TABLE I

Substituted benzaldehydes	Expt.	Ratios							
		Halo acid to other acid				Halo alcohol to other alcohol			
p-Chloro- and *p*-methoxy-	1, 2, 3, 4	2.3:1	2.3:1	1.6:1	1.6:1	1:2.7	1:2.5	1:2.0	....
p-Chloro- and benz-	5, 6, 7, 8	1.45:1	1.3:1	1.7:1	2.5:1	1:1.3	1:1.3	....	1:2.8
p-Chloro- and (*m*,*p*-methylenedioxy)-	9			1.8:1					1:1.95
p-Bromo- and *p*-methoxy-	10, 11			2.3:1	2.8:1			1:1.8	1:2.1
p-Bromo- and benz-	12, 13, 14		1.4:1	1.3:1	1.2:1				
m-Bromo- and *p*-methoxy-	15, 16			1.9:1	1.7:1			1:1.8	1:2.0
m-Bromo- and benz-	17, 18, 19		2.4:1	2.1:1	2.2:1				

Procedure for Experiments Recorded in Table I (Except Numbers 1, 2 and 8).—A mixture of the two aldehydes (0.05 mole of each) was allowed to drop slowly into a solution of 27.5 g. of potassium hydroxide in 25 cc. of water with vigorous stirring. When the addition was complete, the temperature was raised slowly to 100° and held at that point for two hours. The solution was diluted to 400 cc. and extracted with four portions of ether. The ether extracts were combined, treated with bisulfite (which in no case gave more than 0.1 g. of precipitate), washed with water, dried over anhydrous sodium sulfate, and evaporated. The residue was analyzed for halogen by decomposition in the Parr bomb and titration by the Volhard method. The aqueous residue from the ether extractions was acidified with hydrochloric acid, and extracted with four portions of ether. The ether solutions were dried and evaporated and the residue analyzed as described for the alcohols.

Procedure for Experiments 1, 2 and 8 of Table I.—A mixture of five grams of each aldehyde, 10 g. of potassium hydroxide, and 10 cc. of water was shaken vigorously for two hours and allowed to stand a day. The remainder of the procedure was the same as that described above.

In Experiments 7 and 14 the acids were separated by steam distillation. This does not give a sharp separation of *p*-chlorobenzoic acid and benzoic acid, so the ratio given in Experiment 7 is only approximate. The separation of *p*-bromobenzoic acid and benzoic acid is very good, however, the recovered acids melting at 249 and 120° (reported, 251–253 and 122°).

Summary

It has been shown that 50% potassium hydroxide solution, acting on a mixture of benzaldehyde and *p*-dimethylaminobenzaldehyde induces the Cannizzaro reaction for the benzaldehyde only. The other aldehyde is not affected. A mixture of *m*-nitrobenzaldehyde and benzaldehyde, under the action of 14% potassium hydroxide, gives nitrobenzoic acid and nitrobenzyl alcohol, without attacking the benzaldehyde.

Seven reactions have been studied in which a crossed Cannizzaro reaction takes place between aromatic aldehydes. One member of the aldehyde pair in each of these was halogen substituted, and in every case, the halogen substituted molecule showed a tendency to be oxidized to the acid at the expense of the other aldehyde.

URBANA, ILL. RECEIVED AUGUST 19, 1936

Dipole Moment and Structure of Organic Compounds. XVI.[1] The Electric Moments of Some Chlorinated Diphenyls

BY G. C. HAMPSON AND A. WEISSBERGER

It has been suggested[2] that the electric moments of mono- and dichloronaphthalenes indicate a polarization of the naphthalene system by the polar C–Cl link, this polarization causing the observed moments to deviate considerably from those calculated when this effect is neglected, and a similar behavior has been found with the chlorodiphenyls. In the case of the dichlorodiphenyls with substituents in *both* rings, in either the ortho or meta position, a further complication is introduced, for there the moment will depend primarily on the configuration of the two rings about the diphenyl link. In view of the forces which govern the probability of the various configurations, special attention has been drawn to the case of *o,o'*-dichlorodiphenyl. The moment of this compound is larger than that of the *m,m'*-isomeride, and this is even more surprising in view of the fact that in the *o,o'*-compound the *cis*-configuration and a wide range of positions in the neighborhood of the *cis*-position which would contribute to a large moment are precluded for steric reasons. To account for the facts we suggested that *London forces* play an important role in determining the inner configuration of the molecule.

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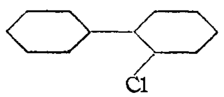
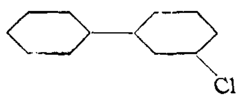
[1] Hampson and Weissberger, Paper XV, *J. Chem. Soc.*, 393 (1935).

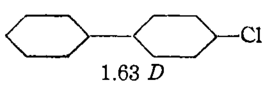
[2] Weissberger, Sängewald and Hampson, *Trans. Faraday Soc.*, **30**, 884 (1934).

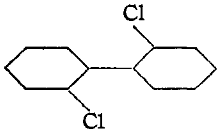
In the preceding paper[1] the polarization effect in the case of the chloronaphthalenes has been treated quantitatively. The present paper deals in a similar way with the three monochlorodiphenyls, and also attempts to give a quantitative treatment of the factors governing rotation about the diphenyl link in the case of the *o,o'*- and *m,m'*-dichlorodiphenyls.

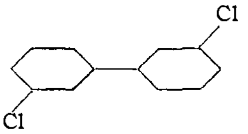
The moments of the compounds under consideration have been redetermined to obtain consistent data of sufficient accuracy. They are


1.45 *D*


1.64 *D*


1.63 *D*


1.91 *D*


1.80 *D*

In calculating the polarizing influence of the C–Cl bond, each of the monochlorodiphenyls has been regarded as a chlorobenzene molecule to which a polarizable benzene ring has been attached, the method of calculation following precisely as in the case of the monochloronaphthalenes.[1] Each of the rings has been assumed to be a regular hexagon of side 1.4 Å.,[3] the length of the internuclear C–C bond being taken as 1.48 Å.[4] The substituted chlorine atom has been assumed to be directed as from the center of the ring and μ_{C-Cl} has been taken as 1.55 *D*.[5] Since a benzene molecule is more polarizable in the plane of the ring than perpendicular to the ring, the magnitude of the polarization in the case of the chlorodiphenyls will vary with the relative configurations of the two rings.

Table I gives the calculated moments for *o*-, *m*- and *p*-monochlorodiphenyl (a) when the rings are co-planar, (b) when they are mutually perpendicular, (c) when there is free rotation, the polarizability of a benzene ring in the plane of the ring being taken as 12.5×10^{-24} and perpendicular to the ring 6.2×10^{-24}.[6]

TABLE I

	Rings co-planar	Rings perpendicular	Free rotation
o-Chlorodiphenyl	1.31	1.40	1.355
m-Chlorodiphenyl	1.601	1.604	1.603
p-Chlorodiphenyl	1.64	1.64	1.64

The results are in quite good agreement with the experimentally determined values, especially as one would expect that in *o*-chlorodiphenyl there would be a tendency for the rings to be perpendicular for steric reasons. An obvious cause of the small discrepancies is the fact that the moment 1.55 of chlorobenzene has been assumed to be located solely in the C–Cl bond, whereas part of it is certainly spread over the rest of the molecule.

In dealing with the *o,o'*- and *m,m'*-dichlorodiphenyls the most important factor in deciding the resultant moment of the molecules is the disposition of the two rings about the diphenyl link. The forces which regulate the probabilities of the various configurations are (a) electrostatic repulsions and attractions, (b) quantum mechanical attractions (London forces), (c) quantum mechanical repulsions (impenetrability of colliding atoms).

In the calculation of these forces the authors have enjoyed the help of Dr. F. London and they acknowledge with sincere thanks his valuable assistance.

Suppose that in any molecule the two rings are oriented about the diphenyl link so that the angle between their planes is ϕ; if now the component moment of each of the two C–Cl bonds perpendicular to the axis of rotation is μ'

$$\text{the resulting moment of the molecule} = 2\mu' \cos \phi/2 \quad (1)$$

In calculating the electric moment of an assemblage of such molecules the problem is to determine the mean angle ϕ. Now the measured polarization is a function of the square of the dipole moment, which in turn is a function of cos $\phi/2$, hence the measured polarization is made up of a series of terms characteristic of the various orientations, each term being a function of $\cos^2 \phi/2$. Having performed the summation and deduced the mean square of cos $\phi/2$, the dipole moment is calculated from the root mean square according to equation (1).

The potential as a function of the disposition of the rotating groups has been calculated and discussed for ethane by Eyring[7] and by Teller and

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(3) J. M. Robertson, *Proc. Roy. Soc.* (London), **A142**, 659 (1933); Pauling and Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

(4) Pickett, *Proc. Roy. Soc.* (London), **A142**, 333 (1933).

(5) Table of Dipole Moments, *Trans. Faraday Soc.*, Appendix, **30** (1934).

(6) Debye, "Handbuch der Radiologie," Vol. VI, Leipzig, 1925, p. 786, and Landolt-Börnstein–Roth, "Tabellen," 5th ed.

(7) Eyring, THIS JOURNAL, **54**, 3191 (1932).

Weigert.[8] A general quantum mechanical treatment which involves all forces between the hydrogen atoms results in showing minima for the positions in which the hydrogen atoms of one CH_3 group are not eclipsing those of the other CH_3 group when viewed along the C–C axis. The potential differences however are so small in comparison with kT, that at ordinary temperatures free rotation is developed; *i. e.*, all positions from 0 to 2 π have practically the same probability. Calculations for 1,2-dichloroethane have been made by Meyer[9] and by Smyth, Dornte and Wilson.[10] Meyer treats the problem classically and considers only the electrostatic effect of the C–Cl moments on each other. These are assumed to be located on the C–Cl axis in a point one-eighth of the C–Cl distance from the center of the chlorine atom.

The calculation gives a minimum of the potential for the *trans*-position, and the potential difference between the *cis*- and *trans*-positions is sufficiently large in comparison with kT to establish a distinct preference for the *trans*-position at ordinary temperatures. This result has been confirmed by Smyth, Dornte and Wilson[10] with a different location of the C–Cl moment and also taking into consideration the effect of the C–H dipoles. These authors further undertake a wave-mechanical treatment and show that the classical treatment of the problem is adequate.

More recently a complete mathematical treatment of the interaction between rotating polar groups in a molecule has been given by Lennard-Jones and Pike[11] and by Altar.[12] Altar introduces a factor neglected hitherto by considering the effect of the variation of the moment of inertia of the molecule with rotation of the polar groups. In a molecule such as 1,2-dichloroethane, for example, where the polar groups are heavy in comparison with the rest of the molecule and unsymmetrically distributed about the molecular axis, the three moments of inertia of the molecule do not remain constant, but vary with the internal configuration of the molecule. Also since the probability of a molecule existing in a given configuration depends on the moment of inertia of the molecule in that configuration, the probability being greater the greater the moment of inertia, one cannot apply simply a Boltzmann formula in order to deduce the mean angle ϕ, but one has to consider the statistics of all degrees of freedom involved, *i. e.*, one must weigh each individual configuration according to its moment of inertia, by multiplying by an appropriate weight factor. The weight factors calculated[12] in the case of 1,2-dichloroethane for several configurations are as follows:

	ϕ	W
cis config.	0°	0.68
	45°	.96
	90°	1.20
	135°	1.02
trans config.	180°	0.96

the effect of the moment of inertia being to favor the 90° configuration.

In the case which we are considering, namely, *o,o'*-dichlorodiphenyl, the variation of the moment of inertia with rotation will be smaller since the molecule is a comparatively large and heavy one and the only dissymmetry is caused by the two chlorine atoms. Also since configurations with small values of ϕ are precluded for steric reasons, the variations in the weight factor will certainly not be more than 10%, which, in view of the other uncertainties involved in these calculations, justifies the neglect of this effect.

Stuart,[13] in discussing the equilibrium between *cis* and *trans* dichloroethylene, also considers the London forces and the induction effect which in this case is high, due to the great polarizability of the double bond. These calculations, owing to the rigidity of the double bond, deal only with the two "plane" configurations of the geometrical isomers. They show, in agreement with the experimental facts, that the potential for the *cis*-position is lower than that for the *trans*-position.

With dichlorodiphenyl, as with dichloroethane, rotation about a single bond is involved, and one needs to know the potential over the whole range of a revolution.

The general method of procedure was to calculate the sum of the potentials Σv due to the electrostatic and quantum mechanical forces for various values of ϕ and construct Boltzmann terms $e^{-\Sigma v/kT}$ giving the probabilities of the molecules existing in the different configurations. The dipole moment μ was then calculated from the formula

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[8] Teller and Weigert, *Nachr. Ges. Wiss. Göttingen*, **2**, 218 (1933).

[9] Meyer, *Z. physik. Chem.*, **B8**, 27 (1930).

[10] Smyth, Dornte and Wilson, THIS JOURNAL, **53**, 4242 (1931).

[11] Lennard-Jones and Pike, *Trans. Faraday Soc.*, **30**, 830 (1934).

[12] Altar, *J. Chem. Phys.*, **3**, 460 (1935).

[13] Stuart, *Physik. Z.*, **32**, 793 (1931).

$$\mu = 2\mu' \sqrt{\frac{\int_0^{\pi} e^{-\Sigma v/kT} \cos^2 \frac{\phi}{2}\, d\phi}{\int_0^{\pi} e^{-\Sigma v/kT}\, d\phi}} \qquad (2)$$

In computing the *electrostatic* potentials we have adopted a method which is different from that of either Meyer or of Smyth, Dornte and Wilson. We consider the dipole as being formed by positive and negative charges of magnitude ϵ at the centers of the constituting atoms, ϵ being equal to μ/d where μ is the moment and d the distance between the atomic centers. The electrostatic potential is then given by $\Sigma(\epsilon_i\epsilon_j/r_{ij})$; r is the distance between the point charges ϵ_i and ϵ_j and varies with the angle of rotation ϕ.

The variable distances are calculated from the formulas

$$\begin{aligned} r &= \sqrt{b^2 + 4a^2 \sin^2 \phi/2} \\ r' &= \sqrt{b'^2 + (a - a')^2 + 4aa' \sin^2 \phi/2} \qquad (3) \\ r'' &= \sqrt{b''^2 + 4a'^2 \sin^2 \phi/2} \end{aligned}$$

where r, r' and r'' are the distances Cl_1 to Cl_2, Cl_1 to C_2, and C_1 to C_2, respectively; the significance of the symbols is evident from Fig. 1.

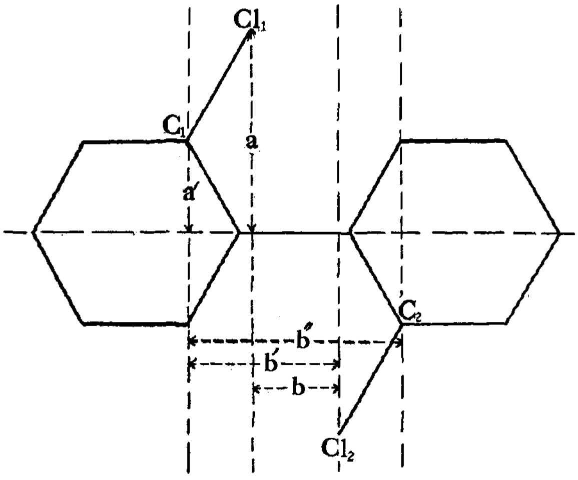

Fig 1.

The numerical data used are those given on page 2112; the distance C–Cl has been taken as 1.69 Å.;[14] $\phi = 0$ indicates the co-planar *cis* configuration. The total electrostatic potential for each angle is $\epsilon^2(1/r + 1/r'' - 2/r')$.

As was shown by Smyth, Dornte and Wilson,[10] the nature of the potential energy curve varies somewhat with the arbitrary location of the dipoles. We have no reason to believe that our convention, just described, is any more exact than that of other authors, and so for the purpose of comparison we have also calculated the electrostatic potential energies by Smyth's method. The results obtained by the two methods are shown in Fig. 2, U_1 being the electrostatic potential energy curve calculated by the charge-separation method, and U_2 the electrostatic potential energy curve calculated by Smyth's method.

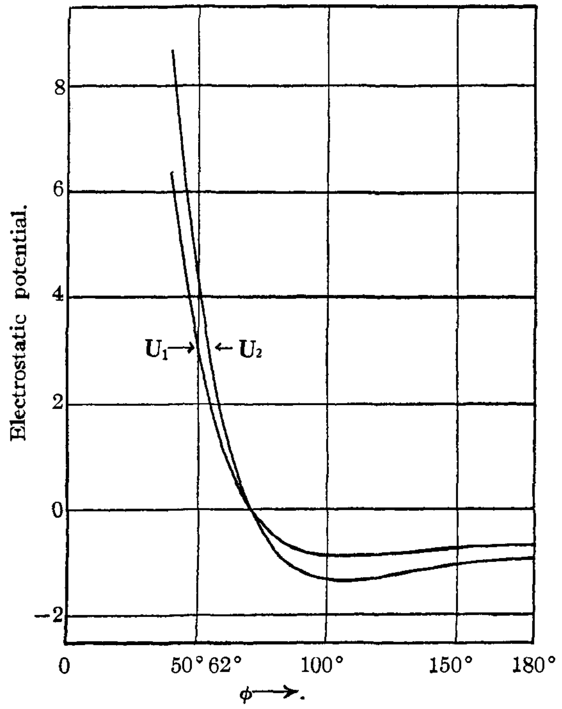

Fig. 2.

They have the same general shape and give approximately the same potential energy difference between the *cis*- and *trans*-positions. The most important factor, however, in governing the orientation of the molecule is the *London dispersion force*.

The *London forces* are of interest only for the chlorine atoms in *o,o'*-dichlorodiphenyl since for the other atoms they are negligible in their absolute magnitudes and furthermore do not vary much with ϕ. This applies also to the chlorine atoms in *m,m'*-dichlorodiphenyl but in this case they have been evaluated for comparison with the *o,o'*-compound. The London potential for the chlorine atoms has been taken as $115 \times 10^{-60}/r^6$, terms involving higher powers of r, which become important only when the atoms approach very close to each other, being neglected.

The numerical results for *o,o'*- and *m,m'*-dichlorodiphenyl are given in Tables II and III under the appropriate symbols.

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[14] De Laszlo, *Proc. Roy. Soc.* (London), **A146**, 698 (1934).

TABLE II

o,o'-DICHLORODIPHENYL

ϕ	r	r'	r''	$U_1 = \epsilon^2(1/r + 1/r'' - 2/r')$ (ergs × 10^{14})	U_2 (ergs × 10^{14})	$L = (115 \times 10^{-60})/r^6$ (ergs × 10^{14})	$U_1 + L$ (ergs × 10^{14})	$U_2 + L$ (ergs × 10^{14})	$e^{-(U_1+L)/kT}$	$e^{-(U_2+L)/kT}$	$e^{-(U_1+L)/kT} \cos^2 \phi/2$	$e^{-(U_2+L)/kT} \cos^2 \phi/2$
40°	2.184	2.793	2.997	6.34	8.70	−105.9	−99.56	−97.2	3.897×10^{10}		3.44×10^{10}	
45°	2.369	2.861	3.025	4.52	6.35	− 65.05	−60.53	−58.7	2.748×10^{6}	1.753×10^{6}	2.346×10^{6}	1.496×10^{6}
50°	2.555	2.933	3.056	3.08	4.42	− 41.32	−38.24	−36.9	1.169×10^{4}	8.416×10^{3}	9.60×10^{3}	6.913×10^{3}
55°	2.743	3.008	3.089	1.98	2.88	− 26.97	−24.99	−24.09	4.554×10^{2}	3.653×10^{2}	3.58×10^{2}	2.874×10^{2}
60°	2.929	3.087	3.125	1.14	1.67	− 18.22	−17.08	−16.55	65.63	57.62	49.22	43.22
65°	3.112	3.167	3.161	0.52	0.75	− 12.65	−12.13	−11.90	19.53	18.45	13.89	13.12
70°	3.293	3.248	3.199	.03	.07	− 9.01	− 8.98	− 8.94	9.025	8.944	5.98	6.00
75°	3.467	3.331	3.237	− .25	− .43	− 6.62	− 6.87	− 7.05	5.381	5.629	3.387	3.543
80°	3.641	3.414	3.275	− .50	− .78	− 4.94	− 5.44	− 5.72	3.788	4.063	2.223	2.384
85°	3.807	3.493	3.313	− .67	−1.02	− 3.78	− 4.45	− 4.80	2.975	3.245	1.617	1.764
90°	3.967	3.575	3.352	− .77	−1.18	− 2.95	− 3.72	− 4.13	2.490	2.751	1.245	1.375
100°	4.269	3.728	3.427	− .87	−1.31	− 1.90	− 2.77	− 3.21	1.970	2.197	0.814	0.908
120°	4.785	4.001	3.564	− .86	−1.26	− 0.96	− 1.82	− 2.22	1.563	1.721	.391	.430
140°	5.168	4.212	3.672	− .75	−1.09	− .60	− 1.35	− 1.69	1.392	1.513	.163	.177
160°	5.403	4.344	3.741	− .67	−0.96	− .46	− 1.13	− 1.42	1.319	1.418	.040	.043
180°	5.482	4.388	3.764	− .65	− .92	− .42	− 1.07	− 1.34	1.299	1.388	.0	.0

TABLE III

m,m'-DICHLORODIPHENYL

ϕ	r	r'	r''	$U = \epsilon^2(1/r + 1/r'' - 2/r')$ (ergs × 10^{14})	$L = (115 \times 10^{-60})/r^6$ (ergs × 10^{14})	$U + L$ (ergs × 10^{14})	$e^{-(U+L)/kT}$	$e^{-(U+L)kT} \cos^2 \phi/2$
0°	7.370	6.687	5.680	1.064	−0.072	+0.992	0.784	0.784
10°	7.385	6.694	5.684	1.057	− .071	+ .986	.785	.779
20°	7.428	6.716	5.696	1.042	− .068	+ .974	.788	.764
30°	7.499	6.752	5.715	1.020	− .065	+ .955	.791	.738
40°	7.594	6.800	5.740	0.991	− .060	+ .931	.796	.703
50°	7.709	6.858	5.771	.957	− .055	+ .902	.802	.659
60°	7.841	6.926	5.808	.921	− .049	+ .872	.808	.606
70°	7.984	6.999	5.848	.884	− .044	+ .840	.814	.546
80°	8.134	7.077	5.890	.850	− .040	+ .810	.820	.481
90°	8.285	7.156	5.933	.821	− .036	+ .785	.825	.413
100°	8.434	7.234	5.976	.793	− .032	+ .761	.830	.343
110°	8.576	7.309	6.017	.770	− .029	+ .741	.834	.275
120°	8.706	7.379	6.055	.756	− .026	+ .730	.836	.209
130°	8.824	7.442	6.090	.739	− .024	+ .715	.840	.150
140°	8.923	7.495	6.120	.726	− .023	+ .703	.842	.099
150°	9.003	7.539	6.143	.720	− .022	+ .698	.843	.057
160°	9.061	7.570	6.161	.712	− .021	+ .691	.844	.026
170°	9.097	7.589	6.172	.708	− .020	+ .688	.845	.006
180°	9.108	7.595	6.176	.705	− .020	+ .685	.846	.0

The case of m,m'-dichlorodiphenyl, where the centers of the chlorine atoms even in the *cis*-position do not come nearer to each other than to a distance of 7.37 Å., is not of any special interest except for comparison with the o,o'-compound. Figure 3 shows the probability $e^{-(U+L)/kT}$ for the m,m'-isomeride. It indicates a slight preference for the *trans*-position, but the potential energy $(U + L)$ difference between the *cis*- and *trans*-positions (*ca.* 0.3×10^{-14} ergs) is so small in comparison with kT (*ca.* 4×10^{-14} ergs) that free rotation is virtually established. The moment for free rotation ($\sqrt{2} \times 1.55 \cos 30°$) would be 1.90 *D*, that calculated from eq. (2) is 1.89 *D*,[15] the measured moment is 1.80 D. The difference is probably due to induced effects by the two dipoles, similar to those calculated in the case of the monochlorodiphenyls on page 2112.

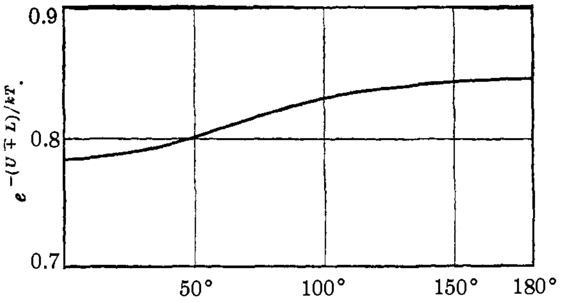

Fig. 3.—Probability distribution curve for m,m'-dichlorodiphenyl.

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[15] The integrals were evaluated graphically.

For *o,o'*-dichlorodiphenyl the data reveal the striking fact that the electrostatic potentials (U_1 or U_2 according to the mode of calculation), which favor the *trans*-position, are largely overcompensated by the London potentials, and that the internal configuration of the molecule depends almost entirely on the latter. As these decrease with the sixth power of r, they produce a considerable preference for positions with small angles ϕ. The probability of the various configurations as a function of ϕ is given by the numerical values of $e^{-(U_1+L)/kT}$ and by the full line in Fig. 4.[16] This proves our suggestion of the influence of the London forces as previously stated.[2] The curve indicates that the smaller the angle ϕ the greater is the probability. A limit, of course, must be set by a steric factor. In agreement with the resolvability of *o*-substituted diphenyl compounds, the table of values of r shows that no chance of a co-planar *cis*-configuration exists. Already at an angle $\phi = 35°$, the Cl–Cl distance is that of two chlorine atoms in a chlorine molecule. At a value $\phi = 60°$ they are at the distance 2.93 Å. which has been measured for the two chlorine atoms in methylene chloride,[17] where there still seems to be a slight repulsion between the chlorine atoms as is indicated by a deflection (2–3°) of the carbon valences. Configurations with a smaller angle ϕ can have only a small probability, and so the probability function must be characterized by a maximum where the repulsion forces (electrostatic and steric) are in equilibrium with the London attraction forces.

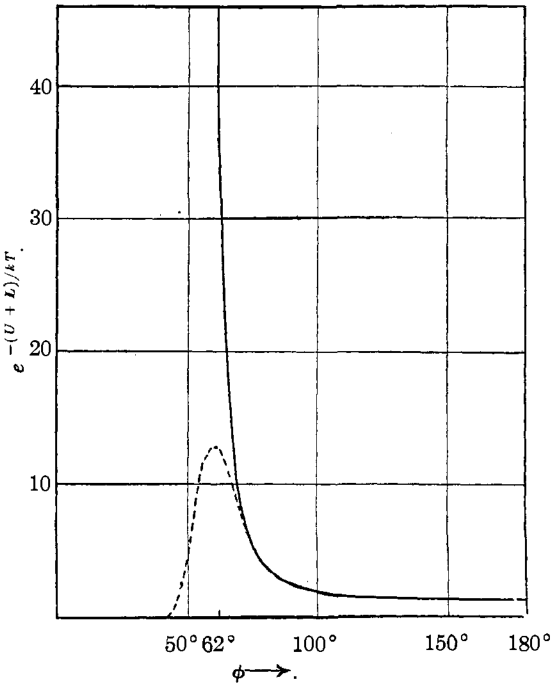

Fig. 4.—Probability distribution curve for *o,o'*-dichlorodiphenyl.

Little is known about the law of steric repulsion in question. For ions Born and Mayer[18] use a repulsion law of the form $be^{-r/\rho}$ (4) where b is a constant characteristic of the ions in question and they found that for the alkali halides ρ has a mean value of 0.345×10^{-8} cm. It seems reasonable to assume that such a law holds also in the case of covalently bound atoms but there is, of course, no reason for assuming that ρ especially equals 0.345.

In order to get an idea of the equilibrium distance the value for 60°, whose significance has been pointed out above, will be taken as a lower limit. The close packing distance between two chlorine atoms not belonging to the same molecule, and found to be 3.74 Å. for hexachlorobenzene,[19] gives the upper limit. The distance of equilibrium for *o,o'*-dichlorodiphenyl should be smaller than that owing to the smaller freedom of motion. Sidgwick's suggestion to add 0.5 Å. to the radius of the bound atom[20] gives a value of about 2.98 Å. for the distance of equilibrium. No other data appear to be available. In these circumstances the least hypothetical treatment will be to consider the repulsion potential as a rigid barrier, and to try at what angle we must cut the probability curve by a straight line parallel to the ordinate to obtain the experimental value for the moment from equation (2). This angle is 62° and it corresponds to a distance of 3.0 Å. between the chlorine atoms. If instead of this vertical barrier we multiply the probability function by an exponentially increasing repulsion term of the form $e^{-be^{-r/\rho}/kT}$ we get a probability curve shown by the dotted line in Fig. 4. Owing to the uncertainty in the law of repulsion, however, a calculation of the moment from this probability curve hardly seems justified.

Another effect which should be considered is the induction effect of the two C–Cl dipoles. This will tend to make the resultant moment of the compound low, especially in the case of the

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[16] $e^{-(U_2+L)/kT}$ gives essentially the same type of curve.

[17] Sutton and Brockway, THIS JOURNAL, **57**, 473 (1935).

[18] Born and Mayer, *Z. Physik*, **75**, 1 (1932).

[19] Hendricks and Blicke, THIS JOURNAL, **48**, 3007 (1926).

[20] "Annual Reports," 1933, p. 119.

o,o'-compound where the two dipoles come close to one another. On the other hand, this induction will contribute to the forces which favor molecules with smaller angles ϕ, and since both effects will be small and of inverse influence on the measured moment, their evaluation *in extenso* has not been undertaken.

The main results of our investigation may be summarized thus. The moments of the monochlorodiphenyls are explained if one takes into account the inducing effects of the polar group on the unsubstituted nucleus, as in the case of the chloronaphthalenes. The configuration of *o,o'*-dichlorodiphenyl is governed predominantly by the London forces.

Experimental

Polarization Results.—The measurements were carried out in benzene solution at 25.0°. The symbols have their usual significance.

o-Chlorodiphenyl

f_2	d	ϵ	n^2	P_2	eP_2
0.012289	0.8801	2.3167	2.26559	101.1	57.4
.008942	.8784	2.3039	2.26321	99.9	57.0
.006342	.8771	2.2951	2.26166	100.4	56.8
.003451	.8756	2.2846	2.25978	99.4	56.1
.0	.87385	2.2727	2.25797	...	..

$P_{A+O} = 100.2 - 56.8 = 43.4$ cc. $\mu = 1.45\ D$.

m-Chlorodiphenyl

0.022820	0.8858	2.3722	2.27285	112.3	58.0
.017568	.8833	2.3503	2.26952	113.0	57.8
.011424	.8801	2.3231	2.26542	113.2	57.9
.010396	.8796	2.3180	2.26480	112.4	57.9
.0	.8743	2.2727	2.25797	...	..

$P_{A+O} = 113.5 - 57.9 = 55.6$ cc. $\mu = 1.64\ D$.

p-Chlorodiphenyl

0.017357	0.8833	2.3501	2.27008	112.9	57.7
.013914	.8815	2.3333	2.26754	111.4	57.5
.008394	.8785	2.3096	2.26384	112.2	57.8
.006196	.8774	2.2998	2.26228	111.6	57.4
.0	.8740	2.2727	2.25797	...	..

$P_{A+O} = 112.6 - 57.6 = 55.0$ cc. $\mu = 1.63\ D$.

o,o'-Dichlorodiphenyl

0.011263	0.8825	2.3367	2.26505	135.0	60.9
.009917	.88145	2.3299	2.26398	136.3	60.6
.008776	.88055	2.3228	2.26304	135.6	60.2
.007935	.8799	2.3173	2.26256	134.3	60.2
.0	.8737	2.2727	2.25797	...	..

$P_{A+O} = 136 - 60.5 = 75.5$ cc. $\mu = 1.91\ D$.

Remeasurement of *o,o'*-dichlorodiphenyl. (This was made on an independent sample of material.)

0.017073	0.88675	2.3703	.....	135.4	..
.010177	.8814	2.3313	2.26412	136.4	60.7
.0	.8735	2.2727	2.25797	...	..

m,m'-Dichlorodiphenyl

0.014915	0.8854	2.3514	2.26893	128.7	62.1
.011293	.8826	2.3320	2.26568	128.3	61.3
.008686	.8805	2.3187	2.26423	129.2	61.9
.0	.8736	2.2727	2.25797	...	..

$P_{A+O} = 129.2 - 61.8 = 67.4$ cc. $\mu = 1.80\ D$.

The substances were either identical with, or prepared by, the same methods as those described by Weissberger and Sängewald.[21] A slight alteration has been made in the preparation of *o,o'*-dichlorodiphenyl. The Ullmann reaction was carried out for twelve hours at 260° with an *o*-chloroiodobenzene obtained from *o*-chloroaniline (purified according to Orton and King),[22] and worked up by vacuum distillation; b. p. (16 mm.) 145–165°; m. p. 52–55°; yield 40%; m. p. after repeated recrystallization from alcohol and finally from hexane 60.7–62°.

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Summary

The electric moments of the monochlorodiphenyls and the dichlorodiphenyls with the substituents in identical position in both rings have been determined.

The moments of the monochlorodiphenyls are explained by taking into account the inducing effects of the polar group on the unsubstituted nucleus, as in the case of the chloronaphthalenes.

The forces which determine the configuration of *m,m'*- and *o,o'*-dichlorodiphenyl have been evaluated. Since the electrostatic attraction and repulsion forces largely compensate each other, the configuration of the latter substance is predominantly determined by the London dispersion forces between the chlorine atoms. This explains the high moment of *o,o'*-dichlorodiphenyl.

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(21) Weissberger and Sängewald, *Z. physik. Chem.*, **B20**, 145 (1933).

(22) Orton and King, *J. Chem. Soc.*, **99**, 1380 (1911).