217. *Some Calculations of the Activation Energies for Inversion of Diphenyl and a Number of* ortho-*Halogenated Diphenyls.*

By K. E. Howlett.

Westheimer and Mayer's method for calculating minimal energy states for various molecular conformations which involve intramolecular non-bonded interactions is modified and extended. In this form it is used to determine the energy barriers hindering free rotation of the benzene rings in diphenyl and a number of 2,2′- and 2,6-dihalogeno- and 2,2′,6,6′-tetrahalogeno-diphenyls. The calculated values are discussed in relation to the available experimental information.

In an earlier paper,[1] some calculations of non-bonded interactions involving hydrogen atoms were presented. These calculations were relatively crude in that Cartesian, rather than normal co-ordinates were used throughout, and limited allowance was made for molecular deformation. The results did indicate, however, that Hirschfelder and Linnett's potential function [2] for the $^3\Sigma$ repulsive state of the hydrogen molecule is suitable for the description of non-bonded interactions between hydrogen atoms which are already bound to other atoms. Some years ago Hill,[3] and Westheimer and Mayer [4] derived more general and less approximate methods for the calculation of intramolecular non-bonded energies and illustrated their uses for, *inter al.*, boron trifluoride complexes and substituted diphenyls. Detailed calculations of non-bonded interactions have also been presented by Hughes, Ingold, de la Mare, and their co-workers [5] for the transition complexes in certain bimolecular substitutions. Sustained interest in the stereochemistry of diphenyl and its derivatives, together with the advent of experimental values for certain non-bonded interaction energies prompted the work now described. The object was to calculate the activation energies for inversion of diphenyl itself and of a number of poly-*o*-halogenated diphenyls. In practice this is reduced to the estimation of the energy difference between the planar and the orthogonal conformations for each compound, a modified form being used of the treatment developed by Westheimer and Mayer, and used by Westheimer for 2,2′-dibromo-[6] and 2,2′-di-iodo-diphenyl [7] derivatives and in extended form for 5,5′,6,6′-tetraiododiphenyl-3,3′-dicarboxylic acid.[7] The chief errors in this type of calculation are considered by Westheimer.

The argument and method of calculation adopted here are given first.

The inversion of a diphenyl molecule involves passage through the planar state. The difference between the energies of this transition state and the normal (near orthogonal) state may be considered to arise from four causes: (*a*) van der Waals forces operate between the 2-, 2′-, 6-, and 6′-groups. These forces, being non-bonding, are entirely repulsive at the internuclear distances involved, and are much higher in the planar than in the orthogonal state. (*b*) The change in energy caused by (*a*) is reduced by deformation, the deformation extending ideally over all the normal co-ordinates of the molecule. (*c*) In the planar state the molecule has a stabilisation energy due to π-electron overlap between the rings. This is absent from the orthogonal conformation. (*d*) There are significant alterations in dipole–dipole interaction effects between *ortho*-carbon–halogen bonds as their relative orientations change.

It is, however, very difficult to carry out a variational treatment minimising all these

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[1] Howlett, *J.*, 1957, 4353.

[2] Hirschfelder and Linnett, *J. Chem. Phys.*, 1950, **18**, 130.

[3] Hill, *ibid.*, 1946, **14**, 465; 1948, **16**, 399, 938.

[4] Westheimer and Mayer, *ibid.*, 1946, **14**, 733.

[5] Dostrovsky, Hughes, and Ingold, *J.*, 1946, 173; de la Mare, Fowden, Hughes, Ingold, and Mackie, *J.*, 1955, 3200.

[6] Westheimer, *J. Chem. Phys.*, 1947, **15**, 252.

[7] Rieger and Westheimer, *J. Amer. Chem. Soc.*, 1950, **72**, 19.

energy effects to find the ground state, even when only the planar and orthogonal conformations are studied. The effects of (*a*) and (*b*) are therefore minimised first and the effects of (*c*) and (*d*) added to the result. This involves no error for (*c*) but implies a slight overestimate for (*d*). It is easily seen, however, that the error from this cause is much lower than 1 kcal. mole^{-1} because dipole–dipole repulsion energies diminish relatively slowly with distance.

Accordingly, the energy of a diphenyl molecule over that of its ordinary bonded state is written initially as

$$E = \sum_i \tfrac{1}{2} k_i q_i^2 + A_1 \exp(-d_1/\rho_1) + A_2 \exp(-d_2/\rho_2) \quad . \quad . \quad . \quad . \quad (1)$$

where q_i is a displacement in a normal co-ordinate, k_i is the attendant force constant, and the two steric repulsion terms caused by close approach of *ortho*-groups are assumed to have the form given, in which A_i and ρ_i are constants for a particular atomic pair which are separated by a distance d_i. The summation should be made over all the normal co-ordinates. These are, however, unknown for the cases being considered, and therefore, following the suggestion of Westheimer and Mayer, normal co-ordinates for the carbon atoms of the benzene rings together with force constants for the central part of the molecule are used.

For small displacements one can write the distances d_i as linear functions of the changes in the co-ordinates. These functions are calculable from the molecular geometry. Thus

$$d_1 = d_{10} + \sum_i b_i q_i \text{ and } d_2 = d_{20} + \sum_i c_i q_i \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which d_{10} and d_{20} are the internuclear distances in the absence of molecular distortion, and the summations extend over all co-ordinates. Substitution of eqns. (2) into eqn. (1) yields

$$E = \tfrac{1}{2}\sum k_i q_i^2 + A_1 \exp\{-d_{10}/\rho_1 - (\sum b_i q_i)/\rho_1\} + A_2 \exp\{-d_{20}/\rho_2 - (\sum c_i q_i)/\rho_2\} \quad (3)$$

The energy may be minimised by setting $\delta E/\delta q_i$ equal to zero, *i.e.*,

$$0 = k_i q_i^* - (A_1 b_i/\rho_1) \exp\{-d_{10}/\rho_1 - (\sum b_i q_i^*)/\rho_1\} - (A_2 c_i/\rho_2) \exp\{-d_{20}/\rho_2 - (\sum c_i q_i^*)/\rho_2\} \quad (4)$$

where q_i^* is the displacement in the distorted configuration of minimum energy. Since this configuration is a definite one, the q_i^* values and the van der Waals potentials for this state are definite and have single values. These particular repulsion terms

$$V_1 = A_1 \exp\{-d_{10}/\rho_1 - (\sum b_i q_i^*)/\rho_1\}$$

and

$$V_2 = A_2 \exp\{-d_{20}/\rho_2 - (\sum c_i q_i^*)/\rho_2\} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

simplify eqn. (4) to

$$k_i q_i^* - b_i V_1/\rho_1 - c_i V_2/\rho_2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

for each co-ordinate, whence

$$q_i^* = b_i V_1/\rho_1 k_i + c_i V_2/\rho_2 k_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Two cases must now be considered.

(A) If the two pairs of passing *ortho*-groups in the transition state are identical, so that $V_1 = V_2$, $\rho_1 = \rho_2$, $d_{10} = d_{20}$, and $d_1 = d_2$, then

$$q_i^* = (b_i + c_i) V_1/\rho_1 k_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

For this symmetrical case, combination of eqns. (8) and (5), for example by setting $V_1 = \sqrt{(V_1 V_2)}$, gives

$$V_1 = A_1 \exp\{-d_{10}/\rho_1 - (V_1/2\rho_1^2)\sum(b_i + c_i)^2/k_i\} \quad . \quad . \quad . \quad . \quad (9)$$

This is easily solved numerically if the values of $(b_i + c_i)^2/k_i$ are tabulated. We now have

$$E_{\text{min.}} = \sum \tfrac{1}{2} k_i (q_i^*)^2 + 2V_1 = (V_1^2/2\rho_1^2)\sum(b_i + c_i)^2/k_i + 2V_1 \quad . \quad . \quad (10)$$

(B) For the unsymmetrical case in which the pairs of passing groups are dissimilar it is convenient to effect some simplification of the symbolism. Substitution of eqn. (7) into eqn. (5) yields

$$V_1 = A_1 \exp\{-d_{10}/\rho_1 - (1/\rho_1)\textstyle\sum b_i(b_iV_1/\rho_1k_i + c_iV_2/\rho_2k_i)\}$$

and

$$V_2 = A_2 \exp\{-d_{20}/\rho_2 - (1/\rho_2)\textstyle\sum c_i(b_iV_1/\rho_1k_i + c_iV_2/\rho_2k_i)\}$$

which can be written

$$V_1 = B_1 \exp(-\mathrm{p}V_1 - \mathrm{q}V_2)$$

and

$$V_2 = B_2 \exp(-\mathrm{q}V_1 - \mathrm{r}V_2)$$

in which p, q, and r represent the summations $\sum b_i^2/k_i\rho_1^2$, $\sum b_ic_i/k_i\rho_1\rho_2$, and $\sum c_i^2/k_i\rho_2^2$ and $B_i = A_i \exp(-d_{i0}/\rho_i)$.

Then $\log_e V_1 + \mathrm{p}V_1 = \log_e B_1 - \mathrm{q}V_2$ and $\log_e V_2 + \mathrm{r}V_2 = \log_e B_2 - \mathrm{q}V_1$

which can be solved to give

$$\log_e[\{\log_e(B_1/V_1) - \mathrm{p}V_1\}/\mathrm{q}B_2] + \mathrm{r}\{\log_e(B_1/V_1) - \mathrm{p}V_1\}/\mathrm{q} + \mathrm{q}V_1 = 0$$

and

$$\log_e[\{\log_e(B_2/V_2) - \mathrm{r}V_2\}/\mathrm{q}B_1] + \mathrm{p}\{\log_e(B_2/V_2) - \mathrm{r}V_2\}/\mathrm{q} + \mathrm{q}V_2 = 0 \quad . \quad (11)$$

or alternatively, V_1 being found,

$$V_2 = \{\log_e(B_1/V_1) - \mathrm{p}V_1\}/\mathrm{q}$$

The equations (11) can be solved in the same way as eqn. (9), and finally

$$E_{\text{min.}} = \mathrm{p}V_1^2/2 + \mathrm{q}V_1V_2 + \mathrm{r}V_2^2/2 + V_1 + V_2 \quad . \quad . \quad . \quad . \quad (12)$$

Eqns.(10) and (12) thus represent the energy minima of (say) planar conformations when effects caused by (*a*) and (*b*) only are considered.

For certain of the polyhalogenodiphenyls, changes in dipole–dipole interaction energies with intramolecular rotation are significant. For 2,6-dihalogenodiphenyls there is no difference in dipolar interaction energy for any conformational isomer obtained by rotation about the 1,1′-bond. For 2,2′-dihalogenodiphenyls which invert through the *trans* activated state, dipolar repulsions are negligible in the transition state, but just appreciable in the normal state. For these molecules, therefore, polarity of the bonds in the *ortho*-positions slightly lowers the activation energy of inversion.

For some compounds, *e.g.*, the tetra-*ortho*-substituted diphenyls, dipolar repulsions become important. For these cases an assessment of the effect in the planar state requires the calculation of the actual molecular configuration in this state. This is accomplished by using eqn. (7) or (8). For both normal and transition states the dipolar energy is estimated by assuming point dipoles to be situated on the carbon–halogen bonds 0·75 Å from the aromatic carbon atoms. These point dipoles are assumed to be separated by a medium of dielectric constant 2·5. Any dipolar character of C–C and C–H bonds is neglected.

The stabilisation energy of the planar state of all the diphenyls considered here is taken [8] as 6·96 kcal. mole^{-1}. This figure was estimated for diphenyl itself and is presumably an overestimate for all the other compounds considered because the 1,1′-bond is elongated in minimising the repulsion energy between the *ortho*-substituents. However, the maximum variation in the calculated displacement co-ordinate for the extension of this bond is from 0·025 Å in diphenyl to 0·078 Å in tetraiododiphenyl so that the stabilisation energy arising from electron overlap is not likely to change markedly.

In order to make the computations detailed above, it is necessary to assume values for

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[8] Guy, *J. Chim. phys.*, 1949, **46**, 469.

the molecular dimensions, bond dipole moments of the carbon–halogen linkages, bond bending and stretching force constants, and the van der Waals potentials between *ortho*-substituents. When relevant, these assumed quantities are taken to apply to all the molecules considered.

The 1,1′-bond in all compounds is assumed to have an unstrained length of 1·54 Å in the orthogonal conformation, and 1·50 Å in the planar state. The former assumption is not critical, but some degree of shortening must attend the assumed increase in overlap of electron density as the phenyl groups approach coplanarity. Other assumed bond lengths are given in Table 1; they are generally within 0·01 Å of the values recommended by Sutton *et al.*[9] All unstrained interbond angles are taken to be 120°. The carbon–halogen bond electric moments used in the calculations are the dipole moments of the corresponding monohalogenobenzenes. These are also listed in Table 1.

TABLE 1. *Assumed bond lengths and dipole moments.*

Bond	C–C	C–H	C–F	C–Cl	C–Br	C–I
Bond length (Å)	1·40	1·08	1·31	1·69	1·86	2·02
Dipole moment (D)	—	—	1·57	1·69	1·71	1·50

TABLE 2. *Assumed force constants.*

Bond	C–H	C–F	C–Cl	C–Br	C–I
k (dyne cm.$^{-1}$ × 10^{-5})	5·02	6·2	3·8	3·3	2·8
Interbond angle	C–C–H	C–C–F	C–C–Cl	C–C–Br	C–C–I
k (dyne rad.$^{-2}$ × 10^{11})	0·86	1·42	1·08	0·97	0·84

Force constants for the deformations of the benzene skeletons are taken from Wilson[10] and from Westheimer,[6] and the latter's suggestion for the force constant of the 1,1′-bond is taken to apply to the planar state for all the molecules. The other force constants for the central parts of the molecules are, in general, not available experimentally, but are estimated by analogy as follows. Kohlrausch[11] gives $k = 5{\cdot}02 \times 10^5$ dyne cm.$^{-1}$ for radial stretching of the C–H bonds in benzene. This was obtained by applying Wilson's equations to his own assignment of the Raman spectrum of benzene. More accurate assignments of the benzene fundamentals are now available[12] and use of these data in conjunction with Wilson's equations gives $5{\cdot}06 \times 10^5$ dyne cm.$^{-1}$ for this force constant. This minor correction is here disregarded because the last figure is of doubtful significance. Crawford and Brinkley[13] calculated $k = 4{\cdot}79 \times 10^5$ dyne cm.$^{-1}$ for the stretching of the aliphatic C–H bond. The values, also given by Crawford and Brinkley, for the stretching force constants of aliphatic C–halogen bonds are therefore increased by the fraction 5·02/4·79 in order to obtain the desired aromatic C–halogen stretching force constants. A somewhat similar method is used for estimating bond bending force constants. Kohlrausch gives $k = 0{\cdot}737 \times 10^5$ dyne cm.$^{-1}$ for in-plane bending of the C–H bonds in benzene. In conjunction with Westheimer's assumed dimensions (C–C = 1·40 Å; C–H = 1·08 Å) this is equivalent to $0{\cdot}86 \times 10^{-11}$ dyne radian^{-2}. Kohlrausch considered, however, that this constant was the least satisfactory of his assignments, but the result is confirmed by modern assignments of the fundamentals. It is most directly obtained from Kohlrausch's eqn. 3

$$0{\cdot}05863\,\bar{\nu}_3^2 = k_{\mathrm{CCH}}\,[1 + m_{\mathrm{H}}\,(d_{\mathrm{CC}} + d_{\mathrm{CH}})^2/m_{\mathrm{C}}(d_{\mathrm{CC}})^2]/m_{\mathrm{H}}$$

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[9] " Tables of Interatomic Distances and Configurations in Molecules and Ions," Ed. Sutton, *Spec. Publ. Chem. Soc.*, 1958.

[10] Wilson, *Phys. Rev.*, 1934, **45**, 706.

[11] Kohlrausch, *Z. phys. Chem.*, B, 1935, **30**, 305.

[12] See compilation by Herzberg, " Infrared and Raman Spectra," Van Nostrand, New York, 1945, based largely on Angus, Ingold, and Leckie, *J.*, 1936, 925; and Bailey, Hale, Ingold, and Thompson, *J.*, 1936, 931.

[13] Crawford and Brinkley, *J. Chem. Phys.*, 1941, **9**, 69.

$\bar{\nu}$ being in wave numbers and masses (m) in relative atomic weights. The Raman line at 2454 cm.$^{-1}$ has been assigned [12] as $2\bar{\nu}_3$, so that $\bar{\nu}_3 \approx 1230$ cm.$^{-1}$, whence $k_{\mathrm{CCH}} = 0{\cdot}71 \times 10^5$ dyne cm.$^{-1}$, which is not significantly different from the value used by Westheimer. It may be noted that use of Pitzer's tentative alternative assignment [14] for $\bar{\nu}_3$ would yield a force constant some 11% higher. Crawford and Brinkley's value for $\mathrm{H{-}\widehat{C}{-}H}$ bending is $0{\cdot}557 \times 10^{-11}$ dyne radian^{-2}, and since no consistent set of $\mathrm{C{-}\widehat{C}}$–halogen bending constants is available, their $\mathrm{H{-}\widehat{C}}$–halogen figures were increased by the fraction 0·86/0·557. The force constants obtained by these two methods are given in Table 2. Where direct comparison can be made with Westheimer's figures the agreement is close for bond bending constants but poorer for C–halogen stretching force constants, but these have virtually no effect upon the final results because the contribution of this co-ordinate to the sum $\sum(b_i + c_i)^2/k_i$ is always small.

For the repulsive van der Waals potentials, no really good functions were available to Westheimer and he was forced to modify theoretical repulsion curves for neon–neon interactions for use in the hydrogen–bromine case. This was unsatisfactory. In the meantime, however, Amdur and Mason [15] published repulsion potentials obtained directly from collisional experiments with inert-gas atoms. Since these potential functions apply over the precise ranges of internuclear distance involved in the present calculations, they are used as follows. The non-bonded fluorine–fluorine potential is set equal to the reported experimental neon–neon interaction energy, and the heavier halogens are regarded as interacting in the same manner as the corresponding heavier inert gases. For hydrogen–hydrogen interactions, however, the experimental helium–helium potential [16] is considered to be a very bad approximation because of the discrepancy in nuclear charge, so that, as in the earlier paper,[1] Hirschfelder and Linnett's energy for the repulsive state of H_2 is used (it is shown later that use of the helium–helium potential leads to an obviously incorrect answer for diphenyl). Very similar assumptions of non-bonding interactions were made by Mason and Kreevoy [17] in dealing, for example, with rotational isomers in aliphatic molecules. Amdur and Mason [18] have further shown that the geometric mean of the M–M and N–N potentials is a good approximation for that of the M–N atomic pair. In the present work therefore the appropriate geometric mean between Hirschfelder and Linnett's function and an inert gas–inert gas potential is used for hydrogen–halogen interactions. For convenience all the van der Waals potential functions have been recast in the form $V = A \exp(-d/\rho)$. The constants A and ρ for the various atomic pairs are listed in Table 3. Non-bonded interactions other than those between *ortho*-groups are neglected.

TABLE 3. *van der Waals's potential parameters with internuclear distances, in Å.*

Atoms	$10^{11}A$ (erg molecule^{-1})	ρ (Å)
H...H	6·65	0·3917
F...F	670	0·2101
Cl...Cl	553	0·2760
Br...Br	679	0·3031
I...I	352	0·3953
H...F	82·4	0·2660
H...Cl	84·3	0·3104
H...Br	14·4	0·4379
H...I	53·7	0·3983

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[14] Pitzer and Scott, *J. Amer. Chem. Soc.*, 1943, **65**, 803.

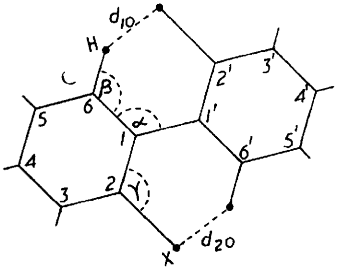
[15] Amdur and Mason, *J. Chem. Phys.*, 1954, **22**, 670; 1955, **23**, 415, 2268; 1956, **25**, 624.

[16] Amdur and Harkness, *ibid.*, 1954, **22**, 664.

[17] Mason and Kreevoy, *J. Amer. Chem. Soc.*, 1955, **77**, 5808; Kreevoy and Mason, *ibid.*, 1957, **79**, 4851.

[18] Amdur, Mason, and Harkness, *J. Chem. Phys.*, 1954, **22**, 1071; Amdur and Mason, *ibid.*, 1956, **25**, 630, 632.

The compounds considered in this paper are diphenyl, 2,2′-difluoro-, -dichloro-, -dibromo- and -di-iodo-diphenyl, the corresponding 2,6-compounds, and 2,2′,6,6′-tetrafluoro-, -tetrachloro-, -tetrabromo-, and -tetraiodo-diphenyl. The 2,2′-dihalogeno-compounds are expected to be inverted more easily through the *trans* transition state. This point will be considered in a forthcoming paper.



One general simplification is possible in the calculation of the b_i and c_i geometrical factors in the transition state. To a first approximation any non-planar distortion has no effect on d_1 or d_2 so that only planar deformations need be considered. The deformation modes for which allowance must be made are therefore (cf. Westheimer [6]), I extension of the 1,1′ bond, II, III, and IV, opening of the angles α, β, and γ respectively (see Figure), and contractions of the *ortho* C–H (V) and C–halogen (VI) bonds, together with planar normal modes of the carbon atoms of the benzene nuclei. These latter are given in Table 4. Displacement co-ordinates of the carbon atoms are R for radial movement and Y for clockwise motion round each ring at right angles to R.

TABLE 4. *Normal co-ordinates of the benzene nuclei.*

$$q_1 = R_1 + R_2 + R_3 + R_4 + R_5 + R_6$$
$$q_{6a'} = R_1 - R_3 + R_4 - R_6$$
$$q_{6b'} = (R_1 - 2R_2 + R_3 + R_4 - 2R_5 + R_6)/\sqrt{3}$$
$$q_{8a'} = -(Y_1 - 2Y_2 + Y_3 + Y_4 - 2Y_5 + Y_6)/\sqrt{3}$$
$$q_{8b'} = Y_1 - Y_3 + Y_4 - Y_6$$
$$q_{12} = R_1 - R_2 + R_3 - R_4 + R_5 - R_6$$
$$q_{14} = Y_1 - Y_2 + Y_3 - Y_4 + Y_5 - Y_6$$
$$q_{19a} = 2R_1 + R_2 - R_3 - 2R_4 - R_5 + R_6 + \sqrt{3}(Y_2 + Y_3 - Y_5 - Y_6)$$
$$q_{19b} = \sqrt{3}(R_2 + R_3 - R_5 - R_6) - (2Y_1 + Y_2 - Y_3 - 2Y_4 - Y_5 + Y_6)$$

Co-ordinates 6′ and 8′ must be combined to give true normal co-ordinates. The true normal co-ordinates are [6] $q_{(6+8)} = q_{6'} - 0{\cdot}481\, q_{8'}$, and $q_{(6+8)^*} = q_{6'} + 2{\cdot}08\, q_{8'}$. The force constants for these co-ordinates, which are derived *via* Wilson's potential function, are given in Table 5.

In calculating the geometrical factors some assumption is also necessary for the motion of a radial bond as the benzene skeleton is distorted. It is invariably assumed that such a bond remains both unaltered in length and directed along the bisector of the ring angle throughout any displacement of the benzenoid carbon atoms. For example, in determining the $b_{(6a+8a)}$ contribution to d_1 between (say) a 6-hydrogen atom and a 2′-substituent, caused by distortion of the unprimed ring (Fig.) in this co-ordinate, not only must the displacements $q_{6a'}$ and $-0{\cdot}481 q_{8a'}$ be considered, but also (for positive values of $q_{(6a+8a)}$) the effect of anticlockwise twisting motions of the $C_{(6)}$–H and the 1,1′ bonds relative to the unprimed ring, in order to maintain them along the bisectors of the ring angles at the 6- and 1-positions respectively.

TABLE 5. *Normal co-ordinate force constants.*

Co-ordinate	Force constant
I	$5{\cdot}5 \times 10^5$ dyne cm.$^{-1}$
II	$1{\cdot}13 \times 10^{-11}$ dyne rad.$^{-2}$
III—VI	See Table 2
q_1	$45{\cdot}9 \times 10^5$ dyne cm.$^{-1}$
$q_{(6+8)}$	$13{\cdot}7 \times 10^5$ dyne cm.$^{-1}$
$q_{(6+8)}$ *	450×10^5 dyne cm.$^{-1}$
q_{12}	$46{\cdot}2 \times 10^5$ dyne cm.$^{-1}$
q_{14}	138×10^5 dyne cm.$^{-1}$
q_{19}	$74{\cdot}6 \times 10^5$ dyne cm.$^{-1}$

The contribution of each co-ordinate to the sum $\sum(b_i + c_i)^2/k_i$ must be suitably weighted; *e.g.*, C–H bond bending terms due to q_{III} have statistical weight 4 in diphenyl and 2 in the dihalogeno-compounds. For all the 2,2′,6,6′- and 2,2′-compounds the benzene deformation contributions are doubly weighted, *i.e.*, they are counted once for each ring. In the remaining cases, however, contributions from most of the benzene deformation modes are different for each ring.

Tables 6 and 7 give the statistically weighted values of $(b_i + c_i)^2/k_i$ for the compounds investigated. In Table 7 the priming indicates the ring from which the contribution comes. Table 8 lists the computed energy components of the orthogonal and planar states of the molecules, and also the finally calculated barriers to internal rotation. The van der Waals and dipolar repulsion terms for the orthogonal states were calculated by assuming no molecular deformation. Since these energy terms are all small, and also the geometrical factors comparable to b_i and c_i tend to be small, this involves little error.

TABLE 6. *Values* of $10^6(b_i + c_i)^2/k_i$.

Co-ordinate	Diphenyl	2,2′-Difluoro-diphenyl	2,2′-Dichloro-diphenyl	2,2′-Dibromo-diphenyl	2,2′-Di-iodo-diphenyl
I	7·273	7·171	6·495	5·944	5·342
II	0	0·536	4·319	7·250	10·603
III	40·618	17·441	11·592	8·767	6·337
IV	—	20·349	51·030	70·872	97·152
V	2·000	1·421	2·286	2·703	3·070
VI	—	0·506	0·182	0·041	0·002
1	0·436	0·429	0·388	0·356	0·321
(6a + 8a)	9·168	10·501	12·362	12·912	13·156
(6a + 8a) *	2·234	2·732	3·562	3·879	4·116
(6b + 8b)	3·052	2·422	1·351	0·848	0·522
(6b + 8b) *	0·744	0·411	0·048	0·000	0·039
12	3·896	3·839	3·477	3·184	2·859
14	0	0·018	0·141	0·238	0·347
19a	24·033	25·716	27·100	26·842	27·740
19b	0	0·144	1·096	1·888	2·766
$\Sigma(b_i + c_i)^2/k_i$	93·454	93·636	125·429	145·723	174·372

Co-ordinate	Tetrafluoro-diphenyl	Tetrachloro-diphenyl	Tetrabromo-diphenyl	Tetraiodo-diphenyl
I	7·273	7·273	7·273	7·273
II	0	0	0	0
III	—	—	—	—
IV	36·224	79·381	106·891	145·500
V	—	—	—	—
VI	1·613	2·632	3·030	3·572
1	0·436	0·436	0·436	0·436
(6a + 8a)	10·345	12·430	13·420	14·394
(6a + 8a) *	2·435	2·788	2·956	3·112
(6b + 8b)	3·444	4·140	4·471	4·793
(6b + 8b) *	0·811	0·928	0·984	1·037
12	3·896	3·896	3·896	3·896
14	0	0	0	0
19a	27·936	35·013	38·439	41·810
19b	0	0	0	0
$\Sigma(b_i + c_i)^2/k_i$	94·413	148·924	181·796	225·822

The calculated barriers to rotation are, apart from small quantum effects, equal to the activation energies for inversion of configuration and, where comparison can be made with published data, the agreement is good.

The barrier for diphenyl itself is considerably lower than that calculated earlier [1] when insufficient allowance was made for molecular deformation. The present result is more consistent with the fact that the conjugation electronic absorption band is so strongly developed in this compound.[19] The 2,2′-compounds are dissymmetric in any non-planar conformation and therefore might be shown to be optically active if their half racemisation times were as long as one or two minutes. The rate constant for racemisation depends upon both the activation energy and the entropy of activation which is reflected in the non-exponential term. For such relatively simple inversion reactions the non-exponential

[19] O'Shaughnessy and Rodebush, *J. Amer. Chem. Soc.*, 1940, **62**, 2906.

TABLE 7. *Values of* $10^6(b_i + c_i)^2/k_i$.

Co-ordinate	2,6-Difluoro-diphenyl	2,6-Dichloro-diphenyl	2,6-Dibromo-diphenyl	2,6-Di-iodo-diphenyl
I	7·171	6·495	5·944	5·342
II	0	0	0	0
III	17·441	11·592	8·767	6·337
IV	20·349	51·030	70·872	97·152
V	1·421	2·286	2·703	3·070
VI	0·506	0·182	0·041	0·002
1	0·310	0·499	0·589	0·669
1′	0·137	0·030	0·006	0·000
(6a + 8a)	4·761	4·817	4·569	4·324
(6a + 8a)′	2·308	5·103	5·034	4·874
(6a + 8a) *	1·276	1·504	1·566	1·595
(6a + 8a) *′	1·038	0·829	0·710	0·590
(6b + 8b)	1·586	1·582	1·526	1·439
(6b + 8b)′	1·625	1·704	1·651	1·634
(6b + 8b) *	0·421	0·500	0·522	0·531
(6b + 8b) *′	0·345	0·276	0·236	0·196
12	1·670	1·110	0·844	0·608
12′	2·189	2·508	2·579	2·597
14	0	0	0	0
19a	15·693	22·536	25·462	30·394
19a′	10·305	6·838	5·203	3·746
19b	0	0	0	0
$\sum(b_i + c_i)^2/k_i$	90·553	121·420	138·822	165·100

TABLE 8. *Energy components and barriers in kcal. mole*$^{-1}$.

		E (planar)		*E* (orthogonal)			
Compound	*V*	(*a* + *b*)	*d*	(*a* + *b*)	*c*	*d*	Barrier
Diphenyl	3·97	11·27	0	0·43	6·96	0	3·9
2,2′-Difluorodiphenyl	3·59	13·09	0	0·06	6·96	0·11	6·0
2,2′-Dichlorodiphenyl	5·57	25·17	0	0·26	6·96	0·13	17·8
2,2′-Dibromodiphenyl	7·58	30·33	0	1·32	6·96	0·13	21·9
2,2′-Di-iododiphenyl	7·73	38·27	0	1·72	6·96	0·10	29·5
2,6-Difluorodiphenyl	3·66	13·31	0	0·06	6·96	0	6·3
2,6-Dichlorodiphenyl	5·70	25·63	0	0·26	6·96	0	18·4
2,6-Dibromodiphenyl	7·83	31·07	0	1·32	6·96	0	22·8
2,6-Di-iododiphenyl	8·05	39·53	0	1·72	6·96	0	30·9
2,2′,6,6′-Tetrafluorodiphenyl	3·55	16·50	4·86	0·01	6·96	0·44	13·9
2,2′,6,6′-Tetrachlorodiphenyl	7·25	50·13	2·76	0·18	6·96	0·51	45·2
2,2′,6,6′-Tetrabromodiphenyl	8·60	67·97	2·28	0·49	6·96	0·52	62·3
2,2′,6,6′-Tetraiododiphenyl	12·17	98·66	1·38	4·04	6·96	0·40	88·6

term is expected to be of the order of $10^{11.5}$—10^{12} sec.$^{-1}$. This implies a minimum activation energy impeding racemisation of about 17 kcal. mole^{-1} if optical activity is to be observed at 0°. This general consideration agrees well with the calculations. 2,2′-Difluoro- and 2,2′-dichloro-diphenyl have calculated activation energies of 6 and 18 kcal. mole^{-1}, respectively, and have never been obtained optically active, whilst 2,2′-dibromo- and 2,2′-di-iodo-diphenyl have calculated activation energies of 22 and 29 kcal. mole^{-1} respectively, and suitable 4,4′-derivatives of both have been obtained optically active.[7,20] The calculated figure of 21·9 kcal. mole^{-1} for racemisation of the dibromo-compound can be compared with Westheimer's calculated result of 18 (ref. 6) or 18·2 (ref. 21) kcal. mole^{-1} for 2,2′-dibromodiphenyl-4,4′-dicarboxylic acid. Searle and Adams[20] determined the rate of racemisation for this optically labile compound at one temperature (0°). From their result the free energy of activation is 19·5 kcal. mole^{-1}. The activation energy for the racemisation has recently been determined by Harris[21] as 19·0 kcal. mole^{-1}. Overall agreement is thus good for this compound. Rieger and Westheimer[7,22] have both calculated and determined the activation energy for racemisation of a 2,2′-di-iododiphenyl derivative. Their figures are, respectively, 21·4—23·6 and 21·0 kcal. mole^{-1}.

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[20] Searle and Adams, *J. Amer. Chem. Soc.*, 1934, **56**, 2112.
[21] Harris, *Proc. Chem. Soc.*, 1959, 367.
[22] Westheimer, " Steric Effects in Organic Chemistry," Ed. Newman, Wiley, New York, 1956.

Beaven and Hall[23] have calculated probable upper limits to rotational barriers in *o*-fluorinated diphenyls from blue shifts in electronic absorption spectra and phosphorescence spectra. From these two sources they obtain values of 7·7 and 4·6 kcal. mole^{-1}, respectively. From similar evidence Lewis and Kasha[24] conclude that inhibition of stabilisation of the planar state is substantially complete with two *o*-chlorine substituents. The calculated barrier, of course, leads to similar conclusions. Exact concordance with conclusions from ultraviolet spectra is not necessarily expected, for it has previously been observed " that the ultraviolet absorption spectra of a substituted diphenyl must be used with considerable reserve as a criterion of coplanarity or otherwise."[25]

It may be noted that the 2,6-compounds all have slightly higher activation energies for inversion than the 2,2′-analogues.

Comparisons with the results for the 2,2′,6,6′-tetrasubstituted compounds can only be made qualitatively or by analogy. Compounds with four *o*-fluorine atoms seem to be unresolvable,[26] even though the potential asymmetry is attained by buttressing 3- and 3′-substituents. This is in harmony with the low rotational barrier found here. The higher barrier in compounds with four *o*-chlorine atoms is, however, well recognised both from ultraviolet absorption spectra data[27] and from the preferential diradical nature of Muller and Neuhoff's compound.[28] Semi-quantitative comparisons are possible by various analogies with compounds of known optical stability. Buttressed compounds with four *o*-chloro-groups are, of course, easily resolvable.[26] Dipolar studies on steric inhibition of mesomerism[29] indicate that the methyl group is, on the average, sterically equivalent to bromine, whilst the amino-group is somewhat less obstructive. This suggests that the compound 6,6′-diamino-*o*-ditolyl resolved by Meisenheimer[30] should have an activation energy of racemisation between 45 and 62 kcal. mole^{-1}, the values calculated for tetrachloro- and tetrabromo-diphenyl. Kistiakowsky and Smith,[31] in fact, determined this activation energy as 45 kcal. mole^{-1}.

It is pertinent to demonstrate the unsuitability of the helium–helium interaction potential as an approximation to that for hydrogen atoms. Insertion of this potential into eqn. (9) for diphenyl gives a value for V_1 of $7{\cdot}55 \times 10^{-14}$ erg molecule^{-1}, whence $E_{\text{min.}}$ for the planar state is 3·8 kcal. mole^{-1}. When this result is coupled with the stabilisation energy of the planar state it is apparent that the planar state would be the preferential conformation; whereas for the free molecule this is known to be false.[32,33] It is clear therefore that the potential function for helium–helium interaction gives values which are much lower than the true potentials between hydrogen atoms.

For all the compounds studied the stabilisation energy of the planar state is taken as 6·96 kcal. mole^{-1}. It is clear from the resultant energy barrier in diphenyl itself that this figure is not likely to be an underestimate otherwise the calculated barrier would be improbably small.

The results reported here have been obtained by approximation methods, and various corrections, designed to remove errors arising from the use of quantities appropriate to infinitesimal displacements throughout, may be applied. These will be considered in a forthcoming paper.

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[*Received, March 9th,* 1959; *revised November 4th,* 1959.]

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[23] Beaven and Hall, *J.*, 1956, 4637.
[24] Lewis and Kasha, *J. Amer. Chem. Soc.*, 1944, **66**, 2100.
[25] Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854.
[26] Cf. Adams and Yuan, *Chem. Rev.*, 1933, **12**, 261.
[27] Pickett, Walter, and France, *J. Amer. Chem. Soc.*, 1936, **58**, 2296.
[28] Muller and Neuhoff, *Ber.*, 1939, **72**, 2063.
[29] Smith, *J.*, 1957, 4050.
[30] Meisenheimer and Horing, *Ber.*, 1927, **60**, 1425.
[31] Kistiakowsky and Smith, *J. Amer. Chem. Soc.*, 1936, **58**, 1043.
[32] Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408.
[33] Littlejohn and Smith, *J.*, 1954, 2552.