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ON THE ORIGIN OF POTENTIAL BARRIERS TO INTERNAL ROTATION IN MOLECULES*

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It is well known that in molecules such as ethane (CH_3—CH_3) one part of the molecule can rotate relative to the other part about the single bond (here C—C) joining the two halves. This phenomenon has considerable importance; for instance, it permits the coiling and uncoiling of protein molecules and other polymers. It has also been known[1] for some time that this internal rotation is not free but is hindered by a potential energy barrier of a magnitude beyond theoretical expectations. Various hypotheses have been put forward concerning the origin of these forces, but no satisfactory conclusion has been reached.

Recent developments in microwave spectroscopy and the related theory[2–10] have provided powerful new tools for the study of this phenomenon. For a certain class of molecules it is now possible to obtain values of the potential barrier with an accuracy of 5 per cent or better, and with much greater certainty than was associated with older methods. Further, the structure and interatomic distances can be obtained and the equilibrium orientation of the rotating groups, as well as other detailed information mentioned below.

Current theories of the forces between atoms suggest a number of types of interaction which could possibly account for the observed barriers. All these forces are of course fundamentally electrostatic interactions among the electrons and nuclei involved. Eyring[11,12] and collaborators early made a quite detailed attempt to find the origin of the barriers by means of the quantum-mechanical approximations then available, but without success. Recently Mason and Kreevoy[13] and also van Dranen[14] have made new estimates of the importance of the van der Waals repulsion between the attached groups, a repulsion which appears between separate gas molecules at close distances, due to overlap of the charge clouds and quantum-mechanical exchange. At somewhat longer distances than occur in most examples of hindered rotation, this repulsion should be replaced by a weak attraction due to inductive and dispersion effects.

The separate atoms and chemical bonds in a molecule will surely interact, due to the direct electrostatic force between the charge distributions, even if there is no important contribution from overlap, exchange, dispersion, or induction. If the electron distribution were known, this term could be calculated with purely classical methods. This effect has been invoked and investigated by Lassettre and Dean,[15] Oosterhoff,[16] and Au-Chin Tang.[17]

Finally, it has several times been suggested[18] that the potential might not appreciably involve direct interactions of the attached atoms or their bonding electrons at all but might be in some way an intrinsic lack of cylindrical symmetry in the axial chemical bond itself.

Recent microwave data throw some light on the relative importance of these forces. Table 1 shows some barrier values and equilibrium orientations, all but

TABLE 1

Some Potential Barriers and Equilibrium Orientations

Molecule	V (Kcal/Mole)	Orientation	Ref.
CH_3CH_3	(2.7–3.0)	(Staggered)	1
CH_3CH_2F	3.30		2
CH_3CHF_2	3.18		2
CH_3CH_2Cl	....	Staggered	3
CH_3OH	1.07		4
CH_3SH	0.71		5
CH_3CHO	1.15	H—H staggered	6
CH_3CFO	1.08	H—F staggered	7
CH_3CClO	1.35	H—Cl staggered	8
CH_3COCN	1.27		9
CH_3NH_2	1.90		10
CH_3SiH_3	1.70	Staggered	11
CH_3SiH_2F	1.56	Staggered	12
CH_3SiHF_2	1.32		13
CH_3CHOCH_2	2.56		14
CH_3CHCH_2	1.98		15
CH_3CHCCH_2	1.59		15
CH_3CHCHF (*trans*)	2.15		16
CH_3COOH	0.48		17
CH_3GeH_3	>2.5		18
CH_3NO_2	0.006	6-fold	19
CH_3BF_2	0.014	6-fold	20

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ethane from microwave frequency measurements. First of all, the equilibrium orientations so far well established (some by electron diffraction[19] as well as spectroscopic methods) show that the forces act like repulsions between the attached atoms. Second, it is notable that in methyl silane and in the aldehyde group of acetaldehyde the replacement of hydrogen by fluorine lowers the barrier. If van der Waals repulsion were the dominant force, this would seem very surprising. In the ethane derivatives, the first fluorine increases the barrier, but not greatly, and the second lowers it. Even the substitution of chlorine for the aldehyde hydrogen in acetaldehyde raises the barrier by only a small amount, and the somewhat uncertain data for the ethane series do not suggest a large increase, as long as one end remains a methyl group. Furthermore, the current picture of van der Waals forces calls for them to decrease very rapidly with distance. Consequently, even if the whole barrier in ethane were due to this cause, simple calculations[20] show that only a fraction of the observed barrier in methyl silane could come from this source. The equilibrium orientation of acetaldehyde has a methyl hydrogen opposite the oxygen and therefore as far as possible from the aldehyde hydrogen. Even granting the different distances, one has difficulty understanding this in terms of van der Waals forces. In view of this whole picture, it seems unlikely that the van der Waals basis is acceptable, although when there are large atoms on both ends or specially short distances, it would be expected to play a role.

The work of Lassettre and Dean[15] reopened the electrostatic-interaction hypothesis by postulating large quadrupole moments in C—H bonds. They expanded the effect of the charge distribution in multipoles, about the midpoint of the bond, including, however, only the dipole and quadrupole terms. Lacking empirical data on the quadrupole moments, they adjusted these to fit the observed barriers and obtained values which have been criticized by some as being unreasonably large. However, the main difficulty was suggested by Lassettre and Dean themselves and is that the multipole expansion as they used it is almost certainly an inadequate approximation. Oosterhoff[16] modified this method by directly calculating the Coulomb interaction of the protons and the spherical electron clouds shielding the protons, reserving the multipole expansion for that part of the electron distribution not expected (on simple quantum-mechanical grounds) to be spherically distributed about either carbon or hydrogen, i.e., the overlap charge between hydrogen and carbon. Further, he included octupole terms. It is therefore much more likely that his expansion was convergent. His treatment was based on a particular quantum-mechanical approximation and gave the result that the observed barrier in ethane could be accounted for, but only if the C—H bond were surprisingly ionic, with a much larger bond dipole moment than is currently supposed.

It is possible to make simple Coulomb calculations of electrostatic interactions based on charge distributions consisting of spheres of charge (with any radial distribution as long as overlap between bonds is negligible) about the hydrogen, the central atom, and any desired point in the bond. Such distributions presumably cannot reproduce accurately the true electron distribution, but they have considerable flexibility, and it would be surprising if they did not permit at least a rough representation of the actual situation. For both ethane and methyl silane they show that the observed barriers can be obtained only by very ionic distributions. For example, in CH_3SiH_3 the maximum possible electrostatic barrier, that which would arise from bare protons, i.e., a completely ionic state, is calculated to be only 2.8 Kcal., compared with the observed value of 1.7. In methyl germane (CH_3GeH_3) the bare proton calculation gives 2.5 Kcal. Although no experimental value is available for the barrier in this molecule, a preliminary analysis[21] of the microwave spectrum appears to exclude any value below about 2.5 Kcal. These results rule out the electrostatic mechanism as the primary cause in such molecules.

In addition to the above arguments, there is the fact that substitution of the acetyl hydrogen by fluorine does not reverse the equilibrium orientation found in acetaldehyde, despite the general belief that fluorine is more electronegative than oxygen.

There exists another source of information which is in principle more searching than any of the above, partly because it avoids the necessity for comparing different molecules. Rotational transitions are observed in the microwave region not only for molecules in the ground vibrational state but also for those in the lower excited energy levels of vibration and especially internal torsion. These latter, particularly, are found to be well displaced from the ground-state lines, presumably because of the distortion of the molecule produced during the torsional motion by the forces responsible for the barrier. For example, if direct repulsions between the hydrogens were important, the hydrogens should be pushed back as the internal torsion brings them opposite one another. This effect has been treated in a very general way by Kivelson,[4] and his formulas can be applied to several molecules. If a sufficient number of isotopic species are measured, it is possible to obtain values of the derivatives of the hindering potential with respect to the various molecular coordinates. For example, one can solve for the effect on the barrier of pushing the hydrogens further apart. Hecht and Dennison[22] have given approximate results for methyl alcohol. I have carried out such calculations for methyl silane,[4] methyl mercaptan,[23] and methyl alcohol.[22] With the reasonable assumption that there is little effect of stretching the X—H bonds (X = C, O, or Si) and that the vibrational force constant matrix is approximately diagonal, the result obtained is that moving the hydrogens has less effect on the barrier than changing the length of the axial bond.

Unfortunately, the geometrical factors are such as to make the calculations somewhat insensitive to the displacement of the hydrogen atoms; furthermore, only estimates are available for the force constants. These results are therefore not completely conclusive, but they nevertheless provide an important argument against any theory involving direct forces between the hydrogens or bonding electrons to the hydrogens. Calculations based on an inverse power of the distance between hydrogens (or between midpoints of bonds) give an effect of bending the X—H bonds which is somewhat bigger than the effect of stretching the axial bond, whether the power used is 1 (Coulomb law), 4, or 10 (van der Waals), and these are therefore all in conflict with the experimental results.

It should also be mentioned that Linnett and collaborators,[24] from a study of the vibrational potential functions for water and for methane, found that direct forces of repulsion between the hydrogens seemed to be unimportant.

The conclusion to which all these arguments lead is that potential barriers to internal rotation, at least in the case where one group carries only hydrogen atoms, must in some way be an inherent property of the axial bond itself and not due in any substantial measure to direct forces between the attached atoms or those parts of the electron distribution which are out on the attached bond any considerable distance.

A possible way of obtaining confirmation of this conclusion is to measure barriers in various excited vibrational states. The larger amplitudes of vibration should lead to changes in barrier that are approximately predictable on the basis of the various hypotheses, since the average of the square of the vibrational amplitude will be important. Thus excitation of stretching of the axial bond should have a relatively larger effect than excitation of the bending modes, if the above conclusion is correct. Such observations would be difficult but are probably possible.

This conclusion that it is the electron distribution in and near the axial bond which must play a major role suggests that the quantum-mechanical description of this situation should now be re-examined.

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