# 4,5-BIS-(*m*-AMINOPHENYL)-CARBAZOLE.

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This investigation was undertaken with a view to elucidate the spatial relations of the two phenyl nuclei contained in 4,5-diphenyl-carbazole. Although the work has not so far progressed as was originally intended, it has been thought advisable, for the reasons which will be given at the end of this introduction, to communicate some of the results already obtained.

In a previous paper[1], a brief account was given of the structure of 4,5-diphenyl-carbazole. It was there stated that, as the two phenyl nuclei cannot occupy their normal positions owing to the collision with each other, the valencies carrying the phenyl groups will have to be in a strained condition. Assuming that the atoms of the carbazole nucleus lie in a single plane[2], and taking into account that the molecule would assume the least strained form possible in the circumstances, it was suggested that the most probable structure representing the substance would be one in which the two phenyl nuclei lie in planes approximately perpendicular to the plane in which the carbazole nucleus lies. This is shown by Fig. 1, which is constructed on the assumption that the interatomic distances, C–C and C–N, is approximately 1.42 Å and also that valency distortion is possible only in the same planes as those in which the benzene nuclei lie. The thick lines indicate the sides of hexagons which are nearer to the reader. The directions of the valencies carrying the phenyl groups are those when the two carbon atoms of the *p*-positions of the phenyl nuclei are in mutual contact with the interatomic distance 1.42 Å, in other words, when the angle $\alpha$ is 125.1°. Since, however, it is inconceivable that the two atoms which is not in actual combination should be in such close proximity, actually the angle $\alpha$ will be somewhat larger than this. At any rate, this figure serves to indicate that, when the molecule assumes the structure represented by Fig. 1, the intramolecular strain is not large. The

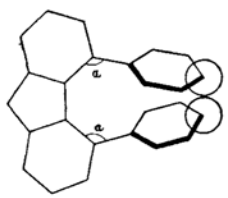


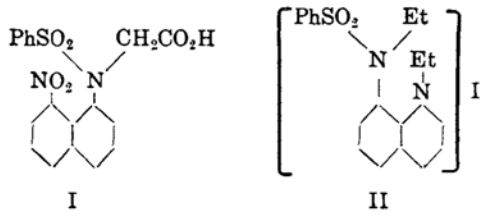
Fig. 1.

(1) Sako, this Bulletin, **9** (1934), 63.

(2) That the carbazole nucleus has a coplanar configuration has been shown by the fact that when *d*- or *l*-2,2′-diamino-1,1′-dinaphthyl is heated with HCl, inactive naphthocarbazole is produced (Kuhn and Goldfinger, *Ann.*, **470** (1929), 183). See also Adams and Yuan, *Chem. Rev.*, **12** (1933), 289.

facile formation of 4,5-diphenyl-carbazole[3] from 2,2′-diamino-6,6′-diphenyl-diphenyl and also of 4,5-bis-(*m*-aminophenyl)-carbazole (XV) from 2,2′-diamino-6,6′-bis-(*m*-aminophenyl)-diphenyl (XIV) may be attributed to this cause.

If Fig. 1 represents the stable form of 4,5-diphenyl-carbazole, a question which is naturally raised is whether or not there is a possibility of the rotation of the two phenyl nuclei around the bond carrying them. The observations such as those by Mills and his co-workers that benzenesulphonyl-8-nitronaphthylglycine (I)[4] and 8 benzenesulphonylethylamino-1-ethyl-quinolinium iodide (II)[5] can be obtained in optically active forms and the resolvability of many of the ortho-substituted diphenyl compounds due to the restricted rotation of the two nuclei seem to indicate that the rotation of the phenyl nuclei of 4,5-diphenyl-carbazole should also be restricted in a similar manner. The probability that the rotation of one of the phenyl groups will be obstructed by the other is perhaps more clearly indicated in the diagrammatical representation of this compound given in Fig. 2, which is constructed on the assumption



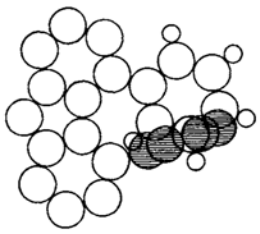



Fig. 2.

that the atoms of carbon and nitrogen may be regarded as spheres of a diameter approximately 1.42 Å, and that the hydrogen atoms as spheres of a diameter approximately one half of the diameter of the carbon atom. The carbazole nucleus is shown in the left half of the figure, and the hydrogen-atoms attached to this nucleus are omitted to simplify the diagram. The six carbon atoms of one of the phenyl groups, which are assumed to lie in the same plane as that in which the carbazole nucleus lies, are indicated in the upper-right of the figure, and the small spheres attached to five of these carbon atoms represent the hydrogen atoms[6]. The horizontally shaded spheres

(3) Sako, this Bulletin, **9** (1934), 70.

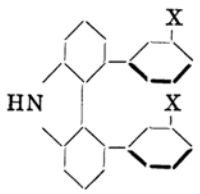
(4) Mills and Elliot, *J. Chem. Soc.*, **1928**, 1291.

(5) Mills and Breckenridge, *J. Chem. Soc.*, **1932**, 2209.

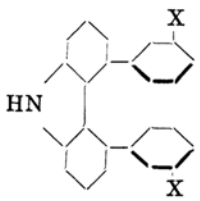
(6) That the hydrogen atoms in the nucleus do act as obstacles and are not embedded in the nuclear carbon atoms has been proved by the fact that diphenyl with only two substituents of proper size in opposite nuclei is resolvable (Turner and his co-workers, *J. Chem. Soc.*, **1932**, 2021, 2394; *ibid.*, **1933**, 135. Searle and Adams, *J. Am. Chem. Soc.*, **55** (1933), 1649. See also *Chem. Soc. Annual Reports*, **1933**, p. 258).

represent the four of the six carbon atoms of the other phenyl group which are assumed to be lying in a plane perpendicular to the plane of the paper. The positions of the two phenyl nuclei indicated in the figure are those when they are in their supposed normal positions.

It will be seen that, for the rotation of one of the phenyl nuclei by sweeping the obstacles presented by the other, the molecule will have to be distorted very considerably, the magnitude of this distortion being perhaps comparable to, if not larger than, that required in the case of the compounds I and II examined by Mills and his co-workers. The compound should therefore be represented by the structure given in Fig. 1, which appears to be the least strained condition of the molecule attainable in the circumstances. If the rotation of the phenyl nuclei are in fact thus limited, it follows that a 4,5-diphenyl-carbazole derivative, which contains each of a substituent in the meta- (or ortho-) positions of the two phenyl nuclei, should exist in a pair of geometrical isomers, one cis and the other trans, as shown respectively by the formulæ IIIa and IIIb, and that, since the transform (IIIb) does not possess a plane of symmetry, it should exist in two enantiomorphous modifications.



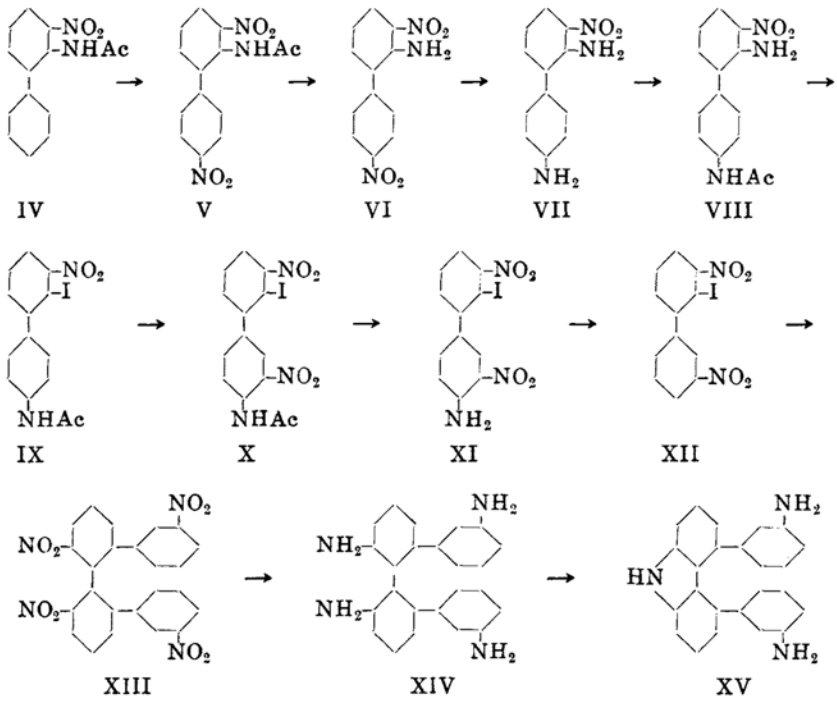

III a




III b

It seemed therefore that the simplest way to test those views stated above experimentally would be through the examination of such a type of 4,5-diphenyl-carbazole derivative as indicated by formulæ IIIa and IIIb. The compound which was selected for examination was 4,5-bis-(*m*-aminophenyl)-carbazole (XV) which has been obtained in the following way. 3-Nitro-2-acetamidodiphenyl (IV), which has been prepared through a series of processes from diphenyl by Sako's method[7], can be successively converted into 3,4′-dinitro-2-acetamidodiphenyl (V), 3,4′-dinitro-2-amino-diphenyl (VI), 3-nitro-2,4′-diaminodiphenyl (VII), 3-nitro-2-amino-4′-acetamidodiphenyl (VIII), 2-iodo 3-nitro-4′-acetamidodiphenyl (IX), 2-iodo-3,3′-dinitro-4′-acetamidodiphenyl (X), 2-iodo-3,3′-dinitro-4′-aminodiphenyl (XI), 2-iodo-3,3′-dinitrodiphenyl (XII), and the latter treated according to the Ullmann method with copper powder. 2,2′-Dinitro-6,6′-bis-(*m*-nitrophenyl)-diphenyl(XIII), produced in this way, on reduction, passes into 2,2′-diamino-6,6′-bis-(*m*-aminophenyl)-diphenyl (XIV), which, upon heating with HCl, yields 4,5-bis (*m*-aminophenyl)-carbazole (XV):

(7) This Bulletin, **9** (1934), 65.




Scarborough and Waters[8] have found that, although it contains the acetamido-group which tends to promote substitution in the same nucleus, 2-acetamidodiphenyl is nitrated in the 4′-position in the presence of acetic acid and conc. $H_2SO_4$, 4′-nitro-2-acetamidodiphenyl being obtained in a good yield[9]. This anomalous behaviour must be attributed to the presence of conc. $H_2SO_4$ which in general weakens, most probably due to the salt formation, the directive influence of the acetamido-group. This view is supported by the fact that when nitrated in the presence of acetic acid alone, 2-acetamidodiphenyl affords the 5-nitro-derivative[10] as the primary product. From these facts and also from the fact that 3-nitro-2-acetamidodiphenyl (IV) contains the nitro-group which tends to prevent substitution from occurring in the same ring, it is to be expected that the compound IV, when nitrated in the presence of conc. $H_2SO_4$ and acetic acid, should give mainly 3,4′-dinitro-2-acetamidodiphenyl (V). The experiment fully justified this expectation, for it has been found that under the conditions the compound (V) is produced in 73% yield. A conclusive proof of the position of the entering nitro-group has been

(8) *J. Chem. Soc.*, **1927**, 95.
(9) Sako, this Bulletin, **10** (1935), 585.
(10) Bell, *J. Chem. Soc.*, **1928**, 2773.

afforded by oxidizing 3,4′-dinitro-2-aminodiphenyl (VI), which is obtained by the hydrolysis of V, with chromic acid in acetic acid, when *p*-nitrobenzoic acid is obtained as one of the products.

The partial reduction of compounds V and VI, and 2-iodo-3,4′-dinitro-diphenyl, with sodium sulphide of which the latter can be obtained from VI by the usual method, was attempted in the hope of effecting the reduction of only the 4′-nitro-group contained in these substances. As a matter of fact, however, the partial reduction of compound VI has been found to be the only workable method, the yield of VII being 89% of the theoretical. That a nitro-group adjacent to an amino-group resists reduction with an alkaline sulphide has already been observed in the case of *o*-nitroaniline which is recovered unchanged after being heated with ammonium sulphide[11]. This behaviour of *o*-nitro-aniline is in marked contrast with that of *o*-nitro-acetanilide, of which compound V is a derivative, for under similar conditions the acetylated base can be reduced with ammonium sulphide[12]. As will be foreseen from this, when compound V was treated with sodium sulphide, both nitro-groups appeared to be attacked, and the chance of partial reduction taking place in the desired manner only seemed remote. It has been found that when 2-iodo-3,4′-dinitro-diphenyl is heated with alcoholic sodium sulphide, the resulting substance contains no halogen. This observation is in accord with that of Beilstein and Kurbatow[13] that the reaction, which occurs when *o*-chloronitro-compounds such as 1-chloro-2,4-dinitrobenzene are heated with $(NH_4)_2S$, $K_2S$, or better with KSH, is the elimination of halogen.

In the monoacetylation of 3-nitro-2,4′-diaminodiphenyl (VII), advantage was taken of the fact that the amino-group adjacent to the nitro- and also to the phenyl group is not attacked by acetic anhydride, the theoretical yield of the monoacetylated product VIII being obtained easily. This was a matter which had been anticipated, for it had been known that 3,5-dinitro-2-amino-diphenyl[14] and 3-nitro-2-aminodiphenyl[15], which, like compound VII, have each a nitro- and a phenyl-group in positions adjacent to the amino-group, cannot be acetylated even by boiling with acetic anhydride.

2-Iodo-3-nitro-4′-acetamidodiphenyl (IX), on nitration with nitric acid of D. 1.45–1.46, yields dinitro-compound X, but with nitric acid of D. 1.51–1.52, the trinitro-compound, 2′-iodo-3,5,3′-trinitro-4-acetamidodiphenyl (XVI). The constitution of this dinitro-compound (X) follows from the following considera-

(11) *Ber.*, **25** (1892), 987.

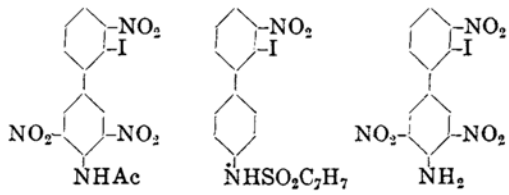
(12) Lassar-Cohn, "Arbeitsmethoden f. org. Chem. Lab.", 5 Ed., p. 861; cf. Niementowski, *Ber.*, **43** (1910), 3024.

(13) *Ber.*, **11** (1878), 2056.

(14) Bell, *J. Chem. Soc.*, **1928**, 2774.

(15) Sako, this Bulletin, **9** (1934), 68.

tions: (i) since there is a nitro-group in one of the nuclei of IX, the second nitro-group would naturally go to the other nucleus containing the acetamido-group which tends to promote substitution, and this should be more so as the nitration was conducted in the presence of nitric acid alone; (ii) that the compound appears to be a derivative of *o*-nitroacetanilide and not that of *m*-nitroacetanilide has been shown by the fact that free base (XI) obtained by its hydrolysis does not form the hydrochloride in a dil. HCl solution, and also that the deamination of the free base (XI) through the diazonium salt resulting in 2-iodo-3,3′-dinitrodiphenyl (XII) takes place with utmost readiness; (iii) by the nitration of 2-iodo-3-nitro-4′-*p*-toluenesulphonamidodiphenyl (XVII), a product is obtained, which, on hydrolysis, yields a trinitroamino-compound identical with that obtained by the hydrolysis of the trinitroacetamido-compound (XVI). In view of the very powerful ortho-para-directing influence exerted by the *p*-toluenesulphonamido-group as has been shown by Bell[16], the most probable structure of this trinitro-amine would be formula XVIII.




XVI XVII XVIII

There was no difficulty presented in the preparations of 2,2′-dinitro-6,6′-bis-(*m*-nitrophenyl)-diphenyl (XIII), 2,2′-diamino-6,6′-bis-(*m*-aminophenyl)-diphenyl (XIV), and 4,5-bis-(*m*-aminophenyl)-carbazole (XV). The free base of the latter crystallized, however, with difficulty. This property, coupled with the fact that it is rather readily oxidized in the air, rendered obtaining the free base XV in pure crystalline condition impossible. The hydrochloride and the diacetyl derivative of XV could be obtained readily in a state of purity. The sharp melting point possessed by this diacetyl compound indicated that it was a single substance, but since compound XV has been produced at such a high temperature as over 200° in the presence of HCl, it is possible that the more stable form (probably the trans form (IIIb)) alone is produced.

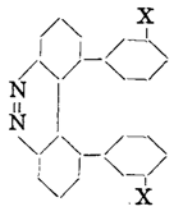
Attempts to resolve compound XV with *d*-camphor-sulphonic acid and *d*-tartaric acid have not been successful. The former acid gave no crystalline salt, and, although the latter acid gave a difficultly soluble tartarate in alcohol, the deep brown colour of this salt rendered the polarimetric examination impossible. This colour was undoubtedly caused by the oxidation in the air, which appeared to occur more readily when the base exists as a salt than when it is free. On account of this property and also of the small quantity

(16) *J. Chem. Soc.*, **1928**, 2770.

of the material (XV), a detailed examination of these salts had to be postponed till a later date (as already stated, for the synthesis of XV, no fewer than fifteen stages of preparations are required).

Compound XV was then submitted to the action of *l*-menthoxyacetyl chloride, when the stable 4,5-bis-(*m*-*l*-menthoxyacetamidophenyl)-carbazole was obtained in 73% yield. Its sharp melting point indicated that the *l*-menthoxyacetyl derivative was a single substance, although it does not necessarily follow from the good yield that the bis-(aminophenyl)-carbazole portion of the *l*-menthoxyacetyl compound is optically inactive, since there is a possibility that the substance might have been obtained as a result of processes of optical activation, similar to those observed, for example, by Pope and Peachy[17] with methyl-ethyl-*n*-propyl-tin-*d*-camphor-sulphonate, by Mills and Elliot[4] with the brucine salt of benzenesulphonyl-8-nitro-naphthyl-glycine, and by Yuan and Adams with the brucine salt of 2′-nitro-2,5-dimethoxydiphenyl-6′-carboxylic acid. Unfortunately, however, attempts to eliminate the *l*-menthoxyacetyl group by means of hydrolysis have so far been failures. That the rotation of an active substance is greatly influenced by the nature of solvents has been demonstrated once again by the bis-*l*-menthoxyacetyl derivative of XV. Thus, although it has $[\alpha]_D$ −22.27° in EtOH and −24.65° in acetone, the sign of rotation is completely reversed in benzene, in which $[\alpha]_D$ is +14.2°.

Although, owing to lack of material, the behaviour of the active acids on XV has not been examined so thoroughly as otherwise would have been possible, it seemed that the rather unstable nature of XV and its salts was unsuited or at least not advantageous for the investigation of this kind. It is proposed, therefore, to investigate the matter in other compounds of similar type which fulfil the conditions mentioned above, including, if possible, those containing a 6-membered ring in place of the 5-membered ring of XV, such as, for example, shown in formula XIX. From similar considerations regarding the probability of restriction of rotation of the phenyl groups, it is apparent that, since XIX should be more highly strained than XV, the rotation of the phenyl groups will be more difficult in XIX than in XV.



XIX

## Experimental.

**3,4′-Dinitro-2-acetamidodiphenyl** (V). A solution of 42.8 g. of 3-nitro-2-acetamidodiphenyl in 85 c.c. each of glacial acetic acid and conc. $H_2SO_4$ was cooled with ice and

(17) *J. Chem. Soc., Proc.*, **16** (1900), 12, 42, 116.

treated gradually with a mixture of 8.6 c c. of fuming $HNO_3$ of D. 1.52, 15 c.c. of glacial acetic acid, and 15 c.c. of conc. $H_2SO_4$ with constant stirring, the mixed acids being added at such a rate that the temperature of the reaction mixture was maintained below +2°. After the mixed acids had been added, stirring was continued one more hour. The mixture was then poured on ice, and the precipitated so id collected. The dried crude product weighed 49.2 g. It was dissolved in 1600 c.c. of boiling EtOH and left overnight. The yellow crystals (30.5 g.) thus separated were almost pure 3,4′-dinitro-2-acetamidodiphenyl (V). By concentration of the mother liquor, somewhat impure crystals were obtained, which on recrystallization gave a second crop (6.4 g.). The yield of V was therefore 73% of the theoretical. Pure 3,4′-dinitro-2-acetamidodiphenyl had m.p. 207.5° with previous sintering (Found : N, 14.2. Calc. for $C_{14}H_{11}O_5N_3$ : N, 14.0%).

The mother liquors separated from the main product, on further concentration, deposited more soluble nitration products in crystalline condition, but they have not been investigated so far. 3,4′-Dinitro-2-acetamidodiphenyl (V), when treated with alcoholic sodium sulphide, yielded a product which contained at least two substances, one yellow and the other red, the latter being identified with compound VII by the mixed melting point method.

**3,4′-Dinitro-2-amino-diphenyl** (VI). 3,4′-Dinitro-2-acetamidodiphenyl (V) (37 g.) was refluxed with a mixture of 450 c.c. each of EtOH and conc. HCl on the water bath for 7 hours. The free base separated as orange needles during the heating. After cooling, the product (31.1 g.) was collected, dried, dissolved in 900 c.c. of boiling benzene, and the solution allowed to cool. The orange leaflets thus obtained, 28 g., melted at 196–197° (Found : N, 16.5. Calc. for $C_{12}H_9O_4N_3$ : N, 16.2%).

The dinitroamino-compound (VI), on oxidation with chromic anhydride in acetic acid, gave *p*-nitrobenzoic acid as one of the products, showing that in the nitration of IV, the second nitro-group entered the 4′-position : a suspension of 3,4′-dinitro-2-aminodiphenyl in 10 parts of glacial acetic acid was treated with 5 parts of chromic anhydride with agitation. The substance disappeared with the evolution of heat, forming a dark-green, thick liquid. After standing for some hours, it was diluted with water, when a yellow precipitate separated. It was collected, dissolved in dil. ammonia solution and some insoluble matter was filtered off. The filtrate, on acidifying with HCl, deposited a yellow crystalline solid, which, on recrystallization, gave yellow crystals, which showed no depression of the melting point when mixed with the authentic specimen of *p*-nitrobenzoic acid.

**2-Iodo-3,4′-dinitrodiphenyl.** 3,4′-Dinitro-2-aminodiphenyl (VI) (1.3 g.) was dissolved in 5 c.c. of conc. $H_2SO_4$ at ordinary temperature. The vessel was then surrounded by ice, and 3.5 g. of cracked ice and 0.38 g. of powdered sodium nitrite were added with stirring. After a time, 2.5 g. of ice was added and stirring continued for an hour. A large quantity of ice was then added, and some suspended matter removed by filtration. The filtrate, on addition of 1.0 g. of KI, decomposed at once, the iodo-compound being precipitated. It was dissolved in ether, and the ethereal solution was shaken with a KOH solution and dried. On removal of the ether, a crystalline solid remained, which after being treated with animal charcoal in alcohol, was twice crystallized from the solvent (50 c.c.). It formed yellow, flat needles melting at 139–140° (Found : I, 34.33. Calc. for $C_{12}H_7O_4N_2I$ : I, 34.31%). The yield was 1.4 g.

In an attempt to effect the partial reduction of the 4′-nitro-group only, the iodo-dinitro-compound was treated with sodium sulphide in EtOH and a small quantity of

water, when fine needles separated, which contained no halogen. This product has not been studied.

**3-Nitro-2,4′-diaminodiphenyl** (VII). The procedure described below for the partial reduction of 3,4′-dinitro-2-aminodiphenyl (VI) is the outcome of a number of comparative experiments which were made to determine the best conditions. A suspension of 26 g. of 3,4′-dinitro-2-amino-diphenyl (VI) in 600 c.c. of EtOH was mixed with a solution of 40 g. of $Na_2S \cdot 9H_2O$ in 150 c.c. of water, and refluxed on the boiling water bath for an hour. The original substance disappeared in a quarter of an hour, forming a red solution. After the requisite time, the hot solution was diluted with 250 c.c. of water, when 3-nitro-2,4′-diaminodiphenyl (VII) separated immediately in crystalline state. The red crystals were collected, washed with EtOH–$H_2O$, and dried. The substance thus obtained was almost pure, had m.p. 156–157°, and may be used for a further experiment. The yield was 20.5 g. or 89.1% of the theoretical. On crystallization from EtOH, it gave red crystals melting at 157° (Found : N, 18.6. Calc. for $C_{12}H_{11}O_2N_3$ : N, 18.3%).

**3-Nitro-2-amino-4′-acetamidodiphenyl** (VIII). Acetic anhydride (6.9 g.) dissolved in a few c.c. of benzene was added to a suspension of 13.8 g. of 3-nitro-2.4′-diaminodiphenyl (VII) in 80 c.c. of benzene. The reaction commenced to occur at once, but it was heated on the boiling water bath for 30 minutes, during which time the original red crystals were replaced by the yellow crystals of the acetyl compound (VIII), which is practically insoluble in benzene. 3-Nitro-2-amino-4′-acetamidodiphenyl (VIII) thus obtained was pure and had m.p. 174–175° (Found : N, 15.80. Calc. for $C_{14}H_{13}O_3N_3$ : N, 15.50%). The yield was 16.2 g. (theoretical).

**2-Iodo-3-nitro 4′-acetamidodiphenyl** (IX). 3-Nitro-2-amino-4′-acetamidodiphenyl (VIII) (17.4 g.) was added in small portions to 77 c.c. of conc. $H_2SO_4$ at ordinary temperature with agitation. The resulting clear solution was cooled with ice water, treated with 60 g. of ice and then with 5.0 g. of $NO_2Na$ which was added during 30 minutes. As soon as the thick foam had subsided, a large quantity of ice was added, and the red solution thus obtained treated with a solution of 14 g. of KI in the cold. Shortly afterwards, a vigorous reaction took place. External heating was not necessary, as the decomposition was complete even in the ice-cold temperature. The precipitated product was filtered and washed successively with a $Na_2S_2O_3$ solution and water. The dried crude product weighed 24.5 g. It was dissolved in 2240 c.c. of boiling alcohol and allowed to stand for crystallization. The yellow leaflets thus obtained melted at 239° with previous softening (Found : I, 33.1. Calc. for $C_{14}H_{11}O_3N_2I$ : I, 33.2%). The yield of the pure substance was 22 g. or 90% of the theoretical.

**2-Iodo-3-nitro-4′-aminodiphenyl and its hydrochloride.** A suspension of 1.9 g. of 2-iodo-3-nitro-4′-acetamidodiphenyl (IX) in a mixture of 20 c.c. each of alcohol and conc. HCl was refluxed on the water bath for 1.5 hours during which time the original crystals were replaced by the yellow crystals of the hydrochloride of 2-iodo-3-nitro-4′-aminodiphenyl. After cooling, it was collected, washed with EtOH–conc. HCl and then with ether (Found : Cl, 9.32. Calc. for $C_{12}H_9O_2N_2I \cdot HCl$ : Cl, 9.42%.). The yield of the hydrochloride was 1.8 g. It can be crystallized from water.

To obtain the free base, the hydrochloride obtained above was shaken with an excess of NaOH solution and ether, and the upper layer, after being dried with $K_2CO_3$, evaporated up. The residual crystals, on crystallization from EtOH, gave yellow crystals melting at 126–127° (Found : I, 37.16. Calc. for $C_{12}H_9O_2N_2I$ : I, 37.33%).

**2-Iodo-3-nitro-4′-*p*-toluenesulphonamidodiphenyl** (XVII). To a solution of 1.12 g. of 2-iodo-3-nitro-4′-aminodiphenyl in 3 c.c. of pyridine was added 0.66 g. of *p*-toluenesulphonyl chloride, and the reddish solution thus obtained was heated on the water bath until the colour had almost disappeared. It was then diluted with water and shaken with benzene. The benzene solution, when shaken with a $CaCl_2$ solution, separated a gummy material which solidified on rubbing. On crystallization from EtOH, 2-iodo-3-nitro-4′-*p*-toluenesulphonamidodiphenyl separated as beautiful yellow, transparent crystals which melted at 136–137° (Found I, 25.44; S, 6.56. Calc. for $C_{19}H_{15}O_4N_2IS$: I, 25.69; S, 6.49%).

**2-Iodo-3,3′-dinitro-4′-acetamidodiphenyl** (X). At first, the preparation of this compound from 2-iodo-3-nitro-4′-acetamidodiphenyl (IX) presented unexpected difficulties, and it was only after a large number of comparative experiments, in which nitric acid of varied concentrations was employed, that this compound (X) became obtainable in an almost theoretical yield. The success of the nitration depended essentially upon the concentration of nitric acid, according to which either the dinitro-compound (X) or the trinitro-compound (XVI) was obtained exclusively.

To 40 c.c. of nitric acid of D. 1.456 which was cooled with ice water, was gradually added 7.64 g. of 2-iodo-3-nitro-4′-acetamidodiphenyl (IX) with stirring. The substance disappeared almost instantaneously after each addition. The addition of the original substance took about one hour, and the agitation was continued one more hour. Some of the product separated towards the end of the reaction. Reaction mixture was then poured into ice, and the solid thus appeared collected. The dried crude product weighed 8.6 g. On crystallization from 615 c.c. of EtOH, it formed yellow leaflets melting at 196–197° (Found: N, 10.11. Calc. for $C_{14}H_{10}O_5N_3I$: N, 9.84%). The yield of the purified substance was 8 g. or 93.7% of the theoretical.

**2-Iodo-3,3′-dinitro-4′-aminodiphenyl** (XI). A suspension of 7.26 g. of powdered 2-iodo-3,3′-dinitro-4′-acetamidodiphenyl (X) in a mixture of 100 c.c. each of EtOH and conc. HCl was refluxed on the water bath for 1.5–2.0 hours. Fifty c.c. of water was then added to the hot mixture, and the crystalline product thus separated filtered after cooling. The substance (6.5 g.) was the almost pure free base (XI). Crystallized from EtOH, it formed yellow needles which melted at 178–178.5° (Found: N, 11.22, Calc. for $C_{12}H_8O_4N_3I$: N, 10.91%).

**2′-Iodo-3,5,3′-trinitro-4-acetamidodiphenyl** (XVI). 2-Iodo-3-nitro-4′-acetamidodiphenyl (IX) (0.57 g.) was added during 15 minutes and with stirring to 6 c.c. of fuming $HNO_3$ of D. 1.52 which was cooled in an ice bath. After a short time (it has been found essential that the reaction mixture should be poured into ice without delay, for otherwise an amorphous product would result, from which no crystalline substance can be isolated), the reaction mixture was poured on ice and the yellow solid thus separated collected and dried. It was dissolved in 300 c.c. of boiling EtOH and the solution, after being concentrated, left overnight. The crystals thus obtained, on one more crystallization from EtOH, yielded slightly yellow needles melting at 263–264° (Found: N, 11.96. Calc. for $C_{14}H_9O_7N_4I$: 11.86%). The yield of the pure substance was 0.4 g.

**2′-Iodo-3,5,3′-trinitro-4-aminodiphenyl** (XVIII). This base was obtained by the hydrolysis of 2′-iodo-3,5,3′-trinitro-4-acetamidodiphenyl (XVI) and also of the product obtained by nitrating 2-iodo-3-nitro-4′-*p*-toluenesulphonamidodiphenyl (XVII).

A mixture of 2′-iodo-3,5,3′-trinitro-4-acetamidodiphenyl (XVI), conc. HCl and EtOH was refluxed on the water bath for a long time. The free base began to appear when

there was still a considerable quantity of the original acetyl compound left unaffected in the reaction mixture. The base was purified by crystallization from EtOH, from which it separated as yellow thin needles melting at 220–221° (Found : N, 13.12. Calc. for $C_{12}H_7O_6N_4I$ : N, 13.02%). It is readily soluble in cold benzene.

The same base was also obtained from 2-iodo-3-nitro-4′-*p*-toluenesulphonamidodiphenyl as follows. 2-Iodo-3-nitro-4′-*p*-toluenesulphonamidodiphenyl (XVII) (0.25 g.) was added in small portions to 0.5 c.c. of fuming $HNO_3$ of D. 1.51 at ordinary temperature with agitation. After some time, water was added and the precipitated product filtered off. The product, 0.29 g., after crystallization from EtOH, was dissolved in 1 c.c. of conc. $H_2SO_4$ by gentle heating, and the solution, after cooling, poured into water. The yellow precipitate thus obtained, on crystallization from EtOH, gave yellow needles which melted, either alone or when mixed with the base obtained by the hydrolysis of the acetyl compound (XVI), at 220–221°.

**2-Iodo-3,3′-dinitrodiphenyl** (XII). 2-Iodo-3,3′-dinitro-4′-aminodiphenyl (XI) (6.6 g.) was added slowly to 28 c.c. of conc. $H_2SO_4$ at ordinary temperature with constant stirring, and the stirring continued until the substance had disappeared (1.5 hours). With continued stirring and with cooling with ice water, it was treated with 19 g. of ice and then 1.4 g. of $NO_2Na$, the latter being added in small portions. After an hour, 9 g. of ice was added and stirring continued for some time. The reaction mixture was then added gradually to 280 c.c. of boiling EtOH and the solution, after being refluxed on the water bath for an hour, filtered while hot to remove a trace of the red byproduct which was deposited during the reaction. The clear filtrate was concentrated, diluted with water, and the precipitate thus obtained extracted with ether. The ether was then removed, when 6.3 g. of the crystalline product was left behind, which, on vacuum distillation, gave 6.0 g. of the distillate boiling at 239°/6 mm. Upon crystallization from EtOH, 2-iodo-3,3′-dinitrodiphenyl separated in beautiful yellow needles which melted at 130–131° (Found : N, 7.72. Calc. for $C_{12}H_7O_4N_2I$ : N, 7.57%).

**2,2′-Dinitro-6,6′-bis-(*m*-nitrophenyl)-diphenyl** (XIII). Copper powder (1.27 g.) was added during 4 minutes to 3.70 g. of well-stirred 2-iodo-3,3′-dinitrodiphenyl (XII) which was heated in an oil bath at 190–195°. After the copper powder had been added, the heating was continued for 5 to 7 minutes more, during which time the mass solidified completely. The product was extracted with a large quantity of boiling benzene, and the blue benzene extract shaken with water to remove the colour which was due probably to the presence of a copper compound. The benzene was then evaporated off, and the yellow residue (2.35 g.) crystallized from glacial acetic acid. 2,2′-Dinitro-6,6′-bis-(*m*-nitro-phenyl)-diphenyl thus obtained was yellow needles melting at 259.5–260° (Found : N, 11.70 Calc. for $C_{24}H_{14}O_8N_4$ : N, 11.52%.) The yield of the pure substance was 90.5% of the theoretical. Compound XIII was not so easily soluble in cold benzene, but once dissolved by heating, it did not crystallize from this solvent even when it was greatly concentrated. One gram of it dissolves in about 55 c.c. of boiling acetic acid.

**2,2′-Diamino-6,6′-bis-(*m*-aminophenyl)-diphenyl** (XIV). A suspension of 3.9 g. of powdered 2,2′-dinitro-6,6′-bis-(*m*-nitrophenyl)-diphenyl (XIII) in a solution of 26 g. of stannous chloride in 96 c.c. of glacial acetic acid which contains dry HCl was gently heated with occasional shaking until a clear solution resulted, dry HCl being passed in all the time. It was observed that, when the reaction mixture was heated at a higher temperature (over 70° or so), the product separated as a gelatinous mass which redissolved

when HCl was passed into the cooled mixture, showing that the solubility of the product decreases with the decrease of the HCl content in the reaction mixture. When the reaction was over, the solvent was removed by distillation in vacuum, and the residue dissolved in water, made alkaline, and the free base collected. It was purified by vacuum distillation and then by crystallization from EtOH, from which 2,2′-diamino-6,6′-bis-(*m*-aminophenyl)-diphenyl (XIV) separated as almost colourless, large crystals which melted at 169–170° (Found: N. 15.43. Calc. for $C_{24}H_{22}N_4$: N, 15.30%). The yield of the pure crystals was 2.5 g. The tetramino-compound, unlike most of the aromatic amines, is sparingly soluble in ether and benzene. It is moderately soluble in EtOH when hot and sparingly so in the cold.

Attempts to isolate the tetramine as its hydrochloride from the reaction mixture were also made, but besides some other reason which has not been made clear, as the hydrochloride is very soluble even in conc. HCl, the result was not satisfactory.

**4,5-Bis-(*m*-aminophenyl)-carbazole** (XV). A solution of 0.61 g. of 2,2′-diamino-6,6′-bis-(*m*-aminophenyl)-diphenyl (XIV) in 20 c.c. of 0.5 N HCl solution in the nitrogen atmosphere was heated in a sealed tube in an oil bath at 200–205° for 7 hours, and then left overnight in the cold. As it is difficultly soluble even in a greatly diluted HCl, the carbazole derivative (XV) separated almost completely as a gray powdery dihydrochloride, but a few c.c. of conc. HCl was added to complete its separation, the dihydrochloride was collected, washed with dil. HCl and dried in vacuum over soda lime. The product (0.69 g.) was the almost pure dihydrochloride of XV. The method of purification such as the redissolution of the dihydrochloride in water, followed by the addition of conc. HCl after being treated with animal charcoal did not remove a trace of the impurity present. The crude product was therefore dissolved in water, made alkaline, and the base thus set free extracted with ether, when a trace of the dark impurity remained undissolved. The ethereal solution thus obtained was still somewhat coloured, but on leaving overnight with the addition of anhydrous $K_2CO_3$ or KOH, it became almost colourless. The ether was then removed at as low a temperature as possible to avoid oxidation of the base which tends to darken in colour at higher temperatures. The gummy residue was subsequently dried in high vacuum. It weighed 0.57 g. All attempts to purify the base by crystallization from a solvent and from mixed solvents failed, but on rubbing this gum with a small quantity of EtOH, a small portion of it was obtained as a solid form, which melted fairly sharply at 180–182° after softening at 175°.

The free base is readily soluble in ether, benzene, MeOH, and EtOH, and insoluble in petroleum ether. The solutions had a violet fluorescence, as was also observed in solutions of its salts and the acyl derivatives prepared so far. As stated above, the base, when heated at higher temperatures, darkens in colour and passes into a substance or substances insoluble or difficultly soluble in ether and benzene.

To obtain the pure dihydrochloride, the gummy base obtained above was dissolved in the calculated quantity of dil. HCl, and the dihydrochloride precipitated by the addition of a few c.c. of conc. HCl. It was collected and dried in vacuum over soda lime at ordinary temperature. It formed nearly colourless powdery crystals containing two molecules of water of crystallization (0.1858 g. of the dihydrcchloride lost 0.0136 g. at 100° and 7 mm. pressure. Found: $H_2O$, 7.32; N, 9.42; Cl, 15.28. Calc. for $C_{24}H_{19}N_3 \cdot 2HCl \cdot 2H_2O$: $H_2O$, 7.86; N, 9.17; Cl, 15.48%). Aqueous solutions of the dihydrochloride darkened gradually when left in the air. This rather easily oxidisable nature was also

observed in solutions of the other salts of this base. Apparently, in solutions, these salts were oxidized more readily than the free base.

As already stated in the introduction, attempts to resolve this base with *d*-camphor sulphonic acid and *d*-tartaric acid have not been successful. No crystalline substance was formed when a conc. solution of this base in EtOH or in a mixture of EtOH and benzene was treated with *d*-camphor sulphonic acid. With *d*-tartaric acid, the base formed a difficultly soluble salt or salts in EtOH, but the deep brown colour of this salt rendered polarimetric examination impossible. Furthermore, as the material available for the investigation was very small, it was not possible to make a detailed examination of these salts.

**4,5-Bis-(*m*-acetamidophenyl)-carbazole.** The gummy 4,5-bis-(*m*-aminophenyl)-carbazole (XV) (0.20 g.) was dissolved in 12 c.c. of benzene and treated with an excess of acetic anhydride. The very difficultly soluble diacetyl derivative separated at once as an amorphous mass, which slowly but completely crystallized when the mixture was heated under reflux. After two hours' heating almost colourless crystals (0.21 g.) melting at 257–258° were obtained (Found: N, 9.90. Calc. for $C_{28}H_{23}O_2N_3$: N, 9.70%). There was no indication of the existence of the two forms.

**4,5-Bis-(*m*-*l*-menthoxyacetamidophenyl)-carbazole.** To a mixture of 0.32 g. of anhydrous $K_2CO_3$ and a solution of 0.20 g. of 4,5-bis-(*m*-aminophenyl)-carbazole (XV) in 20 c.c. of benzene was added 0 40 g. of *l*-menthoxyacetylchloride prepared from *l*-menthoxyacetic acid[18] by the method of Holmes and Adams[19], and the mixture refluxed on the water bath for two hours. It was then shaken with water to remove the excess of *l*-menthoxyacetic acid, and the upper layer, after being dried with $Na_2CO_3$, evaporated up. The residual syrup, on being left in a basin, partly crystallized, but as the residual mass was not easily brought into crystallization it was rubbed with 12 c.c. of ether, and the crystals thus obtained were collected and washed. The colourless powder thus obtained weighed 0.19 g. It was dissolved in 10 c.c. of boiling EtOH, and the solution evaporated until the bulk was 6 c.c. and left overnight. In this way, all the dissolved substance (0.19 g.) slowly separated in almost colourless, well-defined crystals melting at 190–191° (Found: N, 5.77. Calc. for $C_{48}H_{59}O_4N_3$: N, 5.67%). Rotation: 0.0741 g. made up to 15 c.c. with benzene gave $\alpha_D$+0.14° ($l = 2$), $[\alpha]_D$+14.2°, 0.0741 g. made up to 15 c.c. with EtOH gave $\alpha_D$−0.22° ($l = 2$), $[\alpha]_D$−22.27°, 0.0852 g. made up to 15 c.c. with acetone gave $\alpha_D$−0.28° ($l = 2$), $[\alpha]_D$−24.65°.

The ethereal mother liquor and the washings obtained above were evaporated up and the residue twice crystallized from a few c.c. each of EtOH. The crystals thus obtained (0.12 g.), though had somewhat lower melting point (188° after sintering at 185°) than the main crop, showed no depression of the melting point when they were mixed together, and possessed the same crystalline form and the same rotation as the main crop, showing that they were one and the same substance. The total yield of the *l*-menthoxyacetyl compound was therefore 0.31 g. or 73% of the theoretical.

The *l*-menthoxyacetyl compound was hydrolysed with great difficulty. Thus, in one instance, when 0.14 g. of the diacyl compound was refluxed with a mixture of 5 c.c. of conc. HCl and 7 c.c. of EtOH for 14 hours, 0.06 g. of the original substance was recovered unchanged. In addition, there was also deposited from the reaction mixture 0.04 g. of

(18) Frankland and O'sullivan, *J. Chem. Soc.*, **99** (1911), 2329.
(19) Holmes and Adams, *J. Am. Chem. Soc.*, **56** (1934), 2093.

a crystalline hydrochloride which was quite stable in the air. The free base could be precipitated by adding alkali to its solution in water. This hydrochloride had $\alpha_D = 0$ in water, and so was the rotation of the free base in benzene. From these properties it is inferred that this hydrochloride might have been a product obtained by the removal of one of the menthoxyacetyl groups and also of the menthoxyl group of the other menthoxyacetamido-group. The analysis of the nitrogen content in the hydrochloride showed that the figure found agreed fairly well with that calculated for the monoglycolyl derivative of XV containing one molecule of water of crystallization. The conclusive proof of the structure of this substance could not be obtained on account of lack of material.

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