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E. R. Andrew

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Molecular Motion in Certain Solid Hydrocarbons

E. R. ANDREW*

Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts

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An investigation has been made of the variation of the nuclear resonance absorption line width with temperature for four long chain aliphatic compounds and eight aromatic hydrocarbons. The aliphatic compounds are dimorphous; in the lower temperature modification it is concluded that the molecules are rigid at the lowest temperatures, but that an increasing number of molecules rotate about their length as the temperature increases; in the upper temperature modification all the molecules rotate. The naphthalene crystal lattice is found to be rigid up to the melting point. Benzene and anthracene, however, show sharp line-width transitions at about 110° and 190°K, respectively. It is suggested that in benzene this is due to tunnelling or rotation of the molecules about their hexagonal axes. The explanation for anthracene is less clear, but it is suggested that each molecule rotates about its long diad axis. The xylenes, mesitylene, and hexamethylbenzene show internal rotation of the CH₃ groups at all temperatures above 95°K. In addition, hexamethylbenzene has a line-width transition over the range 135–210°K, attributed to tunnelling or rotation of the molecules about their hexagonal axes.

A calculation is made of the reduction of the intramolecular contribution to the resonance line second moment caused by rotational oscillation of molecules in a crystal lattice. The effects of certain types of molecular motion on the intermolecular contribution are also calculated.

I. INTRODUCTION

GUTOWSKY and Pake¹ have shown that the magnetic dipolar broadening of nuclear resonance absorption lines in solids is reduced by molecular motion in the crystal lattice. For a number of compounds such motion was found to set in as the temperature was increased, and by a quantitative analysis of the resonance lines they obtained information concerning the nature of the molecular motion encountered. The present paper gives the results of an investigation by this method, of molecular motion in certain hydrocarbons and in a related alcohol.

The twelve compounds studied were:

Long chain paraffins:

n-Octadecane
n-Octacosane
Dicetyl

Long chain alcohol:

Lauryl alcohol

Aromatic hydrocarbons:

Benzene
o-, *m*- and *p*-Xylene
Mesitylene
Hexamethylbenzene
Naphthalene
Anthracene

All the materials were supplied by Eastman Kodak (highest purity grade).

The apparatus was that used by Gutowsky and Pake, and the experimental technique was essentially the same. The temperature range of measurement, which in their experiments had been from 90°K to room temperature, was extended upwards by use of an oil bath and immersion heater. The samples under investi-

gation were powdered solids occupying about 1 cc volume. Proton resonances were used throughout this investigation in the applied field of 6774 gauss from a permanent magnet (resonance frequency 28.8 Mc/sec.). The apparatus did not enable the shape of the resonance line to be plotted out directly; a phase-sensitive amplifier, which serves to give a good signal to noise ratio, together with a small sinusoidal modulation of the applied field, yields the first derivative of the resonance line-shape. The line-shape itself may be obtained, if required, by direct integration of the measured derivative. For comparison with theory the second moment of the resonance line-shape about its center has to be computed; this, however, can be done directly from the derivative curve. Values of second moment quoted later in this paper are the mean of those obtained from about three sets of derivative measurements. The probable error of the mean ranged from 0.2 gauss² for the narrowest lines to about 0.8 gauss² for the broadest lines. A subtraction of 0.2 gauss² from the mean computed values has been made to allow for field inhomogeneity over the sample. The line-shape could be completely plotted only at steady temperatures; in the intervals 100–200°K and 210°–270°K the sample warmed up continuously, giving only time enough at each temperature to measure the width between the stationary points of the derivative curve. This, however, was sufficient to indicate the temperature range in which changes in line-shape occurred, and their order of magnitude; the complete line-shape and second moment could be obtained at fixed temperatures on both sides of the change.

Before proceeding to an account of the experimental results and their detailed explanation, some general remarks will be made concerning the information which the theory allows us to deduce from the experimental results. It may be said at once that unless the reorien-

* Commonwealth Fund Fellow. Now at the Department of Natural Philosophy, University of St. Andrews, Scotland.

¹ H. S. Gutowsky and G. E. Pake, *J. Chem. Phys.* **18**, 162 (1950); see also earlier experiments by N. L. Alpert, *Phys. Rev.* **75**, 398 (1949).

tation frequency¹ characteristic of a type of motion in the crystal lattice exceeds that represented by the half-width of the resonance line, the second moment of the line will be unaffected by the motion; this type of experiment is therefore unable to detect such motion. (The half-width is of the order of 30 kc/sec. for the solids considered here.) Therefore, whenever the statement is made later in this paper that a reduction in line-width is to be explained by a certain type of motion, it should not be assumed that the motion was altogether absent before the reduction took place (although this *may* have been the case), but merely that the motion took place too infrequently to be effective in these measurements.

The various types of molecular motion about a rotational axis which may be encountered in a crystal include:

- (i) Rotation.
- (ii) Quantum mechanical tunnelling through the potential barrier. The rotational axis must also be a symmetry axis if this motion is to be possible.
- (iii) Rotational oscillation.

Provided the frequency of rotation, tunnelling or oscillation exceeds the minimum reorientation frequency, all these forms of motion cause a reduction of line width and of second moment. Moreover, if the axis of rotation is an axis of three-, four-, or sixfold symmetry, the rotation in (i) need not be maintained all the time, provided the necessary number of reorientations are made per second. Thus a small fraction of the time may be spent in excited states of high rotational frequency and the remainder of the time in the various equivalent

fixed positions. This type of motion is almost equivalent in results to tunnelling, merely providing a different mechanism for the angular changes.

The effect of rotation (including the non-continuous form just mentioned) on the second moment is identical with that of tunnelling about a three-, four-, or sixfold axis¹ (except insofar as there may be a slight difference in the intermolecular contributions). Second moment data are therefore unable to distinguish between these forms of motion. A distinction can, however, usually be made from rotational oscillation, and in principle from tunnelling about a twofold axis, although the difference in the expected reduction of second moment from that for higher symmetry tunnelling is not always very large.

A further piece of evidence which may be used in determining the type of motion encountered comes from x-ray structural determinations. If the structure of the crystal has been successfully determined at temperatures where the motion is found to occur, then we may rule out uniform or nearly uniform continuous rotation of the heavier atoms in the crystal. In molecular crystals this will usually imply that such motion for the hydrogen atoms is also ruled out.

II. LONG-CHAIN PARAFFINS

Experimental Results

(i) *n*-Octadecane, $n\text{-C}_{18}\text{H}_{38}$. At the lowest temperature of measurement, 95°K, the derivative of the resonance line, shown in Fig. 1, indicated no fine structure in the line itself. The mean second moment was 23.9 gauss². There was evidence of fine structure, however, at 208°K, Fig. 1, where the second moment was 20.3 gauss². This fine structure became more pronounced at higher temperatures, the second moment decreasing to 16.2 gauss² at 297°K, a few degrees below the melting point (300°K). The second moment is plotted against temperature in Fig. 2. It decreased smoothly until the melting point was reached, at which temperature the narrow line characteristic of liquids was obtained.

(ii) *n*-Octacosane, $n\text{-C}_{28}\text{H}_{58}$. At 99°K and at 205°K there was no evidence of fine structure; the second moment was 26.6 gauss². At 228°K fine structure of the kind found for octadecane began to appear; the second moment decreased smoothly until a temperature of 326°K was reached, as indicated in Fig. 2. Here a discontinuity in second moment occurred, and the line narrowed rapidly over the last seven degrees before the solid melted.

(iii) Dicetyl, $n\text{-C}_{32}\text{H}_{66}$. The behavior was similar to that of octacosane. At the lowest temperatures the second moment was 27.1 gauss². Fine structure of the kind encountered in octadecane and in octacosane appeared at 235°K, and as shown in Fig. 2, the second moment decreased continuously until 318°K where it remained steady at 14 gauss² until 336°K. At this temperature the second moment fell rapidly over the last six degrees before reaching the melting point at 342°K.

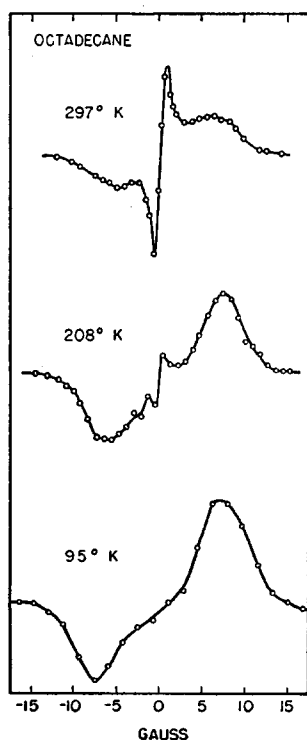


FIG. 1. Resonance line derivatives for octadecane.

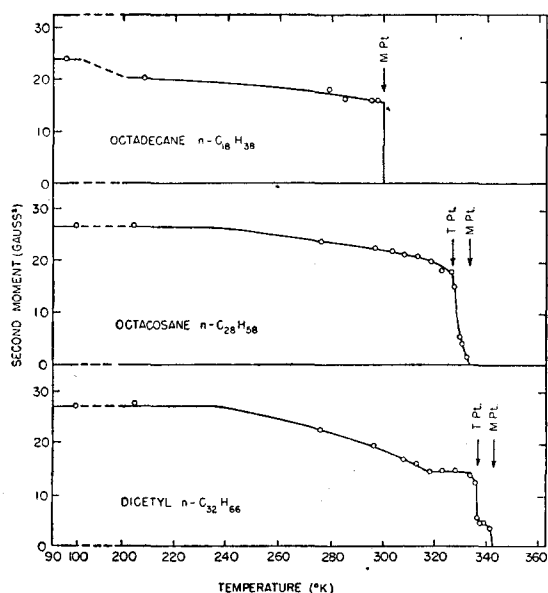


FIG. 2. The variation with temperature of the second moment of the resonance line for three long chain paraffins.

Discussion

The structures of the normal paraffins have been investigated by Müller² using x-rays; for one member of the series, $C_{29}H_{60}$, the structure has been completely determined. The molecule consists of a plane zig-zag chain of carbon atoms with the characteristic tetrahedral interbond angle of $109\frac{1}{2}^\circ$. The carbon chains are all arranged parallel to the c -axis of an orthorhombic unit cell as the projection on the basal plane shown in Fig. 3 indicates. Other members of the series studied less completely show the same kind of molecular structure and parallel packing, but with differences in detail. Several members of the series are polymorphous showing structural changes about 6° below the melting point. The structural transition temperatures have been measured for the whole series by Piper *et al.*³

If the structure of a crystal is known and the lattice can be assumed rigid, Van Vleck's formula⁴ makes possible the calculation of the second moment of the proton resonance line.⁵ For the paraffins the intramolecular contribution to the second moment predominates. The x-ray analysis does not give the position of the hydrogen atoms, but it may be reasonably assumed that the C—H bonds are tetrahedrally distributed with respect to the C—C bonds of the chain; the C—C bond length is taken as 1.54 Å from Müller's work, and the C—H distance as 1.094 Å from spectroscopic data.⁶

² A. Müller, Proc. Roy. Soc. A120, 437 (1928); 127, 417 (1930); 138, 514 (1932).

³ Piper, Chibnall, Hopkins, Pollard, Smith, and Williams, Biochem. J. 25, 2072 (1931).

⁴ J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

⁵ Gutowsky, Kistiakowsky, Pake, and Purcell, J. Chem. Phys. 17, 972 (1949).

⁶ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 440.

For the general member C_nH_{2n+2} the intramolecular contribution is found to be $[18.5 + 19.1/(n+1)]$ gauss². For the smaller intermolecular contribution, it is good enough to use Müller's structure for $C_{29}H_{60}$ despite the slight differences in packings for the various members of the series. The intermolecular contribution is then found to be 7.8 gauss², the total second moment thus becoming $[26.3 + 19.1/(n+1)]$ gauss². For $n=28$ (octacosane), the calculated second moment is 27.0 gauss², which is in good agreement with the experimental value of 26.6 gauss² for temperatures below 228°K. For $n=32$ (dicetyl), the calculated second moment is 26.9 gauss², which is in good agreement with the experimental value of 27.1 gauss² for temperatures below 235°K. Thus at the lower temperatures the molecules are effectively stationary for these two paraffins. For $n=18$ (octadecane), the calculated second moment is 27.3 gauss², which is appreciably higher than the experimental value of 23.9 gauss² at 95°K. This suggests that the molecules are not quite stationary and there is still some motion of the kind to be discussed, which is found at higher temperatures in all three paraffins.

Müller found that as the temperature increased the axial ratio a/b changed progressively toward that of a higher symmetry hexagonal form. (In Fig. 3 this means that the angle ψ tends to 30° .) For $21 \leq n \leq 29$, members of the series C_nH_{2n+2} reached hexagonal symmetry before melting. For $n \leq 23$ the change in axial ratio was continuous, but for $n \geq 24$ an abrupt transition took place about 6° below the melting point.

Müller explained the higher symmetry hexagonal form by supposing that all the molecular chains were in rotation about their lengths at this temperature; the structure was then that of close-packed cylindrical molecules. At the lower temperatures he assumed that there would be rotational oscillation of the molecules; an increasing number would have sufficient energy to surmount the potential barrier as the temperature increased, thus causing the progressive transition of axial ratios. As a result of later work on the dielectric

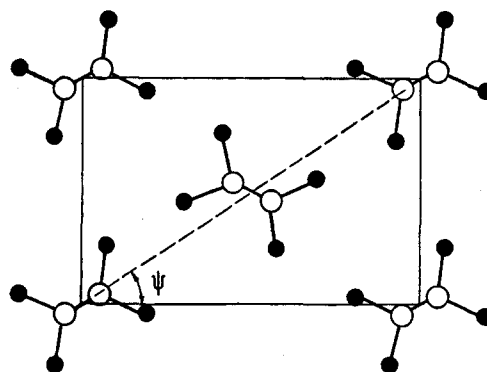


FIG. 3. Diagram illustrating the packing of the long chain paraffins in the unit cell. The molecules are shown projected on the base of the unit cell. The open circles represent carbon atoms; the solid circles represent hydrogen atoms.

constant of long chain di-ketones, Müller⁷ concluded that the chains had considerable torsional flexibility, and that torsional oscillations might, at least in part, be the cause of the increase in symmetry.

In comparing the present results with the work of Müller, it may first be noted that the discontinuous changes in second moment found for octacosane and dicetyl correspond to the structural changes found by him; for octadecane he found that the axial ratio changed continuously, and in fact no discontinuity in second moment was found.

To further test the compatibility of the present results with Müller's conclusions, it is necessary to calculate the reduction in second moment caused by rotation or oscillation of the molecules. Gutowsky and Pake¹ have given formulas for the reduction of the intramolecular contribution to the second moment caused by rotation or quantum-mechanical tunnelling between equivalent positions. (Tunnelling is not a possibility here, however, since the axis of rotation is not an axis of symmetry.) Using these formulas, it is found that this contribution is reduced from the rigid lattice value of $[18.5 + 19.1/(n+1)]$ gauss² to $[6.8 - 11.6/(n+1)]$ gauss² if all the molecules rotate. The values are 6.2, 6.4, 6.4 gauss² for $n=18, 28, 32$, respectively. Gutowsky and Pake assumed for the purpose of their calculations that the intermolecular contribution would not be appreciably affected by the rotation. In Appendix II the effects of certain kinds of motion on this contribution are calculated, and as an example, it is shown there that for the paraffins, the intermolecular contribution is, however, reduced by a factor of three from 7.8 gauss² to 2.6 gauss². Intra- and inter-

molecular contributions are thus reduced by about the same factor. The total second moments to be expected if all the molecules rotate are therefore 8.8, 9.0, 9.0 gauss² for octadecane, octacosane, and dicetyl, respectively.

A comparison of these values with the experimental second moment values shown in Fig. 2 indicates that for octadecane up to the melting point, and for the other two paraffins up to their transition points, the second moments are too great for all the molecules to be rotating. It seems reasonable to suppose, therefore, that the progressive reduction of second moment is due to the rotation of some, but not all, of the molecules. Those molecules which do not rotate presumably oscillate; we must, therefore, find what reduction of second moment is caused by rotational oscillation in order to know how much of the observed reduction can be ascribed to this cause. The necessary calculation is carried out in Appendix I, where the reduction factor is given as a function of the amplitude of oscillation. As an approximation in applying these results to the paraffins, it will be assumed that the intermolecular contribution is reduced by the same factor; this was almost exactly the case for uniform rotation. It is found that for angular oscillation amplitudes of 30°, 45° and 60° that the reductions in second moment below the rigid lattice values for the paraffins are 6.2, 10.8 and 13.9 gauss², respectively. For octadecane the second moment was 11 gauss² below the rigid lattice value at the melting point, while for octacosane and dicetyl at their transition points the corresponding reductions were 10 and 12 gauss². If the experimental reductions are to be accounted for on the basis of oscillation alone, it is necessary to assume oscillatory amplitudes of at least 45°. Without a detailed knowledge of the shape and size of potential barrier we cannot make a definite pronouncement, but it seems more likely that at lower temperatures the molecules occupy oscillatory energy levels and that as the temperature rises the amplitude of oscillation increases with an increasing number of molecules occupying rotational levels. It should be noted in this connection that for C₂₈H₆₀, whose structure Müller determined completely, only a small fraction of the molecules could have been rotating at the temperature of his investigation, 293°K. The reduction of second moment for octacosane, the next member in the series, is in fact quite small at this temperature (see Fig. 2).

In the case of dicetyl, the second moment appears to maintain a steady value of 14.5 gauss² over a 15° range below the transition point. As we have noticed, this value is greater than the 9.0 gauss² which would be expected if all the molecules rotated. If this effect is real, it suggests a stable arrangement with about two-thirds of the molecules rotating and one-third merely oscillating. A possible explanation of such an arrangement is as follows. The molecules in plan pack together in an almost hexagonal array. The molecules themselves are far from having circular symmetry about their axes,

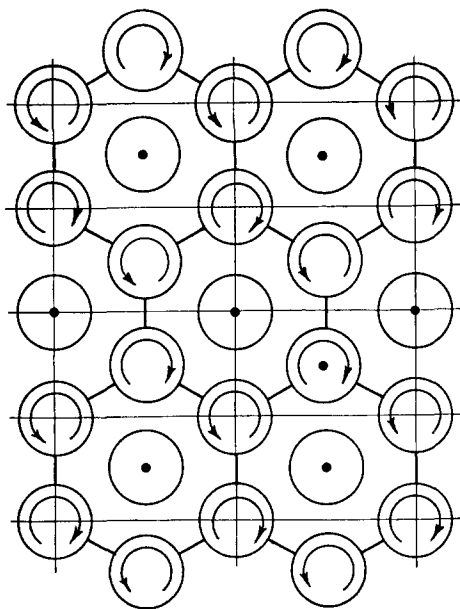


FIG. 4. A suggested arrangement of rotating molecules for dicetyl, shown projected on the basal plane of the unit cell.

⁷ A. Müller, Proc. Roy. Soc. A174, 137 (1940).

and would tend to rotate like a set of meshed gear-wheels. However, a closed train of identical gears will only rotate if it contains an even number of members, and it will be seen on examination that it is not possible for the whole hexagonal array of molecules to rotate in this manner since it is made up of a set of almost equilateral triangular groups containing three members. If, however, one-third of the molecules do not rotate, one can imagine satisfactory systems of meshing molecules such as that indicated schematically in Fig. 4.

We now have to account for the much lower values of second moment which were found for octacosane and dicetyl above their transition temperatures. The values are rather lower than those calculated for uniform rotation of all the molecules. Presumably the structural change at the transition point lowers the potential barriers hindering rotation to an extent permitting all the molecules to rotate. It is likely that other forms of motion will also be present such as torsional oscillations, lateral and longitudinal motion and flexing. These motions, which would also be present to some extent below the transition point, would cause the second moment to be still lower than that calculated for rotation alone.

Finally, an attempt should be made to explain the nature of the fine structure of the resonance line. Only a qualitative explanation will be attempted since the molecular proton system is a complicated one. The characteristic features are the sharp positive and negative peaks on the derivative curve, which reflect a sharp central peak in the resonance line itself. Because it is sharp, this peak only represents a small fraction of the total energy of the resonance line.

The paraffin chain may be grouped as a set of CH_2 groups with a CH_3 group at each end. Taken separately, only the CH_3 groups give a central peak. As shown by Andrew and Bersohn⁸ the resonance line for an equilateral triangular group of protons has a central component, which for a rigid lattice and a powdered sample, contains a fraction 0.19 of the line intensity of the whole group. When the triangle rotates about the paraffin chain axis, which makes an angle $35^\circ 16'$ with the normal to the plane of the three protons, this fraction is slightly enhanced to 0.25. In the rigid lattice this central line is presumably not visible as fine structure owing to the considerable broadening caused by protons of other molecules and of adjacent groups in the same molecule. When the molecule rotates or oscillates with large amplitude, the broadening due to neighbors becomes several times smaller as we have seen, thus perhaps allowing this central component to be resolved. This hypothesis could be tested by substituting some other nucleus for one of the protons in each end group.

III. LAURYL ALCOHOL

Lauryl alcohol, $n\text{-C}_{12}\text{H}_{26}\text{OH}$, like several other members of the normal primary alcohol series is dimor-

⁸ E. R. Andrew and R. Bersohn, *J. Chem. Phys.* **18**, 159 (1950).

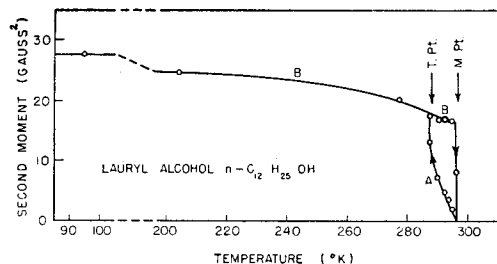


FIG. 5. The variation with temperature of the second moment of the resonance line for lauryl alcohol.

phous.^{9,10} In both structural forms the carbon chain has the same form and dimensions as in the paraffins, and the chains are arranged parallel to each other in the unit cell. Bernal¹¹ found that lauryl alcohol solidified at 297°K into a hexagonal form, with the parallel chains normal to the base of the unit cell. On cooling to 289°K this transformed to a monoclinic structure with the chains inclined at an angle of 57° to the cell base. The transition was found to be irreversible, however, since the hexagonal structure could not be reproduced without first melting. Bernal suggested that the hexagonal structure followed from rotation of the molecules about their chain lengths.

The mean experimental values of second moment are plotted against temperature in Fig. 5, and a series of resonance line derivatives for various temperatures is shown in Fig. 6. At the lowest temperature, 95°K , the mean second moment 27.7 gauss^2 is in good agreement with the calculated value 27.1 gauss^2 for a rigid lattice. In obtaining this calculated value it was assumed that the intermolecular contribution was the same as that for the corresponding paraffin since the detailed structure of lauryl alcohol is not known.

On raising the temperature, the second moment decreased continuously until the melting point was reached as with octadecane, sharp peaks appearing in the derivative curve (Fig. 6). On solidifying again the hexagonal form was first obtained with a much narrower line than that for the monoclinic form, giving the hysteresis loop in Fig. 5. Below 287°K the same resonance lines were obtained as when heating up.

These results find the same explanation as that for the paraffins. For the monoclinic form, the motion is the same as for octadecane up to the melting point; for the hexagonal form, the motion is the same as for octacosane and dicetyl above their transition points.

IV. BENZENE, NAPHTHALENE, AND ANTHRACENE

Benzene, C_6H_6

At 94°K the mean second moment was 11.4 gauss^2 . At this and higher temperatures the resonance line was single-humped showing no fine structure. At both

⁹ T. Malkin, *J. Am. Chem. Soc.* **52**, 3739 (1930).

¹⁰ D. A. Wilson and E. Ott, *J. Chem. Phys.* **2**, 231 (1934).

¹¹ J. D. Bernal, *Zeits. f. krist.* **83**, 153 (1932).

205°K and 273°K the line was much narrower, with second moment values 2.1 and 2.0 gauss², respectively. In Fig. 7 the line width (reckoned between the stationary points of the derivative curve) is plotted against

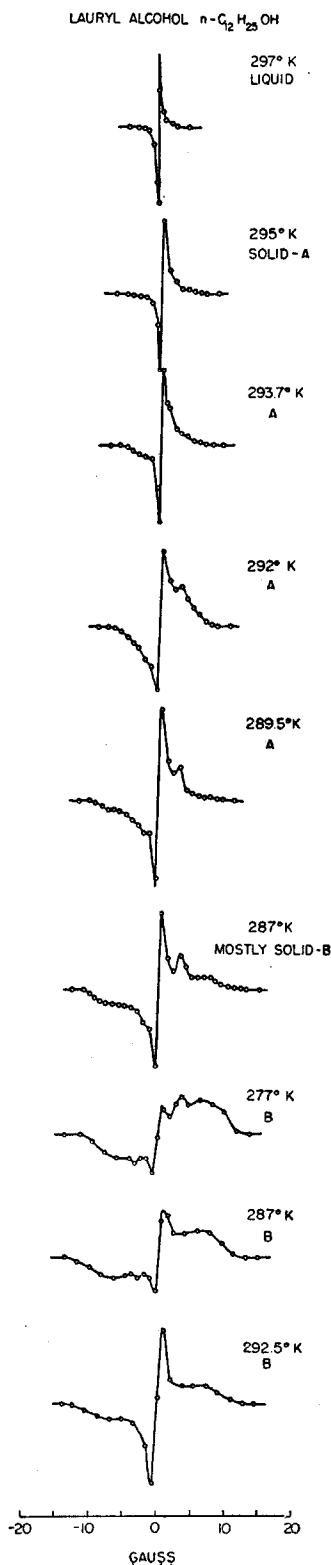


FIG. 6. Resonance line derivatives for lauryl alcohol, illustrating the hysteresis loop shown in Fig. 5.

temperature, and it will be seen that a sharp drop occurs over the range 100–118°K.

The benzene molecule is known to be a plane hexagon of carbon atoms each with a side-bond hydrogen atom in the plane, thus producing a plane hexagon of protons. In calculating the theoretical intramolecular contribution to the second moment, Brockway and Robertson's¹² value 1.39A has been taken for the carbon-carbon bond length; for the carbon-hydrogen bond length we have taken the value 1.08A, intermediate between 1.09A for $-C-H$ and 1.07A for $=C-H$.⁶ The contribution is 3.3 gauss². Using the structure of benzene determined by Cox,¹³ the intermolecular contribution is found to be 5.3 gauss² for the temperature of Cox's determination, 251°K, and approximately 6.4 gauss² at 94°K, assuming the contraction of solid benzene at the lower temperature is not very different from that of naphthalene for which a value of the contraction is available. The total calculated second moment for a rigid lattice is therefore 9.7 gauss² at 94°K. The experimental value is 1.7 gauss² larger than this; the discrepancy is probably due to the use of a rather larger modulating field than usual on account of the very weak signal obtained at this temperature. The lattice can therefore be treated as rigid at 94°K.

The sharp drop in line-width over the range 100–118°K must indicate the commencement of some considerable motion in the lattice; the reduction is more than can be accounted for by mere rotational oscillation or vibration. An examination of the lattice structure suggests that rotation or tunnelling of the benzene molecules about their hexagonal axes is the motion likely to require the least energy. The evidence of the x-ray analysis (see Section 1) suggests that of these forms of motion, the more likely are tunnelling and non-uniform rotation.

This rotational motion would reduce the intramolecular contribution by a factor of four. The effect on the intermolecular contribution is not covered by the cases considered in Appendix II, but if we assume that this contribution is reduced by the same factor as the intramolecular contribution, as was the case for the paraffins, the total theoretical second moment would be 2.4 gauss² at 120°K and 2.1 gauss² at 273°K in good agreement with the experimental values. This agreement should not, however, be interpreted as ruling out other forms of motion such as rotation or tunnelling about the diad axes, which though less likely (since the potential barrier is probably much greater) would give roughly the same theoretical values of second moment. By studying line-width changes in substituted benzene compounds it may be possible to make a more definite decision between these forms of motion.

¹² L. O. Brockway and J. M. Robertson, J. Chem. Soc. 1934 (1939).

¹³ E. G. Cox, Proc. Roy. Soc. A135, 491 (1932).

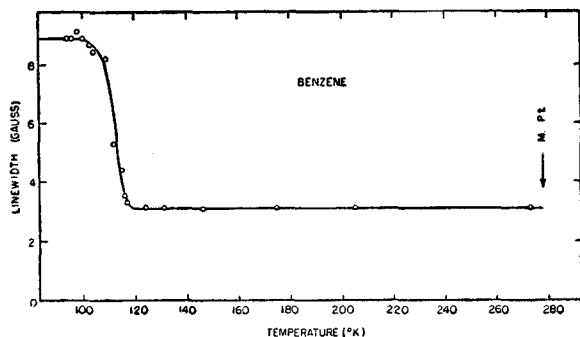


FIG. 7. The variation with temperature of the resonance line width for benzene.

The specific heat of benzene¹⁴ shows no anomaly in the region of 100°K. The motion does not, therefore, accompany a structural change. An explanation of the breadth of the temperature range over which the line narrows is given by Purcell, Sachs, and Turner¹⁵ in conjunction with their measurements of relaxation times for benzene and other solids exhibiting similar line-width changes.

Naphthalene, C₁₀H₈

The line-width did not change appreciably over the whole range of measurement from 96°K to the melting point 353°K. There appeared to be a decrease of the order of 10 percent in line width at the higher temperatures, but the accuracy was not good because the signal was weak. The resonance line was a single-humped curve showing no fine structure; the mean experimental second moment was 9.1 gauss². The structure of naphthalene has been determined by Robertson.¹⁶ Using a carbon-hydrogen bond length of 1.08 Å as for benzene, the intramolecular contribution is found to be 3.2 gauss². Together with an intermolecular contribution of 6.9 gauss², the total theoretical second moment is 10.1 gauss². Thus the naphthalene lattice is essentially rigid at all temperatures; the slight reduction of line width at higher temperatures, if real, can be explained as due to lattice expansion and to some vibrational motion.

Anthracene, C₁₄H₁₀

At 97°K the mean experimental second moment was 11.4 gauss²; the resonance line was again a single-humped curve at all temperatures. As Fig. 8 indicates, the line width remains unchanged until about 184°K, when it suddenly narrows by a factor of five over a temperature range of about 16°. Above 200°K the line width remains at this narrow value. At 203°K and 298°K the mean experimental second moments were 0.75 and 0.65 gauss², respectively.

¹⁴ Huffman, Parks, and Daniels, *J. Am. Chem. Soc.* **52**, 1547 (1930).

¹⁵ Sachs, Turner, and Purcell, *Bull. Am. Phys. Soc.* **24**, 21 (1949).

¹⁶ J. M. Robertson, *Proc. Roy. Soc. A* **142**, 674 (1933); **140**, 79 (1933).

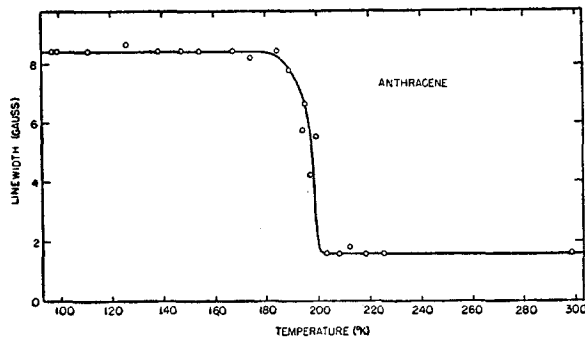


FIG. 8. The variation with temperature of the resonance line width for anthracene.

The structure of anthracene has been determined by Robertson.¹⁶ For a rigid lattice the intra- and intermolecular contributions are 3.2 and 7.1 gauss², respectively, making a total of 10.3 gauss². This indicates that the lattice is effectively rigid below 184°K.

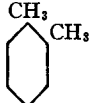
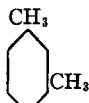
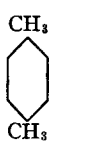
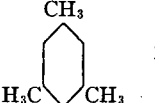
The line-width change was a surprise in view of the lack of motion shown by naphthalene, which has a similar structure. Moreover, the magnitude of the reduction of the second moment, namely by a factor of 16, is difficult to explain. Rotation about the two diad axes normal to the length of the hexagon chain seems to be ruled out by lack of room in the lattice for the molecule to turn end over end. Rotation or tunnelling about the third diad axis lying along the length of the hexagon chain seems a possibility. However, tunnelling merely reduces the theoretical intramolecular component from 3.2 gauss² to 2.5 gauss², while the *total* observed value is only 0.75 gauss²; even uniform rotation about this axis only reduces this contribution to 2.0 gauss². It seems necessary, therefore, to assume other motions besides tunnelling or rotation involving bending, twisting, and side-bond deformation, in order to account for such a low, almost liquid-like, value. This explanation cannot be regarded as entirely convincing, and it is possible that more radical ideas should be considered, such as motion or tunnelling of the protons about a rigid carbon skeleton. The size of the potential barriers involved seems, however, to render this explanation improbable. There is, of course, the possibility that the resonance line has very wide skirts whose energy is too low to detect, but whose contribution to the second moment is quite finite. It is clear that more experiments, particularly on related compounds, are needed before a satisfactory explanation can be put forward.

From the results of this section, the general remark may be made that line-width transitions are to be found in substances for which there are no obvious reasons to expect them.

V. THE XYLENES AND MESITYLENE

There were no important changes in the resonance lines of these compounds from 95°K to their melting

TABLE I. Mean experimental second moment values for the xylenes and mesitylene.

Substance	Molecular formula	Melting point °K	Mean second moment (gauss ²)			Theoretical rigid lattice second moment (gauss ²)
			95°K	205°K	277°K	
<i>o</i> -Xylene		245	9.8	8.8	Liquid	21.1
<i>m</i> -Xylene		219	9.8	8.9	Liquid	20.7
<i>p</i> -Xylene		288	9.9	8.9	7.7	20.7
Mesitylene		220	9.8	7.6	Liquid	23.8

points. The mean experimental second moments are given in Table I. For the most part the resonances were single-humped curves, although for *m*-xylene and mesitylene there was some evidence of a central peak being resolved at 205°K.

In calculating the rigid lattice second moments, which are also given in Table I, the following assumptions have been made:

(a) that the six bonds were coplanar with the benzene ring, adjacent bonds subtending angles of 60°;
 (b) C—H bond lengths in CH₃ groups of 1.094Å as in Section II;

(c) C—H side bond lengths of 1.08Å as in Section IV;

(d) C—C side bond lengths of 1.53Å and C—C ring bond lengths of 1.39Å;¹¹

(e) that as the lattice structure of these compounds has not been determined, the intermolecular contribution is 5.4 gauss² since it is 5.3 gauss² for benzene and 5.6 gauss² for hexamethylbenzene (Section VI); these are related compounds and all have apolar molecular structures;

(f) that the orientation of the CH₃ groups is that which maximizes the shortest distance between a hydrogen atom of the CH₃ group and any other hydrogen atom elsewhere in the molecule.

It will be seen from Table I that the experimental second moment is less than the calculated rigid lattice value by more than a factor two for all four substances from 95°K to their melting points. Since the molecules are all of different shape and symmetry the most obvious explanation of the low second moment value common to all four is to assume there is rotation or threefold tunnelling of the CH₃ groups about the direction of the C—C sidebond. Such motion reduces the

second moment contribution of the protons of the CH₃ groups, which is, in all cases, the predominant contribution, by a factor four. Since the molecule as a whole is not rotating, the intermolecular contribution will probably only be reduced slightly by the motion, and in fact it will be assumed not to change. The remaining intramolecular contributions are small anyway; if they too are assumed not to change, the theoretical second moment values for *o*-, *m*-, *p*-xylene, and mesitylene are respectively 11.2, 10.8, 10.8, 11.5 gauss². If, however, these remaining intramolecular contributions were reduced even as much as to zero, the values are only slightly lower, namely 9.3, 9.3, 9.3, 9.5 gauss². The experimental values at 97°K do all lie between these limiting calculated values, and lend support to the internal rotational motion suggested. The slightly lower values of second moment at higher temperatures are probably caused by the combined effects of lattice expansion and vibrational motion.

VI. HEXAMETHYLBENZENE

Resonance line derivatives taken at 96°K and 280°K are shown in Fig. 9(a). The line-width is plotted against temperature in Fig. 9(b). It is seen to have a steady value from 95°K to 135°K and to decrease gradually over a range 135–210°K to another steady value which remains unchanged at 380°K, the highest temperature of measurement. The mean experimental second moment at 96°K was 13.0 gauss² and above 210°K was 2.5 gauss².

The structure of hexamethylbenzene has been determined by Lonsdale,¹⁷ and confirmed with slightly more accurate bond lengths by Brockway and Robertson.¹² In calculating the theoretical intramolecular contribution to the rigid lattice second moment it has been assumed that each CH₃ group lies symmetrically with respect to the plane of the benzene ring, with one proton in the plane and the other two equally spaced on either side. By arranging all the CH₃ groups in the same sense round the ring, the closest approach of hydrogen atoms from different groups was a maximum. The intra- and intermolecular contributions were found to be 27.1 gauss² and 5.6 gauss² respectively, giving a total of 32.7 gauss².

Since the observed second moment in the range 95°–135°K is less than half the rigid lattice value, it is natural to look for the explanation in terms of rotation or tunnelling of the CH₃ groups about the C—C sidebonds, since this was found to be an adequate explanation of the results for the other polymethylbenzenes in Section V. The effect of such motion is to reduce the contribution of the CH₃ groups by a factor four. If it be assumed that all other contributions are unaltered, the calculated second moment becomes 16.4 gauss². By assuming instead that the other contributions are reduced by a factor 0.7, the calculated value

¹⁷ K. Lonsdale, Proc. Roy. Soc. A123, 494 (1929).

can be made to agree with the experimental value of 13.0 gauss². Such a reduction factor seems quite reasonable in the light of the previous sections and of the fact that the molecule as a whole is not moving.

It is now necessary to seek an explanation of the still lower second moment (2.5 gauss²) found at temperatures above 210°K. Uniform rotation of the molecule as a whole is ruled out by the evidence of the x-ray analysis. Moreover, if there were such rotation of the whole molecule, one might expect to find a structure of higher symmetry than the triclinic structure actually found. Sixfold tunnelling or nonuniform rotation of the molecule about the hexagonal axis seem the most likely possibilities therefore. If the CH₃ groups were fixed, such molecular motion would reduce the rigid second moment by a factor of about three. No attempt has been made to calculate the expected second moment for the very complicated case of the two superimposed forms of motion, but it is clear that the observed second moment is of the order of magnitude to be expected, and we may therefore adopt this explanation.

The specific heat of hexamethylbenzene has been measured by Huffman, Parks, and Daniels,¹⁴ and is shown as a function of temperature in Fig. 9. The authors explained the specific heat discontinuity at 108°K in terms of a structural change; since the structure is triclinic above this temperature, it is presumably also triclinic below, but with different lattice constants. The change does not, however, affect the resonance line. The authors could offer no explanation of the specific heat hump at 135–165°K. The present work suggests that this hump may be associated with the onset of rotational motion of the molecules about their hexagonal axes.

ACKNOWLEDGMENTS

The author wishes to thank Professor E. M. Purcell for his interest and helpful advice. He is greatly

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APPENDIX I

The Effect of Rotational Oscillation on Second Moment

For a rigid pair of like nuclei Van Vleck's formula for the second moment of the resonance line contains the geometrical factor $[(3 \cos^2 \theta - 1)/r^3]^2$ which we will call y^2 , where θ is the angle between the applied field and the pair direction, and r is the internuclear distance. Gutowsky and Pake¹ have shown that when the nuclei are in sufficiently rapid motion, y must be replaced in the above factor by its mean value over the motion.

We may express $\cos \theta$ in terms of other angles of the system:

$$\cos \theta = \cos \theta' \cos \gamma + \sin \theta' \sin \gamma \cos(\phi - \phi_0) \quad (1)$$

where θ' is the angle between the applied field and the axis of rotational oscillation, γ is the angle between the pair direction and the axis of rotational oscillation, ϕ_0 is the azimuth of the plane containing the field direction and the axis of oscillation, ϕ is the azimuth of the pair direction.

We shall assume that the oscillation is simple harmonic so that we may write $\phi = \phi_1 + \alpha \sin \omega t$, where ϕ_1 is the azimuth of the mean position of the pair direction and α is the angular amplitude.

The mean value of y over the motion merely requires the evaluation of $\langle \cos^2 \theta \rangle_{\text{av}}$ since r remains constant. Performing the necessary integration, this is found to be

$$\langle \cos^2 \theta \rangle_{\text{av}} = \cos^2 \theta' \cos^2 \gamma + 2 \sin \theta' \cos \theta' \sin \gamma \cos \gamma \cos \delta J_0(\alpha) + \frac{1}{2} \sin^2 \theta' \sin^2 \gamma (1 + \cos 2\delta J_0(2\alpha)),$$

where $\delta = \phi_1 - \phi_0$.

The ratio of second moments for the oscillatory and rigid cases is then given by \bar{y}^2/y^2 . For a powdered

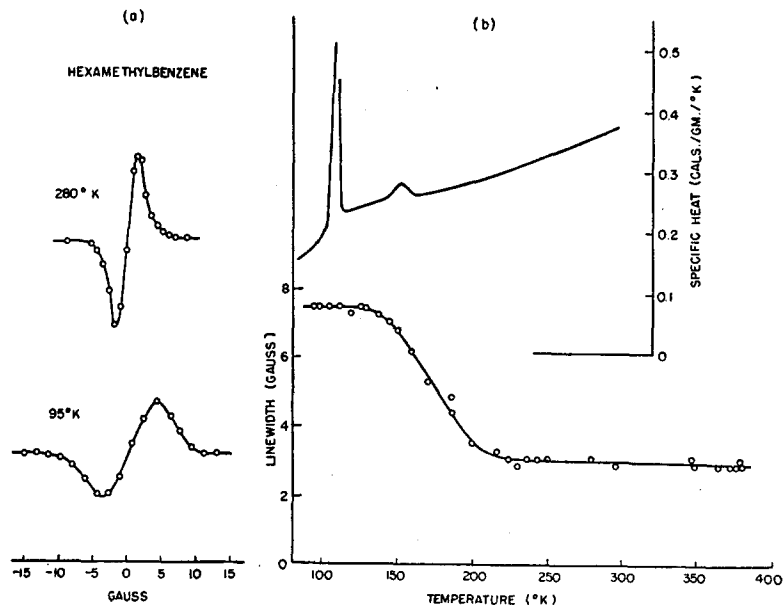


FIG. 9. (a) Resonance line derivatives for hexamethylbenzene; (b) the variation with temperature of the resonance line width and of the specific heat for hexamethylbenzene.

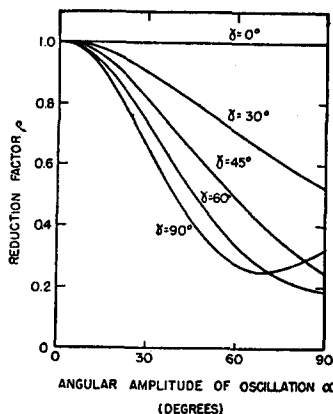


FIG. 10. The variation of the second moment reduction factor ρ with amplitude of angular oscillation α , for various orientations γ of the oscillation axis with respect to the nuclear pair direction.

sample, it is now necessary to average this result for: (i) all values of ϕ_0 over a circle; (ii) all values of θ' over a sphere. After averaging it is found that the ratio of second moments is

$$\rho = 1 - \frac{3}{4}[(1 - J_0^2(\alpha)) \sin^2 2\gamma + (1 - J_0^2(2\alpha)) \sin^4 \gamma]. \quad (2)$$

For small angles α , this gives the approximate result

$$\rho = 1 - \frac{3}{2}\alpha^2 \sin^2 \gamma. \quad (3)$$

Values of ρ from Eq. (2) are plotted in Fig. 10.

APPENDIX II

The Change of Contribution to Second Moment Due to Coplanar Motions

We shall consider only the case where the two nuclei are confined to a single plane. The procedure and notation of Appendix I will be used. If angles of azimuth are measured in the plane, then $\gamma = 90^\circ$, and

$$\cos \theta = \sin \theta' \cos(\phi - \phi_0). \quad (4)$$

We need the mean value of y over the motion, where $y = (3 \cos^2 \theta - 1)/r^3$; that is, we require

$$\bar{y} = \frac{3}{2} \sin^2 \theta' (A \cos 2\phi_0 + B \sin 2\phi_0 + C) - C$$

where

$$A = \langle [\cos 2\phi / r^3] \rangle_{Av}; \quad B = \langle [\sin 2\phi / r^3] \rangle_{Av}; \quad C = \langle [1/r^3] \rangle_{Av}.$$

A , B , C will be evaluated later in this Appendix for particular types of motion.

For powdered samples, it is now necessary to form \bar{y}^2 (which we will call z) and average (i) for ϕ_0 over a circle and (ii) for θ' over a sphere.

- (i) gives $\bar{z}^{(0)} = (9/8) \sin^4 \theta' (A^2 + B^2 + 2C^2) + C^2(1 - 3 \sin^2 \theta')$
- (ii) gives $\bar{z} = \frac{3}{8}(A^2 + B^2) + \frac{1}{2}C^2$.

For a rigid pair of nuclei separated by distance r_0 , $\bar{z} = \frac{1}{2}r_0^{-6}$. The ratio ρ of the second moments for moving and rigid cases is therefore

$$\rho = \frac{1}{4}r_0^6(3A^2 + 3B^2 + C^2). \quad (5)$$

In principle the problem is now determined and it only remains to find A , B , and C for the type of motion encountered. Several simple cases will now be considered.

Case (i). One nucleus fixed and the other executing uniform motion round a circle. This is a case encountered when one molecule is fixed and the neighbor molecule is uniformly rotating. In Fig. 11, P is the fixed nucleus, Q is the nucleus moving uniformly round a circle of radius p and center O . Let OP , PQ be q , r respectively. OPQ is ϕ and POQ will be called β .

$$r^2 = q^2 + p^2 - 2qp \cos \beta = (q+p)^2(1 - k^2 \cos^2 \beta/2)$$

where

$$k^2 = \frac{4qp}{(q+p)^2}.$$

Since β takes all values equally from 0 to 2π ,

$$C = \langle [1/r^3] \rangle_{Av} = \frac{1}{\pi(q+p)^3} \int_0^\pi \frac{d\beta}{(1 - k^2 \cos^2 \beta/2)^{3/2}} = -\frac{2}{\pi} \frac{E(k)}{(q+p)(q-p)^2}.$$

$$A = \langle [\cos 2\phi / r^3] \rangle_{Av} = C - 2D,$$

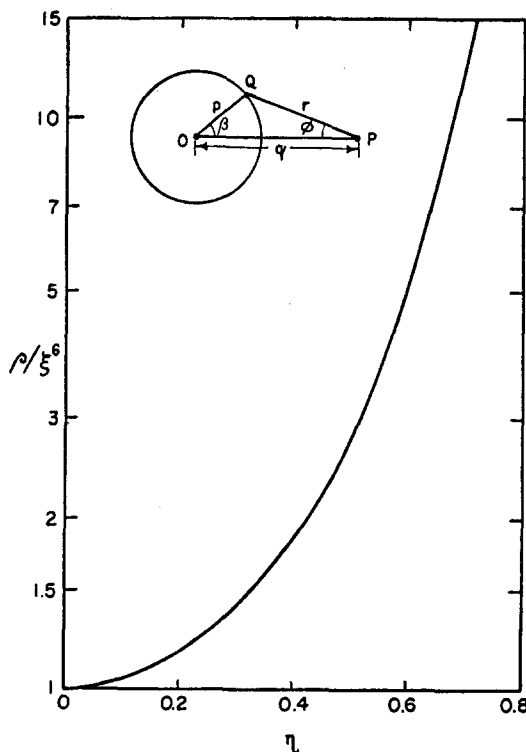


FIG. 11. The variation of the second moment reduction factor ρ with $\eta (= p/q)$, when one nucleus (P in the inset diagram) is fixed, and the other, Q , moves uniformly round a circle.

where $D = \langle [\sin^2 \phi / r^3] \rangle_{\text{av}}$. Since $r \sin \phi = p \sin \beta$

$$D = \frac{1}{\pi} \cdot \frac{1}{(q+p)^5} \int_0^\pi \frac{p^2 \sin^2 \beta d\beta}{(1 - k^2 \cos^2 \beta / 2)^{5/2}}$$

$$= \frac{1}{3\pi} \cdot \frac{1}{(q-p)^2 (q+p) q^2} [(q^2 + p^2) E(k) - (q-p)^2 K(k)],$$

$$B = 2 \langle [\sin \phi \cos \phi / r^3] \rangle_{\text{av}} = \frac{2p}{\pi (q+p)^5} \int_0^\pi \frac{\sin \beta (q - p \cos \beta) d\beta}{(1 - k^2 \cos^2 \beta / 2)}$$

$$= \frac{2}{3\pi q} \cdot \frac{q-p}{(q+p)^3} \left[\left(\frac{q+p}{q-p} \right)^3 - 1 \right]$$

$$+ \frac{4p}{3\pi q^2 (q+p)} \left[\frac{q}{(q+p)^2} - \frac{1}{(q-p)} \right].$$

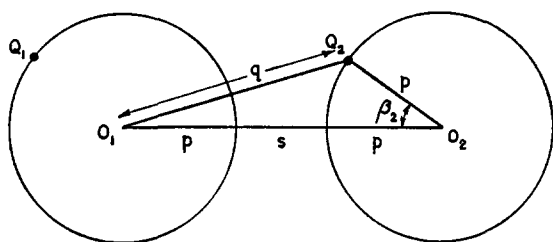


FIG. 12. Diagram illustrating the motion discussed in Appendix II, Case (ii).

Putting $\eta = p/q$ and $\xi = r_0/q$, we have

$$\rho = [c^2 + \frac{3}{4}b^2 - 3cd + 3d^2] \xi^6,$$

with

$$b = \frac{4\eta(\eta^3 + 3\eta^2 - 3\eta + 3)}{3\pi(1+\eta)^3(1-\eta)^2}$$

$$c = \frac{2E(k)}{\pi(1+\eta)(1-\eta)^2}$$

$$d = \frac{(1+\eta^2)E(k) - (1-\eta)^2K(k)}{3\pi(1-\eta)^2(1+\eta)}.$$

Values of ρ/ξ^6 obtained from these relations are plotted in Fig. 11.

Case (ii). Both nuclei rotating. We shall consider the case in which the nuclei Q_1 and Q_2 move uniformly round circles of the same radius p , centers O_1 and O_2 (Fig. 12). It will be assumed that there is no phase correlation between the two rotations. The closest distance of approach of the two circles is called s , and the distance O_1Q_2 is q . If the second nucleus had been fixed while the first rotated, then the value of the means A , B , C would be those given in Case (i) for the particular value of q concerned. In this case, however, Q_2 also takes all points equally round a second circle.

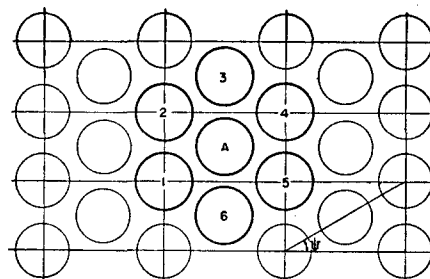


FIG. 13. Diagram illustrating the application of Appendix II, Case (ii) to long chain paraffins.

It is, therefore, necessary to average the values given in Case (i) over all q . Thus, for example,

$$C = \langle [1/r^3] \rangle_{\text{av}} = \frac{2}{\pi^2 p^3} \int_0^\pi \frac{\eta^3 E(k) d\beta_2}{(1+\eta)(1-\eta)^2}.$$

For a given s/p , η can be expressed as a function of β_2 , and the integral evaluated graphically. Evaluations have been made for $s/p = \frac{2}{3}$, 1 and $\frac{3}{2}$. Writing Eq. (5) in the form $\rho = (\mu r_0/p)^6$, the respective values of μ are found to be 0.503, 0.406, 0.304. Other values of μ in this range may be readily interpolated.

As an example of the application of this result, the effect on the intermolecular contribution for the normal paraffins will be considered. Figure 13 shows a section through several unit cells of the crystal lattice normal to the length of the carbon chains. There is one molecule at the corner of each rectangle, and one at each center. Except for one atom in each end group, all the hydrogen atoms are equidistant from the rotational axis of the molecule. The circles in Fig. 13 are then a projection of the loci of all the protons in these molecules (the neglected protons at each end of the chain describe a smaller circle). Consider molecule A. The only neighboring molecules we need consider are those numbered 1-6. If ψ is still somewhat greater than 30° , that is to say, if the orthorhombic axial ratio has not quite reached the hexagonal value, then molecules 3 and 6 will be slightly farther away from A than the other four. Consider one proton somewhere in the middle of molecule A. Its nearest neighbors in molecule 1 will be the two in its plane of rotation and the four bonded to the next carbon atoms above and below the plane. Since the motions of the latter four are not coplanar with the proton from A the theory is not strictly applicable to them. However, the line joining the centers of rotation is only 16° above the plane, so that the theory should be a good approximation provided the correct distances are preserved. The three approximately equidistant molecules A, 1, 2, cannot rotate as a set of meshed gear wheels so the assumption that there is no phase correlation seems reasonable. The assumption of uniformity of rotation is only seriously invalidated if the energy of a molecule is barely greater than the potential barrier

against rotation. If, however, the temperature is such that practically all the molecules are rotating, the assumption will be good enough.

Applying the foregoing theory to the six neighboring protons in each of the molecules 1-6, the contribution to the second moment is found to be 2.0 gauss². The other protons belonging to the neighboring molecules are elevated at much greater angles above the plane of rotation, and the results of this section are not appli-

cable to them. Fortunately, however, they are also much farther away so that their motion is less effective, and in any case their contribution is much smaller. In the non-rotating case their contribution was 0.6 gauss², and little inaccuracy will be caused in the total if their contribution is assumed unchanged in the rotating case. The total intermolecular contribution is, therefore, 2.6 gauss² for the rotating case, compared with 7.8 gauss² in the rigid case.

The Logical Position of the "Average Bond Energy," the "Dissociation Energy of a Bond," and the "Force Constant"

M. SZWARC AND M. G. EVANS

Department of Chemistry, University of Manchester, England

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The concepts of "bond dissociation energy" and "average bond energy" are analyzed. A mathematical treatment is suggested which makes it possible in principle to distribute the energy of atomization among the various bonds of the molecule. The relationship between the "bond dissociation energy," "average bond energy," and "reorganization energy" is examined in the light of various molecular force fields.

THE idea of "bond energy" was introduced into the chemical literature by Fajans,¹ who assumed that the amount of energy necessary for breaking any particular bond was a constant magnitude, characteristic for each type of bond, and independent of the environment of the bond within the molecule. Therefore, the heat of atomization of any molecule was regarded as an additive property, being given by the sum of all bond energies corresponding to the bonds existing in that particular molecule. The assumption of constancy of the bond energy led to the conclusion that the bond energy $M-A$ was given by $1/n$ of the heat of atomization of the molecule MA_n . Similarly the bond energy $M-B$ might be computed from the heat of atomization of the molecule MA_kB_i by subtracting from it the k -fold value of the bond energy $M-A$, obtained from the heat of atomization of MA_n , and dividing the remaining quantity by i . Thus a system of bond energies was evolved which was based on the experimental material provided by heats of combustion of various compounds. The data concerned with the energies required for the direct dissociation of the molecule into two parts, formed by breaking any particular bond, were available only for a few diatomic molecules; and, of course, these dissociation energies were identified with the bond energies.

The subsequent, very fruitful development of the idea of bond energy² demonstrated clearly that the assumption of constancy of bond energy could not be

retained. About the same time several experimental methods were invented which made it possible to determine the dissociation energy of various bonds in polyatomic molecules. It was soon realized that the bond energy and the "dissociation energy of a bond" are not identical magnitudes. Thus, the intrusion of the idea of the dissociation energy of a bond and the accepted principle of variations of bond energies have caused a great deal of confusion in the present literature on these subjects. We decided, therefore, to examine the logical position of both concepts: Of bond energy, subsequently referred to as the "average bond energy," and of the dissociation energy of the bond. We shall also try to point out the interrelations existing between the various measured magnitudes, usually correlated with the average bond energy, and to clear up, to some extent, the ambiguities accumulated in the literature.

We start by defining the dissociation energy of the bond. The dissociation energy of the bond $A-B$ in the molecule (or radical) M is the endothermicity of the reaction in which M is decomposed into two fragments R_1 and R_2 (atoms, radicals or molecules) formed by breaking the bond $A-B$ only.*

$$M = R_1 + R_2 - D(A-B) \text{ kcal./mole.}$$

It should be stressed that this endothermicity must be computed for the state in which both the reactant M and the products R_1 and R_2 are in gas phase at zero pressure and at 0°K. It follows from this definition that the dissociation energy of the bond is unambigu-

¹ K. Fajans, *Ber.* **53**, 643 (1920); **55**, 2826 (1922).

² L. Pauling, *The Nature of Chemical Bond* (Cornell University Press, Ithaca, 1940).

* In cyclic molecules the breaking of certain bonds may produce one fragment only.