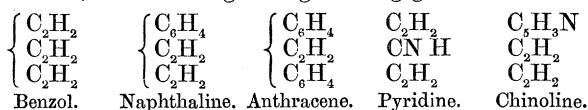


$$\cos ax = \frac{\sin(a\pi)}{\pi} \left[\frac{1}{a} + 2a \left(\frac{\cos x}{1^2 - a^2} - \frac{\cos 2x}{2^2 - a^2} + \frac{\cos 3x}{3^2 - a^2} - \frac{\cos 4x}{4^2 - a^2} + \&c. \right) \right]$$

$$\sin ax = \frac{2 \sin(a\pi)}{\pi} \left(\frac{\sin x}{1^2 - a^2} - \frac{2 \sin 2x}{2^2 - a^2} + \frac{3 \sin 3x}{3^2 - a^2} - \frac{4 \sin 4x}{4^2 - a^2} + \&c. \right)$$

II. "Studies in the Chinoline Series.—I. Transformation of Leucoline into Aniline." By Prof. JAMES DEWAR. Communicated by Prof. A. W. WILLIAMSON, Foreign Secretary of the Royal Society. Received February 19, 1877.

In a previous research* on the pyridine series of bases the formation and properties of dicarbopyridinic acid were described. This acid derivative is related to pyridine in the same manner as phthalic acid to benzol. It was then pointed out that the members of the pyridine and chinoline series bear to one another a similar relation to that of benzol and naphthaline, the following analogies being given :—



An extension of the work was promised in support of these theoretical relations.

Our knowledge of the chinoline series has made little progress since the masterly and exhaustive investigation of Greville Williams†, proving the isomerism of the tar and cinchona bases. The relations of these bodies are still very obscure, owing to the great stability of the bases preventing the formation of derivatives of a simpler type. Indeed some of the most interesting products obtained from these bases, such as

* "On the Oxidation Products of Picoline," Trans. Royal Soc. Edinb. vol. xxvi.

† Trans. Royal Soc. Edinb. vol. xxi.

the blue colouring-matter cyanine, have a more complicated structure, all attempts to reach gradationally simpler substances of known constitution having been unsatisfactory. Gerhardt remarked that "En général les réactions de la quinoleine sont fort peu nettes"*. It is the object of this communication to render the relations of this substance a little more definite.

In the paper above referred to it was shown that pyridine might be obtained by the distillation of dicarbopyridinic acid with soda-lime; and as the acid had been made from the oxidation of picoline this may be regarded as a means of passing from the six- to the five-carbon base. It seemed, therefore, important to ascertain if the members of the chinoline series yielded on oxidation any similar acid, and if a simpler base could be obtained by subjecting it to a like treatment.

In order to carry out this investigation, a quantity of the crude high boiling-point bases occurring in coal-tar was procured, and after repeated fractionation on the large scale was treated in the following manner, to ensure its freedom from pyrrols, phenols, and high boiling-point hydrocarbons. The bases were dissolved in strong nitric acid, separated by means of soda, distilled, and again treated with nitric acid. The addition of small quantities of arsenious acid to the solution was continued for some hours. The bases now liberated from the solution of the nitrate were fractionally distilled, and the specimens boiling between 220° C. and 240° C. were regarded as tolerably pure leucoline. It has been satisfactorily proved by Greville Williams that no amount of fractional distillation will yield chemically pure members of this series; so that this product must be regarded as a mixture of leucoline and iridoline, the names given to the bases in coal-tar isomeric with the chinoline and lepidine obtained from cinchona. In various experiments specimens were used which had been more carefully fractionated, the boiling-point not varying more than 2° C.; but the products obtained were in all cases similar.

The mode in which the oxidation was conducted was similar in all respects to that described in my former paper; but the high boiling-point of the base and the rapidity of the action rendered the use of the condenser unnecessary. The general method of working was as follows:—129 grams of leucoline were dissolved in an equivalent of sulphuric acid and the solution diluted to 600 cubic centimetres. This was then divided into three equal parts, to each of which was added a hot solution of 100 grams of permanganate of potash in about a litre of water, with constant stirring so as to avoid too vigorous an action. In a few minutes the whole of the permanganate is reduced, and the solution, which ought to be neutral, having been made slightly alkaline, is filtered from the oxide of manganese and evaporated to a small bulk, when a large proportion of the sulphate of potash crystallizes on cooling. The mother-liquor was next carefully acidulated with dilute sulphuric acid, when a

* 'Traité de Chimie Organique,' par M. C. Gerhardt, tom. iv.

resinous mixture of acids separates. The crude acids may also be obtained as potash salts by evaporating to dryness the product of the reaction and extraction with alcohol. The aqueous solution of these potash salts, on the addition of acetate of lead, yields a white insoluble lead salt from which the acids may also be separated.

The crude mixture of acids thus obtained, boiled with water for a considerable time and filtered from an oily matter, yields, after treatment with a little animal charcoal, crystals of a well-defined acid.

Leucolinic Acid, $C_9H_9NO_3$.—The crystalline substance obtained as above described is mainly composed of this acid, which may be obtained in colourless plates or needles by a few crystallizations. The acid melts at $162^\circ C.$, is slowly volatilized when heated to $110^\circ C.$ in a current of hydrogen, and communicates a characteristic aromatic odour to the vapour from a hot aqueous solution. The acid may be most conveniently crystallized from an aqueous solution, being slightly soluble in cold water. Although soluble in alcohol and ether the acid is generally rendered slightly coloured, from an apparent oxidation, when crystallized from these menstrua.

The salts of this acid are for the most part soluble, the more notable exceptions being the lead, mercurous, and ferric salts. The silver salt crystallizes in fine needle-shaped crystals.

Analyses of different specimens of the acid and silver salt yielded the following results:—

Acid.	I.	II.	III.
Weight of acid taken	0·1625	0·3345	0·2315
Carbonic anhydride produced..	0·3620	0·7450	0·5110
Water	0·0790	0·1595	0·1060

Calculated centesimally these figures give:—

	I.	II.	III.	$C_9H_9NO_3$.
Carbon	60·75	60·74	60·20	60·33
Hydrogen	5·40	5·30	5·09	5·02

Silver Salt.	I.	II.	III.
Weight of salt taken	0·5115	0·3206	0·4925
Carbonic anhydride produced..	0·7080	0·4390	0·6933
Water produced	0·1300	0·0850	0·1276
Silver	—	—	0·1868

Calculated centesimally these figures give:—

	I.	II.	III.	$C_9H_9AgNO_3$.
Carbon	37·73	37·34	38·39	37·76
Hydrogen	2·82	2·94	2·88	2·79
Silver	37·93	37·76

A quantity of the silver salt, weighing 0·1274 gram, ignited, left 0·04815 gram of silver, corresponding to 37·79 per cent.

Nitrogen Determination.—The nitrogen was found by Gottlieb's method to bear to the carbonic anhydride produced the volume ratio of 1 to 18·4 and 1 to 18·8.

An absolute determination of the nitrogen was made with the following results:—

Weight of acid taken	0.1087 gram.
Volume of nitrogen at 0° C. and 760 millimetres pressure . . . }	7.37 cubic centimetres.
Weight of nitrogen0092 gram.

This gives the percentage of nitrogen as 8.5 instead of 7.8, as required by theory. The acid used in this experiment was not quite pure, and the quantity taken too small for an accurate determination.

Equivalent of the Acid.—A quantity of the acid, weighing 0.445 gram, titrated with pure caustic soda solution, every 1.73 cubic centimetre of which contained 23*milligrams of sodium, required 4.28 cubic centimetres of this solution to neutralize the quantity of acid taken. Hence the equivalent of the acid is 179.

Professor Liveing has kindly determined the following crystallographic constants:—

“The acid crystallizes from solution of ether in tufts of thin plates which show the form of fig. 1.

“The face *a* is the only one which is largely developed. They cleave readily in plane *c* at right angles to *a*. The faces *b*, *b'* are equally inclined to *a*, their normals making an angle of about 53° with that of *a*. The normals to *b*, *c* make an angle of about 69°. The normal to face *d* is inclined to that of *a* at about 42°.

“Many of the crystals do not show the faces *d*, but are terminated by faces parallel to *c*. Some show some smaller facets at the apex, barely discernible.

“There are occasionally twin crystals, with the twin face parallel to the edge *b* and at right angles to *a*.

“The crystals appear to belong to the oblique prismatic system, with the inclined axes in a plane parallel to *a*.

“The uncertainty about the measurements is due to the minuteness of all the faces except *a*, and will perhaps be overcome when a fresh crop of crystals is obtained.”—G. D. L.

Fig. 1.

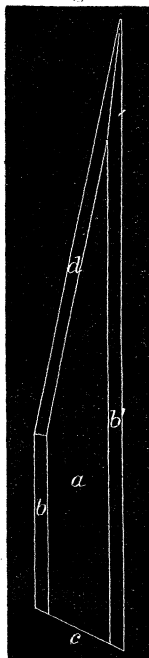
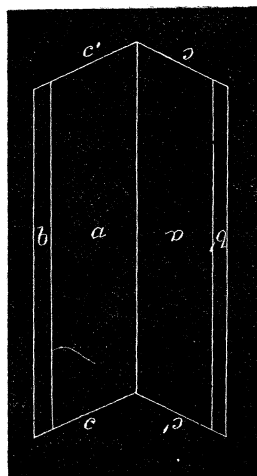
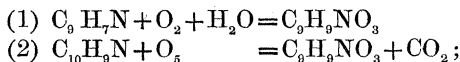


Fig. 2.



The acid may be regarded as formed by one or other of the following reactions :—



but (1) probably represents the chief source of the acid. Whether perfectly pure leucoline free from traces of iridoline would give the acid must, however, in the mean time remain an open question, as large quantities of material are required to procure the pure base. The yield of acid only amounts to three per cent. of the bases used.

Decompositions of the Acid.

Action of heat.—The acid heated rapidly above its melting-point becomes dark brown, evolves water, and gives an oily sublimate which ultimately solidifies, leaving a mass of porous carbon. The acid sublimate, which probably contains the anhydride, boiled with water regenerates the acid.

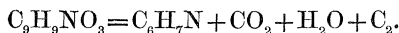
Action of soda-lime.—The acid heated with soda-lime to a low red heat leaves a deposit of carbon and yields an alkaline oily distillate. This oil is soluble in dilute hydrochloric acid, and gives the characteristic reactions of pyrrol. The solution evaporated leaves the hydrochlorates of the bases as a crystalline mass, which, after several solutions and evaporations with dilute hydrochloric acid, is freed from pyrrol. The hydrochlorates of the basic substances produced were now heated with potash, when the bases distilled as a colourless oil. This oil has all the physical and chemical characters of pure aniline.

In order to demonstrate the transformation of leucoline into aniline the crude product of the oxidation may be used instead of the isolated acid. A cubic centimetre of leucoline dissolved as sulphate, treated with a solution of 3 grams of permanganate of potash, filtered, evaporated to dryness, and the residue mixed with some soda-lime, yields on distillation sufficient aniline to give all its characteristic reactions. If potash-lime be used instead of soda-lime, the product of the distillation is found to be almost free from pyrrol.

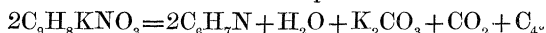
In order to ascertain if any base other than aniline was present, 3 grams of the acid was heated with potash-lime and the distillate collected in dilute hydrochloric acid. This was fractionally precipitated by chloride of platinum, when 0.1248 gram of the first fraction gave 0.0425 gram of platinum, equal to 34.05 per cent., aniline requiring 32.99 per cent. The second fraction, 0.2101 gram, gave 0.0688 gram of platinum, equal to 32.74 per cent.

The only substance associated with aniline seems to be ammonia, as appears from the following experiment, undertaken to ascertain whether any nitrile bases occurred in the distillate. The distillate from other 3 grams of acid was collected in nitric acid, and fragments of nitrite of potash added, until all the aniline was decomposed. The solution after being boiled was treated with caustic soda and distilled. The distillate

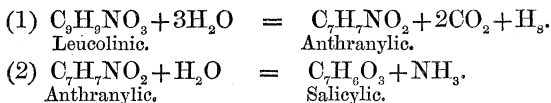
was slightly alkaline, and gave a platinum salt, of which 0.216 gram yielded 0.0954 of platinum, equal to 44.16 per cent. of platinum, the double chloride of platinum and ammonium requiring 44.23 per cent. The mother-liquor yielded nothing apparently but the ammonium salt. The acid on heating with potash-lime mainly undergoes the following reaction :—



When the crude mixture of potash salts resulting from the oxidation is taken, instead of the pure acid, and distilled with soda-lime, there appears to be associated with the aniline and pyrrols a small quantity of a nitrile base having a lower boiling-point than leucoline. If the pure potash salt is heated alone it fuses, aniline distils along with the vapour of water, and a mixture of carbonate of potash and carbon is left. Thus



If the potash salt is fused with excess of potash, ammonia is evolved and salicylic acid is found in solution. Probably anthranilyc acid is the first product, and this is subsequently changed into ammonia and salicylic acid, viz.—

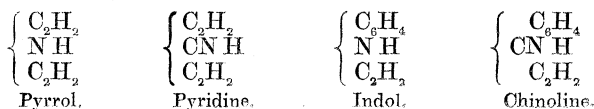


A similar series of reactions take place when indigo is carefully treated with fused potash. The formation of salicylic acid explains the origin of the ammonia found associated with the aniline when the acid is heated with potash-lime.

A solution of the acid in glycerine, heated to the boiling-point of the latter, gives a distillate of glycerine, aniline, and a substance in small quantity having the characters of indol. No free carbon is separated in this reaction. That indol or an isomeric body is likely to occur amongst the products of decomposition appears from the following likely decomposition :—



This reaction is rendered probable from the relations of indol and aniline, indol being readily obtained from the reduction of isatine, and isatine yielding aniline, carbonate of potash, and hydrogen on fusion with potash. The relations of chinoline, leucoline, and indol will be fully investigated in the second part of this paper, after I have had an opportunity of examining the isomeric cinchona bases. In the mean time it may be remarked that pyrrol and pyridine have a similar relation to indol and chinoline, thus—



In my paper before referred to it was suggested that, "considering the stability and mode of formation of these bases, it is not at all improbable that they may be produced by the simultaneous action of acetylene and its derivatives on hydrocyanic acid; thus as three molecules of acetylene condense and form benzol, so may two molecules of acetylene and one of hydrocyanic acid condense and produce pyridine."

A synthetical experiment of the kind suggested has been executed by Mr. Ramsay*, who finds that by transmitting a mixture of acetylene and hydrocyanic acid through a red-hot tube bases were unquestionably produced. Pyrrol, which may be so readily identified by means of its characteristic reaction with fir wood moistened with hydrochloric acid, may be formed synthetically by substituting ammonia for the hydrocyanic acid in the above experiment. The acetylene employed, however, contained a small quantity of bromide of vinyl, and it is possible the reaction may have taken place between that substance and ammonia. Only a small quantity of pyrrol is formed in this reaction, the principal substance formed being cyanide of ammonium; and the success of the experiment seems to depend on the maintenance of a carefully regulated temperature and a certain extent of porous surface. These and similar reactions are under investigation.

The theoretical bearings of this investigation have not been touched upon in the present paper, as an extensive research will be necessary before structural relations can be predicted with any certainty.

I am greatly indebted to Mr. W. F. Sell, B.A., and Mr. A. Scott, B.Sc., assistants in the Chemical Department, for aid in the course of the investigation.

Laboratory, Cambridge University.

III. "On the Density of Solid Mercury." By Prof. J. W. MALLETT, University of Virginia. Communicated by Prof. STOKES, Sec.R.S. Received February 22, 1877.

I have lately taken advantage of a heavy fall of very cold and finely pulverulent snow, well adapted to the preparation of freezing-mixtures, to redetermine, with accuracy I believe, the density of mercury in the solid state and at a definite temperature.

Such redetermination was not superfluous, as appeared from a collation of the statements to be found in various standard works. In the tables of specific gravities compiled by Prof. F. W. Clarke, and published by the Smithsonian Institution†, there are four authorities quoted, with the numbers given by these, as follows:—

* "On Picoline and its Derivatives," *Phil. Mag.* 1876, vol. ii. p. 269.

† "The Constants of Nature.—Part I." *Smithsonian Miscell. Coll.* 255, Washington 1873, p. 24.

Fig. 1.

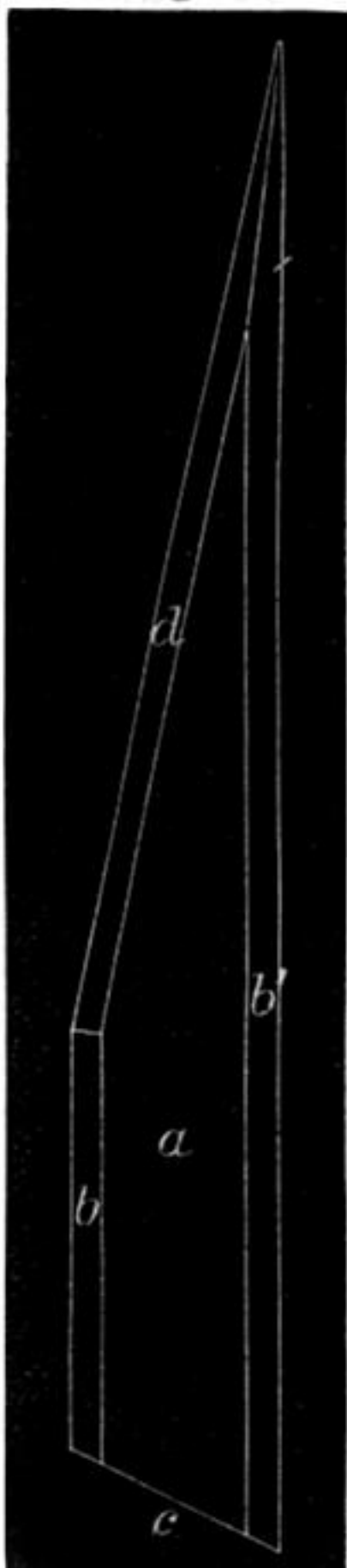


Fig. 2.

