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Edwin N. Lassettre and Laurence B. Dean Jr.

Citation: *The Journal of Chemical Physics* **16**, 151 (1948); doi: 10.1063/1.1746802

View online: <http://dx.doi.org/10.1063/1.1746802>

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Origin of the Potential Barrier Hindering Rotation in Ethane and Related Substances

EDWIN N. LASSETTRE AND LAURENCE B. DEAN, JR.
Department of Chemistry, The Ohio State University, Columbus, Ohio
December 9, 1947

ATTEMPTS have been made by Aston, Isserow, Szasz, and Kennedy¹ to systematize the calculation of potential barriers hindering rotation around single bonds by assuming a repulsion between hydrogens which was found empirically to vary inversely as the fifth power of the distance. Since the energy of interaction of two quadrupoles varies inversely as the fifth power of the distance² these results have suggested to us that the barriers arise, not from the repulsion of hydrogen atoms, but from the electrostatic interaction of the charges of *one bond* with the charges of *another bond*. We have investigated the potential barrier for ethane on the basis of this model with results which are in rather satisfactory agreement with experiment and which suggest that the ideas are of general applicability. The results are briefly described below.

In considering the magnitude of interaction between bonds the following specific hypotheses are employed. (i) A single-bond charge distribution consists of a unit positive charge at each nucleus and a pair of electrons. (ii) The electron distribution of a single bond is cylindrically symmetric with respect to the internuclear axis. (iii) The charge distributions of two bonds, which have no atom in common, do not significantly overlap and, hence, exchange interactions are negligible. (iv) The electrostatic potential due to a single-bond charge distribution is sufficiently well characterized by its dipole and quadrupole moments, calculated relative to an origin midway between the nuclei. These hypotheses are in qualitative accord with the accepted ideas concerning the distribution of molecular electrons. If, however, this theory is to account satisfactorily for potential barriers, it is essential that the bond quadrupole moments have reasonable magnitudes.

In the first calculations, an approximate quadrupole moment for the negative charge of the C—H bond was calculated by assuming that the electron pair forming the bond is distributed in a localized molecular orbital which is a linear combination of atomic orbitals for carbon and hydro-

gen. The molecular orbital used is

$$\sigma = aN_1r_1 \exp[-(1.62r_1)(\frac{1}{2} + \frac{3}{2}\cos\theta)] + bN_2 \exp(-r_2),$$

where r_1 and r_2 are the distances, in atomic units, of an electron from the carbon and hydrogen nuclei, respectively, and θ is the angle between r_1 and the line of centers. N_1 and N_2 are normalizing constants. The factor $(\frac{1}{2} + \frac{3}{2}\cos\theta)$ is Pauling's tetrahedral orbital,³ and the radial factor is obtained from Slater's functions and screening constants.⁴ The constants a and b can be determined from the normalizing condition and the bond dipole moment (0.4 Debye). Since, however, the sign of the dipole moment is uncertain, we have preferred to vary a/b over a considerable range which includes both signs for the dipole moment. This procedure also indicates how sensitive the calculated barrier is to alterations in bond ionic character since a/b can be considered a measure of ionic character. The results are given in Table I. In Table I the second column contains

TABLE I.

| a/b | $\mu \times 10^{18}$ e.s.u. | P atomic units | D-D kcal. | D-Q kcal. | Q-Q kcal. | Barrier V kcal. | V (stag.) kcal. |
|-------|--------------------------------|----------------------|--------------|--------------|--------------|--------------------|--------------------|
| 1.0 | -2.30 | 3.16 | 1.58 | -3.33 | 5.63 | 3.88 | 147.1 |
| 1.5 | -1.51 | 3.22 | 0.68 | -2.22 | 5.84 | 4.30 | 96.4 |
| 2.0 | -0.98 | 3.22 | 0.29 | -1.45 | 5.84 | 4.68 | 70.3 |
| 4.0 | 0.03 | 3.13 | 0.00 | 0.05 | 5.52 | 5.57 | 38.3 |
| 5.75 | 0.40 | 3.07 | 0.05 | 0.56 | 5.30 | 5.91 | 33.1 |

the calculated bond dipole moment and the third column the bond quadrupole moment. The "quadrupole moment," P , is defined for a cylindrically symmetric distribution of charge density ρ by the formula

$$P = \int (r^2 - 3x^2)\rho d\tau,$$

where x is the coordinate perpendicular to the axis of symmetry. This is the only parameter required to characterize the quadrupole field of such a distribution. The interaction energy of the three C—H bonds of one methyl group with the three of the other methyl group was calculated for both the staggered (D_{3d}) and the eclipsed (D_{3h}) configurations. The difference between these is given in column seven and the separate dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole energies are also given in columns four, five, and six, respectively. The interactions between C—C and C—H bonds need not be calculated since they remain unchanged as a methyl group is rotated around its symmetry axis.

The results may be briefly summarized as follows:

1. The staggered configuration has lower energy for every value of a/b .
2. The calculated potential barrier is larger than that observed (2750 cal.⁵), but is of the proper order of magnitude.
3. For those values of a/b which give the correct magnitude to the bond dipole moment (0.4D) the quadrupole-quadrupole interaction predominates, and hence an inverse fifth-power dependence on distance between bonds is confirmed.
4. The barrier is not very sensitive to bond ionic character.
5. In performing the calculations it was observed that,

although certain quadrupoles attract and others repel, the net interaction of methyl groups in ethane is one of repulsion both for the staggered and the eclipsed configurations.

6. The calculated potential barriers are small, being the difference between interactions in two configurations, but the total interaction energy is large. (See column eight.)

Since a considerable weight of indirect evidence now exists in favor of the staggered configuration for ethane,^{3,6} the above are seen to be in as good agreement with experiment as could be expected in view of the rough approximation to the negative charge distribution which has been employed. Accurate agreement between the calculated and the experimental barrier (2750 cal.) is obtained with quadrupole moment 2.03 (atomic units) if $\mu = 0.4D$ and 2.35 if $\mu = -0.4D$. The calculated interaction energies are given in Table II. It is interesting to note that both of these quadrupole moments are considerably smaller than those of Table I. This implies that the actual bonding distributions overlap even less than is indicated by the rough molecular orbital used here, hence is consistent with our initial hypothesis. It seems, therefore, that the potential barrier for ethane can be accounted for by means of a quadrupole moment of reasonable magnitude, and the staggered configuration is favored. Thus far the mutual polarization of bonding distributions has been ignored. It is obvious that such polarization occurs but it is difficult to see how such interactions can stabilize the staggered configuration.

It is of interest that quadrupole moments obtained from observed potential barriers (which depend only on energy differences) may be used to calculate the force exerted by one bond on another which contains no common atom. The large energy of interaction of methyl groups in ethane (see Table II, column 7) indicates that such forces are appreciable. In this way a more quantitative treatment of the dependence of interatomic distances, hydrogenation energies, dissociation energies, etc., on bond environment, along the lines proposed by Conn, Kistiakowsky, and Smith,⁶ becomes possible.

Although we have found the same dependence on *distance* for interacting bonds of small dipole moment as did Aston and collaborators, the present model also provides for dependence on the quadrupole moments of two interacting bonds as well as their orientation relative to each other and to the line joining them. Moreover, in a complex substance, such as tetramethyl methane, substantial interactions between C-H and C-C bonds are expected, and hence the similar dependence on distance may be fortuitous.

The conception of interaction of bonding distributions as constituting the source of potential barriers is essentially similar to that proposed by Kistiakowsky, Lacher, and Ransom⁷ several years ago. In certain respects the present treatment may be considered as a quantitative extension of their ideas.

TABLE II.

| $\mu \times 10^{18}$ e.s.u. | P atomic units | D-D kcal. | D-Q kcal. | Q-Q kcal. | Barrier kcal. | V (stag.) kcal. |
|--------------------------------|----------------------|--------------|--------------|--------------|------------------|--------------------|
| 0.40 | 2.03 | 0.05 | 0.37 | 2.33 | 2.75 | 14.2 |
| -0.40 | 2.35 | 0.05 | -0.43 | 3.13 | 2.75 | 29.0 |

A further investigation of the electrostatic interaction of bonding distributions is in progress along two lines: (a) A more accurate calculation of the electrostatic potential than is provided by dipole and quadrupole terms, (b) the empirical calculation of quadrupole moments from the observed potential barriers of compounds other than ethane, and the use of such moments in the prediction of other properties in order to check the accuracy of these values. The calculations will be fully reported when this investigation is complete.

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² H. Marganau, *Rev. Mod. Phys.* **11**, 1 (1939).

³ L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), p. 86.

⁴ J. C. Slater, *Phys. Rev.* **36**, 57 (1930).

⁵ G. B. Kistiakowsky, J. R. Lacher, and F. Stitt, *J. Chem. Phys.* **7**, 289 (1939). See also J. D. Kemp and K. S. Pitzer, *J. Chem. Phys.* **4**, 749 (1936).

⁶ J. B. Conn, G. B. Kistiakowsky, and E. A. Smith, *J. Am. Chem. Soc.* **61**, 1868 (1939).

⁷ G. B. Kistiakowsky, J. R. Lacher, and W. W. Ransom, *J. Chem. Phys.* **6**, 900 (1938).

Physical Basis of a Concept about the Mechanism of Viscosity of Liquids

R. PARSHAD

Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts

December 15, 1947

A THEORY of viscosity of liquids should explain the following: (1) decrease of viscosity with temperature; (2a) increase of viscosity with pressure; (2b) the rate of increase of viscosity increasing with increase of pressure; (3) increased viscosity of associated liquids over that of normal liquids.

The current theories of viscosity generally relate cohesion with viscosity. Cohesion may be taken as a measure of total attraction energy of molecules and is indicated in magnitude by latent heat of vaporization or inverse function of compressibility. While the relation between cohesion and viscosity is generally true, there are significant departures from this correspondence. These originate in the difference between the mechanisms of viscosity and cohesion. Viscosity arises because of the resistance to the displacement of a molecule at right angles to the intermolecular line (taking an ideal case of two molecules), and is, in general, due to the resistance offered to change of configuration of the molecules, or the resistance against changing of places of individual molecules in the same configuration, while the intermolecular distances remain unchanged. Cohesion arises due to resistance offered to a direct change of intermolecular distances, the configurations remaining the same. These differences have been discussed more fully elsewhere.¹

We assume that viscosity, or the resistance offered to change of position of molecules, is due to the existence of potential barriers around the molecules in the liquid. The steeper these potential barriers, the more the viscosity will be. This is why liquids of anisotropic molecules have, in general, higher viscosity than liquids of more symmetrical molecules. Now we postulate that these potential