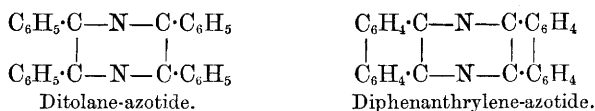


XV.—On some Azines.

By FRANCIS R. JAPP, F.R.S., and COSMO INNES BURTON, B.Sc.

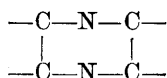
IN a recent communication (Trans., 1886, 826), it was suggested by one of us, in conjunction with Dr. W. H. Wilson, that the compound $C_{28}H_{20}N_2$, obtained from benzoïn and ammonia, and the compound $C_{28}H_{16}N_2$, obtained from phenanthraquinone and ammonia, were related in the manner expressed by the (partially-developed) formulæ—



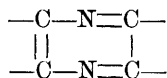
and the nature of this relation was further denoted by the names *ditolane-azotide* and *diphenanthrylene-azotide*.

An experimental proof of this relation was subsequently furnished (Japp and Burton, Trans., 1886, 843) by the conversion of ditolane-azotide, with elimination of hydrogen, into diphenanthrylene-azotide, when the former compound was distilled over heated soda-lime.

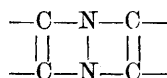
In the above formulæ the distribution of the unsatisfied affinities in the closed-chain complex—



has been left undecided. This complex might either have the constitution—



in which case the compounds would belong to the class of the ketines (see Economides, *Ber.*, **19**, 2524); or it might be formulated—



when the compounds would have to be regarded as azines.

In the present communication, we shall endeavour to show that the latter view is correct.


In the first place, assuming that ditolane-azotide is a ketine, it

ought to be possible to obtain this compound by the action of nascent hydrogen upon Wittenberg and V. Meyer's benzil-hydroxime* :—



We therefore prepared the hydroxime and reduced it with tin and hydrochloric acid, but, as the compound formed was in every way distinct from ditolane-azotide, it was not further examined. This negative result appeared to render it improbable that ditolane-azotide was a ketine.

In the meantime, however, an investigation was published by O. N. Witt, which promised to throw light on the constitution of these compounds. Witt has prepared (*Ber.*, 19, 2794) $\alpha\beta$ -naphthazine,

C_{10}H_5  C_{10}H_5 , by the condensation of β -naphthaquinone with

$\alpha\beta$ -diamidonaphthalene, an application of Hinsberg's quinoxaline reaction.† He further shows that this compound is identical with Laurent's "naphthase," the latter having the formula $\text{C}_{20}\text{H}_{12}\text{N}_2$, instead of the formula $\text{C}_{20}\text{H}_{14}\text{N}_2$, hitherto assigned to it.

Now, between this $\alpha\beta$ -naphthazine and diphenanthrylene-azotide, there is a very marked resemblance in properties. Both are substances of high melting point, volatile at a high temperature without decomposition, and sparingly soluble in most solvents. With concentrated sulphuric acid, naphthazine gives a violet solution which changes to orange on gradual dilution with water, whilst still further dilution precipitates the original compound. Diphenanthrylene-azotide behaves with concentrated sulphuric acid in a precisely similar manner, except that the solution in the concentrated acid is deep-blue instead of violet; the change to orange and the subsequent precipitation occur in this case also.

$\alpha\beta$ -Naphthazine stands to β -naphthaquinone in the same relation as diphenanthrylene-azotide stands to phenanthraquinone :—

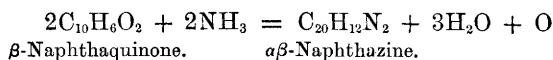
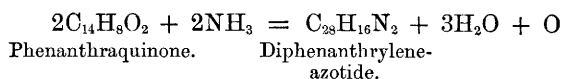
β -Naphthaquinone	$\text{C}_{10}\text{H}_6\text{O}_2$.
$\alpha\beta$ -Naphthazine	$\text{C}_{20}\text{H}_{12}\text{N}_2$.
Phenanthraquinone	$\text{C}_{14}\text{H}_8\text{O}_2$.
Diphenanthrylene-azotide	$\text{C}_{28}\text{H}_{16}\text{N}_2$.

Both phenanthraquinone and β -naphthaquinone contain the CO·CO-group. Phenanthraquinone, when heated with ammonia, yields, among other products, diphenanthrylene-azotide. It seemed to us, therefore,

* Cf. Ceresole and Koeckert, *Ber.*, 17, 820.

† Hinsberg's "quinoxalines" are, as Witt shows, in all probability azines, whilst the constitution ascribed by Hinsberg to the "quinoxalines" is in reality that of the ketines.

that if we could succeed in synthesising $\alpha\beta$ -naphthazine from β -naphthaquinone and ammonia, the parallelism between diphenanthrylene-azotide and $\alpha\beta$ -naphthazine would be complete, and we should be justified in classing diphenanthrylene-azotide, and also its analogue ditolane-azotide, with the azines :—



Instead of heating the β -naphthaquinone in sealed tubes with alcoholic ammonia, we adopted the process described on a former occasion (*Trans.*, 1886, 829) in connection with the preparation of ditolane-azotide and diphenanthrylene-azotide, and fused the β -naphthaquinone with ammonium acetate. (For the details of the process, see *loc. cit.*) The product of the reaction was a black friable mass, which was powdered and washed with boiling water. The smallest trace of this substance gave with concentrated sulphuric acid an intense violet coloration, indicating the presence of the desired $\alpha\beta$ -naphthazine. By sublimation, needle-shaped crystals of this compound were obtained, which gave the sulphuric acid reaction, the violet changing to orange on gradual dilution; a tarry substance distilled, however, at the same time, rendering the purification of the sublimate a matter of difficulty. We therefore adopted a process of sublimation which had on a previous occasion yielded excellent results in the case of diphenanthrylene-azotide. The crude product was mixed with a small quantity of powdered soda-lime and distilled over a short layer of granulated soda-lime, heated just sufficiently to keep the distillate from condensing in it. The part of the tube containing the mixture was not heated more than was necessary to volatilise the substance, so as to reduce to a minimum all decomposition of the substance by soda-lime. In this way, the tar was retained by the soda-lime, and a yellow sublimate was obtained from which a small quantity of a greenish oily matter was removed by boiling it with alcohol. As Witt's method of purification by recrystallising from boiling naphthalene is somewhat inconvenient, we employed, instead of the naphthalene, a coal-tar oil boiling between 160—180°, which at its boiling point readily dissolved the substance, and on cooling deposited it in tufts of pale-yellow needles, which were washed, first with benzene and afterwards with hot alcohol. This process of purification was twice repeated. The substance, thus purified, melted constantly at 275°, sublimed in thin yellow needles, and was very sparingly soluble in alcohol, the alcoholic solution showing a violet fluorescence. In all

these particulars, the behaviour of the compound agreed with Witt's description, except as regards the melting point, which Witt gives as 275°. The substance also showed the sulphuric acid reaction already mentioned.

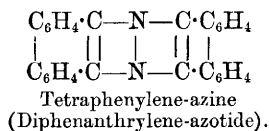
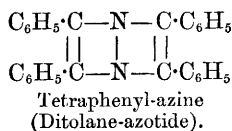
The yield of $\alpha\beta$ -naphthazine by the above method is very small.

Analysis of the substance dried at 140° gave the following results:—

- I. 0.1134 gram substance gave 0.3551 gram CO₂ and 0.0455 gram H₂O.
- II. 0.0751 gram, burnt with copper oxide in a vacuum, gave 13.79 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 14.5° and under 372.5 mm. pressure. After absorption of the nitric oxide there remained 13.79 c.c. of dry nitrogen at 14.8° and under 334.5 mm. pressure.

	Calculated for		Found.	
	C ₂₀ H ₁₂ N ₂ .		I.	II.
C ₂₀	240	85.71	85.40	—
H ₁₂	12	4.29	4.45	—
N ₂	28	10.00	—	10.18
	—	—		
	280	100.00		

The two compounds—ditolane-azotide and diphenanthrylene-azotide—are therefore to be classed as azines, and in accordance with this view we propose to change the names to *tetraphenyl-azine* and *tetraphenylene-azine*. The relation of the two compounds to each other is expressed by the formulæ—



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