RESTRICTED FREE ROTATION AND
CYCLIC MOLECULES

L. J. OOSTERHOFF

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LUITZEN JOHANNES OOSTERHOFF

GEBOREN TE LEEUWARDEN

PROMOTOR: PROF. Dr H. A. KRAMERS

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INTRODUCTION

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   In organic molecules the energies of formation of chem-
ical bonds usually are of the order of magnitude of about 50
to 100 kcal/mol. These energies account for the stability of
the molecules with respect to thermal dissociation and also
for many phenomena in chemical equilibria and chemical reac-
tions which involve important heat effects. As these energies
often are a roughly constant property of chemical bonds they
can profitably be tabulated and used in calculations and in
theoretical considerations in which one need not trouble about
minor details.   The theories of resonance are an example of
this procedure.

   The interactions between the atoms within a molecule
are not confined to those leading to chemical bonds but there
also occur a great number of interactions involving energies
of the order of magnitude of a few kcal/mol. These are for
instance the electrostatic interactions of dipoles, v.d.Waals-
London attraction, several kinds of steric hindrance, the
forces which hinder the free rotation around single bonds and
so on.   Although the energies involved are much smaller than
those bringing about the chemical valence they are, at ordi-
nary temperature, still large as compared with kT and there-
fore still of considerable importance. At room temperature kT
is about 0.6 kcal/mol and energy changes of a few kcals can
shift an equilibrium entirely to the opposite side or change
the course of a chemical reaction in an essential way.   Exam-
ples are known that minor differences in molecular structure
may cause a normal monomolecular chemical reaction to switch
over to a chain mechanism.
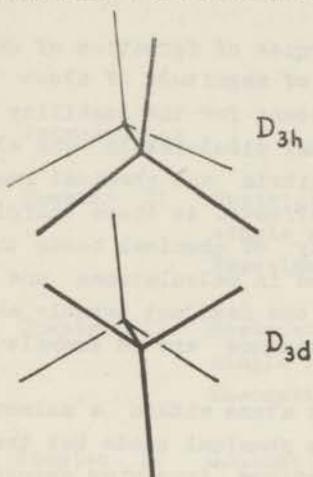
   Without these small energy effects the immense variety
of chemical substances and chemical processes would not exist
to such an extent as it does. Especially the phenomena in
living matter which occur within such a small interval of
temperature often appear to be closely connected with the
small energy interactions.

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   In the present investigation one of these interactions

viz. the forces which hinder the free rotation around single bonds, will be considered more closely.

The potential energy barriers hindering the free rotation in hydrocarbons appear to be of such a shape that the staggered configuration, which corresponds to the D_{3d} symmetry of the ethane molecule is the most stable one, whereas the potential energy is a maximum in the eclipsed configuration which corresponds to the symmetry D_{3h} in ethane. On a superficial view this phenomenon may be described as a repulsion of the atoms bound to the two carbon atoms connected by a single bond. Whatever the true cause of this effect may be it seems that also in most other molecules the forces hindering the free rotation can be held to be repulsions between atoms not connected by a bond.

The potential barriers hindering the free rotation give evidence of their existence in a great number of phenomena in chemistry and physics.

In the first place the thermodynamic properties of the molecules in the gaseous state are influenced thereby to such an extent that e.g. specific heats and entropies can be used as a source of knowledge about the magnitude of these barriers.

Also the properties of the liquid state of many long chain molecules might undergo their influence. According to a suggestion of v a n A r k e l and of K r a m e r s [1] the slow increase of the boiling point T_b of normal paraffins with increasing number n of carbon atoms ($T_b \sim \sqrt{n}$) might be due to the tendency of the molecules to reconcile a maximum of intermolecular attraction with the greatest possible randomness in shape and position. If this tendency is realized partly at the cost of molecular configurations which are unfavourable from a point of view of the energy barriers hindering free rotation it may be that the transition of the molecules to the gaseous phase, where they can assume the most favourable configuration with respect to the inner energy, will involve a relatively low heat of evaporation, which is roughly proportional to the boiling point.

The interaction of non-bonded atoms has also a bearing on the structure of cyclic molecules. According to the ideas of v a n 't H o f f on the directional properties of the carbon bonds one can expect the existence of two isomeric forms of cyclohexane. As has been shown by S a c h s e [35] one of the isomers usually indicated as boat form is capable of passing continuously through a sequence of configurations without any change in bond lenghts or bond angles. The boat configuration which in text books generally is represented is only one extreme configuration of this movable form.The other isomer, the chair form, exists only in one configuration. (Schematic figures of both forms are given on page 40).

When considering these models one would presume the movable form to be capable of an internal motion which at ordinary temperatures will be fully excited. The lowering of the free energy in consequence of this degree of freedom will be more important than the effect of the corresponding vibration of the chair form which will be only slightly excited. Therefore one may expect the movable form to be thermodynamically more stable.

In contrast with this expectation experimental evidence points to the practically exclusive occurrence of the chair form. This suggests some kind of energetical interaction between the atoms which will make the movable form less stable.

It is a remarkable fact that in most molecules containing a free sixmembered saturated ring the chair configuration occurs irrespective of whether the ring contains only carbon atoms or contains also other atoms as oxygen or nitrogen. Probably dioxane has the chair configuration; the same is true for the derivatives of trioxane and for the pyranose ring in sugars and cellulose and starch.Only a few exceptions are known.

Cyclohexanedione-1,4 has a dipole moment which can only be explained by assuming a movable configuration.

The blue coloured starch-iodine complex seems to possess a structure which can be thought of as a spiral formed by a chain of pyranose rings in the boat configuration around iodine molecules and ions lying in the axis [16].Similar structures probably are present in the dextrines of Schardinger. According to X-ray investigations these products of the destruction of starch contain rings of six or seven pyranose rings in the boat configuration giving the same kind of iodine

complexes.

As ringstructures, five as well as sixmembered satu-
rated rings, frequently occur in important natural products,
for instance in steroids and sugars, an insight into the for-
ces which, although of much smaller magnitude than the valence
forces, also determine the shape of the molecules, is of im-
portance. The more so as the shape of a molecule often is a
dominating factor in its biochemical activity.

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A satisfactory insight in the forces restricting free
rotation about single bonds is still lacking. The experimental
results give no clear indication as to the nature of these
forces. I A further study of cyclic molecules might be
especially useful since in these molecules the relative pos-
itions of the atoms are more defined than in the open chain
molecules, whereas the possibility of several isomers involves
enough freedom to compare the energies of the different con-
figurations.

From the theoretical side one meets with the difficulty
that the current methods of applying wave mechanics to prob-
lems of molecular structure involve serious approximations.
For this reason the resulting wave functions may account for
important energy effects but it looks doubtful whether these
wave functions are sufficiently accurate to account unambigu-
ously for the small energy effects involved in the restricted
free rotation.

The usual ways to describe the state of a molecule with
a wave function which one hopes is not too far remote from
the solution of Schrödinger's equation are known as the mo-
lecular orbital (MO) method and the valence bond (HLSP) meth-
od. These methods are usually applied in an unrefined form in
so far as one builds up the total wave function as sums of
products of atomic wave functions. Besides in the MO method
one usually does not give the wave function the proper symmetry
whereas in the valence bond method the higher order permutations
and ionic contributions are mostly not taken into account.
Used in these crude forms both methods predict in the case of
ethane free rotation or at most a potential barrier which is
ten times too small.

Now one might proceed by taking into account some of
the obvious refinements. This procedure has been tried several

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times in different directions with results which sometimes look satisfactory. In all cases, however, the difficulty remains that other improvements of the crude theory which are left out of consideration might give effects of at least the same magnitude in the same or in the opposite sense.

One way to get out of this difficulty is to look for feasible ways of solving Schrödinger's equation more accurately by wave functions of a systematic type which do not confront us with such dilemma's. As an example we may perhaps think of the H a r t r e e - F o c k method as developed by L e n n a r d - J o n e s [25] for the case of molecules. Such a procedure might serve as a base for an appropriate discussion of the forces hindering free rotation.

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In the following chapters a review will be given of the empirical knowledge and theoretical insight pertaining to the problem of the hindering of the free rotation of ethane and some other molecules. Some results of our own calculations will be included which may contribute to clarify some points.

Next the actual knowledge of the structure of cyclohexane and related molecules will be reviewed. A method will be developed to treat adequately the inner motion of the movable isomers which serves as a preliminary to the calculation of the free energy and other properties of these molecules. In the case of cyclohexane the symmetry of the molecule facilitates the calculations to such an extent that the difference between the free energies of the rigid and the movable isomer can be estimated rather accurately. The cyclohexanedione-1,4 molecule is more difficult to treat, but it is plausible that the experimentally determined dipole moment may be in accord with our present knowledge about the forces restricting free rotation.

CHAPTER II
RESTRICTED FREE ROTATION
ABOUT SINGLE BONDS
EXPERIMENTAL DATA

1.

The main information about the magnitude of the poten-
tial barriers hindering the free rotation about single bonds
has resulted from measurements of thermodynamic quantities
such as specific heat, entropy of chemical equilibria. In the
case of ethane the specific heat measured at low temperatures,
the entropy determined with the Nernst theorem and the equi-
librium constant of the hydrogenation of ethylene indicate a
potential barrier of about 2750 cal/mol as first has been
suggested by K e m p and P i t z e r[20]. (For a review see
e.g. Z e i s e[42].One is led to this value assuming a barrier
of the shape.

(1) $$V = V_3 \cos 3\varphi$$

where φ is the angle of rotation about the C–C bond with $\varphi = 0$
in the eclipsed or in the staggered configuration.If an other
dependence on φ is assumed a somewhat different value of V_3
might result.

Probably the staggered configuration is the stable one.
This is in accord with the zig-zag configuration of paraffin
molecules in the cristalline state and with the preponderant
occurrence of the rigid isomer of cyclohexane which we will
discuss more fully afterwards. Spectroscopic evidence also
supports the assumption of a potential barrier of the said
order of magnitude with the staggered position as the stable
one (S m i t h[36]).

Beside ethane a great number of other molecules have
been investigated in order to get information about the mag-
nitudes of the potential barriers. The data given in table I
are taken from a paper of F r e n c h and R a s m u s s e n[13],
where further references may be found.

TABLE I

Compound	Potential barrier (cal/mol)
Ethane	2750
Propane	3300
Isobutane	3870
Neopentane	4800
Methylamine	>1520
Dimethylamine	3460
Trimethylamine	4270
Methylalcohol	1350
Dimethylaether	2700
Aceton	560 – 1240
Methyl mercaptan	1460
Dimethyl sulfide	2000
Tetramethyl silane	1100 – 1500

2.

The barrier heights are determined by comparing measured thermodynamic quantities with the results of calculations
using various values of the height of the barriers. In order
to give an idea of the kind of information which can be obtained along these lines we will briefly indicate the method
developed by P i t z e r [30] for the calculation of thermodynamic functions of paraffins and other molecules.

This procedure consists of a calculation of the classical partition function assuming free rotation and afterwards
correcting for the influence of the potental barriers and
quantum effects. This can easily be done using the tables of
P i t z e r and G w i n n [32] in which the corrections are
given for each restricted free rotation as functions of the
classical partition function Q_f of the rotation and the ratio
of the height of the potential barrier to RT.

Now for many single bonds a formula for the potential
barrier like (1) is not correct since the trigonal symmetry
is lacking.This is for instance the case for the central bond
of n-butane. In this molecule the planar zig-zag configuration is considered to be the most stable one. The two gauche
positions which result from a rotation around the central bond
by either + or $-\frac{2\pi}{3}$ are presumably also positions of minumum
energy,but according to Pitzer these minima have an increased
energy of 0.8 cal/mol with respect to the first-mentioned
configuration. Similar considerations can be applied to each
sequence of four carbon atoms.

Now the procedure adopted by Pitzer for calculating the free energy of molecules like n-butane is to consider an ideal gas of these molecules as a mixture of isomers, each isomer corresponding to a configuration where each bond is in a position of minimum energy. For each isomer the internal rotations need to be considered only for a region $0 \leqslant \varphi \leqslant \frac{2\pi}{3}$. It proved to be consistent with the experimental data of a number of paraffins if within this region the potential barrier was assumed to depend on φ according to

(2) $$V = V_3 \cos 3\varphi$$

with V_3 = 3600 cal/mol. Clearly the shape of the potential barrier in the neighbourhood of the maxima at $\varphi = 0$ and $\varphi = \frac{2\pi}{3}$ can not exactly be given by (2) in the case of for instance the central bond in n-butane since there the potential energy would change discontinuously when passing from a planar zig-zag isomer to a gauche isomer. .But this is quite irrevelant for the calculation of the partition function since the configurations near the potential maxima contribute only slightly to this quantity. On the other hand this proves that one can not expect to deduce precise information about the shape of the potential barrier in the positions of maximum energy from a study of the thermodynamical properties of paraffins. This might, however, be possible in the case of saturated cyclic molecules where in consequence of the ring structure some bonds may be forced into a position of unfavourable potential energy. In the boat configuration of cyclohexane for instance four bonds are in the staggered and two bonds in the eclipsed position.Now at ordinary temperatures this configuration will occur at most to a very slight extent as has been shown by P i t z e r et al. [5]. But in some cases of cyclic molecules configurations corresponding to the movable isomer of cyclohexane may be present even at ordinary temperatures as has been shown to occur with the naphtodioxanes which have a non zero dipole moment (B o e s e k e n et al. [8] and with cyclohexanedione -1,4 which has also a dipole moment (L e F è f r e 24).

A further study of these molecules might therefore be useful in order to obtain more detailed information about the shape of the potential barrier then can be deduced from thermodynamical data of open chain compounds.

3.

To account for the magnitudes of the potential barriers in a great number of molecules A s t o n et al. [2]. Assumed a repulsive potential between non bonded atoms of the form k/r_{ij}^{n}, where r_{ij} is the distance between the atoms i and j and k and n are constants. In the case of hydrogen atoms Aston et al. found the best fit with the experimental data assuming a value $n = 5$. Along these lines the potential barriers for a number of molecules could be calculated in fair agreement with the experimental values.

A still simpler method giving as good results has been suggested by F r e n c h and R a s m u s s e n [13]. In this method the closest distance of approach of two atoms in a molecule is considered as a measure of the interaction of these atoms which contributes to the potential barrier. By constructing an empirical curve showing the relation between the shortest distance of two atoms and their contribution to the potential barrier it proved possible to calculate a number of potential barriers with satisfying results.

Although these methods may be very useful in predicting the potential barriers in molecules for which experimental data are lacking it is not clear how far they indicate the lines along which an theoretical explanation may be tried.

CHAPTER III
RESTRICTED FREE ROTATION
ABOUT SINGLE BONDS
THEORETICAL EXPLANATIONS

1.

   For a review of the various theoretical explanations
of the origin of the hindering of the free rotation around
single bonds it will be useful to consider first one of the
standard methods of treating the electronic structures of sat-
urated molecules such as ethane, usually indicated as valence
bond method or HLSP (Heitler – London – Slater – Pauling)
method. This procedure has the advantage that it closely links
up with the classical structural formulae used in organic
chemistry.

   Following the ideas of Lewis one considers each line
in a valence pattern as a symbol of an electron pair respon-
sible for the stability of the bond. An approximate descrip-
tion of the behaviour of the two electrons is obtained by
building a wave function out of atomic orbitals in a similar
way as has been done by Heitler and London for the hydrogen
molecule. A wave function for the whole molecule is written as
a product of the electron pair wave functions, which has to
be made antisymmetric according to the Pauli principle.

   If we indicate by the symbol

$$a - b \qquad c - d \qquad \ldots\ldots$$

that the bonds are formed by the atomic orbitals a and b and
also by c and d etc. the corresponding wave function is

(1) $\qquad \Psi = (n!)^{-\frac{1}{2}} \sum_p \delta_p P \left\{ a_1 b_2 + b_1 a_2 \right\} \left\{ c_3 d_4 + d_3 c_4 \right\} \ldots\ldots$ [12][34]

n is the number of electrons

P indicates a permutation of the coordinates of the elec-
trons

δ_p is +1 or −1 according to whether P is an even or odd
permutation

a_1 means the wave function a depending on the coordinates
of electron 1.

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[12] is an abbreviation of the spin function $\dfrac{\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)}{\sqrt{2}}$

Wave function (1) may also be written as

(2) $\Psi = (n!)^{-\frac{1}{2}} \sum\limits_{P} \delta_P\, P\, a_1\, b_2\, c_3\, d_4 \ldots\ldots [12]\,[34] \ldots\ldots$

and introducing the abbreviations

$\psi = a_1\, b_2\, c_3\, d_4 \ldots\ldots$ $\qquad\qquad \varphi = [12]\,[34] \ldots\ldots$

we get

$$\Psi = (n!)^{-\frac{1}{2}} \sum\limits_{P} \delta_P\, P\, \psi\, \varphi$$

The corresponding energy is

$$E = (\Psi\, H\, \Psi)\big/(\Psi\, \Psi) \qquad\qquad\qquad\qquad *)$$

which can be transformed in

(3) $E = \sum\limits_{P} (P\psi\,|\,H\psi)(\delta_P\, P\varphi\,|\,\varphi)\big/\sum\limits_{P} (P\psi\,|\,\psi)(\delta_P\, P\varphi\,|\,\varphi)$

Pauling as well as Eyring et al. have given useful directions
for the evaluation of the scalar products $(\delta_P\, P\varphi\,|\,\varphi)$.

It has become a common practice to neglect in (3) all
terms involving permutations of higher order than the inter-
change of two electrons. This procedure would be exact if the
functions a, b, .. were mutually orthogonal. Although this is
not the case the influence of the non orthogonality expressed
by the overlap integrals like

$$S_{ab} = \int a\, b\, d\tau$$

is assumed to be small enough to justify this procedure
In a similar way one neglects in the normalization in-
tegral $(\Psi\, \Psi)$

all permutations except the identity operation. After intro-
duction of these approximations one gets the simple energy
formula

(4) $E = Q + \sum J_{\alpha\beta} - \frac{1}{2} \sum J_{ij}$

Q is the coulomb integral $(\psi H \psi)$. $J = (T\psi\,|\,H\psi)$ is a single ex-
change integral where T is a single interchange of two elec-

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trons. The indices $\alpha\beta$ or ij refer to the orbitals of the two interchanged electrons.The coulomb integral is a sum of terms which give the interactions of the charge clouds a^2, b^2 , ... with one another and with the atom cores. In the exchange integrals one finds terms giving the interactions of overlap charges like $a_1 b_1$ and $a_2 b_2$ with each other and also the interactions of the overlap charges with the atom cores and the other charges but multiplied into appropriate weight factors. The summation $\sum J_{\alpha\beta}$ has to be taken over all pairs of atomic wave functions linked up by a line in the valence pattern.The summation $\sum J_{ij}$ has to be taken over all pairs of   functions occuring in different bonds.

For the treatment of the total binding energy of molecules which in organic chemistry are pictured by one valence structure the above formula is convenient and instructive,but it involves a number of crude approximations.

2.

Along the lines indicated P e n n e y [29)] and E y r i n g [12)] have treated the ethane molecule. One of the results was that to this approximation the rotation around the C-C bond would be practically free. According to Eyring the potential barrier would not exceed a 300 cal/mol with the staggered position the more stable one.
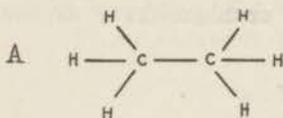
The atomic wave functions which were used in the wave function describing the normal valence state A of the ethane molecule were 1s hydrogen functions as far as the hydrogen atoms are concerned and for each carbon atom four carbon functions constructed as linear combinations of hydrogen like 2s and 2p functions. Following S l a t e r and P a u l i n g [28a)], these linear combinations can be chosen in such a manner that four equivalent or, as may be required, nearly equivalent wave functions result. For the case of four equivalent wave functions suited to form four tetrahedrally arranged bonds these carbon functions are

$$\psi_t = \tfrac{1}{2}\, \psi_{2s} + \tfrac{1}{2}\, \sqrt{3}\, \psi_{2p}$$

where that particular ψ_{2p} function has been chosen which has rotational symmetry around the line joining the two bonded atoms.

In ethane one of these carbon ψ_t functions will have

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its axis in the C-C direction. The other three form a set
with trigonal symmetry about the C-C direction, each pointing
to one of the three hydrogen atoms. Each of the last mentioned
functions can be written as the sum of three terms, one term
being cylindrically symmetric around the C-C direction and two
terms being proportional to $\cos X$ and $\sin X$ if X is the angle
of rotation around the C-C bond. Now the exchange integrals
containing the products of two carbon ψ_t functions belonging
to different carbon atoms can contain no terms of higher than
the second degree in $\sin X$ and $\cos X$. If these integrals are
added together the terms depending on X give either zero or a
constant value in consequence of the trigonal symmetry.

The same applies to the exchange integrals containing
the products of a carbon function with a hydrogen function
belonging to the other methyl group. The coulomb interactions
are also independent of the angle of rotation because the
charge cloud of the trigonal set of ψ_t functions has cylin-
drical symmetry around the C-C bond.

The only X -dependent terms which remain in (4) are
the coulomb and exchange hydrogen – hydrogen interactions,
which are very small in consequence of the large distances
between the hydrogen atoms. The repulsive interactions have
been estimated by Eyring, who takes also a Van der Waals-
London attractive potential into account and arrives at the
afore-mentioned result.

Clearly in this method of attack one has neglected too
much to get the right order of magnitude for the potential
barrier and so the question arises in which direction the im-
provement of the crude method most advantageously may be
sought.

3.

The effect of a number of refinements of the valence
bond method has been studied by E y r i n g et al.[17] These
refinements consist of using other carbon orbitals instead of
the ψ_t functions and also of the introduction of other wave
functions corresponding to structures like (B) [*] which, after
multiplication with the appropriate coefficients, are added to
the principal wave function.

The carbon wave functions may be improved by adding to
the function ψ_t hydrogen like functions fitting in with the

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[*] see fig. p. 19

symmetry of the molecule. The orbital of lowest energy which can be added to the ψ_t orbital forming the C-C bond and may influence the calculated potential barrier is a 4f orbital

$$\psi_{4f} = f(r) \sin^3 \theta \cos 3 X$$

The carbon orbital is changed thereby into

$$c_1 \psi_t + c_2 \psi_{4f}$$

By a variational calculation the coefficient c_2 was shown to be of the order of magnitude of $0.015 c_1$ which gives such a small distortion of the carbon orbital that the contribution of the f orbitals to the potential barrier is negligible.

The calculated potential barrier may also change by the addition of d functions to the ψ_t orbitals in the C-H bonds. A set of equivalent tetrahedral functions can be obtained by taking linear combinations of one 2s three 3p and three 3d functions as has been shown by Pauling. For instance along an axis which makes equal angles with the three coordinate axis this function becomes

$$\psi_{III} = c_1 s + \frac{c_2}{\sqrt{3}} (p_x + p_y + p_z) + \frac{c_3}{\sqrt{3}} (d_{xy} + d_{yz} + d_{zx})$$

For methane Eyring et al. estimate a value of about 0.15 for c_3 when ψ_{III} is normalized. Assuming a similar value in ethane it is possible to calculate the coulomb interaction between the charge distributions on the two carbon atoms which now no longer are cylindrically symmetrical about the C-C bond, but contain a $\cos 3 X$ term. This gives a contribution of about 500 cal/mol favouring the staggered configuration. The exchange effects are presumably small. A larger effect in the opposite direction was calculated for the coulomb interaction of the hydrogen atoms with the charge distributions on the carbon atoms, which was estimated to 1440 cal. This might be diminished to about 700 cal/mol if exchange interactions are included.

So improving the atomic orbitals one is led to a number of effects in opposite directions of which it is very difficult to decide how important the total result will be. Eyring et al. estimate the sum of all these interactions to give a barrier of about 600 cal/mol with the opposed configuration the stable one.

Beside the corrections applied to the atomic orbitals

which were used as a starting point in constructing the total
wave function, Eyring et al. have also considered the influe-
ence of the introduction of other valence structures, in par-
ticular those which imply a double bond between the carbon
atoms e.g.

B

H————————H

H——C===C——H

H   H
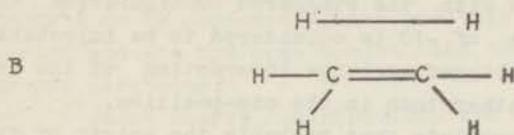
The wave functions corresponding to these structures can be
added to the principal wave function (A) multiplied with co-
efficients which may be determined by a variational method.

It should be kept in mind that the double bond in the
valence structure (B) is quite different from the double bond
in olefins. One of the lines indicates an ordinary single
bond but the other a bond between two ψ_t orbitals on different
carbon atoms having their axis in the carbon—hydrogen direc-
tions. The overlap of these orbitals is much less than of the
π orbitals taking part in the normal double bond. Accordingly
the second bond is a very weak one.

The energy difference of the „excited" structure (B)
and the normal valence structure of ethane will be rather
high, because two C—H bonds have been broken and are replaced
by carbon—hydrogen repulsions and only two weak bonds have
been formed replacing two weak repulsions. Therefore the wave
functions of the excited structures will take part in the
whole wave function only to a slight extent. Nevertheless it
is indicated by the calculations of Eyring et al. that their
influence on the potential barrier may be important.

The exchange integrals pertaining to two ψ_t orbitals
on different carbon atoms consist of three terms, one term
not depending on the angle of rotation around the C—C direc-
tion χ, one term proportional to $\cos \chi$ and one proportional
to $\cos^2 \chi$. Only the second term may contribute to the poten-
tial barrier when the total effect of all these exchange in-
teractions is considered. Unfortunately the magnitude of this
term is rather uncertain. The calculations have been made
with successively assuming that the coefficient of $\cos \chi$
equals 0, 2 or -10 kcal/mol. In the first case the effect of
the exchange interactions of the ψ_t orbitals vanishes. The
only effect which remains comes from the interactions of the
hydrogen atoms of one methylgroup with the hydrogen atoms and

carbon orbitals of the other methylgroup. The magnitude of this contribution to V_3 is estimated to lie between 0.7 and 1.3 kcal/mol favouring the eclipsed configuration.

In the second case the barrier is raised to 1.3 to 2.2 kcal/mol. If one assumes a value − 10 the barrier is again 2.2. kcal/mol but now with the staggered configuration the stable one. This value of −10 is considered to be improbable because it implies a bigger exchange interaction of the orbitals in the trans rather than in the cis-position.

Eyring et al. conclude that probably the origin of the potential barrier has to be sought in the effects indicated above leading to the opposed form as the stable one.

Since now all the experimental evidence is in favour of the staggered form as the more stable, one has to conclude that either a more exact calculation will change the results of Eyring et al. or otherwise that still other effects may be large enough to turn the results into the opposite direction.

4.

A quite different suggestion of P i t z e r [31] is based on the idea that the length of for instance the carbon-carbon bond in ethane is determined by the equilibrium of the interaction of the bonding electrons tending to shorten the bond and the repulsion of the other valence electrons of the carbon atoms.

If the charge distributions on the carbon atoms deviate from the cylindrical symmetry, for example because of a contribution of the d-orbitals to the C-H bonds, the resulting trigonal distributions will always give a larger repulsion if the hydrogens of one methyl group line up with those of the other methyl group than in the staggered position. The de - creased repulsion in this configuration will allow the C-C bond to shorten a little thereby increasing its binding energy and stabilizing the staggered form.

Without an explicit calculation it is difficult to see whether this effect may account for the magnitude of the experimentally determined barriers.

5.

An other way of attack of this problem is followed by L a s s e t t r e & D e a n [23]. As their reasoning in many respects goes along the same line as our own calculation relating to this problem we will give here only a brief review and

come back to some points in the next chapter.

According to the ideas of Lassettre and Dean the bar-
riers restricting the rotation about single bonds originate
in the coulomb interactions of the charge distributions of
the C-H bonds. Each bond which is electrically neutral is
thought to be composed of two positive charges located in the
carbon and the hydrogen nuclei and the two negative charges
of the electrons.

These charge distributions are calculated using for
each C-H bond molecular orbitals of the type

$$a\,\psi_t + b\,\psi_h$$

With these orbitals the dipole moment and the quadrupole mo-
ment with respect to a point midway between the carbon and the
hydrogen atom are calculated. These moments are used for a
calculation of the electrostatic interactions of the bonds.

The moments are defined in the following way

the dipole moment $\quad \mu = \sum qz + \int u\,z\,d\tau$

the quadrupole moment $\quad P = \sum q\left(\frac{3}{2}z^2 - \frac{1}{2}r^2\right) + \int u\left(\frac{3}{2}z^2 - \frac{1}{2}r^2\right)d\tau$

The summations extend over the discrete positive charges q ,
the integration over the continuous charge distribution with
density u of the electrons. The positive sense of the z axis
is taken along the line linking up the nuclei going from C to
H. The other components of the two moments are zero in conse-
quence of the cylindrical symmetry.

The dipole moment and the quadrupole moment have been
calculated for a series of values of the ratio of the con –
stants a and b . The quadrupole moment is not very sensitive
to the variations in the ratio b/a in contrast with the dipole
moment. The value of the dipole moment is assumed to be either
+ or – 0.4 Debye in agreement with current views about the
magnitude of this quantity. Since this is an important assump-
tion we will come back to this point at the end of this chap-
ter.

These two moments are supposed to give a sufficiently
accurate characterization of the bond for the calculation of
the coulomb interactions of the bonds. Lassettre and Dean ex-
plicitly state that the higher moments are probably negligible
so that it is only necessary to consider dipole-dipole ,
dipole-quadrupole and quadrupole-quadrupole interactions .
These interactions have been calculated for the staggered and

for the eclipsed configuration of ethane, using the usual formulae giving the potential energy of two moments in dependence of the distance and the orientation.

In consequence of the assumption of a very small value of the dipole moment the main contribution to the calculated value of the potential barrier comes from the interaction of the quadrupole moments. The calculated value of the potential barrier being too small Lassettre and Dean have reversed their reasoning and have concluded that the real quadrupole moment is larger than the calculated one. It proves necessary in order to get a value of $V_3 =$ 2750 cal/mol to assume a value $P = 2.71$, if μ is taken to be $+ 0.4$ and $P = 3.14$, if $\mu = -0.4$.

An argument in favour of this procedure is that the ratio of the calculated quadrupole moment of the hydrogen molecule according to the crude molecular orbital method and the accurate value calculated by James & Coolidge, which is about 30 percent higher, is about the same as the ratio of the calculated and „empirical" values of the C-H bonds in ethane.

In the same manner Lassettre and Dean have determined empirical values of the quadrupole moments of a number of bonds. The value for the C-C bond could be determined from the propane molecule. Herewith the barriers in isobutane and neopentane could be calculated, the results being in fair agreement with the experimental values. It is, however, difficult to see whether this is an independent argument in favour of the theory.

A typical result of the investigations of Lassettre and Dean is the dependence of the quadrupole moments on the interatomic distance. For a number of bonds the calculated as well as the „empirical" values prove to be proportional to the square of the interatomic distance. In the series of „empirical" moments the accurately calculated value for the hydrogen molecule fits in very well.

One of the objections which may be raised against this theory refers to the way in which the interactions of the bonds have been calculated. The use of dipole moments and higher moments in the calculation of electrostatic interactions of charge clouds is useful if the resulting series development in powers of the reciprocal distance of the clouds converges quick enough. In that case the series may be broken off after a term which is sufficiently small. In the calculations of Lassettre and Dean, however, the first two terms of

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the series, the dipole-dipole and the dipole-quadrupole in-
teractions, are small. The quadrupole-quadrupole interaction
which is a part of the third term is much bigger and than the
series is stopped assuming the contribution of the other terms
to be negligible.

A further discussion of this theory will be given in
the next chapter together with the results of our own calcu-
lations pertaining to the problem of the coulomb interactions
of C-H bonds. We will conclude this chapter with some consid-
erations of the dipole moment of the C-H bond which is an im-
portant quantity in the discussion of the character of the
C-H bond.

7.

In chemistry the C-H bond usually is considered to be
a typical covalent bond. Therefore, on the analogy of co-
valent diatomic molecules, one is inclined to attribute at
most a small dipole moment to the C-H bond. C o u l s o n [9]
pointed out, however, that a purely covalent wave function,
which may be used for the description of the C-H bond in
methane, is connected with a large dipole moment of 1.9 Debye
in the sense of (C^+H^-). This dipole moment was calculated for
a charge distribution consisting of the positive charge of the
hydrogen nucleus, an equal charge at the carbon nucleus and
the charge cloud of the two electrons involved in the
formation of the bond. The high value of the moment is due to
the asymmetrical carbon orbital, ψ_t, taking part in the bond
wave function, and projecting considerably towards the
hydrogen.

In order to reconcile the calculated bond dipole mo-
ment with the usual assumption that it has a small value, it
proved necessary to mix the covalent wave function with an
ionic wave function of the type C^-H^+ to a rather high extent.

The empirical arguments in favour of a small value of
the dipole moment of the C-H bond, say smaller than 0.7, have
recently been reviewed by G e n t [14]. The main arguments have
for the greater part been derived either from the analysis of
measured dipole moments or from the intensities in vibration
spectra.

The arguments of the first type always refer to the
division of the total measured dipole moment of a molecule
into contributions of bonds or groups. Since there is no def-
inite prescription how the total dipole moment has to be di-

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vided into separate bond moments this procedure always in-
volves some arbitrary assumptions.

More definite arguments can be deduced from the inten-
sities in vibration spectra. These intensities are determined
by the change of the dipole moment connected with the relative
motions of the vibrating atoms, for instance with the stretch-
ing or bending of a C-H bond.

M e c k e and T i m m [39, 26] deduced from the intensities
of the harmonics of a stretching vibration the dependency of
the dipole moment on the bond length. By extrapolating to in-
finite length they determined that part of the dipole moment
which disappears on dissociation of the bond. In this way a
value of 0.3 Debye was found for the moment of the C-H bond
in $CHCl_3$.

But now the difficulty arises how this value has to be
related to the dipole moment calculated according to Coulson.
If the extrapolation refers to a dissociation of the H-atom
preserving the pyramidal configuration of the CCl_3 group then,
disregarding polarisation effects, the atomic dipole connected
with an electron in an asymmetrical ψ_t function remains and
only the difference of the total bond dipole moment and the
remaining atomic dipole is about 0.3 Debye. This would corre-
spond with a nearly covalent bond.

However, if the extrapolation corresponds with a dis-
sociation of the H-atom leaving a flat CCl_3 group, then the
value of the disappearing dipole should be equal to the total
dipole moment of $CHCl_3$ (1,2 Debye) which is not the case.

The same difficulties are met in the determination of
the dipole moments from the C-H bending vibrations for in-
stance in ethylene (B r i g h t W i l s o n et al. [38]) and
benzene (B e l l, T h o m p s o n and V a g o [6]). In ethylene
the moments connected with various vibrations are 0.37, 0.52
and 0.77. An analysis of out of plane vibrations of a number
of alkyl- and halogen-substituted benzenes have led to a moment
of 0.4 (C^-H^+). In these cases one may ask whether the
hybridization of the carbon orbitals is such that the relative
positions of the electrons with respect to the nuclei remain
unchanged during the bending vibration or that for instance
the hybridization is constant and only the effective charge
of the hydrogen atom and the overlap charge are moving. In
this case also a nearly covalent bond would be indicated.

In view of these considerations we do not think it
necessary to lay much stress on the idea that a calculation

of the dipole moment of the C—H bond according to Coulson has
to lead to a value of 0.4 Debye. On the other hand we will
not deny that a closer examination of the meaning of the
spectroscopic dipole moments might give support to the assump-
-tion of a small value of the dipole moment.

CHAPTER IV
COULOMB INTERACTIONS IN THE
PROBLEM OF HINDERED ROTATIONS

1.

In the foregoing chapter it has been mentioned that in the standard procedure of calculating the energy corresponding to a wave function it is a common use to neglect the higher order permutations (Chapter IV, 1). This is a reasonable method in the case of overlap integrals which are small as compared with unity. But for a C-H bond S is of the order of magnitude of 0.6 and so it is an obvious task to ascertain whether it would be advisable to take account of the higher permutations.

From the examination of a four electron problem it can easily be seen that, as long as these electrons can be divided up into two pairs belonging to different bonds which do not overlap to an appreciable extent, the simultaneous interchange of the electrons within each pair is the only important contribution of the higher permutations. Physically, the introduction of these permutations, means that one takes account of the coulomb interactions of the overlap charges in different bonds. These interactions will be included in the following calculations which pertain to the electrostatic interaction of the methylgroups in ethane. Our procedure will be to evaluate the charge distribution in each bond and from them to calculate the coulomb interaction. (Thus we follow the same principles as Lassettre and Dean although the treatments differ in detail).

In the case of the C-H bonds in ethane, belonging to different methylgroups, it is difficult to ascertain whether the bond wave functions overlap so little that the other higher order permutations are of minor importance. According to the calculations of Eyring, already referred to in Chapter III, the exchange integral, which is a measure of the degree of overlapping, is rather small in the case of two ψ_t orbitals belonging to C-H bonds on different carbon atoms but by no means is negligible.

Still we will for the present consider only the coulomb interactions of the charge distributions of different C-H bonds thereby assuming that these charge distributions do

not overlap.

2.

In the calculation of the charge distribution in a C-H bond we will make use of the wave functions which were used by C o u l s o n [9] in the discussion of the dipole moment of this bond. These functions are either localized two centre molecular orbitals or electron pair wave functions of the HLSP-type including ionic contributions. In the first case

(1) $\qquad X = \frac{1}{N}\left\{\kappa\,\psi_t\,(1) + \psi_h\,(1)\right\}\left\{\kappa\,\psi_t\,(2) + \psi_h\,(2)\right\}$

with $\qquad N^2 = \kappa^2 + 2\,\kappa\,S + 1 \qquad\qquad S = \int \psi_t\,\psi_h\,d\tau$

In the second case

(2) $\qquad X = \frac{1}{N}\left[\frac{1}{(2+2\,S^2)^{\frac{1}{2}}}\left\{\psi_t\,^{(1)}\,\psi_h\,^{(2)} + \psi_h\,^{(1)}\,\psi_t\,^{(2)}\right\} + \lambda\,\psi_t\,^{(1)}\,\psi_t\,^{(2)}\right]$

(3) $\qquad N^2 = 1 + \frac{4\,\lambda\,S}{(2+2\,S^2)^{\frac{1}{2}}} + \lambda^2$

Coulson does not introduce a term with $\psi_h\,^{(1)}\,\psi_h\,^{(1)}$ since the energy of a negative hydrogen ion and a positive carbon ion at the C-H distance of the normal C-H bond is supposed to be very high. Although we do not think this argument very convincing since the situation indicated by $\psi_h\,^{(1)}\,\psi_h\,^{(2)}$ is rather different from a negative hydrogen ion we will likewise leave this function out of consideration mainly because a really satisfactory investigation of the problem along the present lines would anyhow require a much more refined discussion of the individual bonds.

The charge distribution of each electron can be considered as a linear combination of the three normalized charge clouds ψ_t^2, $\psi_t\,\psi_h/S$ and ψ_h^2. For instance in the case of (2) the charge distribution of one electron is given by

(4) $\qquad \alpha\,\psi_t^2 + \beta\,\psi_t\,\psi_h\,/S + \gamma\,\psi_h^2$

where

(5)
$$\alpha = \frac{1}{N^2}\left\{\frac{1}{2+2S^2} + \frac{2\lambda S}{(2+2S^2)^{\frac{1}{2}}} + \lambda^2\right\}$$
$$\beta = \frac{1}{N^2}\left\{\frac{2S^2}{2+2S^2} + \frac{2\lambda S}{(2+2S^2)^{\frac{1}{2}}}\right\}$$
$$\gamma = \frac{1}{N^2}\,\frac{1}{2+2S^2}$$

and N^2 is given by (3).

Using wave function (1) one gets other coefficients

α, β and γ but by adjusting the constant κ the charge distributions may be made nearly the same. This does not necessarily imply that the energies corresponding to these wave functions are also nearly equal since the spatial correlations of the two electrons are always different.

3.

We are only interested in that part of the coulomb interaction of the methylgroups which changes on rotation about the C-C bond. Now the sum of the ψ_t^2 distributions of the three C-H bonds of one methylgroup is a distribution with cylindrical symmetry about the C-C direction. So the interaction with these distributions can be left out of the calculation.

A ψ_h^2 charge distribution has spherical symmetry around the hydrogen nucleus. So in a calculation of the magnitude of the coulomb interaction with this distribution we may reckon as if the total charge is concentrated at the hydrogen nucleus.

More complicated are the calculations in which the overlap charges are involved. To a first approximation it is allowed to replace a charge cloud distributed according to $\psi_t \psi_h /S$ by an equal charge placed in the centre of charge. For a further approximation it is necessary to consider also the higher moments of this distribution.

Summing up we have three kinds of coulomb interactions to take account of viz. the $(\psi_h^2 - \delta) \leftrightarrow (\psi_h^2 - \delta)$ the $(\psi_h^2 - \delta) \leftrightarrow \psi_t \psi_h /S$ and the $\psi_t \psi_h /S \longleftrightarrow \psi_t \psi_h /S$ interactions where δ stands for the point charge of the proton.

4.

The coulomb interaction of two charge clouds with densities u_1 and u_2 is given by the integral

(6)
$$\iint \frac{u_1 u_2}{L} d\tau_1 d\tau_2$$

L is the distance between a point in the first cloud and a point in the second one.

The charge distributions which enter into the present calculations always have cylindrical symmetry around a C-H bond. Therefore the centre of charge lies on the line through the carbon and the hydrogen nucleus. For the evaluation of integral (6) it is convenient to consider the reciprocal distance L^{-1} as a function of the distance between the charge

centres and the distances between the two above-mentioned
points and the charge centres. We will proceed in the follow-
ing way.
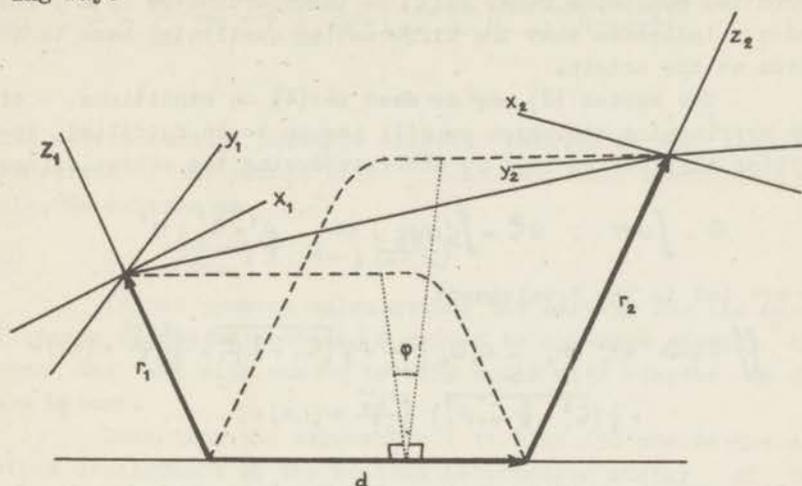
In the figure the two carbon nuclei are indicated a dis-
tance d apart. The charge centres are lying at distances r_1
and r_2 from the carbon nuclei. Each charge centre serves as
the origin of a coordinate system. The z-axis lies along the
C-H line in the sense C-H. The x-axis lies in the plane
through the C-C bond and the C-H bond, the positive sense
pointing to the other methylgroup. The y-axis is fixed by a
right-handed coordinate system. The two coordinate systems
can be distinguished by the indices 1 or 2. φ is the angle of
rotation around the C-C bond; $\varphi = 0$ if the two C-H bonds lie
in one plane.

We call L the distance between the points (x_1, y_1, z_1)
and (x_2, y_2, z_2), L_o being the distance between the points
(o, o, o) and (o, o, o). Assuming tetrahedral bond angles we
get

(7) $L_o^2 = R^2 - \frac{16}{9} r_1 r_2 \cos \varphi$; $R^2 = r_1^2 + r_2^2 + \frac{2}{3} r_1 d + \frac{2}{3} r_2 d + \frac{2}{9} r_1 r_2 + d^2$

We will now develop L^{-1} into a power series in x_1, y_1, z_1 and
x_2, y_2, z_2. This may conveniently by written as

(8) $\frac{1}{L} = \frac{1}{L_o} + \sum_{i=1}^{\infty} \frac{1}{i!} \left\{ (\vec{\sigma_1} \nabla_1) + (\vec{\sigma_2} \nabla_2) \right\}_o^i \frac{1}{L}$

$(\vec{\sigma} \nabla) = \xi \frac{\partial}{\partial x} + \eta \frac{\partial}{\partial y} + \zeta \frac{\partial}{\partial z}$

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The greek letters, which have the same meaning as the latin letters, have been used to bring out explicitly that the differential quotients refer only to the coordinates in L . The index o indicates that the differential quotients have to be taken at the origin.

The series (8) may be used in (6) on conditions of non overlapping etc.which we will assume to be fulfilled. Inserting this series in (6) and introducing the abbreviations

$$Q = \int u d\tau \quad ; \quad Q\,\overline{\varsigma} = \int \varsigma\, u d\tau \quad ; \text{ etc.} \qquad \rho^2 = \xi^2 + \eta^2$$

we are led to the development

$$(9) \qquad \iint \frac{u_1\, u_2}{L}\; d\tau_1\;\; d\tau_2 \; = Q_1 Q_2 \left[\frac{1}{L_o} + \frac{1}{2} \overline{\left(\varsigma_1^2 - \frac{1}{2}\rho_1^2\right)}\; \frac{\partial^2 L_o^{-1}}{\partial r_1^2} + (1,2) + \right.$$
$$\left. + \frac{1}{6} \overline{\left(\varsigma_1^3 - \frac{3}{2}\varsigma_1 \rho_1^2\right)}\; \frac{\partial^3 L_o^{-1}}{\partial r_1^3} + (1,2) + \ldots \ldots \right.$$

(1,2) means that the same term as the foregoing has to be added but with the indices 1 and 2 interchanged. $Q_1 \overline{\left(\varsigma_1^2 - \frac{1}{2}\rho_1^2\right)}$ is the only non-zero component of the quadrupole moment of the charge distribution 1. $Q_1 \overline{\left(\varsigma_1^3 - \frac{3}{2}\varsigma_1 \rho_1^2\right)}$ is the only non-zero component of the octupole moment. The dipole moment $Q_1 \varsigma_1$ and the other components of the quadrupole moment and the octupole moment are zero in consequence of the choice of the origin in the centre of charge and of the cylindrical symmetry of the charge clouds.

5.

It has already been said that we are only interested in that part of the coulomb interaction which changes on rotation of the methylgroups around the C-C bond.In consequence of the trigonal symmetry of the methylgroups the interaction energy may be expected to depend on the angle of rotation φ according to

$$(10) \qquad V = V_o + \frac{1}{2} V_3 \cos 3\varphi + \frac{1}{2} V_6 \cos 6\varphi + \ldots \ldots$$

provided that the zero of φ has been suitably chosen. This formula suggests that it will be advantageous to insert in the energy expression (9) a Fourier development of the reciprocal distance, for in the resulting development only the coefficients of $\cos 3\varphi$, $\cos 6\varphi$, etc. need to be considered. The other terms cancel when adding together all the interactions between the charge distributions of the two methylgroups. Expanding the reciprocal distance

$$\frac{1}{L_o} = \left(R^2 - \frac{16}{9} r_1 r_2 \cos \varphi \right)^{-1}$$

in a Fourier series yields the result.

$$(11) \qquad \frac{1}{L_o} = \sum_{m=0}^{\infty} \cos m\varphi \sum_{n=0}^{\infty} \frac{\varepsilon_m}{R} \binom{4n+2m}{2n+m}\binom{2n+m}{n}\left(\frac{2 r_1 r_2}{9 R^2}\right)^{2n+m}$$

$$\varepsilon_o = 1 \qquad \varepsilon_m = 2 \qquad m = 1, 2, \ldots$$

The coefficient of $\cos m\varphi$ is closely related to the Legendre functions of the second kind [41]. In fact this coefficient may also be written as

$$(12) \qquad \frac{\varepsilon_m}{\pi \sqrt{r_1 r_2}} \sqrt{\frac{2}{8}} \ Q_{m-\frac{1}{2}} \left(\frac{9 R^2}{16 r_1 r_2}\right)$$

In the present calculations the series for the coefficients of $\cos 3\varphi$ and $\cos 6\varphi$ proved to converge rapidly and even the term with $\cos 6\varphi$ is very small with respect to the $\cos 3\varphi$ term.

Inserting the expression (11) in (9) yields the desired development of the coulomb interaction energy of two charge clouds. The interaction of point charges can be calculated easily. For the computation of the interaction energy of the higher moments the derivatives of L_o^{-1} are required which involves a somewhat lenghty but quite feasible numerical calculation.

6.

The charge densities u have been calculated using Slater functions for the carbon ψ_{2s} and ψ_{2p} functions which figure in ψ_t. ψ_h is a 1s hydrogen function. C o u l s o n & D u n c a n s o n [10] have shown in a discussion of the momentum distribution in CH_4 that there are reasons for increasing Slater's screening constants (1 for hydrogen, 1.625 for carbon 2s and 2p) by a factor $\omega = 1.1$. Following this suggestion we get the set of functions (in atomic units)

$$(13) \qquad \begin{aligned} \psi_h &= \left(\frac{\omega^3}{\pi}\right)^{\frac{1}{2}} e^{-\omega r} & \omega &= 1.1 \\ \psi_{2s} &= \left(\frac{\omega^5 c^5}{3\pi}\right)^{\frac{1}{2}} e^{-\omega c r} & c &= 1.625 \\ \psi_{2p} &= \left(\frac{\omega^5 c^5}{\pi}\right)^{\frac{1}{2}} e^{-\omega c r} & \psi_t &= \frac{1}{2}\psi_{2s} + \frac{1}{2}\sqrt{3}\ \psi_{2p} \end{aligned}$$

The length of a carbon-hydrogen bond is taken as 1.093 Å. The value of the overlap integral $S = 0.636$. The moments of the overlap charge $\psi_t \psi_h / S$ with respect to the centre of charge are

Table II

λ	α	β	γ	μ	P	O
0	0.356	0.288	0.356	-1.95	1.65	-0.175
0.5	0.495	0.341	0.177	-0.90	2.07	0.283
1.0	0.601	0.297	0.101	-0.22	2.19	0.576
1.5	0.678	0.258	0.064	0.20	2.22	0.763
2.0	0.731	0.225	0.044	0.47	2.22	0.886
3.0	0.799	0.198	0.024	0.81	2.20	1.038
4.0	0.841	0.144	0.015	1.00	2.19	1.128

Table III

λ	point charge	quadrupole	octupole	V_3	V_3^1
0	39	60	- 53	46	626
0.5	294	74	165	533	1066
1.0	931	48	285	1264	1458
1.5	1485	32	324	1841	1597
2.0	1934	21	325	2280	1670
3.0	2574	9	295	2878	1725
4.0	2989	2	261	3252	1725

$$\overline{\varsigma^2} = 0.115 \text{ Å}^2 \qquad\qquad \overline{\varsigma^3} = 0.1078 \text{ Å}^3$$

$$(14) \qquad \overline{\rho^2} = 0.423 \text{ Å}^2 \qquad\qquad \overline{\varsigma\rho^2} = 0.0026 \text{ Å}^3$$

$$\overline{\varsigma^2 - \tfrac{1}{2}\rho^2} = -0.096 \text{ Å}^2 \qquad \overline{\varsigma^3 - \tfrac{3}{2}\varsigma\rho^2} = 0.1039 \text{ Å}^3$$

The distance of the charge centre to the carbon nucleus is 0.794 Å.

The moments of the ψ_t^2 distribution are

$$\overline{\varsigma^2} = 0.213 \text{ Å}^2 \qquad\qquad \overline{\varsigma^3} = -0.082 \text{ Å}^3$$

$$(15) \qquad \overline{\rho^2} = 0.307 \text{ Å}^2 \qquad\qquad \overline{\varsigma\rho^2} = 0.021 \text{ Å}^3$$

$$\overline{\varsigma^2 - \tfrac{1}{2}\rho^2} = 0.059 \text{ Å}^2 \qquad \overline{\varsigma^3 - \tfrac{3}{2}\varsigma\rho^2} = -0.114 \text{ Å}^3$$

The distance of the centre of the ψ_t^2 distribution from the carbon nucleus is 0.370 Å.

Now α, β and γ measure the chance for one electron to be found in one of the three charge distributions ψ_t^2, $\psi_t\psi_h/S$ or ψ_h^2. $-2\alpha e$ is the charge of the electrons in the ψ_t^2 distribution (e is the positive electron charge). $-2\beta e$ is the charge in the normalized overlap distribution $\psi_t\psi_h/S$ and $(1-2\gamma)e$ is the total charge of the hydrogen atom.

The values of α, β and γ are given in table II for a series of values of λ. In addition the values of the dipole moment μ, the quadrupole moment P and the octupole moment O of the C-H bond are given. These moments have been calculated with the purpose of comparing the energies calculated according to the method developed in this chapter with the energies calculated along the lines suggested by Lassettre and Dean.

The moments are defined by the formulae

dipole moment $\qquad \mu = \sum \varsigma q \qquad\qquad + \int \varsigma u \, d\tau$

quadrupole moment $\quad P = \sum (\varsigma^2 - \tfrac{1}{2}\rho^2) q + \int (\varsigma^2 - \tfrac{1}{2}\rho^2) u \, d\tau$

octupole moment $\qquad O = \sum (\varsigma^3 - \tfrac{3}{2}\varsigma\rho^2) q + \int (\varsigma^3 - \tfrac{3}{2}\rho^2) u \, d\tau$

The summations refer to the two equal positive charges of the nuclei. The integrations extend over the charge cloud of the

two electrons. The origin of the coordinate system has been chosen midway between the two nuclei. The units are based on a unit of charge equal to 10^{-10} electrostatic unit and the $\mathring{A}$ as a unit of length. So μ is expressed in Debye.

6.

The calculation of the coulomb interaction energy in particular of the coefficient V_3 can be performed with the equations (9) and (11) . From these equations the following formula can be deduced.

$$(16) \quad \begin{aligned} V_3 \,(cal/mol) = &\; 4706\,(1-2\,\gamma)^2 - 5714\,(1-2\,\gamma).2\beta + 1802 \times 4\beta^2 \\ &+ \overline{\left(\zeta^2 - \tfrac{1}{2}\,\rho^2\right)} \left\{ 555\,(1-2\,\gamma).2\beta - 2156 \times 4\beta^2 \right\} \\ &+ \overline{\left(\zeta^3 - \tfrac{3}{2}\,\zeta\rho^2\right)} \left\{ 11089\,(1-2\,\gamma).2\beta - 7074 \times 4\beta^2 \right\} \end{aligned}$$

The quadrupole and the octupole moment refer to the overlap charge distribution. With this formula the value of V_3 for a number of values of λ have been calculated. The results are given in table III together with the separate contributions of the interactions of the point charges, of the quadrupole moments with the point charges, and of the octupole moments with the point charges.

It is gratifying that the main contribution to the $\cos 3\varphi$ term in the interaction energy results from the inter - action of the point charges. The contribution of the terms involving the quadrupole moments is very low but the contribution of the octupole moments is rather high. So we do not feel sure that the higher moments will give a negligible contribution. We do not expect, however, that the values of V_3 given in the table will change very much if they are calculated exactly using the same charge distributions.

In table III are also given the values of V_3 calculated according to the method of Lassettre and Dean which are indicated by V_3' . Lassettre and Dean give in their paper the formula (converted to the units used in the present investigation.)

$$(17) \quad V_3' = 297,5\,\mu^2 + 339,9\,\mu\,P + 311,3\,P^2$$

From the equations (8) and (11) we have derived the formula

$$(18) \quad V_3' = 296,0\,\mu^2 + 343,9\,\mu\,P + 315,9\,P^2 - 736,7\,\mu\,O$$

which agrees very well with (17) except that the dipole-oc-

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tupole interaction has been included. This latter term is only of importance for high values of μ corresponding to a high degree of ionicity of the bond.

From table III it can be seen that the agreement between the values of V_3 and V_3' is not impressive but the general trend is the same.

7.

In view of our poor knowledge of the C-H bond it is difficult to arrive at a definite conclusion from the data of table III. Since to our opinion it is at present not justified to use the bond dipole moment as a guide in selecting the most appropriate value of λ, we may only say that one has to reckon with the possibility that the potential barrier restricting the free rotation in ethane is due to the coulomb interaction of C-H bonds with a rather high degree of ionicity.. On the other hand it can by no means be excluded that the C-H bond is a nearly covalent bond and in that case the origin of the potential barrier will have to be sought in a quite different direction.

If, however, one would like to discuss more closely the possibility of a C-H bond having a strongly ionic character then the wave functions we have used in the present calculations are less appropriate. In fact a high value of λ, say 3.0, corresponds with a rather negative carbon atom which involves the use of quite different screening constants in the functions ψ_t.

Perhaps it may be useful to approximate the electronic structure of the ethane molecule by considering a model consisting of a negative C_2-molecule and six protons bedded in the electron cloud. If the cylindrical symmetry of the charge cloud would not be disturbed a potential barrier of 4706 cal/mol would result as follows from equation (16). Now it would be interesting to find some method to estimate the distortion of the electron distribution and the influence on the potential barrier. If this distortion could be described mainly by a quadrupole moment then an interaction between the hydrogen atoms as has been suggested by A s t o n et al.[2] (see chapter II) might result.

CHAPTER V

THE STRUCTURE OF CYCLOHEXANE
AND RELATED MOLECULES

1

Cyclohexane resembles in many respects the saturated
paraffinic hydrocarbons. This has led to the hypothesis that
the valence state of the carbon atom in cyclohexane is similar
to the valence state in saturated molecules where according
to V a n 't H o f f and L e B e l one has to assume a
tetrahedal arrangement of the four valencies. On the basis of
this hypothesis S a c h s e [35] derived by geometrical con-
siderations that in principe two isomers of the cyclohexane
molecule should be possible. The angles between two consecu-
tive carbon-carbon bonds being less than 120° - in our case
109°28'16'' - it is possible to construct an infinite number
of configurations which can be divided into two groups. In
one group the six ring can pass continuously through an infi-
nite number of configurations. The other group consists of
only one configuration which cannot change into the other
configurations without a temporary alteration of the valence
angles.

The first group may be indicated as the movable isomer,
the second as the rigid isomer. Current names are boat and
chair form but these are less appropriate since the boat con-
figuration is only one of all the possible configurations of
the movable isomer whereas the pictures which are supposed to
suggest a similarity with a chair do not emphasize the high
symmetry (D_{3d}) of the rigid isomer.

The ideas of S a c h s e have not been accepted for
a long time mainly because there were not found any indica-
tions as to the existence of isomers of this kind. On the
contrary this was regarded as supporting the hypothesis of a
plane structure advocated by B a e y e r [3].

A solution was offered by M o h r [27] who pointed out
that already a slight distortion of the bond angles would be
sufficient to change one isomer into the other one. This would
involve a high rate of isomerization making it impossible to
isolate one of the isomers.

The hypothesis of a puckered structure of the cyclo-

hexane ring was the guiding and fruitful idea in many inves-
tigations of B o e s e k e n [7], H e r m a n s [19] and co-
workers into the properties of substituted cyclohexanes. Their
results made it very likely that the ideas of Sachse and Mohr
were correct. A more definite indication, however, was
obtained by a number of physical methods. In the first place
the measurements of the entropy and the specific heat in the
ideal gaseous state (P i t z e r [20]) and the analysis of
infrared (R a s m u s s e n [34]) and Raman spectrum
(K o h l r a u s c h [22], G e r d i n g [15]) have to be men-
tioned. These methods unambiguously prove the predominating
occurrence of the rigid isomer.

X-ray analysis of the crystal and electron diffraction
of the gaseous molecules also lead to the abandoning of the
plane structure. It is more difficult, however, to decide by
these methods whether the rigid or the movable isomer is of
general occurrence.

These methods have also been applied to determine the
structure of cyclohexane derivatives. If these molecules con-
tain atoms which introduce a certain degree of polarity they
lend themselves also to an investigation with the aid of di-
pole measurements.

In most cases (cf. H a s s e l [18]) one has come to the
conclusion that the cyclohexane ring preferably has the rigid
structure. This holds as well in cases where the six-membered
saturated ring contains not only carbon atoms but also oxygen
or nitrogen. A few exceptions, however, are known. Cyclo-
hexanedione-1,4 has a dipole moment of 1.3. Debye which
proves that at least in part the movable structure is present,
the rigid structure having a zero dipole moment.
(L e F è v r e [24]).

Dioxane probably is dipole free and accordingly may be
assumed to have the rigid structure. But in naphtodioxanes
where two of the carbon atoms simultaneously take part in two
dioxane rings, the joining of the two rings may be such that
the dioxane ring is stabilized in one or more configurations
of the movable isomer. Two isomers characterized by different
dipole moments and melting points could be isolated (B o e -
s e k e n et al [8]).

The structure of 1,2-dichlorocyclohexane and 1,2-di-
bromocyclohexane could not be determined up to now because
neither the dipole moment nor the electrondiffraction data
could be related to one of the possible isomers with a rigid

cyclohexane ring although the interpretation in terms of the
movable structure seems also to lead to difficulties
(D a l l i n g a [11]).

So it might be that a systematic investigation of the
substituted cyclohexanes will reveal more examples of mole-
cules containing movable rings.

The boat configuration very often occurs in bridged
ringsystems of which campher and a great number of other ter-
penes are the well known examples.Here the configuration which
seldom occurs in the free cyclohexane and therefore has to be
regarded as having a high free energy is stabilized by the
threefold ringsystem. The internal strain which is present in
these compounds probably is responsible for the great variety
of isomerisations which lend a peculiar charm to the chemis-
try of the terpenes. As the study of the reactions of the
terpenes often are of basic importance to many fields in re-
action kinetics, an insight into the behaviour of these ring-
systems may be of wide interest.

Another example of the boat configuration can be found
in the Schardinger dextrines and in the blue iodine-starch
complex. Probably more examples can be found but in general
and in particular in the gaseous state of molecules containing
free, six-membered saturated rings, the rigid form appears
mostly to be the more stable one.

2

At first sight the higher free energy of the movable
isomer is somewhat astonishing. The internal movability may
be expected to add to the free energy the (negative) contri -
bution of a fully excited degree of freedom whereas the
corresponding degree of freedom of the rigid form will be a
partly excited vibration.Besides the rigid form has the higher
symmetry and therefore also for this reason would have a higher
free energy. So one is led to the conclusion that there will
be a difference in potential energy making the movable isomer
less stable.

It is a plausible suggestion to hold the interactions
between the C-H bonds responsible for this potential energy
difference as will be clear from a closer inspection of the
geometry of both isomers.

On page 40 the rigid form and two configurations of
the movable form are pictured. The rigid form has a threefold
axis together with the other symmetry elements of the symmetry

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group D_{3d}. The boat configuration has the symmetry C_{2v}, one twofold axis and two planes of symmetry containing this axis. The second configuration of the movable form has the symmetry V, three mutually perpendicular twofold axis. The other configurations of the movable isomer have a twofold axis only.

From the figure it can be seen that in the rigid structure all pairs of consecutive CH_2 groups are in the staggered position, whereas in the boat configuration two pairs are in the eclipsed and four pairs are in the staggered position. If,following Pitzer, we assume an energy difference of 2750 cal/mol between the staggered and the eclipsed position, the energy difference between the rigid and the boat configuration is 5500 cal/mol. The potential energy of the other configurations is more difficult to determine but in the next chapter we will show that the potential energy is nearly a constant as far as the interactions of consecutive CH_2 groups are concerned.

P i t z e r [5], in the interpretation of the experimentally determined entropy of cyclohexane, reduced to the ideal gas state, only takes account of the boat configuration when comparing the calculated entropies of the two isomers. Therefore the difference between these entropies is mainly due to the different symmetry. This difference is equal to Rln 3 which is large enough to conclude, on the basis of the experimental value of the entropy, to the preponderant occurrence of the rigid form at least at ordinary temperatures. If one takes account of the other configurations of the movable isomer as well, the calculated value of the entropy of this isomer will be increased which strengthens the argument of Pitzer.

It would not be correct, however, to set the free energy difference equal to 5500 - RT ln 3 and to conclude that this value is in accord with the slight occurrence of the movable isomer, since for a calculation of the equilibrium between both isomers one has to consider accurately the effect of the internal movability.

In the next chapter we will develop a method enabling the calculation of the free energy contribution of the internal motion of the movable isomer, from which an estimate of the equilibrium ratio of the two isomers will be derived.
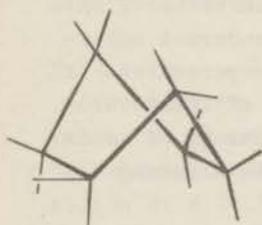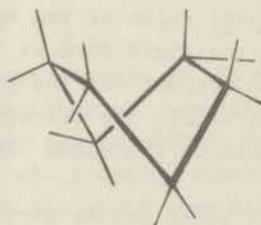
Rigid
D_{3d}

Stretched
V

$\theta = 0$

$\theta = \pi$
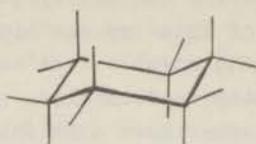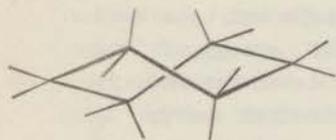
boat
C_2

$\theta = \dfrac{\pi}{2}$

$\theta = \dfrac{3\pi}{2}$

Configurations of cyclohexane

THE ISOMERS OF CYCLOHEXANE

1.

For a calculation of the equilibrium concentrations of the rigid and of the movable isomer in gaseous cyclohexane one has to know the difference in free energy of these molecules or which amounts to the same, the ratio of the partition functions.

In consequence of the equal masses the translational contributions to the free energy are the same for both isomers. The moments of inertia belonging to the overall rotation are nearly equal as may be calculated along the lines indicated further on. So the rotational parts of the free energy are also equal except for the difference in symmetry number. The symmetry number σ_r of the rigid isomer is 6 (symmetry D_{3d}, see fig.p.40). The symmetry number of the movable isomer σ_m depends on the configuration. Therefore we will come back to this point after these configurations have been treated more in detail.

The vibrational contributions of the free energy are difficult to compare since the movable isomer has not been investigated spectroscopically. Nor has a calculation of the vibration frequencies been tried. For want of better information we will assume that to each of the vibrations of the rigid isomer there corresponds a vibration of the movable isomer which on the average gives the same contribution to the free energy. With the exception, however, of one carbon skeleton vibration of the rigid isomer which will be considered as the counterpart of the internal motion of the movable isomer which has the character of a (restricted) free rotation.

In order to calculate the free energy contribution of this internal motion we will first try and find an analytical formulation of the geometrical relations in the movable isomer.

---

*) The main results of this chapter have been derived in 1943 along somewhat different lines by P.Hazebroek and the present author. Because of war-time restrictions their results have thus far only been communicated at the session of the Netherlands Chemical Society on 20.VII.1944, but will form the subject of a joined paper.

2. Geometrical considerations

In the description of the possible configurations of the cyclohexane molecule we will provisionally leave the hydrogen atoms out of consideration and fix our attention on the relative positions of the carbon atoms. Thus we have to treat the problem of an appropriate description of the configurations of equilateral and equiangular hexagon with angles of $109^\circ 28'16''$. The length of a side we put equal to 1. The six sides are represented by six unit vectors $\vec{a}_1, \vec{a}_2, \ldots \ldots \vec{a}_6$ which fulfill the equation
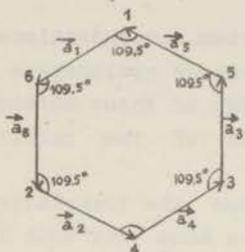
$$(1) \qquad \sum \vec{a}_i = 0$$

Scalar multiplation with successively $\vec{a}_1, \ldots \ldots \vec{a}_6$ leads to the equations

$$(2) \qquad \sum_{i=0}^{6} S_{ij} = 0 \qquad j = 1, \ldots \ldots 6$$

with

$$S_{ij} = (\vec{a}_i\, \vec{a}_j)$$

According to the suppositions

$$(3) \qquad S_{ii} = 1$$

and

$$(3) \qquad S_{ij} = \tfrac{1}{3}$$

when i and j refer to consecutive vectors. In consequence of these equations and $S_{ij} = S_{ji}$ there remain nine unknown S_{ij}, which have to be determined by the six equations (2) and by additional equations which may be derived in the following way. Four vectors $\vec{a}_i$ are always linearly dependent so that we may write e.g.

$$(4) \qquad \begin{vmatrix} S_{11} & S_{16} & S_{12} & S_{14} \\ S_{61} & \cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots \\ S_{41} & \cdots\cdots\cdots S_{44} \end{vmatrix} = 0$$

and similar equations for all other four-rowed determinants contained in the matrix S_{ij}. Of the equations (4) only two need be added to the six equations (2) as the other ones in the case of the movable isomer do not restrict the consequences of the light equations mentioned, thus leaving one degree of freedom.

We will now try and find a variable on which the S_{ij}

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will depend in a symmetrical way. Substituting in (2) the numerical values (3) of S_{11} and S_{ij} we get the equations

(5)
$$
\begin{aligned}
S_{12} + S_{13} + S_{14} &= -\tfrac{5}{3} \\
S_{12} \qquad\; + S_{23} + S_{25} &= -\tfrac{5}{3} \\
S_{13} \qquad\; + S_{23} \qquad\qquad + S_{36} &= -\tfrac{5}{3} \\
S_{14} \qquad\qquad\qquad\qquad\; + S_{45} + S_{46} &= -\tfrac{5}{3} \\
S_{25} \qquad\; + S_{45} \qquad\; + S_{56} &= -\tfrac{5}{3} \\
S_{36} \qquad\qquad + S_{46} + S_{56} &= -\tfrac{5}{3}
\end{aligned}
$$

Addition and substraction leads to

(6)
$$ S_{12} = S_{45} ; \quad S_{23} = S_{56} ; \quad S_{31} = S_{46} $$

The nine unknown quantities S_{ij} are thereby reduced to six and introducing the abbreviations

(7)
$$ S_{12} = z ; \quad S_{23} = x ; \quad S_{31} = y $$

equations (5) can be written as

(8)
$$
\begin{aligned}
S_{14} &= -\tfrac{5}{3} - z - y \\
S_{25} &= -\tfrac{5}{3} - x - z \\
S_{36} &= -\tfrac{5}{3} - y - x
\end{aligned}
$$

Substitution of the scalar products S_{14}, S_{25}, S_{36} in (4) leads to the equation

(9)
$$
\begin{vmatrix}
1 & \tfrac{1}{3} & x & z \\
\tfrac{1}{3} & 1 & \tfrac{1}{3} & y \\
x & \tfrac{1}{3} & 1 & \tfrac{1}{3} \\
z & y & \tfrac{1}{3} & 1
\end{vmatrix} = 0
$$

Writing

(10)
$$ \xi = 3x + 1 ; \quad \eta = 3y + 1 ; \quad \zeta = 3z + 1 $$

equation (9) becomes

(11)
$$ \xi^2 \eta^2 - 24 \left(\xi^2 + \eta^2 + \xi\eta \right) - 32 \left(\xi + \eta \right) = 0 $$

By cyclic permutations one finds

(11)
$$
\begin{aligned}
\eta^2 \zeta^2 - 24 \left(\eta^2 + \zeta^2 + \eta\zeta \right) - 32 \left(\eta + \zeta \right) &= 0 \\
\zeta^2 \xi^2 - 24 \left(\zeta^2 + \xi^2 + \zeta\xi \right) - 32 \left(\zeta + \xi \right) &= 0
\end{aligned}
$$

In accordance with what has been stated above these three equations are interdependent in the sense that they possess a

one dimensional manifold of solutions beside the trivial solution $\xi = \eta = \zeta = 0$. Substracting these equations in pairs gives the following three equations

(12) $$\left\{ \xi^2 (\eta + \zeta) - 24 (\xi + \eta + \zeta) - 32 \right\} (\zeta - \eta) = 0 \qquad \text{(cycl.)}$$

One solution of these equations is $\xi = \eta = \zeta$ which after substitution in (12) gives

(13)
$$\xi = \eta = \zeta = 0$$
$$x = y = z = -\tfrac{1}{3}$$

This solution corresponds with the rigid configuration as may be demonstrated quite easily.

If the three quantities ξ, η and ζ are unequal
$$\xi \neq \eta; \quad \eta \neq \zeta; \quad \zeta \neq \xi$$
the following equations hold

(14) $$\xi^2 (\eta + \zeta) - 24 (\xi + \eta + \zeta) - 32 = 0 \qquad \text{(cycl.)}$$

which on substracting yield

(15) $$(\xi \eta + \eta \zeta + \zeta \xi)(\eta - \zeta) = 0$$

Therefore

(16) $$\xi \eta + \eta \zeta + \zeta \xi = 0$$

which together with (14) leads to

(17) $$\xi \eta \zeta + 24 (\xi + \eta + \zeta) + 32 = 0$$

Equations (16) and (17) are two independent equations from which the geometrical relations pertaining to the configurations of the movable isomer can be deduced. The case of only two of the three quantities ξ, η, ζ being equal e.g. $\xi = \eta \neq \zeta$ can easily be shown to lead to values of these quantities which even occur in the solutions of equations (16) and (17).

Equation (16) suggests the introduction of new variables S and θ by the substitutions

(18)
$$\xi \eta = S^2 \cos 3\theta \cos \theta$$
$$\eta \zeta = S^2 \cos 3\theta \cos \left(\theta + \tfrac{2\pi}{3}\right)$$
$$\zeta \xi = S^2 \cos 3\theta \cos \left(\theta - \tfrac{2\pi}{3}\right)$$

or

(19)
$$\zeta = - S \left[\tfrac{3}{2} - 2 \cos^2 \theta \right]$$
$$\xi = - S \left[\tfrac{3}{2} - 2 \cos^2 \left(\theta + \tfrac{2\pi}{3}\right)\right]$$
$$\eta = - S \left[\tfrac{3}{2} - 2 \cos^2 \left(\theta - \tfrac{2\pi}{3}\right)\right]$$

The minus signs have been chosen so as to get a positive value of S. The value of this quantity follows from (17) which after substituting ξ , η and ζ reads

(20) $$-\frac{S^3}{2} \cos^2 3\theta + 36 S - 32 = 0$$

It is interesting to see that S varies only little with varying θ.

To a first approximation

(21) $$S = \frac{8}{9}$$

and a more accurate value is

(22) $$S = \frac{8}{9}\left[1 + \frac{8}{729}\cos^2 3\theta\right]$$

This variable θ is appropriate to define the possible configurations of the movable isomer in a symmetrical way. The equations (19) and (20) allow the calculation of various properties of this isomer as a function of θ .

The value $\theta = 0$ corresponds with a configuration of symmetry V where the distance between the carbon atoms 1 and 4 is as large as possible and which accordingly may be indicated as a stretched configuration (see page 40). $\theta = \frac{\pi}{2}$ corresponds with a boat configuration, where the carbon atoms 1 and 4 have the closest approach to one another. $\theta = \pi$ corresponds again with a stretched configuration with respect to the carbon atoms 1 and 4 and $\theta = \frac{3}{2}\pi$ with a boat configuration but with the atoms 1 and 4 bent to the opposite side as in the case $\theta = \frac{\pi}{2}$. The same applies to the atoms 2 and 5 and 3 and 6 but with θ values shifted by $\pm\frac{2\pi}{3}$.

3. Potential energy

For a calculation of the potential energy of the isomers of cyclohexane it is necessary to make an assumption about the interaction of the CH_2-groups. It looks plausible to assume an interaction of the same kind as between the CH_2-groups in n-butane and other straight chain paraffins for which Pitzer suggests a value of 3600 cal/mol for the potential barrier . On the other hand S p i t z e r and H u f f m a n [37] on account of heat of conbustion data of cycloparaffins consider even a value of 2750 cal/mol too high. This latter value has been used by Pitzer considering cyclic molecules. Provisionally we will also assume a value of 2750 cal/mol.

Beside these interactions between neighbouring CH_2-groups there may also occur important repulsions between H-atoms linked to opposite carbon atoms, since in a boat config-

uration the distance between two of these hydrogen atoms
(1.84 Å) is much lower than the sum of the v.d. Waals radii
(2.4 Å) according to P a u l i n g [28].

To begin with, however, we will restrict ourselves to
the first type of interactions for which we will assume the
formula

(23)
$$V = 1375 \cos 3 \varphi$$

The angle φ can be defined as the angle between the vectors
$[\vec{a}_1, \vec{a}_6]$ and $[\vec{a}_6, \vec{a}_2]$ for instance. Indicating this angle
by φ_3 we find

(24)
$$\cos \varphi_3 = \tfrac{1}{8} \left(4 - 3 \varsigma \right)$$
$$\cos 3\varphi_3 = -1 + \tfrac{27}{32} \varsigma^2 - \tfrac{27}{128} \varsigma^3$$

and similar formulae for the other angles.
The total energy according to formulae (23) is

(25)
$$V = 2750 \left(-3 + \tfrac{27}{32} \sum \xi^2 - \tfrac{27}{128} \sum \xi^3 \right)$$

The rigid isomer is characterized by

$$\xi = \eta = \varsigma = 0$$

In this case we get the result

(26)
$$V \text{(rigid)} = -3.2750$$

For the movable isomer we have to make use of (19) and (21) lead-
ding to

(27)
$$V \text{(movable)} = -\tfrac{95}{81} \cdot 2750 - \tfrac{7}{81} \cdot 2750 \left(1 - \cos 6 \, \theta \right)$$

The energy of the movable isomer is seen to be nearly constant
the term proportional to $\cos 6\theta$ not exceeding RT at room temper-
ature.

This picture may change if we include the repulsive in-
teractions between the hydrogen atoms linked to opposite car-
bon atoms. These repulsions which are most pronounced in the
boat configurations and, to a less extent, in the neighbouring
configurations will increase the potential energy of the mov-
able isomer at values of θ equal to $30°$, $90°$, $150°$, etc. So
we may add to (27) a term of the type

(28)
$$V_R \left(1 - \cos 6 \, \theta \right)$$

The magnitude of V_R is difficult to assess. According to cal-
culations of B a r t o n [4] it may be as high as several
kcal/mol. In the free energy calculations we will consider
also the effect of a term like (28).

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4. Moment of inertia of the internal motion.

For a calculation of the moment of inertia of the internal motion it is advantageous to introduce cylindrical coordinates to mark the position of the atoms. The twofold axis is taken as z-axis, r measures the distance to this axis and X the azimuth. The centre of gravity of the molecule is taken as origin. In order to study the internal motion separately not perturbed by the overall rotation the moment of momentum of the molecule has to be zero. This condition is expressed by

$$(29) \qquad \sum m r^2 \frac{dX}{d\theta} = 0$$

the summation extending over all atoms. The moment of inertia can be calculated from

$$(30) \qquad J = \sum m \left\{ \left(\frac{dz}{d\theta}\right)^2 + \left(\frac{dr}{d\theta}\right)^2 + r^2 \left(\frac{dX}{d\theta}\right)^2 \right\}$$

The coordinates of the carbon atoms are easily found from the expressions of S_{ij} as functions of s and θ

$$(31)$$

$$Z_1 = \frac{\sqrt{s}}{3} \sin \theta \qquad\qquad r_1^2 = \frac{11-s}{12} + \frac{5}{6} \cos 2\theta$$

$$Z_2 = \frac{\sqrt{s}}{3} \sin \left(\theta + \frac{2\pi}{3}\right) \qquad r_2^2 = \frac{11-s}{12} + \frac{5}{6} \cos \left(2\theta - \frac{2\pi}{3}\right)$$

$$Z_3 = \frac{\sqrt{s}}{3} \sin \left(\theta - \frac{2\pi}{3}\right) \qquad r_3^2 = \frac{11-s}{12} + \frac{5}{6} \cos \left(2\theta + \frac{2\pi}{3}\right)$$

$$r_1 r_2 \cos (X_2 - X_1) = -\frac{5}{12} \qquad X_1 \cong \frac{4}{135} \sin 2\theta$$

$$r_2 r_3 \cos (X_3 - X_2) = -\frac{5}{12} \qquad X_2 \cong \frac{4}{135} \sin \left(2\theta - \frac{2\pi}{3}\right) + \frac{2\pi}{3}$$

$$r_3 r_1 \cos (X_1 - X_3) = -\frac{5}{12} \qquad X_3 \cong \frac{4}{135} \sin \left(2\theta + \frac{2\pi}{3}\right) + \frac{4\pi}{3}$$

It is not excluded that the exact expressions of the X's should contain also a small term linear in θ, the same for each of them.
The coordinates of the hydrogen atoms are given by much more involved formulae which we will not repeat here. Using these formulae we find

$$J \cong 39.6 \times 10^{-40} + 0.4 \times 10^{-40} \cos 6\theta \ g \, cm^2$$

The main contribution of the value of J comes from the Z-coordinates which alone would yield the results $J = 25.0 \times 10^{-40}$

In many calculations on the internal motions of hydrocarbons it is a common use to account for the contributions of the hydrogen atoms by attaching an effective mass to the carbon atoms. In the case of propane and the higher paraffins P i t z e r [30] used the value 18.2. In an investigation

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of the structure of cyclopentane [21] 28.1 was suggested. In our case an effective mass of 21.8 would be necessary.

5. Free energy of the internal motion

In consequence of the nearly constant value of the moment of inertia the calculation of the partition function of the internal motion of the movable isomer is particularly simple. In the case of a constant value of the potential energy the partition function of the completely free rotation is given by

$$(32) \qquad Q_f = \frac{2\pi}{\sigma_i} \frac{(2\pi \, \mathfrak{I} k T)^{\frac{1}{2}}}{h}$$

where σ_i is the symmetry number of the internal motion.

The symmetry number of the internal motion can best be discussed using a graph of the z coordinates of the carbon atoms as functions of θ. Considering the
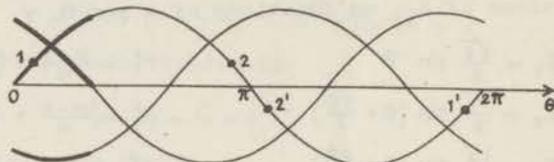
CH_2-groups as indistinguishable it can easily be seen from an inspection of a model that the points marked 1 and 1' represent the same configuration since they can be made to cover by a rotation of the molecule as a whole. The same applies to the points 2 and 2'. The points 1 and 2, however, represent configurations which are optical isomers. Now it will be clear that all the points of the z_1 curve in the range $0 < \theta < \pi$ would represent different configurations if only opposite CH_2 groups were indistinguishable. Since no CH_2-group can be distinguished from an other one, all configurations represented by the same set of z values with the same or the opposite signs are to be considered as identical immaterial on which curves these points are lying. Now it may readily be seen from the figure that all the distinguishable configurations are already represented by the sets of z-values in the range $0 < \theta < \frac{\pi}{3}$ So the symmetry number has to be put equal to six. Inserting the values of σ_i and $\mathfrak{I}$, disregarding the $\cos 6\theta$ term, in (32) leads to the formula

$$Q_f = 0.293 \sqrt{T}$$

Now if we add to the constant potential energy a term $V_6 (1-\cos 6\theta)$

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the value of the partition function can easily be deduced from the tables of P i t z e r and G w i n n [ ). In these tables $R \ln Q/Q_f$ is given as a function of Q_f and of the ratio of the height of the potential barrier to RT. For Q we find for a series of values of V_6 the following values

T $^\circ$K	Q_f	$Q(V_6=238)$	$Q(V_6=1200)$	$Q(V_6=2400)$	$Q(V_6=3600)$
300	5,08	4,64	2,98	2,19	1,82
400	5,86	5,45	3,77	2,73	2,28
500	6,55	6,19	4,51	3,34	2,75
600	7,18	6,85	5,22	3,95	3,42
700	7,76	7,43	5,83	4,55	3,94
800	8,29	8,03	6,42	5,07	4,47

6.

Equilibrium concentrations of the isomers of cyclo-hexane.

For a calculation of the equilibrium concentrations of the isomers in gaseous cyclohexane we have to estimate the contribution to the partition function of the rigid isomer of the vibration which we will consider as the counterpart of the internal motion of the movable isomer. From a table of calculated vibration frequencies of the rigid isomer (R a m s a y and S u t h e r l a n d [33]) we will select the vibration with the lowest frequency ($\omega = 206$ cm^{-1}) which will give an upper estimate for the partition function and hence for the concentration of the rigid isomer as far as this vibrational contribution is concerned. Using the Einstein function $Q_\omega = \left(1 - e^{-\frac{h\omega c}{kt}}\right)^{-1}$ we find for this contribution

Since the symmetry number of the rigid isomer is 6 and of the overall rotation of the movable isomer is 2 the ratio of the number of molecules of the movable isomer N_m to the number of molecules of the rigid isomer N_r is given by

$$\frac{N_m}{N_r} = \frac{\sigma_r}{\sigma_m} \frac{Q}{Q_\omega} e^{-\frac{U}{RT}} = 3 \frac{Q}{Q_\omega} e^{-\frac{2750.148/81}{RT}}$$

where U is the potential energy of the movable isomer, without the $(1 - \cos 6\theta)$ term, minus the potential energy of the rigid isomer. This formula gives the following values for the ratio N_m/N_r:

T °K	$V_6 = 238$	1200	2400	3600
300	0.002	0.001	0.001	0.001
400	0.016	0.008	0.011	0.006
500	0.053	0.029	0.039	0.025
600	0.120	0.069	0.091	0.060
700	0.209	0.128	0.164	0.111
800	0.320	0.202	0.256	0.178

$\dfrac{N_m}{N_r}$:

This table indicates that at ordinary temperatures the movable isomer will occur at most to a very slight extent. At higher temperatures it may occur at concentrations which are large enough to allow an experimental confirmation for instance from measurements of the specific heat over a large range of temperatures.

It is interesting to note that at high values of V_6 (strong repulsion between hydrogen atoms) the movable isomer occurs practically only in the stretched configuration. Although this configuration has a symmetry number 4 this does not change formula (p.49) since there are two such configurations which are optical isomers as may be seen on page 40.

THE STRUCTURE OF
CYCLOHEXANEDIONE -1,4

1.

When studying the structure of the cyclohexanedione-
1,4 molecule one is confronted with problems of the same kind
as in the case of cyclohexane. In fact geometrical considera-
tion of the dione molecule leads likewise to the expectation
that two isomers may occur a rigid and a movable isomer.

As may be seen on page 52 the two C=O-groups in the
rigid configuration are parallel but have opposite directions.
Therefore the dipole moment of this isomer is zero.The same is
true for the stretched configuration*) of the movable isomer.
The other configurations of this isomer all have a non-zero
dipole moment which may be rather high. Assuming the dipole
moment of the C=O-group to be equal to the moment of acetone
(2.84 Debye) one finds a dipole moment of 4.23 Debye for the
boat configuration. Each of the configurations of the movable
isomer has a twofold axis which is the direction of the total
dipole moment. Indicating by γ the angle between a C=O-dipole
moment and the twofold axis the total dipole moment is equal
to 2 cos γ x 2.84 Debye.

The experimental value of the dipole moment is much
less viz. 1.3 Debye (L e F è v r e [24]). Since quantum effects
presumably are of minor importance for the value taken by the
dipole moment we may consider the value 1.3 as the root mean
square of the dipole moments of the various configurations
distributed according to a Boltzmann factor $e^{-\frac{U}{kT}}$ where U is
the potential energy of the configuration. From this it fol-
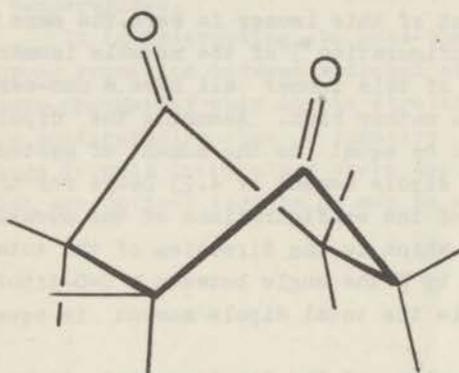lows that $\overline{\mu^2} = 4\ \overline{\cos^2\gamma} \times 2.84^2 = 1.3^2$ or

$$4\ \overline{\cos^2\gamma} = 0.21$$

The value of 4 $\cos^2\gamma$ in the boat configuration is 2.22.   So
one may expect that even slight deflections from the stretched
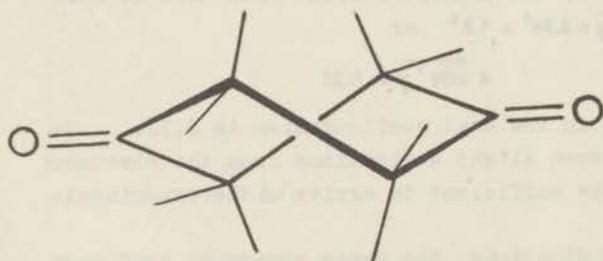configurations will be sufficient to arrive at the experiment-

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*) Without further indications the names stretched configura-
   tion and boat configuration refer to the peculiar positions
   of the C=O-groups.
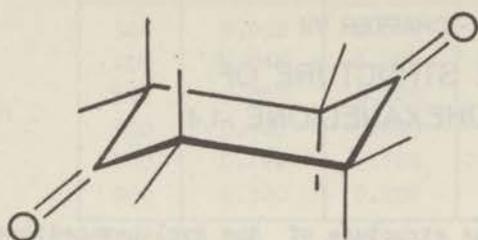
rigid

boat
$\theta = \dfrac{\pi}{2}$

stretched
$\theta = 0$

Configurations of Cyclohexanedione - 1,4

al value. In order to calculate theoretically the mean square
of $\cos \gamma$ we will first consider more closely the geometrical
relations in the cyclohexanedione molecule.

2. Geometrical considerations

Cyclohexanedione-1,4 may be thought to be derived
from cyclohexane by replacing two opposite CH_2-groups by C=O-
groups. The carbon skeleton changes in so far as the bond an-
gles at the carbon atoms of the C=O-groups are probably about
120° as in acetone.
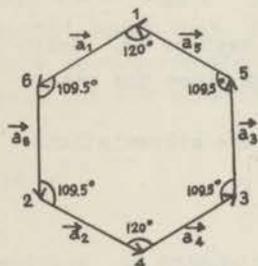
We will assume all bonds to be of equal
length.

The bond angles at the CH_2-groups will be
assumed to be $109^{\circ}28'16''$ and at the C=O
groups 120°. So we have to solve the prob-
lem of the description of an equilateral
hexagon with angles as has been indicated.
The treatment of this problem is similar
to that given in the case of cyclohexane.

Starting from the equation

(1)
$$\sum_{i=1}^{6} \vec{a}_i = 0$$

and multiplying successively with $\vec{a}_1, \vec{a}_2, \ldots \ldots \vec{a}_6$ one is led
to the equations

(2)
$$\sum_{i=1}^{6} S_{ij} = 0 \qquad j = 1, \ldots \ldots, 6$$

Putting the length of a side of the hexagon equal to
one and substituting the values of the scalar products

(3)
$$S_{ii} = 1 \qquad S_{15} = S_{24} = \tfrac{1}{2}$$
$$S_{16} = S_{26} = S_{34} = S_{35} = \tfrac{1}{3}$$

the equations (2) are transformed in

(4)
$$
\begin{aligned}
S_{12} + S_{13} + S_{14} & & & & & = -\tfrac{11}{6} \\
S_{12} & + S_{23} + S_{25} & & & & = -\tfrac{11}{6} \\
S_{13} & + S_{23} & + S_{36} & & & = -\tfrac{10}{6} \\
S_{14} & & & + S_{45} + S_{46} & & = -\tfrac{11}{6} \\
& S_{25} & & + S_{45} & + S_{56} & = -\tfrac{11}{6} \\
& & S_{36} & + S_{46} & + S_{56} & = -\tfrac{10}{6}
\end{aligned}
$$

From these equations one can deduce

(5)
$$S_{12} = S_{45} ; \qquad S_{23} = S_{56} ; \qquad S_{31} = S_{64}$$

and

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$$S_{14} = -\frac{11}{6} - S_{31} - S_{12}$$

(6)
$$S_{25} = -\frac{11}{6} - S_{12} - S_{23}$$

$$S_{36} = -\frac{10}{6} - S_{23} - S_{31}$$

Beside these equations we can deduce equations of the kind

(7)
$$\begin{vmatrix} S_{11} & S_{16} & S_{12} & S_{14} \\ S_{61} & \cdots & & \\ \cdots & \cdots & & \\ S_{41} & \cdots & & S_{44} \end{vmatrix} = 0 \quad \text{and} \quad \begin{vmatrix} S_{66} & S_{62} & S_{64} & S_{63} \\ S_{26} & \cdots & & \\ \cdots & \cdots & & \\ S_{36} & \cdots & & S_{33} \end{vmatrix} = 0$$

which express the linear dependence of four vectors $\vec{a}_i$. Only three of these equations need to be considered since the other ones are not independent.

It is advantageous to make use of the abbreviations

(8)
$$\zeta = 3\,S_{12} + \tfrac{3}{2}$$
$$\xi = 3\,S_{23} + 1$$
$$\eta = 3\,S_{31} + 1$$

which are similar to the equations (10) in chapter VI. Substituting (3) (5) (6) and (8) in (7) we get the result

(9)
$$4\,\xi^2\eta^2 + 4\,(\xi^2\eta + \xi\eta^2) - 95\,(\xi^2 + \eta^2) - 82\,\xi\eta - 90\,(\xi + \eta) = 0$$

(10)
$$\xi^2(4\,\zeta^2 - 4\,\zeta - 95) - (108\,\zeta + 90)(\xi + \zeta) = 0$$

and by reason of symmetry

(11)
$$\eta^2(4\,\zeta^2 - 4\,\zeta - 95) - (108\,\zeta + 90)(\eta + \zeta) = 0$$

One solution is

(12)
$$\xi = \eta = \zeta = 0$$

which corresponds to the rigid configuration. Substracting (11) from (10) gives

(13)
$$(\xi - \eta)\left\{(4\,\zeta^2 - 4\,\zeta - 95)(\xi + \eta) - (108\,\zeta + 90)\right\} = 0$$

Assuming $\xi \neq \eta$ leads to

(14)
$$(4\,\zeta^2 - 4\,\zeta - 95)(\xi + \eta) - (108\,\zeta + 90) = 0$$

which together with (10) yields the result

(15)
$$\xi\eta + \eta\zeta + \zeta\xi = c$$

Substituting this equation in (9) one gets

(16)
$$4\,\xi\eta\zeta - 4\,\xi\eta + 95\,(\xi + \eta) + 108\,\zeta + 90 = 0$$

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Now one may use just as in the case of cyclohexane the substitutions

$$\xi\eta = s \cos 3\theta \cos\theta$$

(17)
$$\eta\zeta = s \cos 3\theta \cos\left(\theta + \tfrac{2\pi}{3}\right)$$

$$\zeta\xi = s \cos 3\theta \cos\left(\theta - \tfrac{2\pi}{3}\right)$$

which transforms (16) into

(18) $-S^3\left(1 + \cos 6\theta\right) + 2S^2\left(\cos 2\theta + \cos 4\theta\right) + S\left(149 - 13\cos 2\theta\right) = 90$

To a first approximation (accurate to about 1%)

(19) $S = \frac{90}{149}\left(1 + \frac{13}{149}\cos 2\theta\right)$

which shows that in this case the dependence of s on θ is more pronounced than in the case of cyclohexane. One might as well use the substitution

$$\xi\eta = -2p\cos\alpha\cos\theta$$

(20)
$$\eta\zeta = p\cos(\theta + \alpha)$$

$$\zeta\xi = p\cos(\theta - \alpha)$$

and try to determine a value of α which makes the dependence of p on θ as simple as possible, but for the present purpose this has no special advantage.

3.

For a discussion of the potential energy of the con-figurations of the movable isomer it is necessary to know the angle of rotation about a C–C bond as a function of θ . We indicate by φ_3 the angle of rotation about a bond between two CH_2-groups and by φ_1 and φ_2 the angles of rotation about the bonds between a CH_2- and a C=O-group.

φ_3 is equal to the angle between the vectors $[\vec{a}_4, \vec{a}_3]$ and $[\vec{a}_3, \vec{a}_5]$.   From the scalar product of these vectors it can be derived that

(21)
$$\cos\varphi_3 = \tfrac{11}{6} - \tfrac{3}{8}\zeta$$

$$\cos 3\varphi_3 = -\tfrac{1}{128}\left\{\tfrac{787}{8} + \tfrac{513}{4}\zeta - \tfrac{297}{2}\zeta^2 + 27\zeta^3\right\}$$

Similary we put φ_1 equal to the angle between the vector $[\vec{a}_5, \vec{a}_1]$ and $[\vec{a}_1, \vec{a}_6]$ and φ_2 equal to the angle between $[\vec{a}_6, \vec{a}_2]$ and $[\vec{a}_2, \vec{a}_4]$.   From this follow the formulae

(22)
$$\cos\varphi_1 = \tfrac{1}{\sqrt{24}}(3 - 2\xi)$$

$$\cos\varphi_2 = \tfrac{1}{\sqrt{24}}(3 - 2\eta)$$

$$(22) \qquad \cos 3\,\varphi_1 = \frac{1}{\sqrt{24}} \left(\frac{9}{2} + 7\,\xi - 6\xi^2 + \frac{4}{3}\,\xi^3 \right)$$

$$\cos 3\,\varphi_2 = \frac{1}{\sqrt{24}} \left(\frac{9}{2} + 7\,\eta - 6\eta^2 + \frac{4}{3}\,\eta^3 \right)$$

When substituting ξ, η and ζ as functions of θ the resulting formulae are not easily surveyable. Therefore we give in table IV the values of the cosines for a number of values of θ together with the values they take in the rigid configuration. In the same table we mention the values of $\cos \gamma$ and of $4\,\overline{\cos^2 \gamma}$. $\left(\cos \gamma = \sqrt{5}\,\sin \theta \right)$

TABLE IV

Movable isomer	$\cos 3\varphi_3$	$\cos 3\varphi_1$	$\cos 3\varphi_2$	$\cos 3\varphi_1 + \cos 3\varphi_2$	$\cos \gamma$	$4 \cos^2 \gamma$
$\theta =$ 0	$- 0.97$	0.08	0.08	0.16	0	0
15	$- 0.94$	0.56	0.71	0.15	0.21	$0,17$
30	$- 0.76$	0.92	0.99	0.07	0.40	0.64
45	$- 0.40$	$- 1.00$	0.71	$- 0.29$	0.55	1.23
60	$+ 0.26$	$- 1.00$	$- 0.09$	$- 1.09$	0.66	1.76
90	$+ 1.00$	$- 0.92$	$- 0.92$	$- 1.84$	0.75	2.22
Rigid isomer	$- 0.76$	$- 0.92$	$- 0.92$	$- 1.84$		

In the potential energy we have to reckon with four effects.

First there is a change in potential energy with the rotation around the bonds between the CH_2-groups. Just as in the case of cyclohexane we will assume the contribution of the two bonds to be equal to

$$2750 \cos 3\,\varphi_3$$

The change of potential energy on rotation about one of the other bonds is more difficult to assess. The only datum which can be used to estimate the magnitude of the energies involved is the barrier height in the rotation of the methyl groups in acetone. As has been mentioned in chapter II the experimental data indicate a barrier which is much lower than the barrier in ethane. There is, however, much uncertainty as to the exact value of the height of the barrier, the suggested values varying between 560 and 1240 cal/mol. Nor is it known whether the opposed or the staggered configuration has the

lower energy, although there are indications derived from a study of the Kerr effect of diethylketone that the planar zig-zag configuration of the carbon chain is the stable one (V o l k m a n n [49]).For the present problem the precise value of the height of the barrier appeared to be of secondary importance as far as the dipole moment of the movable isomer is concerned as has been ascertained by using the values 1200 as well as 800 cal/mol. More important is the sign of the term proportional to $\cos 3\varphi_1 + \cos 3\varphi_2$ since this determines to a large extent the relative stability of the rigid and the movable isomer.

A third effect which is difficult to estimate is the interaction between the two C=O-groups which may be important on account of the large dipole moments. One cannot be sure, however, that this interaction can be adequately accounted for as a dipole-dipole interaction because of the small distance of these groups and even if so one meets with the difficulty that the bond dipole moment is not known with certainty. For want of better data the only thing which we can do is to calculate the energy of the dipole-dipole interaction assuming a bond dipole moment of the C=O-group equal to the moment of acetone 2.84 Debye. Locating the dipole in a point midway between the carbon atom and the oxygen atom the calculation yields a result which is given in table V in the column under E.In addition the interaction energy of two C=O bonds has also been computed assuming point charges of equal magnitude but opposite sign to be located in the carbon and the oxygen atoms. The magnitude of the charges was chosen so as to give the same bond moment as before. The results are given in the column under E'.

TABLE V

Movable isomer	$2750 \cos 3\chi_3$	$1200(\cos 3\chi_1 + \cos 3\chi_2)$	E	E'	U_+	U_-	U_+'	U_-'
$\theta = 0$	-2670	195	3210	3525	0	0	0	0
15	-2580	180	3260	3570	125	155	120	150
30	-2090	85	3395	3665	655	875	610	830
45	-1100	-345	3625	3840	1445	2525	1345	2425
60	$+720$	-1305	3890	4045	2570	5570	2410	5410
90	$+2750$	-2205	4210	4290	4020	8820	3785	8585
Rigid isomer	-2095	-2205	3170	3650	-1865	2935	-1700	3100

In the next columns headed U_+, U_-, U_+' and U_-' are given the sums of the three energy effects just mentioned

$$U_\pm = 2750 \cos 3\varphi_3 \pm 1200 (\cos 3\varphi_1 + \cos 3\varphi_2) + E$$

$$U_\pm = 2750 \cos 3\varphi_3 \pm 1200 (\cos 3\varphi_1 + \cos 3\varphi_2) + E'$$

In each of these cases the energy of the stretched configuration ($\theta = 0$) has been taken as zero.

Now we may use these energies for a calculation of the dipole moment of the movable isomer. Since the moment of inertia belonging to the internal motion is probably somewhat larger than in the case of cyclohexane and the range of configurations which is accessible at ordinary temperatures is fairly large we presume that it is justified to disregard quantum effects and to calculate the mean square of the dipole moment along classical lines. A rough estimate of the magnitude of the moment of inertia belonging to the internal motion yields a value of about 70.10^{-40} g/cm^2. This would be an average value since in this case the moment of inertia is rather strongly dependent on θ. From the values of U it can be deduced that in the range of θ values which are of importance the potential energy may be approximated by for instance

$$U = 3100 \; \theta^2 \; \text{cal/mol} = 2,09.10^{-13} \; \theta^2 \; \text{erg/molecule}$$

when θ is expressed in radians. This corresponds with a value of $h\nu = 120$ cal/mol which is much smaller than the value $kT = 600$ cal/mol at ordinary temperatures.

In the classical calculation we have to evaluate the expression

$$\overline{4\cos^2\gamma} = \frac{\int 4\cos^2\gamma \, e^{-\frac{U}{RT}} \, d\theta}{\int e^{-\frac{U}{RT}} \, d\theta}$$

By a numerical procedure we find the following results

$$U = U_+ \qquad\qquad 4\,\overline{\cos^2\gamma} = 0.28$$
$$U = U_- \qquad\qquad 4\,\overline{\cos^2\gamma} = 0.22$$
$$U = U'_+ \qquad\qquad 4\,\overline{\cos^2\gamma} = 0.29$$
$$U = U'_- \qquad\qquad 4\,\overline{\cos^2\gamma} = 0.23$$

In all these cases the calculated value is a little higher than the experimental value 0.21. The reason for this may be sought in an interaction of the hydrogen atoms in those boat configurations where the carbon atoms of two opposite CH_2-groups are close together. This occurs at values of θ which are nearly $\pm 30°$. A slight repulsion between these hydrogen atoms, making the configurations belonging to $\theta \cong 30°$ less stable and diminishing the calculated values of $4\,\overline{\cos^2\gamma}$ a little may be in agreement with the experimental result.

It appears that it makes little difference for the dipole moment of the movable isomer if one takes the + or the − sign in the term pertaining to the rotation about the CH_2 − C = O bond. It makes, however, quite a difference in the relative stability of the rigid and the movable isomer. If we take the + sign the rigid isomer is energetically more stable to such extent that it seems highly improbable that the free energy contribution of the internal motion of the movable isomer may outweigh that effect. Now as soon as the movable isomer is not predominantly present the mean square of the dipole moment will be too low. Even if we take a much lower coefficient of $(\cos 3\varphi_1 + \cos 3\varphi_2)$ for instance + 800 cal/ mol. which lowers the values of $\overline{\cos^2\gamma}$ only slightly we estimate that the equilibrium concentration of the rigid isomer is still too large to give the right value of the dipole moment.

Therefore we conclude that probably the interaction between the CH_2 and C=O-groups is of such a nature that the potential energy has the opposite sign as $(\cos 3\varphi_1 + \cos 3\varphi_2)$ although this disagrees with the planar zig-zag structure

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which (V o l k m a n n[40]) suggests for diethyl ketone. In view
of the crude and perhaps unwarranted assumptions which have
been made in the foregoing calculations we do not attach much
value to the nice agreement of the experimental and calculated
magnitudes of the dipole moment. To our opinion the most
important result is that there is no contradiction between
the experimental results and the assumptions underlying the
calculations. So we may say that the dipole moment of the
cyclohexanedione-1,4 molecule may be understood just as well
as the preponderant occurrence of the rigid isomer of
cyclohexane on the basis of our present knowledge of the
interactions between non bonded atoms in cyclic molecules.

A more definite conclusion can only be reached by a
further experimental investigation for instance by electron-
diffraction and also by measuring quantities as dipole moment
and specific heat as a function of temperature over as large
a range as possible. A study of the infrared spectrum may be
especially fruitful in deciding whether the rigid isomer is
present to a certain extent.

SUMMARY

1.

 The interactions restricting the free rotation about single bonds have also a bearing on the structure of saturated cyclic molecules. A study of these interactions may therefore contribute to a better understanding of such molecules.On the other hand a closer study of cyclic molecules may add to our knowledge of the potential barriers restricting free rotation.

2.

 With regard to the problem of the restricted free rotation we have investigated the coulomb interaction between the methylgroups in ethane. The basic idea was the same as in the investigation of Lassettre and Dean, published in 1949, but the calculations have been performed along different lines.

 The charge distributions were calculated with wave functions of the same type as used by Coulson when discussing the dipole moment of the C-H bond.By expanding the reciprocal distance, which occurs in the coulomb interactions, in a Fourier series it proved possible to calculate directly the $\cos 3\varphi$ term as well as the $\cos 6\varphi$ term in the interaction energy (φ being the angle of rotation about the C-C bond). The $\cos 6\varphi$ proved to be negligible with respect to the $\cos 3\varphi$ term.

 The results of the calculations differ in detail from those of Lassettre and Dean but the general trend is the same. With a purely covalent bond the coulomb energy of the methylgroups depends only to a negligible extent on the angle of rotation φ . In order to get the right order of magnitude of the potential barrier it proved necessary to add to the covalent wave function a considerable ionic contribution. If this ionic contribution is of the type C^-H^+ the potential barrier is of the right order of magnitude when the bond dipole moment is about 0.7 Debye with the sense C^-H^+. Experimental results, mainly from the domain of spectroscopy, lead to an empirical bond dipole moment of about either + or − 0.4 Debye, but we are not convinced that these dipole moments refer to the same quantities calculated along the lines indicated by Coulson. So to our opinion it is premature to conclude to the electrostatic interactions of bonds with fixed charge distributions as the origin of the potential barrier in ethane.

3.

The structure of saturated cyclic molecules containing a six-membered ring is particularly interesting since at least two isomers may be expected to occur, one possessing a rigid structure of the ring, whereas the movable isomer is capable of an internal motion having the character of a restricted free rotation. In the case of cyclohexane a calculation of the free energy difference between both isomers has been performed assuming for the rotation of the CH_2-groups about a C-C bond a potential barrier of the same shape and magnitude as is found in ethane. The equilibrium ratio's calculated from the free energy differences indicate that at ordinary temperatures the movable isomer occurs at most to a very slight extent. At higher temperature it may occur in concentrations which are large enough to allow an experimental confirmation.

In contrast with cyclohexane cyclohexanedione - 1,4 occurs at least partly in the movable configuration as appears from the non zero dipole moment. Although our present knowledge about the potential barrier connected with the rotation about the bond between a C=O group and a CH_2-group is very scanty, it can be made plausible that the same forces which occur in open chain compounds are also responsible for the stability of the movable isomer and will lead to the right dipole moment.

SAMENVATTING

1.

De krachten, die de vrije draaibaarheid om enkelvoudige bindingen beperken, zijn ook van invloed op de structuur van verzadigde cyclische moleculen. Een studie van deze krachten zal daarom een beter inzicht in het gedrag van deze moleculen geven. Aan de andere kant zal een nadere bestudering van cyclische moleculen tot onze kennis van de beperkt vrije draaibaarheid bijdragen.

2.

In verband met het probleem van de beperkt vrije draaibaarheid hebben wij de Coulombse wisselwerking tussen de methylgroepen in aethaan berekend. De grondgedachte was dezelfde als die waar Lassettre en Dean in hun onderzoek (1949) van uit gingen. De berekeningen werden echter volgens een andere methode uitgevoerd.

De ladingsverdelingen werden berekend met behulp van golffuncties van dezelfde soort als die waarvan Coulson gebruik maakte bij zijn beschouwingen over het dipoolmoment van de C-H binding. Door de reciproke afstand, die in de formules voor de Coulombse wisselwerking voorkomt in een Fou rierreeks te ontwikkelen, bleek het mogelijk om de $\cos 3\varphi$ term, evenals de $\cos 6\varphi$ term, voorkomende in de wisselwerkingsenergie, direct te berekenen (φ is de rotatiehoek om de C-C binding). De term met $\cos 6\varphi$ bleek te kunnen worden verwaarloosd naast de term die $\cos 3\varphi$ bevat.

De resultaten van de berekeningen vertonen allerlei verschillen met die welke door Lassettre en Dean werden verkregen, maar de algemene lijn is dezelfde. Voor een zuiver covalente binding hangt de Coulomb energie van de methylgroepen vrijwel niet af van de rotatiehoek φ. Teneinde de juiste orde van grootte van de potentiaalberg te verkrijgen, bleek het noodzakelijk om aan de covalente golffuncties andere functies, die een ionenbinding beschrijven, toe te voegen. Op deze wijze kan de berekening een potentiaalberg van de juiste orde van grootte leveren, wanneer de bijdrage van de ionenstructuur C^-H^+ zo groot is, dat het bindingsdipoolmoment 0,7 Debye bedraagt, met de richtingszin C^-H^+. Experimentele resultaten, welke voornamelijk van het gebied van de spectroscopie afkomstig zijn, leiden tot een empirisch dipoolmoment van + of - 0,4 Debye.

Het lijkt ons echter geenszins juist deze dipoolmomenten te be-
schouwen als grootheden, die dezelfde betekenis hebben als de
bindingsmomenten die volgens Coulson worden berekend. Volgens
onze mening is het voorbarig om de gevolgtrekking te maken,
dat de electrostatische wisselwerking van de bindingen met on-
veranderlijke ladingsverdelingen als de oorzaak van de poten-
tiaalbergen in aethaan moet worden beschouwd.

3.

De structuur van verzadigde cyclische moleculen die een
verzadigde zesring bevatten, vertoont bijzondere eigenschappen,
op grond waarvan men het voorkomen van tenminste twee isome-
ren mag verwachten. Bij de ene is de ring star, terwijl bij de
andere de ring een inwendige beweging kan uitvoeren, die het
karakter heeft van een beperkt vrije draaiing.

Voor het geval van cyclohexaan werd het verschil in
vrije energie van de beide isomeren berekend, uitgaande van de
veronderstelling, dat de potentiaalberg, die bij draaiing van
de CH_2-groepen om een C-C binding optreedt, dezelfde vorm en
grootte heeft als in aethaan. De evenwichtsconcentraties
welke uit de vrije energieverschillen werden uitgerekend, laten
zien, dat bij gewone temperatuur de bewegelijke isomeer tot een
zeer gering bedrag voorkomt. Bij hogere temperaturen kan de
bewegelijke vorm echter voorkomen in een concentratie die wel-
licht een experimenteel onderzoek van deze vorm mogelijk maakt.

In tegenstelling met cyclohexaan komt cyclohexaandion-
1,4 tenminste gedeeltelijk in de bewegelijke configuratie voor,
zoals blijkt uit het van nul verschillende dipoolmoment. Of-
schoon onze huidige kennis van de krachten, die de draaiing
om de binding tussen een C=O groep en een CH_2-groep belemmeren
nog zeer gering is, kan het toch waarschijnlijk worden gemaakt,
dat krachten van dezelfde aard als die, welke in verbindingen
met open ketens voorkomen, verantwoordelijk zijn voor de sta-
biliteit van het bewegelijke isomeer, en bovendien het juiste
dipoolmoment opleveren.

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STELLINGEN

1. De wijze, waarop Lassettre en Dean de invloed van "unshared electron pairs" op de beperking van de vrije draaibaarheid in moleculen als methylalcohol en methylamine in rekening brengen, is onjuist.

   E.N.Lassettre, L.B.Dean, J.Chem.Phys.
   17 (1949) 317

2. Bij de bepaling van de structuur van cyclohexaan met behulp van electronendiffractie is onvoldoende rekening gehouden met de mogelijke configuraties van het bewegelijke isomeer.

   O.Hassel, B.Ottar, Arch.f.Math.og Naturv.
   XLV nr. 10 (1942)
   L.Pauling, L.O.Brockway, J.Am.Chem.Soc.
   59 (1937) 1223

3. De door Heitler gebruikte methode om via de "Bindungsgleichungen" een vergelijking af te leiden voor de eerste orde storingsenergie van een systeem met veel electronen, is onjuist.

   W.Heitler, Quantentheorie und homöopolare chemische Bindung (1934), hfdst.III, § 8.
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   Vgl.G.W.Wheland,J.Chem.Phys. 3 (1935)230.

4. Soms kan het begrip chemisch evenwicht met vrucht worden uitgebreid op mechano-chemische systemen, met name op reacties onder invloed van visceuze stroming.

   H.A.Kramers, J.Chem.Phys. 14 (1946) 415
   J.G.Kirkwood, Rec.trav.chim.68 (1949)649.

5. Indien men tracht de afleiding van de mengentropie van vloeistofmengsels volgens Planck met voorbeelden te illustreren, blijkt dat deze afleiding vrijwel nooit van toepassing is.

6. Voor de katalytische activiteit van een mengsel van zinkoxyde en het vrije radicaal α,α-diphenyl-β-pikrylhydrazyl bij de ortho-para-waterstof reactie wordt door Turkevich en Selwood een verklaring gegeven, die in strijd is met de "transition state" theorie. Een dergelijke verklaring komt slechts dan in aanmerking, indien voor de snelheidsbepalende stap een tunneleffect van belang is.

   J.Turkevich, P.W.Selwood, J.Am.Chem.Soc.
   63 (1941) 1077

7. De naam perzoutzuur voor $HOCl$ is te verkiezen boven die van onderchlorigzuur.

8. De door Pitzer voorgestelde structuur van B_2H_6 is in overeenstemming met de gemakkelijke isomerisatie van carboniumionen.

   K.S.Pitzer, J.Am.Chem.Soc. 67 (1945) 1126.

9. De door Wizinger voorgestelde formule voor diphenyl-chlooramine is in strijd met de door Weitz beschreven reactie tussen tetra-p-tolylhydrazine en chloor-tetraoxyde.

   R.Wizinger, Organische Farbstoffe (1933) 22.
   E.Weitz, B. 60 (1927) 1203.
   E.Müller, Neuere Anschauungen der Organischen
   Chemie (1940) 279.

10. De bestudering van technische werkwijzen leidt tot verrijking van organisch preparatieve methoden in het laboratorium.

11. Bij de wiskunde-opleiding van chemici en physici dienen numerieke methoden niet verwaarloosd te worden.

12. Het verschil tussen chemie en physica is in de grond een verschil tussen chemici en physici.

13. De door Bode c.s. voorgestelde opleiding tot "scientific generalist" is in hoge mate verwerpelijk.

    H.Bode, F.Mosteller, J.Tukey, C.Winsor,
    Science, 109 (1949) 553.

14. De mening van Clarence A.Mills als zou conceptie in het zomerjaargetijde ongunstig zijn voor het bereiken van de functie van president van de Verenigde Staten van Noord-Amerika, houdt tegen statistische analyse geen stand.

    C.A.Mills, Science 110 (1949) 267.