

PROCEEDINGS

OF

THE ROYAL SOCIETY.

March 6, 1862.

Major-General SABINE, President, in the Chair.

In accordance with the Statutes, the names of the Candidates for election into the Society were read, as follows :—

Alexander Armstrong, M.D.	Henry Fawcett, Esq.
Henry Foster Baxter, Esq.	Frederick Field, Esq.
George Bentham, Esq.	George Gore, Esq.
Sir Charles Tilston Bright.	Robert Philips Greg, Esq.
William Brinton, M.D.	Robert Harley, Esq.
Henry William Bristow, Esq.	John Braxton Hicks, M.D.
Samuel Brown, Esq.	William Charles Hood, M.D.
Alexander Ross Clarke, Capt.	The Very Rev. Walter Farquhar
R.E.	Hook, D.D., Dean of Chi-
Edward William Cooke, Esq.	chester.
William White Cooper, Esq.	Edmund C. Johnson, Esq.
Joseph Cubitt, Esq.	Waller Augustus Lewis, M.B.
Henry Duncan Preston Cunning-	Edward Joseph Lowe, Esq.
ham, Esq., R.N.	Charles Watkins Merrifield, Esq.
John W. Dawson, Esq.	Gavin Milroy, M.D.
Alexander John Ellis, Esq.	Sir Joseph F. Olliffe, M.D.
Frederick John Owen Evans, Esq.,	George Wareing Ormerod, Esq.
R.N.	Frederick William Pavy, M.D.
John Evans, Esq.	William Pengelly, Esq.

VOL. XII.

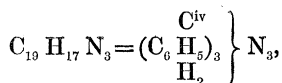
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Charles Bland Radcliffe, M.D.	Balfour Stewart, Esq.
George Rolleston, M.D.	Thomas Tate, Esq.
Edward Romilly, Esq.	Thomas Pridgin Teale, Esq.
Henry E. Roscoe, Esq.	Sir James Emerson Tennent.
William Henry Leighton Russell, Esq.	Isaac Todhunter, Esq.
Samuel James Augustus Salter, Esq.	Charles Tomlinson, Esq.
Charles William Siemens, Esq.	C. Greville Williams, Esq.
Maxwell Simpson, M.B.	Charles Wye Williams, Esq.
	Frederick Marow Eardley Wil- mot, Lieut.-Col. R.A.

The following communications were read :—

- I. "Notes of Researches on the Poly-Ammonias."—No. XX.
On the Colouring Matters produced from Aniline. By
A. W. HOFMANN, Ph.D., LL.D., F.R.S. &c. Received
February 20, 1862.

In a note on the Action of Tetrachloride of Carbon on Aniline submitted to the Royal Society on the 17th of June, 1858, I have described a crystalline basic derivative of aniline formed by the coalescence of three molecules of ammonia, viz. carbtriphenyltri-amine,



the formation of which is accompanied by that of a colouring matter of a magnificent crimson colour.

It may be useful to quote here the passage* of the paper referred to, in which the formation of the colouring matter is mentioned. "On submitting a mixture of $3\frac{1}{2}$ parts by weight of aniline and 1 part of bichloride of carbon, both in the anhydrous state, for about thirty hours to a temperature of 170°C. , the liquid will be found to be converted into a black mass, either soft and viscid, or hard and brittle, according to time and temperature.

"This black mass, which adheres firmly to the tubes in which the reaction has been accomplished, is a mixture of several bodies. On

* Proceedings of the Royal Society, vol. ix. p. 284.

exhausting with water, a portion dissolves, while a more or less solid resin remains behind.

“The aqueous solution yields, on addition of potassa, an oily precipitate containing a considerable portion of unchanged aniline; on boiling this precipitate with dilute potassa in a retort, the aniline distils over, whilst a viscid oil remains behind, which gradually solidifies with a crystalline structure. Washing with cold alcohol and two or three crystallizations from boiling alcohol render this body perfectly white and pure, a very soluble substance of a magnificent crimson colour remaining in solution.

“The portion of the black mass which is insoluble in water dissolves almost entirely in dilute hydrochloric acid, from which it is reprecipitated by the alkalies in the form of an amorphous pink or dingy precipitate soluble in alcohol with a rich crimson colour. The greater portion of this body consists of the same colouring principle which accompanies the white crystalline substance.”

The action of tetrachloride of carbon on aniline yields only a comparatively small quantity of the crimson pigment; the temperature of the exposure, and the relative proportions in which the two substances act upon one another, have the greatest influence upon the results of the reaction. The white crystalline base, and the base dissolving with a crimson colour, are by no means the only products; other bases, most of them amorphous and accessible only in the form of platinum-salts, are produced, and complicate, owing to the similarity of their chemical characters, the purification of the new compound. Notwithstanding many efforts, I failed in obtaining the new colouring matter in a state fit for analysis, and for the time abandoned the inquiry.

Industry, however, was not long in discovering new and much more appropriate methods for the production of the crimson aniline dye. Certain metallic chlorides (tetrachloride of tin) and nitrates (mercurous nitrate), and numerous oxidizing agents are capable of converting aniline into the crimson colouring matter. It was M. Verguin who first prepared this colour upon a large scale by the action of tetrachloride of tin on aniline. Since that time the production of the aniline-crimson has become an important industry, which, in the hands of Messrs. Simpson, Maule, and Nicholson in this country, of Messrs. Renard frères in France, has rapidly attained

to colossal proportions. The interest attached to the subject is sufficiently evident by a glance at the periodical literature of the day. The journals of applied chemistry teem with the descriptions of processes for the production of the aniline-crimson, for which the names fuchsine, magenta, and others more fanciful have been proposed. Even the action of tetrachloride of carbon on aniline, little promising as it appeared at first, has been used upon the large scale; and interesting papers upon the industrial production of the colour by this process have been published by M. Charles Dolfus Galline*, by Messrs. Monnet et Dury†, and lastly by M. Lauth‡, who have proved that aniline-crimson, prepared upon the large scale by means of tetrachloride of carbon, may be applied in dyeing with exactly the same result as the colouring matter produced by other processes. It is not the object of this Note to enter into a detailed account of the development of this new industry, which has been admirably traced by M. E. Kopp in a series of interesting articles published in the 'Répertoire de Chimie Appliquée;' but I thought it right to quote the above authorities in order to show that the basic colouring matter obtained by me in 1858, while studying the action of tetrachloride of carbon upon aniline, is identical with the aniline-crimson which is now by various processes manufactured upon an enormous scale.

A substance possessing such remarkable properties as aniline-crimson, and accessible, moreover, as a commercial product, could not fail to attract the attention of scientific inquirers. The subject has been examined in succession by M. Guignet§, M. Béchamp||, M. Wilm¶, Messrs. Persoz, De Luynes et Salvétat**, M. Schneider††, and more recently by M. Emile Kopp‡‡ and M. Bolley§§. The conclusions, however, at which these experimentalists have arrived are far from concordant. I attribute this discrepancy in the results obtained by such able observers to the extreme difficulty of procuring the colouring matter in a state of purity, and to the circumstance

* Répertoire de Chimie Appliquée, 1861, p. 11. † Ibid. p. 12.

‡ Ibid. p. 416. § Bull. Soc. Chim. Séance du 23 Déc. 1859.

|| Annales de Chim. et de Phys. [3] tome lix. p. 396.

¶ Bull. Soc. Chim. Séance du 27 Juillet 1861.

** Comptes Rendus, li. 538. †† Ibid. li. 1087.

‡‡ Annales de Chim. et de Phys. tome xii. p. 222.

§§ Dinger's Journal, clx. 57.

that the slightest contamination with other bodies is capable of altogether masking the properties of this remarkable compound.

The red colouring matter of aniline and its saline compounds have been obtained for the first time in the state of purity by my friend and former pupil Mr. Edward Chambers Nicholson, a chemical manufacturer equally distinguished for his scientific attainments as for the skill and indomitable energy with which in many instances he has succeeded in rendering the results of purely scientific inquiries available for the purposes of life.

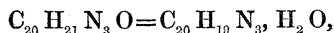
Mr. Nicholson has, with the utmost liberality, placed at my disposal not only a very considerable supply of the beautiful compounds which he produces, but also the vast and precise information which in his protracted experiments upon this subject he has accumulated. It is entirely through the kindness of Mr. Nicholson that I was enabled to resume the study of these remarkable bodies, a short account of the composition and of the chemical nature of which I beg leave to submit to the Royal Society.

Mr. Nicholson designates the pure base of the red colouring matter by the name of Roseine, which appears very appropriate, since this substance, which furnishes such splendidly coloured solutions, is absolutely white in the solid condition. Nevertheless, since the compound in question appears to be the prototype of a number of similar substances obtainable by similar processes from the homologues, and probably also from the analogues, of aniline, it may be useful to commemorate the origin of the compound in its name, and I accordingly propose the term *Rosaniline* for the designation of the new substance.

Rosaniline.—The material from which the base may be most conveniently obtained is the acetate which in practice is generally used for dyeing. This acetate Mr. Nicholson produces on the large scale in a state of perfect purity. The boiling solution of this salt, when supersaturated with a large excess of ammonia, furnishes a rose-red somewhat crystalline precipitate, which constitutes the base in a tolerably pure state. The colourless liquid filtered off while boiling from this precipitate deposits, on cooling, perfectly white needles and plates, which are the rosaniline in a state of absolute purity. Unfortunately the solubility of rosaniline in boiling ammonia, and even in boiling water, is extremely limited, so that only a

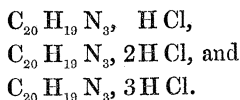
very small proportion of the compound is obtained in the perfectly white condition. The base is somewhat more soluble in alcohol, the solution having a deep-red colour; it is insoluble in ether. Exposed to the action of the atmosphere, rosaniline turns rapidly pink, and ultimately dark red. No perceptible alteration of weight is observed during this change. At the temperature of 100° the base rapidly loses a minute quantity of water of interposition; it may then be heated to 130° without further losing weight. At a higher temperature rosaniline is decomposed with evolution of an oily liquid containing much aniline, a quantity of charcoal remaining behind.

The combustion of rosaniline has led to the formula



which has been corroborated by the examination of numerous well-characterized salts and derivatives.

Rosaniline is a well-defined powerful base, which forms several series of salts, nearly all remarkable for the facility and beauty with which they crystallize. The proportions in which this substance unites with acids characterize it as a triacid triamine. Like several other triamines which I have examined, it will probably be found to produce three classes of salts, viz.,



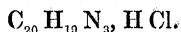
Up to the present moment, however, I have been able to obtain only representatives of the first and the third of these classes. The predilections of rosaniline are essentially monacid. The salts with one equivalent of acid are wonderfully stable compounds. I have recrystallized them four and five times without producing the slightest alteration in their composition. The salts with three equivalents of acid present comparatively little stability, being, in fact, decomposed by the action of water or by exposure to 100° .

By a glance at the formula given, it is obvious that the white crystals of the base itself, which were submitted to examination, are a hydrate,—the saline compounds of rosaniline, as might have been expected from many of the processes of their formation, containing no oxygen. The salts of rosaniline may be obtained by two different processes: either by the direct action of the respective acids, or

by submitting the ammonium-compounds of the several acids to ebullition with an excess of the free base. Both processes yield the salts equally pure and of exactly the same composition. The salts with one equivalent of acid exhibit for the most part, in reflected light, the splendid metal-lustrous green of the wings of the rose-beetle; in transmitted light the crystals are red, becoming opaque when they acquire certain dimensions. The solutions of these salts in water or alcohol possess the magnificent crimson colour for which rosaniline has become so justly celebrated. The salts with three equivalents of acid, on the other hand, are yellowish brown, both in the solid state and in solution. They are much more soluble in water and alcohol than the monacid salts, which for the most part are comparatively sparingly soluble. Both classes of rosaniline-salts crystallize readily, more especially the monacid compounds; some of them Mr. Nicholson has obtained in perfectly well-formed crystals, which are at present in the hands of Quintino Sella for crystallometrical examination.

Chlorides.—These substances, and more especially the monacid salt, were of particular use in fixing the formula of rosaniline. Prepared either by the action of hydrochloric acid, or by means of chloride of ammonium, the salt is deposited from the boiling solution in well-defined rhombic plates, frequently united in stellar forms. The chloride is difficultly soluble in water, more soluble in alcohol, insoluble in ether.

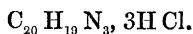
The salt retains a minute quantity of water at 100°, but becomes anhydrous at 130°. At this temperature it contains



The salt, like most of the rosaniline-salts, is very hygroscopic, a character which must not be lost sight of in the analysis of these compounds.

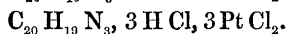
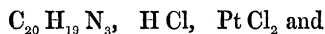
The monacid chloride dissolves more readily in moderately strong hydrochloric acid than in water. If this solution, gently warmed, be mixed with very concentrated hydrochloric acid, it solidifies, on cooling, into a network of beautiful brown-red needles, which have to be washed with concentrated hydrochloric acid and dried *in vacuo* over sulphuric acid and lime, since water decomposes them with reproduction of the monacid compound. The salt obtained by the

action of concentrated hydrochloric acid is the compound with three equivalents of acid,

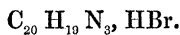


Exposed to 100° this salt gradually loses acid, the brown crystals becoming indigo-blue; and if the exposure be continued until the weight becomes constant, the original green salt with one equivalent of acid is reproduced, which was identified by analysis.

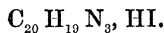
The two chlorides combine with *dichloride of platinum*. The compounds thus produced, being uncrystallizable, are not easily obtained in a state of purity. From platinum-determinations, which have given only approximative results, I infer that they contain respectively,



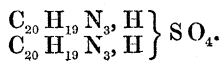
The *Hydrobromate of Rosaniline* resembles in every respect the hydrochlorate; it is even more difficultly soluble than the latter; it contains



Hydriodate of Rosaniline.—Green, very difficultly soluble needles of the composition

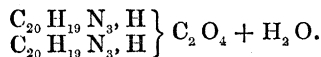


Sulphate of Rosaniline is readily obtained by dissolving the free base in boiling dilute sulphuric acid. On cooling, the salt is deposited in green metal-lustrous crystals, which by one recrystallization become perfectly pure. At 130° , at which temperature it loses a small quantity of water, the formula of the salt is



The acid sulphate crystallizes with difficulty. I have not analysed it.

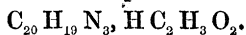
Oxalate of Rosaniline.—The preparation and properties of this salt are similar to those of the sulphate. The salt retains at 100° one equivalent of water, and is at this temperature represented by the formula



The water may be expelled at a higher heat; but the temperatures at which the water is lost and the salt commences to be decomposed are so close to each other, that it is not quite easy to obtain the salt

in the anhydrous state. I have not been able to procure an oxalate with a larger amount of acid.

Acetate of Rosaniline.—This is probably the finest salt of the series. Mr. Nicholson has obtained it in crystals an inch in diameter, which, on analysis, were found to be the pure monacid acetate, viz.,

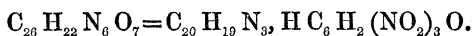


The acetate is one of the more soluble salts, both in water and in alcohol; it cannot be conveniently recrystallized.

The *Formiate of Rosaniline* is similar to the acetate.

Of the remainder of the salts of this base I may mention the *Chromate*, which is obtained by adding chromate of potassium to the solution of the acetate in the form of a brick-red precipitate, becoming a green, crystalline, almost insoluble powder on ebullition with water.

The *Trinitrophenate* also deserves to be noticed; it crystallizes in beautiful reddish needles, likewise very difficultly soluble in water, which contain



Multiplied and varied though the analytical results may be which support the formulæ of rosaniline and its compounds, it appeared desirable to seek additional experimental evidence for the expressions derived from simple analysis. With this view I have studied the products of decomposition of rosaniline. They are both numerous and interesting. I must limit myself to-day to quote one or two compounds which claim some attention, not only because they unmistakably confirm the formula which I have proposed, but also on account of the light which they throw upon the nature of the class of substances to which rosaniline belongs.

Action of reducing agents upon Rosaniline.—This action appeared to promise the simplest mode of controlling the formula of the new base. My anticipations have not been disappointed. Rosaniline is readily attacked by nascent hydrogen or sulphuretted hydrogen. A solution of the base in hydrochloric acid, when left in contact with metallic zinc, is rapidly decolorized. The liquid thus produced contains, together with chloride of zinc, the hydrochlorate of a new triamine, which, perfectly colourless as it is in the free state and in its saline compounds, I propose to designate by the term *Leucaniline*. The separation of the new compound from the zinc being tedious and troublesome, I prefer to prepare it by the action of sulphide of

ammonium. A salt of rosaniline, when digested for some time with sulphide of ammonium, furnishes a yellow, half-fused, scarcely crystalline, brittle compound, which constitutes the leucaniline in a state approaching purity. It is, however, by no means necessary to employ for the preparation of this compound a rosaniline-salt in the pure state. In most cases I have produced the leucaniline from the commercial article sold under the name of fuchsine or magenta.

To purify the product thus obtained, the yellow resinous mass is powdered, washed with water to remove the sulphide of ammonium, and dissolved in dilute hydrochloric acid, when sulphur, together with impurities, are left behind. The dark-brown solution thus obtained yields, with concentrated hydrochloric acid, a copious crystalline precipitate, which, according to the degree of purity of the commercial colouring matter, is either brown or yellow. Washing with concentrated hydrochloric acid, in which the precipitate is insoluble, effects a considerable purification; but in most cases it is necessary to repeat the process of dissolving in dilute and reprecipitating by concentrated hydrochloric acid once or twice. If the solution, before the last addition of concentrated acid, be heated to ebullition, the liquid remains clear, and the new chloride crystallizes out only on cooling. The crystals are beautiful, white, rectangular plates, which are, however, always very small. Recrystallization from water, in which they are extremely soluble, renders them perfectly pure. Or they may be dissolved in alcohol and precipitated by ether, in which they are quite insoluble.

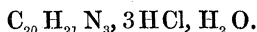
The chloride thus purified yields, on addition of ammonia, the leucaniline as a dazzling white powder, which assumes the faintest rosy tint when left for some time in contact with the atmosphere of the laboratory. It is scarcely soluble in cold, very little soluble in boiling water, from which it is deposited, on cooling, in the form of small crystals. It is very soluble in alcohol, and, although less so, in ether. I have not been able to get it in good crystals from these solvents. The best solvent appears to be a solution of the chloride above described, in which leucaniline is freely soluble, and from which, on cooling, it is deposited in the form of interlaced needles, which are frequently united to spherical aggregations. Leucaniline may be dried *in vacuo* over sulphuric acid without changing its colour. When slightly heated it becomes red, and at 100° it fuses

to a deep-red liquid which, on cooling, solidifies to an indistinctly crystalline mass of lighter colour. Leucaniline is anhydrous. The analysis of the substance, dried *in vacuo*, and at 100°, has given results which correspond to the formula



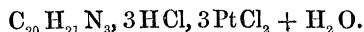
This formula has been verified by the examination of the chloride already mentioned, of a splendidly crystallized platinum-salt, and, lastly, of the nitrate, which may be likewise obtained in good crystals.

Hydrochlorate of Leucaniline.—The preparation of this compound has been mentioned. It is triacid, and retains, when dried *in vacuo*, one equivalent of water, its formula being



The salt cannot be dried at 100°, at all events in air; but the water may be expelled, although with great difficulty, by exposing the salt for a considerable length of time to 100° in a current of hydrogen. I have endeavoured to convert this compound into a salt with less acid by boiling the solution with an excess of leucaniline, but without result. The boiling solution deposits, on cooling, beautiful crystals of the base, the triacid salt remaining in solution.

Platinum-salt of Leucaniline.—On adding dichloride of platinum to a moderately concentrated, gently warmed solution of the chloride, a splendid bright orange-yellow platinum-salt separates, on cooling, in well-formed prisms, generally aggregated to triangular stars. The salt is difficultly soluble in cold water; boiling water decomposes it. At 100° this salt retains one equivalent of water, which can be expelled, although with difficulty, at higher temperatures. Numerous analyses of this beautiful compound have established the formula



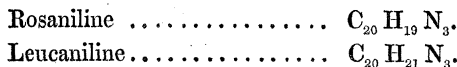
Nitrate of Leucaniline.—Well-formed white needles, soluble in water and alcohol, insoluble in ether. The salt is rather difficultly soluble in nitric acid. When dried *in vacuo* this salt contains



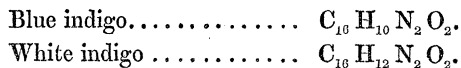
I have not succeeded in separating the water of crystallization, the salt being decomposed at 100°.

The salts of leucaniline are, in general, well crystallized. They are all very soluble in water, and precipitated from the aqueous solu-

tion by the addition of the respective acids. The sulphate crystallizes readily. I have submitted leucaniline to the action of disulphide of carbon, chloride of benzoyl, and several other agents. In all these cases new compounds are generated, some of them remarkable for their crystallizing power. The study of these substances does not belong to the present inquiry; I shall return to them in a future communication, in which I propose to examine the constitution of rosaniline and leucaniline, and their derivation from aniline. The object of the present Note was only to fix the composition of the two new bases, and their mutual relations to each other. This relation, as will be obvious by a glance at their formulæ, is of the simplest kind. In the anhydrous condition the two substances respectively contain,



Leucaniline differs from rosaniline simply by containing two equivalents of hydrogen more. The two bases hold to each other the relation which obtains between blue and white indigo :



Leucaniline, as might have been expected, is readily reconverted into the red colouring matter by oxidizing agents. The reaction succeeds with peroxide of barium, perchloride of iron, or chromate of potassium. On gently heating the colourless solution of the chloride with one of these reagents, the liquid at once reassumes the splendid colour of the rosaniline-salts. An excess of the oxidizing agents is, however, to be avoided, lest the action should go too far and the regenerated compound be converted into further products of oxidation. Both rosaniline and leucaniline, when submitted to protracted ebullition with highly oxygenated compounds, yield a brown amorphous powder, the composition of which remains at present unknown.

The two bases which I have described in the preceding paper are the prototypes of two series of homologous colouring matters which cannot fail to be obtained from the homologues of aniline. Toluidine appears to yield perfectly similar bases. I have not, in the present Note, examined into the nature of the reaction by which aniline is transformed into rosaniline; in most of the processes which give rise

to this substance, it is accompanied by several other bases, the study of which is not yet completed. Nor am I at present in a position to offer any definite opinion regarding the constitution of the new compounds, tempting though it appears to venture on speculations. It is in the hope of rendering the formulæ of the new bases more transparent that I have commenced to examine some of the products of decomposition. Their study is likewise far from being completed; but I may mention, even now, that both rosaniline and leucaniline, when in nitric solution, are powerfully acted upon by nitrous acid, new bases being thus generated, the platinum-salts of which are remarkable for their fulminating properties. A splendid crystalline base also deserves to be mentioned, which, associated with aniline, appears among the products of distillation of rosaniline.

The results obtained in the further prosecution of these studies I propose to lay before the Royal Society in a future communication.

II. "On the Integration of Simultaneous Differential Equations." By GEORGE BOOLE, Esq. Received March 4, 1862.

It is well known that a system of $n-1$ simultaneous differential equations of the first order connecting n variables always admits of $n-1$ integrals, each of which is the form $P=c$, i. e. each of them is expressible by a function of the variables equated to an arbitrary constant.

But when the number of the variables exceeds by more than by unity the number of the differential equations, no existing theory assigns the number of theoretically possible integrals, or guides us to their discovery.

Yet cases such as this occur in problems of the greatest importance. The solution of partial differential equations of the second order by Monge's method depends ultimately on the solution of a system of *three* ordinary differential equations of the first order between *five* variables.

I wish here briefly to indicate the results of a theory which enables us in all such cases, 1st, to assign *à priori* the number of possible integrals; 2ndly, to reduce the determination of the integrals to the solution of a system of differential equations equal in number to the