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The Theory of the Racemization of Optically Active Derivatives of Diphenyl

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T. L. Hill has recently shown that it is possible to compute the magnitude of steric strain in certain organic molecules. The present paper summarizes the results of a similar but independent investigation directed towards a computation of the rate of racemization of optically active (i.e., sterically hindered) derivatives of diphenyl. The energy of the planar form of a sterically hindered diphenyl can be approximated by the equation:

$$E = \sum_i \frac{1}{2} a_i q_i^2 + A_1 \exp(-d_1/\rho_1) + A_2 \exp(-d_2/\rho_2),$$

where the q_i are the normal coordinates of the unstrained molecule in question and the exponential terms are approximations (over the limited range of interest) to the steric repulsions of the non-bonded groups which repel each other. There are two such exponential terms, for in most sterically hindered diphenyls the repulsion is caused by two pairs of ortho substituents. The equation for E_0 , the activation energy for racemization, has been found for the symmetrical case by minimizing E ; the constants a_i , A , and ρ , and the dimensions of the diphenyl derivative appear in the expression for E_0 . It is also possible to derive equations for the vibration frequencies of the planar form of the sterically hindered molecule (and, therefore, find the entropy of activation); these equations are complicated by the essential degeneracy of the vibrations in question.

I

IN a recent letter to the editor, T. L. Hill¹ has presented the outline of a general method for the quantitative (or at least semi-quantitative) evaluation of steric strain.² The method applies to those molecules where neighboring but non-bonded groups have been forced together so that they are separated by a distance less than the sum of their van der Waals radii. (An example of the type discussed by Hill is the addition compound of boron trifluoride and α, α' -lutidine, where the methyl groups in the base are forced close to the fluorine atoms in the boron derivative.^{2b} Investigations by the same method as that suggested by Hill have been under way here for the past nine months, with special reference to the rate of racemization of optically active diphenyls. It seems therefore appropriate to supplement Hill's publication with those results obtained here which are of general applicability.

Hill suggested that the energy of a strained molecule is distributed among many bonds and is by no means concentrated in the energy of

repulsion of the groups which have been pressed together. Quantitatively, Hill's equation is similar to Eq. (1), where E is the energy of the strained molecule in excess of that of a hypothetical molecule, identical in every way with the first, except that it has no steric strain.

$$E = \sum_i \frac{1}{2} a_i q_i^2 + E(\text{steric}). \quad (1)$$

Here $E(\text{steric})$ is a function of the distance d , between the groups or atoms which are involved in the steric interference. $E(\text{steric})$ may be negative (attraction) or positive (repulsion) but for most cases of interest, and certainly in the case studied here, it is positive. The variables q_i are coordinates which for the molecule in question are proportional to the displacements of all the atoms from their equilibrium positions. Equation (1) is written without cross-product terms, that is, without terms $a_{ij} q_i q_j$. The assumption is thus made that the coordinates, q_i , are mutually independent. This assumption is satisfied for the "normal" coordinates of the molecule but not in general for the increments (decrements) to the Cartesian coordinates of the various atoms. The sum in Eq. (1) must extend over all those coordinates, q_i , changes in which will affect the value of d . The force constant associated with each coordinate q_j is represented by a_j . The values of the coordinates, q_i , are to be

¹ T. L. Hill, *J. Chem. Phys.* **14**, 465 (1946). See also I. Dostrovsky, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.* 173 (1946).

^{2a} R. Adams and H. C. Yuan, *Chem. Rev.* **12**, 261 (1933);

^{2b} H. C. Brown, H. I. Schlesinger, and S. Z. Cardon, *J. Am. Chem. Soc.* **64**, 325 (1942).

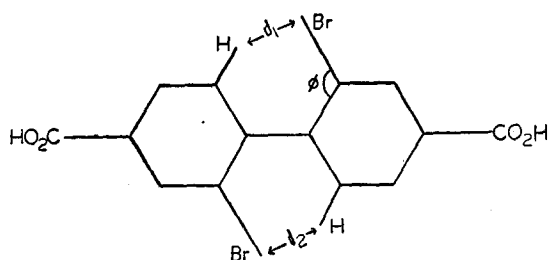


FIG. 1. Planar form (the activated complex) of the diphenyl.

chosen in such a way that E is a minimum. It should be noted that the larger the number of terms in Eq. (1) the lower will be the minimum value of E . This is the usual situation which obtains in a variation treatment, and is a necessary consequence of the fact that the energy depends upon a power of the displacement coordinates higher than the first.

II

The rest of this article is concerned with the quantitative treatment for the rate of racemization of optically active diphenyls such as 2,2'-dibromo-4,4'-dicarboxydiphenyl.³ The racemization of a compound of this type will occur only if the molecule passes through the planar configuration (Fig. 1). This will be the "activated complex" for the racemization of sterically hindered diphenyls.

It is worth noting in passing that the proposed treatment of steric strain assumes that the racemization involves (among other displacements) an increase in the angle, ϕ , between each ortho substituent and the benzene ring. This increase in angle will be sterically hindered by a substituent in the adjacent meta position. This conclusion is consistent with the experimental fact⁴ that the rate of racemization of some diphenyl derivatives is uniformly and considerably decreased by substituents in this meta position. Substituents in other positions, although they affect the rate of racemization, do so to a much smaller extent, and they occasionally increase, rather than decrease, the racemization rate.

In the particular example chosen, only the hydrogen and bromine nuclei are close enough

together to interfere strongly. (It is assumed that the bromine-bromine repulsions are so strong as to preclude the possibility of racemization through an activated complex in which these atoms are adjacent to one another.) The distance between a pair of hydrogen and bromine nuclei in the activated complex is represented by d ; the distance between these nuclei which would obtain if there were no deviations from normal bond lengths and angles is called d_0 . In the case under consideration, the energy of the two neighboring but non-bonded groups is predominately repulsive in character. It is convenient to approximate this repulsive energy by $A \exp(-d/\rho)$; this approximation should be valid for the values of d in question. The constants A and ρ can be evaluated by comparing the expression above with the energy curve computed from the second virial coefficient⁵ for molecules which contain the same groups (here hydrogen and bromine) which repel each other in the activated complex.

In the case under discussion (2,2'-dibromo-4,4'-dicarboxydiphenyl) each of the two bromine atoms must be forced close to a hydrogen atom in the activated complex. The repulsive energy for any distance, d , will then be twice that calculated from the energy curve to which reference has been made above. The same considerations will apply to other cases in which the diphenyl derivative is symmetrically substituted in the ortho positions. In the case of unsymmetrically substituted diphenyls, the sum of the repulsive energy for the two different sets of repelling groups would have to be used for $E(\text{steric})$ in Eq. (1). The energy of activation for the present case is that shown in Eq. (2):

$$E = \sum_i \frac{1}{2} a_i q_i^2 + 2A \exp(-d/\rho). \quad (2)$$

Here the constants a_i are the force constants⁶ associated with the normal coordinates q_i . Normal coordinates are chosen so that both the potential and kinetic energies involve only square and no cross-product terms. We wish to use such coordinates that the potential energy involves only squares but we are not primarily interested in the kinetic energy terms. It is

⁵ See, for example, O. K. Rice, J. Am. Chem. Soc. **63**, 3 (1941).

⁶ For a discussion of these constants for benzene see E. Bernard, C. Manneback, and A. Verlayen, Ann. Soc. Sci. Bruxelles **60**, 45 (1940); F. A. Miller and B. L. Crawford, J. Chem. Phys. **14**, 282 (1946).

³ W. I. Patterson and R. Adams, J. Am. Chem. Soc. **57**, 762 (1935).

⁴ R. Adams and H. R. Snyder, J. Am. Chem. Soc. **60**, 1411 (1938).

therefore possible (except in Part III of this paper, in which the entropy of activation is discussed) to use bastardized coordinates which are not true normal coordinates but involve true normal coordinates of part of the molecule (the benzene rings) and force constants for other parts. In fact, the normal coordinates for the substituted diphenyls are not now available. However, the normal coordinates for benzene are known. In order to carry through the calculations, it will be necessary to assume that the force constants for the various deformations in each benzene ring are unaffected by the other aromatic nucleus. It will further be necessary to make some assumption about the magnitude of the force constant for the stretching vibration of the central carbon to carbon bond in the diphenyl derivative. The value of the activation energy computed on the basis of these assumptions should be the same as that which would be obtained from the normal coordinates of diphenyl provided only that a correct value for the stretching force constant of the central bond has been chosen. It should be noted, however, that the summation in (2) extends over all the normal coordinates in both benzene rings.

Preliminary calculations have shown that for diphenyls which racemize at measurable rates, only small changes in bond lengths and angles are necessary to attain the planar configuration. Because the displacement of each atom from its equilibrium position is small, it is possible as a good approximation to represent d as a linear function of the Cartesian displacement coordinates, x_i . Here, however, it will be necessary to

set up separate functions for the distances d_1 and d_2 between the two hydrogen-bromine pairs, since the distances between the atoms in the two pairs are affected differently by changes in the various Cartesian displacement coordinates.

$$d_1 = d_0 + \sum_i l_i x_i, \quad d_2 = d_0 + \sum_i l'_i x_i. \quad (3)$$

There is a linear relationship⁷ (Eq. (4)) between the Cartesian displacement coordinates of each atom and the normal coordinates, q_i .

$$x_j = \sum_i c_{ij} q_i. \quad (4)$$

(The normal coordinates of the benzene molecule, for example, are known in terms of the Cartesian displacement coordinates of each atom.⁸) Because of the considerations cited above, Eq. (3) may be written in the form (5)

$$d_1 = d_0 + \sum_i b_i q_i, \quad d_2 = d_0 + \sum_i b'_i q_i, \quad (5)$$

where

$$b_i = \sum_k l_k c_{ik} \quad \text{and} \quad b'_i = \sum_k l'_k c_{ik}. \quad (6)$$

The sum in Eq. (2) extends over all the normal coordinates, q_i . There will be some of these coordinates, however, changes in which do not change the internuclear distance, d ; for example, this applies as a first approximation to the non-planar vibrations of the aromatic rings in a diphenyl derivative. For such a coordinate, q_k , the corresponding constant b_k is zero. It will be seen below (Eq. (10)) that when any particular b_i , say b_k , is zero, the value of q_k in the activated complex is also zero; the term in Eq. (2) involving this coordinate therefore contributes nothing to the energy, E , and may be omitted from the calculation if this for any reason seems desirable.

The combination of Eq. (2) and Eq. (5) leads to (7)

$$E = \sum_i \frac{1}{2} a_i q_i^2 + E_{d_0} \exp \left[-\left(\frac{1}{\rho} \right) \sum_i b_i q_i \right] + E_{d_0} \exp \left[-\left(\frac{1}{\rho} \right) \sum_i b'_i q_i \right], \quad (7)$$

where $E_{d_0} = A \exp \left[-\left(\frac{d_0}{\rho} \right) \right]$. Here E_{d_0} is the repulsive potential which would have obtained if no bond lengths or angles had been distorted. It is now possible to find the minimum value for E ; the values of the normal coordinates, q_i , in the activated state are represented by q_i^0

$$\left(\frac{\partial E}{\partial q_j} \right) = a_j q_j^0 - \left(\frac{b_j}{\rho} \right) E_{d_0} \exp \left[-\left(\frac{1}{\rho} \right) \sum_i b_i q_i^0 \right] - \left(\frac{b'_j}{\rho} \right) E_{d_0} \exp \left[-\left(\frac{1}{\rho} \right) \sum_i b'_i q_i^0 \right] = 0. \quad (8)$$

Let

$$E_{d_0} \exp \left[-\frac{1}{\rho} \sum_i b_i q_i^0 \right] = E_{d_0} \exp \left[-\frac{1}{\rho} \sum_i b'_i q_i^0 \right] = Z. \quad (9)$$

Since only definite values of the normal coordinates, corresponding to the "equilibrium" state of the

⁷ Cf. G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, New York, 1945).

⁸ E. B. Wilson, *Phys. Rev.* **45**, 706 (1934).

activated complex, occur in Z , it follows that Z itself is a constant for any particular optically active diphenyl. Further, from what has already been said about the constants b and b' and about the symmetry of the problem, it is clear that the two sums in Eq. (9) must be equal; this will also later be apparent from physical considerations. Then

$$q_j^0 = \frac{(b_j + b'_j)Z}{\rho a_j} = \frac{2B_j Z}{\rho a_j}, \quad (10)$$

where Eq. (10) defines B_j ; Z can be obtained in terms of known constants by the numerical solution of Eq. (11), which equation results from the combination of (9) and (10).

$$Z = E_{d0} \exp -[(2Z/\rho^2) \sum_i B_i^2/a_i]. \quad (11)$$

Substitution of the values of q_j^0 (Eq. (10)) into Eq. (7) yields E_0 , the minimum value of E ; E_0 is, therefore, the activation energy for racemization.

$$E_0 = \sum_i \frac{1}{2} a_i (q_i^0)^2 + 2Z = \frac{2Z^2}{\rho^2} \sum_i \frac{B_i^2}{a_i} + 2Z. \quad (12)$$

Z is therefore analogous to $E(\text{steric})$ of Eq. 1. It is the actual energy of repulsion of one pair of neighboring non-bonded groups in the activated state, and is of course much less than E_{d0} . It is also clear that, for symmetrically substituted diphenyls, Z must be the same for the two halves of the molecule (i.e., Eq. (9) is valid).

Equation (12) for the energy of activation for the racemization of diphenyl derivatives is not precisely correct, since the resonance energy of the molecule has been neglected. However, the resonance energy for diphenyl itself, in excess of that for two benzene rings, amounts only to a few kilocalories⁹; the precise value of this energy term is, however, uncertain. When a satisfactory estimate of this resonance energy is available, the true activation energy can be found by subtracting the resonance energy from E_0 . In the calculation of this latter quantity, the observed length of the carbon-carbon bond between the benzene rings in diphenyl should be used; this length is needed to evaluate the constants l_i and l'_i , of Eq. (3).

However, until an accurate estimate of the resonance energy is available, an approximate method of calculation must be employed. The resonance in the planar form of diphenyl decreases the lengths of the carbon-carbon bond between the benzene rings. It follows, therefore, that the repulsion between the ortho substituents in the planar form of a sterically hindered diphenyl will be increased, because of resonance, over that which would have obtained in the absence of resonance.¹⁰ This additional steric hindrance will diminish the absolute magnitude of the contribution of resonance to the energy of the planar configuration. Since the contribution of resonance even before it is diminished by steric effects, is small, the net effect on E_0 can probably be neglected.¹¹ It should be noted, however, that in any computation where resonance is neglected, the normal (i.e., aliphatic) carbon-carbon bond length should be used for the central bond in a diphenyl derivative.

Approximate numerical calculation of the activation energy for the racemization of 2,2'-dibromo-4,4'-dicarboxydiphenyl has led to a value of the order of 20 kcal.; a more refined calculation is in progress.

⁹ G. W. Wheland, *The Theory of Resonance* (John Wiley and Sons, Inc., New York, 1944).

¹⁰ M. Calvin, *J. Org. Chem.* **4**, 256 (1939).

¹¹ The net effect, however, of resonance is to lower the energy of activation, E_0 , although the amount by which E_0 is lowered is less than the resonance energy of diphenyl (in excess of that in the benzene rings). This conclusion follows because (a) resonance will be more important in the planar than in the non-planar structure of any diphenyl and (b) the energy of a resonance hybrid is always less (although perhaps only slightly less) than that predicted for the most stable individual structure which contributes to the ground state of the molecule in question. The stabilization of the activated complex by resonance, therefore, appears inevitable. The opposite viewpoint, which has previously (reference 10) been expressed, would appear to be in error.

III

The free energy of activation for racemization is given by the equation

$$\Delta F^* = E_0 - RT \ln (f^*/f), \quad (13)$$

where f^* is the partition function for the planar activated state and f the partition function for the non-planar normal state. The partition function for the normal state can be approximated by the product of partition functions, one for each vibrational and one for each rotational degree of freedom in the molecule; a similar statement applies to the activated complex. The partition functions depend, of course, on the vibration frequencies ν_i^* (of the activated complex) and ν_i (of the normal molecule). As a rough first approximation, each term in f^* will cancel the corresponding one in f . This approximate cancellation is the result in part of the fact that the vibration frequencies in the activated complex will not differ very much from those in the unstrained molecule. The cancellation is also the result in part of the fact that, for most of the vibrations in question, $h\nu_i$ is large compared with kT ; the contribution of such a vibration to the entropy of activation will be small. An exception to the approximate cancellation of corresponding terms in the twisting vibration of the unstrained molecule about the central carbon-to-carbon bond in diphenyl, since this is the motion which, in molecules of high energy, leads to racemization.

Corresponding terms, however, do not precisely cancel since steric hindrance somewhat modifies the vibrational frequencies and energies on the activated complex. The energy of the activated complex is in fact represented by Eq. (14),

$$\begin{aligned} E &= \sum_i \frac{1}{2} a_i (q_i^0 + q_i')^2 + E_{d0} \exp \left[-(1/\rho) \sum_i b_i (q_i^0 + q_i') \right] + E_{d0} \exp \left[-(1/\rho) \sum_i b_i' (q_i^0 + q_i') \right] \\ &= \sum_i \frac{1}{2} a_i (q_i^0 + q_i')^2 + Z \exp \left[-(1/\rho) \sum_i b_i q_i' \right] + Z \exp \left[-(1/\rho) \sum_i b_i' q_i' \right], \end{aligned} \quad (14)$$

where the q_i' are small displacements from the "equilibrium" configuration of the activated complex, denoted by q_i^0 . For sufficiently small values of the displacements, q_i' , the exponential terms in (14) can be expanded in terms of the new coordinates, q_i' ; this expansion together with Eqs. (10) and (12) lead to (15).

$$E - E_0 = \sum_i \frac{1}{2} a_i (q_i')^2 + (Z/2\rho^2) \sum_i \sum_j (b_i b_j + b_i' b_j') q_i' q_j', \quad (15)$$

where the double summation is carried out over all values of i and j , including $i = j$. Whenever the potential energy, $E - E_0$, can be represented by a quadratic function of this sort, it is in principle⁷ possible to eliminate the cross product terms $q_i' q_j'$. Further, if the coordinates q_i are true, normal coordinates, and if they have been normalized (i.e., if $T = \sum_i \dot{q}_i^2$), then the elimination of cross-product terms from Eq. (15) will lead to a new set of normal coordinates such that

$$E - E_0 = \sum_i \alpha_i Q_i^2 \quad (16)$$

and

$$T = \sum_i \dot{Q}_i^2. \quad (16')$$

The frequencies of vibration for the activated complex are related to the new force constants α_i , by the expression

$$\alpha_i = 4\pi^2 \nu_i^{*2} \quad (17)$$

just as the vibration frequencies of the unstrained (non-planar) molecule are related to the corresponding force constants a_i by the expression

$$a_i = 4\pi^2 \nu_i^2. \quad (17')$$

The general transformation of (15) to (16) demands the solution of a secular equation with n roots, where n is the number of vibrational degrees of freedom of the molecule in question. The solution of such an equation, in the general case, is very difficult, and in many cases cannot reasonably be performed. However, in the event that the cross-product terms in (15) are small compared to the terms $a_i (q_i')^2$, the secular equation can be solved by perturbation methods. The actual solution leads to expressions for the force constants α_i , the frequencies of vibration ν_i^* , of the activated state, and finally by way

of Eq. (13) to the free energy of activation and the absolute rate of reaction. Unfortunately, the perturbation method is considerably complicated by the essential degeneracy of many of the benzenoid vibrations. Since for the cases under consideration the two benzene rings are identically substituted, every vibration of the diphenyl molecule is at least doubly degenerate and those corresponding to the doubly degenerate levels of the benzene ring are fourfold degenerate. In principle, these degeneracies can be eliminated, and the perturbation method can be carried through to completion. However, since the steps necessary to this solution are concerned with the details of the particular example chosen, it seems best to postpone the presentation of the explicit solution of this case. The authors hope soon to

carry out numerical calculations based on this development.

IV

Although the present treatment has been restricted to a consideration of the racemization of diphenyls, it is clearly of much broader application. An equation analogous to (12) will predict the energy of reaction for those cases in which an equilibrium constant rather than a rate constant can be observed.

V

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On the Equation of State for Gases at Extremely High Pressure

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On the basis of the thermo-hydrodynamic theory of the explosive detonation—developed by Chapman, Jouguet, and R. Becker—a procedure is developed permitting the deduction of the equation of state for gaseous mixtures from explosive processes. The equation is established by starting from several sets of experimental data. In this way one can semi-empirically derive the equation of state for gases compressed up to 10^4 – 10^5 atmos. The results of numerical calculations are reported.

1

DIRECT experimental measurements allow one to derive the equation of state for gases up to pressures of some thousand atmospheres. But we have little knowledge about the properties of gases compressed up to 10^4 – 10^5 atmos.; this is the order of the instantaneous pressures of gaseous products resulting from the detonation of solid explosives. Therefore, the fundamental importance, from the chemical-physical viewpoint, presented by the knowledge of the properties of gases at these particular conditions is evident.

The purpose of this work is in the first place to show that, when one admits the validity of the thermo-hydrodynamic theory of detonation

as developed by Chapman,¹ Jouguet,² and R. Becker,³ and makes use of a few experimental data, then one can determine the equation of state for gases applicable during the detonation: the pressures of these gases can be of the order of 10^5 atmos.

In order to make more comprehensible our

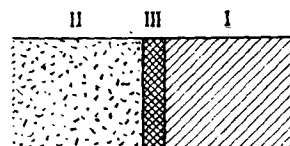


FIG. 1. Explosion process.

¹ D. L. Chapman, *Phil. Mag.* **47**, 90 (1899).

² Jouguet, *J. de Math.* **1**, 347 (1905); **2**, 6 (1906).

³ R. Becker, *Zeits. f. Physik* **8**, 321 (1922).