

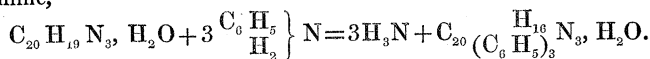
without losing its solubility or passing into the pectous state, but at a temperature near redness it undergoes a molecular change, losing at the same time 2·42 per cent. of water. When water is added to unchanged tungstic acid, it becomes pasty and adhesive like gum; and it forms a liquid with about one-fourth its weight of water, which is so dense as to float glass. The solution effervesces with carbonate of soda, and tungstic acid is evidently associated with silicic and molybdic acids. The taste of tungstic acid dissolved in water is not metallic or acid, but rather bitter and astringent. Solutions of tungstic acid containing 5, 20, 50, 66·5, and 79·8 per cent. of dry acid, possess the following densities at 19°, 1·0475, 1·2168, 1·8001, 2·396, and 3·243. Evaporated *in vacuo* liquid tungstic acid is colourless, but becomes green in air from the deoxidating action of organic matter. Liquid silicic acid is protected from pectizing when mixed with tungstic acid, a circumstance probably connected with the formation of the double compounds of these acids which M. Marignac has lately described.

*Molybdic Acid* has hitherto been known (like tungstic acid) only in the insoluble form. Crystallized molybdate of soda dissolved in water is decomposed by the gradual addition of hydrochloric acid in excess without any immediate precipitation. The acid liquid thrown upon a dialyzer may gelatinize after a few hours, but again liquefies spontaneously, when the salts diffuse away. After a diffusion of three days, about 60 per cent. of the molybdic acid remains behind in a pure condition. The solution of pure molybdic acid is yellow, astringent to the taste, acid to test-paper, and possesses much stability. The acid may be dried at 100°, and then heated to 200° without losing its solubility. Soluble molybdic acid has the same gummy aspect as soluble tungstic acid, and deliquesces slightly when exposed to damp air. Both acids lose their colloidalty when digested with soda for a short time, and give a variety of crystallizable salts.

XV. "Researches on the Colouring-matters derived from Coal-tar. —III. Diphenylamine." By A. W. HOFMANN, LL.D., F.R.S.,  
Received June 16, 1864.

In the course of last year\* I published an account of some experiments upon the composition of the blue colouring-matter discovered by MM. Girard and De Laire when studying the action of aniline upon rosaniline.

These experiments had established a simple relation between aniline-red and aniline-blue, the latter exhibiting the composition of triphenylated rosaniline,

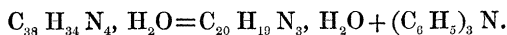


The composition of aniline-blue has since been also investigated by M. Schiff†, who, in a paper published shortly after my first communication

\* Proceedings of the Royal Society, vol. xii. p. 578; and vol. xiii. p. 9.

† Comptes Rendus, lvi. 1234.

upon this subject, attributes to this compound a formula differing from the expression at which I had arrived. According to M. Schiff, aniline-blue is not a *triamine*, as I had found, but a *tetramine*, which may be looked upon as a combination of rosaniline with triphenylamine,



This formula is less simple than the one I had given; it attributes to aniline-blue a constitution not supported by analogy, and involves the necessity of assuming, for the formation of this substance, a reaction which ceases to be a simple process of substitution.

M. Schiff's formula is given as the result of an unfinished inquiry, and the author himself appears to have but limited confidence in its correctness. Nevertheless, the publication of his Note imposed upon me the duty of confirming by new experiments the result of my former researches upon this subject.

The material used in these new experiments was likewise furnished to me by Mr. Nicholson; it had been taken from the product of an operation perfectly different from the one which had supplied the first specimen. In the following synopsis the experimental numbers of the former analyses are marked (*a*), in contradistinction to those (*b*) recently performed.

#### Free Base.

$\text{C}_{38} \text{H}_{36} \text{N}_4 \text{O}$ (Schiff).			$\text{C}_{33} \text{H}_{33} \text{N}_3 \text{O}$ (Hofmann).		
$\text{C}_{38}$	456	80.85	$\text{C}_{38}$	456	83.36
$\text{H}_{36}$	36	6.38	$\text{H}_{33}$	33	6.03
$\text{N}_4$	56	9.93	$\text{N}_3$	42	7.69
$\text{O}$	16	2.84	$\text{O}$	16	2.92
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	564	100.00		547	100.00

#### Analyses (Hofmann).

	<i>a.</i>		<i>b.</i>	
Carbon	83.81	83.89	83.13	—
Hydrogen	6.20	6.18	6.04	—
Nitrogen	—	—	—	8.16

#### Chloride.

$\text{C}_{38} \text{H}_{35} \text{N}_4 \text{Cl}$ (Schiff).			$\text{C}_{38} \text{H}_{32} \text{N}_3 \text{Cl}$ (Hofmann).		
$\text{C}_{38}$	456	78.28	$\text{C}_{38}$	456	80.64
$\text{H}_{35}$	35	6.01	$\text{H}_{32}$	32	5.66
$\text{N}_4$	56	9.61	$\text{N}_3$	42	7.43
$\text{Cl}$	35.5	6.10	$\text{Cl}$	35.5	6.27
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	582.5	100.00		565.5	100.00

## Analyses (Hofmann).

	a.				b.		
Carbon	80.58	80.57	—	—	80.67	—	—
Hydrogen	5.70	5.71	—	—	5.67	—	—
Nitrogen	—	—	—	—	—	7.76	—
Chlorine	—	—	6.10	6.73	—	—	6.12

*Bromide.*

$C_{38}H_{35}N_4Br$ (Schiff).				$C_{38}H_{32}N_3Br$ (Hofmann).			
$C_{38}$	456	72.73		$C_{38}$	456	74.75	
$H_{35}$	35	5.58		$H_{32}$	32	5.25	
$N_4$	56	8.93		$N_3$	42	6.88	
Br	80	12.76		Br	80	13.12	
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	627	100.00			610	100.00	

## Analyses (Hofmann).

	a.		
Carbon	74.60	—	—
Hydrogen	5.37	—	—
Nitrogen	—	7.59	—
Bromine	—	—	12.59

*Nitrate.*

$C_{38}H_{35}N_5O_3$ (Schiff).				$C_{38}H_{32}N_4O_3$ (Hofmann).			
$C_{38}$	456	74.88		$C_{38}$	456	77.03	
$H_{35}$	35	5.75		$H_{32}$	32	5.40	
$N_5$	70	11.49		$N_4$	56	9.46	
$O_3$	48	7.88		$O_3$	48	8.11	
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	609	100.00			592	100.00	

## Analyses (Hofmann).

Carbon	77.55	77.17
Hydrogen	5.36	5.41

*Triphenylic Leucaniline.*

$C_{38}H_{33}N_3$			
$C_{38}$	456	85.88	85.75
$H_{33}$	33	6.21	6.15
$N_3$	42	7.91	—
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	531	100.00	

The preceding analyses appear to establish beyond a doubt the composition of aniline-blue; and I do not hesitate to maintain the formula originally established by me as the true expression of the constitution of this compound.

The resumption of this inquiry has led me to some observations which afford an additional support of the composition of aniline-blue.

*Rosaniline*, when submitted to dry distillation, undergoes an irregular decomposition. Ammonia is evolved, a large amount of liquid bases (from 40 to 50 per cent.) passes over, and a porous mass of charcoal remains in the retort. The principal constituent of the liquid product is *aniline*.

*Ethyl-rozaniline*, the commercial aniline-violet, already manufactured on a large scale by Messrs. Simpson, Maule, and Nicholson, when distilled, exhibits similar phenomena. There is no difficulty in separating from the liquid product an appreciable amount of *ethylaniline*, the presence of which has been established by the examination of the platinum-salt.

The relation existing between aniline-violet, obtained by the action of iodide of ethyl, and aniline-red, cannot possibly be doubtful. Now, since analysis points out similar relations between aniline-blue and aniline-red, it became perfectly legitimate to anticipate, among the products of distillation of aniline-blue, *i.e.* of *phenylated rosaniline*, the presence of *phenylated aniline*, or *diphenylamine*, a substance which chemists had often, but vainly, endeavoured to prepare. Experiment has verified this anticipation.

Some weeks ago my friend, M. Charles Girard, Director of the Works of the Fuchsine Company at Lyons, had the kindness to transmit to me for examination some basic oils of high boiling-point which he had obtained by the destructive distillation of a considerable quantity of aniline-blue. The product of distillation which he forwarded to me was brown and viscid. When rectified, it furnished a slightly coloured liquid; at 300° the thermometer indicated the distillation of a definite compound.

The distillate which had passed between 280° and 300° solidified on addition of hydrochloric acid, a chloride difficultly soluble (more especially in concentrated hydrochloric acid) being formed. By washing with alcohol, and ultimately by crystallization from this liquid, the chloride was obtained in a state of purity. When treated with ammonia, it furnished colourless oily drops, which, after a few moments, solidified to a white crystalline mass.

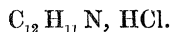
The crystals thus obtained possess a peculiar flower-like odour; their taste is aromatic, and afterwards burning. At 45° they fuse to a yellowish oil, distilling constantly, and without alteration, at 312° (corr.). They are almost insoluble in water, easily soluble in alcohol and ether. Neither in aqueous nor in alcoholic solution has the substance any alkaline reaction. When brought into contact with concentrated acids, the crystals are converted into the corresponding salts, which are remarkable for their instability. On the addition of water, the base separates in oily drops, rapidly solidifying to

crystals. The chloride, when washed with water, loses every trace of hydrochloric acid.

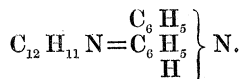
The analysis of the base has led to the formula



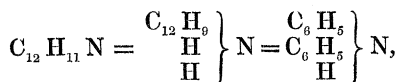
The composition of the chloride, which crystallizes from alcohol in concentrically grouped needles, assuming a bluish tint by contact with the air, is



I do not believe that I am deceived in considering this compound as diphenylamine,



It deserves, however, to be stated that the strict experimental demonstration of this mode of viewing the compound is still wanting, the ethylation of the substance presenting difficulties that I have not yet been able to overcome. I regret this gap, since the experience acquired in the study of xenylamine, isomeric with diphenylamine,



and which for several weeks I regarded as the secondary phenyl-base, points out the necessity of consistently carrying out the process of ethylation in the examination of bases of this kind.

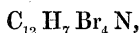
Diphenylamine exhibits a peculiar reaction, which, while it appears to reveal its relation to the colour-generating aniline, enables us to recognize the presence of the new base. In contact with concentrated nitric acid, diphenylamine, as well as its salts, assumes at once a magnificent blue coloration. The reaction succeeds best by pouring concentrated hydrochloric acid upon a crystal of the base, and then adding the nitric acid drop by drop. Immediately the whole liquid becomes intensely indigo-blue. Minute quantities of diphenylamine may in this manner be readily traced. I have thus been enabled to ascertain the presence of this body, or, at all events, of a substance exhibiting this particular reaction, in the products of distillation of rosaniline, leucaniline, and even of melaniline. The last experiment deserves particularly to be noticed, since it affords the general method for the production of the secondary aromatic monamines, which was hitherto wanting.

The substance possessing the blue colour is formed also by the action of other oxidizing agents. On adding chloride of platinum to a solution of the chloride, the liquid at once assumes a deep-blue colour. Only, from

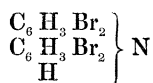
very concentrated solutions, a platinum-salt is deposited exhibiting an undesirably blue tint.

When a mixture of diphenylamine and toluidine is submitted to one of the processes (treatment with chloride of mercury or arsenic acid) which, if phenylamine and toluidine had been employed, would have furnished rosaniline, a mass is formed which dissolves in alcohol with a magnificent blue coloration, and possesses the characters of a true colouring-matter.

An alcoholic solution of diphenylamine furnishes, on addition of bromine, a yellow crystalline precipitate, difficultly soluble in cold alcohol, but crystallizing from boiling alcohol in beautiful needles of a satiny lustre. According to analysis, they contain

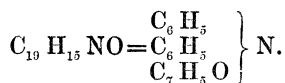


a formula which renders the grouping

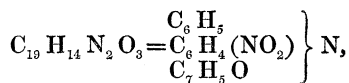


probable.

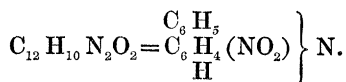
A mixture of diphenylamine and chloride of benzoyl, when heated, furnishes a thick oil, which solidifies on cooling. Washed with water and alkali, and recrystallized from boiling alcohol, in which it dissolves with difficulty, the new compound is obtained in beautiful white needles. Analysis has confirmed the theoretical anticipation,



This substance has become the starting-point of some experiments which I shall here briefly mention, but to which I intend to return hereafter. On addition of ordinary concentrated nitric acid, the benzoyl-compound liquefies and dissolves. From this solution, water precipitates a light-yellow crystalline compound,

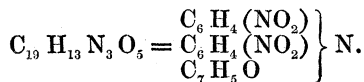


which dissolves in alcoholic soda with a scarlet colour, splitting on ebullition into benzoic acid and reddish-yellow needles of nitro-diphenylamine,



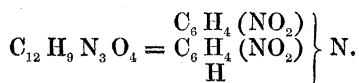
If, instead of ordinary nitric acid, a large excess of the strongest fuming nitric acid be employed, the solution deposits, on addition of water, a crys-

talline compound of a somewhat deeper yellow colour, containing probably



This substance dissolves in alcoholic soda with a most magnificent crimson colour. Addition of water to the boiling liquid furnishes a yellow crystalline deposit, benzoate (?) of sodium remaining in solution.

The yellow powder is dinitro-diphenylamine. From boiling alcohol, it crystallizes in reddish needles, exhibiting a bluish metallic lustre. The analysis of the compound has led to the formula



The chemical history of these compounds will be the subject of a special communication.

XVI. "A Table of the Mean Declination of the Magnet in each Decade from January 1858 to December 1863, derived from the Observations made at the Magnetic Observatory at Lisbon; showing the Annual Variation, or Semiannual Inequality to which that element is subject." Drawn up by the Superintendent of the Lisbon Observatory, Senhor DA SILVEIRA, and communicated by Major-General SABINE, R.A., President of the Royal Society. Received June 6, 1864.

I have much pleasure in communicating to the Fellows of the Royal Society a copy of a Table which I have received from the Superintendent of the Magnetic Observatory at Lisbon, containing the mean values of the Declination in each Decade from the commencement of 1858 to the close of 1863, with corrections applied for the mean secular change, and showing, in a final column, the difference in each decade of the observed from the mean annual value derived from the 216 decades. This Table is a counterpart of Table VII. in Art. XII. of the Philosophical Transactions for 1863, p. 292, differing only in the substitution in the Lisbon Table of decades for weeks, and the addition of the year 1863.

This general confirmation by the Lisbon Observatory of the annual variation to which the Declination is subject, "the north end of the magnet pointing more towards the East when the sun is north of the Equator, and more towards the West when the sun is south of the Equator," is very satisfactory. In the Lisbon Table the disturbances have not been eliminated.