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A Relation between Internuclear Distances and Potential Barriers of Methyl Groups

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An empirical relation is shown between contributions of various groups to the potential barriers of methyl groups and the minimum distance of approach of atoms of these groups to the methyl group. The use of this relation to derive barrier values for other molecules is demonstrated.

I. INTRODUCTION

THE existence of barriers hindering the rotation of groups about bonds has been known for some time. Methods have been described for the calculation of these potential barriers by the comparison of the results of thermodynamic measurements with the results of statistical mechanical calculations.¹

A method of estimating potential barriers where no thermodynamic data exist is highly desirable for the calculation of thermodynamic functions. The available evidence indicates that the equilibrium configuration of groups on opposite ends of a CC axis is staggered rather than opposed.² A plausible explanation of the origin of these barriers is that they arise from repulsive forces between the atoms of the groups in relative rotation. In the barriers considered here (methyl groups rotating on various molecular frames) these forces are presumably of the Van der Waals type, operating between the CH bonding electrons of the methyl group and the other atoms of the molecule.³

It may be possible that energy *vs.* distance relationships, similar to the usual type of interatomic energy curves, exist for pairs of atoms on

opposite ends of a bond about which rotation is occurring. From such curves it would then be possible to calculate the energy changes which occur when groups rotate relative to one another. This approach was used in a recent paper by Aston, Isserow, Szasz, and Kennedy.⁴ An interatomic potential of the form $V = k/r_{ij}^n$ was assumed between pairs of atoms ij . The constants were evaluated from known barriers in ethane and neopentane and other barriers were calculated with fair success. A simpler and more empirical approach has been adopted by the present authors. This method reproduces the barriers of methyl groups in a certain class of molecules with somewhat greater accuracy and is easier to apply.

As is the common practice, the assumption of independence of torsional coordinates is made, i.e., the absence in the potential energy function of cross terms involving products of torsional coordinates of different groups. Although such cross terms, particularly between adjacent torsional rotators, certainly do exist and have been evaluated for one simple case (see Pitzer, reference 6), the difficulty of their evaluation and the fact that they would seem to be small compared to the "pure" potential terms have led to the use of effective barriers obtained by ignoring them.

II. DEPENDENCE OF BARRIERS ON MINIMUM INTERNUCLEAR DISTANCES

The barrier on a single methyl group is regarded as being due to a summation of contributions from interactions with groups on the other end of the rotational axis. For example, the

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¹ K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.* **10**, 428 (1942). This is the most recent paper on the theory and gives references to earlier work.

² V. Schomaker and D. P. Stevenson, *J. Chem. Phys.* **8**, 637 (1940); K. W. F. Kohlrausch and H. Wittek, *Zeits. f. physik. Chemie* **B48**, 177 (1941).

³ Effects due to unshared electron pairs have been ignored. The ultimate justification for this lies in the success achieved when only hydrogen-hydrogen interactions are considered. In other cases than those considered here it may be necessary to take into account the additional effect of dipole-dipole interactions: J. Y. Beach and D. P. Stevenson, *J. Chem. Phys.* **6**, 635 (1938); J. Y. Beach and K. L. Palmer, *J. Chem. Phys.* **6**, 639 (1938).

⁴ J. G. Aston, S. Isserow, G. J. Szasz, and R. M. Kennedy, *J. Chem. Phys.* **12**, 336 (1944).

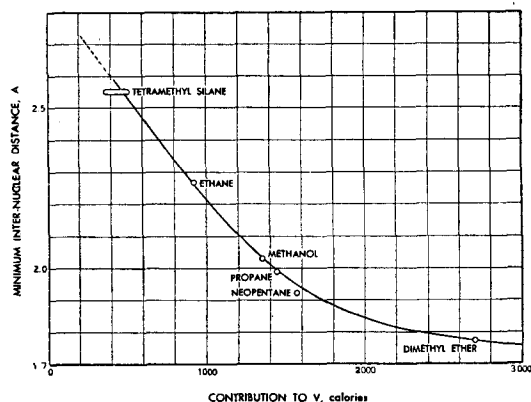


FIG. 1. Relation of barrier contributions to minimum internuclear distance.

barrier of 2750 calories found for ethane⁵ may be looked upon as three times the barrier offered to a methyl group by a single CH bond at the other end of the CC rotation axis. Hence, this barrier contribution may be taken as 920 cal. The observed barrier of 3300 cal. restricting the rotation of a methyl group in propane⁶ may be regarded, similarly, as being a summation of two 920-cal. contributions from the hydrogen atoms on the central carbon atom and a contribution due to the other methyl group. Thus this contribution has a value of $3300 - 2 \times 920 = 1460$ cal. The observed barriers to the methyl group rotations in methanol and dimethyl ether may be regarded as being entirely due to the hydrogen atom and the methyl group, respectively, while those in neopentane and tetramethylsilane are three times the individual contribution from a methyl group on the other end of the rotation axis.

The minimum distance of approach of a hydrogen nucleus of the methyl group to any hydrogen nucleus of the opposing group has been chosen as a convenient measure of the amount of interaction giving rise to a barrier contribution. This minimum distance of approach is taken with respect to the rotation of the groups with all parameters other than rotational orientation held constant. Thus for ethane the minimum distance is that from a hydrogen nucleus on one

end to the corresponding hydrogen nucleus on the other end of the CC axis when the groups are in the opposed (D_{3h}) configuration. For propane the minimum distance between methyl groups is calculated with both methyl groups in the "opposed" configuration with respect to the CH_2 group. Other molecules are treated in a similar fashion. When these minimum distances are plotted against the barrier contributions from the respective groups, the points may be fitted remarkably well by a single smooth curve (Fig. 1). It is an oversimplification to assert that all the forces giving rise to the barrier are functions of this single parameter; nevertheless the excellence of the fit and the adequacy of the predictions made from the curve indicate that this parameter (minimum distance of approach) is a useful measure of the magnitude of the interactions of the groups involved.

The barriers used in obtaining data for the construction of Fig. 1 are listed in Table I. All values given are taken directly from the indicated literature references with the exception of the one for dimethyl ether, which together with methanol requires special discussion.

For methanol an analysis of the fine structure of the infra-red absorption spectrum by Koehler and Dennison⁷ led to an estimate of 1340 calories for the barrier. Crawford⁸ calculated a barrier of 3400 calories using the third law entropy obtained for liquid methanol by Kelley⁹ and the

TABLE I. Barrier contributions used in construction of Fig. 1.

Compound	Measured barrier, cal.	Distances, A	Barrier contributions, cal.	References
Ethane	2750	2.270	920	5
Propane	3300	2.261, 1.991	930, 1440	6, a
Neopentane	4800	1.923	1570	b
Methanol	1350	2.030	1350	7
Tetramethylsilane	1100-1500	2.556	370-500	c
Dimethyl ether	2700	1.774	2700	see text

^a The values shown here for barrier contributions differ very slightly from those used in the text. This is due to a slight adjustment made in the methyl-to-methylene closest hydrogen distance, resulting from the non-tetrahedral angles about the central carbon, and making this distance somewhat shorter than the analogous ethane distance.

^b J. G. Aston and G. H. Messerly, *J. Am. Chem. Soc.* **58**, 2354 (1936); K. S. Pitzer, *J. Chem. Phys.* **5**, 473 (1937); K. S. Pitzer, *Chem. Rev.* **27**, 39 (1940).

^c J. G. Aston, R. M. Kennedy, and G. H. Messerly, *J. Am. Chem. Soc.* **63**, 2343 (1941).

⁷ J. S. Koehler and D. M. Dennison, *Phys. Rev.* **57**, 1006 (1940).

⁸ B. L. Crawford, Jr., *J. Chem. Phys.* **8**, 744 (1940).

⁹ K. K. Kelley, *J. Am. Chem. Soc.* **51**, 181 (1929).

⁵ G. B. Kistiakowsky, J. R. Lacher, and F. Stitt, *J. Chem. Phys.* **7**, 289 (1939).

⁶ G. B. Kistiakowsky and W. W. Rice, *J. Chem. Phys.* **8**, 610 (1940). A value of 3400 cal. was recently derived by K. S. Pitzer, *J. Chem. Phys.* **12**, 310 (1944).

latent heat of vaporization measurements of Fiock, Ginnings, and Holton.¹⁰ However, since methanol has only a single hydrogen-methyl interaction at each maximum, it would be expected to have a barrier much smaller than that of ethane where three interactions contribute to each maximum. Much higher latent heats than those of Fiock, Ginnings, and Holton, which are *a priori* as acceptable, have been reported in the literature.¹¹ Third law entropies calculated using these data give a barrier in close agreement with the spectroscopic value of 1340 calories. For these calculations the frequency assignment of Noether¹² and the moments of inertia shown in Table II were used. Consequently, the spectroscopic value was adopted. Since there has been considerable lack of agreement on the barrier for this molecule, the data referred to above are discussed in detail in an appendix to this paper.

For dimethyl ether an accurate third law entropy has been determined by Kennedy, Sagenkahn, and Aston.¹³ Using the frequency assignment of Crawford and Joyce¹⁴ they obtained a barrier of 3100 cal. Unpublished infra-red data from these laboratories led to a frequency assignment sufficiently different from that of Crawford and Joyce to warrant recalculation of the barrier, leading to a value of 2700 cal. This frequency assignment together with the moments of inertia used is shown in Table II. The heat capacity data of Kistiakowsky and Rice¹⁵ on dimethyl ether vapor unfortunately cannot be used to determine the barrier, since contributions from the internal rotations in the temperature range of the measurements are nearly constant over a fairly broad range of barrier values. Small errors in either the frequency assignment or the heat capacity measurements would lead to large errors in the barrier. However, the calculated and observed heat capacities are in substantial agree-

TABLE II. Moments of inertia and vibrational frequencies used in statistical calculations.

Compound	Product of moments of inertia, g ² cm ⁴	Reduced moment for internal rotation, g cm ²	Vibrational frequencies, cm ⁻¹
Dimethyl ether	$1.708 \cdot 10^{-115}$	$4.33 \cdot 10^{-40}$	412, 920, 1102, 1180(2), 1260(2), 1425(2), 1450(2), 1462(2), 2930(6)
Methanol	$7.748 \cdot 10^{-117}$	$1.08 \cdot 10^{-40}$	1034, 1209, 1260, 1340, 1430, 1455, 1477, 2845, 2978(2), 3683
Methylamine	$1.101 \cdot 10^{-116}$	$1.82 \cdot 10^{-40}$	620, 783, 1064, 1120, 1174, 1426, 1460(2), 1625, 2930(3), 3350(2)
Acetone	$1.398 \cdot 10^{-114}$	$4.99 \cdot 10^{-40}$	391, 488, 531, 787, 900(2), 1066, 1070, 1220, 1350, 1353, 1420, 1423, 1430, 1438, 1710, 2930(6)
Dimethyl sulfide	$7.867 \cdot 10^{-116}$	$4.90 \cdot 10^{-40}$	Same as those of Osborne, Doescher, and Yost. ^a

All physical constants used were taken from R. T. Birge, Rev. Mod. Phys. **13**, 233 (1941). Thermodynamic contributions for restricted rotators were from the tables of Pitzer and Gwinn, reference 1.

^a Osborne, Doescher, and Yost, J. Am. Chem. Soc. **64**, 169 (1942).

ment. Consequently the value of 2700 calories was accepted.

The molecular constants used in calculating the minimum internuclear distances used in Fig. 1 are given in Table III. The CH bond length of 1.093A from spectroscopic work on methane¹⁶ and the CC bond distance of 1.542A from x-ray diffraction work on diamond¹⁷ were used throughout. The bond angles in methyl groups were assumed to be tetrahedral. All other values used and their sources are indicated in Table III. Interatomic distances were carried to 0.001A in all cases. This is well beyond the accuracy with which these parameters are known for most molecules. However, since small changes in these distances were significant, this procedure gave a greater degree of internal consistency than would have been obtained with values rounded off to the experimentally significant limit of 0.01A.

III. TESTS OF THE METHOD

A number of calculations have been made to illustrate the use of the curve of Fig. 1 in esti-

¹⁶ D. M. Dennison, Rev. Mod. Phys. **12**, 210 (1940).

¹⁷ Value given by L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1939), first edition, p. 150.

¹⁰ E. F. Fiock, D. C. Ginnings, and W. B. Holton, Bur. Stand. J. Research **6**, 881 (1931).

¹¹ E. Bartoszewicz, Roczniki Chem. **11**, 90 (1931); Chem. Abs. **25**, 5343 (1931); S. Young, Proc. Roy. Dublin Soc. **12**, 374 (1911).

¹² H. D. Noether, J. Chem. Phys. **10**, 693 (1942).

¹³ R. M. Kennedy, M. Sagenkahn, and J. G. Aston, J. Am. Chem. Soc. **63**, 2267 (1941).

¹⁴ B. L. Crawford, Jr. and L. Joyce, J. Chem. Phys. **7**, 307 (1939).

¹⁵ G. B. Kistiakowsky and W. W. Rice, J. Chem. Phys. **8**, 618 (1940).

TABLE III. Molecular structural parameters used in calculating minimum distances of approach of rotating groups.

Molecule	Parameters (lengths in Å)
Ethane	standard values (see text)
Propane	<CCC, 111° 30'
Neopentane	standard values; <CCC tetrahedral
Methanol	CO, 1.420; OH, 0.959; <COH, 104° 40'
Tetramethylsilane	CSi, 1.93; <CSiC tetrahedral
Dimethyl ether	CO, 1.420; <COC, 111°
Methylamine	CN, 1.470; NH, 1.016; <CNH, 108°; <HNH, 108°
Dimethylamine	CN, 1.470; NH, 1.016; <CNH, 108°; <CNC, 110°
Trimethylamine	CN, 1.470; <CNC, 110°
Methyl mercaptan	CS, 1.82; SH, 1.35; <CSH, see text, Section III
Dimethyl sulfide	CS, 1.82; <CSC, 96°
Acetone	CO, 1.21; CC, 1.52; <CCC, 120°
Isobutane	<CCC, 111° 30'
Trimethylborane	BC, 1.56; <CBC, 120°
Trimethylphosphine	PC, 1.87; <CPC, 100°
Methyl hydroselenide	CSe, 1.93; SeH, 1.49; <CSeH, 90°
Methyl hydrotelluride	CTe, 2.10; TeH, 1.68; <CTeH, 90°
Tetramethylgermane	CGe, 1.98; <CGeC tetrahedral
Tetramethyltin	CSn, 2.18; <CSnC tetrahedral
Tetramethyllead	CPb, 2.23; <CPbC tetrahedral

These parameters were taken from the electron diffraction results summarized by: L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1939), first edition, Chaps. III and V. V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.* **63**, 37 (1941).

In addition, spectroscopic results were utilized for certain of the parameters of methanol (OH distance; see A. Borden and E. F. Barker, *J. Chem. Phys.* **6**, 553 (1939)), the amines (NH distance and HNH angle taken from NH₃), and methyl mercaptan (SH distance taken from H₂S).

mating barriers and to demonstrate the accuracy and practicality of this method. The comparisons of estimated barriers and those reported in the literature, for molecules other than those used in constructing the curve, are given in Table IV. In addition the potential barriers have been estimated for a number of molecules that are amenable to statistical treatment and for which no calorimetric measurements have been published. Molecular constants used in calculating minimum internuclear distances for these molecules are given in Table III.

The following discussion of the check calculations will illustrate the method as applied to the methylamines, methyl mercaptan, dimethyl sulfide, acetone, and isobutane.

The closest distance of approach of a methyl-group hydrogen to the hydrogen of an NH group linked to the methyl is 2.151Å, using the molecular dimensions in Table III for methylamine. Therefore, from Fig. 1, the barrier contribution of the NH bond is 1110 cal. The closest distance between a methyl-group hydrogen and a hydrogen of another methyl-group bonded to the same nitrogen atom is 1.823Å, leading to a contribution of 2130 cal. offered by the -NCH₃ group to a methyl group in di- and trimethyl-

amine. A small expansion of the CNC angle over the HNH angle was assumed for di- and trimethylamine analogous to the known increase in the CCC angle of hydrocarbons over the tetrahedral value. Summing the contributions from the proper groups, the following barriers are obtained for methyl groups in the methylamines:

monomethylamine = $2 \times 1110 = 2220$ calories,
dimethylamine = $1130 + 2130 = 3260$ calories,
trimethylamine = $2 \times 2130 = 4260$ calories.

These values are in close agreement with experimentally determined values, as shown in Table IV.¹⁸

The third law entropy of methyl mercaptan leads to a barrier of 1460 calories. The value from Fig. 1 is 930–1010 depending on the CSH angle assumed. In the case of dimethyl sulfide, while an accurate third law entropy has been determined, the uncertainty in the CSC angle makes an accurate determination of the barrier impossible. Using an angle of 96° for calculation of the moments of inertia leads to a barrier of 1990 calories for each methyl group. This same angle gives a minimum hydrogen-hydrogen distance between methyl groups of 1.867Å and a barrier of 1870 calories from Fig. 1, in satisfactory agreement.

In the case of acetone, the third law entropy of the liquid,¹⁹ various reported heats of vaporization, the heat capacity of the gas,²⁰ and the frequency assignment shown in Table II gave barriers ranging from 560 to 1240 calories compared to 970 calories from Fig. 1.

For isobutane the third law entropy led to a barrier of 3870 calories.²¹ Using a CCC angle of 111°30' a barrier of 3850 calories was obtained from Fig. 1.

¹⁸ Using the gaseous heat capacity data of Felsing and Jesson, *J. Am. Chem. Soc.* **55**, 4418 (1933), and the frequency assignment for methylamine given in Table II, values of $C_p(\text{calc.}) - C_p(\text{obs.})$ of +.59 at 0°C, -.05 at 25°C, and -.52 at 50°C were obtained. A similar trend was noticed by Aston, Eidinoff, and Forster, *J. Am. Chem. Soc.* **61**, 1539 (1939), in comparing calculated and observed C_p 's of Felsing and Jesson for dimethylamine. These trends cannot be accounted for by any reasonable modifications of barrier or frequency assignments.

¹⁹ K. K. Kelley, *J. Am. Chem. Soc.* **51**, 1145 (1929).

²⁰ K. Bennewitz and W. Rossner, *Zeits. f. physik. Chemie* **B39**, 126 (1938).

²¹ J. G. Aston, R. M. Kennedy, and S. C. Schumann, *J. Am. Chem. Soc.* **62**, 2059 (1940).

IV. APPLICATION TO OTHER CLASSES OF MOLECULES

This method for estimating barriers is, as emphasized above, applicable only to methyl groups, since it is only by virtue of the threefold symmetry that it becomes legitimate to split the barrier up into independent contributions from the groups giving rise to the barrier. However, some fairly successful attempts have been made to estimate barriers for other simple groups bearing hydrogens.

Thus in ethanol the methyl-group barrier was calculated from the interactions with two methylene-group hydrogens at 2.270Å and one-third of the contribution from the hydroxyl hydrogen, whose closest approach is at 1.798Å. Similarly, the barrier for the OH group was calculated from Fig. 1, using an average of values obtained from the minimum distances of approach of the OH hydrogen to the methylene-group hydrogens and to the nearest methyl-group hydrogen:

$$V_{\text{OH}} = \frac{2400 + 2 \times 1340}{3} = 1690 \text{ cal.}$$

$$V_{\text{Me}} = 2 \times 916 + \frac{2400}{3} = 2630 \text{ cal.}$$

In isopropyl alcohol the analogous values are

$V_{\text{OH}} = 2070$, $V_{\text{Me}} = 3240$, and in tertiary butyl alcohol $V_{\text{OH}} = 3400$ and $V_{\text{Me}} = 4010$. These values for the OH group barriers are believed to be reliable. If, however, the oxygen atom has any large effect the methyl barrier estimates may be low. Preliminary comparisons of statistical calculations for these alcohols with the results of all known measurements are satisfactory. The data on these alcohols are from various sources, which are often in serious disagreement. Hence, a complete treatment of the data, which will be presented in a later paper, is required to clarify the picture.

In molecules such as butane where the rotating groups are highly unsymmetrical the present method does not seem to be applicable, and in such cases it will probably be necessary to use a more difficult but more fundamental treatment such as that of Aston.

A consideration of the barriers hindering the rotation of methyl groups attached to ethylenic frames has been omitted from this correlation for several reasons. In the rotation of these groups there may be six maxima per rotation and the barrier contributions might be expected to be different from those predicted from Fig. 1, which was constructed from data on molecules having three maxima per rotation.

TABLE IV. Barriers derived from Fig. 1, and comparison with experimental values.

Compound	Distances, Å	Contributions from Fig. 1, cal.	Total barrier from contributions, cal.	Measured barrier, cal.	References
Methylamine	2.151	1110	2220	1520 or more	<i>a</i>
Dimethylamine	2.140, 1.823	1130, 2130	3260	3460	<i>b</i>
Trimethylamine	1.823	2130	4260	4270	<i>c</i>
Methyl mercaptan	2.208–2.262*	1010–930	1010–930	1460	<i>d</i>
Dimethyl sulfide	1.867**	1870	1870	2000	<i>e</i>
Acetone	2.271	920	920***	560–1240	see text, Section III
Isobutane	2.232, 1.991	970, 1440	3850	3870	<i>f</i>
Trimethylborane	2.302	860	1720		
Trimethylphosphine	2.098	1210	2420		
Methyl hydroselenide	2.340	800	800		
Methyl hydrotelluride	2.548	470	470		
Tetramethylgermane	2.638	~400	~1200		
Tetramethyltin	2.965	~0	~0		
Tetramethyllead	3.046	~0	~0		

* Assuming a CSH angle of 90° and 92° 20', respectively.

** Assuming a CSC angle of 96°.

*** Assuming the whole barrier to be due to the other methyl group. The barrier derived on this assumption fits the available experimental data within their probable errors.

^a J. G. Aston, C. W. Siller, and G. H. Messerly, *J. Am. Chem. Soc.* **59**, 1743 (1937); J. G. Aston and P. M. Doty, *J. Chem. Phys.* **8**, 743 (1940).

^b J. G. Aston, M. L. Eidinoff, and W. S. Forster, *J. Am. Chem. Soc.* **61**, 1539 (1939).

^c J. G. Aston, M. L. Sagenkahn, G. J. Szasz, G. W. Moessen, and H. F. Zuhre, *J. Am. Chem. Soc.* **66**, 1171 (1944).

^d H. Russell, Jr., D. W. Osborne, and D. M. Yost, *J. Am. Chem. Soc.* **64**, 165 (1942).

^e D. W. Osborne, R. N. Doescher, and D. M. Yost, *J. Am. Chem. Soc.* **64**, 169 (1942).

^f J. G. Aston, R. M. Kennedy, and S. C. Schumann, *J. Am. Chem. Soc.* **62**, 2059 (1940).

V. CONCLUDING REMARKS

This method, like any other method of estimating barriers based on an exact knowledge of interatomic distances, is very sensitive to changes in these parameters, particularly in the region of short internuclear distances. For this reason an effort has been made to use a consistent set of molecular constants. Values consistent with those which entered into the construction of Fig. 1 must be used in making barrier estimates from this curve. The arbitrariness in the choice of molecular constants is particularly evident in the choice of hydrogen angles. It is impossible, at present, to state the precise values for these angles in complex molecules because they cannot be obtained by current spectroscopic and electron diffraction methods. It has been assumed, for example, that the COH angle is the same as the water angle and that HCC and HCH angles are tetrahedral, except in cases where this is obviously untrue (such as the HCC angle of the tertiary hydrogen in isobutane).

An additional point of question lies in the uncertainties of the values of the barriers used in constructing Fig. 1. These uncertainties may, in some cases, be as high as ± 500 calories. However, the excellence of fit of the barrier contributions to a smooth curve, and the relatively small deviations between the barriers estimated from the curve and those estimated by the usual methods from calorimetric data indicate that this method will yield values which are entirely adequate for practical thermodynamic calculations.

The concept that repulsive forces give rise to potential barriers in the types of molecules considered is supported further by the electron diffraction evidence that CCC angles are greater than tetrahedral in propane, isobutane, and tertiary butyl chloride.²² In addition the change in some methyl rocking frequencies from approximately 1160 wave numbers in methyl groups attached to secondary and tertiary C atoms to

approximately 1250 in methyl groups attached to quaternary C atoms is readily interpreted as being due to the increased repulsion from adjacent groups.

APPENDIX: THE BARRIER IN METHANOL

The entropy of methanol vapor at 298.16°K and one atmosphere can be derived from available data as follows:

Entropy of liquid, 298.16°K (Kelley ⁹)	30.26 e.u.
Entropy of vaporization ^{10,11}	30.015, 30.447, 30.688
Gas imperfection correction (Berthelot Eq.)	0.02
Entropy change, vapor pressure to one atmos.	-3.586
Entropy of vapor at 298.16°K and one atmos.	56.71, 57.14, 57.38 e.u.

The three values given for entropy of vaporization are those derived from the latent heat values of Fiock, Ginnings, and Holton,¹⁰ Young,¹¹ and Bartoszewicz,¹¹ respectively. These values are 8949.4 cal., 9078 cal., and 9150 cal.

The statistically calculated entropy, except for the internal rotational contribution, is (using constants and frequencies shown in Table II):

Vibrational	0.220 e.u.
Translational-rotational	55.291
	55.511 e.u.

Thus the contribution from internal rotation is 1.20, 1.63, or 1.87 e.u., respectively, obtained from the three latent heat values. The first value, 1.20 e.u., derived from the Fiock, Ginnings, and Holton datum, leads to a barrier of 2360 cal. The spectroscopic value for the barrier (1340 cal.) gives an internal rotational contribution of 1.65 e.u., in essential agreement with the latter two values. The discrepancy between the barrier (2360 cal.) derived here using the Fiock, Ginnings, and Holton latent heat and that given by Crawford⁸ (3400 cal.) derived from the same latent heat and liquid entropy is due mainly to the more recent physical constants and frequency values used here.

²² L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.* **59**, 1223 (1937); J. Y. Beach and D. P. Stevenson, *J. Am. Chem. Soc.* **60**, 475 (1938); J. Y. Beach and J. Walter, *J. Chem. Phys.* **8**, 303 (1940).