CCXXXIII.—*Orientation Effects in the Diphenyl Series. Part II. The Constitution of Bandrowski's Dinitrobenzidine.*

By RAYMOND JAMES WOOD LE FÈVRE and EUSTACE EBENEZER TURNER.

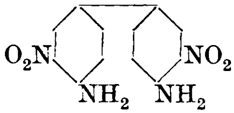
CAIN, COULTHARD, and MICKLETHWAIT (J., 1912, **101**, 2298), in discussing the constitutions of the dinitrobenzidines (compare also Cain and Micklethwait, J., 1914, **105**, 1444), assumed that unsymmetrical nitration in the diphenyl series is " extremely unlikely." Since, however, it has recently been shown (Dennett and Turner, this vol., p. 476) that the nitration of 4 : 4′-dichloro- and 4 : 4′-dibromo-diphenyl affords exclusively unsymmetrical derivatives, Cain's argument would appear to be less admissible. We have therefore re-examined the structures of the two isomeric dinitrobenzidines prepared by Strakosch (I) (*Ber.*, 1872, **5**, 236) and Bandrowski (II) (*Monatsh.*, 1887, **8**, 471). The former has been shown definitely to contain two *o*-nitroaniline residues (Brunner and Witt, *Ber.*, 1887, **20**, 1024; Brady and McHugh, J., 1923, **123**, 2047) and we accordingly directed our attention to the latter.

If the nitration of acylated benzidines could follow a course similar to that of the dihalogenodiphenyls,* 2 : 3′-*dinitrobenzidine*

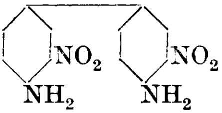
---

* The apparent meta-directing influence of phthalylamino-groups has been observed by Cain and Micklethwait (J., 1914, **105**, 1442) and by Brady, Quick, and Welling (*ibid.*, 1925, **127**, 2264).

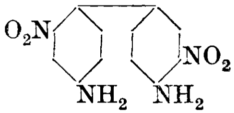
(III) would be one of the products. This hitherto undescribed compound was therefore synthesised from the diacetyl derivative of 2-nitrobenzidine. The dinitro-compound, m. p. 236°, was readily converted into the corresponding dibromodinitrodiphenyl (m. p. 148°), the latter being identical with the product of nitration of 4 : 4′-dibromodiphenyl, and it thus has the 2 : 3′-structure.



(I.)



(II.)



(III.)

It seemed possible that Bandrowski's (3 : 3′-)dinitrobenzidine, m. p. 233°, might be identical with our 2 : 3′-compound. It was therefore prepared by the method described by previous authors (Bandrowski, *loc. cit.*; Cain, Coulthard, and Micklethwait, *loc. cit.*), and was found to melt at 230—233°. Its melting point was raised by admixture with 2 : 3′-dinitrobenzidine, but it was converted through its bisdiazo-compound into a dibromodinitrodiphenyl melting, not at 148°, but at 137—138°, as described by Cain, Coulthard, and Micklethwait (*loc. cit.*). This result seemed to show that the melting points of mixtures of Bandrowski's dinitrobenzidine and 2 : 3′-dinitrobenzidine gave misleading evidence, since these compounds appeared to give rise to two distinct dibromodinitro-derivatives. When, however, Bandrowski's dinitrobenzidine was purified *via* the hydrochloride, and then twice crystallised from phenol, it melted sharply at 236°, produced no depression of the m. p. of the 2 : 3′-compound, and gave a dibromodinitrodiphenyl melting at 148°, which produced no depression of the m. p. of 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl.

These observations apparently proved that Bandrowski's dinitrobenzidine and 2 : 3′-dinitrobenzidine are one and the same substance, and the identity was established beyond doubt by means of two more pairs of compounds, derived from each, *viz.*, the diacetyl derivatives and the two bromopiperidino-compounds obtained as described previously (Dennett and Turner, *loc. cit.*), which also were identical. It might be urged that Bandrowski's diamine is a mixture of 2 : 3′- and 3 : 3′-dinitrobenzidines. Against this view, however, are the following facts : (1) Our " Bandrowski " dinitrobenzidine, purified by the methods previously used, melted at 230—233°. (2) Although we had little difficulty in repeating Cain's observations on this dinitrobenzidine, the dibromodinitrodiphenyl, etc., we found that the m. p.'s of all the compounds in this series were raised by admixture with pure specimens of 2 : 3′-compounds.

It is certain, therefore, that we were working with the substance hitherto called " 3 : 3′-dinitrobenzidine."

For purposes of comparison, we also prepared Strakosch's dinitrobenzidine. When the amino-groups in this compound were replaced by bromine, 4 : 4′-dibromo-3 : 5′-dinitrodiphenyl was obtained, having the properties described by Cain, Coulthard, and Micklethwait (*loc. cit.*) and being converted by hot piperidine into 4 : 4′-*dipiperidino*-3 : 5′-*dinitrodiphenyl.* The formation of the latter confirms the work of the above authors on the structure of Strakosch's dinitrobenzidine, and clearly differentiates the 3 : 5′- from the 2 : 3′-series, in which the dibromo-compound reacts with only one molecule of piperidine.*

Cain's dibromodinitrodiphenyl (melting, according to our observation, at 137—138° to give a turbid liquid) gave a bromopiperidino-compound which became pure only after several recrystallisations, whereas the piperidino-derivative obtained from the pure 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl was pure after one crystallisation.

It is important now to review the evidence on which 3 : 3′–3 : 5′ isomerism has hitherto rested. Cain, Coulthard, and Micklethwait accepted Brunner and Witt's proof of the constitution of Strakosch's dinitrobenzidine, and assigned a symmetrical structure to Bandrowski's diamine for two reasons : (1) That when reduced it gave a tetra-amine which, with benzil, yielded a product apparently identical with the diquinoxaline similarly derived from Strakosch's dinitrobenzidine. (2) That unsymmetrical nitration was unlikely (an assumption originally made also by Dennett and Turner in connexion with the nitration of dihalogenodiphenyls).

The preparation of a whole series of compounds of the 3 : 3′- and 3 : 5′-types appeared to establish the isomerism on a sure footing, although the non-interconvertibility of corresponding pairs has always given rise to a sense of doubt (compare Brady and McHugh, *loc. cit.*). When, however, Cain and Micklethwait (*loc. cit.*) described the interconversion of a pair of *o*-dinitrotolidines, one of the main objections to the conception was removed. Ferriss and Turner (J., 1920, **117**, 1140) showed that Cain's evidence for the Kaufler structure of benzidine (J., 1914, **105**, 1437) was not altogether satisfactory, and the fact that Brady and McHugh (*loc.*

---

* 4 : 4′-Dichloro- and 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl react readily with alcoholic ammonia, aniline, methylaniline, potassium phenoxide, etc., to give well-defined, crystalline substances. In all cases these compounds (in contradistinction to those obtained from the definitely diortho-3 : 5′-dinitro-4 : 4′-dihalogenodiphenyls) are produced by the reaction of only one halogen atom, and thus the results obtained with piperidine are confirmed. Further details will be published in a later paper.

cit.) considered it worth while to prove again the constitution of one of the dinitrobenzidines shows that other workers in this field have entertained doubts as to the structure of one or other of the isomerides. We cannot now explain Cain's isomeric dinitrotolidines, but hope to investigate the matter in the course of these studies of the laws of substitution in the diphenyl series. It will, however, be generally agreed that the evidence on which rests the conversion of *o*-dinitrotolidine II into *o*-dinitrotolidine I is far from satisfactory.

As far as the benzidine series is concerned, if there is isomerism of the 3 : 5′–3 : 3′ type, the second isomeride still remains to be discovered; for the present, the 3 : 5′-compounds should be called 3 : 3′- and the 3 : 3′-, 2 : 3′-.*

EXPERIMENTAL.

Preparation of 2 : 3′-*Dinitrobenzidine.*—(a) 2-*Nitrodiacetylbenzidine.* Benzidine (72 g.) was dissolved in 830 c.c. of 100% sulphuric acid and nitrated as described by Täuber (*Ber.*, 1894, **27**, 2628). It is unnecessary to prepare benzidine sulphate first as recommended by this author.

The *diacetyl* compound was prepared by gradually adding 26 c.c. of acetic anhydride to 30 g. of 2-nitrobenzidine suspended in about 50 c.c. of boiling glacial acetic acid and heating the mixture under reflux for 1·5 hours. The product was treated with water, filtered off, and twice extracted with boiling methylated spirit, the crude diacetyl compound (33·5 g.) being thus obtained as a light yellow powder, m. p. above 300°.

(b) 2 : 3′-*Dinitrodiacetylbenzidine.* 2-Nitrodiacetylbenzidine (25 g.) was slowly added with stirring to 175 c.c. of nitric acid (*d* 1·5) kept at 0° (nitration at the ordinary temperature caused marked hydrolysis). After 15 minutes, the mixture was poured on to crushed ice and the solid was filtered off and extracted repeatedly with boiling methylated spirit. The product was a yellow powder which, after being twice crystallised from much glacial acetic acid, melted at 220—222° (Found : N, 15·7. $C_{16}H_{14}O_6N_4$ requires N, 15·6%).

(c) *Hydrolysis of* 2 : 3′-*Dinitrodiacetylbenzidine.* A solution of the acetyl compound (36 g.) in 190 c.c. of concentrated sulphuric acid was heated at 140° for 20 minutes, cooled, and poured on to ice. The dark red precipitate was well washed with water and dried at 120°; it then melted at about 206°. It separated from hot rectified spirit as a gelatinous mass (this behaviour has also been observed with some specimens of Bandrowski's diamine). A suspension in hot rectified spirit was saturated with hydrogen

---

* In the present paper, in order to avoid confusion, all compounds derived from Strakosch's dinitrobenzidine are called 3 : 5′-derivatives.

chloride and the yellow hydrochloride obtained on cooling was decomposed with ammonium hydroxide; the bright red product, m. p. about 230°, was crystallised from phenol, giving deep red needles of constant m. p. 236° (Found : N, 20·5. $C_{12}H_{10}O_4N_4$ requires N, 20·4%).

In one experiment, hydrolysis of the dinitrodiacetyl compound with very concentrated alcoholic potassium hydroxide produced a brown powder quite different in appearance from the above compound, m. p. 236°, and we suggest that in this case hydrolysis was accompanied by loss of ammonia.

Conversion of 2 : 3′-*Dinitrobenzidine into* 4 : 4′-*Dibromo*-2 : 3′-*dinitrodiphenyl*.—The dinitrobenzidine (5 g.) was dissolved in 40 c.c. of concentrated sulphuric acid, and water added until incipient precipitation occurred. The solution, cooled to 5°, was bisdiazotised with solid sodium nitrite and thereafter diluted, filtered, and treated with a solution of 2 c.c. of bromine in 18 c.c. of 48% hydrobromic acid. The precipitated perbromide was collected, washed with water, and boiled with a little glacial acetic acid until bromine evolution ceased. On dilution with water, a yellow substance, m. p. about 135°, was obtained; this, after crystallisation once from fuming nitric acid and once from benzene, melted at 148° and produced no depression of the m. p. of pure 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl obtained by nitrating dibromodiphenyl. The identity of the two compounds was further established through the bromopiperidino-compounds (m. p.'s and mixed m. p.'s).

Bandrowski's Dinitrobenzidine.—This was prepared as exactly as possible by the method used by previous workers. The crude dinitrobenzidine, after being crystallised from rectified spirit, melted at about 220°. (Repeated crystallisation from this solvent afforded a product, m. p. 230—233°, evidently corresponding to Cain's 3 : 3′-compound.) It was converted, by the method described above, into the hydrochloride; the base recovered from this, after being crystallised three times from phenol, formed bright red needles, m. p. 236° (Found : N, 20·1. Calc. : N, 20·4%). It produced no depression of the m. p. of 2 : 3′-dinitrobenzidine. The product obtained by crystallising a mixture of the two bases from phenol melted at 236°, as did also the ground-up product of fusion of the two bases.

Although the two dinitrobenzidines are thus shown to be chemically identical, they have not been obtained of the same colour, the Bandrowski preparation having a brighter shade. The amount of the impurity present is revealed neither by the m. p. nor by analysis and is evidently exceedingly small.

Bandrowski's dinitrobenzidine was bisdiazotised and converted into the corresponding dibromodinitrodiphenyl by the method described above : (*a*) From the dinitrobenzidine melting at 230—233°, the dibromo-compound obtained melted at 137—138° to a turbid liquid. A mixture of this product with pure dibromodinitrodiphenyl (m. p. 148°) melted at 145°. After being crystallised once from fuming nitric acid and then several times from glacial acetic acid, it still melted at 137—138°, and when condensed with piperidine gave a bromopiperidinodinitrodiphenyl which, after one crystallisation from rectified spirit, melted at 130°; a mixture with pure 4-bromo-4′-piperidino-2 : 3′-dinitrodiphenyl melted at 134°. (*b*) The crude dibromodinitrodiphenyl obtained from the dinitrobenzidine of m. p. 236° melted at 137—138°. After being once crystallised from fuming nitric acid, it had m. p. 148° and did not depress the m. p. of pure 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl. The derived bromopiperidino-compound, after one crystallisation from alcohol, melted at 137°, either alone or when mixed with pure 4-bromo-4′-piperidino-2 : 3′-dinitrodiphenyl.

Bandrowski's dinitrobenzidine, when acetylated, gave the diacetyl derivative of m. p. 220—222° (compare Cain, Coulthard, and Micklethwait, *loc. cit.*). This m. p. was not affected by admixture with 2 : 3′-dinitrodiacetylbenzidine.

4 : 4′-*Dipiperidino*-3 : 5′-*dinitrodiphenyl*.—4 : 4′-Dibromo-3 : 5′-dinitrodiphenyl was prepared by the perbromide method from 3 : 5′-dinitrobenzidine, obtained by the usual method, and had the properties described by Cain. It was heated at 100—110° for 1 minute with piperidine, the resulting solution carefully diluted with water, the solid collected, and crystallised from a large bulk of rectified spirit. Orange plates, m. p. 159—160°, were obtained (Found : N, 13·8. $C_{22}H_{26}O_4N_4$ requires N, 13·7%).

A part of the expense of this investigation was met by a grant from the Chemical Society, for which the authors express their thanks.

East London College,
University of London.

[*Received, March 4th*, 1926.]