CCLXXX.—N-*Methyl Derivatives of 2-Phenylnaphthylene*-1 : 3-*diamine*.

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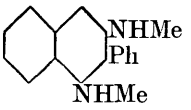
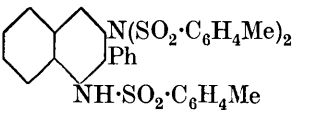
IT was observed by Lees and Thorpe (J., 1907, **91**, 1296) that when 2-phenylnaphthylene-1 : 3-diamine is methylated two isomeric dimethyl derivatives (I) are obtained, the particular isomeride formed depending on the conditions of methylation. Since these two methylated bases, being di-secondary amines, could not be structurally different, the nature of the isomerism remained unexplained at the time. With the kind permission and encouragement of Professor J. F. Thorpe, we have attempted the elucidation of this problem.

(I.) 



(II.)

We have confirmed in almost all particulars the work of Lees and Thorpe; we have been successful in elaborating somewhat more convenient methods for the preparation of the two bases, more especially of the β-base, and we have also succeeded, although indirectly, in converting the α-base into the β-base. The α-base, which is dimorphic, is formed when the diamine is treated with methyl sulphate in the presence of alkali (see p. 2136) and, by a slight modification of the original method, we have greatly increased the yield of the base. At the same time, a not inconsiderable amount of the tetramethyldiamine is produced together with a small quantity of the trimethyldiamine.

Lees and Thorpe prepared the β-base by heating the parent diamine with an excess of methyl sulphate, but the base is not readily obtained pure by this method and the yield varies considerably with small changes in the temperature of heating. When the reaction is carried out at 94° the β-dimethyldiamine and the trimethyldiamine are produced in approximately equal quantities, and the best yield of the former substance is obtained at 90°. The β-dimethyldiamine is, however, best obtained in a state of purity by the following method in which the formation of higher methylated products is avoided.

Di-p-*toluenesulphonyl*-2-*phenylnaphthylene*-1 : 3-*diamine* is very readily prepared by the action of *p*-toluenesulphonyl chloride on the original diamine in pyridine solution. The products of this reaction have been exhaustively examined, since it was of interest to determine whether isomeric di-substitution products are also

formed in this case. The main product of the reaction is a substance, *α-di-*p-*toluenesulphonyl-2-phenylnaphthylene-*1 : 3-*diamine*, which is soluble in alkali and, like the α-dimethyldiamine, is dimorphic, the two forms having m. p. 188—189° and 203—205°, respectively. The lower-melting form, which has been designated α_1-, is obtained when the sulphonamide is precipitated from alkaline solution by acidification or when it is recrystallised from ethyl alcohol in such strength that crystallisation does not take place until the ordinary temperature is reached. When the lower-melting form is melted in a capillary tube and allowed to resolidify, it undergoes conversion into the higher-melting form. The α-, or stable, form of the disulphonamide separates when crystallisation takes place from a hot solution. Both forms crystallise in prisms and the dimorphic relationship was confirmed by Sidgwick's method (J., 1915, **107**, 672).

The alcoholic mother-liquor from which the α-disulphonamide had been removed contained a second disulphonamide, which, after repeated crystallisation from methyl alcohol, was obtained in soft needles, m. p. 173—175°. This substance was only obtained in sufficient quantity for analysis, but in all probability it is β-*di*-p-*toluenesulphonyl*-2-*phenylnaphthylene*-1 : 3-*diamine* corresponding to the β-form of the dimethyl base.

In addition to the α- and β-disulphonamides, which are soluble in alkali, two other substances were isolated from this reaction. One of these, having m. p. about 213°, was not obtained crystalline and therefore was not analysed. Since, however, it gave the original diamine on hydrolysis, it was probably the tetrasulphonyl derivative. The other crystallised from methyl alcohol in needles, m. p. 153—154°, and proved to be a *trisulphonyl* derivative, probably having the constitution (II).

The α-disulphonamide is readily methylated by methyl sulphate in the presence of alkali, yielding NN′-*dimethyldi*-p-*toluenesulphonyl*-2-*phenylnaphthylene*-1 : 3-*diamine*, which, on hydrolysis, yields the β-dimethyldiamine in theoretical amount. This is the most convenient method for preparing the pure β-base in quantity.

The important investigations by Kenner and his collaborators (J., 1922, **121**, 614 and subsequent papers) on the resolution of substituted diphenylcarboxylic acids have shown that, whilst the molecular asymmetry necessitates the impossibility of free rotation of the two benzene nuclei, the formula suggested by Kaufler to account for certain supposed cases of isomerism is unnecessary (compare Le Fèvre and Turner, J., 1926, 2476). It is significant that molecular asymmetry has been realised only in diphenyl derivatives which have at least three of the four positions

(2 : 2′ : 6 : 6′) substituted and it appears that the substituents should be large (*e.g.*, Cl, NO_2, CO_2H). An adequate explanation of this has been suggested by Mills (*Chem. and Ind.*, 1926, **45**, 883, 905) on a purely mechanical basis (compare Turner and Le Fèvre, *ibid.*, p. 831).

From formula (I), it is clear that in the two *NN′*-dimethyl derivatives of 2-phenylnaphthylene-1 : 3-diamine we have substituted derivatives of diphenyl each with all the substituents in one nucleus. It was found on preparing a model, using ordinary atomic diameters as indicated by Mills (*loc. cit.*), that free rotation of the unsubstituted phenyl group in the dimethyl base is prevented owing to interlocking if all the nuclei and the substituent groups are co-planar. In the light of Mills's suggestion, therefore, it seemed not improbable that one or both forms of this base should be resolvable into optically active forms.

The salts of both α- and β-*NN′*-dimethyl-2-phenylnaphthylene-1 : 3-diamine with optically active acids did not prove satisfactory for the purpose and no evidence of resolution of either of the bases was obtained. We therefore investigated the methylenecamphor derivatives prepared by condensation of each of the two bases with *d*-hydroxymethylenecamphor—a method which, in the hands of Pope and his collaborators (Pope and Read, J., 1913, **103**, 1516; Kipping and Pope, J., 1926, 494), has proved of great value for the optical resolution of primary and secondary amines.

The α-base, when treated with *d*-hydroxymethylenecamphor, gave a quantitative yield of α-NN′-*dimethyl*-2-*phenylnaphthylene*-1 : 3-*diaminomono*-d-*methylenecamphor*, only one of the secondary amino-groups reacting. This substance, which crystallised well, was perfectly homogeneous and there was no sign of the formation of optical isomerides. The remaining secondary amino-group is singularly unreactive and cannot be acetylated by acetic anhydride. This abnormal behaviour of the α-dimethyldiamine is exhibited in other reactions, since it only yields a *monoacetyl* and a *mono*-p-*toluenesulphonyl* derivative.

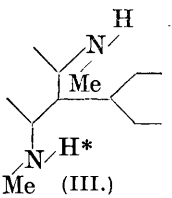
Similar interaction of the β-base with *d*-hydroxymethylenecamphor resulted in the formation of a very sparingly soluble *dimethylenecamphor* derivative, which, like the mono-derivative of the α-base, showed no signs of heterogeneity. The difference in reactivity of the α- and β-bases was further exemplified by the β-base readily yielding a diacetyl derivative and the disulphonamide (m. p. 305°) referred to above.

Although the possibility of the resolvability of the α- and β-dimethyldiamines (compare Gibson and Simonsen, J., 1915, **107**, 115) is not excluded, the facts so far established are adequately explained

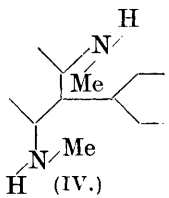
by assuming *cis-trans* isomerism of the two bases. This being so, the conversion of the one form into the other should be possible. We have succeeded in converting the α-form into the β-form by an indirect method.

Lees and Thorpe showed that both bases yielded dinitrosoamines on treatment with nitrous acid, the formation taking place very slowly from the α-base (*loc. cit.*, p. 1286) and immediately from the β-base. According to these authors (pp. 1298, 1299) the dinitrosoamine prepared from the α-base has m. p. 174—175°, that from the β-base, m. p. 179°; we have now found that these two dinitrosoamines are identical and, when carefully purified, both have m. p. 180—181°. This identity was confirmed by the method of Sidgwick. When the dinitrosoamine prepared from either of the bases is reduced with tin and hydrochloric acid, it gives a quantitative yield of the β-dimethyldiamine, and it follows, therefore, that it is the dinitrosoamine of the β-base. This explains the retarded separation of the dinitrosoamine when prepared from the α-base, the course of the change probably being the conversion of the mononitrosoamine of the α-base, which is obviously the first product of the reaction, into the mononitrosoamine of the β-base, followed by formation of the dinitrosoamine. This is in complete accord with the facts that the α-base only yields monoacetyl, mono-*p*-toluenesulphonyl, and monomethylenecamphor derivatives.

The conversion of the α-dimethyldiamine into the β-dimethyldiamine by the nitrosoamine reaction strongly supports the view that these two bases are *cis-trans*-isomerides of a type not previously observed. There would appear to be four possible formulæ (partly represented by III—VI) for these bases on the assumption that the rings and nitrogen atoms with attached groups are co-planar.



(III.)



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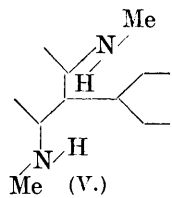

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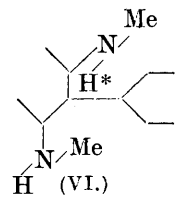


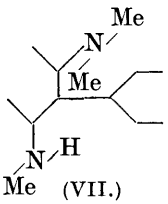
(VI.)

There can be little doubt that the β-dimethyldiamine must be represented by the *trans*-form (IV), since both the hydrogen atoms of the secondary amino-groups are highly reactive. It is further clear that (V) cannot represent the α-dimethyldiamine, since in it both hydrogen atoms might be expected to be subject to steric hindrance. We have no means of distinguishing between the formulæ (III) and (VI), in each of which one of the hydrogen atoms,

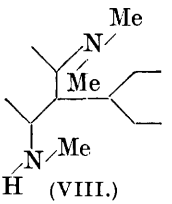
H*, would appear to be likely to be affected by steric hindrance; but we prefer (III), since the base is more reactive than would be anticipated if the hydrogen were in the 1-position in the naphthalene nucleus.

Pending further investigation of related compounds, the suggested uniplanar configuration of the two *NN'*-dimethyldiamines adequately explains their *cis-trans* isomerism. The evidence so far accumulated lends additional support to the generally accepted view that the valencies of a tervalent nitrogen atom lie in one plane.

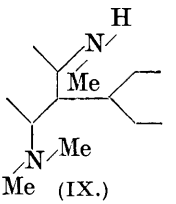
Lees and Thorpe (*loc. cit.*, p. 1299) described a trimethyldiamine, and we have obtained this base in a somewhat higher state of purity (see p. 2139). It can obviously be represented by partial formulæ (VII—X).



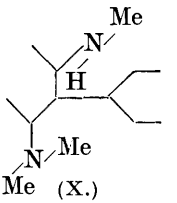
(VII.)



(VIII.)



(IX.)



(X.)

Since this base can be acetylated readily and is also formed by the direct methylation of the β-dimethyldiamine, we consider that it is most probably represented by (VIII). We had hoped to prepare one of the other possible trimethyl bases by the methylation of the α-dimethyldiamine or its *p*-toluenesulphonyl derivative, but in this we were not successful. In alkaline solution the diamine is not methylated, and it is converted into the tetramethyl base by methyl sulphate at 110°. The *p*-toluenesulphonyl derivative was very resistant and was not attacked by methyl sulphate at 145°; above this temperature sulphur dioxide was evolved and decomposition commenced.

EXPERIMENTAL.

2-Phenylnaphthylene-1 : 3-diamine was prepared by the method of Lees and Thorpe (*loc. cit.*, p. 1287). We found it advantageous to interrupt the steam distillation as soon as the xylene had passed over, the excess of nitrile being allowed to remain in the distillation flask. The yield of the base was approximately 50% and after crystallising six times from alcohol and once from light petroleum it had m. p. 113·5° (Lees and Thorpe give 116°). The acetyl acetate, prepared by boiling the base with acetic anhydride containing a trace of pyridine, crystallised from alcohol in prisms, m. p. 175°. The m. p. 185° given by Atkinson and Thorpe (J., 1906, **89**, 1935) is possibly a misprint (Found: C, 71·3; H, 5·8. Calc.: C, 71·4; H, 5·9%).

α-NN′-*Dimethyl*-2-*phenylnaphthylene*-1 : 3-*diamine*.—The yield of the methylated base was somewhat improved by the following modification of Lees and Thorpe's method. The base (15 g.) was dissolved in methyl alcohol (200 c.c.) and after the addition of methyl sulphate (150 g.) potassium hydroxide solution (600 c.c.; 25%) was added gradually, the temperature being kept below 5° and the mixture mechanically stirred. The crude granular methylation product was dried and boiled with methyl alcohol (50 c.c.), which dissolved the bulk of the impurities. The residue after two crystallisations from light petroleum (b. p. 80—100°) had m. p. 168° (yield, 30%).

As shown by Lees and Thorpe, the base is dimorphic, being obtained either in needles or in prisms according to the conditions of crystallisation. The long needles are obtained most readily if either an alcoholic or light petroleum solution of the base be allowed to crystallise at 30°. If such a solution is allowed to crystallise in the ice-chest, the prism form separates. At 17° the colourless needles become yellow and opaque and are seen under the microscope to be pseudomorphs composed of minute prisms. These gradually pass into large yellow prisms. Both forms have m. p. 170°.

The methyl alcoholic and light petroleum solutions from which the α-base had been obtained gave on removal of the solvents a somewhat gummy residue. This was repeatedly crystallised from alcohol and large colourless prisms were ultimately obtained, m. p. 122° (yield, 35%). This substance was identified as the tetramethyl derivative of the diamine by analysis (Found : N, 9·7. Calc. : N, 9·6%), by the method of mixed m. p., and by conversion into the nitroso-derivative, m. p. 135°.

In another experiment the solid from the mother-liquor was dissolved in hydrochloric acid and treated with sodium nitrite solution. A portion of the nitrosoamines formed was soluble in acid and was identified as the nitrosoamine of the trimethyldiamine (yield, 6%). The crude insoluble nitrosoamine, on reduction with tin and hydrochloric acid, gave, in addition to a resin which was insoluble in acids, a quantity of β-*NN′*-dimethyl-2-phenylnaphthylene-1 : 3-diamine. This was best purified by distillation in superheated steam (yield, 25%).

Methylation of α-NN′-*Dimethyl*-2-*phenylnaphthylene*-1 : 3-*diamine*.—When the α-base was heated for 1 hour at 100° or 115° with an excess of freshly distilled methyl sulphate, the mixture gradually became solid and yielded the tetramethyldiamine, m. p. 122°, in a theoretical yield. The diamine could not be further methylated by treatment with methyl sulphate in alkaline solution.

Monoacetyl-α-NN′-*dimethyl*-2-*phenylnaphthylene*-1 : 3-*diamine* was

obtained when the α-base was digested for some hours with acetic anhydride. It crystallised from alcohol in iridescent prisms, m. p. 203° (Found : N, 9·3. $C_{20}H_{22}ON_2$ requires N, 9·2%).

p-*Toluenesulphonyl*-α-NN′-*dimethyl*-2-*phenylnaphthylene*-1 : 3-*diamine*.—A solution of the base (2 g.) and *p*-toluenesulphonyl chloride (5 g.) in pyridine (15 c.c.) was heated on the water-bath for 4 hours, and poured into water. The white solid (3·2 g.) obtained crystallised from alcohol, in which it was somewhat sparingly soluble, in needles, m. p. 219—220° (Found : C, 72·2; H, 5·8. $C_{25}H_{24}O_2N_2S$ requires C, 72·2; H, 5·8%). The *monosulphonamide* was soluble in concentrated hydrochloric acid, and when hydrolysed with a mixture of acetic and sulphuric acids the original α-base was regenerated. It could not be acetylated or methylated, being unaffected by methyl sulphate at 145°.

α-NN′-*Dimethyl*-2-*phenylnaphthylene*-1 : 3-*diaminomono*-d-*methylenecamphor*.—The α-base (2·6 g.) was dissolved in a mixture of alcohol (140 c.c.) and acetic acid (25 c.c.) and after the addition of *d*-hydroxymethylenecamphor (5·4 g.) in alcohol (15 c.c.) the mixture was heated on the water-bath for 30 minutes. On cooling and dilution with water a crystalline solid (2·7 g.), m. p. 168°, separated and a further quantity (1·7 g.) was obtained from the mother-liquor after treatment with alkali to remove the excess of *d*-hydroxymethylenecamphor. The product, which was quite homogeneous, crystallised from methyl alcohol, in which it was somewhat readily soluble, in colourless prisms, m. p. 167—168°. It depressed the m. p. of the original α-base (Found : N, 6·7. $C_{29}H_{32}ON_2$ requires N, 6·6%*). In alcohol at 20° ($c = 0{\cdot}2484$, $l = 4$), it gave $\alpha_{5461} = +4{\cdot}04°$, whence $[\alpha]_{5461} = +406{\cdot}5°$.

Attempts to prepare an acetyl derivative by treatment with acetic anhydride were unsuccessful.

The salt which formed when equivalent quantities of α-*NN′*-dimethyl-2-phenylnaphthylene-1 : 3-diamine and *d*-camphor-10-sulphonic acid were mixed in hot aqueous alcohol and the mixture allowed to cool separated in glistening prisms and was homogeneous.

The α-base (3·5 g.) was added to a hot solution of *d*-α-bromocamphor-π-sulphonic acid (8·52 g.) in water (445 c.c.), and alcohol (30 c.c.) added to give a clear solution. A voluminous mass of fine needles separated and after 2 days changed to yellow prisms of the α-base, which were optically inactive. The filtrate, on evaporation to dryness in a vacuum over sulphuric acid, gave a deep red resin which slowly crystallised in nodules on being kept in acetone–ethyl

* We are indebted to Mr. A. Bennett, of the Microanalytical Laboratory, University of Manchester, for the microanalyses of this compound and of the dimethylenecamphor compound described on p. 2140.

acetate. The salt, which appeared to be homogeneous, could not be recrystallised, since it was insoluble in acetone, ethyl acetate, benzene, and light petroleum. It was readily soluble in water or alcohol but underwent hydrolysis in these solvents.

β-NN'-*Dimethyl*-2-*phenylnaphthylene*-1 : 3-*diamine*.—(1) The base (10 g.), heated with methyl sulphate (65 g.) at 100° for 2 hours, gave a solid which had m. p. 93° after crystallisation from alcohol and was evidently a mixture. When the reaction was carried out at 115—120°, an almost theoretical yield of the tetramethyldiamine, m. p. 122°, was obtained and this was characterised by conversion into the nitroso-derivative, m. p. 136°. A series of experiments was carried out at temperatures between 90° and 100°, since it was found that below 90° the product contained much unchanged primary amine. At 90°, the dimethyl derivative was the main product. It was found possible to estimate fairly accurately the percentages of dimethyl and trimethyl derivatives in the product by treatment with nitrous acid, since the mononitrosoamine of the trimethyl base was soluble in mineral acids, and the dinitrosoamine of the dimethyl base insoluble. The results are in the following table, 2 g. of the crude methylation product being used in each case.

Temp. of methylation.	Dinitroso-amine.	Mononitroso-amine.	% Me_2.	% Me_3.
90°	2·12 g.	0·24 g.	87	11
94	1·20	1·11	49	50
100	0·73	1·55	30	70

(2) The β-base was prepared in quantity by the methylation of *di*-p-*toluenesulphonyl*-2-*phenylnaphthylene*-1 : 3-*diamine*, followed by hydrolysis. A solution of the diamine (50 g.) and *p*-toluenesulphonyl chloride (150 g.) in pyridine (400 c.c.) was heated on the water-bath for 4 hours and poured into water. The thick brown oil obtained was washed with dilute hydrochloric acid to remove pyridine and heated on the water-bath for 30 minutes with sodium carbonate solution to remove the excess of acid chloride; the remainder solidified on cooling and then had m. p. 175—183° (yield, 114 g.). It was best purified by solution in sodium hydroxide (10%), which left undissolved a small quantity of a red solid (*A*). When the filtrate was acidified the sulphonamide was deposited as an almost colourless, crystalline powder. It was recrystallised from alcohol, α-*di*-p-*toluenesulphonyl*-2-*phenylnaphthylene*-1 : 3-*diamine* being obtained pure; the mother-liquor contained a small quantity of a second substance (see below).

The sulphonamide was dimorphic. When crystallised from methyl alcohol, the α-form separated in fine glistening prisms, m. p. 203—205°, and the same form resulted if the amide was allowed to

separate from a *hot* solution in either alcohol or acetic acid. If this form was crystallised from a dilute solution in alcohol, so that deposition took place in the cold, prisms were also obtained which had, however, m. p. 188—189°, rapidly resolidified, and then melted at 203—205°. This low-melting α_1-form was also obtained when an alkaline solution of the sulphonamide was acidified (Found : for α, C, 66·4; H, 4·9; for α_1, S, 12·0. $C_{30}H_{26}O_4N_2S_2$ requires C, 66·4; H, 4·8; S, 11·8%). The sulphonamide was somewhat sparingly soluble in alcohol, benzene, and acetic acid and insoluble in water and light petroleum. The dimorphic relationship of these two forms was established by Sidgwick's method (*loc. cit.*) with benzene as the solvent, the following depressions being observed :

Depression of f. p. by	α_1 alone	0·086°
,, ,, ,,	α ,,	0·025
,, ,, ,,	$\alpha + \alpha_1$	0·029

The original mother-liquor from the first crystallisation of the sulphonamide contained a small quantity of a second substance which, after repeated crystallisation from methyl alcohol, in which it was somewhat readily soluble, was obtained in soft needles, m. p. 173—175°. It is possible that this m. p. is not quite accurate, since the amount of material available for purification was small (Found : C, 66·8; H, 4·9. $C_{30}H_{26}O_4N_2S_2$ requires C, 66·4; H, 4·8%). *β-Di-p-toluenesulphonyl-2-phenylnaphthylene-1 : 3-diamine* is much more readily soluble in the ordinary organic solvents than either of the α-forms and when mixed with these causes a marked depression in m. p.

The solid (*A*) (see above), which was insoluble in alkali, dissolved in hot alcohol, yielding a deep red solution from which a brown amorphous solid, m. p. about 213°, was slowly deposited. This product could not be obtained pure enough for analysis, but was probably the tetrasulphonyl derivative of the diamine, since on hydrolysis with a mixture of acetic and sulphuric acids it gave the original base. The deep red mother-liquor on concentration yielded a small quantity of a crystalline solid, which after repeated crystallisation from methyl alcohol was obtained in fine, colourless needles, m. p. 153—154°. Analysis showed this to be *tri-p-toluenesulphonyl-2-phenylnaphthylene-1 : 3-diamine* (II) (Found : C, 63·7; H, 4·6. $C_{37}H_{32}O_6N_2S_3$ requires C, 63·8; H, 4·6%).

Di-p-toluenesulphonyl-NN'-dimethyl-2-phenylnaphthylene-1 : 3-diamine.—The α-disulphonamide (50 g.) was dissolved in sodium hydroxide solution (270 c.c.; 10%) and methyl sulphate (200 c.c.) was added gradually with constant agitation, the solution being kept alkaline. An oil separated which rapidly solidified (53 g.); it

crystallised from pyridine in small plates, m. p. 305° (Found : C, 67·5; H, 5·3. $C_{32}H_{30}O_4N_2S_2$ requires C, 67·3; H, 5·3%). The methyl derivative was very sparingly soluble in all the ordinary organic solvents.

*Hydrolysis of Di-*p*-toluenesulphonyl-*NN*′-dimethyl-2-phenylnaphthylene-*1 : 3*-diamine.*—The amide (100 g.) was dissolved in a mixture of acetic acid (100 c.c.) and sulphuric acid (200 c.c.) and heated on the water-bath for 2 hours. The clear brown solution was poured on ice and made alkaline with ammonia. An oil separated which rapidly solidified (yield, 46 g.); after crystallisation from alcohol it had m. p. 159—160° and was pure β-*NN*′-dimethyl-2-phenylnaphthylene-1 : 3-diamine. When this base was treated with *p*-toluenesulphonyl chloride in pyridine solution, it was reconverted into the above-mentioned sulphonamide, m. p. 305°. On treatment with methyl sulphate at 100° it was converted quantitatively into the tetramethyl base, m. p. 122°, and in alkaline solution it was partly converted into the trimethyldiamine, which was identified by the preparation of the nitrosoamine.

*Diacetyl-*β*-NN′-dimethyl-2-phenylnaphthylene-*1 : 3*-diamine.*—The β-base was boiled for 2 hours with acetic anhydride, and after removal of the excess of the anhydride by evaporation with alcohol the *acetyl* derivative was recrystallised from dilute methyl alcohol or benzene and obtained in rosettes of small prisms, m. p. 207—208° (Found : N, 8·2. $C_{22}H_{22}O_2N_2$ requires N, 8·1%).

β-*NN′-Dimethyl-2-phenylnaphthylene-*1 : 3*-diaminodi-*d*-methylenecamphor.*—The β-base (2·6 g.) was dissolved in a mixture of alcohol (75 c.c.) and acetic acid (20 c.c.; 50%) and after the addition of *d*-hydroxymethylenecamphor (5·4 g.) in alcohol (15 c.c.) the mixture was heated on the water-bath for 30 minutes. On cooling in the ice-chest over-night, a hard, crystalline cake (4·25 g.), m. p. 274—277°, had separated. By evaporation of the filtrate and removal of the excess of *d*-hydroxymethylenecamphor with alkali a further quantity (1·6 g.) was obtained. It crystallised from alcohol in nodules of colourless prisms, m. p. 277—279° (Found : N, 5·2. $C_{40}H_{46}O_2N_2$ requires N, 4·8%). In alcohol at 20° ($c = 0·2142$, $l = 4$), it gave $\alpha_{5461} = +5·57°$, whence $[\alpha]_{5461} = +650·1°$.

The β-base (2 g.) was added to a hot solution of *d*-camphor-10-sulphonic acid (3·54 g.) in water (7 c.c.). On cooling, the viscid, red solution deposited a mass of fine needles. This salt dissolved in its own water of crystallisation at 105° and was very readily soluble in water, acetone, and alcohol, less soluble in ethyl acetate. The salt and the mother-liquor were separately made alkaline; the base recovered was in each case optically inactive.

The β-base (2 g.), when added to a hot solution of *d*-β-bromo-

camphor-π-sulphonic acid (4·74 g.) in water (25 c.c.), slowly dissolved, giving a reddish-brown solution which deposited an oil on stirring. On cooling, the oil redissolved, but there was no separation of crystals. The solvent was evaporated in a vacuum and the residual resin, which was readily soluble in acetone, crystallised slowly from a solution in ethyl acetate. It was recrystallised from acetone–ethyl acetate, from which it was deposited in nodules. The bases recovered from the crystalline salt and from the mother-liquor were inactive.

The Dinitrosoamines of α- *and* β-NN′-*Dimethyl*-2-*phenylnaphthylene*-1 : 3-*diamines.*—α-*Base.* The dinitrosoamine was prepared as described by Lees and Thorpe (*loc. cit.*, p. 1297) and obtained in a yield of 85%. After recrystallisation from alcohol and then from benzene, it was obtained in clusters of yellow needles, m. p. 180°.

β-*Base.* The dinitrosoamine was obtained from the β-base in a somewhat better yield (95%). The final crystallisation was from benzene. It had m. p. 180—181°.

These two dinitrosoamines were found to be identical. They have the same m. p. and mixtures in all proportions melt at this temperature. The identity was confirmed by the application of Sidgwick's method (*loc. cit.*), benzene being used as the solvent. The following depressions were observed :

Depression of f. p. with				β-form alone, 0·759°
,,	,,	,,	,,	β- + α-forms, 0·764
,,	,,	,,	,,	α-form alone, 0·750
,,	,,	,,	,,	α- + β-forms, 0·761

NN′-*Trimethyl*-2-*phenylnaphthylene*-1 : 3-*diamine.*—The crude nitrosoamine of the trimethyl base obtained by the action of methyl sulphate on the diamine (see p. 2136) crystallised from alcohol in buff-coloured needles, m. p. 151°. These (5 g.) were dissolved in acetic acid (25 c.c.) and, after the addition of an excess of tin and hydrochloric acid, heated on the water-bath for ½ hour, the red solution rapidly becoming colourless. The solution was made alkaline with sodium hydroxide, boiled to decompose tin salts, and extracted with benzene. The dried benzene solution was evaporated, leaving the colourless base, which crystallised from alcohol in needles, m. p. 104—105° (Lees and Thorpe, *loc. cit.*, give 98—99°) (yield, 4·4 g.) (Found : C, 82·8; H, 7·3. Calc. : C, 82·6; H, 7·2%).

The *acetyl* derivative, prepared by means of acetic anhydride, crystallised from alcohol in needles, m. p. 178° (Found : N, 9·0. $C_{21}H_{22}ON_2$ requires N, 8·8%).

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