In conclusion the writer wishes to thank Professor Hugh S. Taylor for his active interest and encouragement during the course of this work.

Summary

1. The decomposition of gaseous hydrogen iodide has been investigated at concentrations from 0.02 to 7 moles per liter.

2. The rate of decomposition is bimolecular in the whole range of concentrations investigated and is not influenced by extreme drying.

3. At higher concentrations a correction taking care of the volume of the molecules in the expression for the number of bimolecular collisions must be introduced in order to retain the bimolecular character of the reaction rate.

4. Calculations of the reaction rate from the data on the activation energy show that the effective cross section of activated molecules in collisions leading to reaction are smaller than the average kinetic cross section of molecules.

5. A way of deciding which forms of molecular energy are contributing to the activation process has been indicated from considerations on the nature of the volume correction obtained from the rate measurements here recorded.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE PHYSIKALISCHES INSTITUT AND CHEMISCHES LABORATORIUM DER UNIVERSITÄT, LEIPZIG]

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. VII. THE ELECTRIC MOMENTS OF CERTAIN DIPHENYL DERIVATIVES. THEIR RELATION TO THE SEVERAL STRUCTURES

BY JOHN WARREN WILLIAMS[1] AND ARNOLD WEISSBERGER[2]

RECEIVED APRIL 16, 1928 PUBLISHED SEPTEMBER 5, 1928

A study of the chemical properties of diphenyl and its derivatives has led to interesting speculations concerning the structures of the various molecules. For the purpose in hand it is considered unnecessary to review the work which has been done in this field; it will be sufficient simply to state the conclusions given in two more recent publications These articles contain numerous references to previous investigations.

Adkins, Steinbring and Pickering,[3] as a result of their studies, conclude that the non-formation of the anhydrides is due to the fact that in the dinitro and dihydroxy acids the rings are extended as in the conventional formula, while in the amino or benzidine type of acids the rings are super-

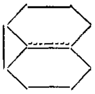
---

[1] National Research Council Fellow in Chemistry.

[2] Privatdozent an der Universität, Leipzig.

[3] Adkins, Steinbring and Pickering, THIS JOURNAL, **46**, 1917 (1924).

imposed. Kuhn and Albrecht,[4] discussing the same question, "come to the conclusion that it is not possible to explain diphenyl and its derivatives by means of a single space formula." In the case of the *p,p'*-disubstituted diphenyl compounds, two types of formula are discussed, as follows. (1) A formula in which the axes of the two benzene rings lie in a straight line. (2) A formula in which the axes of the two benzene rings make an angle with each other or are directed parallel to each other, as indicated in the following diagram.



In the previous papers of this series,[5] the use of electric moment data for the solution (in many cases at least) of problems of chemical structure has been suggested. The purpose of this article is to demonstrate the utility of these data as applied to the question of the structure of certain derivatives of diphenyl.

Experimental

The electric moments of the molecules in question, as well as that of *p*-phenylenediamine, which is necessary for the discussion, have been determined from dielectric constant and density data of their dilute solutions in benzene at 25°. The limited solubility of the diphenyl derivatives in benzene requires that the difference in dielectric constant between the solution and that of the solvent be determined with a high degree of accuracy. For this purpose an apparatus shown diagrammatically in Fig. 1 was built.

It differs from that previously described[6] in that it consists of three distinct circuits, two of which are oscillators and the other a receptor. The heterodyne principle was used as before; in fact, the method of making a dielectric constant measurement was very similar to that previously described. The dielectric constant of benzene was assumed to be 2.2820; that of the solutions was determined by noting the change in capacitance produced when the solution was substituted for the solvent between the plates of the measuring condenser. In the tables the dielectric constants have been expressed to four significant figures only. A fifth and doubtful figure was used in the calculation of the molar polarization of the solution, and therefore in the calculation of the molar polarization of the solute molecule. The uncertainty in the molar polarization of the solute molecule, P_2, is of the order of magnitude of 5%.

---

[4] Kuhn and Albrecht, *Ann.*, **455**, 272 (1927).

[5] Williams and collaborators, THIS JOURNAL, **49**, 1676, 2408, 2416 (1927); **50**, 94, 362 (1928).

[6] Williams and Krchma, *ibid.*, **48**, 1888 (1926).

All substances used for the measurements reported were subjected to a careful purification by the usual methods of crystallization or distillation or both. The melting points of the various solutes were determined, and in no case was the observed melting point different by more than 1° from that given in the literature.

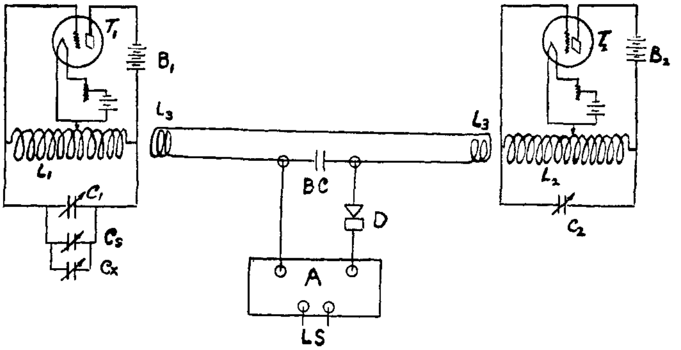


Fig. 1.—Diagram of circuits.

T_1,T_2—Telefunken RE 144 vacuum tubes; B_1,B_2—"B" batteries, 90 volts; L_1,L_2—inductances, 150 turns; C_1,C_2—capacitances, 1000 mmf.; C_s—standard variable air condenser; C_x—dielectric cell; L_3—coupling inductances, 25 turns; BC—block condenser, 0.1 μf; D—detector; A—two-step amplifier; LS—loud speaker.

Table I

Dielectric Constant and Density Data for Mixtures

MF, C_6H_6	d_4^{25}	ϵ	$P_{1,2}$	P_2
		p-Phenylenediamine		
100.00	0.8731	2.282	26.77	37.5
99.84	.8744	2.285	26.79	
		4,4′-Dichlorodiphenyl		
100.00	.8731	2.282	26.77	63
99.84	.8739	2.282	26.82	
99.68	.8752	2.283	26.87	
99.36	.8775	2.286	27.00	
		4,4′-Dinitrodiphenyl		
100.00	.8731	2.282	26.77	65
99.95	.8733	2.281	26.79	
		4,4′-Diaminodiphenyl		
100.00	.8731	2.282	26.77	100
99.75	.8758	2.294	26.94	
		4,4′-Diethoxydiphenyl		
100.00	.8731	2.282	26.77	150
99.82	.8741	2.295	27.03	
99.63	.8755	2.302	27.21	

The results of the experimental determinations are given in Tables I and II. The symbols used in the earlier articles have been retained throughout; therefore their significance need not be repeated here.

TABLE II

ELECTRIC MOMENTS OF SOLUTE MOLECULES AT 25°

Molecule	P_2	P_2''	P_2'	$\mu \times 10^{18}$
p-Phenylenediamine	37.5	35	2.5	0.3[a]
4,4'-Dichlorodiphenyl	63	63	0	0
4,4'-Dinitrodiphenyl	65	65	0	0
4,4'-Diaminodiphenyl	100	60	40	1.3
4,4'-Diethoxydiphenyl	150	75	75	1.9

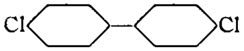
[a] Moment indistinguishable from zero by the method used.

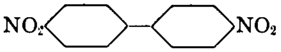
Discussion

In the discussion of these results it is necessary to consider the data not only for the particular derivatives of diphenyl but also for the corresponding derivatives of benzene. The data for *p*-dichlorobenzene,[7] *p*-dinitrobenzene[5] and hydroquinonediethylether[8] are available in the literature; that of *p*-phenylenediamine is reported above.

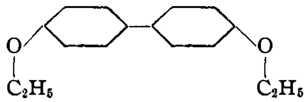
With regard to the structure of the several derivatives of diphenyl, the following statements may be made.

(1) Since the electric moments of the compounds *p*-dichlorobenzene and 4,4'-dichlorodiphenyl, and of *p*-dinitrobenzene and 4,4'-dinitrodiphenyl, are zero, and since the introduction of a single Cl atom or NO_2 group into the benzene nucleus causes a highly unsymmetrical molecule,[5] the conclusion is definite that in the case of the compounds 4,4'-dichlorodiphenyl and 4,4'-dinitrodiphenyl the rings of the diphenyl nucleus are co-axial. They are represented diagrammatically in the following sketches.





(2) The electric moments of the compounds hydroquinonediethylether and 4,4'-diethoxydiphenyl (1.7 and 1.9 × 10^{-18} e. s. u., respectively) must be considered to be of the same order of magnitude. The reason why hydroquinonediethylether gives a finite moment has been discussed previously.[8,9] Since the magnitude of the moment of the corresponding diphenyl derivative is the same, it is highly probable that its structure is similar. The conclusion to be drawn from these considerations is, again, that the benzene rings are extended. This structure is suggested in the following diagram.



---

[7] Smyth and Morgan, THIS JOURNAL, **49**, 1030 (1927).

[8] Williams, *Physik. Z.*, **29**, 271 (1928). In this connection see also Williams, THIS JOURNAL, **50**, 2350 (1928).

[9] Weissberger, *Physik. Z.*, **29**, 272 (1928).

In this connection it may be pointed out that until more accurate experiments are available for this and similar substances, the possibility of a slight deformation from the extended position is not excluded.

(3) The electric moment data for the compounds *p*-phenylenediamine and 4,4′-diaminodiphenyl distinctly indicate a collapsed or folded structure for the latter substance, in benzene solution, at least.[10] The electric moment of the similar benzene derivative is zero; thus there is no tendency for the NH_2 groups to be bent from the plane of the benzene ring. 4,4′-Diaminodiphenyl has a comparatively large moment, $\mu = 1.3 \times 10^{-18}$ e. s. u. If the benzene rings of the diphenyl were extended, as has been shown to be the case for the dichloro, dinitro and diethoxy derivatives, there can be little question that a moment indistinguishable from zero would have resulted for the benzidine molecule as well.

Thus the electric moment data reported in this article indicate the truth of the statement quoted above from the article of Adkins, Steinbring and Pickering, namely, that in the dinitro and dihydroxy derivatives of diphenyl the rings are extended as in the conventional formula, while in the amino or benzidine type the rings are folded. They are also in accord with the conclusions of Kuhn and Albrecht. It is evident, however, that these data are insufficient to establish the general truth of these conclusions; therefore the work is being continued.

The authors take pleasure in thanking Professor P. Debye for facilities placed at their disposal, for his kindly interest in the work and for the inspiration he has given it.

Summary

1. Dielectric constant and density data at 25° have been obtained for benzene solutions of *p*-phenylenediamine, 4,4′-dichlorodiphenyl, 4,4′-dinitrodiphenyl, 4,4′-diethoxydiphenyl and 4,4′-diaminodiphenyl. The electric moments of the various solute molecules have been calculated from these data.

2. The electric moment data have been shown to indicate the truth of statements made by Kuhn and by Adkins with regard to the structure of certain derivatives of diphenyl. In the case of the dinitro and dihydroxyl derivatives, the rings of the nucleus are extended. In the case of the amino derivative the rings cannot be extended.

LEIPZIG, GERMANY

---

[10] For discussion of effect of solvent, see Kuhn and Zumstein, *Ber.*, **59**, 488 (1926).