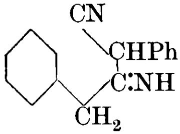
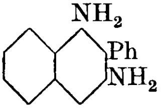
CXCVI.—*The Isomerism of Derivatives of 2-Phenylnaphthylene-*1 : 3-*diamine.*

By Mary Stephen Lesslie and Eustace Ebenezer Turner.

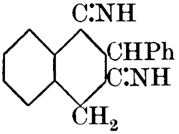
In 1907, Lees and Thorpe (J., **91**, 1282) found that *NN'*-dimethyl-2-phenylnaphthylene-1 : 3-diamine (as II) existed in two forms, although they did not attempt to explain the isomerism. More recently (J., 1928, 2131) Gibson, Kentish, and Simonsen have extended the older work and have suggested an explanation of the isomerism on novel stereochemical grounds.

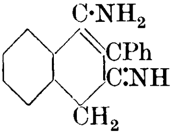
A consideration of the work of Lees and Thorpe (*loc. cit.*) shows, however, that the α- and β-bases are almost certainly *structural* isomerides. 2-Phenylnaphthylene-1 : 3-diamine (II) was obtained by these authors from β-imino-α-cyano-αγ-diphenylpropane (I) :

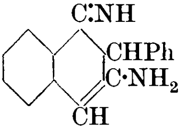

(I.)

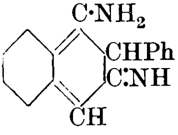

(II.)

It seems probable, however, that (III) would first be formed, and, according to the conditions to which it was submitted, could exhibit the characteristics of one or more of the tautomeric forms (II), (III), (IV) or (V) :


(III.)

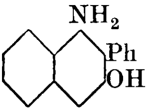

(IV.)

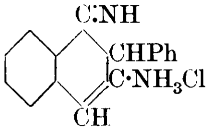

(V.)

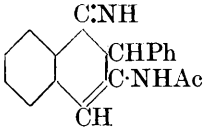

(VI.)

Form (VI) need not be considered, since fused systems of this type appear generally to avoid a single bond fusion.

If (III), (IV) and (V) are probable tautomeric forms of (II), the diamine might under certain conditions exhibit reactions corresponding to one or other of them. Lees and Thorpe actually found that the diamine could be converted into a monohydrochloride which, when heated under pressure in aqueous solution, passed into 1-amino-3-hydroxy-2-phenylnaphthalene (VII). This suggests that the monohydrochloride might be (VIII), corresponding to a " diamine " of structure (V). Such a diamine might form only a


(VII.)

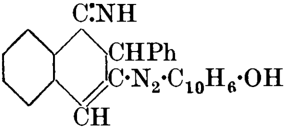

(VIII.)

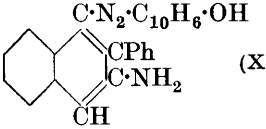

(IX.)

monoacetyl derivative, and Lees and Thorpe found that acetylation with acetic anhydride did in fact give the acetate of a monoacetyl derivative, which might therefore be (IX). It cannot be postulated that (IX), the tautomeric equilibrium of which must be different from that of the parent diamine, would not, under certain conditions, exhibit some of the properties of the tautomeric amino-compound, and, actually, Lees and Thorpe diazotised it and (1) warmed the resulting solution, obtaining 3-amino-1-hydroxy-2-phenylnaphthalene, and (2) added the solution to alkaline β-naphthol : the acetyl-azo-compound obtained, when hydrolysed, gave red plates, m. p. 253°.

Further, the diamine is diazotised once only, a further fact in favour of a structure such as (V), if it is remembered that in all cases, although tautomeric change may appear to be *possible*, one form may under the given conditions predominate. The diazo-solution obtained coupled with alkaline β-naphthol to give a compound which formed purple needles, m. p. 270° : this is probably (X), quite different from the above red azo-compound, which on the present view would be (XI).

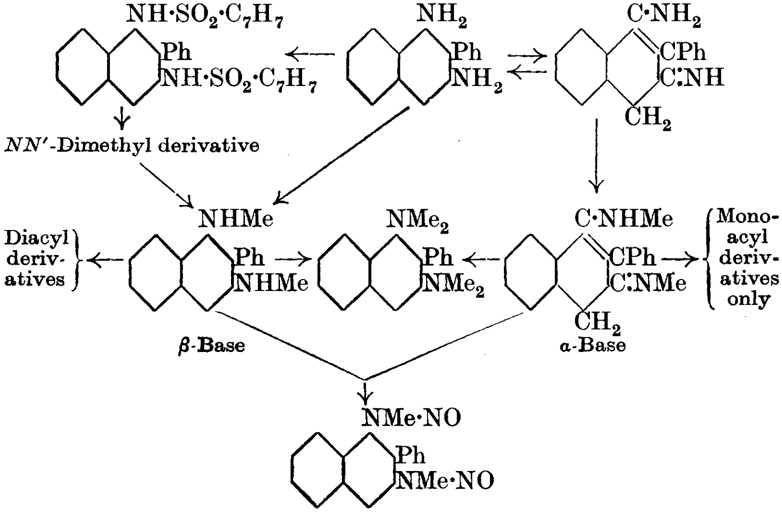
(X.)





(XI.)

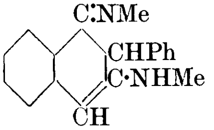
It is at any rate an incontrovertible fact that the diamine usually reacts not as (II), but rather as (V), under the conditions of the particular experiments carried out by Lees and Thorpe. Under different conditions, however, the diamine might be expected to behave as (II) or as (IV), and in this suggestion appears to lie a simple explanation of the isomerism of the α- and β-*NN'*-dimethyl bases. If it be assumed that under the conditions employed for preparing the α-base, namely, cold alkaline methylation, the diamine behaves largely as (IV), whereas in the hot acid methylation giving the β-base it behaves as (II), then all the important known chemistry of the α- and β-bases is explained by the following scheme :



The probability of this explanation being correct is enhanced by the following considerations :

(1) Neither the α- nor the β-base should be capable of optical resolution. Gibson, Kentish, and Simonsen obtained no evidence of resolvability, although they carried out much careful work.

(2) The non-resolvability of the α-base suggests that the formula assigned to it above is more correct than (XII), since a compound having this constitution should be resolvable.



(3) The conditions under which the α-base is convertible into the tetramethyl base are precisely those which favour the formation of the β-type of structure. The α-base cannot be dimethylated under conditions favouring the α-type of structure.

(4) The β-base rapidly gives a dinitrosoamine, whereas the α-base passes rapidly into a mononitrosoamine, which slowly passes into the dinitrosoamine of the β-base (the identity of the dinitrosoamines is required by the present theory, and was first established by Gibson, Kentish, and Simonsen). As we are dealing with tautomeric substances, this slow conversion is particularly instructive. *cis-trans*-Isomerism might explain why a mononitroso-derivative is formed, but it seems highly improbable that nitrous acid would be the only reagent effecting a conversion of a *cis*- into a *trans*-form.

(5) The formation of monoacyl derivatives by the α-base and of diacyl derivatives by the β-base is readily understood on the present theory.

Lees and Thorpe obtained fairly conclusive, though indirect, evidence that their monoacetyldiamine had the acetamido-group in position 3. The feasibility of the theory now put forward at first rested very largely on the correctness of this structure for the monoacetyl compound. We have, however, sought further evidence that 2-phenylnaphthylene-1 : 3-diamine can possess structure (V) under certain conditions. This structure contains an asymmetric carbon atom and a base of formula (V) should therefore be capable of optical resolution. We have succeeded in effecting the resolution. When an aqueous solution of the diamine (1 mol.) in *d*-camphorsulphonic acid (2·2 mols.) was kept, d-2-*phenylnaphthylene*-1 : 3-*diamine dicamphorsulphonate*, $[\alpha]_{5461}^{20^\circ}$ + 40·5°, $[M]_{5461}^{20^\circ}$ + 282·9° (in alcohol) separated, and by using the *l*-acid under precisely similar conditions the l-*base* l-*acid*, having $[\alpha]_{5461}^{20^\circ}$ − 40·7°, $[M]_{5461}^{20^\circ}$ − 284·3°, was obtained. The calculated specific rotations of the base in these salts is + 19·2° and − 19·9°, respectively. When the *d*-salt was treated with ammonia, a diamine was obtained with $[\alpha]^{20^\circ}_{5461}$ + 14·8° (in alcohol).

The only possible explanation of these results appears to be that the diamine is capable of existing as (V).

EXPERIMENTAL.

Preparation of 2-*Phenylnaphthylene*-1 : 3-*diamine*.—The success of this preparation depends to a large extent on the purity of the phenylacetonitrile used. Purchased material was found to contain a considerable quantity of impurity, mainly benzyl alcohol and benzyl ethyl ether. The nitrile was conveniently obtained by a slight modification of the usual method : A mixture of 420 g. of benzyl chloride, 600 c.c. of rectified spirit, and 300 g. of commercial potassium cyanide (previously dissolved in 275 c.c. of hot water) was heated under reflux as usual. The greater part of the alcohol was then distilled off, the residue steam-distilled, the distillate extracted with carbon tetrachloride, and the extract dried over sodium sulphate, freed from solvent, and distilled through a column; 250 g. of phenylacetonitrile, b. p. 234—235°, were obtained (yield, 65%).

The conversion of the nitrile into the diamine appears to be more rapid when the volume of xylene is somewhat reduced. When 250 c.c. of xylene, 150 g. of phenylacetonitrile, and 15 g. of sodium were used, the reaction mixture became solid after 10 minutes' heating on the water-bath. The product was worked up by the method of Lees and Thorpe, as modified by Gibson, Kentish, and Simonsen, and gave 38 g. of crude base, m. p. 107—110°. After one crystallisation from alcohol the base melted at 112·5—113·5°, and further crystallisation did not affect the m. p. (yield of pure base, 35 g., *i.e.*, 23%).

Resolution of the Diamine.—The diamine (2·3 g.; 1 mol.) was dissolved in a warm solution of 5·1 g. (2·2 mols.) of *d*-camphorsulphonic acid in 80 c.c. of water. No solid was deposited on standing, and the solution was therefore concentrated under reduced pressure to 30 c.c.; clumps of fine needles slowly separated (2·9 g.). This substance, d-2-*phenylnaphthylene*-1 : 3-*diamine di*-d-*camphorsulphonate*, gave $\alpha^{20^\circ}_{5461}$ + 0·948° (l = 2; c = 1·1705), whence $[\alpha]^{20^\circ}_{5461}$ = + 40·5° and $[M]^{20^\circ}_{5461}$ = + 282·9° (Found : C, 61·9; H, 7·05. $C_{36}H_{46}O_8N_2S_2$ requires C, 61·8; H, 6·6%. 0·1 G. was equivalent to 14·3 c.c. of 0·0196*N*-barium hydroxide; calc., 14·6 c.c.).

The salt (1 g.) was decomposed with dilute aqueous ammonia, and the product extracted with ether. The ethereal layer was washed twice with ammonia and then yielded a base, m. p. 109—111°, with $[\alpha]_{5461}^{20^\circ} + 14{\cdot}8^\circ$ ($l = 2$; $c = 0{\cdot}5070$; $\alpha_{5461}^{20^\circ} + 0{\cdot}15^\circ$).

By using *l*-camphorsulphonic acid, 1-2-*phenylnaphthylene*-1 : 3-*diamine di*-1-*camphorsulphonate* was obtained. It had $[\alpha]_{5461}^{20^\circ} - 40{\cdot}7^\circ$, $[M]_{5461}^{20^\circ} - 284{\cdot}3^\circ$ ($l = 2$; $c = 1{\cdot}2410$; $\alpha_{5461}^{20^\circ} - 1{\cdot}01^\circ$) (0·1 G. required 14·5 c.c. of 0·0196*N*-barium hydroxide).

In order to prove that the rotation effects were not due merely to solvent (alcoholic diamine) action on the camphorsulphonic acids, 1 mol. of the diamine was dissolved in 2 mols. of *d*-camphorsulphonic acid in alcohol. The dissolved solids had $[M]_{5461}^{20^\circ} + 237{\cdot}2^\circ$ ($l = 1$; $c = 6{\cdot}980$; $\alpha_{5461}^{20^\circ} + 2{\cdot}362^\circ$), whereas the acid present would have $[M]_{5461}^{20^\circ} + 238^\circ$.

When alcoholic solutions of the *d*-base *d*-acid or *l*-base *l*-acid are kept (*e.g.*, in an observation tube), needles of a sparingly soluble salt are precipitated. Again, on one occasion, an evaporated solution of the diamine (11·5 g.) in 2 mols. of aqueous *d*-camphorsulphonic acid deposited a mixture. This was extracted with hot water, in which 1 g. was very sparingly soluble. Evaporation of the filtrate in a vacuum gave 1·1 + 2·4 + 3·2 g. in successive crops of sparingly soluble, small, rectangular crystals (0·1 G. required 14·1 c.c. of 0·0196*N*-barium hydroxide, so the salt was a dicamphorsulphonate), and finally 1·5 + 4·0 g. of the fine needles of the *d*-base *d*-acid. Since the formation of these sparingly soluble compounds does not affect the interpretation of the preceding results, these substances have not been examined in detail. They may be racemic compounds, or salts of another tautomeric form.

It is probable that some at least of the different tautomeric forms of the diamine could be isolated, although there is little doubt that the stability of the α- and β-dimethyl bases is due to the presence of the alkyl groups. We have noticed that in the preparation of the base certain conditions of precipitation from an acid solution give a brown solid product, and when this is stirred with cold alcohol the whole suddenly begins to pass into a greenish-yellow, less soluble form, which is the material normally obtained on crystallisation from alcohol. The type of change most definitely suggests that one tautomeride is being converted into another.

Our thanks are due to Professor J. F. Thorpe for the interest he showed at the inception of this work.

BEDFORD COLLEGE,
UNIVERSITY OF LONDON.

[*Received, April 20th*, 1929.]