

181. The Configuration of Certain Diphenyl Compounds indicated by their Dipole Moments.

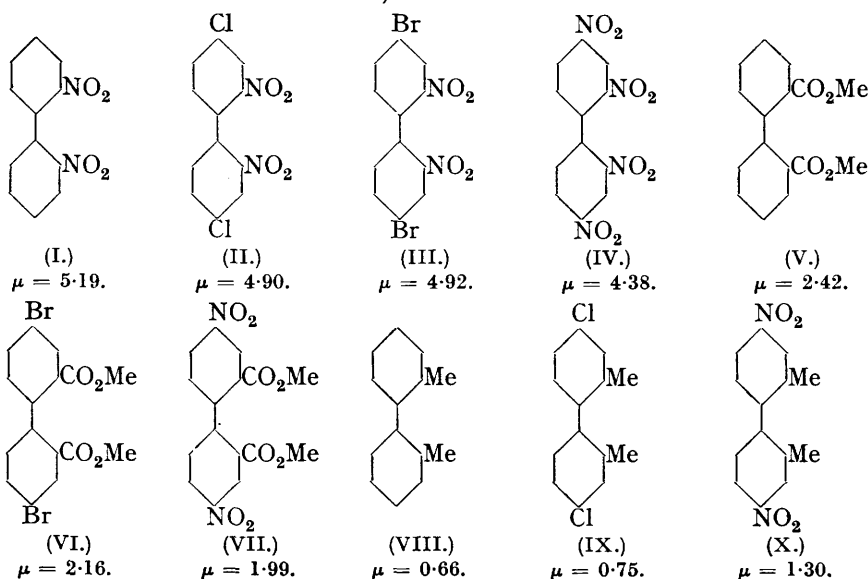
By R. J. W. LE FÈVRE and H. VINE.

An attempt has been made to determine whether a diphenyl molecule in which large ("obstacle") groups are situated in the 2 : 2'-positions has a configuration in which carbon atoms 4 : 1 : 1' : 4' are collinear. The general plan has been to measure the moment of the 2 : 2'-disubstituted diphenyl and compare it with the value for the related substance in which an additional pair of substituents has been inserted in the 4 : 4'-positions. The results are not in disagreement with the generally accepted view that the spatial arrangement of all derivatives of diphenyl is rectilinear. Small changes in moment with every pair of compounds have been found, but it has not been possible to decide whether these have arisen from departures from linearity or from other causes. Several of the compounds appear to be non-planar, with their benzenoid rings approximately at right angles.

ALL discussions of the factors determining the configuration of a dissymmetric diphenyl molecule (Le Fèvre and Turner, *Chem. and Ind.*, 1926, **45**, 831; Bell and Kenyon, *ibid.*, p. 864; J., 1926, 3045; Mills, *Chem. and Ind.*, 1926, **45**, 883, 905) have assumed that, when groups of considerable size are present in the 2 : 2'-positions and are operating to stabilise a non-planar molecule, carbon atoms 4 : 1 : 1' : 4' lie approximately along a straight line. No direct experimental evidence for this assumption has yet been advanced, although the rectilinear configuration of the parent hydrocarbon and a few 4 : 4'-disubstituted derivatives has been indicated by various X-ray and dipole-moment examinations.

In the present work an attempt has been made to supply this deficiency by examining the changes in dipole moments of some 2 : 2'-disubstituted diphenyls caused by the insertion in the 4 : 4'-positions of two radicals whose "group moments" lie along their directions of attachment to the aromatic carbon atoms; on the view that the configuration of the molecule is controlled only by the properties of the two *o*-substituents and that the 4 : 1 : 1' : 4' carbon atoms are collinear, the moment of the tetrasubstituted compound should not differ from that of the disubstituted one by an amount greater than that which might be expected to arise from intramolecular induction effects.

Comparisons have been made among the following substances * (the necessary experimental observations are tabulated later) :



* All dipole moments are given in Debye units (e.s.u. $\times 10^{-18}$).

Without correction it would appear that the two C-X (X = Cl, Br, or NO₂) vectors in (II), (III), and (IV) lie at angles of 165–170°; but before conclusions can be drawn from these data, estimations of the mutual effects of the substituents must be made. As an example, the case of the di- and tetra-nitrodiphenyls may be set out in some detail. A dipole situated at the origin (Fig. 1) and lying along the x axis will induce in a body P of polarisability α a moment whose vertical and horizontal components are μ_y and μ_x respectively. These (Smallwood and Herzfeld, *J. Amer. Chem. Soc.*, 1930, **52**, 1919; Frank, *Proc. Roy. Soc.*, 1935, **152**, A, 171) are given by:

$$\mu_x = \mu\alpha (3 \cos^2 \theta - 1)(\epsilon + 2)/3\epsilon r^3$$

$$\mu_y = 3\mu\alpha (\sin \theta \cdot \cos \theta)(\epsilon + 2)/3\epsilon r^3$$

and may be written as $R_x\mu\alpha(\epsilon + 2)/3\epsilon$ and $R_y\mu\alpha(\epsilon + 2)/3\epsilon$.

The application to the present problem is made on the basis of the dimensions indicated

FIG. 1.

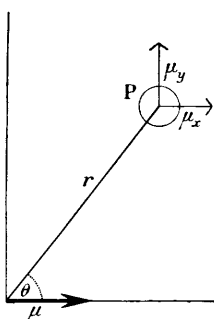
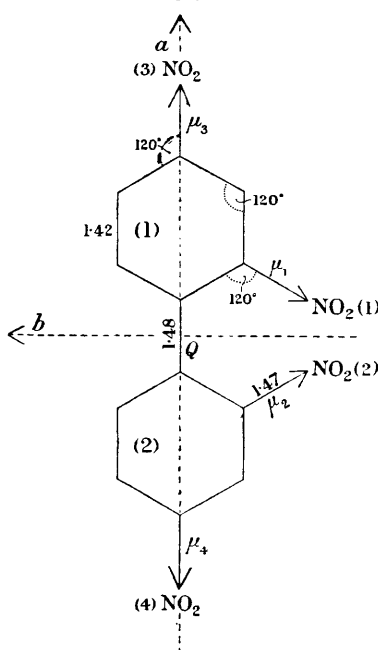


FIG. 2.



in Fig. 2. It is supposed that the plane of the ring (1) is rotated through an angle χ with respect to that of (2), and three axes meeting at Q have been taken, a passing through the centres of the two rings, b in the plane of (1), and c in that of (2). Values of R_x and R_y necessary to the calculation of the component induced moments parallel to b are tabulated below. On account of the symmetry of the model, the sum of the components R_a is zero, and those of R_b and R_c are equal. For the purpose of calculation, angles and distances have been measured between the centres of the nitrogen atoms.

	$r, \text{\AA.}$	$\theta.$		$R_b.$
(A) Induction by μ_1 on $(\text{NO}_2)_3$	5.0	150°	$R_x = 0.0100$	$-0.0087 \times 10^{24} \text{ cm.}^{-3}$
			$R_y = 0.0104$	$+0.0052$
(B) Induction by μ_1 on $(\text{NO}_2)_4$	6.3	83	$R_x = 0.0039$	$+0.0034$
			$R_y = 0.0015$	-0.0008
(C) Induction by μ_3 on $(\text{NO}_2)_1$	5.0	150	$R_x = 0.0104$	$+0.0104$
(D) Induction by μ_4 on $(\text{NO}_2)_1$	6.3	157	$R_x = 0.0043$	$+0.0043$
				$\Sigma R_b = 0.0138 \times 10^{24} \text{ cm.}^{-3}$

The resultant difference to be expected between the moments of the two substances under consideration, due to intramolecular induction, is therefore

$$0.0138 \times 10^{24} \cdot \mu\alpha(\epsilon + 2) \cdot 2\cos \frac{1}{2}\chi/3\epsilon$$

The moment of the C-NO₂ group, μ , is 4.2; the dielectric constant of the medium, ϵ , is assumed to be 2.4 (Le Fèvre and Le Fèvre, *J.*, 1937, 196); χ is probably *ca.* 90° (see below). Smallwood and Herzfeld (*loc. cit.*) used the value $2.75 \times 10^{-24} \text{ cm.}^3$ for the polarisability of the nitro-group, which they derived from the octet refractions. On insertion of these figures in the above expression, the net effect should be to reduce the moment arising from the 2 : 2'-dinitro-groups by 0.14.

The reduction actually observed is 0.81, which could be accounted for if α were as high as 16×10^{-24} . Such a value is considerably greater than that derived from the refraction.

In the other compounds examined, the action of induction effects similarly is scarcely adequate to explain the observed results. It is noteworthy, however, that the ratio between the *reduction* of moment in passing from (I) to (IV) and the *increase* of moment from (VIII) to (X) is almost exactly that between the molecular refractions of the nitro- and the methyl group ($0.81 : 0.64 = 7.3 : 5.7$). This, of course, is consistent with the view that the change of moment has its cause chiefly in polarisation of the 2 : 2'-substituents by the polar links at the ends of the molecule. The cases (V)—(VII) are more complex owing to the size and possibilities of intramolecular rotation inherent in the carbomethoxy-group; nevertheless, they qualitatively resemble (I), (III), and (IV), consistently with the $-I$ polarity common to the $C-NO_2$ and the $C-CO_2Et$ group.

In conclusion, it therefore appears that if any weight can be attached to calculations of the type made above, electrostatic induction effects within the molecules are insufficient to account for the observed changes in moment when the 4 : 4'-groups are introduced. In view, however, of the uncertainties involved, no definite conclusion can be drawn at the present time.

These uncertainties arise, not only in connexion with the actual magnitudes of α , ϵ , r , and θ which are used in the calculations, but also from the unknown "anomalous" solvation effects and the possibility that the average angle χ can be modified by the 4 : 4'-substituents. The former is not likely to be considerable (*p*-dinitrobenzene shows an excess of total polarisation over refractivity in benzene of *ca.* 10 c.c.), but the latter will probably be much more significant (cf. data for the rates of racemisation of certain 5-substituted dissymmetric diphenyls; Yuan and Adams, *J. Amer. Chem. Soc.*, 1932, **54**, 4434; Chien and Adams, *ibid.*, 1934, **56**, 1787).

It is noteworthy that if a uniaxial and regularly hexagonal carbon skeleton be assumed for substituted diphenyl molecules and if link moment values for $C-NO_2$ and $C-CO_2Me$ of 4.2 and 2.0 be adopted (4.2 is the moment of 4-nitrodiphenyl; no value for the corresponding methyl ester is available) then the mean angles χ , which are given by

$$\cos \chi = \frac{2}{3} \mu_{\text{obs}}^2 / \mu_{\text{link}}^2 - 1$$

are in both cases *ca.* 90° ($\cos \chi = 0.017$ and -0.023 respectively).

The moments reported by Bretscher (1.72; *Helv. Physica Acta*, 1929, **2**, 257) and Weissberger, Sängewald, and Hampson (1.77; *Trans. Faraday Soc.*, 1934, **30**, 884) for 2 : 2'-dichlorodiphenyl and by the last authors for 3 : 3'-dichlorodiphenyl (1.68), considered in conjunction with a $C-Cl$ link moment of 1.6, similarly indicate χ values between 90° and 100° . The somewhat greater moment of the 2 : 2'- compared with the 3 : 3'-dichlorodiphenyl has been attributed by Hampson and Weissberger to the operation of London forces (*J. Amer. Chem. Soc.*, 1936, **58**, 2111), leading to a reduction in the angle χ .

The moment of diphenic anhydride is also included in the table of results on p. 972. This substance contains a seven-membered ring, which from its ease of formation is presumably strainless. It is therefore of interest to compare this result with data for three five-ring anhydrides, recently reported by Govinda-Rau and Anantanarayanan (*Proc. Indian Acad. Sci.*, 1937, **V**, 185) as follows :

Succinic anhydride	$\mu = 4.2$	Citraconic anhydride	$\mu = 4.3$
Phthalic anhydride	5.3		

Our value for diphenic anhydride is practically identical with that found by the Indian authors for phthalic anhydride.

EXPERIMENTAL.

Preparation of Materials.—The 2 : 2'-dinitrodiphenyls were prepared by the method of Ullmann and Bielecki (*Ber.*, 1901, **34**, 2176). The reaction with copper powder took place at $240-245^\circ$ in the case of 2-chloro- and 2 : 5-dichloro-nitrobenzene, at 210° with 2 : 5-dibromo-nitrobenzene, and in boiling nitrobenzene solution in the case of 2 : 4-dinitrochlorobenzene. 4 : 4'-Dibromo-2 : 2'-dinitrodiphenyl, recrystallised from benzene, had m. p. 142° , which was 4° higher than that recorded by Ullmann and Bielecki.

Methyl diphenate and diphenic acid were obtained by addition of diazotised methyl anthranilate and anthranilic acid respectively to an ammoniacal solution of cuprous oxide (Vorländer and Meyer, *Annalen*, 1902, **320**, 122). By nitration of diphenic acid with fuming nitric acid, 4 : 4'-dinitrodiphenic acid was formed together with the 4 : 6'-dinitro-derivative, from which it was separated by recrystallisation of the barium salt (Hummel, *Annalen*, 1878, **193**, 131). It was readily esterified with methyl alcohol in the presence of hydrogen chloride (Schultze, *Annalen*, 1880, **203**, 98).

4 : 4'-Dibromodiphenic acid has previously been obtained only by oxidation of 2 : 7-dibromophenanthraquinone (Schmidt and Junghans, *Ber.*, 1904, **37**, 3569; Underwood and Clough, *J. Amer. Chem. Soc.*, 1929, **51**, 585), and from 4 : 4'-diaminodiphenic acid by the Sandmeyer reaction (Schmidt and Junghans, *loc. cit.*). Since 5-bromo-2-aminobenzoic acid is readily obtained by bromination of anthranilic acid (Wheeler, *J. Amer. Chem. Soc.*, 1909, **31**, 568), an application of Vorländer and Meyer's reaction to this substance offered a more convenient means of preparing the required dibromodiphenic acid. The bromoaminobenzoic acid (18 g.) was dissolved in 300 c.c. of 3N-sulphuric acid, and sodium nitrite (6 g.) added at 0°. The filtered liquid was allowed to run slowly into a solution of cuprous oxide (from 26 g. of cuprous chloride) in ammonia (*d* 0.88, 56 c.c.), the mixture being well stirred and the temperature kept below 20°. Nitrogen was evolved, and after standing for $\frac{1}{2}$ hour the mixture was heated to boiling and carefully acidified with concentrated hydrochloric acid, the thick bluish-green precipitate then being replaced by a pale yellow granular one of crude dibromodiphenic acid (16 g.). The product was purified by boiling for 10 minutes with acetic acid (50 c.c.), water (20 c.c.), and powdered zinc (3 g.), 1 g. of animal charcoal being added at the end. After filtration, addition of water, and cooling, the acid crystallised in yellowish-white leaflets, m. p. 277—278°.

Methyl 4 : 4'-dibromo-2 : 2'-diphenate was obtained by saturating a methyl-alcoholic solution of the acid with hydrogen chloride and warming it on the water-bath for a short while. The ester crystallised on cooling, and after being washed with sodium carbonate and recrystallised from methyl alcohol, formed colourless leaflets, m. p. 124° (Found : C, 44.4; H, 2.8. $C_{16}H_{12}O_4Br_2$ requires C, 44.9; H, 2.8%).

Diphenic acid was converted into its anhydride by heating with acetic acid and acetic anhydride (Bischoff and Adkins, *J. Amer. Chem. Soc.*, 1923, **45**, 1032). When 4 : 4'-dibromodiphenic acid (4 g.) was heated with a boiling mixture of acetic acid (8 g.) and acetic anhydride (8 g.), it changed rapidly into a white powder, which, after boiling for 15 minutes, was filtered and dried. It was very sparingly soluble in organic solvents and was not recrystallised, but was found to consist of microscopic transparent needles (Found : C, 44.4; H, 1.8. Calc. for $C_{14}H_6O_3Br_2$: C, 44.0; H, 1.6%). The m. p. was 316°, in disagreement with 304—305°, recorded by Underwood and Clough (*loc. cit.*) for an anhydride prepared by a similar method, but with more prolonged heating and with larger quantities of acetic acid and acetic anhydride.

Attempts to prepare 4 : 4'-dinitrodiphenic anhydride by a similar method were unsuccessful, as reported by Schmidt and Kämpf (*Ber.*, 1903, **36**, 3743) and by Underwood and Kochmann (*J. Amer. Chem. Soc.*, 1924, **46**, 2074).

2 : 2'-Dimethyldiphenyl was obtained by heating *o*-iodotoluene with copper powder in a sealed tube (Ullmann, *Annalen*, 1904, **332**, 42). 4 : 4'-Dichloro-2 : 2'-dimethyldiphenyl was prepared from *m*-tolidine (4 : 4'-diamino-2 : 2'-dimethyldiphenyl) by the Sandmeyer reaction. *m*-Tolidine hydrochloride (100 g.) was suspended in 10N-hydrochloric acid (350 c.c.) and diazotised by addition of sodium nitrite (50 g. in 200 c.c. of water) at 10°. The filtered solution was gradually added to a mixture of cuprous chloride (125 g.) and 10N-hydrochloric acid (200 c.c.), the temperature being kept at about 20°. Nitrogen was evolved and a large amount of sticky brown material precipitated; 41 g. (47% yield) of the required compound were obtained by prolonged steam-distillation, and on recrystallisation from alcohol it formed colourless needles, m. p. 48° (Found : C, 67.0; H, 4.9; Cl, 27.6. $C_{14}H_{12}Cl_2$ requires C, 67.0; H, 4.8; Cl, 28.2%).

Ullmann and Frentzel (*Ber.*, 1905, **38**, 725) recorded the preparation of 4 : 4'-dinitro-2 : 2'-dimethyldiphenyl by diazotisation of 2-amino-5-nitrotoluene and treatment with cuprous chloride in hydrochloric acid solution. Repetition of their procedure gave large yields of 2-chloro-5-nitrotoluene, which was removed by steam-distillation, together with small quantities of tarry residues. A similar result was obtained with *o*-nitroaniline; whether the diazotised solution of this base were added to the cuprous chloride solution or *vice versa*, large amounts of *o*-chloronitrobenzene only were produced, whereas Ullmann and Forgan (*Ber.*, 1901, **34**, 3802) and Ullmann and Frentzel (*loc. cit.*) stated that in this case, as in several others, reversal of the normal procedure of a Sandmeyer reaction gave quite high yields of diphenyl derivatives. We

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have obtained the required substance, 4:4'-dinitro-2:2'-dimethyldiphenyl, by another application of Vorländer and Meyer's reaction. These authors found that reduction of diazotised toluidines with ammoniacal cuprous oxide gave the corresponding azo-compounds, whereas *o*- and *p*-nitroaniline, like anthranilic acid and its ester, gave diphenyl compounds (*loc. cit.*).

w_1 .	$\epsilon_{25^\circ}^{1900}$.	$d_{4^\circ}^{25^\circ}$.	α_{ϵ_2} .	β .	$n_D^{25^\circ}$.	r_{12} .	$[R_L]_D$.
0	2.2725	0.87378	—	—	1.49724	0.33503	—
I. 2:2'-Dinitrodiphenyl.							
0.004174	2.3233	0.87512	12.17	0.367	—	—	—
0.004672	2.3303	0.87528	12.37	0.367	1.49761	0.33473	66.1
0.007903	2.3705	0.87632	12.40	0.367	1.49790	0.33451	65.7
0.008533	2.3804	0.87653	12.64	0.368	—	—	—
0.010091	2.3988	0.87701	12.52	0.366	1.49813	0.33440	66.5
II. 4:4'-Dichloro-2:2'-dinitrodiphenyl.							
0.001697	2.2866	0.87437	8.30	0.35	1.49740	0.33489	79
0.002418	2.2927	0.87466	8.35	0.36	1.49745	0.33481	75
0.005073	2.3161	0.87570	8.59	0.378	1.49767	0.33454	75
0.013879	2.3915	0.87914	8.57	0.386	—	—	—
III. 4:4'-Dibromo-2:2'-dinitrodiphenyl.							
0.004251	2.3013	0.87592	6.77	0.503	1.49761	0.33442	77
0.005904	2.3125	0.87660	6.78	0.478	1.49779	0.33426	82
0.006431	2.3148	0.87682	6.58	0.473	—	—	—
0.007793	2.3250	0.87732	6.74	0.454	1.49789	0.33405	84
0.012293	2.3551	0.87970	6.72	0.482	—	—	—
IV. 2:2':4:4'-Tetranitrodiphenyl.							
0.003040	2.2913	0.87509	6.2	0.431	1.49735	0.33488	71
0.004158	2.2988	0.87557	6.33	0.430	1.49767	0.33452	75
0.005733	2.3093	0.87612	6.42	0.408	—	—	—
0.007791	2.3226	0.87700	6.43	0.413	—	—	—
V. Methyl diphenate.							
0.00537	2.2860	0.87509	2.51	0.244	1.49752	0.33469	73.4
0.00855	2.2936	0.87586	2.47	0.243	1.49777	0.33453	74.5
0.01125	2.2998	0.87652	2.43	0.244	1.49787	0.33434	74.0
VI. Methyl 4:4'-dibromodiphenate.							
0.00415	2.2785	0.87549	1.44	0.472	1.49758	0.33457	95.9
0.00671	2.2818	0.87662	1.38	0.485	1.49769	0.33420	90.3
0.00739	2.2830	0.87693	1.42	0.488	1.49779	0.33414	91.6
0.00850	2.2842	0.87742	1.38	0.490	1.49783	0.33397	89.9
VII. Methyl 4:4'-dinitrodiphenate.							
0.00420	2.2778	0.87523	1.26	0.345	1.49753	0.33464	87.1
0.00476	2.2791	0.87542	1.37	0.345	1.49761	0.33461	88.9
0.00564	2.2801	0.87575	1.40	0.349	1.49766	0.33451	87.5
VIII. 2:2'-Dimethyldiphenyl.							
0.00548	2.2749	0.87434	0.44	0.117	—	—	—
0.00849	2.2770	0.87466	0.53	0.119	—	—	—
0.01166	2.2770	0.87498	0.39	0.118	—	—	—
0.11765	—	0.88608	—	0.119	1.50555	0.33505	61.0
IX. 4:4'-Dichloro-2:2'-dimethyldiphenyl.							
0.00900	2.2765	0.87588	0.44	0.267	1.49784	0.33457	71.3
0.01298	2.2783	0.87682	0.44	0.268	1.49813	0.33437	71.3
0.02334	2.2825	0.87927	0.428	0.269	1.49877	0.33380	70.8
0.03462	2.2873	0.88196	0.428	0.270	1.49967	0.33330	71.5
0.05257	2.2948	0.88627	0.424	0.272	1.50105	0.33245	71.8
X. 4:4'-Dinitro-2:2'-dimethyldiphenyl.							
0.01268	2.2844	0.87748	0.94	0.334	1.49828	0.33421	73.6
0.01946	2.2900	0.87945	0.90	0.333	1.49889	0.33380	73.9
XI. Diphenic anhydride.							
0.001186	2.2901	0.87415	14.8	0.36	1.49742	0.33498	66
0.001763	2.2970	0.87432	13.9	0.35	1.49745	0.33493	62
0.001797	2.2975	0.87431	13.9	0.34	1.49744	0.33493	62
0.003138	2.3171	0.87474	14.2	0.35	1.49754	0.33483	61

2-Amino-5-nitrotoluene (25 g.) was diazotised with concentrated sulphuric acid (60 c.c.), water (100 c.c.), and sodium nitrite (12 g.) at 0°, 350 g. of water added, and the resulting solution poured slowly, with vigorous stirring, into cuprous oxide (25 g.) dissolved in ammonia (d 0.88, 120 c.c.) and water (100 c.c.). Rapid evolution of nitrogen took place, with the formation of a reddish-brown solid. Extraction of this with alcohol gave 12 g. of an orange-coloured solid, m. p. *ca.* 150°, and the residue, after recrystallisation from acetic acid, yielded 5 g. of pure 4 : 4'-dinitro-2 : 2'-dimethylazobenzene, m. p. 258°. The material extracted with alcohol was repeatedly recrystallised from acetic acid (after boiling with animal charcoal), from alcohol, and finally from toluene, the m. p. rising to 168—170°. The purification was very wasteful. Ullmann and Frentzel record m. p. 170° for the substance (*loc. cit.*).

Dipole-moment Measurements.—The necessary observations in benzene solution are tabulated on page 971 under the usual headings. These, and the method of calculation employed, are explained in a recent paper (Le Fèvre and Vine, J., 1937, 1805).

	<i>M.</i>	Mean values.		<i>P</i> ₁ .	[<i>R</i> _L] _D .	μ .
		$\alpha\epsilon_2$.	β .			
I. 2 : 2'-Dinitrodiphenyl *	244	12.43	0.367	623	66	5.19
II. 4 : 4'-Dichloro-2 : 2'-dinitrodiphenyl	313	8.58	0.378	572	76	4.90
III. 4 : 4'-Dibromo-2 : 2'-dinitrodiphenyl ...	402	6.75	0.478	582	81	4.92
IV. 2 : 2' : 4 : 4'-Tetranitrodiphenyl	334	6.42	0.420	470	74	4.38
V. Methyl diphenate †	270	2.47	0.244	195.2	74.0	2.42
VI. Methyl 4 : 4'-dibromodiphenate	428	1.40	0.487	187.5	90.6	2.17
VII. Methyl 4 : 4'-dinitrodiphenate	360	1.37	0.346	173.2	87.8	2.03
VIII. 2 : 2'-Dimethyldiphenyl	182	0.45	0.118	70.1	61.0	0.66
IX. 4 : 4'-Dichloro-2 : 2'-dimethyldiphenyl ...	251	0.428	0.269	82.8	71.3	0.75
X. 4 : 4'-Dinitro-2 : 2'-dimethyldiphenyl ...	272	0.92	0.334	108.8	73.8	1.30
XI. Diphenic anhydride	224	14.0	0.35	640	62	5.29

* Bretscher (*loc. cit.*) found $P = 596$ c.c., $\mu = 5.12$, in benzene.

† For benzene solutions Bretscher (*loc. cit.*) found $P = 190.3$, $\mu = 2.36$, and Weissberger and Williams (*Z. physikal. Chem.*, 1929, B, **3**, 367) $P = 190$, $\mu = 2.3$.

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[Received, April 2nd, 1938.]