STRUCTURE OF MOLECULES and INTERNAL ROTATION

By

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Dedicated to

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Emeritus Professor
of the University of Tokyo

Preface

For several years I have been planning to write a book on internal rotation, a subject in which I, with many coworkers, have been interested during the past twenty years.

The opportunity and incentive to publish this book in English have been prompted by the kind invitations I have accepted to serve as a visiting lecturer and to speak at some symposia. From 1951 to 1953 requests were received from several universities and institutions in the United States and in Europe, including the University of Notre Dame, Cornell University, and Consejo Superior de Investigaziones Cientificas. My decision to write the book at this time has been encouraged by Professor E. Hutchinson, who wished to include this book in his international series. I should like to express my warmest gratitude to Professor P. Debye, Sir Lawrence Bragg, and Professors C. C. Price, O. R. Foz Gazulla, J. W. Williams, F. A. Long, G. Glockler, and P. C. Cross for their cordial invitations. Thanks are also due to Professor P. A. McCusker of the University of Notre Dame for some valuable suggestions.

The first part of this book deals with a description of the development of the investigations on internal rotation. In the second part are presented a more detailed explanation of some of the theoretical aspects of the problem, especially that of normal vibrations, and a description of experimental methods. This is built up as systematically as possible so that this may be understood by the chemists whose special field is in other directions but who wish to increase their knowledge of the general field of structural chemistry. Therefore, it was necessary to include some sections well known to the specialists.

I am deeply indebted to the University of Tokyo for the extension of leave which permitted me to visit the universities and institutions on both sides of the Atlantic and to attend some international congresses and symposia for valuable discussions on the subject matter of this book. I also wish to thank many coworkers of mine, including Professor Y. Morino and Dr. T. Shimanouchi, who have been working with me on this subject for so long, and Drs. M. Yasumi, I. Watanabe, I. Ichishima, S. Nagakura, K. Kuratani, and M. Tsuboi, and Messrs. T. Miyazawa, T. Sugita, and I. Nakagawa for their helpful discussions in preparing this book.

Tokyo, 1954.

S. Mizushima

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PART I

CHAPTER I

Introduction and Earlier Investigations

1. Introduction

The structure of molecules was originally studied by chemical methods of investigation involving the determinations of the composition of substances, molecular weights, the existence of isomers, the nature of the chemical reactions in which substances take part, and so on. From the consideration of facts of this nature chemists succeeded in determining not only the structural formula, but also the spatial configuration of molecules: e. g., van't Hoff and le Bel were led to bring classical organic stereochemistry into its final form by their postulate of the tetrahedral valences of the carbon atom.

Perhaps the most striking advance of the present century in the field of physical chemistry is the more general and quantitative elucidation of such stereochemical problems by the application of various physical methods, including the study of the structure of crystals by the diffraction of X-rays and of gas molecules by electron diffraction, the measurement of electric dipole moments, the interpretation of infrared and Raman spectra, and the determination of entropy and specific heat values.

Among the many interesting results obtained by these methods, that relating to interatomic distances is worthy of note. The values found for the equilibrium distance between two atoms A and B connected by a covalent bond of fixed type in different molecules and crystals are in most cases very nearly the same, so that it becomes possible to assign a constant value to the $A-B$ bond distance for use in any molecule involving this bond. For example, the carbon-carbon distance in diamond (representing a single covalent bond) is 1.542 A, and the values found in many molecules containing this single bond are equal to the diamond value to within their probable errors. This constancy is of interest in view of the varied nature of the molecules. Similar constancy is shown by other covalent bond distances.

Moreover, it is found, that covalent bond distances are in general related to one another in an additive manner: the bond distance $X-Y$ is equal to the arithmetic mean of the distances $X-X$ and $Y-Y$. For example, the C – C distance is 1.54A, as stated above, and the Cl – Cl distance in the element is 1.98A. The arithmetic mean of these, 1.76A, is identical within the probable error of the experimental value with the C – Cl distance found in many organic molecules containing this bond. In consequence it becomes possible to assign to the elements *covalent radii* (shown in Table 1.1) such that the sum of two covalent radii is equal to the equilibrium internuclear distance for the two corresponding atoms connected by a covalent bond.

TABLE 1.1

Covalent radii*

Atom	Single bond	Double bond	Triple bond
H	0.30		
B	0.88	0.76	0.68
C	0.77	0.67	0.60
N	0.70	0.61	0.55
O	0.66	0.57	
F	0.64		
Si	1.17	1.07	1.00
P	1.10	1.00	0.93
S	1.04	0.95	
Cl	0.99		
As	1.21	1.11	
Se	1.17	1.08	
Br	1.14		
Sn	1.40	1.30	
Te	1.37	1.28	
I	1.33		

Thus one might expect to be able to construct any molecular model, even that of a polymer, by using the bond radii and known bond angles. There is, however, a further problem in structural chemistry remaining to be solved: i. e. the question of internal rotation about a single bond as axis, which is the subject of this book. Without the knowledge of the internal rotation we cannot even determine the structure of such a simple molecule as ethane, $H_3C–CH_3$.

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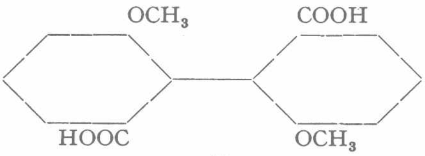
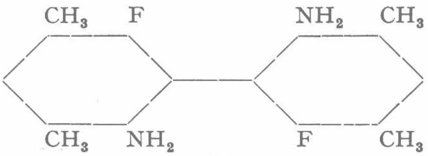
* These values are taken from L. Pauling, The Nature of Chemical Bond, Cornell University Press (1939). See also V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc., 63, 37 (1941). These authors have suggested that corrections should be made for the additivity rule, when the covalent bond acquires ionic character: in other words, when the two atoms forming the bond differ very greatly in their electronegativity.

Such internal rotation about a single bond as axis was for some time supposed to be entirely free and even the term "free rotation" has often been used in chemistry instead of the term "internal rotation" now generally accepted. We must, however, be clear as to what the so called "principle of free rotation" originally meant. It was founded upon the non-existence of isomers whose structures could pass into one another by means of the internal rotation about a single bond: it did not assume that the rotation went on continuously in the molecule, or that all the positions to which it could lead were equally favorable. Actually considerable evidence based on the various physical methods referred to above has been accumulated to indicate that the rotation is not free and that there is in general more than one potential minimum in one complete rotation about a single bond as axis. The rotational isomers corresponding to these minima differ only by small amounts in their properties and any attempt to separate them by the usual chemical methods will not succeed except in some special cases.

The most interesting example of such a special case is afforded by the diphenyl derivatives with three or four substituents in the 2,2′, 6,6′ positions, such as



(I)



(II)

Compounds of this type have been extensively studied by Adams and coworkers.[1] The substituents in the 2,2′, 6,6′ positions restrict, by their spatial interference, the free rotation of the two benzene nuclei around the common axis, thus preventing the rings from becoming coplanar and thereby producing in the molecule an asymmetric configuration. It was found possible by properly modifying the size of the 2,2′, 6,6′ groups to prepare optically active diphenyls with widely varying degrees of stability towards racemization. For example, for the two diphenyl derivatives whose formulae appear above, (II) is completely racemized after 30 minutes boiling in acetic acid, while for (I) the half-life period for boiling in the same solvent is 78 minutes.[1] The racemization of optically active diphenyl derivatives is explained in this case on the basis of the theory of restricted rotation, in that thermal

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[1] R. Adams et al., Chem. Rev. **12**, 261 (1933). See also many other papers published in J. Am. Chem. Soc.

agitation causes the groups in 2,2′, 6,6′ positions to slip by each other (i. e. to cross over the potential barrier) and thus result in internal rotation of the two benzene nuclei.

The simplest molecule with an axis of internal rotation is ethane, $H_3C–CH_3$ for which we can expect a potential curve of the type shown in Fig. 1.1. The potential curve can be obtained theoretically, if we know the interaction of the H atoms of one methyl group with those of the other which prevents free rotation about the C–C axis. Assuming a simple type of interaction energy, Eyring et al. calculated the height of the potential barrier to internal rotation in ethane as 0.3 kcal/mol.[2]

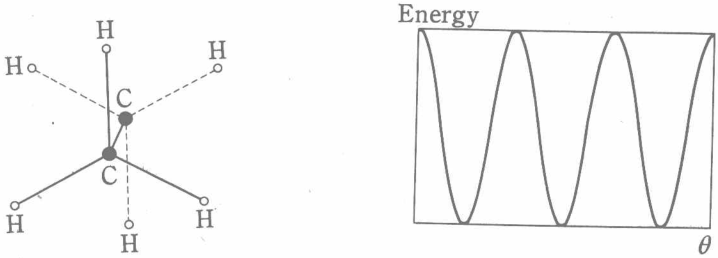

Fig. 1.1. The dependence of the internal potential of ethane on azimuthal angle.

According to classical mechanics, the specific heat of a gas can be calculated by allowing to each degree of freedom of the molecules of gas a mean energy $RT/2$. Thus the specific heat is $nR/2$, where n is the number of degrees of freedom and R is the gas constant, with a value approximately 2 cals. per mole. If ethane were a rigid body, it would have three degrees of translational and three degrees of rotational freedom, and so the value of n would be 6. There is, however, an additional degree of freedom, the twisting of one methyl group relative to the other. This motion is clearly on a different footing from the other six, because it can be inhibited at temperatures still high enough to permit considerable translational and rotational activity. One would expect, therefore, that at low temperatures the specific heat would be 3 R, and that at higher temperatures it would approximate to 7 $R/2$. The temperature dependence of the contribution to the specific heat of the twisting motion can be calculated by quantum mechanics (see Section 10), if we know the form of the potential curve, which can be determined by the calculation of Eyring referred to above.[2]

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[2] H. Eyring, J. Am. Chem. Soc. **54, 3191** (**1932**).

The result of this calculation[3] was in good agreement with the experimental material of Eucken and Weigert[4] and thus the most fundamental problem of the internal rotation seemed to be solved.

However, as we shall see in Section 10, a more accurate determination of specific heat has required the height of the potential barrier to be about 3 kcal./mole which is about ten times as large as that obtained by Eucken and Weigert. We have to consider, therefore, that the calculation of the interaction energy between the two methyl groups of ethane is far more complicated than would appear at first sight. Such being the case, it is desirable to choose other kinds of molecules, for example, 1,2-dihalogenoethane, $XH_2C{-}CH_2X$, for which the interaction between the two halogen atoms might play a much more important part than that between two hydrogen atoms or that between hydrogen and halogen atoms. This seemed quite reasonable in the earlier stages of the investigation of the internal rotation, since as stated above, the interaction between two hydrogen atoms of different methyl groups of ethane was considered to be small.

Therefore, many researchers considered at that time that the internal rotation of 1,2-dihalogenoethanes could be discussed by means of a simple potential function with one potential minimum at the position at which the two halogen atoms are at the farthest distance apart. From the experimental point of view the halogenated ethanes have several advantages over ethane itself: for example, we can apply the dielectric measurement which is the simplest experimental method for attacking the internal rotation problem of such a kind of molecule. Let us first discuss the results of such measurements on 1,2-dihalogenoethanes as earlier studies in this field.

2. Earlier Studies on Dihalogenoethanes

The molecular configuration of 1,2-dihalogenoethanes, $XH_2C{-}CH_2X$, with two like halogen atoms on different movable groups has a center of symmetry, when these two halogen atoms are at the greatest distance apart (see Fig. 1.2). We shall call this configuration the *trans* form and take the origin of the azimuthal angle θ of internal rotation at this position. It is evident that the dipole moment of this configuration is zero while that of any other configuration is finite. It is also evident that the value of the

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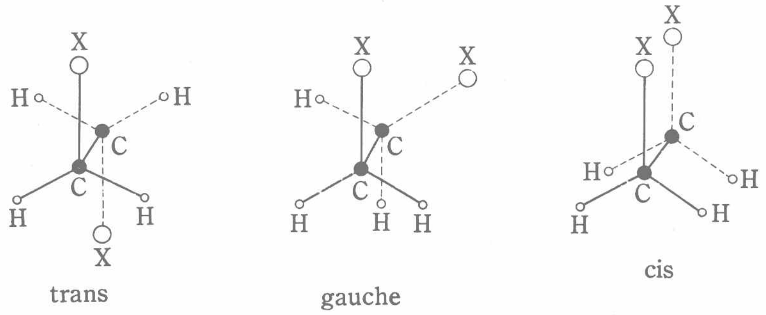
[3] E. Teller and K. Weigert, Nachr. Göttingen Ges., 218 (1933).

[4] A. Eucken and K. Weigert, Z. phys. Chem. **B 23**, 265 (1933).

dipole moment increases with increasing angle of internal rotation, until it reaches the maximum at the *cis* position, in which all the atoms of one movable group eclipse the same kind of atoms of the other group as viewed along the C–C axis.



trans gauche cis

Fig. 1.2. The configurations of $XH_2C–CH_2X$ as viewed along the C–C axis.

According to the experimental results of the earlier investigations in this field[5–9], the apparent moment of 1,2-dihalogenoethanes increases with rising temperature (see Table 1.3). We can, therefore, consider that the *trans* form is the most stable form and as a result of increased thermal energy the molecule tends to take a configuration with larger azimuthal angle θ of internal rotation, as the temperature is raised.

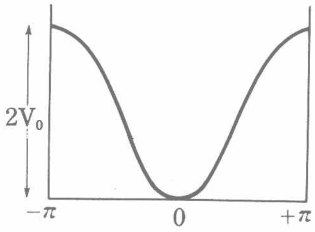


Fig. 1.3. A simple potential curve of internal rotation.

Let us first consider only the interaction between the two $C-X$ groups and assume a potential function for the internal rotation which has only one potential minimum at the *trans* position at which we take the origin of azimuthal angle θ (see Fig. 1.3).

$$V = V_0 (1 - \cos \theta) \tag{1.1}$$

Here $2V_0$ denotes the energy difference between the *cis* and the *trans* forms. Starting from such a simple potential function Mizushima and Higasi[9]

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[5] L. Meyer, Z. physik. Chem., **B 8**, 27 (1930).

[6] C. P. Smyth, R. W. Dornte and E. B. Wilson, J. Am. Chem. Soc. **53**, 4242 (1931).

[7] C. T. Zahn, Phys. Rev. **38**, 521 (1931).

[8] E. F. Greene and J. W. Williams, Phys. Rev. **42**, 119 (1932).

[9] S. Mizushima and K. Higasi, Proc. Imp. Acad. Tokyo, **8**, 482 (1932).

calculated the apparent moment of 1,2-dihalogenoethanes, $XH_2C{-}CH_2Y$, as follows:

Let μ_x and μ_y be the group moments of CH_2X and CH_2Y, repectively, both of which make an angle α with $C-C$ axis (see Fig. 1.4). Then the dipole moment μ of a configuration* with azimuthal angle θ can be calculated as follows:

$$\mu^2 = (\mu_x - \mu_y)^2 + 2\,\mu_x \mu_y \sin^2\alpha\,(1 - \cos\,\theta)$$

The probability that a molecule has the moment value μ is given by the Boltzmann law as

$$e^{-\frac{V_0(1-\cos\theta)}{kT}}$$

Hence we obtain as the average square moment of the molecule at temperature T^0K:

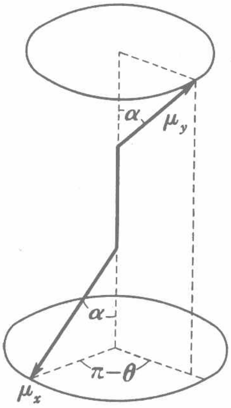

Fig. 1.4.

$$m^2 = \frac{\int_{-\pi}^{+\pi} \mu^2\, e^{-\frac{V_0(1-\cos\theta)}{kT}}\, d\theta}{\int_{-\pi}^{+\pi} e^{-\frac{V_0(1-\cos\theta)}{kT}}\, d\theta}$$

$$= (\mu_x - \mu_y)^2 + 2\,\mu_x\mu_y \sin^2\alpha \left[1 - \frac{\int_{-\pi}^{+\pi} \cos\theta\, e^{-\frac{V_0(1-\cos\theta)}{kT}}\, d\theta}{\int_{-\pi}^{+\pi} e^{-\frac{V_0(1-\cos\theta)}{kT}}\, d\theta} \right]$$

If we put $-\frac{V_0}{k\,T} = i\,z$, then the integrals can be transformed into Bessel's form and we have:

$$m^2 = (\mu_x - \mu_y)^2 + 2\,\mu_x\mu_y \sin^2\alpha \left[1 + \frac{i\,J_1\left(i\,\frac{V_0}{kT}\right)}{J_0\left(i\,\frac{V_0}{kT}\right)} \right] \tag{1.2}$$

where J_1 and J_0 denote the Bessel functions of the order 1 and 0, respectively, In the case $\mu_x = \mu_y = \mu_0$ this formula is reduced to

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* This is the configuration in which the projections of two moments on a plane perpendicular to $C-C$ axis make angle $\pi - \theta$.

$$m^2 = 2\mu_0^2 \sin^2 \alpha \left[1 + \frac{i\,J_1\left(i\,\frac{V_0}{k\,T}\right)}{J_0\left(i\,\frac{V_0}{k\,T}\right)} \right]. \qquad (1.3)^*$$

To obtain a theoretical value of m, it is necessary to know the values of μ_x, μ_y, α and V_0. In the first approximation we can put μ_x or μ_y equal to the moment of the corresponding methyl halide, its direction coinciding with the bond direction linking carbon to halogen. The angle α is therefore, equal to 70°, the tetrahedral structure of carbon valency being assumed.

V_0 is now the only parameter to be determined. This can be calculated from the experimental values of m, using Equations (1.2) and (1.3) and the validity of these equations can be shown by obtaining values of V_0 constant over the whole range of temperature.

Among the values of dipole moments of methyl halides determined by many authors, we shall use the following most probable ones — 1.85 D for CH_3Cl, 1.80 D for CH_3Br and 1.65 D for CH_3I.** Using these values of μ_x and μ_y and putting $\alpha = 70°$ as above, we can obtain a series of constant values of V_0 for each observed values of m in a definite solvent. In Table 1.2 are collected the mean values of V_0 thus obtained.

TABLE 1.2

The values of $V_0 \times 10^{14}$ (in ergs) in various solvents

Solvent	ε	$ClH_2C–CH_2Cl$	$ClH_2C–CH_2Br$	$BrH_2C–CH_2Br$	$IH_2C–CH_2I$
Vacuum	1.00	11.12	13.37	16.85	—
Hexane	1.90	8.13	10.83	—	41
Heptane	1.93	7.83	10.82	14.80	—
Amylene	2.06	7.64	—	—	—
Ethyl ether	4.37	6.65	—	—	—

We shall show in Table 1.3 how the calculated moments (m_{calc}) obtained by substituting these values of V_0 (of Table 1.2) into Equations (1.2) and (1.3) coincide with those observed (m_{obs}).

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* The limiting value of the moment m of the molecule, when $V_0 = 0$ or when there is complete freedom of rotation is evidently

$$m = \sqrt{2}\,\mu_0 \sin a$$

which is identical with the equation derived by Williams for the case of two freely rotating dipoles. See J. W. Williams, *Z.* physik. Chemie **138**, **75** (**1928**).

** D is the Debye unit equal to 10^{-18} e. s. u.

TABLE 1.3

Comparison of observed and calculated moments*

(a) $ClH_2C \cdot CH_2Cl$

Gaseous state			Hexane solution			Heptane solution		
T	m_{obs} (D)	m_{calc} (D)	T	m_{obs} (D)	m_{calc} (D)	T	m_{obs} (D)	m_{calc} (D)
304.95	1.12	1.15	223	1.13	1.15	223	1.16	1.17
341.03	1.24	1.23	248	1.21	1.22	243	1.24	1.23
376.25	1.32	1.30	273	1.30	1.29	263	1.31	1.29
419.00	1.40	1.38	298	1.36	1.36	283	1.36	1.34
456.96	1.45	1.44	323	1.42	1.42	303	1.41	1.39
479.82	1.48	1.47				323	1.42	1.44
484.82	1.48	1.48						
543.66	1.54	1.57						

Amylene solution			Ethyl ether solution		
T	m_{obs} (D)	m_{calc} (D)	T	m_{obs} (D)	m_{calc} (D)
223	1.22	1.20	213	1.25	1.26
248	1.29	1.28	223	1.29	1.29
273	1.33	1.34	233	1.32	1.33
293	1.38	1.39	243	1.35	1.35
			253	1.39	1.39
			263	1.43	1.42
			273	1.45	1.44
			283	1.48	1.47
			293	1.51	1.49

(b) $ClH_2C \cdot CH_2Br$

Gaseous state			Hexane solution			Heptane solution		
T	m_{obs} (D)	m_{calc} (D)	T	m_{obs} (D)	m_{calc} (D)	T	m_{obs} (D)	m_{calc} (D)
338.93	1.08	1.08	248	0.95	1.03	223	0.93	0.96
368.22	1.12	1.14	273	1.04	1.08	243	0.99	1.01
405.28	1.19	1.20	298	1.14	1.14	263	1.06	1.05
435.60	1.27	1.25	323	1.21	1.19	283	1.12	1.10
						303	1.21	1.15
						323	1.20	1.19
						343	1.20	1.23

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* Most of the experimental values are taken from the measurement of Mizushima, Morino and Higasi, Sci. Pap. Inst. Phys. Chem. Res. Tokyo, **25**, 159 (1934); Physik. Z. **35**, 905 (1934). The moments observed by other authors (Smyth, Zahn, etc.) are recalculated by using the following values of $P_E + P_A$: (23.9 for $C_2H_4Cl_2$, 26.9 for C_2H_4ClBr, 29.9 for $C_2H_4Br_2$ and 39.9 c. c. for $C_2H_4I_2$).