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A QUALITATIVE PICTURE OF THE BARRIER RESTRICTING ROTATION ABOUT SINGLE BONDS

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Abstract—The simple model proposed is based on the repulsion between the four substituent or lone electron pairs of a tetrahedral atom and on the strongly anisotropic polarizability of the single bond. Bending back two electron pairs to form a double bond or a small ring, and the introduction of electronegative substituents, reduce the barrier.

A survey of known rotational barriers is given.

MANY attempts have been made to explain theoretically the barrier restricting rotation about single bonds.[1-10] In a critical evaluation of earlier theories, Wilson has concluded[1,4] that for ethane neither Van der Waals interaction between the hydrogen atoms, nor electrostatic interaction between the CH bonds, can explain the potential barrier, and has suggested[1] that it "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 recent more basic quantum mechanical treatment[6] reproduced very satisfactorily the barrier in ethane, but it has not been possible to make the transformation to localized molecular orbitals necessary to describe the barrier in more detail. It is also hard to believe that this very small difference between the large total energies of the eclipsed and staggered form, would come out about unchanged (as it should) when either carbon or hydrogen, or both, are substituted by many other elements (see below). An extended Hückel theory[7] also led to a reasonable barrier for ethane, but the conclusion that transfer of electrons from carbon to hydrogen is associated with greater stability of the staggered form, hence a higher barrier, is in direct contradiction with the experimental data for many molecules (see below). Quite recently a theory,[8] in which "a solution is offered to the mystery of the origin of the barrier", categorically attributes the barrier favouring the staggered form of ethane to the repulsion between protons at one end and protons at the other end, and must therefore be rejected *a priori* and particularly on the basis of the experimental data for N-methylene-methylamine quoted below, where in the equilibrium

[1] E. B. Wilson, *Proc. Natl. Acad. Sci. U.S.A.* **43**, 816 (1957).
[2] L. Pauling, *Proc. Natl. Acad. Sci. U.S.A.* **44**, 211 (1958).
[3] H. Eyring., G. H. Stewart and R. P. Smith, *Proc. Natl. Acad. Sci. U.S.A.* **44**, 259 (1958).
[4] E. B. Wilson, *Adv. Chem. Phys.* (Interscience) **2**, 367 (1959).
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[6] R. M. Pitzer and W. N. Lipscomb, *J. Chem. Phys.* **39**, 1995 (1963).
[7] R. Hoffmann, *J. Chem. Phys.* **39**, 1397 (1963).
[8] R. E. Wyatts and R. G. Parr, *J. Chem. Phys.* **41**, 3262 (1964); **43**, S217 (1965).
[9] H. E. Simmons and J. K. Williams, *J. Amer. Chem. Soc.* **86**, 3222 (1964).
[10] R. A. Scott and H. A. Scheraga, *J. Chem. Phys.* **42**, 2209 (1965).

conformation the methyl-group hydrogens see no hydrogen or other atom in any of the ethane-like positions at the other end.

In spite of the agnostic attitude advocated by Wilson,[1,4] there are nevertheless not only surprising constancies of the barrier in homologous substituted series, but also intriguing variations in seemingly related compounds, which stimulate further speculations about the nature and origin of the barrier. The simple model described may not furnish the final theory of restricted rotation in single bonds, but should serve as a qualitative explanation of the barrier in a variety of compounds and help in organizing the experimental data.

Two observations form the basis of the model:

(1) Calculations in quantum mechanics suggest,[11-13] though not stated in this form, that electron pairs constituting single bonds, as well as lone electron pairs in other "tetrahedral" compounds like NH_3 and H_2O, would like to occupy more space than is available close to the tetrahedral atom (C,N,O etc). By electron repulsion, each of these localized orbitals therefore feels the pressure of the other three.

(2) The polarizability of a single bond is much higher in the bond direction than at right angles to it,[14] and this anisotropy is particularly high for the C—C single bond[15] (although much less so than originally believed[16]).

The "pressure" from the three other electron pairs (in substituent bonds or as lone pairs) will therefore be transmitted preferentially along the rotational axis and felt as a trigonal push by the other atom. which will itself set up a similar trigonal push in the opposite direction. This will then lead to the staggered orientation. The height of the barrier should be influenced by factors which modify the shape of the "orbitals" linking the substituents and by the polarity of the bonds. Bending back two "bonds" to form a double bond or a small ring (cyclopropane) should relieve the "pressure" on the bond orbital forming the rotational axis, hence reduce the barrier. Polar character of substituent bonds, such as C—F or C=O, should also lead to lower barriers at the positive atom according to how strongly the electrons are pulled over to the negative atom. That the crowding at the tetrahedral atom is in fact relieved in this way, is well demonstrated by the fact that a lone pair, having no positive atom pulling it outwards, requires more angular space than a hydrogen substituent[17] ($\angle$HCH in CH_4: $109\frac{1}{2}°$, $\angle$HNH in NH_3: 107°,[18] $\angle$HOH in H_2O: $104\frac{1}{2}°$[19]), and by the observation that when hydrogen is replaced by a more electronegative atom like fluorine, the bond angles decrease further in spite of the supposedly stronger repulsion between substituents ($\angle$FCF in CH_2F_2: 108°,[20] $\angle$FNF in NF_3: 102°[21] and $\angle$FOF in F_2O: 103°[22]).

[11] C. A. Coulson and W. E. Moffit, *Phil. Mag.* **40**, 1 (1949).
[12] C. A. Coulson and H. H. Greenwood, Unpublished results.
[13] A. B. F. Duncan and J. A. Pople, *Trans. Faraday Soc.* **49**, 217 (1953).
[14] H. C. Bolton, *Trans. Faraday Soc.* **50**, 1261 (1954).
[15] C. W. Bunn and R. de P. Dauberry, *Trans. Faraday Soc.* **50**, 1173 (1954).
[16] K. G. Denbigh, *Trans. Faraday Soc.* **36**, 936 (1940).
[17] B. A. Dickens and J. W. Linnet, *Quart. Rev.* **11**, 291 (1957).
[18] M. T. Weiss and M. W. P. Standberg, *Phys. Rev.* **83**, 567 (1951).
[19] D. W. Posener and M. W. P. Strandberg, *Phys. Rev.* **95**, 374 (1954).
[20] D. R. Lide, *J. Amer. Chem. Soc.* **74**, 3548 (1952).
[21] J. Sheridan and W. Gordy, *Phys. Rev.* **79**, 513 (1950).
[22] J. A. Ibers and V. Schomaker, *J. Phys. Chem.* **57**, 699 (1953); L. Pierce, N. DiCianni and R. H. Jackson, *Ibid.* **38**, 730 (1963).

The known values for rotational barriers, most of them determined by the microwave line splitting method,[4] have been arranged in Tables 1 to 8 in a manner which allows comparison both of horizontal and vertical rows; a few compounds had therefore to be listed in more than one Table. The conformation at the potential minimum has been determined in most cases, and it is always found to correspond to a staggered conformation about single bonds with respect to substituents as well as to lone pairs of tetrahedral atoms. For single bonds adjacent to a double bond the two "bent bonds" of the double bond are in this sense equivalent to two substituents.[2] Only for hydrogen peroxide[23,24] and hydrazine[25,26] is there an uncertainty about the stable conformation; as other forms than the normal *gauche* and *trans*-conformers have been assumed, the derived barriers are not directly comparable and have been omitted from Table 1. On the other hand a normal *gauche*-form has been found for tetrafluorohydrazine,[27] and a normal *trans*-form for hydrogen peroxide in the crystal structure of sodium oxalate perhydrate.[28]

The trend (Table 1) when one carbon atom is replaced by larger atoms of the same vertical group of the periodic system (Si, Ge, Sn) is a lowering of the barrier, understandable as a consequence of the increase in the length of the pivot bond, of the greater space available for the four bond orbitals, and of the increased electropositivity. A similar trend is observed in the group N, P, As, and the group O, S, as long as these atoms are not directly bonded to hydrogen (Table 1). In a horizontal row of the periodic system the barrier stays roughly constant, but again only as long as these atoms are not bonded to hydrogen. The particularly low barriers for methanol, for methylmercaptan, and for methylamine, suggest that "active" or easily dissociated protons do not stay long with one electron pair but may dissociate and add to another lone pair of the same atom, and that this may be one mechanism for passing the barrier, rather than a simple rotation (or inversion) of the OH, SH or NH_2 group.

The effect of one halogen substituent (or nitrile group) in ethane is surprisingly small (Table 2) and does not change much when passing from fluorine to iodine. A second or third fluorine substituent on the same carbon atom does not raise the barrier further, possibly because any small additional substituent repulsion terms are cancelled by the pull on the electron pairs over to the electronegative fluorine atoms. A fourth fluorine substituent, now on the other carbon atom, raises the barrier so that a steric interaction must now have come into play, but further fluorine atoms have no added effect. On the contrary, in hexafluoroethane the barrier is slightly lower, suggestive of a very strong pull of electrons away from the carbon atoms. Similarly (Table 2), on substituting the hydrogen atoms in molecules of the general type $CH_2X—CF_3$ with fluorine to give $CF_2X—CF_3$, the barrier decreases when the halogen X is chlorine, and increases slightly when X is bromine and iodine. Apparently, substituent repulsion starts to dominate with the larger halogens (Table 2).

The barrier in methylsilane decreases gradually as SiH bonds are replaced by SiF

[23] R. L. Redington, W. B. Olson and P. C. Cross, *J. Chem. Phys.* **36**, 1311 (1962).
[24] R. H. Hunt, R. A. Leacock, C. W. Peters and K. T. Hecht, *J. Chem. Phys.* **42**, 1931 (1965).
[25] D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard and H. M. Huffman, *J. Amer. Chem. Soc.* **71**, 2293 (1949).
[26] T. Kasuya and T. Kojima, *J. Phys. Soc., Japan* **18**, 364 (1963).
[27] D. R. Lide and D. E. Mann, *J. Chem. Phys.* **31**, 1129 (1959).
[28] B. F. Pedersen and B. Pedersen, *Acta Cryst.* **16**, A75 (1963).

bonds (Table 3). Substituent repulsion must here be even less important than in ethane and one would on this basis at most expect the barrier to stay constant. The observed effect may therefore be due to the much stronger pull of the SiF bond orbital than of the CF bond orbital towards the fluorine atom, silicon being more electropositive than carbon. The extremely low barrier in hexachlorodisilane, as compared with perchlorinated methyl silane and ethane (Table 3), must have the same cause.

The barrier for methyl rotation in propene (Table 4) is significantly lower than in ethane and this can be understood on the basis that two electron pairs are bent back to form the double bond. In perfect analogy with ethane, a fluorine substituent in the methyl group increases only slightly, if at all, the barrier, and replacement of CH_3 by SiH_3 lowers the barrier somewhat. It might have been argued that the double bond causes no interaction here, and that both the barrier and the equilibrium conformation are dictated by the repulsive interaction between the 2-proton and the protons of the methyl group. The decisive proof that this is not so, and that a lone pair, as well as each bent-bond orbital of the double bond, seem just as important as the bond orbital of simple substituent bonds, comes from the microwave study[29] already mentioned of N-methylene–methylamine (Table 4). This compound carries no proton in the corresponding position, but is nevertheless entirely identical with propene both as regards barrier height and equilibrium conformation.[30]

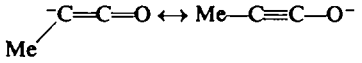
The remaining data in Table 4 illustrate that a further substituent in propene, such as the methyl, halogen or nitrile group, does not increase appreciably the barrier to methyl rotation when it is in *trans* position on the double bond, and only moderately when both groups are on the same carbon. However, very low barriers have been observed when the two groups are in *cis* position on the double bond, and this has been convincingly explained[31,32] as being due to the repulsion between the second substituent and one hydrogen of the methyl group. In the equilibrium conformation this hydrogen atom lies in the plane of the double bond and points directly towards the second substituent; the repulsion must therefore be a maximum in this conformation and raise the energy of the potential bottom, but not the barrier top. In harmony with this picture is the *a priori* surprising trend (Table 4) that the smallest substituents give the highest barriers.

A remarkable lowering of the barrier is observed when the C=C double bond is replaced by the strongly polar C=O double bond (Table 5). Its value stays fairly constant when the aldehydic hydrogen of acetaldehyde is replaced by halogens (acetyl halides) or the nitrile, ethynyl, and vinyl groups. It is even further lowered in trifluoroacetaldehyde, probably because the electron pairs are here drawn away from both carbon atoms. The surprisingly low barrier in acetone (Table 5) must be explained by a stronger polarization of the C=O bond, the methyl groups seemingly stabilizing a positive charge on the carbon atom more than do the halogens. Resonance contributions of the type $Me—C^{\diagup O^+}_{\diagdown X^-}$ which have been invoked[33] to explain the molecular

[29] J. T. Yardley, J. Hinze and R. F. Curl, *J. Chem. Phys.* **41**, 2562 (1964).
[30] D. R. Herschbach and L. C. Krisher, *J. Chem. Phys.* **28**, 728 (1958).
[31] W. G. Dauben and K. S. Pitzer, in M. S. Newman: *Steric Effects in Organic Chemistry*, p. 59. Wiley (1956).
[32] R. A. Beaudet, *J. Chem. Phys.* **40**, 2705 (1964).
[33] L. C. Krischer and E. B. Wilson, *J. Chem. Phys.* **31**, 882 (1959); **33**, 304 (1960).

fine-structure for the former members, would counteract the polarity of the C=O bond, but are less likely when X is methyl. On the other hand, the low barrier in acetic acid may have to do with the important polar resonance structure $Me_3—C^{+OH}_{O^-}$ so that the molecule approaches the situation with a 6-fold barrier (see below).*

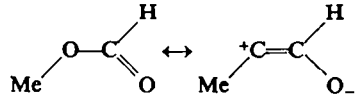
Table 6 compares the barriers for methyl group rotation in olefins, allenes, ketenes and ketones (or aldehydes). From the above discussion, the barrier in dimethylketene would be expected to be as high as in isobutene, and not low as in acetone; this is also actually found (Table 6). However, the rather low barrier in methylketene and in methylallene) cannot be simply understood. One possible explanation is that the allenic hydrogen is quite acidic, since the resulting propargylic anion must be obtained even more easily from an unstable allene than by removing one of the already quite acidic methyl protons from the more stable acetylenic isomer. Similarly, in methylketene the resulting anion would be stabilized by resonance with the ynolate form:



As in methanol etc, the mobility of this active hydrogen atom may then lead to a lower barrier.

If the carbonyl group is considered as a two-membered ring, one would expect the rotational barrier in propylene oxide to be intermediate between that of acetaldehyde and propane, and indeed it is (Table 7). That the barrier is lower in *cis*-2-butene oxide has been plausibly ascribed[35] to repulsion between hydrogens of the methyl groups which raise the potential bottom, just as in *cis*-2-butene (see above). In the analogous three-membered ring containing the less electronegative and larger sulfur atom instead of oxygen, the barrier for rotation of the single methyl group is much higher (Table 7); the carbon is less positive and the longer C—S distance implies that the "substituent bonds" are less bent back.

A comparison (Table 8) of dimethyl ether, which has a normal ethane barrier value for rotation of the methyl group, with methyl formate, in which the barrier for methyl rotation has been more than halved, suggests that the partial positive charge on this "ether oxygen" due to resonance contribution of a polar structure may play a rôle:



In the isoelectronic methyl vinyl ether the analogous polar structure should be less important and the barrier is again rather high.† Similarly, for methyl nitrate no

* Alternatively, if the acidic proton dissociates and adds to the carbonyl oxygen sufficiently frequently, an averaging effect may come into play, which means that in the microwave spectrum one observes the combined effect of methyl rotation and proton-tunneling. In dimers of carboxylic acids, the tunneling of the proton in the hydrogen bond is faster than the frequency of methyl rotation; and this has been expected[34] to make the rotation of CH_3 (and CF_3) nearly free.

† An alternative explanation for the high barrier has been proposed:[36] The structure of the stable *cis*-form (Table 8) is such that a vinyl hydrogen points just between two of the methyl hydrogens in the equilibrium conformation and repulsion will therefore be a maximum at the top of the barrier.

[34] C. C. Costain and G. P. Srivastava, *J. Chem. Phys.* **41**, 1620 (1964).

[35] M. L. Sage, *J. Chem. Phys.* **35**, 142 (1961).

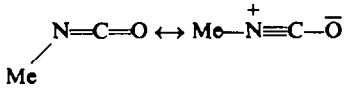
[36] P. Cahill, L. P. Gold and N. L. Owen, *Abstr. 8th Europ. Congr. Mol. Spectroscopy*, p. 102. Copenhagen (1965).

TABLE 1. ROTATIONAL BARRIERS (KCAL/MOLE) FOR C-SUBSTITUTED ETHANES, PROPANES, AND ISOBUTANES

	$[NF_3—NF_3 > 3{\cdot}0^{37}]$	
$CH_3—CH_3$ 2·88[a,b]	$CH_3—NH_2$ 1·94[43]	$CH_3—OH$ 1·07[46]
$CH_3—SiH_3$ 1·70[40]	$CH_3—PH_2$ 1·96[44]	$CH_3—SH$ 1·26[47]
$CH_3—GeH_3$ 1·24[41]	$[CH_3—AsF_2$ 1·32[45]]	
$CH_3—SnH_3$ 0·65[42]		
$CH_3—CH_2—CH_3 > 2{\cdot}7$[48]	$CH_3—NH—CH_3$ 3·28[b,50]	$CH_3—O—CH_3$ 2·72[51]
$CH_3—SiH_2—CH_3$ 1·65[49]		$CH_3—S—CH_3$ 2·13[52]
		$CH_3—\overset{\overset{O}{\|}}{S}—CH_3$ 2·94[53]
$[(CH_3)_3C—C{\equiv}CH \approx 4{\cdot}0$[54]]	$(CH_3)_3N$ 4·41[b,55]	
$(CH_3)_3SiH$ 1·83[55]		
	$(CH_3)_3As$ 1·5–2·5[56]	

[a] From thermodynamic data.
[b] From vibrational spectra.

acceptable resonance structure can be written with a positive charge on the methoxyl oxygen, and the barrier is much higher than in methyl formate (Table 8). For methyl thionylamine the structural data[37] suggest that the nitrogen atom may at most have become slightly positive by an inductive effect and the barrier is low, but not negligible. For methylisocyanate, on the other hand, the observed structure[38] suggests that the nitrogen atom has become positive by resonance and the barrier is far lower:



[37] V. M. Rao, J. T. Yardley and R. F. Curl, *J. Chem. Phys.* **42**, 284 (1965).
[38] R. F. Curl., V. M. Rao., K. V. L. N. Sastry and J. A. Hodgeson, *J. Chem. Phys.* **39**, 3335 (1963).
[39] K. S. Pitzer, *Disc. Faraday Soc.* **10**, 66 (1951).
[40] R. W. Kilb and L. Pierce, *J. Chem. Phys.* **27**, 108 (1957).
[41] V. W. Laurie, *J. Chem. Phys.* **30**, 1210 (1959).
[42] P. Cahill and S. Butcher, *J. Chem. Phys.* **35**, 2255 (1961).
[43] T. Nishikawa, *J. Phys. Soc. Japan* **12**, 668 (1957).
[44] T. Kojima, E. L. Breig and C. C. Lin, *J. Chem. Phys.* **35**, 2139 (1961).
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[54] L. J. Nugent, D. F. Mann and D. R. Lide, *J. Chem. Phys.* **36**, 965 (1962).
[55] L. Pierce and D. H. Petersen, *J. Chem. Phys.* **33**, 907 (1960).
[56] D. R. Lide, *Spectrochim. Acta* **15**, 473 (1959).

When finally a methyl group is linked directly to a trigonal atom like boron, or to a nitro group, or to an aromatic system like pyridine, the barrier essentially disappears (Table 8). The explanation invoked[4] has been that the combination of a rotator of two-fold symmetry with one of three-fold symmetry produces a six-fold potential, but this would not necessarily mean that the barrier is zero. Alternatively, the boron atom can be simply thought of as being electron deficient with bond orbitals bent more away from each other; the nitro group carries a partial positive charge and has the N=O double bond delocalized by resonance; and in pyridine the double bonds are also delocalized by resonance.

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TABLE 2. ROTATIONAL BARRIERS (KCAL/MOLE) FOR H-SUBSTITUTED ETHANES

CH_3—CH_3	2·88[58a]	CH_3—CH_2CN	3·05[67]				
CH_3—CH_2F	3·30[58]	CH_3—CH_2Cl	3·69[59]	CH_3—CH_2Br	3·57[60]	CH_3—CH_2I	3·22[61]
CH_3—CHF_2	3·18[62]						
CH_3—CF_3	3·48[63]						
CH_2F—CF_3	4·58[63b]	CH_2Cl—CF_3	5·79[63b]	CH_2Br—CF_3	6·21[63b]	CH_2I—CF_3	6·13[63b]
CF_3—CF_3	4·35[64a]	CF_2Cl—CF_3	5·67[65b]	CF_2Br—CF_3	6·40[65b]	CF_2I—CF_3	7·09[65b]
		$CFCl_2$—$CFCl_2$	9·65[65c*]				
		CCl_3—CCl_3	10·8[67d]				

* A series of F, Cl, Br mixed derivatives have barriers from 6·9 to 12·0.[66]

[a] From thermodynamic data. [b] From vibrational spectra. [c] From NMR spectra. [d] By electron diffraction.

TABLE 3. ROTATIONAL BARRIERS (KCAL/MOLE) FOR C- AND H-SUBSTITUTED ETHANES

		CH_2Cl—CH_3	3·69[59]	CCl_3—CCl_3	10·8[67a]
CH_3—SiH_3	1·70[40]	CH_2Cl—SiH_3	2·55[68]	CCl_3—$SiCl_3$	4·3[67a]
CH_3—SiH_2F	1·56[69]			$SiCl_3$—$SiCl_3$	1·0[67a]
CH_3—$SiHF_2$	1·28[70]				

[a] By electron diffraction.

[57] V. W. Laurie, *J. Chem. Phys.* **31**, 1500 (1959).
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[65] O. Risgin and R. C. Taylor, *Spectrochim. Acta* **15**, 1036 (1959).
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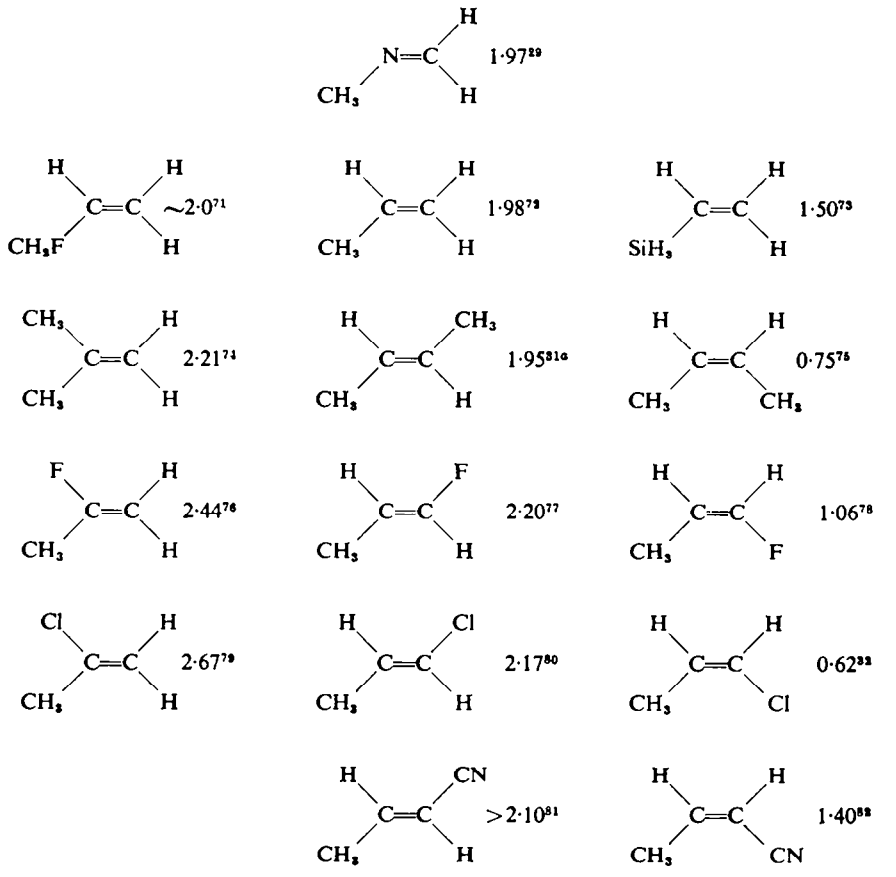
[69] L. Pierce, *J. Chem. Phys.* **29**, 383 (1958).
[70] J. D. Swalen and B. P. Stoicheff, *J. Chem. Phys.* **28**, 671 (1958).

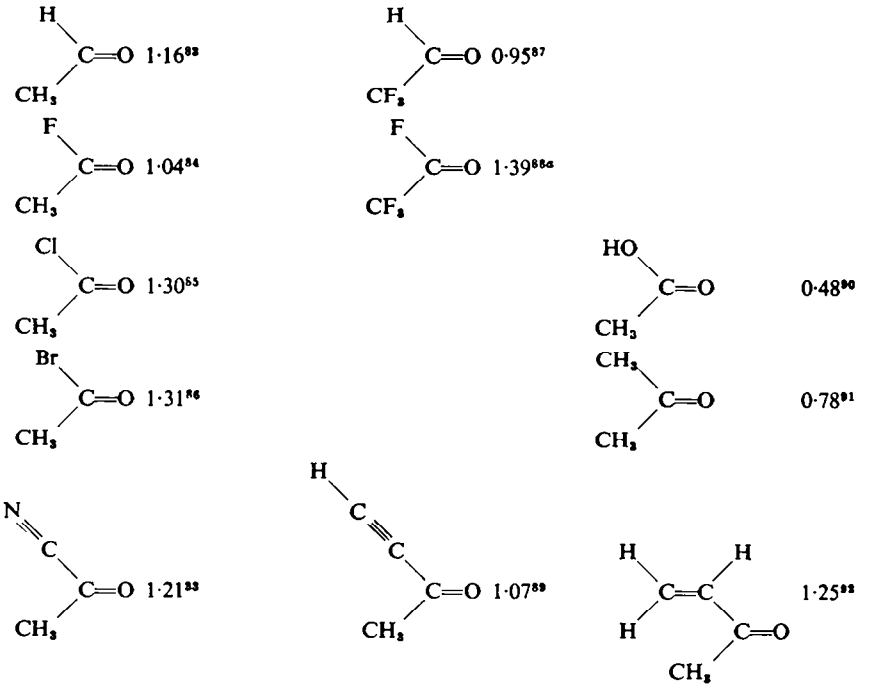
TABLE 4. BARRIERS FOR METHYL ROTATION (KCAL/MOLE) IN C- AND H-SUBSTITUTED PROPENES



[a] From thermodynamic data.

[71] E. Hirota, *J. Chem. Phys.* **42,** 2071 (1965).
[72] D. R. Lide and D. E. Mann, *J. Chem. Phys.* **27,** 868 (1957).
[73] J. M. O'Reilley and L. Pierce, *J. Chem. Phys.* **34,** 1176 (1961).
[74] V. W. Laurie, *J. Chem. Phys.* **34,** 1516 (1961); **39,** 1732 (1963).
[75] T. N. Sarachmann, Quoted in Ref. 32.
[76] L. Pierce and J. M. O'Reilly, *J. Mol. Spectros.* **3,** 536 (1959).
[77] S. Siegel, *J. Chem. Phys.* **27,** 989 (1957).
[78] R. A. Beaudet and E. B. Wilson, *J. Chem. Phys.* **37,** 1133 (1962).
[79] M. L. Unland, V. Weiss and W. H. Flygare, *J. Chem. Phys.* **42,** 2138 (1965).
[80] R. A. Beaudet, *J. Chem. Phys.* **37,** 2398 (1962).
[81] V. W. Laurie, *J. Chem. Phys.* **32,** 1588 (1960).
[82] R. A. Beaudet, *J. Chem. Phys.* **38,** 2548 (1963).

TABLE 5. BARRIERS FOR METHYL ROTATION (KCAL/MOLE) IN CARBONYL COMPOUNDS



[a] From vibrational spectra.

TABLE 6. BARRIERS FOR METHYL ROTATION (KCAL/MOLE) IN ALLENES AND KETENES

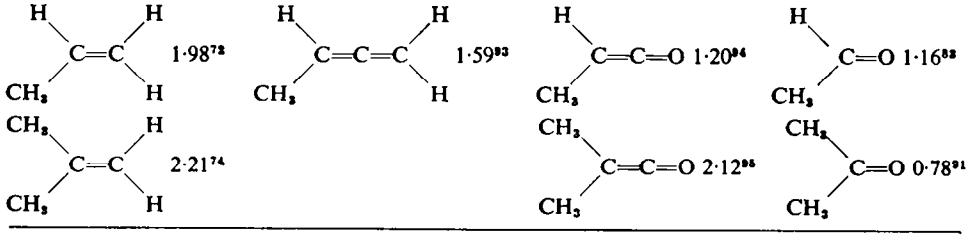


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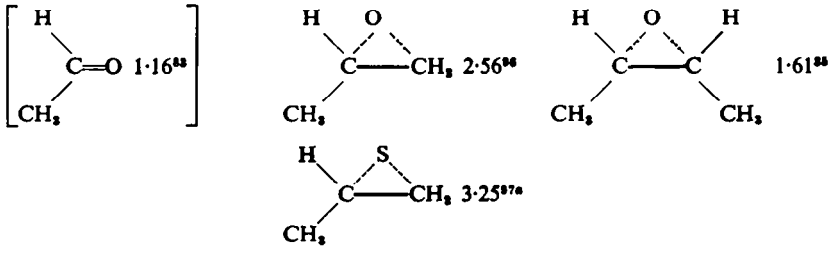
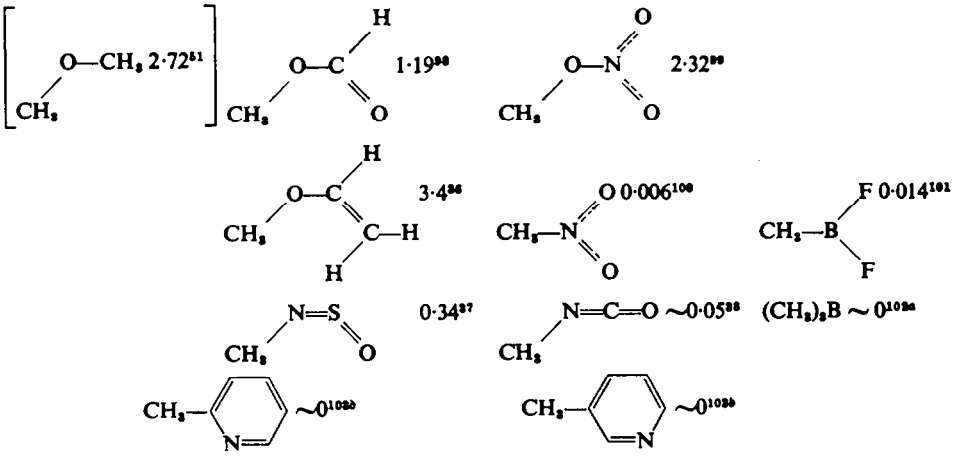
TABLE 7. BARRIERS FOR METHYL ROTATION (KCAL/MOLE) IN THREE-MEMBERED RINGS



[a] From vibrational spectra.

TABLE 8. BARRIERS FOR METHYL ROTATION (KCAL/MOLE) IN RESONATING OR ELECTRON-DEFICIENT MOLECULES



[a] By electron diffraction.
[b] From thermodynamic data.

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