Intra-Molecular Rotation in Organic Compounds.

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AMONG the movements that the atoms can perform inside a molecule, that which is of special interest to the organic chemist is the so-called " inner rotation," *i.e.*, the rotation of molecular parts about each other. The degree of this internal freedom is also of great significance in the study of the physical properties of molecules, such as dipole moments and specific heats: thus in any quantitative calculation of the specific heat of a molecule from the data on the fundamental oscillation frequencies provided by Raman spectra, the degree of internal rotation must also be taken into consideration. It was one of the fundamental assumptions in organic chemistry that atomic groups bound by double or triple bonds could not rotate about each other, but when they were joined by only a single bond a free rotation should be expected. The limitations of this concept have been made evident from two typical investigations. L. Ebert[1] has shown that *cis* and *trans* ethylene isomers can change each into the other at temperatures not by any means high, and reach an equilibrium state. On the other hand, by the resolution of diphenyl derivatives containing two or more substituents in the 2 2′ 6 6′ positions, into optical antipodes by Mills, Adams and others,[2] it has been shown that the rotation about a single bond is not always free, but can be strongly restricted through the influence of substituents. The point is thus clear that rotation about any bond is a possibility and that rotation about each type of bond can be restricted to different extents according to the conditions prevailing inside the molecule. In recent years* the mathematics of quantum and wave mechanics have been applied to this problem by Mullikan,[3] Slater,[4] Pauling,[5] Hückel,[6] Dunkel,[7] Penney,[8] and Penney and Sutherland.[9] Summary reviews of this subject from special points of view have also been very recently published.[10]

The causes for restriction of rotation can be classified into (*a*) steric forces, (*b*) multiple bonds, and (*c*) energy troughs. In general the mechanism for the restriction of rotation is that the potential energy between the rotating parts of the molecule is not independent of the angle of rotation, but changes with it. Let us take a simple case where the potential energy-angle of rotation curve has the shape shown in Fig. 1
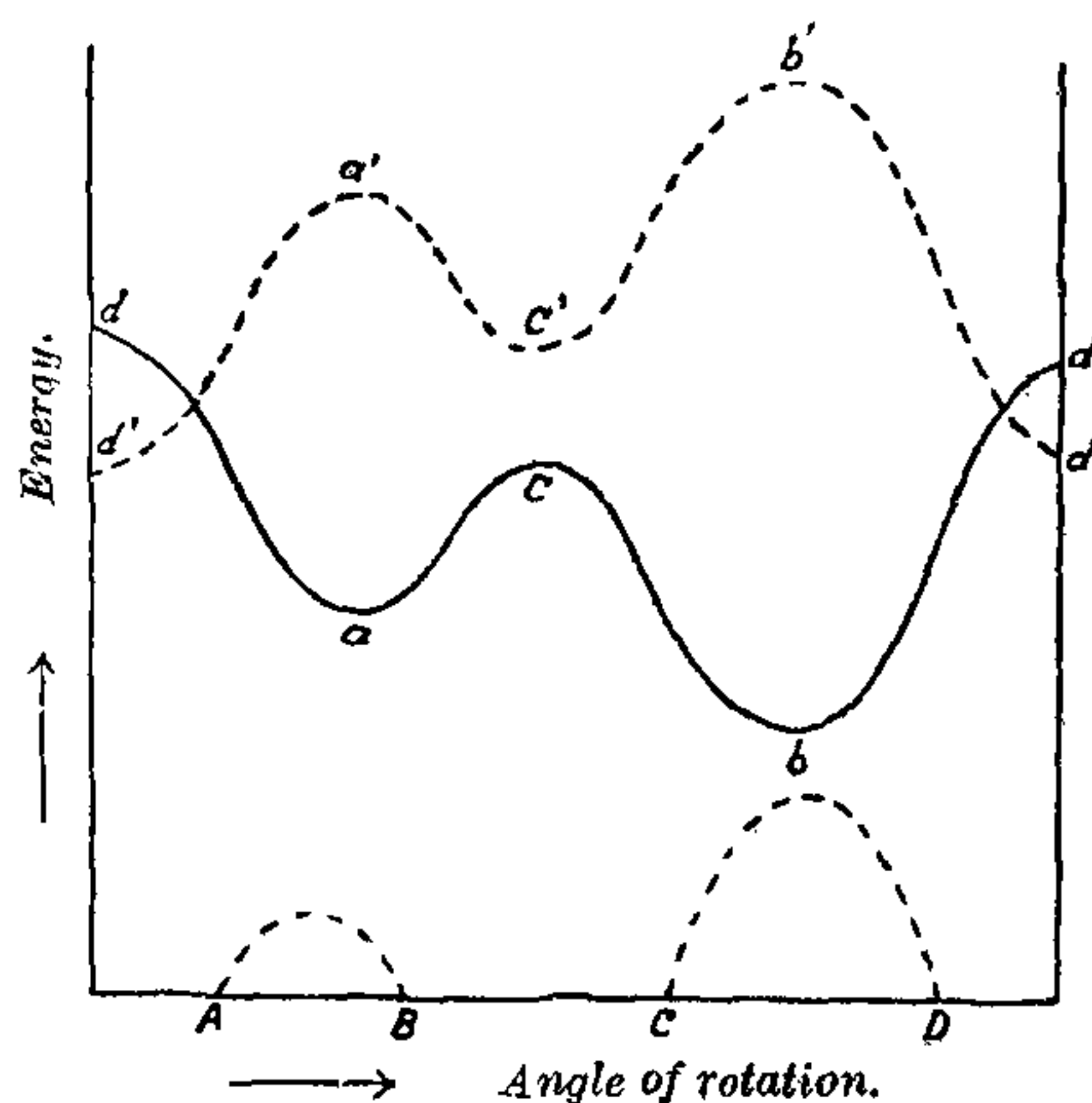

Angle of rotation.

Fig. 1.

(*d a c b d*), with two energy minima *a* and *b*. At a particular high temperature, the kinetic energy of the rotating parts of the molecule can be represented by the dotted line *d′ a′ c′ b′ d′*. Such a line will have a maximum where the potential energy has a minimum, and represents a fully developed rotation. When the temperature is reduced the line of kinetic energy will sink,

[1] L. Ebert and R. Bull, *Z. Physikal Ch.* (A), 1931, **152**, 451.

[2] R. Adams, *Chemical Rev.*, 1933, **12**, 261.

* One of the earliest attempts at a quantitative interpretation of intra-molecular rotation seems to be that of H. Sachse, *Z. Physikal Ch.*, 1893, **11**, 185.

[3] R. Mullikan, *Phys. Rev.*, 1933, **43**, 279.

[4] J. C. Slater, *Ibid.*, 1931, **37**, 481.

[5] L. Pauling, *J. Amer. Chem. Soc.*, 1931, **53**, 1367.

[6] E. Hückel, *Z. Physik.*, 1930, **60**, 423.

[7] M. Dunkel, *Z. Physikal Ch.* (B), 1930, **7**, 81.

[8] W. G. Penney, *Proc. Roy. Soc.*, 1934, **144**, 166; *Proc. Phys. Soc.*, 1934, **46**, 333.

[9] W. G. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.*, 1934, **2**, 492.

[10] P. C. Henriquez, *Chem. Weekblad.*, 1934, **31**, 2. E. Hertel, *Z. Elektrochem.*, 1934, **40**, 105. H. Mark, *Ibid.*, 1934, **40**, 421.

and at some low temperature there will be points where the kinetic energy is zero (A. B, C and D). The rotation is then no more fully developed, and the points A, B, C and D represent inversion points. There will be now only oscillations about the minima a and b. As all the molecules do not have the same "temperature" at any instant of time, there will be a mixture of molecules with small oscillations, with large oscillations, and with fully developed rotation. The intra-molecular rotations will be quantised. The lower the temperature becomes the more the molecules with small oscillations will predominate; quantitatively this can be expressed by the Maxwell-Boltzmann law of distribution. If the average oscillations about a and b are very small, we can speak of two isomers, "rotation isomers", the one characterised by the minimum a and the other by the minimum b. The velocity with which these isomers can pass into one another is determined by the energy levels c and d, and the equilibrium between them by the energy difference $\triangle U$ between a and b.

STERIC FORCES.

Steric force is a better and more precise name given to the organic chemist's mechanical concept of steric hindrance. From a large amount of systematic and semi-quantitative work,[2] chemists have come to the conclusion that in ortho-substituted diphenyl derivatives, the rotation of the two benzene rings is restricted not by the number but by the size of the substituents. The dipole moments of a series of simple di-substituted diphenyl derivatives have been recently measured[11] in order to study quantitatively the nature and degree of restriction of rotation. Weissberger[12] believes that London forces of attraction between substituents even though of the same sign, come into play when they are near enough together, and thus contribute to the restriction of rotation. The question, however, is complicated on account of the still unknown nature of electronic shifts from one ring to the other. The existence of yet another reason for the reduction of

freedom of rotation in the diphenyls will be referred to later.

Another case of restriction of free rotation by steric forces is to be found in compounds of the type Ca_4, where a is a non-axial symmetric substituent of the type CH_2OH, OC_2H_5, CH_2ONO_2, CH_2Br, etc. If a complete free rotation of such substituents about the four tetrahedral valencies of the central carbon atom were possible, then the moment of the molecule will not be zero but will have a definite value[13] given by $\sqrt{4\mu^2{}_k} = 2\mu_k$ where μ_k is the component of the group moment perpendicular to the axis of rotation. However since some of the compounds like $C(CH_2Br)_4$ have zero moment, and the moments of the other compounds do not change with temperature, it is generally concluded that due to lack of space for complete rotation or to the high intra-molecular fields, the groups in these molecules do not freely rotate but take up definite oriented positions.[14]

It would appear that free rotation is also annulled in the crystal state. The magnetic susceptibility measurements of Krishnan[15] and X-ray studies of Hertel[16] have shown that in di-, ter- and quater-phenyls, the benzene rings all lie in one line fixed in definite relative positions in the same plane. This phenomenon of fixing the rings in the crystal state shows interesting possibilities.[17] Thus, m m' diphenyl, although it cannot occur as stable *cis* and *trans* isomers can be fixed by suitably crystallising the substance in these two isomeric forms. Probably on account of the still feeble forces between the two m m' substituents a *trans* form will be more exclusively obtained; but a 3 3′ 5 5′ tetra substitued compound should be capable of being more easily fixed in the two isomeric forms. Such an isomerism would belong to the type called "crystal lattice isomerism", that has been particularly studied by Hertel[18] and others in a different case of inter-molecular compounds.

[11] A. Weissberger and S. Sangewald, *Z. Physikal Ch.* (B), 1933, 20, 145; *Trans. Farad. Soc.*, 1934, 30, 884.

     E. Naeshagen, *Z. Physikal Ch.* (B), 1934, 25, 157.

[12] A. Weissberger, *Trans. Farad. Soc.*, 1934, 30, 852.

[13] W. Hückel, *Z. Physikal Ch.* (B). 1929, 2, 451. C. T. Zahn. *Physical Z.*, 1932, 33, 400.

[14] L. Ebert, *Leipziger Vortrage*, 1929, 65.

[15] K. S. Krishnan, B. C. Guha, and S. Banerjee, *Phil. Trans. Roy. Soc.* (A), 1933, 231, 235.

[16] E. Hertel and G. H. Romer. *Z. Physikal Ch.* (B), 1933, 21, 292; 23, 226.

[17] E. Hertel, *Z. Elektrochem.*, 1934, 40, 407.

[18] E. Hertel, *Z. Elektrochem.*, 1931, 37, 536. E. Hertel and G. H. Romer, *Z. Physikal Ch.* (B), 1932, 19, 288.

Interesting in this connection is the problem of restricted rotation about a single bond in a closed ring which does not seem to have been submitted to theoretical or otherwise quantitative investigations. Sachse[19], and Mohr[20] have postulated a restricted rotation in the cyclohexane ring so that an alternation between the *cis* and *trans* forms of this compound is possible. From his electron interference measurements Wierl[21] concludes that cyclohexane is an equilibrium mixture of the *cis* and *trans*, or what are more picturesquely called boat and chair forms. The measurements by O. Hassel[22] of the dipole moments of cyclohexane derivatives have yielded no definite conclusions. Le Fevre,[22] however, regards that the observed moment of 1 : 4 cyclohexadione is in agreement with a dynamic equilibrium between the *cis* and *trans* forms: and K. L. Wolf[23] has sought to explain the very high negative Kerr constant (−713) of paraldehyde on the basis of the *cis* and *trans* forms of the molecule.

MULTIPLE BONDS.

The power of the double bond between carbon and carbon, or carbon and nitrogen to completely hinder free rotation about it so that only two stable equilibrium positions exist *cis* and *trans*, or *syn* and *anti*, is well known. The precise electronic mechanism which prevents the free rotation about the double bond has been worked out by Mulliken,[4] Hückel[6] and Penney[8]. However, on account of the considerable polarisability of the double bond compared to a single bond, this restricting power of the double bond is susceptible to strong modifications by the presence of substituents. The power for each specific case can be expressed in the shape of a potential energy-angle of rotation curve, which will have a form shown in Fig. 2 with two deep and sharp minima 180° apart. The height of the energy barrier between them could be calculated theoretically for some simple cases,[8] or derived from various physical measurements. Thus from a study of reaction kinetics, in the case of

the fumaric and maleic acids Höjendahl[24] found a value of 15·8 k. cal. per mol, and in the case of dimethyl maleate and fumarate
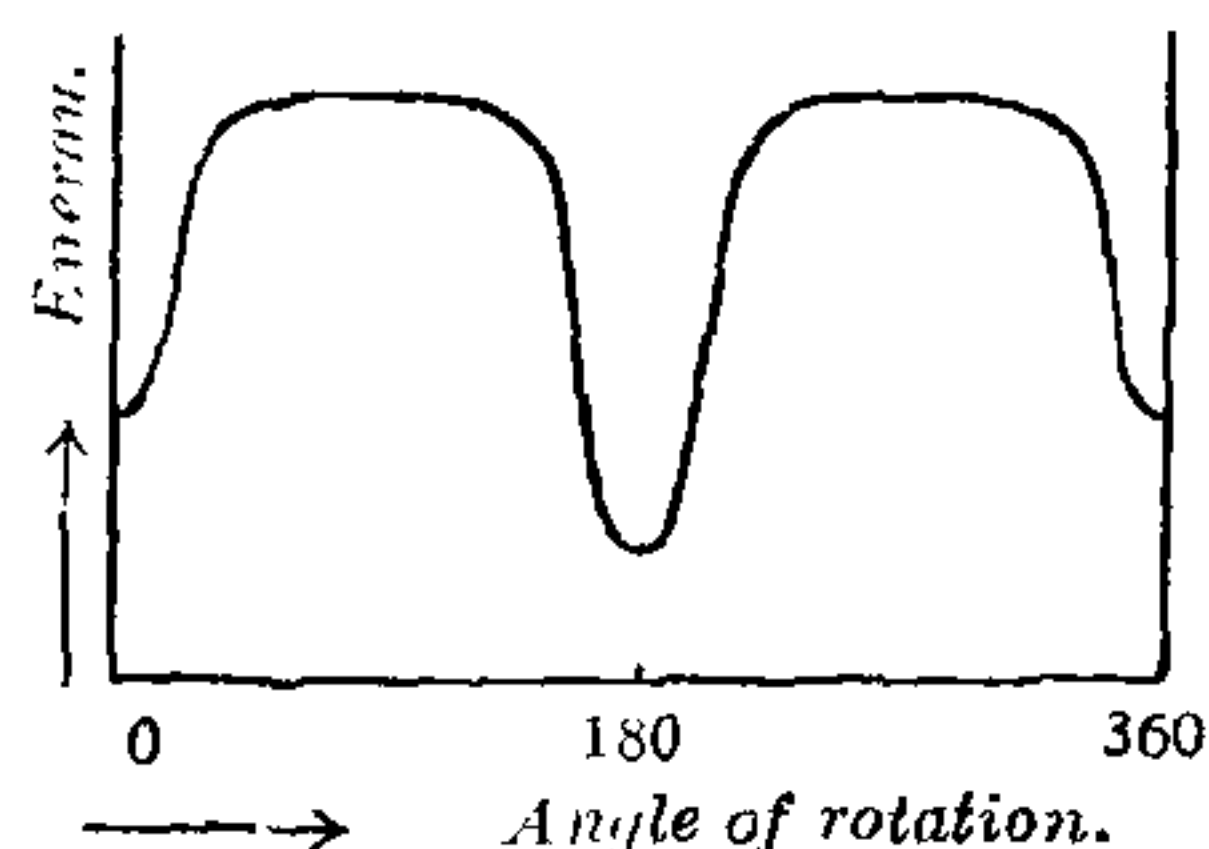

Fig. 2.

Nelles and Kistiakowsky[25] found a value 26·5 k. cal. Again from the fundamental twisting frequency for ethylene[26] the value of the energy barrier between the *cis* and *trans* forms could be estimated[27] to be about 30 k. cal. Ebert and Bull[28] find that at a temperature of 300°C., this energy barrier could be crossed over in the case of the symmetrical dichlor ethylenes. It was also observed that the *cis* form was the more stable of the two, the equilibrium mixture at this temperature consisting of 65% *cis* and 35% *trans*, and the energy difference between the two was estimated as 530 cal./mol. Although this result is contrary to what one would expect from the dipole forces alone, when other influences are taken into consideration[29] such as the London attraction (dispersion effect) between the substituent atoms, and the polarisation of the double bond by the strong field density produced by them in the *cis* position (induction effect), it could be shown that the observations stand theoretically supported. In as much as the induction effect on the double bond for the *cis* compound is very pronounced, it will be interesting to co-relate this with the observed[30] differences in the intensity and magnitude of the C=C frequencies given by the Raman spectra of these two isomers.

[19] H. Sachse, Z. *Physikal Ch.*, 1892, **10**, 203; *Ber.*, 1890, **23**, 1365.

[20] E. Mohr, *J. Praktisch Ch.*, 1918, **98**, 315.

[21] R. Wierl, *Ann. der Physik.*, 1931, **8**, 559; 1932, **13**, 453.

[22] O. Hassel, *Trans. Farad. Soc.*, 1934, **30**, 878. R. J. W. Le Févre, *Ibid.*, p. 874.

[23] K. L. Wolf, *Leip. Vortrage*, 1929, 129.

[24] K. Höjendahl, Z. *Phys. Chem.*, 1924, **28**, 758.

[25] M. Nelles and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, 1932, **54**, 2208; Z. *Physikal Chem.*, 1931, Bodenstein Band, 369.

[26] A. Eucken and A. Parts, Z. *Physikal Ch.* (B), 1933, **20**, 192.

[27] W. G. Penney, *Proc. Phys. Soc.*, 1934, **46**, 333.

[28] L. Ebert and R. Bull, Z. *Physikal Ch.* (A), 1931, **152**, 451.

[29] H. A. Stuart, *Physikal Z.*, 1931, **32**, 793.

[30] Bonino and Brul, Z. *Phys.*, 1929, **58**, 194. M. Pestemer, *Wiener Ber.*, IIA, 1930, **139**, 667.

ENERGY TROUGHS.

In contrast to the double bond the charge distribution in a single bond has a rotation symmetry, and a completely unhindered free rotation should be expected provided there is no interaction between the substituents or between the substituents and the carbon atoms. This ideal case is almost non-existent in the whole field of organic chemistry. Thus Penney[s] has shown that even in the simplest case of ethane, both by the H–L–P–S, and H–M methods of approximation, there will be free rotation of the CH_3 groups around the C–C axis *only* if the interactions of any H atom with the distant C and H atoms are neglected. When, however, the H–H interactions are allowed for, the azimuth ϕ around the C–C axis of one CH_3 group with respect to the other will appear implicitly in the H–H exchange integrals, and the energy will be no more independent of ϕ. The general form of the energy curve can have a number of maxima and minima or energy troughs. Koenig[31] has considered the dynamics of a very general case where the potential field has n maxima and minima in the range $0 \leqslant \phi \leqslant 2\pi$; and, Eyring[32] has calculated the complete shape of the curve for the case of ethane, and finds three maxima corresponding to three paired hydrogen positions and the accompanying three minima corresponding to the *trans* positions of the hydrogen atoms. The separating energy wall is only 350 cal./mol. so that at room temperature, where the mean energy $RT \sim 600$ cal./mol the molecule can go from one trough to another and execute a complete rotation. But if the temperature is lowered this should be no more possible, and the molecule can perform only oscillations about the energy minima. Eucken and Weigert[33] have been actually able to show from measurements of molar heat over a large range of temperatures down to $143°T$, that at low temperatures ethane behaves as a restricted one dimensional rotator, performing only oscillations about a minimum energy point. If a complete free rotation were possible then at these low temperatures, where the other inner degrees of freedom are not yet deve-

loped, the specific heat should be $6+1=7$ calories, while actually it is of the order $7 \cdot 4$: this excess is due to the oscillatory motion which has two degrees of freedom one for the potential energy and another for the kinetic energy. By a simultaneous comparison with the specific heat of ethylene, where there is no inner rotation possible, the increase in specific heat over a free rotating model can be quantitatively accounted for if the potential energy barrier is taken as 350 cal./mol. a value which agrees beautifully with that calculated by Eyring. At room temperatures only about 50% of the molecules have any inner rotation, and among them 45% have quantum number 1 (*i.e.*, oscillation) and 5% quantum number 2 (*i.e.*, free rotation).

In the case of substituted ethanes, the energy curve will be more complicated, the energy minima being of different depths and occupying different positions. An instance where this curve has been worked out in some detail is that of symmetrical dichlorethane.[34] The calculated relation between the distribution of the molecule into its various energy levels, and the effective dipole moment at different temperatures,[35] has been substantiated by careful experimental work,[36] and *vice versa*, from the experimental values of moment, the magnitude of the intra-molecular forces have been estimated. A considerable volume of work has been turned out regarding the possible degrees of rotation inside molecules and their bearing on the observed dipole moments, ever since the first papers on this subject were published by Höjendahl and Williams.[37]

[34] E. H. L. Meyer, *Z. Physikal Ch.* (B), 1930, **8**, 27.
C. P. Smyth, R. W. Dornte and E. B. Wilson, *J. Am. Chem. Soc.*, 1931. **53**, 4242.
[35] S. Mizushima and K. Higashi, *Proc. Imp. Acad., Tokyo*, 1932, **8**, 482.
J. E. Lennard Jones and H. H. M. Pike, *Trans. Farad. Soc.*, 1934, **30**, 830.
J. M. Sturtevant, *J. Am. Chem. Soc.*, 1933, **55**, 4178.
[36] E. W. Greene and J. W. Williams, *Phys. Rev.*, 1932, **42**, 119.
M. A. Govinda Rau and B. N. Narayanaswamy, *Proc. Ind. Acad. Sci.*, 1934, **1**, 14.
S. Mizushima and K. Higashi, *loc. cit.*
[37] J. W. Williams, *Z. Physikal Ch.*, 1928, **138**, 75.
K. Höjendahl, *Physical Z.*, 1929, **30**, 391.
C. T. Zahn, *Ibid*, 1932, **33**, 400, 529, 730, 1933, **34**, 570.
C. P. Smyth and S. E. Kammerling, *J. Am. Chem. Soc.*, 1931, **53**, 2988.
P. C. Henriquez, *loc. cit.*

[31] H. D. Koenig, *Phys. Rev.*, 1933, **44**, 657.
[32] H. Eyring, *J. Amer. Chem. Soc.*, 1932, **54**, 3191.
[33] A. Eucken and K. Weigert, *Z. Physikal Ch.* (B), 1933, **23**, 265.
C. Wagner, *Ibid.* (B), 1931, **14**, 166.
L. Ebert, *Leip. Vortrage*, 1929, **44**.

The existence of oscillations about a position of minimum energy has also been substantiated by X-ray interference diagrams.[38] Evidences for such positions of minimum energy seem also to be obtained from the Raman spectra of a number of molecules, and are neatly marshalled out in one of Kohlrausch's recent reviews.[39] However, the possibilities of these physical measurements to yield more quantitative informations regarding the intra-molecular rotation, have not been completely investigated.

When the two rotating parts are sufficiently separated as by introducing a benzene ring between them, the energy barriers can be smoothed down, and complete rotations made possible: such instances are to be found in p-xylylene dichloride, p-quinone dimethyl ether, etc.[40]

If there are more than one substituent in each of the methyl groups of ethane, there will be in general three pronounced energy minima, with appreciable energy barriers, and at low temperatures there will be a mixture of three rotation isomers, characterised by three equilibrium positions. Wolf[41] has shown that such rotation isomers exist in the case of tartaric acid and dibenzyl derivatives, which are symmetrically substituted ethane compounds of the type

$$a\!\!\searrow\!\!b\!\!=\!\!c\!\!-\!\!c\!\!\searrow^{n}_{\,}\!\!\searrow_{c}$$
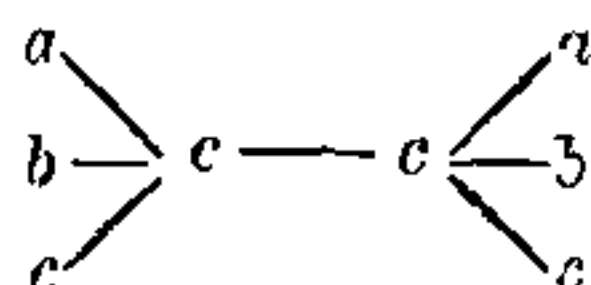
In the meso form of these compounds the substituents a, b and c are so placed that all three can simultaneously occur in the *cis* or *trans* positions, while in the optically active form they cannot do so. If a complete free rotation were possible about the C–C link, both forms of the molecule will have identical moment. As this is not the case, and the active form has in general a higher moment (at the ordinary temperatures) than the meso form, it is obvious that in the latter the molecule tends to get fixed more in the completely *trans* position. Thus at T=0, the meso form will be fixed in this position, and the moment will be zero,

while for the active form the moment will be a finite value—(since all *trans* positions cannot simultaneously occur). As the temperature is increased, on account of the fact that in the meso all the *cis* positions are simultaneously possible, the moment will reach a higher maximum than the *cis*, and the two curves representing moment *vs.* temperature will be separate and cross each other at some particular point. If we regard each form to consist of three isomers in equilibrium, with different optical rotations, then as the temperature rises the ratios between the isomers will shift and thus also the total optical rotation. Now, Lucas[42] has shown that in order that the rotation *vs.* temperature curve should have a maximum there should be at least three isomers present. In the case of ethyl tartrate an actual maximum has been observed. Further measurements on change of rotation with concentration also support the existence of three isomers. These evidences are, however, not altogether quantitative, as the influence of solvent. etc., have also to be taken into consideration.

Recent ideas regarding several possible canonical structures for one and the same molecule existing in a state of quantum mechanical resonance[43] have raised interesting possibilities, as certain bonds which are single in the ordinary structures are double in some others and thus acquire in part the properties of a double bond and *vice versa*. Problems connected with this have been recently discussed by Sutton[44] and Zahn[45]. Sidgwick[46] has, however, questioned the validity of some of the assumptions made although they may be mathematically correct. Another result of the resonance or the interference between the electronic clouds of a pair of singly linked atoms is the possibility of preferred angular positions, such as the highly unsymmetrical skew structures postulated by Penney and Sutherland[27] for H_2O_2 and N_2H_4.

An interesting possibility of the intramolecular rotation is the resulting shape of long chain molecules containing a series of C—C links. If there are two dipoles, each of moment m, at the two ends, one end

[38] F. Erhardt, *Physikal Z.*, 1932, **33**, 605.

[39] K. W. F. Kohlrausch, *Naturwiss.*, 1934, **22**, 166. *Z. Physikal Ch.* (B), 1932, **18**, 61.

[40] A. Weissberger and R. Sangewald, *Physikal Z.*, 1929, **30**, 792.

[41] K. L. Wolf and W. Bodenheimer, *Zeit. Physik. Chem.*, 1931, Bodenstein band, 620.

[42] R. Lucas, *Trans. Farad. Soc.*, 1930, **26**, 418.

[43] L. Pauling and J. Sherman, *J. Chem. Physics*, 1933, **1**, 606, 679.

[44] L. E. Sutton, *Trans. Farad. Soc.*, **1934**, **30**, 789.

[45] C. T. Zahn, *Ibid.*, 1934, **30**, 804.

[46] N. V. Sidgwick, *Ibid.*, 1934, **30**, 821.

moment can set itself in any direction independent of the other, and the resulting moment of the molecule will be $\sqrt{2}\ m$ irrespective of the number of links above a certain limit. This has been experimentally observed.[47] Recently Kuhn[48] has calculated the shape of such molecules to be that of a bean the ratio of whose axes are 6 : 2·3 : 1. Further the electron interference measurements with 1,5-dichlorpentane[49] show that in this case the distance between the end chlorine atoms cannot be defined.

Much of the above review shows how general is the phenomenon of intra-molecular rotation and how our ideas about it are still very qualitative. There is certainly ample scope for precise and quantitative investigations in this field.

Study of Plant Tissue Fluids.*

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CHEMICAL INVESTIGATIONS.

A CHEMICAL study of the plant sap usually consists of a proximate analysis of the more important constituents, like total solids, total ash, total and amino nitrogens, sugars and ash constituents particularly P, K and Ca. In special cases, a determination of some definite constituent pertinent to the investigation, is carried out. In a study of the nature of rust resistance in wheat, Newton and Anderson[114] have determined the phenol content in the press juice of wheat plants varying in rust resistance. Link and others[115] have determined protocatechuric acid in the pigmented variety of onions, which is reputed to resist the fungus disease known as the onion smudge. Power and Chesnut[116] have examined the odorous constituents of the cotton plant, ammonia and trimethyl amine as the possible attractants of the boll-worm. Those varieties of cotton whose content of these constituents is low, are the ones more resistant to the attack of the boll-worm.

For most of the routine estimations, the centrifuged sap can be directly employed but for the estimation of certain constituents like sugars, phenols, a suitable method of clarification has to be adopted, with a view to eliminate substances interfering with the reaction. Immiscible solvents like ether or chloroform can be employed for extracting the constituent from the sap; sometimes a preliminary separation of the associated impurities by precipitating them out with a miscible solvent like alcohol or acetone facilitates subsequent processes of purification. This is elegantly achieved by absorbing the sap on a filter pad or pulp[117] and extracting the impregnated mass with alcohol or acetone

There are other physical methods of fractionating the sap into groups of constituents, which are helpful in the isolation of certain constituents; ultra-filtration, for example, will effect a separation of the sap roughly into two portions, the filtrate containing mostly the crystalloidal constituents of the tissue fluid. The advantage of such a fractionation lies in the fact that both the ultra-filtrate and the residue are obtained in a "pure" state without any admixture of adsorbents, solvents or salts. Electro-ultra-filtration also can be employed with advantage in many instances, to ensure a greater rapidity of separation. The application of such colloid chemical technique has not been extensively employed in a study of the plant tissue fluids.

A line of investigation which has received little attention is the assay of the tissue fluids from the viewpoint of its dynamic nature. It is determined by the presence of the reactive groups on the one hand, and the agents catalysing certain reactions on the other. The reactive groups, aldehydic, ketonic, amino, sulphydryl, hydroxyl, phenolic, carboxyl, can easily be estimated chemically while the existence of the biochemical catalysts present in the fluid is

[47] L. Ebert and K. Höjendahl, *Z. Physikal. Ch.* (B), 1932, 15, 74.

[48] W. Kuhn, *Koll. Z.*, 1934, 68, 2.

* Continued from *Curr. Sci.* 1934, 3, 58.

[114] Newton and Anderson, *Can. J. Res.*, 1929, 1, 85.

[115] Link *et al*, *J. Biol. Chem.*, 1929, 81, 369.

[116] Power and Chesnut, *J. Amer. Chem. Soc.*, 1925, 47, 1751.

[49] R. Wierl, *Ann. der Phys.*, 1931, 8, 521.

[117] Sreenivasaya and Sastri, *J.C.S., abst.*, 1931, A, 1342.