

CVI.—*Aminoamidines of the Naphthalene Series. (Third Communication on Anhydro-bases.)*

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THE azo-derivatives of ethenyltriaminonaphthalene were incidentally referred to in a former communication by one of the authors and Percy P. Phillips (*Trans.*, 1899, **75**, 1016). In continuing the investigation of these compounds we had occasion to prepare some ethenyltriaminonaphthalene by the process of Markfeldt (*Ber.*, 1898, **31**, 1174) for comparison with the original anhydro-base described in 1887 (Meldola and Streatfeild, *Trans.*, **51**, 691). It was found to our surprise that the phenylazo-derivatives obtained from the bases by combination with phenyldiazonium salts were isomeric and not identical, and a further examination of the bases has revealed the fact that the isomerism of the azo-derivatives is due to the isomerism of the ethenyltriaminonaphthalenes which are not identical as assumed by Markfeldt in the paper referred to. This isomerism of the anhydro-bases is certainly unexpected, and is the more remarkable since they are both prepared from the same dinitroacetnaphthalide, the only difference being the nature of the reducing agent, Markfeldt having substituted iron and hydrochloric acid for tin and this acid, as originally employed in 1887. That the isomerism is entirely due to the nature of the reducing agent has been proved by repeated experiments with the same specimen of dinitroacetnaphthalide.

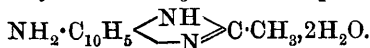
In the present communication, we give a detailed account of the results of our investigation of Markfeldt's base and some of its salts and azo-derivatives, so as to bring into prominence the differences between these and their isomerides obtained from the original ethenyltriaminonaphthalene of 1887. With respect to the nature of the

isomerism, we have come to the conclusion that it is most probably due to structural difference and not to space configuration (stereoisomerism), since the characters of the two sets of compounds are profoundly different. As was indicated in 1887, two constitutional formulæ are possible :



Which of these represents our original base and which Markfeldt's isomeride must for the present remain undecided. The main point established by the present research is that tin and iron behave differently as reducing agents towards 2:4-dinitro-1-acetnaphthalide. The constitution of the isomeric bases will form the subject of future investigation, and it is proposed to extend the study of the difference in the behaviour of the two metals as reducing agents to other nitro-compounds, since evidence has already been obtained that this peculiarity is not manifested only in the naphthalene series.

Markfeldt's Ethenyltriaminonaphthalene,



Meldola and Streatfield's anhydro-base is so soluble in water that it has not yet been isolated (Trans., 1887, 51, 698). Markfeldt's base is much less soluble, and separates out as an oily resin on adding sodium hydroxide solution to a strong aqueous solution of the hydrochloride. The resinous mass becomes crystalline on standing, and the free base can be crystallised from hot water, in which it readily dissolves. The pure compound is probably white, but all our preparations consisted of flat, slate-coloured needles, the colour being no doubt the result of atmospheric oxidation. The melting point of the base, allowed to dry in air at the ordinary temperature, is 84—85°. On analysis :

0·1799 gave 0·4072 CO₂ and 0·1016 H₂O. C = 61·73 ; H = 6·28.

0·1178 „ 17·95c.c. moist nitrogen at 12·2° and 765 mm. N = 18·17.

0·2408, air-dried, lost 0·0354 H₂O in water-oven. H₂O = 14·70.

C₁₂H₁₁N₃·2H₂O requires C = 61·80 ; H = 6·44 ; N = 18·03 ;

H₂O = 15·45 per cent.

The water of crystallisation is not quite driven off at the temperature of the water-oven. The anhydrous base begins to soften and

shrink at 128° and fuses at 135°. Analyses of a specimen, dried as above, gave the following results :

0·1638 gave 0·4386 CO₂ and 0·0896 H₂O. C = 73·03 ; H = 6·08.

0·1112 ,, 19·9 c.c. moist nitrogen at 12·2° and 773·7 mm. N = 21·58.

C₁₂H₁₁N₃ requires C = 73·10 ; H = 5·58 ; N = 21·32 per cent.

This aminoamidine is more distinctly basic in character than its isomeride. It gives a precipitate with silver nitrate in ammoniacal solution, but it is not sufficiently acid to dissolve in aqueous sodium hydroxide. The silver salt is gelatinous, and could not be obtained pure enough for analysis.

Salts of Markfeldt's Base.

Hydrochlorides.—The salt prepared by Markfeldt's process, namely, by crystallisation in presence of excess of hydrochloric acid, is a dihydrochloride of the formula C₁₂H₁₁N₃·2HCl, H₂O.

It consists of pinkish, flat, silky needles, the colour being doubtless the result of atmospheric oxidation. The specimen used for analysis was dried over lime in a desiccator, and had lost some hydrogen chloride under these conditions :

0·2435 gave 0·2322 AgCl. Cl = 23·59.

0·1385 ,, 17·05 c.c. moist nitrogen at 11·8° and 748·1 mm. N = 14·38.

C₁₂H₁₁N₃·2HCl, H₂O requires Cl = 24·65 ; N = 14·58 per cent.

The crystals become opaque on heating in the water-oven, and at 150—160° (in an air-oven) the water and 1 mol. of hydrogen chloride are driven off, leaving a monohydrochloride :

0·210, dried over lime in a desiccator and heated at 150—160° until constant in weight, lost 0·0396 = 18·86 per cent. The loss corresponding to C₁₂H₁₁N₃·2HCl, H₂O - (HCl + H₂O) = 18·92 per cent.

The monohydrochloride can also be prepared from the dihydrochloride by the partial removal of hydrogen chloride by means of dilute cold aqueous ammonia. The first specimen prepared in this way was analysed under the impression that it was the free base, and the results showed that only half the acid is removed under these conditions :

0·2926 gave 0·6187 CO₂ and 0·1516 H₂O. C = 57·67 ; H = 5·76.

0·0886 ,, 12·3 c.c. moist nitrogen at 11° and 766·2 mm. N = 16·67.

0·5503 ,, 0·3260 AgCl. Cl = 14·66.

The above specimen had been crystallised from water from which it separates as small, opaque, white needles melting at about 282° and

darkening with shrinkage from about 265°. This crystalline salt contains 1 mol. of water :

0·8020, dried in air, lost 0·0535 H₂O at 150—160°. H₂O = 6·67.
 C₁₂H₁₁N₃,HCl,H₂O requires C = 57·26; H = 5·57; N = 16·7; Cl = 14·12;
 H₂O = 7·16 per cent.

The isomeric ethenyltriaminonaphthalene forms the hydrochlorides C₁₂H₁₁N₃,2HCl,1½H₂O; C₁₂H₁₁N₃,2HCl,½H₂O; C₁₂H₁₁N₃,2HCl (Meldola and Streatfeild, *loc. cit.*, 694—696).

Sulphate.—The sulphate differs from that of the isomeric base in being much more soluble in hot water. It crystallises from this solvent in small, flat, silky, white needles, becoming pink by atmospheric oxidation. A specimen dried over lime in a desiccator was analysed with the following results :

0·2192 gave 23·75 c.c. moist nitrogen at 10·1° and 751·9 mm. N = 12·81.
 0·6691, dried in desiccator, lost 0·0735 H₂O in water-oven. H₂O = 10·98.
 C₁₂H₁₁N₃,H₂SO₄,2H₂O requires N = 12·69; H₂O = 10·88 per cent.

The anhydrous salt was also analysed :

0·3721 gave 0·2926 BaSO₄. S = 10·80.
 0·2044 gave 24·45 c.c. moist nitrogen at 10·2° and 767·1 mm. N = 14·43.
 C₁₂H₁₁N₃,H₂SO₄ requires N = 14·24; S = 10·85 per cent.

The isomeric sulphate retains ½H₂O at 220° (Meldola and Streatfeild, *loc. cit.*, 692).

Nitrate.—This salt was prepared by dissolving the free base in dilute nitric acid. It crystallises from water in slender needles which soon become coloured by oxidation. A specimen dried in the water-oven was analysed with the following result :

0·0625 gave 11·05 c.c. moist nitrogen at 9·8° and 754·8 mm. N = 21·02.
 C₁₂H₁₁N₃,HNO₃,½H₂O requires N = 20·82 per cent.

The salt could not be dried above the temperature of the water-oven without undergoing decomposition.

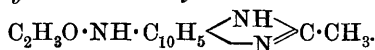
Picrates.—Hot alcoholic solutions of the base and of picric acid, when mixed and allowed to cool, deposit the picrate in the form of yellow, spherical nodules, a mode of crystallisation which is quite characteristic of this salt. After one crystallisation from alcohol, the salt was pure and had a softening point of about 228°, finally melting with decomposition at 236°.

0·0805 gave 13·3 c.c. moist nitrogen at 11·7° and 755·8 mm. N = 19·50.
 C₁₂H₁₁N₃,C₆H₃O₇N₃ requires N = 19·72 per cent.

An attempt to prepare the picrate of the isomeric base showed that no definite compound with picric acid exists. On mixing aqueous

solutions of the hydrochloride of the base and of ammonium picrate, an ochreous, granular precipitate was obtained. The product separates from a hot saturated alcoholic solution in the form of resinous spherules giving no definite results on analysis. The compound could not be crystallised from any solvent, and it is probable that picric acid acts as an oxidising agent towards the base giving rise to indefinite products of decomposition.

Acetyl Derivatives of the Isomeric Bases.



A comparison of the acetyl derivatives of the two bases has shown that they differ considerably in their properties. The process of acetylation employed by Markfeldt (*loc. cit.*) may be applicable to his base, but even in this case we find that the prolonged boiling with excess of acetic anhydride is quite unnecessary. With our own base, this method, as already stated in a former paper (Meldola and Phillips, *loc. cit.*, 1012), is extremely destructive. The chief difference between the acetyl derivatives is the distinctly acid character of that derived from our base (*loc. cit.*, 1013). The isomeride obtained from Markfeldt's base is not acid enough to dissolve in aqueous alkali; it dissolves only in alcoholic alkali, and on the whole is more distinctly basic than acid. The acetyl derivative of Markfeldt's base has been so thoroughly investigated by that author that we have not thought it necessary to make any further examination of it beyond a comparison of certain salts.

The acetyl derivative of our anhydro-base is so difficult to obtain in a state of purity that we have not yet succeeded in getting very satisfactory analytical results. The difficulty of purification is due to the circumstance that the compound is both acid and basic in character, so that it forms salts with both acids and bases. The purest specimen hitherto prepared was obtained by dissolving the crude acetyl derivative in dilute alcoholic ammonia and exactly neutralising the warm solution with acetic acid. The compound separates on cooling in small, glistening, white scales grouped in rosettes. The melting point is about 281—284° with decomposition, Markfeldt's acetyl derivative having a melting point "above 280°" (*loc. cit.*, 1177):*

0.1904 gave 0.4565 CO₂ and 0.0868 H₂O. C = 65.39; H = 5.07.

0.0859 ,, 12.25 c.c. moist nitrogen at 17.2° and 751.5 mm. N = 16.32.

C₁₄H₁₃ON₃·H₂O requires C = 65.37; H = 5.84; N = 16.34 per cent.

* A specimen prepared by us, after crystallisation from water melted at about 286°, but began to shrink from about 270°.

The compound does not lose weight when heated to 190° , and the water of crystallisation could not be driven off without the substance undergoing decomposition. Other preparations in which a slight excess of acetic acid had unintentionally been employed for neutralising the alkaline solution gave on analysis indefinite results indicating mixtures of acetate with free acetyl derivative.

The *hydrochloride*, $C_2H_3O \cdot NH \cdot C_{10}H_5 \left\langle \begin{array}{c} NH \\ \diagdown \quad \diagup \\ N \end{array} \right\rangle C \cdot CH_3, HCl, H_2O$, was prepared by dissolving the acetyl derivative in dilute hydrochloric acid, adding excess of strong hydrochloric acid, and allowing to crystallise. It separates in tufts of very small, white needles. A specimen dried at the ordinary temperature over lime in a desiccator was analysed with the following results :

0.1143 gave 14 c.c. moist nitrogen at 15.7° and 759.3 mm. $N = 14.27$
 0.1530 ,, 0.0745 AgCl. $Cl = 12.09$.

$C_{14}H_{13}ON_3, HCl, H_2O$ requires $N = 14.31$; $Cl = 12.10$ per cent.

The water is not expelled at 180° , the loss at this temperature being 3.16 per cent., and the salt undergoing partial decomposition with discoloration.

An attempt to form a *picrate* showed that the acetyl derivative does not form a definite compound with picric acid. Nothing separates on mixing alcoholic solutions of the acetyl derivative and picric acid, and the product, which is thrown out on dilution with water, on continued crystallisation followed by analysis, gave indications of being a mixture rather than a definite compound. It is possible that, as in the case of the original anhydro-base, picric acid acts as an oxidising agent.

Salts of the Acetyl Derivative of Markfeldt's Base.—For comparison with the foregoing, the hydrochloride and picrate have been prepared from Markfeldt's base.

The *hydrochloride*, $C_2H_3O \cdot NH \cdot C_{10}H_5 \left\langle \begin{array}{c} NH \\ \diagdown \quad \diagup \\ N \end{array} \right\rangle C \cdot CH_3, HCl, H_2O$, was prepared by dissolving the compound in dilute acid and then adding an equal volume of strong (fuming) acid. The salt crystallises in large, flat needles having a silvery lustre and becoming brownish on exposure to light and air. Analysis proved it to have the same composition as the isomeride.

0.1044 gave 13.15 c.c. moist nitrogen at 17.2° and 769.8 mm. $N = 14.78$,
 0.0970 ,, 0.0468 AgCl. $Cl = 11.94$.

$C_{14}H_{15}ON_3, HCl, H_2O$ requires $N = 14.31$; $Cl = 12.10$ per cent.

Heated at 165° , the salt becomes constant in weight and loses 5.53 per cent. of water. The whole of the water could not be expelled without decomposing the compound.

The *picrate* separates at once on mixing alcoholic solutions of the acetyl derivative and picric acid. It is a very definite compound consisting of slender, canary-yellow needles with a beautiful, silky lustre, melting with decomposition at 287°, and beginning to soften at 281°. The product used for analysis was purified by crystallisation from alcohol.

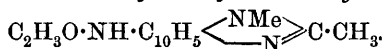
0.1380 gave 0.2610 CO₂ and 0.0448 H₂O. C = 51.58 ; H = 3.61.
 0.1160 „ 17.5 c.c. moist nitrogen at 14.4° and 760.8 mm. N = 17.71.
 C₁₄H₁₅ON₃, C₆H₃O₇N₃ requires C = 51.28 ; H = 3.42 ; N = 17.95 per cent.

Benzoyl Derivative of Markfeldt's Base.

This compound was prepared from the hydrochloride by the method described by one of the authors and Percy P. Phillips last year (*loc. cit.*, 1015). It differs from its isomeride in being more distinctly crystalline, separating from alcohol in the form of dense, ochreous needles melting with decomposition at 278—280°. It is less acid than its isomeride, being insoluble in aqueous alkali solutions.

With respect to the action of benzoyl chloride upon these aminoamidines, we may point out that if our view respecting the nature of the isomerism is correct, both compounds might be expected to yield 1 : 2 : 4-tribenzoyltriaminonaphthalene, C₁₀H₅(NH·CO·C₆H₅)₃, on treatment with this reagent in the presence of aqueous alkali, according to the well-known method of Schotten and Baumann. Experiments in this direction have been commenced, and will be resumed on some future occasion.

N-Methyl Derivative of Markfeldt's Acetyl Derivative,



The acetyl derivative forms a gelatinous silver compound (Meldola and Phillips, *loc. cit.*, 1013), which becomes coherent, but non-crystalline, on standing for some time at a temperature just below the boiling point of the alcoholic solution. As the silver salt was amorphous, no attempt was made to analyse it, but the dry product was digested with methyl iodide in methyl alcohol and treated in the same way as described in the former paper relating to the isomeric compound from our aminoamidine of 1887.

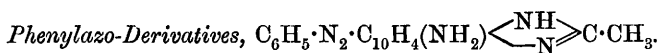
This methyl derivative does not differ in any marked property from its isomeride. It is strongly basic in character and but slightly soluble in hot water. A specimen crystallised from dilute alcohol separated in rosettes of ochreous scales shrinking at 250° and melting with decomposition at about 256°.

0·1323 gave 17·6 c.c. moist nitrogen at 17·6° and 752·2 mm. N = 15·21.
 $C_{15}H_{15}ON_3 \cdot H_2O$ requires N = 15·50 per cent.

It therefore has the same formula as the isomeric compound. In attempting to determine the water, it was found that decomposition occurs at 155—160°, the loss of weight at this temperature being considerably in excess of that required for 1 mol. H_2O , namely, 13·72 instead of 6·6 per cent.

As we had only a small quantity of this compound at our disposal, the remainder was converted into the picrate which separates at once on mixing alcoholic solutions of the base and of picric acid. After one crystallisation from alcohol, it consists of long, slender, silky, yellow needles which fuse and decompose at 273° and begin to shrink and soften at 265—270°.

0·0794 gave 11·8 c.c. moist nitrogen at 16° and 760·3 mm. N = 17·31.
 0·0602 „ 8·85 „ „ „ 16° „ 764·2 mm. N = 17·21.
 $C_{15}H_{15}ON_3 \cdot C_6H_3O_7N_3$ requires N = 17·43 per cent.



The first indication of the isomerism of the anhydro-bases was obtained on preparing a quantity of the phenylazo-derivative by the action of diazotised aniline upon the base in the presence of sodium acetate as described in the previous communication (*loc. cit.*, 1016). Some of Markfeldt's ethenyltriaminonaphthalene having been used for this purpose, it was found that the azo-compound was quite different in appearance and properties from that obtained last year. Instead of being violet and crystallising in bronzy scales almost insoluble in boiling alcohol, the new azo-derivative is red and fairly soluble in alcohol, crystallising from this solvent in brick-red, flat needles. If made to crystallise rapidly by stirring the solution on a watch glass, the small crystals appear bright red. By slow crystallisation from a large bulk of the solution, the compound separates in broad, scale-like needles which appear dull red with a slight metallic lustre when dry. It dissolves readily in toluene or chloroform with a fine red colour. Numerous analyses proved that this azo-derivative contains one mol. of water which can be expelled by heat or by crystallisation from a hydrocarbon with a high boiling point (toluene):

0·1986 gave 0·4928 CO_2 and 0·0981 H_2O . C = 67·67; H = 5·49.
 0·1846 „ 0·4593 CO_2 „ 0·0874 H_2O . C = 67·85; H = 5·26.
 0·0790 „ 14·35 c.c. moist nitrogen at 8·6° and 765·1 mm. N = 22·01.
 0·0776 „ 14·35 c.c. „ „ 9° „ 750·5 mm. N = 21·93.

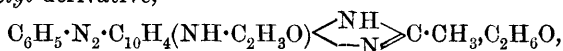
0.4070, dried at 140—150° until constant, lost 0.0241 H₂O. H₂O = 5.92. C₁₈H₁₅N₅·H₂O requires C = 67.71; H = 5.33; N = 21.94; H₂O = 5.64 per cent.

The anhydrous compound dried as above and another specimen crystallised from boiling toluene gave the following results :

0.1365 gave 0.3579 CO₂ and 0.0615 H₂O. C = 71.51; H = 5.01.
 0.2019 „ 0.5328 CO₂ „ 0.0909 H₂O. C = 71.97; H = 5.00.
 0.1899 „ 0.4976 CO₂ „ 0.0846 H₂O. C = 71.46; H = 4.95.
 0.1186 „ 23.1 c.c. moist nitrogen at 10.3° and 755.9 mm. N = 23.14.
 0.1264 „ 24.35 „ „ 8.1° „ 751.4 mm. N = 22.97.
 C₁₈H₁₅N₅ requires C = 71.76; H = 4.98; N = 23.26 per cent.

The azo-compound (hydrate) melts at 220—221°. It dissolves in alcoholic hydrochloric acid with a pale orange colour and a whitish hydrochloride separates out on standing. In alcoholic sodium hydroxide, the colour is not very different from that of the alcoholic solution, but more of an orange than red. When dissolved in glacial acetic acid and treated with sodium nitrite, an orange, crystalline substance is formed, which may be the acetoxy-derivative (Meldola and East, *Trans.*, 1888, 53, 464) resulting from the replacement of the amino-group. The examination of this product is, however, not yet completed and its study will be resumed.

The *acetyl* derivative,



is best prepared by heating the azo-compound with acetic anhydride for about an hour on the water-bath. At the boiling point of acetic anhydride, decomposition is apt to occur. The product crystallises from alcohol in dense oblong tablets of a bright orange colour. The crystals contain alcohol of crystallisation :

0.3313 gave 0.8213 CO₂ and 0.1689 H₂O. C = 67.61; H = 5.66.
 0.1092 „ 16.7 c.c. moist nitrogen at 14.6° and 765.5 mm. N = 18.05.
 0.1265 „ 19.2 „ „ 8.3° „ 750.9 mm. N = 18.06.
 0.1659, dried at 150—155° until constant, lost 0.0203 C₂H₆O. C₂H₆O = 12.24.

C₂₀H₁₇ON₅·C₂H₆O requires C = 67.87; H = 5.91; N = 17.99;
 C₂H₆O = 11.83 per cent.

The compound free from alcohol gave the following results :

0.1244 gave 0.3182 CO₂ and 0.0548 H₂O. C = 69.76; H = 4.89.
 0.1522 „ 25.85 c.c. moist nitrogen at 8.6° and 761 mm. N = 20.46.
 C₂₀H₁₇ON₅ requires C = 69.97; H = 4.96; N = 20.41 per cent.

The crystals of the acetyl derivative become opaque at 160—170°;

they darken at 240—250° and fuse with decomposition at about 253—254°. It is probable that decomposition begins much below the higher limit of temperature, as the loss on heating to determine the alcohol at 150—155° is over 1 per cent. in excess of that required by theory. Nitrogen is evolved, as already indicated, on boiling with acetic anhydride. The compound is completely reduced by zinc and hydrochloric acid in alcoholic solution, but the ethenyltetramino-naphthalene which might be expected to result is apparently very unstable and we have not yet succeeded in isolating it. With zinc dust and acetic acid in alcoholic solution, the acetyl derivative gives a hydrazo-compound crystallising in silvery scales and melting at about 245—250°, but this product requires further examination.

The isomeric phenylazo-derivative of our original anhydro-base has already been partially described (Meldola and Phillips, *loc. cit.*, 1016), and we are now enabled to give further details concerning this compound. The product crystallised from amyl alcohol or from a mixture of aniline and toluene contains, like its isomeride, 1 mol. of water :

0.0852	gave	0.2108	CO ₂	and	0.04	H ₂ O.	C = 67.48 ;	H = 5.21.	
0.2114	„	0.5267	CO ₂	„	0.0935	H ₂ O.	C = 67.95 ;	H = 4.91.	
0.0963	„	18.75	c.c. moist nitrogen	at	23.2°	and	763	mm. N = 21.98.	
0.0884	„	16.85	c.c.	„	„	15.6°	„	749.3	mm. N = 21.92.
C ₁₈ H ₁₅ N ₅ .H ₂ O requires C = 67.71 ; H = 5.33 ; N = 21.94 per cent.									

The water in this azo-compound is not expelled so readily as that of the isomeride. At 150°, the loss is only about 0.5 per cent., but at 200—210° is greater than that required by theory, showing that decomposition occurs at the higher temperature.

The azo-compound is much less soluble in all solvents than the isomeride from Markfeldt's base. The solutions are dull red. It crystallises from amyl alcohol in dull, bronzy scales, and from aniline in dark violet needles with a dull, bronzy lustre. The melting point, as already stated, is between 257° and 260° with decomposition. The compound dissolves in strong sulphuric acid with an orange colour becoming red on dilution with water. In alcoholic hydrochloric acid, the colour is bright reddish-violet, the hydrochloride separating in small, bronzy needles on allowing the solution to stand. This property distinguishes the two isomeric compounds sharply from one another, the azo-derivative of Markfeldt's base dissolving in alcoholic hydrochloric acid with a pale orange colour and depositing a whitish hydrochloride on standing.

The *hydrochloride* of the azo-compound from our anhydro-base, prepared as above, has the composition C₁₈H₁₅N₅.HCl.H₂O, as shown by the following analyses :

0·1201 gave 20 c.c. moist nitrogen at 14·3° and 764·7 mm. N = 19·66.
 0·0682 „ 11·45 „ „ 12·5° „ 758·5 mm. N = 19·82.
 0·1297 „ 0·0520 AgCl. Cl = 9·92.
 $C_{18}H_{15}N_5, HCl, H_2O$ requires N = 19·69 ; Cl = 9·99 per cent.

The azo-compound can be acetylated in the same way as the isomeride, and gives an acetyl derivative which crystallises from alcohol in dense scales of a brown colour with glistening facets. The decomposing point is about 252°, and the compound begins to darken about 240°. Like its isomeride, it retains alcohol of crystallisation :

0·1166 gave 17·5 c.c. moist nitrogen at 12·2° and 772·3 mm. N = 18·07.
 0·1253 „ 19 „ „ 16° „ 765·2 mm. N = 17·78.
 0·1033, dried in water-oven and then at 140—150°, lost 0·0114 C_2H_6O .
 $C_2H_6O = 11·04$.
 $C_{20}H_{17}ON_5, C_2H_6O$ requires N = 17·99 ; $C_2H_6O = 11·83$ per cent.

The alcohol is thus not quite expelled at this temperature, and as at higher temperatures the compound showed signs of decomposing, the product was taken as free from alcohol and analysed :

0·0771 gave 13·6 c.c. moist nitrogen at 19° and 756·9 mm. N = 20·17.
 $C_{20}H_{17}ON_5$ requires N = 20·41 per cent.

The acetyl derivative is much less soluble than its isomeride, and could only be obtained in a satisfactory state of purity by crystallisation from ethyl alcohol, a very large volume of which is required. The acetylation of the azo-compound is best carried out by dissolving in glacial acetic acid and adding acetic anhydride to the solution. On warming on the water-bath, the violet colour of the solution changes to orange when the acetylation is complete. Boiling with acetic anhydride causes decomposition with the evolution of nitrogen and the formation of resinous products.

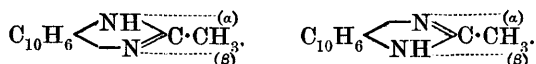
p-Nitrophenylazo-derivative.

Diazotised *p*-nitraniline combines readily with the aminoamidines, and a preliminary examination of the nitroazo-compound obtained from our original anhydro-base was made two years ago, but the investigation was interrupted in order to study the simpler phenylazo-compounds described in the present paper. The introduction of the nitro-group into the molecule modifies the properties of the compound by rendering it less stable, and the nitroazo-derivative appears to be decomposable by alkali with the formation of definite products. As this decomposition is likely to be of interest, we may place upon record the results thus far obtained, reserving for future investigation the nature of the products of the action of alkali upon the azo-compound.

On mixing solutions of diazotised *p*-nitraniline and the anhydro-base in the presence of sodium acetate in the usual way, the acetate of the nitroazo-compound separates as a dark violet, gelatinous precipitate, which dries to a bronzy powder. The compound has only been investigated qualitatively, as its insolubility has rendered it very difficult to obtain in a state of purity. It is distinctly acid in character, dissolving in aqueous and alcoholic sodium hydroxide with a magenta-red colour. It dissolves with a red colour in alcoholic hydrochloric acid, and to a slight extent in boiling fusel oil, nitrobenzene, or aniline. The colour of the solution in the last three solvents is indigo-blue, and it separates from nitrobenzene in small, coppery scales. The nitro-group is reducible by ammonium sulphide without the fission of the azo-group (Meldola, *Trans.*, 1883, 43, 425).

Constitution of the Anhydro-bases and their Azo-derivatives.

The constitution of the azo-derivatives cannot be definitely established until the nature of the isomerism of the anhydro-bases has been ascertained. On the view of the isomerism suggested at the commencement of this paper, the two bases should yield isomeric ethenyldiaminonaphthalenes on replacing the NH_2 group by hydrogen :



It is possible, however, that one or the other of these isomerides is too unstable to exist, and becomes transformed by desmotropic change into the more stable form. This would appear to be the case if the ethenyldiaminonaphthalene of Prager (*Ber.*, 1885, 18, 2161) is identical with that of Liebermann and Jacobson (*Annalen*, 1882, 211, 67), and Fischer and Hepp (*Ber.*, 1887, 20, 1249, 1272). In the first method of preparation (Prager), the reducible nitro-group is in the β_1 -position, whilst in the second method (Liebermann and Jacobson), the nitro-group is in the α_1 -position. It appears, however, that the anhydro-bases obtained by the two methods are identical (Beilstein, *Handbuch*, 3, 992), and, if so, it is most probable that the compound is susceptible of desmotropic change. It will be necessary to re-investigate this subject from the point of view of the discovery of the specific action of the reducing agent upon the nature of the product of reduction as made known in the present paper, and this subject will be taken in hand as soon as possible. A preliminary experiment may be described here, which appears to show that the replacement of the NH_2 group in Markfeldt's base gives rise to the same ethenyldiaminonaphthalene as that already investigated by Prager, &c. Some of Markfeldt's base was diazotised with sodium nitrite in a fairly strong sulphuric acid solution, and then treated with a large excess of abso-

lute alcohol in the usual way. The tarry product obtained after distilling off the alcohol was extracted with dilute sodium hydroxide solution, which dissolves out the amidine by virtue of the acid character of the NH group. The solution, on the addition of excess of hydrochloric acid, deposited a crystalline hydrochloride consisting of white needles, which were collected and purified further by a repetition of the same treatment. The product, washed with water and dried under a desiccator over lime, had the composition of a monohydrochloride :

0.110 gave 12.45 c.c. moist nitrogen at 18° and 751.4 mm. N = 12.91.

$C_{12}H_{10}N_2 \cdot HCl$ requires N = 12.81 per cent.

The picrate, formed by mixing aqueous solutions of the hydrochloride and ammonium picrate, was obtained, after two crystallisations from alcohol, in the form of silky, orange-yellow needles :

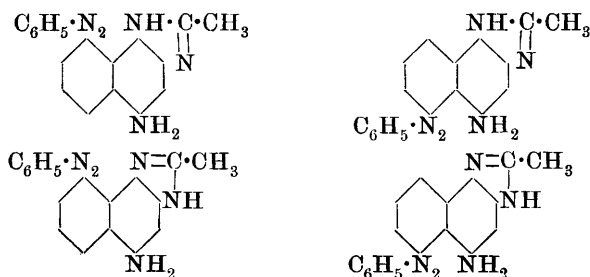
0.0968 gave 13.85 c.c. moist nitrogen at 13.6° and 764.3 mm. N = 16.94.

$C_{12}H_{10}N_2 \cdot C_6H_3O_7N_3$ requires N = 17.03 per cent.

The melting point was 244°, the compound decomposing at about 255°. The melting point assigned to the picrate of Prager's base by Lellmann and Remy (*Ber.*, 1886, 19, 801) is 242°, so that the identity of our base with that of Prager appears to be established.

In view of possible desmotropy, it is still undecided whether in this amidine the NH group is in the α - or β -position, hence the constitution of the base, so far as concerns the amidine ring, is open for investigation, and we give the above result simply as a preliminary step. The corresponding ethenyldiaminonaphthalene from our own anhydro-base will be prepared and described in a future communication.

Apart from the question of the configuration of the amidine ring, the position of the azo-group in the isomeric azo-compounds has yet to be determined. As the bases from which these compounds are derived are homonucleal tri-derivatives of naphthalene, it is most probable that the azo-derivatives are heteronucleal, the α_5 - or α_8 -hydrogen atoms being in the most likely positions for substitution. On this view, the isomerism might be ascribed to such constitutional differences as the following :



Attempts to solve this problem experimentally have already been made, and the research will be continued in this direction. So far as the results go at present, we have only to state that each phenylazo-compound appears to be homogeneous, and not to consist of a mixture of isomerides. The constitution of the aminoamidine thus determines with absolute sharpness the position entered by the azo-group.

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