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## A Calculation of the Energy of Activation for the Racemization of 2,2'-Dibromo-4,4'-Dicarboxydiphenyl

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In a recent article J. E. Mayer and the author presented a method of calculating the energy of activation for the racemization of optically active diphenyl derivatives from known force constants and from the van der Waals repulsion between ortho substituents. In the present paper, the calculation of this activation energy is carried through in detail for the racemization of 2,2'-dibromo-4,4'-dicarboxydiphenyl. The value obtained is 18 kcal./mole. The experimental value is not known, but the free energy of activation for the same process is 19.5 kcal./mole. In the discussion of probable errors, it is shown that the calculated energy of activation is unlikely to be in error by as much as 7 kcal./mole, and that the probable error is only about 4 kcal./mole. The racemization involves distorting the various angles and stretching the various bonds in the molecule, as well as forcing the ortho substituents to approach one another so that the distance between them is less than the sum of their van der Waals radii. In the present treatment, all these deflections and stretchings are computed; that is to say, an accurate model for the activated complex is obtained.

### INTRODUCTION

IN a recent article, J. E. Mayer and the author<sup>1</sup> presented a method for calculating the energy of activation for the racemization of optically active diphenyl derivatives. The calculation makes use of the force constants for the "normal" vibrations of the diphenyl derivative in question and requires a knowledge of the van der Waals repulsion between the non-bonded<sup>2</sup> ortho substituents which must pass one another during the racemization process. The present article presents the details of the calculation of the activation energy for the racemization of 2,2'-dibromo-4,4'-dicarboxydiphenyl. Racemization processes of

the type indicated are especially favorable for the calculation of the energy of activation, since in these reactions, no bonds are formed or broken. It is to be noted that the present computation, although approximate, involves no arbitrary parameters.

During the racemization, the molecule passes through a planar configuration (Fig. 1), which is the activated complex for the reaction. Further, it is assumed<sup>1</sup> that the energy of this planar form exceeds that of the usual, non-planar one by the amount of energy,  $E$ , given in Eq. (1)

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

Here  $a_i$  is the force constant associated with the normal coordinate  $q_i$ ; the exponential term is an approximation, over the limited range which is of interest, to the van der Waals repulsion between two non-bonded bromine and hydrogen atoms separated by the distance,  $d_v$ ;  $A$  and  $\rho$  are constants. Since some of the vibrations of the diphenyl molecule are unsymmetrical, they do not affect the separation of the two bromine-hydrogen pairs equally; hence, the two distances,  $d_1$  and  $d_2$  (Fig. 1) must be considered individually. The distance  $d_1$  between the first pair of bromine and hydrogen atoms and the distance  $d_2$  between the second pair of bromine and hydrogen atoms are given approximately by Eqs. (2) and (2'),

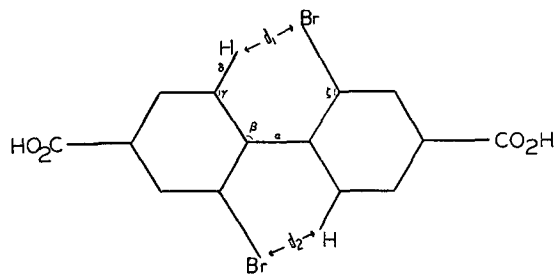


FIG. 1. The planar model of a rigid molecule of 2,2'-dibromo-4,4'-dicarboxydiphenyl.

<sup>1</sup> F. H. Westheimer and J. E. Mayer, *J. Chem. Phys.* **14**, 733 (1946).

<sup>2</sup> "Non-bonded" substituents are atoms or groups which are not bonded to each other; they are, of course, bonded to the carbon atoms of the benzene rings.

respectively.

$$d_1 = d_0 + \sum_i b_i q_i \quad (2)$$

$$d_2 = d_0 + \sum_i b'_i q_i \quad (2')$$

In these equations,  $d_0$  is the separation between bromine and hydrogen atoms which would obtain in the rigid planar molecule (i.e., if there were no deformations of bond angles and no changes in bond lengths). The constants  $b_i$  and  $b'_i$  are proportionality factors (calculable from the geometry of the molecule) which relate the increase in the distances  $d_1$  and  $d_2$  to the magnitude of the displacements  $q_i$ .

The previous paper<sup>1</sup> gives a method of finding the minimum value of  $E$  with respect to all possible variations in all the normal coordinates. This minimum value,  $E_0$ , which is the activation energy for the racemization, can be expressed in terms of a parameter  $Z$ , as shown in Eq. (3).

$$E_0 = \frac{2Z^2}{\rho^2} \sum_i \frac{B_i^2}{a_i} + 2Z \quad (3)$$

where  $B_i = \frac{1}{2}(b_i + b'_i)$ .  $Z$  in turn can be determined by the numerical solution of Eq. (4)

$$Z = E_{d_0} \exp - \left( \frac{2Z}{\rho^2} \sum_i B_i^2 / a_i \right) \quad (4)$$

where

$$E_{d_0} = A e^{-d_0/\rho} \quad (4')$$

$E_{d_0}$  is then the value of the van der Waals repulsion between bromine and hydrogen atoms separated by a distance  $d_0$  (i.e., where the planar molecule is rigid).

In order to calculate the activation energy for the racemization of 2,2'-dibromo-4,4'-dicarboxydiphenyl, it is necessary and sufficient to know the force constants,  $a_i$ , for the normal vibrations of the molecule, to calculate the geometric factors  $b_i$  and  $b'_i$  for these same vibrations, and to evaluate the constants  $A$  and  $\rho$  in the equation  $U = A e^{-d/\rho}$ . This equation gives approximately the van der Waals potential,  $U$ , of a bromine and a hydrogen atom in the region where the energy involved is largely that of repulsion. From  $a_i$ ,  $b_i$ ,  $b'_i$ ,  $A$ , and  $\rho$  the activation energy can be calculated by means of Eqs. (3) and (4).

### THE VIBRATIONS OF THE MOLECULE

In the computation of  $E_0$ , some approximations are necessary. The normal vibrations of substituted diphenyl molecules are unknown, and if they were known, they would be too complex for convenient use. However, as was previously pointed out,<sup>1</sup> a complete set of "normal" coordinates for the diphenyl molecule is unnecessary. Any set of coordinates in which the potential energy,  $E$ , can be expressed as a sum of squares of the form  $q_i^2$  (as in Eq. 1) without any cross-product terms  $q_i q_j$ , is adequate. Although true normal coordinates would be such that the kinetic energy could also be expressed as a sum of squares of the form  $\dot{q}_i^2$ , this additional property is not essential for the problem at hand. Actually, even the thirty normal vibrations of benzene are too complex for convenient use; hence, the set of "bastardized" coordinates suggested in the previous paper is here used.

The normal vibrations of benzene were worked out by E. B. Wilson,<sup>3</sup> and the corresponding vibration frequencies were developed by him in terms of six force constants: (1) a stretching constant,  $K$ , for the carbon-carbon bond; (2) a stretching constant  $q$ , for the carbon-hydrogen bond; (3) a constant  $k$  for the deformation of a ring angle in the plane of the ring; (4) a constant  $H$  for the deformation of the C-C-H angle in the plane of the ring; and (5 and 6) two constants related to the non-planar vibrations of the ring atoms. Although this formulation of the problem may be oversimplified for very precise work, it has proved to be adequate for the purpose at hand.

In the present paper, the six carbon atoms of the benzene ring are considered as a unit, and the problem is simplified by omitting the motions (considered by Wilson) of the hydrogen atoms. The coordinates of the carbon atoms are  $R$ , for

TABLE I. Force constants,  $a_i$ , for vibrations 1, 12, 14, and 19.

Vibration No.	Force constant
1	$6K$
12	$72k$
14	$18K$
19a and 19b	$9(K+k)$

<sup>3</sup> E. B. Wilson, Phys. Rev. **45**, 706 (1934).

radial displacement away from the center of the ring, and  $Y$ , for displacement in the plane of the ring perpendicular to  $R$ ;  $Y$  is positive for motion clockwise around the ring. The normal coordinates are given in the equations of set (5).

$$\begin{aligned}
 q_1 &= R_1 + R_2 + R_3 + R_4 + R_5 + R_6, \\
 q'_{6a} &= R_1 - R_3 + R_4 - R_6, \\
 q'_{6b} &= 1/\sqrt{3}(R_1 - 2R_2 + R_3 + R_4 - 2R_5 + R_6), \\
 q'_{8a} &= -1/\sqrt{3}(Y_1 - 2Y_2 + Y_3 + Y_4 - 2Y_5 + Y_6), \\
 q'_{8b} &= Y_1 - Y_3 + Y_4 - Y_6, \\
 q_{12} &= R_1 - R_2 + R_3 - R_4 + R_5 - R_6, \\
 q_{14} &= Y_1 - Y_2 + Y_3 - Y_4 + Y_5 - Y_6, \\
 q_{19a} &= 2R_1 + R_2 - R_3 - 2R_4 - R_5 + R_6 \\
 &\quad + \sqrt{3}(Y_2 + Y_3 - Y_5 - Y_6), \\
 q_{19b} &= \sqrt{3}(R_2 + R_3 - R_5 - R_6) \\
 &\quad - (2Y_1 + Y_2 - Y_3 - 2Y_4 - Y_5 + Y_6).
 \end{aligned} \tag{5}$$

The above coordinates are closely related to Wilson's, and his numbering is retained throughout. The non-planar vibrations of the ring are omitted for reasons explained below. Coordinates  $q_{19a}$  and  $q_{19b}$  refer to a degenerate pair of vibrations. Coordinates  $q'_{6a}$  and  $q'_{8a}$  must be combined to find two true normal coordinates; and coordinates  $q'_{6b}$  and  $q'_{8b}$  must be similarly treated. The four vibrations thus derived form two degenerate pairs.

The coordinates in set (5) differ from Wilson's in two respects. First, the coordinates  $R$  and  $Y$  here refer simply to distance and not, as Wilson's do, to distance divided by the square root of the mass of the carbon atom. Second, the normalization factors  $-1/\sqrt{3}$  and  $1/\sqrt{3}$  have been included in the respective expressions for  $q_{8a}'$  and  $q_{6b}'$ . Although these factors are not necessary (the

same vibration frequencies are obtained with or without them), unless they are included, the members of a pair of degenerate vibrations do not have the same force constant.

The potential energy and the force constant for each of the vibrations listed above can be found in terms of the stretching and bending force constants  $K$  and  $k$ . Each vibration causes a change in the length of some of the carbon-carbon bonds in the ring, or a change in some of the internal angles of the ring, or both; these changes in length and angle can be found from the geometry of the molecule and the equations of set (5). Following Wilson's procedure, the potential energies and the force constants for vibrations 1, 12, 14, 19a and 19b are written in terms of  $K$  and  $k$ . (Table I.)

Coordinates  $q_6'$  and  $q_8'$  must be combined to find normal modes of vibration. For both combinations, the Lagrangian,  $L$ , is given by Eq. (6)

$$L = T - V = 2M\dot{\psi}^2 + 2M\dot{\omega}^2 - K/2(\psi + 3\omega)^2 - k/2(3\sqrt{3}\psi + \sqrt{3}\omega)^2. \tag{6}$$

Here  $\psi$  is the magnitude of the displacement  $q_6'$  and  $\omega$  is the magnitude of the displacement  $q_8'$ ;  $M$  is the mass of the carbon atom.

The classical equations of motion in Lagrangian form, (7), were then applied to the function

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{q}} - \frac{\partial L}{\partial q} = 0, \tag{7}$$

$L$  of Eq. (6). The resulting differential equations were simplified by introducing the assumption that the motions in question are harmonic. This means that  $\psi = A \sin \lambda t + B \cos \lambda t$  (where  $\lambda$  is the vibration frequency), and that therefore,

$$\frac{d^2 \psi}{dt^2} = -\lambda^2 \psi. \tag{8}$$

Similarly,

$$\frac{d^2 \omega}{dt^2} = -\lambda^2 \omega. \tag{8'}$$

The same value of  $\lambda$  is used in Eqs. (8) and (8'), since the modes of motion in question are just those for which  $q_6'$  and  $q_8'$  have the same frequency. Combining (6), (7), (8), and (8') leads to

TABLE II. Force constants for the benzene ring (Kohlrausch).

Type	Force constant
Stretching C-C bond	$K = 7.65 \times 10^8$ dynes/cm
Stretching C-H bond	$q = 5.02 \times 10^8$ dynes/cm
Bending ring angle (in plane of ring)	$k = 0.642 \times 10^8$ dynes/cm
Bending C-C-H angle (in plane of ring)	$H = 0.737 \times 10^8$ dynes/cm

two simultaneous linear equations, (9), in  $\psi$  and  $\omega$ .

$$\begin{aligned} -4M\lambda^2\psi + K(\psi + 3\omega) + 3\sqrt{3}k(3\sqrt{3}\psi + \sqrt{3}\omega) &= 0, \\ -4M\lambda^2\omega + 3K(\psi + 3\omega) + \sqrt{3}k(3\sqrt{3}\psi + \sqrt{3}\omega) &= 0. \end{aligned} \quad (9)$$

These equations can both be valid only under the condition that (10) is satisfied.

$$4M\lambda^2 = 5K - 15k \pm [(5K + 15k)^2 - 192Kk]^{\frac{1}{2}}. \quad (10)$$

The appropriate numerical values of  $K$  and  $k$  (see below) are then substituted in (10); two values of  $4M\lambda^2$  are thus computed. When these values are substituted in Eq. (9), the two negative reciprocal ratios of  $\psi$  to  $\omega$  are obtained. These values are  $-0.481$  and  $-2.08$ . The two coordinates which result from the combination of  $q'_6$  and  $q'_8$  are then

$$\begin{aligned} q_{6+8} &= q'_6 - 0.481q'_8, \\ q_{6+8}^* &= q'_6 + 2.08q'_8. \end{aligned} \quad (11)$$

In order to obtain Eqs. (11) and in order to obtain numerical values for the force constants of the benzenoid vibrations, numerical values for the force constants  $K$  and  $k$  are needed. Concordant values of  $K$ ,  $k$ ,  $q$ , and  $H$  have been obtained by Kohlrausch<sup>4</sup> and later by Lord and Andrews.<sup>5</sup> Both investigations were based on Wilson's potential functions for the benzene ring, and both led to values of the force constants from which the observed infra-red and Raman frequencies of benzene were predicted with moderate accuracy. The values here used are Kohlrausch's. (Table II.)

From the data in Tables I and II, and from Eqs. (6) and (11), the force constants for all the deformations of the benzene ring have been computed (Table III).

In addition to the deformations of the ring, the following deformations (see Fig. 1) have been considered: (I) the stretching of the interannular bond,  $\alpha$ ; (II) the deformation of the angles,  $\beta$ , between the interannular and the ring bonds; (III) the deformation of the angles,  $\gamma$ , between the ring bonds and the bonds to the ortho-hydrogen atoms; (IV) the stretching (contraction) of the carbon to hydrogen bonds,  $\delta$ ; (V) the

TABLE III. Values of the force constants,\*  $a_i$ .

Vibration No.	Type	$a_i$
I	Stretching interannular bond, $\alpha$	$5.5 \times 10^5$ dynes/cm
II	Deforming C—C—C angle, $\beta$	$1.13 \times 10^{-11}$ dynes cm/radian <sup>2</sup>
III	Deforming C—C—H angle, $\gamma$	$0.86 \times 10^{-11}$ dynes cm/radian <sup>2</sup>
IV	Stretching ring to H bond, $\delta$	$5.0 \times 10^5$ dynes/cm
V	Stretching ring to Br bond, $\epsilon$	$5.0 \times 10^5$ dynes/cm
VI	Deforming C—C—Br angle, $\zeta$	$1.07 \times 10^{-11}$ dynes cm/radian <sup>2</sup>
1	Vibrations of the Benzene Ring	$45.9 \times 10^5$ dynes/cm
(6+8)		$13.7 \times 10^5$ dynes/cm
(6+8)*		$450 \times 10^5$ dynes/cm
12		$46.2 \times 10^5$ dynes/cm
14		$138 \times 10^5$ dynes/cm
19		$74.6 \times 10^5$ dynes/cm

\* It is interesting that computations based on Wilson's equations and Kohlrausch's constants lead to vibration frequencies for the six carbon atom unit which agree well with those obtained in the experiments with models performed by Murray, Dietz, and Andrews (J. Chem. Phys. 3, 180 (1935)). The vibration frequencies obtained by these investigators are given in arbitrary units; only the relative magnitudes of the vibrations of the model can be compared with the values calculated for the carbon ring.

Vibration frequencies of a benzene ring stripped of hydrogen.

Vibration No.	Calc., cm <sup>-1</sup>	Frequency	
		Model, arbitrary units	Ratio
(6+8)	625	575	1.09
1	1040	840	1.24
12	1045		
19	1325	1045	1.27
(6+8)*	1730	1330	1.30
14	1805	1470	1.23

stretching (contraction) of the carbon to bromine bonds,  $\epsilon$ ; and (VI) the deformation of the angles,  $\zeta$ , between the ring bonds and the bonds to the bromine atoms.

The force constant  $H$  for the bending of the carbon to hydrogen bonds and the force constant  $q$  for the stretching of these bonds are taken from Kohlrausch. The force constant for the stretching of the interannular bond in diphenyl was taken to be  $5.5 \times 10^5$  dynes/cm, a value somewhat in excess of the corresponding force constant in aliphatic compounds.<sup>6</sup> The value of the force constant for the stretching of the carbon to bromine bonds was arbitrarily chosen as  $5 \times 10^5$  dynes/cm; actually, the value for this force constant does not affect the calculation. (See Table VI.) No good value of the force constant for the bending of the carbon to bromine bonds in aromatic compounds is available; this value was therefore estimated in the following manner: The force constant,  $H$ , for the bending of the carbon to hydrogen bond was accepted as a first approximation to the desired constant. Then this force

<sup>4</sup> K. W. F. Kohlrausch, Zeits. f. physik. Chemie B30, 305 (1935).

<sup>5</sup> R. C. Lord and D. H. Andrews, J. Phys. Chem. 41, 149 (1937).

<sup>6</sup> See G. Herzberg, *Infra-Red and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945).

TABLE IV. Bond lengths used in calculating  $b$  and  $b'$ .

Bond	Position	Length, $\times 10^8$ cm
C—C	In ring	1.39
C—C	Between rings	1.54
C—H		1.08
C—Br		1.86

constant,  $H$ , was increased in the ratio of the force constants for the corresponding bonds in aliphatic compounds (i.e., in the ratio of the force constant for the deformation of the C—C—Br angle to the force constant for the deformation of the C—C—H angle in aliphatic compounds).<sup>7</sup> The corrected value of  $H$  was then further increased by 10 percent. A similar procedure was used for the force constant for the deformation of the angle  $\beta$ . In each instance, the additional ten percent was added to take into account the stiffening of the bonds caused by resonance.<sup>8</sup> The force constants obtained by the methods outlined are listed in Table III.

#### THE GEOMETRIC FACTORS

Each of the vibrations under consideration (see Table III) changes the distance ( $d_1$  or  $d_2$ ) between the members of at least one pair of ortho-bromine and ortho-hydrogen atoms. As a first approximation and for small amplitudes, the increase or decrease in the bromine-hydrogen distance is proportional to the amplitude of the vibration in question. The proportionality factors  $b$  and  $b'$  (see Eqs. 2 and 2') may be derived from the geometry of the diphenyl molecule, the bond lengths, and the equations of set (5) for the normal vibrations of the ring. It was assumed that, in the planar but undeformed diphenyl molecule, both rings are hexagons and that the C—C—C, C—C—H, and C—C—Br angles are all  $120^\circ$ .

Some of the vibrations of the benzene ring involve changes in the ring angles at the position of the interannular bond or the positions ortho to it. In order to calculate  $b$  and  $b'$ , it was necessary to make some assumption about the nature of these vibrations. It was, therefore, assumed that such vibrations always take place so that the

center of the substituent (bromine or hydrogen or the second ring) remains upon the bisector of the ring angle at the point where the substituent is attached. It was further assumed that the length of the interannular bond was unchanged except during vibration I. Since the individual vibrations of the benzene ring are comparatively unimportant, these assumptions are unlikely to lead to large errors.

For those vibrations which do not change the distance between bromine and hydrogen atoms, the values of  $b$  and  $b'$  are zero. It has been shown<sup>1</sup> that vibrations for which both  $b$  and  $b'$  are zero need not be considered in the determination of the activation energy of racemization. As a first approximation, the non-planar vibrations do not change the bromine-hydrogen distances; they are therefore disregarded.

The bond lengths here used are given in Table IV. They require no comment, except for the value (1.54A) assigned to the length of the interannular bond. This value is slightly in excess of that found experimentally for diphenyl.<sup>9</sup> As previously pointed out,<sup>1</sup> resonance between the two rings may, as a first approximation, be neglected if the longer bond length is used.

The geometric factors  $b_i$ ,  $b'_i$ , and  $B_i$  (where  $B_i = (b_i + b'_i)/2$ ) are given in Table V.

#### THE VAN DER WAALS POTENTIAL

The solution of the problem under consideration requires a knowledge not only of the force constants (Table III) and the geometric factors

TABLE V. Values of the geometric factors.

Vibration No.	$b$	$b'$	$B$
I	0.91	0.91	0.91
II	$2.01 \times 10^{-8}$	$-2.65 \times 10^{-8}$	$-0.32 \times 10^{-8}$
III	$0.62 \times 10^{-8}$	$0.00 \times 10^{-8}$	$0.31 \times 10^{-8}$
IV	-0.82	0.00	-0.41
V	-0.09	0.00	-0.05
VI	$1.89 \times 10^{-8}$	$0.00 \times 10^{-8}$	$0.95 \times 10^{-8}$
1	0.090	0.82	0.45
(6a+8a)	1.10	1.91	1.50
(6a+8a)*	2.19	7.15	4.67
(6b+8b)	1.31	-1.28	0.01
(6b+8b)*	-2.43	0.77	-0.83
12	1.72	1.00	1.36
14	-0.15	1.42	0.63
19a	1.14	0.25	0.70
19b	-0.41	1.71	0.65

<sup>7</sup> B. L. Crawford and S. R. Brinkley, J. Chem. Phys. 9, 69 (1941).

<sup>8</sup> G. W. Wheland, *The Theory of Resonance* (John Wiley and Sons, Inc., New York, 1944).

<sup>9</sup> I. L. Karle and L. O. Brockway, J. Am. Chem. Soc. 66, 1974 (1944).

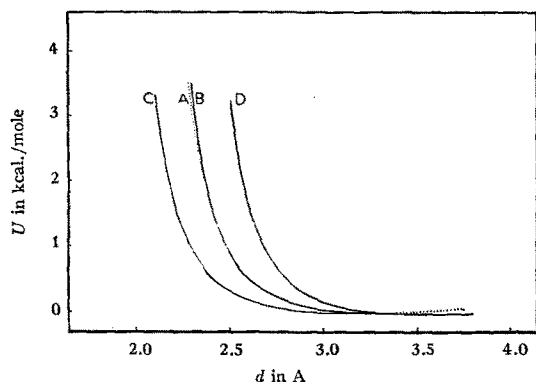


FIG. 2. The van der Waals potential function. Curve *A* is the modified neon potential of Bleick and Mayer, curve *B* is the exponential approximation used in the complete computation. Curves *C* and *D* have been displaced from *B* in opposite directions by 0.2Å.

(Table V), but also of the energy of repulsion between non-bonded bromine and hydrogen atoms. No really good potential function for this energy of repulsion is available; it is, therefore, necessary to approximate one. The form of the expression for the energy of repulsion between atoms with closed electron shells is assumed to be roughly independent of the nature of the atoms involved. The van der Waals potential may be considered to be the sum of two effects: one of attraction and one of repulsion. These combine to give a total potential with a flat, shallow minimum at some inter atomic distance  $d_v$ . Most of the available experimental data for the van der Waals potential deals with the region near the minimum of the curve; the data for argon,<sup>10</sup> for example, are probably valid for that part of the curve where the energy is within 500 small calories of the minimum. Unfortunately, to solve the present problem, it was necessary to know the potential function for an energy region about 3 kcal. above the minimum. Since no experimental values of the van der Waals potential for this region were available, it was necessary to use a theoretical value.

Bleick and Mayer,<sup>11</sup> on the basis of quantum mechanical considerations, have computed the van der Waals repulsion between two neon atoms. It was hoped that the mutual repulsion between two neon atoms would approximate that between

one bromine and one hydrogen atom. Bleick and Mayer's computation for the repulsion effect in the potential should be very nearly precise in the region where  $U \geq 5$  kcal. (i.e., in the region of interest for the present problem). Their computation of the attraction effect in the potential is, as they admitted, crude, and comparison with experimental values of the potential near the minimum<sup>12</sup> suggests that their attraction effect should be doubled. Since the repulsion, in the region under consideration, is almost ten times the attraction, the correction introduced by doubling the latter is small. One slight further modification was also made. The minimum value of the neon potential falls where the distance between neon atoms is 3.2Å.<sup>13</sup> The precise distance between bromine and hydrogen atoms at the minimum of the van der Waals potential is not known, but Pauling<sup>14</sup> has suggested that the van der Waals radius of bromine is 1.95Å and that of hydrogen 1.2Å. The distance,  $d_v$ , between a bromine and a hydrogen atom (non-bonded) at the potential minimum, is thus approximately 3.15Å. The potential curve for neon was therefore shifted through 0.05Å, in order that the minimum might fall at 3.15Å. For convenience, the minimum potential was set equal to zero. The resulting potential curve (see Fig. 2) may be approximated by the exponential expression

$$U = 2.45 \times 10^{-7} e^{-d/0.165 \times 10^{-8}} \text{ ergs/molecule.} \quad (11)$$

A comparison of Eq. (11) with Eq. (1), shows that

$$A = 2.45 \times 10^{-7}, \quad \text{and} \quad \rho = 0.165 \times 10^{-8}.$$

When

$$d = d_0 = 1.61\text{Å}, \\ U = E_{d_0} = 1.44 \times 10^{-11} \text{ erg/molecule.}$$

#### THE ENERGY OF ACTIVATION

In the preceding sections, the values of  $a_i$ ,  $B_i$ ,  $A$ ,  $\rho$ , and  $E_{d_0}$  are all determined. When these values are substituted in Eq. (4), the value of  $Z$  is found to be  $2.02 \times 10^{-13}$  ergs/molecule, or 2.9 kcal./mole. It should be noted that, in forming

<sup>12</sup> See J. E. Leonard-Jones, Proc. Phys. Soc. **43**, 461 (1931).

<sup>13</sup> See S. B. Hendricks, Chem. Rev. **7**, 431 (1930); M. L. Huggins, *ibid.* **10**, 427 (1932).

<sup>14</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, New York, 1939).

<sup>10</sup> O. K. Rice, J. Am. Chem. Soc. **63**, 3 (1941); private communication from O. K. Rice.

<sup>11</sup> W. E. Bleick and J. E. Mayer, J. Chem. Phys. **2**, 252 (1934).

the sum  $\sum_i B_i^2/a_i$  (Eq. 4), the vibrations of both benzene rings must be taken into account. Thus the term  $B_i^2/a_i$  corresponding to each vibration listed in Table V (except vibration I) must be used twice. When the value of  $Z$  (and the values of  $a_i$  and  $B_i$  previously determined) are substituted in Eq. (3), the energy of activation is found to be 18 kcal./mole.

The experimental value of the energy of activation for the racemization of 2,2'-dibromo-4,4'-dicarboxydiphenyl has not yet been determined, but the free energy of activation<sup>15</sup> is 19.5 kcal./mole. However, for the racemization of other optically active diphenyl derivatives<sup>16</sup> and related compounds,<sup>17</sup> both the energy and the free energy of activation are known; they never differ by more than a few kilocalories. The experimental value for the energy of activation for 2,2'-dibromo-4,4'-dicarboxydiphenyl remains to be determined in the future, but probably it will not differ by more than a few kilocalories from the free energy of activation (19.5 kcal./mole).

#### LIMITS OF ERROR

The largest uncertainty in the foregoing computation of the activation energy arises from uncertainties as to the van der Waals potential function. The calculated slope of this function is determined by  $\rho$ ; the particular value ( $0.165 \times 10^{-8}$ ) here assigned to this constant is somewhat less than the value ( $0.2091 \times 10^{-8}$ ) used by Bleick and Mayer<sup>11</sup> in their equation for the repulsion between neon atoms. The effect of including attraction as well as repulsion is to diminish  $\rho$ . Furthermore, the value of  $\rho$  appropriate to neon is considerably smaller than the value ( $0.345 \times 10^{-8}$ ) found by Born and Mayer for the ions in alkali halides,<sup>18</sup> and recently used by Dostrovsky, Hughes, and Ingold in their study of steric effects in substitution reactions.<sup>19</sup> It seems likely that the larger alkali ions and the halide ions are considerably more easily compressed than are hydrogen atoms; hence the

steepness of the van der Waals potential between neon atoms seems a more appropriate approximation to that between bromine and hydrogen atoms than any other approximation now available. In any event, the position of the potential curve is more critical for the present computation than is its slope. A function ( $U = 2.1 \times 10^{-10} e^{-d/0.33 \times 10^{-8}}$ ) was chosen so that, as before, the van der Waals potential is  $2.0 \times 10^{-13}$  ergs/molecule (2.9 kcal./mole) when the bromine and hydrogen atoms are 2.30 Å apart; note, however, that in this function the value of  $\rho$  has been doubled, thus halving the slope of the function. It is unlikely that the chosen value ( $0.165 \times 10^{-8}$ ) of  $\rho$  is in error by such a large amount; the change, moreover, decreases the computed value of  $E_0$  only by 1.5 kcal./mole.

Although the value of  $\rho$  is not in doubt by an amount which is important for the computation of  $E_0$ , the position of the potential curve is important. Admittedly, the van der Waals radii of bromine and hydrogen atoms are uncertain. Pauling rounded off his values to the nearest 0.05 Å; hence, the sum of the radii here used is uncertain by at least that amount. In order to set some reasonable limit of error to the calculated value of  $E_0$ , it was assumed that the position of the potential minimum may be in error (within the region here of interest) by 0.1 Å, i.e., it was assumed that the sum of the van der Waals radii for bromine and hydrogen lies between 3.05 and 3.25 Å. The computation with the smaller sum (3.05 Å) gives an activation energy of 15 kcal./mole; the calculation with the larger sum (3.25 Å) gives an activation energy of 22 kcal./mole. There is no guarantee that these limits are sufficiently wide, but they appear reasonable; the probable error in the calculation is then about three or four kilocalories. If, however, it is assumed that the position of the minimum may be in error by 0.2 Å (i.e., that the sum of the van der Waals radii for bromine and hydrogen lies between 2.95 Å and 3.35 Å) then the calculated activation energy lies between 12 and 26 kcal./mole. These wider limits for the sum of the van der Waals radii appears to the author to be ample, and probably too large. Thus the uncertainty in the computed value of  $E_0$  which is caused by the uncertainty in the van der Waals

<sup>15</sup> W. I. Patterson and R. Adams, *J. Am. Chem. Soc.* **57**, 762 (1935).

<sup>16</sup> G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.* **58**, 1043 (1936).

<sup>17</sup> W. H. Mills and R. M. Kelham, *J. Chem. Soc.* 274 (1937).

<sup>18</sup> M. Born and J. E. Mayer, *Zeits. f. Physik* **75**, 1 (1932).

<sup>19</sup> I. Dostrovsky, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.* 173 (1946).



repulsion is unlikely to exceed 7 kilocalories per mole.

The errors in  $E_0$  which might arise from possible errors in the force constants are much smaller; they may in fact be neglected. Of all the individual force constants, the one for the bending of the carbon-bromine bond is by far the most important. If this force constant has been underestimated by 20 percent, then the calculated activation energy is 1 kcal./mole too low.

The calculated energy of activation represents the saddle-point in the potential energy diagram for the substituted diphenyl molecule. Some other points on this diagram are also of interest, particularly those which correspond to planar configurations of the substituted diphenyl molecule other than the one of minimum energy. One of these configurations is that of a planar molecule in which all of the bond angles and lengths are respectively identical with those in the unstrained, non-planar molecule. For this model, the energy is determined solely by the van der Waals repulsion; it amounts to twice  $E_{d_0}$ , or about 400 kcal./mole. Another interesting configuration is the planar one in which the bromine and hydrogen atoms are separated by 3.15Å, the sum of their van der Waals radii. Here, the stretching of the various bonds and the distortions of the various angles is such as to increase the bromine-hydrogen distance from 1.61Å to 3.15Å; the energy for this configuration exceeds 50 kcal./mole.

Finally, it is of interest to determine the minimum energy for a planar model in which the carbon-bromine bonds can bend, but the molecule is otherwise rigid. This particular model is important because it takes account only of the deflections of the carbon-bromine bonds, which, in the full calculation, account for half of the term  $\sum_i B_i^2/a_i$  in Eqs. (3) and (4). These deflections are by far the most important deformations of the whole molecule. For the calculation in question, the van der Waals potential function was approximated (as before) by  $U = 2.45 \times 10^{-7} e^{-d/0.165 \times 10^{-8}}$  erg/molecule. The minimum energy thus calculated is 26 kcal./mole. Although this value is higher than the one obtained in the complete calculation, it exceeds the latter only by about 50 percent. The result here obtained suggests a rapid method of approximate calculation for similar cases.

An additional uncertainty in  $E_0$ , related to the assumption (Eq. (1) and elsewhere) that all the vibrations are harmonic, is discussed in the next section.

### THE ACTIVATED COMPLEX

On the basis of the computations already presented, it is possible to visualize what actually happens during the racemization of 2,2'-dibromo-4,4'-dicarboxydiphenyl. How much each bond is stretched (or contracted), how much each angle is deformed, how much energy is associated with each vibration, and how much energy of activation is caused by repulsion, may all be estimated. The exact assignments may be somewhat inaccurate, but the limits of error discussed in the previous section show that the general solution here presented is essentially correct.

For each coordinate  $q_i$ , the displacement which occurs in the activated complex is called  $q_i^0$ . It has already<sup>1</sup> been shown that this displacement is equal to  $2ZB_i/\rho a_i$ . Since the values of  $Z$ ,  $B_i$ , and  $\rho$  and  $a_i$  are all known, the values of  $q_i^0$  can be computed; they appear in column 2 of Table VI. The expression  $b_i q_i^0$  gives the amount by which each displacement associated with one benzene ring increases the distance  $d_1$  between the ortho bromine and hydrogen atoms. The same displacement increases the distance  $d_2$  between the second set of bromine and hydrogen atoms by an amount  $b_i' q_i^0$ . Displacements in the two rings are symmetrical about the mid-point of the interannular bond. The total increase in  $d_1$  caused by a displacement of a given type (combining the

TABLE VI. The displacements and energy of the activated complex.

Vibration No.	$q_i^0$	Increase in $d_1$ or $d_2$ , in Å	Energy, kcal./mole
I	$0.040 \times 10^{-8}$ cm	.037	.65
II	-0.069 radian	.044	.78
III	0.088 radian	.055	.96
IV	$-0.020 \times 10^{-8}$ cm	.016	.30
V	$0.004 \times 10^{-8}$ cm	.000	.00
VI	0.216 radian	.409	7.22
1	$0.002 \times 10^{-8}$ cm	.002	.04
(6a+8a)	$0.027 \times 10^{-8}$ cm	.081	1.42
(6a+8a)*	$0.002 \times 10^{-8}$ cm	.024	.42
(6b+8b)	$0.000 \times 10^{-8}$ cm	.000	.00
(6b+8b)*	$-0.003 \times 10^{-8}$ cm	.006	.10
12	$0.007 \times 10^{-8}$ cm	.020	.34
14	$0.001 \times 10^{-8}$ cm	.001	.02
19a	$0.002 \times 10^{-8}$ cm	.002	.06
19b	$0.002 \times 10^{-8}$ cm	.002	.06

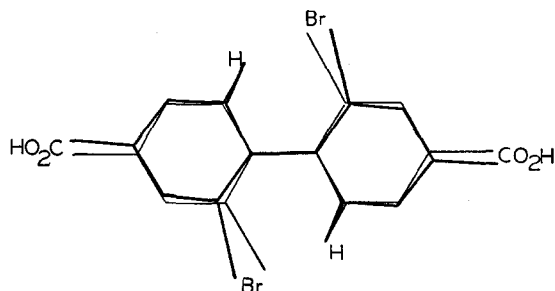


FIG. 3. The activated complex in the racemization of 2,2'-dibromo-4,4'-dicarboxydiphenyl. The light lines show the planar, rigid model (cf. Fig. 1); the heavy lines show the positions of the atoms in the activated complex.

effects of the two displacements associated with the rings) is  $2B_i q_i^0$ . The only exception to this rule is the stretching of the interannular bond, where, since there is only one vibration of this type, the increase is only  $B_i q_i^0$ . The increases in  $d_1$  caused by the various displacements are given (according to bond type) in column 3 of Table VI.

The energies involved in the various displacements are given in the last column of Table VI; here again, the listing is according to the bond type. The value of 7.22 kcal./mole for the bending of the carbon-bromine bond refers to the energy of bending of both the carbon-bromine bonds at once; the value of 0.65 kcal./mole for stretching the interannular bond refers to only one bond.

The sum of the van der Waals radii for bromine and hydrogen is 3.15Å; the value of  $d_0$  is 1.61Å. Table VI shows that, in the activated complex, the bromine and hydrogen atoms are 2.31Å apart (a distance 0.84Å less than the sum of the radii). Here the various bonds are stretched (and the various angles deformed) so as to increase the distance between the bromine and hydrogen atoms by 0.70Å. The difference between the sum of the van der Waals radii and  $d_0$

is thus accounted for in roughly equal amounts by deformations of the molecule and by a "climbing" of the van der Waals potential curve. A picture of the activated complex is presented in Fig. 3.

The energy of activation is divided roughly into three parts; the van der Waals energy of repulsion accounts for 6 kcal., the deflections of the two carbon to bromine bonds accounts for 7 kcal.; all the rest of the deformations account for about 5 kcal./mole. It is of interest that the energy contributed by all the deformations of the benzene rings amounts to only about 2.5 kcal./mole.

Table VI also shows that the carbon-bromine bond in the activated complex is deflected through 0.22 radian, or about  $12^\circ$ . This is so large an angle that the energy of the vibration in question probably cannot be closely approximated by a simple quadratic term,  $\frac{1}{2}a_i q_i^2$ . The anharmonicity in this vibration, although its value is unknown, is not likely to have a large effect upon the energy of activation. It has previously been pointed out that an increase of 20 percent for the force constant in question increases the computed energy of activation only by about 1 kcal./mole.

Since the uncertainties in the force constants are small for the molecules of the sort here treated, it may prove desirable to reverse the procedure here employed, and to use the rates of racemization of optically active diphenyl derivatives to determine van der Waals potential functions.

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