A. Cherniak and C. C. Costain, *J. Chem. Phys.*, 1966, **45**, 104.

[32] J. J. Rush, *J. Chem. Phys.*, 1967, **47**, 3936.

Raman techniques. In principle if a slow neutron undergoes a scattering collision with a molecule in the first torsional excited state, the molecule gives an amount of energy to the neutron equal to the torsional transition 1 → 0. A monoenergetic beam of neutrons is used and the time of their arrival at the detector measured. Those neutrons interacting with the torsional mode have higher energies and thus higher velocities and will arrive ahead of the main beam at the detector. From the difference in time of arrival the frequency of the torsional mode can be estimated. This technique has been recently applied with some success to the study of a number of symmetric rotors.

**C. Approximate Methods.**—In addition to the methods described above which can, in certain circumstances, yield accurate values for barrier heights to internal rotation, a number of methods exist which can provide less accurate values. The concept of internal rotation in molecules originally arose from discrepancies found between the experimentally determined thermodynamic properties for the molecules undergoing internal rotation and those calculated from statistical mechanics using spectral data. The differences found were attributed to internal rotation. In principle the potential energy barrier can be determined from the difference between an experimental and 'statistical' thermodynamic parameter (*e.g.* entropy) by assuming a potential function to describe the internal rotation.[33] This method has been applied with reasonable success to molecules with symmetric potential energy barriers.

In molecules which exist as a mixture of rotational isomers there are, in general, some difficulties encountered in the application of the thermodynamic method. For example, the potential energy makes only a small contribution to the total function; since the calculations are carried out by comparing the experimental and statistical thermodynamic parameter this can lead to large inaccuracies in the actual barrier heights calculated. A further assumption has to be made about the form of the potential function. In some cases a complete vibrational assignment is not always available for the statistical mechanical calculations.

Information on barrier heights has also been obtained from the study of the temperature dependence of dipole moments,[34] electron diffraction data,[35] nuclear quadrupole resonance,[36] and also optical rotatory dispersion studies.[37] In Table 1 values of barriers found from different methods are compared.

**D. Mechanism of Internal Rotation.**—(i) *Substituted ethanes.* Recently some progress has been made towards a quantitative understanding of the mechanism underlying internal rotation in substituted ethanes. Two mechanisms or, more correctly, descriptions of internal rotation have been considered as possibilities

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[33] E. L. Pace and A. C. Plaush, *J. Chem. Phys.*, 1967, **47**, 38.

[34] R. J. W. Le Fèvre and B. J. Orr, *Austral. J. Chem.*, 1964, **17**, 1098.

[35] J. Karle, *J. Chem. Phys.*, 1966, **45**, 4149.

[36] N. E. Ainbender, A. D. Sordeev, V. S. Grechiehkin, Yu. G. Svetlov, and G. B. Soifer *Zhur. Struct. Khim.*, 1961, **2**, 700.

[37] R. E. Ballard, S. F. Mason, and S. M. Vane, *Discuss Faraday Soc.*, 1963, **35**, 43.

**Table 1** *Comparison of experimental barriers found by different techniques*

| *Molecule* | *Method* (kcal./mole) | | | | | |
|---|---|---|---|---|---|---|
| | *Infrared torsional frequency* | *Infrared kinetic* | *Molecular acoustic* | *Nuclear magnetic resonance* | *Micro-wave* | *Dipole moments* |
| 1,2-Dichloroethane | 5·3 | 1·7 | 3·2 | | | 3·0 |
| 1-Fluoro-1,1,2,2-tetrachloroethane | 8·9 | | 8·3 | 7·25 | | |
| Furan-2-carbaldehyde | 8·09 | | 12·1 ± 2 | 11·2 ± 0·2<br>11·7 ± 0·2 | 8·7 | |
| Chlorocyclohexane | | | 12 ± 2 | 10·5 | | 15 ± 5 |

by Newmark and Sederholm.[19,38] The first envisages that an isomer becomes thermally activated to an eclipsed state corresponding to a maximum in the potential energy curve and then is immediately deactivated to the stable isomer in the adjacent potential energy minimum. In the second description the transition form following thermal activation is followed by a state in which the molecule undergoes 'free' internal rotation for some time before deactivation, with equal probability, into any of the three possible potential minima.

The first description of internal rotation is the simplest possible and corresponds to a transition probability, $\kappa$, of unity in the Eyring absolute rate equation (13). Using this description Alger *et al.*[39] showed that for an isomeric transition

$$g \rightarrow t$$

the major contribution to the entropy of activation $\Delta S^{+}{}_{gt}$ will come from the difference in vibrational terms between the transition state and isomer $g$. The only differences in these vibrational terms are in the torsional oscillation which is absent in the eclipsed state. This simple treatment assumes that the vibrational frequencies of isomer $g$ and the eclipsed state in the $g \rightarrow t$ transition will all be the same except there will be no torsional oscillation in the eclipsed conformer. Using the partition function to calculate these entropy contributions it was found that an equation of the form

$$k_{gt} = \nu_0 \exp(-\Delta V_{gt}/RT) \tag{20}$$

can be derived from the Eyring absolute rate equation (13). In equation (20) $\nu_0$ is the torsional frequency of the isomer $g$ and is related to $\Delta V_{gt}$ the 'approximate' potential energy difference between the transition state and $g$, by a simplified version of equation (19):

$$\nu_0 = 3/2\,(\Delta V_{gt}/2I_r)^{\frac{1}{2}} \tag{21}$$

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[38] D. S. Thompson, R. A. Newmark, and C. H. Sederholm, *J. Chem. Phys.*, 1962, **37**, 411.
[39] T. D. Alger, H. S. Gutowsky, and R. L. Vold, *J. Chem. Phys.*, 1967, **47**, 3130.

where $\Delta V_{gt} = V_3$ with $V_1 + 4V_2$ assumed negligible. Equation (20) is identical to the Arrhenius rate equation (6) where

$$E_{gt} = \Delta V_{gt} = \Delta H^{+}_{gt} - RT \tag{22}$$

and $A = \nu_0$. The experimental values of $A$ are compared with the measured spectroscopic values of the torsional frequencies for some substituted ethanes in Table 2.

**Table 2** *Comparison of 'A' factors and torsional frequencies*

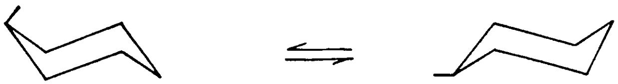
| *Molecule* | $10^{-12}$ '$A$' (sec.$^{-1}$) | $10^{-12}$ $\nu_0$ (sec.$^{-1}$) | *Method** |
|---|---|---|---|
| 1,2-Dichloroethane | 0·1—1 | 3·75 | MA |
| 1,2-Dibromoethane | 1—10 | 2·73 | MA |
| 1,2-Dichloro-2-Methyl propane | 0·4 | 3·3 | MA |
| 1,2-Dibromo-2-Methyl propane | 1·5 | 3·96 | MA |
| *meso*-2,3-Dichlorobutane | 3·98 | 3·0 | MA |
| *meso*-2,3-Dibromobutane | 30·2 | 3·29 | MA |
| Isobutyl chloride | 0·5 | 3·72 | MA |
| Isobutyl bromide | 1·0 | 3·51 | MA |
| 2-Chloro-2-methylbutane | 0·73 | 3·5 | MA |
| 2-Bromo-2-methylbutane | 23·1 | 3·4 | MA |
| 2-Iodo-2-methylbutane | 1170 | 3·5 | MA |
| 1-Fluoro-1,1,2,2-tetrachloroethane | 2·2 | 2·58 | MA |
|  | 0·76 | 2·58 | N.m.r. |
| 1,2-Difluoro-1,1,2,2-tetrachloroethane | 0·45 | 2·40 | N.m.r. |
| Furan-2-carbaldehyde | 20 | 3·9 | N.m.r.—MA |

* MA = Molecular Acoustics

In the second description of internal rotation where the transition state undergoes 'free' internal rotation the molecule has a probability of 1/3 of returning at random to one of the three potential minima. This model leads to a calculated frequency factor of $\nu_0/3$ in equation (20). In this model of delayed deactivation the experimental results must be independent of the highest barrier to rotation because if the energy of a molecule exceeds the second highest barrier, then the molecule can rotate to an angle corresponding to any of the three potential minima without having to pass over the highest barrier.

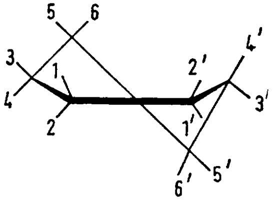
The data listed in Table 2 show that the order of magnitude of the '$A$' factors and torsional frequencies are the same indicating there is no doubt about the basic correctness of these models although several details still remain to be worked out in order to get better agreement.

(ii) *Ring inversion in cyclic molecules.* The phenomenon of ring inversion is a field of conformational analysis that has been studied by several investigators. Most of the barrier heights studies have been focused on six-membered alicyclic and heterocyclic molecules. According to physicochemical evidence the chair form in these molecules is greatly favoured when compared with other conformations,[3] such as boat, half boat *etc.*, mainly because in the chair form the ring atoms are in a staggered conformation of minimum intramolecular energy. In these cyclic molecules internal rotation about the single bonds in the ring can occur giving rise to two chair conformations, this process being known as ring inversion. This statement can be illustrated if we consider methyl cyclohexane which exists in two chair forms, the methyl groups taking up an equatorial or an axial position:



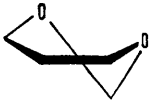
These two conformational isomers are energetically different and are in equilibrium with each other.

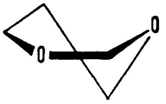
According to current theories[40,41] the transition state in the ring inversion of pure cyclohexane is uniquely defined as a 'cyclohexane'-like conformation:

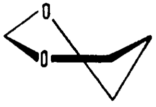


with four ring atoms lying in the same plane. The main arguments for accepting this half-chair transition conformation are based on the calculations of Hendrickson,[40] in which good agreement was found between experimental and theoretical energy barriers to ring inversion in cyclohexane. In the equatorial → axial ring inversion of methyl cyclohexane there are six different positions that the methyl group can occupy in the half-chair transition state. At present it is not possible to estimate the spread of activation energies corresponding to these different transition states and consequently it is difficult to determine which is the isomerisation path or paths that correspond to the ultrasonic barrier height of 13·1 kcal./mole found for this compound.

In the ring inversion of 1,3-dioxan there are three energetically different half-chair forms:







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[40] J. B. Hendrickson, *J. Amer. Chem. Soc.*, 1961, **83**, 4537.
[41] R. K. Harris and R. A. Spragg, *J. Chem. Soc. (B)*, 1968, 684.

and in turn there will be six possible half-chair forms in the ring inversion of a monosubstituted derivative. If these different half-chair transition states differ substantially in energy it may be that only the lower energy conformers need be considered in ring inversion. In monosubstituted cyclic compounds one would expect a positive entropy of activation purely on statistical grounds; entropy contributions in cyclic molecules have been discussed in a recent article.[42]

According to Hendrickson there are three main factors which contribute to the energy of a particular conformer in cyclic compounds: torsional energy resulting from changing the dihedral angles between bonds to neighbouring carbon atoms from the 60° of a staggered conformation; bond angle strain due to distortion of valency angles away from the tetrahedral angle; and repulsion between non-bonded atoms or groups. Of these forces the major contribution to ring inversion barriers comes from torsional strain; this factor accounting for at least 60% of the barrier in alicyclic and also heterocyclic molecules.

## 3 Enthalpy Differences

As shown by equations (2) and (4) the thermodynamic parameters, enthalpy and entropy difference between conformers determine their populations in the isomeric mixture. A literature survey shows that a great deal of experimental information is available on enthalpy differences between various conformers whereas entropies have only been determined in a very few cases. When the relative populations of the isomers in a two-state equilibrium (1) are of the same order of magnitude, techniques such as i.r., Raman, microwave spectroscopy, and also n.m.r. can be used to determine these thermodynamic parameters. For example in the i.r. spectrum of a two-state conformational mixture many of the vibrational bands of the separate isomers will have different frequencies. Since the intensity of a vibrational band is proportional to the population it follows that by choosing two corresponding bands one belonging to each isomer,

$$A_t = \alpha_t c_t l \quad \text{and} \quad A_g = \alpha_g c_g l \tag{23}$$

where the $A$'s are the band areas proportional to band intensities of isomers $t$ and $g$ in equation (1), the $\alpha$'s are the integrated absorption coefficients, and $l$ is the cell length. The expression for the equilibrium constant $K$ can be written as

$$K = c_g/c_t = A_g \alpha_t / A_t \alpha_g \tag{24}$$

and using the van't Hoff isochore, it follows that

$$\ln(A_g/A_t) = -\Delta H/RT + \ln \alpha_g/\alpha_t + \Delta S/R \tag{25}$$

By measuring intensities at different temperatures $\Delta H$ can be derived from the slope of the plot of $\ln(A_g/A_t)$ against reciprocal temperature. This treatment, which is used widely, assumes that $\Delta H$, $\Delta S$ and the quantity $\ln(\alpha_g/\alpha_t)$ are

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[42] R. K. Harris and N. Sheppard, *J. Mol. Spectroscopy*, 1967, **19**, 231.

independent of temperature. In most of the work carried out in this field, optical densities have been used instead of integrated intensities.[1,2]

If $c$ is the total concentration then $c = c_t + c_g$ at all temperatures and from equation (23)

$$A_g/\alpha_g l + A_t/\alpha_t l = c \tag{26}$$

thus

$$A_g = -(\alpha_g/\alpha_t)A_t + \alpha_g l c \tag{27}$$

Assuming the $\alpha$'s are independent of temperature $A_g$ is plotted against $A_t$ at different temperatures and the quantity $-\alpha_g/\alpha_t$ is the slope of the line. The entropy difference, $\Delta S$, can then be found from equation (25).[43] This procedure can only be applied when the integrated intensities of the absorption bands are known. A separate method to determine $\Delta S$ has been used by Mizushima *et al.*[44] where the optical densities (or intensities) of three bands, one belonging to each of the isomers and the third being an absorption band whose frequency is common to both isomers, are compared.

When the rate of isomerisation is so slow that separate n.m.r. parameters can be measured, the thermodynamic quantities of an isomeric equilibrium system can be measured in an analogous way by measuring band areas. In fast conformational equilibria only a single time-averaged n.m.r. parameter $P$ (chemical shift or coupling constant) can be measured from the spectrum which is in a 'collapsed' form. At any temperature $P$ is related to the individual isomeric parameters $P_t$ and $P_g$ through:

$$P = c_g P_g + c_t P_t \tag{28}$$

and combination with equations (2) and (3) gives:

$$K = (P_g - P) / (P_t - P) = \exp(-\Delta H/RT)\exp(\Delta S/RT) \tag{29}$$

The unknown parameters $P_g$, $P_t$, $\Delta H$, and $\Delta S$ are derived from the experimental values of $P$ at different temperatures by means of a computer program employing a curve fitting procedure. The resulting data, however, are uncertain.[45] In favourable cases the individual n.m.r. parameters $P_g$ and $P_t$ can be found from the low-temperature spectrum where the equilibrium is 'frozen'. In some cyclic compounds the conformation of the ring can be fixed by means of a conformational locking group such as a tertiary butyl, which only takes up an equatorial position.[16] This additional information ensures that more reliable thermodynamic quantities can be found from measurements of $P$ at different temperatures.

Another interesting approach to determining enthalpy differences and n.m.r.

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[43] K. O. Hartman, G. L. Carlson, R. E. Witkowski, and W. G. Fateley, *Spectrochim. Acta*, 1968, **24**, *A*, 157.

[44] S. Mizushima, T. Shimanouchi, K. Kuranti, and T. Muyazawa, *J. Amer. Chem. Soc.*, 1952, **74**, 1378.

[45] G. Govil and H. J. Bernstein, *J. Chem. Phys.*, 1967, **47**, 2818.

parameters has recently been used by Abraham and his collaborators.[17] An electrostatic theory has been developed to account for the dielectric solvent effect on the conformational equilibrium. This theory has been used mainly for substituted ethanes. In brief, the enthalpy difference, $\Delta H_s$, between the isomers in a solvent, $s$, is given by

$$\Delta H_s = \Delta H_v - P - D \tag{30}$$

where $\Delta H_v$ is the vapour-phase enthalpy difference, $D$ is the usual dipolar term given by

$$D = (\epsilon - 1) / (2\epsilon + 1) . (\mu_g^2/a_g^3 - \mu_t^2/a_t^3) \tag{31}$$

where $\epsilon$ is the dielectric constant of solution and the $\mu$'s and $a$'s are the isomeric dipole moments and volumes respectively; $D$ is a quadrupolar term which is related to $\epsilon$ and $\mu$ as shown by Böttcher.[46] Experimentally the average coupling constant $P$ is measured in different solvents and from equation (29) and (30), and also a knowledge of $P$ and $D$, the quantities $\Delta H_s$, $\Delta H_v$, $P_t$ and $P_g$ can be found using a curve fitting procedure. Preliminary results are very good although second-order effects such as complexing between solvent and solute and also uncertainties in the calculation of $D$ can be critical.

Several investigators have used dipole moment measurements[1,2] to determine enthalpy differences between rotational isomers in the liquid state. In brief the dipole moment, $\mu$, of an isomeric mixture is related to the individual isomeric dipole moments $\mu_t$ and $\mu_g$ and also the thermodynamic energy parameters through equations identical to equation (28), where $\mu = P$. The individual dipole moments $\mu_t$, $\mu_g$ can be calculated from bond moments and a knowledge of molecular geometry. Experimentally $\mu$ is measured at different temperatures and thus $\Delta H$ and $\Delta S$ can be found by using equations (28) and (29). This procedure is simplified considerably in some systems where one of the isomers has a zero dipole moment, *e.g.* the *trans*-isomer of 1,2-dichloroethane. Kerr constants or molecular polarisabilities can also be used in a similar way to determine enthalpy differences of isomeric equilibria.

The ultrasonic absorption technique[11] can also be used to determine enthalpy and entropy differences for conformational equilibria. In the relationship between the measured acoustic data and the equilibrium parameters there are usually several unknowns, enthalpy, entropy, and volume difference between the isomers and also some thermodynamic properties of the liquid system such as specific heat and dilatation whereas the only experimental information available is the maximum absorption per wavelength and its variation with temperature. In order to evaluate $\Delta H$ several approximations are necessary and, in certain cases, these can lead to enthalpy differences which are incompatible with those found from other techniques.[12]

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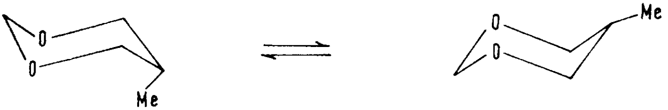
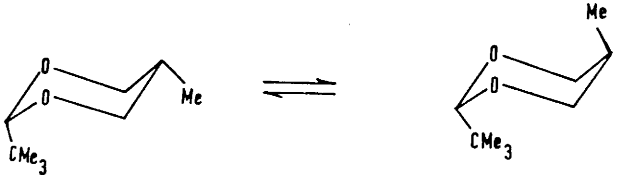
[46] C. J. F. Böttcher, 'Theory of Electric Polarization', Elsevier, Amsterdam, 1952.

In alicyclic and heterocyclic molecules the equilibrium thermodynamic parameters between the axial and equatorial isomers of say 5-methyl-1,3-dioxan:



(32)

can be determined from equilibration studies of the corresponding *cis–trans* isomerism in some related diastereoisomers *e.g.* *cis* and *trans* 2-t-butyl-5-methyl-1,3-dioxan:



(33)

This method uses the configurational equilibrium (33) between the separate *cis*- and *trans*-stereoisomers as a model for the conformational equilibrium between the rapidly converting conformers in (32).[3] In the *cis*- and *trans*-stereoisomers a conformational locking group such as t-butyl or *p*-nitrophenol is used as the second substituent; this group ensures that during the epimerisation (29) only the methyl substituent changes its spacial conformation from axial to equatorial. The equilibration of the *cis*- and *trans*-stereoisomers (33) is carried out chemically and when this configurational equilibrium is reached the composition of the separate stereoisomers is then determined using standard analytical techniques. The equilibrium constant for the equilibrium is then used for the conformational equilibrium (32).

## 4 Theories of Barriers to Internal Rotation in Molecules

Ever since the discovery of internal rotation, attempts have been made to try and describe in simple terms the cause of this phenomenon. The various theories that have been proposed have been reviewed by Wilson[47] and more recently by Dale[48] and Lowe.[49] No attempt will be made to give an exhaustive coverage of the various theories but rather to present methods which make a significant contribution to an understanding of the cause of internal rotation in molecules.

A number of semi-empirical theories in which the parameters describing the potential function are derived from experimentally measurable parameters have been put forward and have met with reasonable success. The success of these methods lies in the fact that for molecules such as $CH_2Br-CH_2Br$, the barrier appears to be described to a good approximation by steric (steric repul-

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[47] E. Bright Wilson jun., *Adv. Chem. Phys.*, 1959, **2**, 1.
[48] J. Dale, *Tetrahedron*, 1966, **22**, 3373.
[49] J. P. Lowe, *Progr. Phys. Org. Chem.*, 1968, **6**, 1.

sion and London attractive forces) and electrostatic (dipole–dipole and dipole-induced dipole forces) forces. Application of such theories to ethane and similar molecules has shown the inadequacies of such calculations and a more complex picture seems to be necessary.

A number of methods of making empirical estimates of the forces producing the barrier may be separated into those attributing the barrier to repulsion between nonaxial bonds (*e.g.* C–H bonds repel C–Cl bonds in $CH_3-CCl_3$); or else to forces between atoms on opposite ends of the rotor axis which are not directly bonded to each other (*e.g.* H - - - Cl interactions in $CH_3-CCl_3$). Estimates of the barrier using the first type of interaction by itself have been made by a number of authors;[50] for the barrier to be totally described by this type of force law an almost purely ionic bond must be predicted to occur in ethane. Clinton[51] has also pointed out that the barrier may not be attributed entirely to potential energy changes, for often the changes in the kinetic energy are of comparable magnitude to the total energy change involved.

Pauling[52] has suggested that an extension of the bond–bond interaction theory related to the earlier valence bond calculations of Gorin *et al.*[53] might be used. To describe the barrier the inclusion of a small amount of *d* and *f* orbital character has to be proposed to produce hybrids with the correct symmetry. In this approach only the exchange interactions between the tetrahedral orbitals are considered and other interactions such as those of the hydrogen on one end of ethane with the tetrahedral orbitals on the other end are ignored. It has however been shown recently that fairly accurate barrier heights can be obtained without the inclusion of *d* or *f* character in the molecular orbital calculations (SCF–LCAO–MO).[54]

Dale[48] has recently suggested that interaction of bonds directly through the trigonal polarisation of the axial bonds may be a major cause of the barrier. Lowe,[49] however, has recently pointed out that this should again require the inclusion of some *f* and *d* character in the non-axial bonds. This makes it difficult to understand Dale's hypothesis that lone pairs of electrons play the same rôle in the barrier production as do bonding electrons.

Nonbonded interactions exist between molecules and it is not unreasonable to predict that the intermolecular forces producing repulsion at very short distances and attraction at long distances, should also exist within the molecule and describe the intramolecular forces giving rise to barriers to internal rotation. Information can be obtained experimentally on the nature of the intermolecular forces from studies of molecular scattering, second virial coefficients, viscosities *etc.* The observed intermolecular interactions are then fitted to theoretical force laws.[55] The reliability of such force laws even when applied to the description of the simplest of interactions has recently been questioned.[55]

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[50] E. N. Lassetre and L. B. Dean, *J. Chem. Phys.*, 1948, **16**, 151, 553; N. W. Luft, *J. Chem. Phys.*, 1954, **22**, 1814.

[51] W. L. Clinton *J. Chem. Phys.*, 1960, **33**, 632.

[52] L. Pauling, *Proc. Nat. Acad. Sci. U.S.A.*, 1958, **44**, 211.

[53] E. Gorin, J. Walter, and H. Eyring, *J. Amer. Chem. Soc.*, 1939, **61**, 1876.

[54] L. Pedersen and K. Morokuma, *J. Chem. Phys.*, 1967, **46**, 3941.

[55] E. B. Smith, *Ann. Reports*, 1966, 25.

Potential functions have been constructed which are repulsive at short distances and attractive at long distances. The attractive part has generally been taken to have the $r^{-6}$ dependence corresponding to the dipole–dipole interaction of the van der Waals force.[55] Several suggestions have been made to describe the repulsive part: the $^3\Sigma$ potential energy curve for the appropriate diatomic (homonuclear) molecule;[56] this same $^3\Sigma$ potential energy curve with angular dependence has been described by Howlett;[57] the negative of the corresponding $^1\Sigma$ has been used by Magnasco,[58] and the function of the form $br^{-12}$ has also been used.[59] The intramolecular force laws have also been generated in terms of Lennard–Jones type of interactions.[60] These approaches give an adequate description of the potential function in cases where steric and electrostatic forces are predominant. The extension of these force laws by the use of additive and commutive operations to make the homonuclear force laws describe the case of the heteronuclear interaction is open to question.

To understand the origin of the barrier in ethane and similar molecules we have to consider recent quantum mechanical calculations. The *ab initio* method has been applied recently to ethane,[54,61,62] methylamine,[54] methyl alcohol,[54,62] hydrazine,[54] and hydroxylamine.[54,62] The agreement between calculated and experimentally observed barriers in ethane and methanol is quite good, but in the case of hydrogen peroxide there are considerable differences. The discrepancy most probably arises from the fact that the calculations do not take into account the possible changes in the structure of the molecule as it undergoes internal rotation. Simple estimates based on force constant calculations[49] indicate that a symmetric deformation of the $O-O-H$ angle by 2° would raise the molecular energy of $H_2O_2$ by *ca.* 300 cal./mole, while a symmetric stretch of the $O-H$ bonds by *ca.* 0·02 Å would account for *ca.* 400 cal./mole. It is thus clear that for an accurate description to be obtained calculations should be carried out on a dynamic framework in which the minimisation of the energy with respect to bond angles and distances is carried out at each torsional angle, but this would require an astronomical amount of computer time. Sovers and Karplus[63] have carried out calculations in which they allowed for changes in the structure in ethane during rotation and have shown that these effects are by no means insignificant.

Pitzer[64] has shown that slight changes in the electron distribution occur on rotation. It appears from localisation of orbitals that the electrons in the $C-H$ bonds drift out towards the protons when the eclipsed form is obtained from the staggered. Comparison of the overlap populations for the two rotamers suggests

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[56] E. A. Mason and M. M. Kreevoy, *J. Amer. Chem. Soc.*, 1955, **77**, 5808.
[57] K. E. Howlett, *J. Chem Soc.*, 1960, 1055.
[58] V. Magnasco, *Nuovo Cimento*, 1962, **24**, 425.
[59] R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, 1966, **44**, 3054.
[60] R. L. McCullough and P. E. McMahon, *Trans. Faraday Soc.*, 1964, **60**, 2089.
[61] R. M. Pitzer and W. N. Lipscomb, *J. Chem. Phys.*, 1963, **39**, 1995.
[62] W. H. Fink and L. C. Allen, *J. Chem. Phys.*, 1967, **46**, 2261.
[63] O. J. Sovers and M. Karplus, *J. Chem. Phys.*, 1966, **44**, 1823.
[64] R. M. Pitzer, *J. Chem. Phys.*, 1964, **41**, 2216.

that changes in bonding and antibonding character between the hydrogen atoms may be a major factor contributing to the barrier. Inclusion of van der Waals interactions into the calculation for ethane requires the mixing of higher orbital contributions on the hydrogen atom which would appear to indicate that such interactions have a marginal importance in the calculations.

The integral Hellmann–Feynmann theorem provides a quite different approach to the problem. The calculations are based on the method developed by Wyatt and Parr[65] for the calculation of the one-electron transition density. The product of the real wavefunctions for the staggered and eclipsed forms of ethane is integrated over all spin co-ordinates and space co-ordinates of all but one electrons and renormalised, which leads to a one-electron spinless transition density $\rho^{(1)}{}_{es}$,

$$\rho^{(1)}{}_{es} = \frac{\int \psi_s(1, 2, \ldots . n)\ \psi_e(1, 2, \ldots . n)\ \partial\tau(2) \ldots .\ \partial\tau(n)\ \partial\omega(1)}{\int \psi_s(1, 2, \ldots . n)\ \psi_e(1, 2, \ldots . n)\ \partial\tau(1) \ldots .\ \partial\tau(n)} \tag{34}$$

This density is merely an overlap between the wavefunctions and may have negative or positive regions. It does not correspond to any actual intermediate state for the process of rotation but represents the transition density symmetrically disposed between the positions of the nucleus before and after the transition. The Hellmann–Feynmann theorem indicates that the total change of energy ($\Delta E^{+}{}_{es}$) for the transition from the staggered to the eclipsed state is equal to the difference in attraction of the eclipsed and staggered nuclear frames for the transition density, plus the change in the internuclear repulsion $V_{nn}$.

$$\Delta E_{es} = \Delta V_{nn} + \int {}_{es}{}^{(1)}\ \Delta V_{ne}(1)\ \partial v(1) \tag{35}$$

The energy of transition is thus zero if both the changes in internuclear repulsion terms are zero and the attraction between the transition density is also zero. This would be the case if the protons in the original and final positions are identical. The barrier in the case of ethane would thus be computed by taking the difference in the attractions between such a transition density, the protons being eclipsed in the one case and staggered in the other, and adding the change in the repulsion terms. Lowe and Parr[66] have extended this approach in a semi-empirical way to other molecules. They neglect the effects of transition density on the rotated end and arrive at a simple electrostatic model which by virtue of its connection with the Hellmann–Feynmann theorem does not neglect kinetic terms.

Goodismann[67] has pointed out that the barrier could in theory be derived knowing the derivative of the barrier at some intermediate point between the staggered and eclipsed states. This derivative may be related to the torque on

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[65] R. E. Wyatt and R. G. Parr, *J. Chem. Phys.*, 1966, **44**, 1529.

[66] J. P. Lowe and R. G. Parr, *J. Chem. Phys.*, 1966, **44**, 3001.

[67] J. Goodismann, *J. Chem. Phys.*, 1966, **44**, 2085; 1967, **47**, 334.

the rotor. His calculations predict a barrier which is 60% too low for ethane. In general the Hellmann–Feynmann calculations are very sensitive to the accuracy of the wavefunctions and so this is not so surprising.

It appears likely that no simple answer will be found for the existence of barriers to internal rotation; most probably it will be found that barriers arise from the combined effect of a number of the interactions outlined above, the magnitude of such interactions varying from molecule to molecule. A complete picture must also contain a more dynamic approach to the molecule to allow for possible distortion during rotation, and these effects remain very difficult to predict.

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