displacement reactions at silicon to pseudorotation of intermediates (1), rather than to the operation of the more prosaic conventional mechanisms,[69] there is at present no compelling evidence which would allow a decision between these alternatives.

As the preceding discussion demonstrates, studies dealing with the role of pseudorotation in the stereochemistry of nucleophilic displacement reactions at centers other than phosphorus are still in their infancy, and one may look forward to the exploration of divers systems[70] in coming years.

Finally, it should be emphasized that even though the pseudorotational mechanisms which form the body of this Account are quite conjectural in nature, and the evidence for them circumstantial rather than direct, they have so far yielded a consistent picture of observed stereochemical events. At least as a heuristic model they have proved remarkably successful, whatever their ultimate fate as representations of the underlying physical processes may turn out to be.

(70) For recent examples, see M. Gielen, M. De Clercq, G. Mayence, J. Nasielski, J. Topart, and H. Vanwuytswinkel, *Recl. Trav. Chim.*, **88**, 1337 (1969); G. J. D. Peddle and G. Redl, *J. Amer. Chem. Soc.*, **92**, 365 (1970); C. A. Udovich and R. J. Clark, *ibid.*, **91**, 526 (1969); J. D. Warren and R. J. Clark, *Inorg. Chem.*, **9**, 373 (1970).

Studies of Internal Molecular Motions and Conformation by Microwave Spectroscopy

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Since its inception shortly after World War II, microwave spectroscopy[1] has proved to be a powerful tool for the study of a wide variety of molecular properties. Although investigators were initially primarily concerned with the accurate determination of molecular structural parameters, research in microwave spectroscopy now encompasses many diverse areas.[2]

One area which has been particularly fruitful is the study of internal molecular motions. Although the main characteristics of a microwave spectrum are normally determined by the molecular geometry and nuclear masses, internal motions affect the spectrum in a number of ways. One way is through the phenomenon of quantum mechanical tunneling. Tunneling can occur when there are two or more equivalent molecular configurations which are interconvertible by some internal motion. Examples are rotation of a methyl group and inversion of amines. Tunneling gives rise to a splitting of some or all of the spectral lines. Since the splittings are quite sensitive to the potential function involved, they provide an accurate way of determining the potential.

Another way in which internal motions affect a spectrum is by shifting the spectral lines. This most commonly occurs through a modification of the moments of inertia. Thus while molecular rotational spectra can in many cases be analyzed as if the molecule were effectively rigid, the moments of inertia obtained always contain vibrational contributions. Although these contributions are often only of the order of 0.1%, they result in frequency shifts which are large compared to the resolution of a microwave measurement. Every vibrational state has a different set of effective moments of inertia and a distinct set of rotational transitions. For some cases, the vibrational perturbations may be sufficiently severe that the effective rigid rotor formulation no longer applies. In such instances very large frequency shifts may result.

Additional information may be obtained from the presence of separate sets of rotational lines for each vibrational state by making intensity measurements. The intensity of a transition is proportional to the number of molecules available to undergo that transition. Thus the intensity of a rotational transition in a given vibrational state is proportional to the population of the vibrational state. Since the population depends on the energy of the state through its Boltzmann factor, intensity measurements can be used to obtain vibrational energies. These energies in turn give information about the potential function governing the vibration.

Through one or more of the vibrational effects mentioned above, microwave studies have been made on internal motions of a number of molecules. The kinds of motion which have been studied so far are internal rotation about single bonds, inversion of amino groups, ring puckering in four-membered rings, and pseudorotation in five-membered rings.

(1) As used here, the term "microwave spectroscopy" means gasphase rotational spectroscopy and does not include electron magnetic resonance.

(2) For a general review of the information which can be obtained from microwave spectroscopy see (a) E. B. Wilson, *Science*, **162**, 59 (1968); (b) D. R. Lide, *Surv. Progr. Chem.*, **5**, 95 (1969).

Related to studies of internal motion, and often concomitant with them, is the determination of molecular conformation. Because of the sensitivity of microwave spectra to molecular geometry, geometrically distinct conformers which are stable appear as separate species, each with its own spectrum. On the time scale of the microwave experiment, their interconversion is slow even when chemical separation is impossible. Microwave spectroscopy has been very successful in studying rotational isomerism and the conformations of ring compounds, including six-membered and larger rings.

It is the purpose of this Account to survey the application of microwave spectroscopy to the study of molecular internal motions and conformation. Of necessity much worthy research could not be mentioned since a comprehensive review is beyond our scope, nor do we consider in detail the methods by which information is extracted. Rather we shall attempt to illustrate the types of problem which can be attacked and the kinds of information which can be obtained.

Internal Rotation about Single Bonds

Threefold Symmetric Internal Rotors. The first type of motion which was studied extensively by microwave spectroscopy was internal rotation of threefold symmetric groups, particularly methyl groups. This subject has been thoroughly reviewed[3-6] and tabulated;[6,7] we shall consider it only briefly here. The distinguishing characteristic of this type of motion lies in the threefold symmetry. The theoretical analysis is simplified since the moments of inertia and the kinetic energy are independent of internal rotation angle.[8] Also the potential function is required to have at least threefold symmetry. The internal rotation manifests itself through tunneling among the three equivalent energy minima. The rotational lines are accordingly split. The potential barrier can usually be determined from the splitting with an uncertainty of a few per cent or less. Of course, if the barrier is too high, no splitting will be resolved. For the most common case, methyl groups, the present practical upper limit is a height of roughly 4 kcal/mol. A large number of molecules have been studied,[6,7] and in general it appears that the potential function can be well represented by a simple cosine term. A great deal of theoretical effort has been devoted to calculation of the origin of such barriers, and the subject has been reviewed by Lowe[6] and by Allen.[9]

Twofold Symmetric Internal Rotors. When internal rotation involves groups with symmetry no greater than twofold, the moments of inertia are no longer independent of the torsional angle. This torsional dependence introduces complications into the theory not present in the threefold case. An analysis has been made by Quade[10] and also by Bauder and Günthard.[11]

Several molecules of this type have been investigated, with the most thoroughly studied being phenol.[12-15] The rotational lines are found to be split into doublets. The splitting arises from tunneling of the light OH group between the two equivalent energy minima which exist at the two planar conformations. From the splittings in a number of isotopic species a barrier height of 3.36 ± 0.06 kcal/mol is obtained.[15]

Another molecule with a twofold symmetric internal rotation which has been studied is benzaldehyde.[16] It is also found to have a planar conformation. However, no splitting due to tunneling is observed since the moments of inertia of the internal rotors are too large. Instead measurements were made of the intensities of transitions of molecules in excited torsional states relative to transitions of molecules in the ground state. In this way the energy of the torsional vibration was found to be 114 cm^{-1} and from this energy a barrier of 4.9 kcal/mol was calculated.

An alternate way to obtain the barrier in cases where torsional states are observed is to analyze the variation of the effective moments of inertia of the molecule with torsional quantum number. Such an analysis is possible[10] if only the torsional motion itself need be considered, with neglect of effects due to all other vibrations. For both nitrosobenzene[14,17] and benzaldehyde,[16] however, it was found that vibration–torsion interactions caused about one-half of the observed variation of the effective moments of inertia with torsional state. This illustrates the care which must be exercised in using one-dimensional models in vibrational analyses.

Asymmetrical Internal Rotors. The situation is qualitatively different when the internal rotors have no axis of symmetry.[18] A common example of this type of rotor is a substituted methyl group. The possibility now exists for energy minima with more than one value. Thus geometrically distinct conformers may be present.

The first systems to be studied involved asymmetrically deuterated methyl groups. Although the potential

(3) C. C. Lin and J. D. Swalen, *Rev. Mod. Phys.*, **31**, 841 (1959).

(4) E. B. Wilson, *Advan. Chem. Phys.*, **2**, 367 (1959).

(5) H. Dreizler, *Fortschr. Chem. Forsch.*, **10**, 59 (1968).

(6) J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 1 (1968).

(7) B. Starck, "Molecular Constants from Microwave Spectroscopy," Landolt-Bornstein, New Series, Group II, Vol. 4, Springer-Verlag, Berlin, 1967.

(8) Strictly speaking, only conformers with the same potential energy will have exactly the same moments of inertia since there may be some distortion as the molecule goes through a potential maximum. For example, the staggered and eclipsed forms of ethane probably have slightly different moments of inertia. However, this small variation is a higher order correction to the theory and is generally not considered.

(9) L. C. Allen, *Annu. Rev. Phys. Chem.*, **20**, 315 (1969).

(10) (a) C. R. Quade, *J. Chem. Phys.*, **47**, 1073 (1967); (b) J. V. Knopp and C. R. Quade, *ibid.*, **48**, 3317 (1968).

(11) A. Bauder, E. Mathier, R. Meyer, M. Ribeaud, and H. H. Günthard, *Mol. Phys.*, **15**, 597 (1968).

(12) T. Kojima, *J. Phys. Soc. Jap.*, **15**, 284 (1960).

(13) H. Forest and B. P. Dailey, *J. Chem. Phys.*, **45**, 1736 (1966).

(14) C. R. Quade, *ibid.*, **48**, 5490 (1968).

(15) T. Pedersen, N. W. Larsen, and L. Nygard, *J. Mol. Struct.*, **4**, 59 (1969).

(16) R. K. Kakar, E. A. Rinehart, C. R. Quade, and T. Kojima, *J. Chem. Phys.*, **52**, 3803 (1970).

(17) T. Hanyu, C. O. Britt, and J. E. Boggs, *ibid.*, **45**, 4725 (1966).

(18) The usual *n*-fold rotation axis C_n is referred to here. A kind of rotational symmetry may still exist, however. An example is *n*-propyl fluoride. There are two equivalent gauche forms related by an internal rotation.

function maintains threefold symmetry,[19] the kinetic energy is no longer independent of torsional angle. Furthermore, distinct species can exist. An example is acetaldehyde.[20] The equilibrium conformation is such that one methyl hydrogen lies in the heavy atom plane eclipsing the carbonyl bond while the other two methyl hydrogens are above and below the plane. Thus there are two kinds of methyl hydrogen; if one deuterium is introduced, two different conformers are possible. One has a plane of symmetry while the other does not. The moments of inertia are quite different, and the microwave spectrum shows two distinct species. Although interconversion of the different conformers is quite rapid, their lifetime is long compared to the time of the microwave measurement. A similar situation obtains if two deuterium atoms replace hydrogen atoms. The moments of inertia of a molecule like acetaldehyde are quite sensitive to the orientation of an asymmetrically deuterated methyl group; it is in this way that the equilibrium conformation of methyl groups in a number of molecules has been determined.[6,7] The asymmetrically deuterated species of acetaldehyde which lack a plane of symmetry possess two equivalent conformations related by a methyl group rotation of 120°. Splitting of spectral lines due to tunneling between these equivalent forms has been observed.[20] An analysis has been given by Quade and Lin,[21] who developed a theoretical treatment for internal rotation of this type.

If a methyl group is substituted with anything other than a hydrogen isotope, the potential function loses its threefold symmetry. Two or more different potential minima may now exist; the physical properties of the different conformers which result will in general not be the same. Since each conformer can be studied separately by microwave spectroscopy, it is possible to determine such parameters as dipole moments and molecular geometry independently. From relative intensity measurements, the relative populations of different conformers can be determined and the differences in energy calculated. If transitions from molecules in enough excited torsional states are observed, it may also be possible to map out in detail the potential function governing the interconversion of conformers.

One of the first and most thorough experimental studies was that made of n-propyl fluoride by Hirota.[22] Both trans and gauche forms are present. The rotational spectrum in the ground vibrational state of each can be fit with three effective rigid rotor constants. To illustrate the sensitivity of the rotational constants to conformation, they are listed in Table I. Since the rotational constants (which are inversely related to the

Table I

Dependence of Ground-State Rotational Constants[a] on Conformation in n-Propyl Fluoride[b]

	Trans	Gauche
A	26,986.73	14,503.69
B	3,748.32	5,085.71
C	3,509.88	4,299.28

[a] In megahertz.   [b] Reference 22.

moments of inertia) are determined to a small fraction of a megahertz, there is clearly no ambiguity in assigning spectra to specific conformers. By making intensity measurements, Hirota established that the gauche form was more stable by 0.5 ± 0.3 kcal/mol. He also observed rotational transitions of excited states of the methyl torsion in both conformers. Splittings due to tunneling were observed, and the barrier to internal rotation of the methyl group was found to be 2.69 kcal/mol for the trans form and 2.87 kcal/mol for the gauche form.

In another study, Hirota[23] has investigated 3-fluoropropene, $CH_2FCH=CH_2$. Here the two conformers are cis and gauche.[24] The cis form has a plane of symmetry with the CF and C=C bonds eclipsed while in the gauche form the CH_2F group is rotated by 127°. The cis form is found to be more stable by 166 ± 67 cal/mol. The dipole moment of the cis form is 1.76 ± 0.01 D; for the gauche form it is 1.94 ± 0.02 D. In both cases the direction is very nearly parallel to the CF bond. A number of isotopic species were studied, eight for the cis form and nine for the gauche. Values for almost all of the geometrical parameters could thus be obtained separately for each conformer. Small apparent differences in structure were observed, but no simple interpretation of their meaning is obvious. Excited torsional states of the gauche form showed splitting due to tunneling between the two equivalent gauche-form conformations. Recently, Harris, et al.,[25] have developed a general (one-dimensional) theory which they have used to analyze the entire potential function in 3-fluoropropene. Combining the microwave data with infrared torsional frequencies, they obtained the potential function shown in Figure 1. Since both the CH_2F group and the rest of the molecule possess a plane of symmetry, the potential must be symmetric about the cis conformation. Denoting the internal rotation angle by θ and taking the cis conformation as $\theta = 0$, the potential energy may be written

$$V = \sum_n {}^1/_2 V_n (1 - \cos n\theta) \qquad (1)$$

If the CH_2F group were a CH_3 or CF_3 group, only terms where n is a multiple of three would be nonvanishing. Thus many new terms are introduced by the removal of threefold symmetry. The potential con-

(19) There is reason to believe that there is an isotope effect that makes this statement not quite true. It is, however, presumed to cause a quite small deviation from threefold symmetry and is neglected in the theory.

(20) R. W. Kilb, C. C. Lin, and E. B. Wilson, J. Chem. Phys., **26**, 1695 (1957).

(21) C. R. Quade and C. C. Lin, ibid., **38**, 540 (1963).

(22) E. Hirota, ibid., **42**, 2071 (1962).

(23) E. Hirota, ibid., **42**, 2071 (1965).

(24) Y. Morino and E. Hirota, Annu. Rev. Phys. Chem., **20**, 139 (1969), have suggested the use of skew rather than gauche when an sp² atom is involved. However, since gauche is in common usage we shall conform to the prevalent notation.

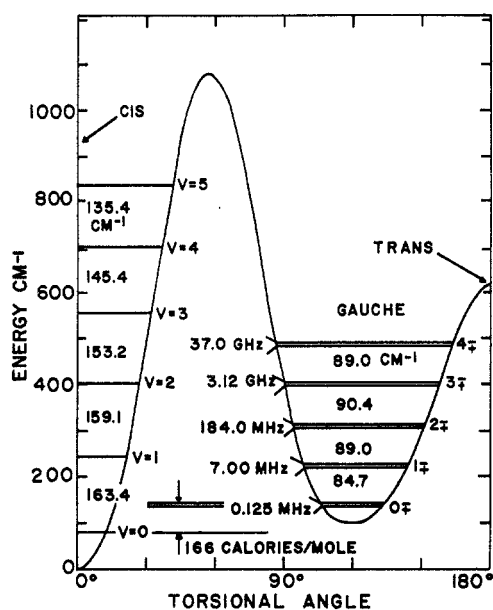(25) P. Meakin, D. Harris, and E. Hirota, J. Chem. Phys., **51**, 3775 (1969).

Figure 1. Potential function for internal rotation of the CH_2F group in 3-fluoropropene. The Fourier coefficients are (cal/mol): $V_1 = -707$, $V_2 = 530$, $V_3 = 2449$, $V_4 = 538$, $V_5 = 20$, $V_6 = 265$ (see ref 25).

tains a trans barrier height of 1.49 ± 0.09 kcal/mol and a cis–gauche barrier of 3.11 ± 0.21 kcal/mol. The error limits do not include any effects from neglect of other vibrations.

Other examples are some of the molecules studied by Wilson and coworkers. These include fluoroacetyl fluoride[26] (CH_2FCFO) and propionyl fluoride[27] (CH_3-CH_2CFO). In both cases the V_3 term of eq 1 is found to be close to that found for the methyl barrier in CH_3CFO.[28] Fluoroacetyl fluoride is interesting in that the two stable isomers are trans and cis with no gauche form observed. The notation refers to the relative positions of the two F atoms. The trans form is more stable by 0.9 ± 0.1 kcal/mol. For propionyl fluoride the conformers are cis and gauche. Here the notation refers to the relative positions of the methyl and carbonyl groups. The cis form is more stable by 1.29 ± 0.05 kcal/mol. For this form it was also possible to determine the barrier to internal rotation of the methyl group.

From the data for those molecules studied so far where substituted methyl groups are involved, two indicative trends have emerged and have been discussed by Wilson[26,27] and coworkers. One of these is that the potential expression of eq 1 converges reasonably fast. Evidence to date indicates that four or five terms may be sufficient to describe the potential. This is in accord with experience in the case of threefold symmetric rotors where convergence is rapid.[6,7] The higher terms are quite difficult to obtain experimentally, but in systems studied so far threefold or lower terms appear to be dominant. More definitive conclusions about the role of the higher terms will require study of

the influence of interaction with other vibrations and assessment of the errors associated with use of a one-dimensional model. A second important indication to emerge is that the V_3 term may be characteristic of a particular linkage and relatively insensitive to substituent. This is a well-established situation in the case of a number of threefold symmetric systems.[4-6] A large number of ethyl derivatives, for example, have barriers not very different from that of ethane. Noting the apparent constancy of V_3 and assuming convergence to be rapid, Stiefvater and Wilson[27] have proposed a formulation which would permit the prediction of potential functions for related molecules. By expressing the potential function as a sum of interactions of individual atoms or groups and assuming these to be transferable among related molecules, they have calculated the change in potential expected for an acetyl system when a H atom is replaced by a CH_3 group. They have pointed out that constancy of V_3 under substitution would imply that its origin is the same as that of the barrier in molecules such as ethane and thus not steric in nature. On the other hand, V_1 and V_2 might then be expected to be largely steric or electrostatic in origin and would be very helpful in studying such interactions. More data are necessary before the extent of the validity of this picture is known; however, it is clear that even if only approximately correct, it will be very useful in understanding intramolecular forces.

Several molecules have been studied in which intramolecular hydrogen bonding is possible. In the 2-haloethanols[29,30] it is found that the only observable form is the gauche conformer which allows close approach of the halogen and hydroxyl hydrogen. The distance between these atoms is quite small, indicating a strong attractive interaction. In glycol aldehyde[31] (CH_2-OHCHO) hydrogen bonding stabilizes the conformation consisting of a ring structure with a plane of symmetry.

Molecules containing conjugated double bonds are another system of compounds where rotational isomerism is of interest, and a number of microwave studies have been made. Butadiene and several of its derivatives have been investigated. Fluoroprene,[32] isoprene,[33] and 1,1-difluorobutadiene[34] have all been found in a planar trans form with no evidence of another form.[35] Butadiene[36] itself shows no detectable microwave spectrum, indicating the absence of appreciable quantities of any form other than the nonpolar, planar trans form. It is estimated[36] that any other form must have an energy greater than the trans form by more than 2 kcal/mol. Similarly, no absorption has been

(26) E. Saegebarth and E. B. Wilson, *J. Chem. Phys.*, **46**, 3088 (1967).

(27) O. Stiefvater and E. B. Wilson, *ibid.*, **50**, 5385 (1969).

(28) L. Pierce and L. C. Krisher, *ibid.*, **31**, 875 (1959).

(29) R. G. Azrak and E. B. Wilson, *ibid.*, **52**, 5299 (1970).

(30) K. S. Buckton and R. G. Azrak, *ibid.*, **52**, 5652 (1970).

(31) M. A. Simons and R. C. Woods, Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 1969, Paper U7.

(32) D. R. Lide, *J. Chem. Phys.*, **37**, 2074 (1962).

(33) D. R. Lide and M. Jen, *ibid.*, **40**, 252 (1964).

(34) R. A. Beaudet, *ibid.*, **42**, 3758 (1965).

(35) Recently in our laboratory a microwave spectrum of perfluorobutadiene has been observed. It presumably arises from a cisoid, nonplanar form, but no definite assignment has been made.

(36) D. R. Lide, *Trans. Amer. Cryst. Ass.*, **2**, 106 (1966).

detected[36] in biacetyl or glyoxal. Also acrolein[37] and methyl vinyl ketone[38] show only the planar trans form. Therefore, it is interesting that acryloyl fluoride[39] (CH_2=CHCFO) exists as planar trans and cis forms of essentially equal energy.

Internal rotation and rotational isomerism have been studied in many more molecules than can be mentioned here. For a more comprehensive listing the reader is referred to the reviews by Morino and Hirota[24] and by Rudolph.[40]

Inversion of Amines and Amides

Inversion occupies a special place in microwave spectroscopy for the first microwave absorption ever observed was due to the inversion spectrum of ammonia.[41] Inversion involves a tunneling between two equivalent molecular configurations which are related by the mirror reflection of one or more atoms. The tunneling gives rise to a splitting of the rotational energy levels. In ammonia the observed microwave absorptions involve transitions between two inversion levels of the same rotational level, but in general different rotational levels are involved in at least some transitions. Accordingly, the inversion splitting is superimposed on the rotational spectrum. The amount of splitting is very sensitive to the potential function and to the reduced mass. For this reason microwave investigations have thus far been limited to molecules containing at least one NH or ND bond. Heavier amino substituents reduce tunneling to an unresolvable level.[42]

Other than ammonia, amines whose inversion splitting have been observed include methylamine,[43-45] dimethylamine,[46] *gauche*-ethylamine,[47] and hydrazine.[48] The barriers to inversion range from 2.8 kcal/mol in hydrazine to 5.8 kcal/mol in ammonia.

The question of planarity and inversion in amides is one of considerable importance, and several molecules have been investigated. Pauling[49] predicted that the bonding at N in an amide should be planar due to resonance interaction. An analysis of the spectrum of formamide[50] indicates that, while the molecule is not planar, there is a much smaller planar potential maxi-

mum than in ordinary amines. The inversion levels are much further apart in this case and become infrared vibrational levels. From analysis of the intensity of rotational lines in the first excited state of the wagging motion of the NH_2 group, Costain and Dowling concluded that a barrier of 1.06 kcal/mol exists. A similar situation is observed in cyanamide.[51] It is concluded that the equilibrium structure is nonplanar with a barrier smaller than that of ammonia but perhaps larger than that in formamide. From a vibration-rotation interaction, the lowest inversion splitting in D_2NCN is estimated[51,52] to be 15 cm^{-1}.

Ring Motion and Conformation

Puckering of Four-Membered Rings. Four-membered rings have one skeletal vibration which involves a puckering of the ring. In the case of a planar ring it is an out-of-plane motion. The potential governing this motion is symmetric about the planar conformation and for a nonplanar ring takes the form of a double minimum function. The motion, therefore, is similar to an inversion. Since the vibrational frequencies are often quite low, the problem is accessible to investigation by microwave spectroscopy. A low vibrational frequency means that a number of excited vibrational states will have sufficient population that their rotational transitions can be detected. Furthermore, if the fundamental vibrational frequency is much lower than those of other vibrations, interaction with the other vibrations may be sufficiently small that a one-dimensional model will be adequate.

The way in which information is obtained about the ring-puckering motion is through analysis of the dependence of the effective moments of inertia on vibrational quantum number together with a knowledge of at least one vibrational spacing. The vibrational spacing is necessary since the rotational constant analysis yields a reduced potential with a poorly determined scale factor.[53] The vibrational spacing fixes the scale factor. The spacing may be obtained from infrared measurements, from microwave intensity measurements, or in some cases through analysis of vibration-rotation coupling between two vibrational levels.

The potential function reflects the competing factors which determine whether or not the ring is planar. These are the ring strain and the torsional forces. Since puckering introduces additional angle reduction, angle strain tends to keep the molecule planar. On the other hand, in the planar conformation adjacent groups such as methylenes are eclipsed; thus torsional forces tend to pucker the ring. Inasmuch as knowledge of the potential function gives detailed information about the balance between these opposing forces, motion in four-membered rings has been the subject of a number

(37) E. A. Cherniak and C. C. Costain, *J. Chem. Phys.*, **45**, 104 (1966).

(38) P. D. Foster, V. M. Rao, and R. F. Curl, *ibid.*, **43**, 1064 (1965).

(39) J. J. Kerns and R. F. Curl, *ibid.*, **48**, 3773 (1968).

(40) H. D. Rudolph, *Annu. Rev. Phys. Chem.*, in press.

(41) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York, N. Y., 1955, Chapter 12, give an extensive discussion of the ammonia spectrum.

(42) For a sufficiently low barrier, this need not be true. However, this statement is applicable to all molecules studied so far.

(43) K. Shimoda, T. Nishikawa, and T. Itoh, *J. Phys. Soc. Jap.*, **9**, 974 (1954); *J. Chem. Phys.*, **22**, 1456 (1954); **23**, 1735 (1965).

(44) T. Itoh, *J. Phys. Soc. Jap.*, **11**, 264 (1956).

(45) D. R. Lide, *J. Chem. Phys.*, **27**, 343 (1957); D. Kivelson and D. R. Lide, *ibid.*, **27**, 353 (1957).

(46) J. E. Wollrab and V. W. Laurie, *ibid.*, **48**, 5058 (1968).

(47) Y. S. Li and V. W. Laurie, unpublished results.

(48) T. Kasuya and T. Kojima, *J. Phys. Soc. Jap.*, **18**, 364 (1963).

(49) L. Pauling, "Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1948, p 133.

(50) C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960).

(51) D. J. Millen, G. Topping, and D. R. Lide, *J. Mol. Spectry.*, **8**, 153 (1962).

(52) D. R. Lide, *ibid.*, **8**, 142 (1962).

(53) In principle, this is not necessarily true, but applies to cases discussed here.

of microwave investigations,[54] particularly by Gwinn and coworkers.

The first such study was carried out on trimethylene oxide.[55-57] By means of an extensive investigation which combined microwave and far-infrared measurements, Chan, et al, determined the ring-puckering potential function in detail. The sensitivity of the method of investigation is shown by the fact that they could detect and accurately determine the very small potential maximum of 15.3 cm^{-1} (44 cal/mol) present at the planar conformation. Because of zero-point energy the ground vibrational level lies 12 cm^{-1} above the top of the maximum. The ring is therefore effectively planar. As predicted by Bell,[58] a very large quartic contribution to the potential was found.

In a related study, Harris,[59] et al., have characterized the potential function for trimethylene sulfide. In this case the potential maximum is found to be much greater with a value of 274 cm^{-1} (784 cal/mol). The higher barrier pushes together the ground and first excited ring-puckering states so that their separation is only 0.27461 cm^{-1} (8232.5 MHz). Very strong mixing between these states occurs, and this perturbation results in large deviations from an effective rigid rotor for their rotational transitions. From analysis of these deviations an accurate value for the separation of the two states was calculated. Knowledge of this spacing together with the variation of the rotational constants with ring-puckering quantum number would be enough to characterize the potential function, but Harris, et al., also used vibrational spacing data from microwave intensities[60] and far-infrared measurements.[61] Four puckering levels lie below the potential maximum. Thus the ring may be regarded as permanently bent, at least in the lower levels. Analysis using a model for the molecular motion showed that bending is mostly along a CS diagonal and that the dihedral angle is about 30°. The higher barrier compared to trimethylene oxide is attributed to a smaller amount of ring strain due to the tendency of S to form smaller angles than O.

The isoelectronic pair cyclobutanone[62] and methylenecyclobutane[63] offer an opportunity to study substituent effects. In cyclobutanone a very small barrier of 7.6 cm^{-1} (22 cal/mol) is obtained. The barrier is in accord with the idea that the presence of a nominally sp^2-hybridized carbon in the ring should increase the ring strain. In methylenecyclobutane, the barrier is increased to about 160 cm^{-1} (0.46 kcal/mol). The effect of a relatively high barrier on the ring-puckering energy level structure is shown in Figure 2. It is
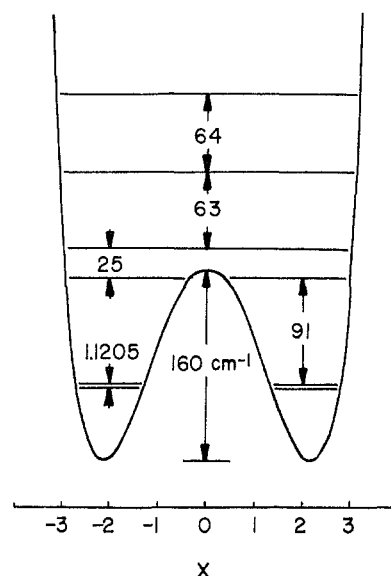

Figure 2. Potential function in cm^{-1} for ring puckering in methylenecyclobutane (see ref 63). X is the reduced ring-puckering coordinate.

interesting to note the methyl barriers in isobutylene[64] (2.21 kcal/mol) and acetone[65] (0.78 kcal/mol). Since the ring structures and ring strain of cyclobutanone and methylenecyclobutane are likely similar, the acetone-isobutylene barrier difference suggests that torsional forces are the origin of the difference in ring-puckering potential.

The prototype molecule cyclobutane has no dipole moment and cannot be investigated by microwave spectroscopy. However, several halogen derivatives have been studied. Cyclobutane itself has the puckered D_{2d} conformation[66] with a barrier of 1.28 kcal/mol and the halogen-substituted molecules studied so far are likewise puckered. In the monohalogen species two conformers, axial and equatorial, are possible. In their study of cyclobutyl chloride and fluoride, Kim and Gwinn[67] found only the equatorial form. They set a lower limit of 1.1 kcal/mol for the energy of the axial form relative to the equatorial.

Pseudorotation and Conformation of Five-Membered Rings. Five-membered rings have two ring-puckering vibrations; if they are close in frequency a strong interaction may occur which has been called pseudorotation.[68] Pseudorotation was introduced by Kilpatrick, et al.,[68] to explain the unusually high entropy of cyclopentane. In cyclopentane the ring-puckering modes are degenerate. Their vibrational motion consists of a ring puckering whose phase rotates around the ring. This gives rise to vibrational levels of quite low energy. The resulting density of energy levels causes the unusually high entropy observed in cyclopentane. When a molecule has less symmetry than cyclopentane, the two ring-puckering modes will no longer be degenerate.

(54) For a more comprehensive listing, see ref 24 and 40.
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However, if they are not too different in energy, pseudo-rotation effects can still occur. The phase of the puckering no longer rotates freely around the ring but encounters potential energy maxima and minima. Thus this case has been designated[69] as hindered pseudorotation. Very low energy vibrational states can exist in this case also, and significant vibration–rotation effects can be present. Since many vibrational states will have appreciable population, it is possible to study these effects by microwave spectroscopy.

The theory of the effects to be expected has been treated in detail by Harris, et al.,[69] and applied to tetrahydrofuran.[70] Rotational transitions of nine vibrational states were observed. All nine vibrational states had energies of less than 200 cm^{-1}, with the lowest four being very close in energy. These four states deviate significantly from rigid rotor behavior because of vibration–rotation coupling. Analysis showed that the ground and first excited states are separated by only 0.65 cm^{-1}, while the second and third excited states are separated by only 1.5 cm^{-1}. These splittings and the variation of the rotational constants were used to obtain the detailed potential function. Assuming a model for the molecular motion, Engerholm, et al.,[70] found that the equilibrium conformation is one which is twisted about an axis containing the O. The planar conformation is estimated to be about 1220 cm^{-1} higher in energy than the pseudorotation track. Thus the barrier for direct inversion of the ring through the planar form is much higher than the 57-cm^{-1} barrier found for inversion through the pseudorotation path.

In other five-membered rings studied to date, there are distinct bending and twisting vibrations with a high barrier to pseudorotation. Thus these molecules are permanently localized in a particular conformation in their ground states. Cyclopentanone[71] and germacyclopentane[72] ($C_4H_{10}Ge$) are twisted with a twofold axis. On the other hand, cyclopent-2-en-1-one[73] is planar. Apparently the conjugation of the two double bonds overcomes the repulsion expected for two eclipsed methylene groups.

Cyclopentene presents a slightly different case. Because of the energy associated with torsion around a double bond, the frequency of the twisting motion is considerably higher than that of the bending motion. The molecule is nonplanar with the C_4 atom bent out of the plane.[74] The dihedral angle is 22°. The bending motion involves this dihedral angle and is symmetric about the planar conformation. Thus the double minimum formulation used in treating inversion or puckering in four-membered rings is applicable. The ground state and first excited ring-bending state are very close in energy; they interact sufficiently that non-

rigid rotor effects occur. Analysis[75] of these effects using the theory of Lide[52] gave a value of 0.91 cm^{-1} for the separation of the two states. This separation together with the variation of the rotational constants was used[76] in combination with far-infrared data[77] to obtain a barrier value of 232 cm^{-1} (663 cal/mol).

Conformation of Six-Membered Rings. Six-membered rings have three ring-puckering vibrations; in principle these could interact to give complicated effects. In practice, however, the potential barriers involved appear to be quite high; to date, no detailed potential study has been reported. On the other hand, a number of studies have been made of the conformation of six-membered rings.

Pierce and coworkers[78] have investigated the spectrum of cyclohexyl fluoride and have observed both equatorial and axial forms of the chair conformer. Scharpen[79] has made accurate intensity measurements and has determined that the equatorial form is more stable by 259 ± 25 cal/mol.

Piperidine,[80] a nitrogen analog of cyclohexane, also has been found to have two chair forms. Intensity measurements show that the equatorial form is more stable by 248 ± 150 cal/mol. In contrast, a study of morpholine,[81] whose ring contains both a N and an O, revealed only the equatorial form.

Other six-membered rings which have been studied are cyclohexanone,[82] cyclohexadiene,[83] and cyclohexene.[84] None of these studies found more than one conformer. Cyclohexadiene and cyclohexene both have twofold symmetry and are twisted. Cyclohexanone has the expected chair structure.

Low-Resolution Studies

The great power of microwave spectroscopy is its tremendous resolution and accuracy. As molecules get larger, however, the number of spectral lines increases rapidly. Analysis may become quite difficult because of the sheer amount of information available. It becomes, very simply, a case of not being able to see the forest for the trees. In such situations, Scharpen[85] has shown that often it is possible to obtain some information by *lowering* the resolution. Under very low resolution many molecules present pseudosymmetric-top spectra, and an approximate rotational constant can

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be obtained very quickly. Since different conformers often have rather different rotational constants (see Table I), this provides a way for very easily detecting the presence of more than one conformer. Furthermore, with reasonable structural assumptions the approximate rotational constants obtained from the low-resolution spectra can usually be definitive in establishing the identity of the conformers present. Thus it appears that low-resolution microwave spectroscopy may be very useful in the study of molecular conformation.

Conclusion

From the wealth of detailed information already obtained from microwave spectral studies, our knowledge of the factors involved in determining molecular con-

formation has been greatly increased. Also a substantive beginning has been made toward understanding the nature of the intramolecular forces involved in nonbonded interactions. The area of molecular internal motions and conformation is an active one in microwave spectroscopy, and further advances in our understanding can be expected. Recent improvements in microwave intensity measuring techniques and overall technology should substantially aid in this endeavor by making it much easier to obtain accurate relative energies for different conformations and for vibrational spacings.

Thallium in Organic Synthesis

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Thallium was discovered in 1861 almost simultaneously by Sir William Crookes and by the French chemist Lamy. It is a soft white metal, slowly oxidized by air or water at room temperature, but rapidly at 100°. It is unique among the group IIIb metals in possessing a stable 1+ oxidation state; interplay between the 1+ and 3+ states forms the basis for much of the chemistry to be described in this review.

Although inorganic thallium salts are generally more stable in the lower oxidation state, organothallium compounds are usually stable only in the 3+ oxidation state; cyclopentadienylthallium appears to be the only stable organothallium compound with an oxidation state of 1+.

For an element relatively unknown to organic chemists, thallium is surprisingly abundant. Recent estimates, in fact, place its abundance in the earth's crust at about 1 g/metric ton, a figure somewhat higher than that for several more commonly known metals such as mercury, antimony, bismuth, cadmium, and silver.[1] The metal is prepared commercially as a by-product from the smelting of lead and zinc ores, and is also found in "flue dust" along with cadmium, indium, selenium, and tellurium. It is supplied commercially in a wide variety of thallium(I) salts, a few thallium(III) salts, and, in rod form, as the metal itself.

Some physical properties of thallium metal are summarized in Table I.

Table I
Thallium[1]

Atomic weight	204.37
Atomic number	81
Electronic configuration	(Xe) $6s^2 5d^{10} 4f^{14} 6p^1$
Density at 20°, g/cm³	11.85
Mp, °C	303
Bp, °C	1437
Isotopes	^{203}Tl (spin $^1/_2$), 29.5%
	^{205}Tl (spin $^1/_2$), 70.5%
Oxidation potentials[2]	Tl → Tl$^+$ + e$^-$; $E° = 0.3363$
	Tl$^+$ → Tl^{3+} + 2e$^-$; $E° = -1.25$

Thallium is also unique in group IIIb as the only soft acid on the hard acid–soft base classification of Pearson.[3,4] Both thallium(I) and thallium(III) are soft acids, with thallium(III) definitely softer than thallium(I). Thus, thallium(I) would be expected to show properties characteristic of both silver(I) (soft acid) and potassium(I) (hard acid), which is found to be the case. By contrast, thallium(III) resembles mercury(II) and lead(IV) (soft acids) rather than aluminum(III) (hard acid).

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