

246. *Molecular Compound Formation in the Polyphenyl Series. Part I.
Some Compounds formed by 4 : 4'-Dinitrodiphenyl.*

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Molecular compounds of 4 : 4'-dinitrodiphenyl with various diphenyl derivatives are described. It is demonstrated from their chemical compositions and from their crystal structures (to be described in detail elsewhere) that the molecular ratios in which the components of these compounds unite are determined almost exclusively by geometrical considerations. Interaction of dipoles and not an ionization process is visualized as the basis of compound formation in this series.

THE formation of deeply coloured molecular compounds from quinones and nitro-compounds on the one hand and certain unsaturated hydrocarbons and their derivatives on the other has been attributed (Weiss, *J.*, 1942, 245) " to a complex molecule, essentially ionic in character, which is formed from the two components by an electron transfer from the unsaturated hydrocarbon or its derivative (donor A) to the polynitro-compound (acceptor B) according to the net reaction $A + B \rightleftharpoons [A]^+ [B]^-$." This postulate of an integral electron transfer from A to B can be regarded, however, as possibly valid only in limiting cases " where deep coloration accompanies molecular compound formation, and where the presence of ions or ion pairs is supported by other evidence " (*idem*, *J.*, 1943, 463). The very great variations in colour and stability encountered in these molecular compounds suggest that in most cases interaction of dipoles, leading perhaps to an incipient oxidation-reduction reaction (Hammick and Yule, *J.*, 1940, 1539; Gibson and Loeffler, *J. Amer. Chem. Soc.*, 1940, 62, 1324) is the more probable basis of compound formation.

The union of the components in simple stoichiometric ratio (usually 1 : 1, though sometimes 2 : 1) has provided strong support for the former hypothesis of integral electron transfer as the basis of compound formation; for in the comparatively few cases where a molecular ratio of 2 : 1 has been observed in the past (cf. Kuhn and Winterstein, *Helv. Chim. Acta*, 1928, 11, 144; Hammick and Sixsmith, *J.*, 1939, 972) the molecule of at least one of the components has contained two groupings capable of resonating separately, and therefore of acting separately as donor or acceptor units. Less simple ratios than these occur, however, and are difficult to explain in terms of any process of integral electron transfer. Thus Hertel and Römer (*Z. physikal. Chem.*, 1930, B, 11, 84) have reported that *s*-trinitrobenzene and fluorene combine in the molecular ratio of 4 : 3. Of

even greater complexity, however, are the molecular compounds of 4 : 4'-dinitrodiphenyl with various diphenyl derivatives described below and listed in Table I.

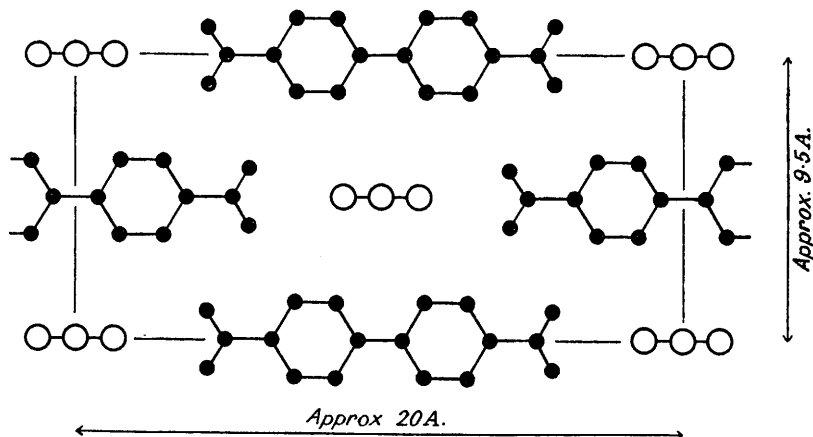
TABLE I.
Molecular Compounds of 4 : 4'-Dinitrodiphenyl.

"Donor" component.	Colour.	M. p.	<i>d.</i>	<i>l.</i>	<i>n.</i>	Mol. ratio of components.
4 : 4'-Diacetoxydiphenyl	Cream	224—226°	—	17—18	4.6—4.9	5 : 1
4-Acetoxydiphenyl	Cream	191—221	—	14.0—14.5	3.8—3.9	4 : 1
NNN'N'-Tetramethylbenzidine	Dark red	233	1.42	15.3	4.1	4 : 1
	Steel-grey	224	—	—	—	1 : 1
Benzidine	Red	240	1.44	13.9	3.8	4 : 1
4 : 4'-Dimethoxydiphenyl	Canary-yellow	216—218	—	14.8—15.3	4.0—4.1	3.5 : 1
4-Iododiphenyl	Pale yellow	192—220	1.56	13.1	3.5	3.5 : 1
4-Bromodiphenyl	Cream	192—220	1.52	12.8	3.5	3.5 : 1
4 : 4'-Dihydroxydiphenyl	Orange-yellow	249—250	1.45	12.5	3.4	3 : 1
4-Aminodiphenyl	Orange	220	—	12.2	3.3	3 : 1
4-Hydroxydiphenyl	Yellow	228—230	1.43	11.9	3.2	3 : 1
Diphenyl	Cream	191—221	—	10.7	2.9	3 : 1

l = Approximate length (A.) of "donor" molecule (allowing for approach of next molecule in end-on position).

n = Number of molecules of 4 : 4'-dinitrodiphenyl separated by 3.7 A. that can be accommodated at right angles to each "donor" molecule.

4 : 4'-Dinitrodiphenyl has been found to exhibit great selectivity in the formation of molecular complexes, which have been isolated only with 4-substituted and 4 : 4'-disubstituted diphenyls. Diphenyl derivatives with strong electron-donating substituents such as $-\text{NH}_2$ or $-\text{OH}$ in one or both of the *ortho* positions have failed even to generate colour on admixture with 4 : 4'-dinitrodiphenyl in solution. No evidence has been obtained of compound formation between 2 : 2'-dinitrodiphenyl and any of a large number of simple diphenyl derivatives which have been applied to it.



Idealized type of structure for the complexes of 4 : 4'-dinitrodiphenyl.

Each molecule of 4 : 4'-dinitrodiphenyl, denoted by black circles, should be seen as several molecules, one above the other, separated by 3.7 A. The larger plain circles represent the diphenyl nucleus of the "donor" component seen end-on.

The compounds of 4 : 4'-dinitrodiphenyl with benzidine and its tetramethyl derivative appear to be by far the most stable of those studied. They are much more intensely coloured (Table I) than those with 4-amino-, 4 : 4'-dihydroxy-, 4-hydroxy-, and 4 : 4'-dimethoxy-diphenyl. These in turn are much more deeply coloured than the remaining complexes listed, all of which have approximately the same colours as the substances from which they are derived. Almost all of these lightly coloured complexes melt with decomposition (over approximately the same range of temperature), indicating that they are less stable than their more deeply coloured analogues. In the cases studied, no complex formation has been observed between 4 : 4'-dinitrodiphenyl and diphenyl derivatives with electron-accepting groups in a *para* position. In this series, therefore, it appears that electron-donating substituents favour, and electron-accepting substituents inhibit, compound formation. Of interest from this point of view is the formation of a highly coloured and stable compound from 4-nitrodiphenyl and NNN'N'-tetramethylbenzidine (which contains strongly electron-donating dimethyl-amino-groups). This compound is the only stable and easily prepared molecular complex formed by a simple mononitro-derivative which is known to us, and is the only compound formed by 4-nitrodiphenyl which we have isolated. (A red colour is produced when solutions of 4-nitrodiphenyl and benzidine are mixed; but we have not succeeded in isolating the complex formed.)

In a series of X-ray crystallographic studies (shortly to be published elsewhere) the crystal structures of six of the molecular compounds listed in Table I have been examined, namely, those from 4-hydroxy- and 4 : 4'-

dihydroxy-diphenyl, benzidine, *NNN'*-tetramethylbenzidine, and 4-iodo- and 4-bromo-diphenyl. The structure of the first of these complexes has been worked out in detail, and the studies of the others carried sufficiently far to demonstrate that they all possess structures of the type indicated in the figure. In this projected structure the dinitrodiphenyl (acceptor) molecules are to be seen one above the other separated by 3.7 Å., whilst the donor molecules are seen end-on perpendicular to the plane of the paper. In the actual structures geometrical and symmetry considerations require that individual molecules should be tilted in varying degrees; but the type of structure still remains essentially the same as the idealized structure of the figure.

The following are significant points arising from the crystallographic studies:

(a) In the molecular compound with 4-hydroxydiphenyl (a complete *X*-ray crystallographic analysis of which has been carried out) all the molecules are approximately equally spaced from one another, and none of the intermolecular distances is shorter than those normally found in crystals of aromatic nitro-compounds, bonding in which is attributed to ordinary van der Waals forces (Table II). The only exception is one OH—O distance of 3.0 Å. At this distance very weak hydrogen bonding *might* be possible; but this could not explain compound formation, because the molecular ratio of the components is 3 : 1. The closest intermolecular approaches are those between the oxygen atoms of the nitro-groups and the carbon atoms of the benzene rings; but it is unlikely that these could provide a mechanism for compound formation, particularly as the approach of the nitro-groups to the benzene rings of the hydroxydiphenyl molecules is no closer than their approach to the benzene rings of the dinitrodiphenyl molecules themselves. The *X*-ray data, like those of Powell, Huse, and Cooke (*J.*, 1943, 153) on the complex between *s*-trinitrobenzene and *p*-iodoaniline, therefore reveal no localized bonding between the units in the crystal structure. The same almost certainly holds good for the other compounds in Table I for which preliminary structures have been worked out: in no cases is there any necessity to assume closer approaches between the molecules of the components than those determined for the dinitrodiphenyl-hydroxydiphenyl complex; *i.e.*, there is sufficient space in the unit cell in each case for the molecules to pack quite normally. Furthermore, the crystal densities (Table I) are quite normal, and no higher than those recorded for the aromatic nitro-compounds listed in Table II.

TABLE II.

Distances (Å.) of Closest Intermolecular Approach observed in Various Compounds.

Compound.	O—O Distance between oxygen atoms of nitro-groups.	O—C Distance from oxygen atom of nitro-group to carbon of benzene ring.	C—C Distance ⁶ between carbon atoms of adjacent molecules.
Molecular compound of 4 : 4'-dinitrodiphenyl with 4-hydroxydiphenyl ¹ ...	3.5	3.2	3.6
<i>p</i> -Dinitrobenzene ²	3.1(9)	3.3(0)	3.6(3)
<i>m</i> -Dinitrobenzene ³	3.2(0)	2.9(5)	3.6(0)
4 : 4'-Dinitrodiphenyl ⁴	3.4	2.9	3.6
Molecular compound of <i>s</i> -trinitrobenzene with <i>p</i> -iodoaniline ⁵	3.2(5)	3.3(5)	3.5

¹ Saunder, shortly to be published elsewhere. ² James, King, and Horrocks, *Proc. Roy. Soc.*, 1935, *A*, 153, 225. ³ Archer, unpublished work. ⁴ van Niekerk, *Proc. Roy. Soc.*, 1943, *A*, 181, 314. ⁵ Powell, Huse, and Cooke, *J.*, 1943, 153. ⁶ Compare also the C—C distances of 3.60—3.72 Å. for naphthalene, and 3.77—3.80 Å. for anthracene (Robertson, *Proc. Roy. Soc.*, 1933, *A*, 140, 79).

(b) In all these complexes very pronounced thermal vibrations occur, as shown by the strong "optical ghosts" accompanying certain spectra. This is an indication of comparatively weak bonding between the "layers" of atoms concerned, and is most pronounced for the spectra arising from the planes most nearly containing the dinitrodiphenyl molecules. There is thus weak bonding between these units in the crystal structure. Powell and Huse (*J.*, 1943, 435) have found similar diffuse spectra in the complex of hexamethylbenzene with picryl chloride, indicating weak bonding between layers consisting each of one kind of molecule.

(c) In the cases of the complexes of 4-iodo- and 4-bromo-diphenyl with 4 : 4'-dinitrodiphenyl, further optical ghosts (distinct from those produced by thermal vibration) have been observed. These optical ghosts are the result of a periodic error in the structure, the nature of which is still under investigation. It is perhaps significant that these two complexes are amongst the most lightly coloured and least stable of the series of compounds examined. Powell and Huse (*loc. cit.*) have also observed similar optical ghosts in the study of the complex of hexamethylbenzene with picryl chloride, and have suggested that in this case errors in the structure are due to alternate layers of molecules not being completely regular; *i.e.*, sometimes two adjacent layers of the same type of molecule may exist.

(d) It seems clear that the molecular ratios in which the components unite are determined almost exclusively by geometrical considerations. In compounds conforming to the type of structure depicted in the figure the number of 4 : 4'-dinitrodiphenyl molecules that can be accommodated by each molecule of the "donor" component depends on the length of the molecule of this component. In Table I are listed molecular ratios calculated on this basis for a number of compounds, together with the ratios actually observed. The agreement between the observed and the calculated values is surprisingly good in view of the differences which are to be expected in consequence of the tilting of the various molecules. It seems evident that the exact stoichiometric

ratios observed in these molecular compounds are a result more of the requirements of crystal structure than of any specific bonding mechanism.

EXPERIMENTAL.

Preparation of Molecular Compounds.—All the molecular compounds of 4 : 4'-dinitrodiphenyl, except the 1 : 1 compound with *NNN'N'*-tetramethylbenzidine, were prepared as follows. A considerable excess of the "donor" component dissolved in acetone (in the case of tetramethylbenzidine, in chloroform) was added to a boiling, almost saturated solution of 4 : 4'-dinitrodiphenyl in acetone. The crystals of the molecular compound which separated on slow cooling were filtered off rapidly, washed on the filter with a little acetone, and dried.

1 : 1-Compound of 4 : 4'-dinitrodiphenyl and *NNN'N'*-tetramethylbenzidine. A solution of 4 : 4'-dinitrodiphenyl in acetone was added to a considerable excess of *NNN'N'*-tetramethylbenzidine dissolved in chloroform, both solutions being at room temperature. Crystals of the molecular compound separated immediately. An attempt to prepare a 1 : 1 compound with benzidine was unsuccessful.

1 : 1 Compound of 4-nitrodiphenyl and *NNN'N'*-tetramethylbenzidine. This could be prepared from the components in acetone solution by the general method described above; but it was most conveniently made by adding the tetramethylbenzidine in chloroform solution to a hot, well-stirred solution of 4-nitrodiphenyl in alcohol. A deep red coloration appeared on mixing, and the compound separated in rouge-coloured crystals, m. p. 150°.

Compound formation between 4-nitrodiphenyl and benzidine. When solutions of 4-nitrodiphenyl and benzidine in acetone or alcohol were mixed a bright red coloration appeared. No compound could be isolated, however, although the relative concentrations of the components were varied over a wide range.

No crystals other than those of the components were isolated, and no colour was generated in solution, when 4 : 4'-dinitrodiphenyl was treated with :

(a) the following compounds containing electron-donating groups in *ortho* position : 2 : 2'-diamino-, 2-amino-, 2-hydroxy-, 2 : 2'-di-iodo-, and 2 : 2'-dibromo-diphenyl;

(b) the following compounds containing electron-accepting groups in *para* position : diphenyl-4-carboxylic acid and -4 : 4'-dicarboxylic acid, and 4-acetyldiphenyl.

Analysis of Molecular Compounds.—The compounds with amines were decomposed by digestion with 5*N*-hydrochloric acid (90% formic acid in the case of 4-aminodiphenyl, on account of the insolubility of the hydrochloride), and the nitro-compound was separated by filtration from the solution of the amine hydrochloride, washed with water, dried at 80–90°, and weighed. The amine was precipitated from the filtrate with alkali, filtered off, washed with water, dried, and weighed.

An analogous procedure was used for compounds with phenols, decomposition being effected with 5*N*-sodium hydroxide solution instead of hydrochloric acid.

4 : 4'-Dinitrodiphenyl	+ tetramethylbenzidine	(4 : 1).	Found : ratio, 3.96, 4.01.
	+ tetramethylbenzidine	(1 : 1)	" " 0.98, 1.01.
	+ benzidine	(4 : 1)	" " 3.89, 3.99.
	+ 4-aminodiphenyl	(3 : 1)	" " 2.96, 3.01.
	+ 4 : 4'-dihydroxydiphenyl	(3 : 1)	" " 2.96, 3.06.
	+ 4-hydroxydiphenyl	(3 : 1)	" " 3.10, 3.12.
4-Nitrodiphenyl	+ tetramethylbenzidine	(1 : 1)	" " 1.02, 1.03.

The compositions of the remaining complexes were found by determining their nitrogen contents.

4 : 4'-Dinitrodiphenyl	+ 4 : 4'-diacetoxydiphenyl	(5 : 1).	Found : N, 9.35, 9.38. $5C_{12}H_8O_4N_2, C_{16}H_{14}O_4$ requires N, 9.40%.
	+ 4-acetoxydiphenyl	(4 : 1).	Found : N, 9.40, 9.47. $4C_{12}H_8O_4N_2, C_{14}H_{12}O_2$ requires N, 9.43%.
	+ 4 : 4'-dimethoxydiphenyl	(3.5 : 1).	Found : N, 9.14, 9.21. $3.5C_{12}H_8O_4N_2, C_{14}H_{14}O_2$ requires N, 9.18%.
	+ 4-iododiphenyl	(3.5 : 1).	Found : N, 8.58, 8.65. $3.5C_{12}H_8O_4N_2, C_{12}H_9I$ requires N, 8.64%.
	+ 4-bromodiphenyl	(3.5 : 1).	Found : N, 8.97, 9.03. $3.5C_{12}H_8O_4N_2, C_{12}H_9Br$ requires N, 9.01%.
	+ diphenyl	(3 : 1).	Found : N, 9.53, 9.53. $3C_{12}H_8O_4N_2, C_{12}H_{10}$ requires N, 9.48%.

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