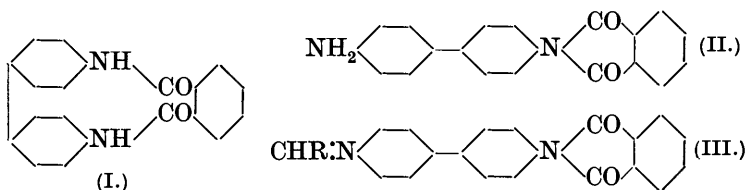


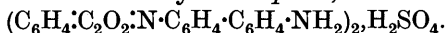
CCCXXVI.—*The Space Formula of Diphenyl.*

By RAYMOND JAMES WOOD LE FÈVRE and EUSTACE EBENEZER TURNER.

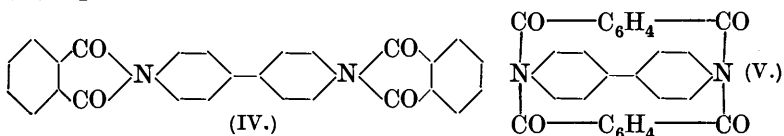
In a recent communication (Le Fèvre and Turner, this vol., p. 2042), it was recorded that, when monophthalylbenzidine is nitrated, the main product is the 2- and not, as stated by Koller (*Ber.*, 1904, **37**, 2882), the 3-nitro-derivative. It occurred to us at the time that, although the formula (I) hitherto assigned to monophthalylbenzidine does not enable one to predict, with any degree of certainty, the orientation of the mononitro-compound, formula (II) would do so adequately, in view of the well-known meta-directing influence of the amino-sulphate group. In accordance with this formula (II) monophthalylbenzidine dissolves in boiling benzaldehyde and salicylaldehyde, the solutions on cooling depositing *benzylidene-* and *salicylidene-monophthalylbenzidine*, respectively (III). Moreover,



although monophthalylbenzidine is apparently reprecipitated unchanged when its solution in concentrated sulphuric acid is diluted, the product is actually the *sulphate*,



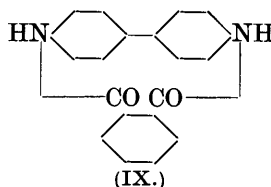
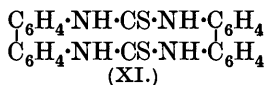
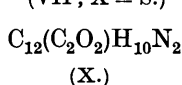
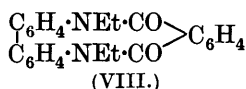
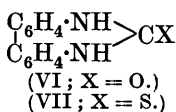
Finally, monophthalylbenzidine may be diazotised in concentrated sulphuric acid solution to give a sparingly-soluble solid *diazonium sulphate*, which is very stable and couples with alkaline  $\beta$ -naphthol to form a red *azo-dye*. Formula (II) also readily explains the conversion of mono- into di-phthalylbenzidine (IV). Shimomura (*Mem. Coll. Sci. Kyōtō*, 1925, **8**, 19), accepting Kaufler's formula for diphenyl and a symmetrical structure for monophthalylbenzidine (I), formulated the change, by the action of a further molecule of phthalic anhydride, as being the conversion of (I) into (V). Formula (II) explains this conversion in a normal manner.



Kaufler (*Annalen*, 1907, **351**, 151; *Ber.*, 1907, **40**, 3250) advanced his formula for diphenyl compounds in order to account for the

existence of a number of derivatives of benzidine "in which the amino-groups were linked either through one or two neighbouring carbon atoms." \*

The actual examples he cited were carbonylbenzidine (Michler and Zimmermann, *Ber.*, 1881, **14**, 2178), thiocarbonylbenzidine (Borodine, *Jahresb.*, 1860, 356; Strakosch, *Ber.*, 1872, **5**, 240), diethylphthalylbenzidine (Schiff and Vanni, *Annalen*, 1890, **258**, 363), monophthalylbenzidine (Koller, *loc. cit.*) and oxalylbenzidine, † to which substances the original discoverers had already assigned formulæ (VI), (VII), (VIII), (IX), and (X), respectively.



Kaufler made the assumption that the two benzene nuclei in diphenyl are inclined towards each other ("gegen einander geneigt"), and not that they are parallel, as is usually stated, although in his formulæ the 1:1'- and 4:4'-positions are represented as being equidistant. His formulæ for the above compounds merely had the benzene ring written instead of the grouping  $\text{C}_6\text{H}_4$ . Strakosch recognised the possibility that thiocarbonylbenzidine might be (XI), but owing to the insolubility of this compound he was unable to determine its molecular weight. The new experimental evidence published by Kaufler (as far as diphenyl derivatives are concerned), consisted of determinations of the molecular weights of monophthalylbenzidine, monophthalyl-dianisidine and thiocarbonyl-dianisidine, the last two compounds only being prepared by him. He therefore doubted, not the mode of linking of the amino-groups, but what he termed the "unimolecular" nature of the compounds. For, finding that the molecules of the above three substances contained only one benzidine residue, he concluded that "for the other derivatives named, an analogous constitution was made very probable."

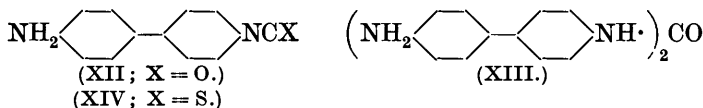
The discovery that monophthalylbenzidine, the most fully investigated Kaufler compound, has a constitution other than that

\* Kaufler also considered that naphthalene and other polynuclear molecules had folded configurations. It is hoped to deal with these in a subsequent communication.

† For this substance Kaufler gives two references: Borodine, *Jahresb.*, *loc. cit.*, and Strakosch, *loc. cit.* The latter paper contains no mention of oxalylbenzidine; the *Jahresb.* contains only a brief abstract. The correct reference is *Z. Chem. Pharm.*, 1860, 641.

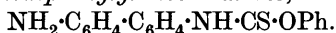
hitherto assumed, made it imperative to examine a number of other compounds of a supposedly similar structure. Carbonyl- and thiocarbonyl-benzidine were therefore prepared by the methods described in the literature.

The former was found to form a *sulphate*, and to condense with aromatic aldehydes, and therefore to contain a free amino-group. In view of the fact that the interaction of carbonyl chloride and amines usually leads to the production either of carbamyl chlorides or of carbamides, it appears probable that carbonylbenzidine is (XIII) rather than (XII), since carbimides are usually only produced by the action of carbonyl chloride on amine hydrochlorides at comparatively high temperatures. This view, which cannot be



completely substantiated, owing to the insolubility of carbonylbenzidine in cryoscopic or ebullioscopic solvents, is supported by the observation that carbonylbenzidine is apparently unaffected by boiling aniline. In any case, formula (VI) is excluded.

Thiocarbonylbenzidine has been found definitely to have formula (XIV).\* As an amine, it condenses with aldehydes, and, as a thiocarbimide, it is converted by aniline into 4'-aminodiphenylphenylthiocarbamide,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CS} \cdot \text{NHPh}$ , and by phenol into phenyl 4'-aminodiphenylthiocarbamate,

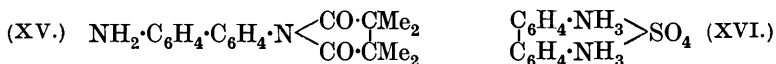


Further, although thiocarbonylbenzidine is stated in the literature (*loc. cit.*) to be precipitated unchanged when its solution in concentrated sulphuric acid is diluted, the precipitate actually consists of the *sulphate*,  $(\text{SCN} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$ .

It seems probable that the condensation products discussed by Kaufler are the substances that are isolated mainly because of their extreme insolubility. An interesting example of the formation of a mono-derivative under conditions where a di-derivative was expected is given, without reference to the present problem, by von Auwers (*Annalen*, 1896, **292**, 177) : benzidine was heated in benzene solution with two molecules of tetramethylsuccinic anhydride; compound (XV) then separated almost quantitatively. In this

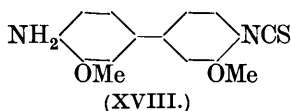
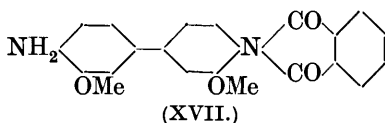
\* Reuland (*Ber.*, 1889, **22**, 3014) found that diphenylene (2 : 4'-diaminodiphenyl) was converted by alcoholic carbon disulphide into a compound which he called thiocarbonyldiphenylene, and wrote as (VII) with complete benzene rings. There is little doubt that the substance is actually an amino-diphenylthiocarbimide, analogous to (XIV).

particular case the product formed a soluble hydrochloride and was thus recognised as a base.



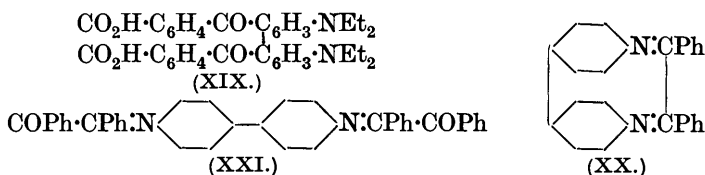
Whereas benzidine dihydrochloride is soluble in water, the monohydrochloride is sparingly soluble (Schmidt and Schultz, *Annalen*, 1881, 207, 330), and therefore we suggest that benzidine sulphate has the formula  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_3 \cdot \text{HSO}_4$  rather than (XVI).

There seems no reason to doubt that Kaufler's monophthalyl- and thiocarbonyl-dianisidine are respectively (XVII) and (XVIII); this



author's molecular-weight determinations support these structures and the structure (II) assigned to monophthalylbenzidine as well as they do the formulæ he suggested. Of the other Kaufler compounds mentioned above, there remain to be considered oxalylbenzidine and diethylphthalylbenzidine. The former has been found (qualitatively) to condense with benzaldehyde and thus to contain a free amino-group or groups, whilst the latter, although apparently a condensation product, with phthalic anhydride, of a compound containing no primary amino-group—therefore furnishing the most convincing evidence adduced by Kaufler in favour of his formula—was not a chemical individual. Schiff and Vanni (*loc. cit.*), who first described it, heated phthalic anhydride with “diethylbenzidine” and assigned formula (VIII) to the product. At the same time, tetraethylbenzidine was stated to give the compound (XIX). P. Hofmann (*Annalen*, 1860, 115, 365) first ethylated benzidine, obtaining a “diethylbenzidine” melting at  $65^\circ$ . This was presumably the material used by Schiff and Vanni, since they say nothing about the preparation of their specimen. It was evidently regarded by Beilstein (compare “Handbuch,” 3rd ed., Vol. IV, 967, 963) as the symmetrical diethyl derivative. Bamberger and Tichwinsky (*Ber.*, 1902, 35, 4179) found that symmetrical diethylbenzidine melted at  $115.5^\circ$  and isolated it from the product obtained by Hofmann's process. Later, Tichwinsky (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 675) showed that this product was a mixture of 15% of tetra- and 85% of *s*-di-ethylbenzidine. It is therefore evident that no conclusions whatever can be drawn from Schiff and Vanni's results.

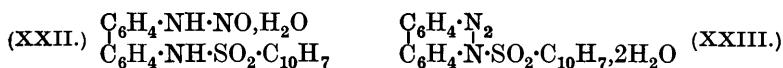
Cain (J., 1914, **105**, 1437) described a condensation product of benzidine and benzil, assumed to have formula (XX), which he was unable to free from methyl or ethyl alcohol of crystallisation. Ferriss and Turner (J., 1920, **117**, 1140) showed that the condensation product could readily be obtained free from solvent of crystallisation, but failed to realise what is now evident, that the condensation product is *s*-dibenzoylbenzylidenebenzidine (XXI). It was observed (*loc. cit.*) that more than a 70% yield of the condensation product could not be obtained. Since the maximum yield of dibenzoylbenzylidenebenzidine could not be more than 74%, calculated on the old basis, this result is entirely satisfactory and the experiment becomes evidence against and not for the Kaufler formula.



Adams, Bullock, and Wilson (*J. Amer. Chem. Soc.*, 1923, **45**, 521) condensed *iso*- and *tere*-phthalaldehydes with benzidine and obtained amorphous compounds which were regarded as of the "unimolecular" type, without any supporting experimental evidence being put forward. We have not examined these substances, as they do not affect the position.

Similarly, the diazoidimides obtained by Vaubel and Scheuer (*Z. Farb. Tech. Ind.*, 1906, **5**, 61) were, from the description given, ill-defined compounds of unknown molecular complexity, and it is difficult to see on what lines they could be examined from the point of view of the present paper.

Morgan and Micklethwait (J., 1908, **93**, 614) found that whilst naphthalene- $\beta$ -sulphonylbenzidine was readily convertible into a substance which they formulated as (XXII) or (XXIII), *as*-naphthalene- $\beta$ -sulphonylethylbenzidine,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NEt}\cdot\text{SO}_2\cdot\text{C}_{10}\text{H}_7$ , could not be converted into a similar substance, a result which



supports formula (XXIII) rather than (XXII). The presence of water of crystallisation, however, makes a decision uncertain, as the authors pointed out (compare also Kenner and Mathews, J., 1914, **105**, 2473), and the meaning of this work as regards the Kaufler

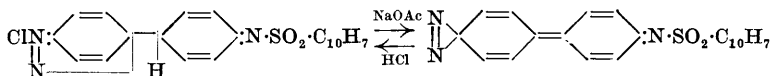
formula is not clear. The compound,\* like that from benzenesulphonylbenzidine (Morgan and Hird, J., 1905, **91**, 1505), is a crystalline substance differing from most of Kaufler's compounds in appearance.

The most important phenomena in connexion with which the Kaufler formula has been discussed are, first, the isomerism of the dinitrobenzidines (Cain, Coulthard, and Micklethwait, J., 1912, **101**, 2998, etc.) and of the 6:6'-dinitrodiphenic acids (Kenner and Stubbings, J., 1921, **119**, 593), and, secondly, the optical activity of the substituted diphenic acids (Christie and Kenner, J., 1922, **121**, 614, etc.). The former phenomena have been shown not to exist (Le Fèvre and Turner, this vol., p. 1759; Christie, Holderness, and Kenner, *ibid.*, p. 671), whilst the explanation of the second, well-established phenomenon has still to be discovered.

Kaufler (*loc. cit.*) considered that his formula explained not only the reactions of benzidine already discussed, but also, on the assumption of steric hindrance between groups in the 4- and 4'-positions, (1) the difficulty of diazotising the second amino-group in benzidine, (2) the slowness of coupling of the second diazo-group in diphenyl-bisdiazonium salts, and (3) the benzidine change. As has been pointed out by Vignon (*Compt. rend.*, 1906, **142**, 159) and by Cain ("Chemistry and Technology of Diazo Compounds," 1920, p. 27), difficulty (1) does not exist. The second point would appear to be sufficiently explained by the insolubility of the intermediate mono-azo-dye produced during the coupling of bisdiazotised benzidine (compare Georgevics and Grandmougin, "Text-book of Dye Chemistry," trans. by Mason, 1920, p. 129, for many technical applications).

As regards the benzidine change, we are unable to see any advantage in Kaufler's formulation, which, incidentally, does not explain the formation of diphenylene. We are also unable to understand why Raiford and Clark (*J. Amer. Chem. Soc.*, 1926, **48**, 483) should, on the basis of the Kaufler formula, have expected 4-amino-4'-hydroxydiphenyl to behave, as regards migrations of its acyl derivatives, like *o*-aminophenol.

\* Professor Morgan informs me that he now regards the scheme



as explaining more satisfactorily the formation and properties of the naphthalenesulphonyl derivative. This explains why a similar compound is not obtained from the ethyl derivative, and would appear to remove the last remaining evidence in favour of Kaufler's formula.—E. E. T.

Kuhn and Zumstein (*Ber.*, 1926, **59**, 488) determined the dissociation constant of benzidine and compared it with the corresponding values for the three phenylenediamines; their conclusion is that the amino-groups in benzidine are farther apart than Kaufler's formula suggests.

The views expressed by one of us in 1915 (*J.*, **107**, 1495) would thus appear to be fully justified, since the inconsistencies then referred to have now been explained. We do not regard the present work as proving anything beyond the fact that there is no satisfactory evidence for the existence of compounds of the type to be expected if Kaufler's formula for diphenyl were the correct one. At the same time, since no authentic cases of "cis-trans" isomerism are known to occur among the diphenic acids capable of resolution, it would probably be justifiable to regard our results as indicating that the diphenyl molecule has not a folded structure. It seems very unlikely that the cause of stereoisomerism in the diphenyl series is a mere matter of the angle between the two benzene nuclei.

#### EXPERIMENTAL.

*Monophthalylbenzidine* (II) prepared by Koller's method (*loc. cit.*) was repeatedly extracted with alcohol and crystallised from phenol (Found: N, 9.0. Calc.: N, 8.9%). The latter solvent is readily removed from the solid, whereas nitrobenzene, recommended by Koller, is tenaciously retained.

Monophthalylbenzidine dissolved in concentrated sulphuric acid with a slight evolution of heat. The brown solution was poured into a large bulk of water, the bluish-grey *sulphate* precipitated was filtered off, thoroughly extracted with boiling water, and dried at 100° [Found: N, 7.8. (C<sub>20</sub>H<sub>14</sub>O<sub>2</sub>N<sub>2</sub>)<sub>2</sub>.H<sub>2</sub>SO<sub>4</sub> requires N, 7.7%].

*Benzylidene- and Salicylidene-monophthalylbenzidine* (III).—Monophthalylbenzidine (1 g.) was heated with 25 c.c. of the appropriate aldehyde, the condensed water being removed in the usual manner from time to time. When the whole of the monophthalylbenzidine had dissolved, the solution was filtered; on cooling, it set to a solid magma. The filtered crystals were washed first with the parent aldehyde, then with alcohol, and dried at 100°.

*Benzylidenemonophthalylbenzidine* forms yellow needles, m. p. above 300° (Found: N, 7.3. C<sub>27</sub>H<sub>18</sub>O<sub>2</sub>N<sub>2</sub> requires N, 7.0%). *Salicylidenemonophthalylbenzidine*, microscopic platelets, melts above 300° (Found: N, 6.6. C<sub>27</sub>H<sub>18</sub>O<sub>3</sub>N<sub>2</sub> requires N, 6.7%). It is hydrolysed by boiling alkali or acid.

*Diazotisation of Monophthalylbenzidine*.—A solution of 5 g. of monophthalylbenzidine in 50 c.c. of concentrated sulphuric acid was treated gradually at -10° to -5° with the calculated quantity of

solid sodium nitrite. Dilution, by addition of ice, gave a yellow paste of the *diazonium sulphate*, which was insoluble in water. When it was added to sodium  $\beta$ -naphthoxide solution, a deep red *azo-dye* was formed, and coated the sulphate. The diazonium sulphate is recovered unchanged when shaken with a solution of bromine in hydrobromic acid. As Armstrong has pointed out (P., 1899, **15**, 176), diazosulphanilic acid also is indifferent to the action of the same reagent.

*Carbonylbenzidine* (XIII) was prepared as described by Michler and Zimmermann (*loc. cit.*) and purified by sublimation in a current of carbon dioxide (Found: N, 13.6. Calc.: N, 13.3%). Addition of its solution in concentrated sulphuric acid to an excess of water led to the precipitation of the whitish-yellow *sulphate* (Found: N, 10.9.  $C_{25}H_{22}ON_4 \cdot H_2SO_4$  requires N, 11.4%).

The *salicylidene* and *benzylidene* derivatives were sparingly soluble in the respective aldehydes, from which they separated as yellow powders. Salicylidene derivative: Found, N, 9.0.  $C_{39}H_{30}O_3N_4$  requires N, 9.3%. Benzylidene derivative: Found, N, 9.6.  $C_{39}H_{30}ON_4$  requires N, 9.8%.

*Thiocarbonylbenzidine* (XIV), prepared as described by Strakosch (*loc. cit.*), was purified by repeated extraction with boiling methylated spirit (Found: N, 13.0. Calc.: N, 12.4%). When its solution in sulphuric acid was added to an excess of water, the *sulphate* was precipitated as a grey powder, which, after being well washed, was dried at 100° [Found: N, 9.4.  $(C_{13}H_{10}N_2S)_2 \cdot H_2SO_4$  requires N, 10.1%]. When boiled with the appropriate aldehyde, thiocarbonylbenzidine was converted into the *benzylidene* derivative (Found: N, 8.3.  $C_{20}H_{14}N_2S$  requires N, 8.9%), and the *salicylidene* derivative (Found: N, 8.4.  $C_{20}H_{14}ON_2S$  requires N, 8.5%).

*Acetylthiocarbonylbenzidine*.—The suspension obtained by heating thiocarbonylbenzidine under reflux for one day with an excess of acetic anhydride and a trace of sulphuric acid was poured into water; after the acetic anhydride had decomposed, the cream-coloured solid was boiled with alcohol and dried at 100° (Found: N, 11.1.  $C_{15}H_{12}ON_2S$  requires N, 10.5%).

*Diazotisation of Thiocarbonylbenzidine*.—A solution of thiocarbonylbenzidine in concentrated sulphuric acid (10 parts) was treated at 0° with water until the sulphate began to be precipitated. It was then diazotised with solid sodium nitrite. On dilution, a sparingly soluble, bright orange *diazo*-compound was precipitated, which coupled with alkaline  $\beta$ -naphthol solution to give a red *azo-dye*.

*Phenyl 4'-Aminodiphenylthiocarbamate*.—Thiocarbonylbenzidine (2 g.) was boiled under reflux with 40 g. of phenol for 8 hours. It gradually became white and assumed a crystalline appearance.



The suspension was diluted with alcohol, filtered, and the product washed repeatedly with water and hot methylated spirit. The *thiocarbamate* was thus obtained as a white powder, m. p. above  $300^{\circ}$  (Found : N, 9.0.  $C_{19}H_{16}ON_2S$  requires N, 8.7%).

*4'-Aminodiphenylphenylthiocarbamide*.—Thiocarbonylbenzidine was boiled under reflux with an excess of aniline for 1 hour. The solution was poured into water, and dilute hydrochloric acid added until the grey precipitate was quite hard. It crystallised from much glacial acetic acid as a grey, microcrystalline powder (Found : N, 12.9.  $C_{19}H_{17}N_3S$  requires N, 13.2%).

*Action of Benzaldehyde on Oxalylbenzidine*.—Oxalylbenzidine, prepared by Borodine's method (*loc. cit.*), was heated under reflux for a short time with benzaldehyde. Water was formed.

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