## 707. *Polynuclear Heterocyclic Systems. Part IV.* The Linear Pentacyclic Compounds.*

By G. M. Badger and R. Pettit.

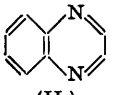
The linear heterocyclic compounds pyrazine, quinoxaline, phenazine, 2 : 3-benzophenazine, etc., have been compared with their carbocyclic analogues, and Dutt's claim (*J.*, 1926, 1179) to have prepared 5 : 7 : 12 : 14-tetra-azapentacene (VII) and 5 : 7 : 9 : 14 : 16 : 18-hexa-azaheptacene (VIII) is disputed. A dihydro-derivative of (VII) has been prepared by a number of methods, and has been given the structure (IX). On reductive acetylation it gave 5 : 7 : 12 : 14-tetra-acetyl-5 : 7 : 12 : 14-tetrahydro-5 : 7 : 12 : 14-tetra-azapentacene (XI). Mild oxidation failed to give the aromatic structure (VII), and more vigorous oxidation gave 5 : 7 : 12 : 14-tetra-azapentacene-6 : 13-quinone (XII), which was converted into 6 : 13-diacetoxy-5 : 7 : 12 : 14-tetra-acetyl-5 : 7 : 12 : 14-tetrahydro-5 : 7 : 12 : 14-tetra-azapentacene (XIII) on reductive acetylation. The quinonoid dihydro-compound (IX) seems to be more stable than the aromatic structure (VII).

It is well known that in the series of linear benz-homologues of benzene, namely, benzene, naphthalene, anthracene, naphthacene, pentacene, etc., there is a very pronounced increase in the " reactivity " of the *meso*-positions as the number of rings increases. This is also correlated with the increased stability of the *meso*-dihydro-derivatives, with an increasing shift in the positions of the absorption bands towards the red, and with an increasing depth of the colours of the compounds themselves (Clar, " Aromatische Kohlenwasserstoffe," Springer-Verlag,

* Part III, preceding paper.

Berlin, 1941). It does not seem to have been noted previously, however, that similar relations in the reactivity of the *meso*-position and in the stability of the related dihydro-derivatives may be observed among the heterocyclic analogues of these compounds. The " reactivity " of the heterocyclic compounds, and the stability of the *meso*-dihydro-compounds increases progressively with the number of rings. For example, in the azine series, pyrazine (I) and quinoxaline (II) do not seem to give stable dihydro-derivatives. Phenazine (III) gives a dihydro-derivative which is only moderately stable, for it is oxidised in air to a molecular compound of phenazine and dihydrophenazine. This complex itself is oxidised very readily, even with mild oxidising agents such as ferric chloride. On the other hand, 2 : 3-benzophenazine (IV) gives a dihydro-compound with the greatest of ease and, although this is stable in air, it can be oxidised to the aromatic structure with dichromate (Hinsberg, *Annalen*, 1901, **319**, 257). 2 : 3-6 : 7-Dibenzophenazine (6 : 13-diazapentacene) (V) has never been prepared, for it cannot be obtained by oxidation of the dihydro-derivative, the latter being exceptionally stable (Hinsberg, *loc. cit.*). The dihydro-derivative of the aromatic compound 5 : 6 : 13 : 14-tetra-azapentacene (VI) is also exceptionally stable, and resisted attempts to oxidise it (Hinsberg, *loc. cit.*).


(I.)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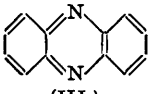
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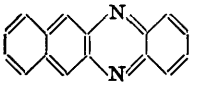
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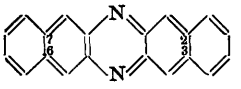
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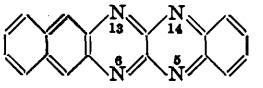
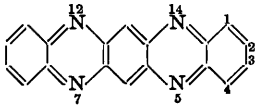
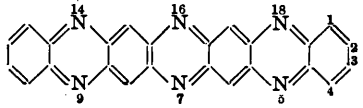
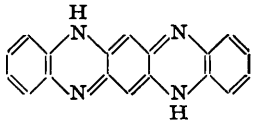

(VI.)

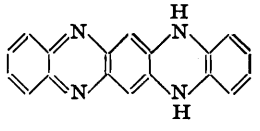
That the colour of the linear heterocyclic compounds should deepen as the number of rings increases follows from the similarities between the absorption spectra of the aromatic hydrocarbons and azahydrocarbons, as already discussed in Part I (*J.*, 1951, 3199). Thus pyridine, quinoline, and acridine are colourless, but 2 : 3-benzacridine, like the analogous hydrocarbon naphthacene, is orange-red. Similarly, pyrazine (I) and quinoxaline (II) are colourless, but phenazine (III), which begins to absorb at slightly longer wave-lengths than anthracene or acridine (see Part I, *loc. cit.*), is yellow. In the same way, 2 : 3-benzophenazine (IV) must absorb at slightly longer wave-lengths than naphthacene, for it is a red compound. The same relationship may be observed in other series of aromatic azahydrocarbons. The naphthacene analogue, 5 : 6 : 11 : 12-tetra-azanaphthacene, for example, is red-brown (Hinsberg, *loc. cit.*). There is no doubt, therefore, that all the azahydrocarbons should be of very nearly the same colour, often somewhat deeper, as their hydrocarbon analogues.

This evidence clearly invalidates Dutt's claim (*J.*, 1926, 1178) to have prepared 5 : 7 : 12 : 14-tetra-azapentacene (VII) and 5 : 7 : 9 : 14 : 16 : 18-hexa-azaheptacene (VIII). Dutt condensed 2 : 3-diaminophenazine with *o*-benzoquinone in concentrated sulphuric acid solution, and isolated a yellow crystalline solid, apparently having the correct composition (nitrogen analysis given). The compound isolated cannot have been a tetra-azapentacene, however, for the analogous aromatic hydrocarbon, pentacene, is deep blue (Clar, *loc. cit.*). Similarly, the compound isolated by Dutt by condensation of 2 : 3-diaminophenazine and 2 : 3-dihydroxy-phenazine in sulphuric acid cannot have been a hexa-azaheptacene. The compound isolated was described as forming microscopic yellow needles, but the analogous hydrocarbon, heptacene, would be deep green, almost black (Clar, *loc. cit.*).


(VII.)


(VIII.)


(IX.)

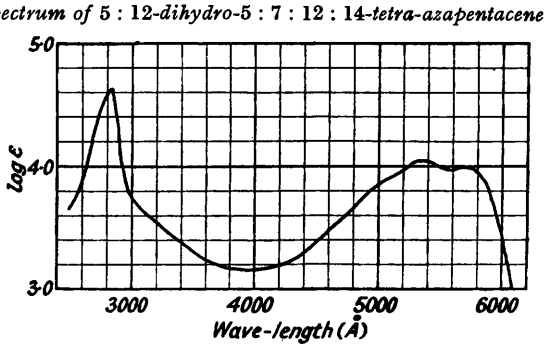

(X.)

Numerous attempts have now been made to repeat Dutt's preparation of tetra-azapentacene (VII), but all have been unsuccessful. Only unchanged 2 : 3-diaminophenazine could be

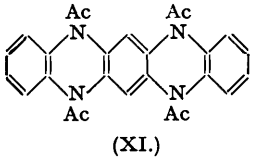
isolated from the reaction mixture. This is not surprising, for *o*-benzoquinone is extremely unstable and would not be expected to survive long in sulphuric acid. Attempts have also been made to carry out the condensation under other, usually milder, conditions, but no pure condensation product could be isolated. Attempts have also been made to use the more stable *o*-toluquinone, but these also failed to yield any product analogous to tetra-azapentacene. These experiments may be compared with those of Hinsberg (*loc. cit.*), who likewise failed to obtain other aromatic aza-pentacenes, and it seems likely that these substances must be too unstable to be prepared. Hinsberg found the dihydro-derivatives of his azapentacenes to be quite stable, and the same appears to hold with the present type of aza-compound. A dihydro-5 : 7 : 12 : 14-tetra-azapentacene has long been known under the name of " homofluorindine," and it is the parent substance of a group of coloured compounds known as " fluorindines." It was prepared by Fischer and Hepp (*Ber.*, 1890, **23**, 2791) by fusing together 2 : 3-diaminophenazine and *o*-phenylenediamine, but on p. 3214 we give an improved preparation, affording a purer product. It has also been obtained by heating *o*-phenylenediamine and its hydrochloride in the presence of air, and an additional method of preparation is described below. No conclusion seems to have been reached regarding the structure of this dihydro-compound, but in view of its very deep blue colour and its absorption spectrum (see figure), there can be no doubt that it has the asymmetrical " quinonoid " structure (IX), and is not the symmetrical dihydro-compound (X).

Catalytic reduction of the dihydro-compound (IX) gave a colourless solution (presumably of the tetrahydro-compound) but this was rapidly oxidised in air to give a deep blue solution

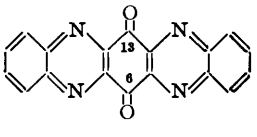
*Absorption spectrum of* 5 : 12-*dihydro*-5 : 7 : 12 : 14-*tetra-azapentacene in methanol.*



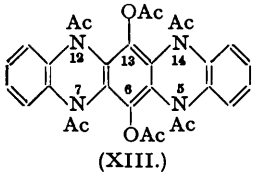

of the original dihydro-compound. On reductive acetylation, however, 5 : 7 : 12 : 14-tetra-acetyl-5 : 7 : 12 : 14-tetrahydro-5 : 7 : 12 : 14-tetra-azapentacene (XI) was obtained. This derivative is useful as, unlike the deep blue (IX), it has a melting point, and may therefore be used for purposes of identification. Many attempts to oxidise the dihydro-compound (IX) to the aromatic structure (VII) were made, but all proved unsuccessful. It seems certain, there-



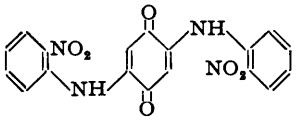
(XI.)



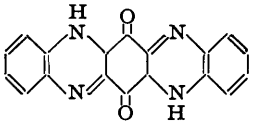
(XII.)



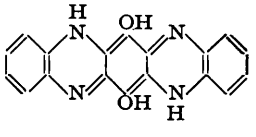
(XIII.)



(XIV.)



(XV.)



(XVI.)

fore, that the quinonoid system present in (IX) is more stable than the aromatic system (VII), and this is of some theoretical importance. Satisfactory conditions have, however, been found for the oxidation of the dihydro-compound (IX) to the quinone (XII), which has also been con-

verted into 6 : 13-diacetoxy-5 : 7 : 12 : 14-tetra-acetyl-5 : 7 : 12 : 14-tetrahydro-5 : 7 : 12 : 14-tetra-azapentacene (XIII) by being boiled with zinc dust and acetic anhydride.

According to Leicester (*Ber.*, 1890, **23**, 2794), 2 : 5-di-*o*-nitroanilinobenzoquinone (XIV) is reduced by alcoholic hydrogen sulphide in a sealed tube to a blue compound, which was given the structure (XV). The only evidence supporting this structure was the analysis, and it is significant that the calculated and the found value for hydrogen differed by as much as 1·6%. In any case the structure (XV) is impossible as it involves two tervalent carbon atoms. The structure (XVI), however, seems reasonable, and moreover, agrees with Leicester's analysis. Nevertheless, the formation of such a compound seemed unlikely, especially in view of the synthesis of " azophenine " from *p*-benzoquinone and aniline; the synthesis has therefore been reinvestigated. The reduction of (XIV) has now been carried out, not only by Leicester's method, but also with sodium sulphide and acetic acid, with sodium sulphide and ammonium chloride, with hydrogen and Raney nickel, and with Raney nickel alloy and sodium hydroxide solution. In every case the dihydrotetra-azapentacene (IX) was obtained and identified by reductive acetylation to the tetra-acetyl-derivative (XI). It seems certain, therefore, that the reaction proceeds by reduction of nitro- to amino-groups, followed by elimination of water with the quinone (or quinol) groups.

## Experimental.

*Attempts to prepare* 5 : 7 : 12 : 14-*Tetra-azapentacene.*—The following experiments are typical: (i) *o*-Benzoquinone (0·54 g.) was added, in small portions with stirring, to a solution of 2 : 3-diaminophenazine (1·05 g.) in concentrated sulphuric acid (40 c.c.). After 1 hour, the mixture was poured into water, and the precipitated dark brown powder (0·7 g.) was collected. Attempts to obtain a pure substance by recrystallisation from nitrobenzene (cf. Dutt, *loc. cit.*) and other solvents were unavailing. After sublimation at 280°/0·2 mm., a small amount of light yellow material, identified as 2 : 3-diaminophenazine, was obtained. Similar experiments were carried out in 80% and in 50% sulphuric acid, and in acetic acid.

(ii) A suspension of finely powdered lead tetra-acetate (2 g.) in glacial acetic acid (20 c.c.) was slowly added with vigorous stirring to a solution of catechol (0·5 g.) and 2 : 3-diaminophenazine (1 g.) in glacial acetic acid (30 c.c.). After a further 90 minutes' stirring the mixture was poured into water. Purification of the resulting black material gave only a small quantity of 2 : 3-diaminophenazine.

(iii) In an attempt to prepare the methyl derivative, the relatively stable *o*-toluquinone was used. 2 : 3-Diaminophenazine (0·42 g.) in glacial acetic acid (25 c.c.) was added to a solution of *o*-toluquinone (0·25 g.) in glacial acetic acid (10 c.c.), and the mixture kept overnight. A dark red-brown solid was obtained, but all attempts to purify it, either by recrystallisaion or by sublimation, failed.

5 : 12-*Dihydro*-5 : 7 : 12 : 14-*tetra-azapentacene* (IX.).—(i) (cf. Fischer and Hepp, *loc. cit.*) A mixture of 2 : 3-diaminophenazine (8 g.) and *o*-phenylenediamine (6 g.) in benzyl alcohol (60 c.c.) was refluxed for 14 hours. After cooling, the dark blue-green crystals, having a metallic lustre, were collected, and washed with ethanol. The product was boiled with dilute sulphuric acid (100 c.c.), then with alcoholic ammonia (200 c.c.), and filtered off and dried. 5 : 12-Dihydro-5 : 7 : 12 : 14-tetra-azapentacene was obtained as a deep blue-purple powder (7·8 g.). It was only very sparingly soluble in all the usual organic solvents, giving deep blue solutions with a red fluorescence. It also dissolved in concentrated sulphuric acid to give a blue solution with a red fluorescence. For analysis and spectrographic examination, a sample was sublimed at 280—290°/0·1 mm. (Found: C, 75·8; H, 4·1. Calc. for $C_{18}H_{12}N_4$: C, 76·0; H, 4·2%).

(ii) A mixture of *o*-phenylenediamine (4·3 g.) and *o*-phenylenediamine dihydrochloride (3·5 g.) in naphthalene (60 g.) was heated at 210—215° for 20 minutes, a slow stream of oxygen being passed through the molten mass. After cooling somewhat, the molten mixture was poured into ethanol (200 c.c.), and the suspension boiled and filtered. The residue was extracted with more boiling ethanol (200 c.c.) and the resulting small shiny dark green crystals were further purified by boiling them with alcoholic ammonia (50 c.c.). The dihydrotetra-azapentacene (0·75 g.) was identified by reductive acetylation and direct comparison with an authentic specimen of the tetra-acetyltetrahydrotetra-azapentacene (XI) (see below).

5 : 7 : 12 : 14-*Tetra-acetyl*-5 : 7 : 12 : 14-*tetrahydro*-5 : 7 : 12 : 14-*tetra-azapentacene* (XI).—A mixture of 5 : 12-dihydro-5 : 7 : 12 : 14-tetra-azapentacene (0·5 g.), zinc dust (0·5 g.), sodium acetate (0·2 g.), and acetic anhydride (20 c.c.) was boiled under reflux until the blue colour disappeared (45 minutes). After cooling, the product was collected, and the zinc, which had coagulated into one piece, was removed. After recrystallisation from nitrobenzene, 5 : 7 : 12 : 14-*tetra-acetyl*-5 : 7 : 12 : 14-*tetrahydro*-5 : 7 : 12 : 14-*tetra-azapentacene* (0·4 g.) formed colourless needles, which began to darken at 340°, finally melting at 375—378° (sealed tube) (Found: C, 68·25; H, 5·2. $C_{26}H_{22}O_4N_4$ requires C, 68·7; H, 4·9%). It was very sparingly soluble in the usual organic solvents, such as alcohol and benzene. On treatment with mineral acids it was very readily hydrolysed (and oxidised in the air) to 5 : 12-dihydro-5 : 7 : 12 : 14-tetra-azapentacene.

*Dihydrotetra-azapentacene* (IX) *by Reduction of* 2 : 5-*Di-o-nitroanilinobenzoquinone.*—(i) A mixture of nitroanilinobenzoquinone (0·5 g.) and alcoholic ammonium sulphide (12 c.c.; containing *ca.* 5 g. of ammonium sulphide) was heated in a sealed tube at 100° for 2 hours. After it had cooled, no colourless crystals could be seen in the tube as stated by Leicester (*loc. cit.*). The product (0·45 g.) was obtained

as shiny, very dark-green, metallic-looking crystals, and was identified as dihydrotetra-azapentacene. Reductive acetylation in the usual way gave tetra-acetyltetrahydrotetra-azapentacene (XI) as colourless needles, m. p. 374—376°, alone or mixed with an authentic specimen.

(ii) A mixture of the nitroanilinoquinone (2·0 g.), sodium sulphide hydrate (15 g.), and ammonium chloride (2·5 g.) in water (400 c.c.) was boiled under reflux for 3 hours. Further quantities of sodium sulphide (7·5 g.) and ammonium chloride (1·7 g.) were then added, and the refluxing continued for a further 2 hours. The product (1·2 g.) obtained by filtration was again identified as dihydrotetra-azapentacene. The same compound was also obtained in less satisfactory yield by reduction and cyclisation with sodium sulphide and acetic acid, with hydrogen and Raney nickel catalyst at 100—120° and 1000 lb./in.$^2$, and by addition of Raney nickel alloy in small portions to a solution of the nitroanilinoquinone in aqueous sodium hydroxide, at 90°.

*Oxidation of* 5 : 12-*Dihydro*-5 : 7 : 12 : 14-*tetra-azapentacene*.—Attempts to oxidise dihydrotetra-azapentacene to tetra-azapentacene with hydrogen peroxide in acetic acid, either at room temperature or under reflux, were unsuccessful. In these experiments, and in runs with other oxidising agents, mixtures were obtained, from which no pure product could be isolated. Under more vigorous conditions, however, the quinone was obtained. 5 : 12-Dihydro-5 : 7 : 12 : 14-tetra-azapentacene (0·5 g.) was dissolved in concentrated sulphuric acid (180 c.c.), and the resulting deep blue solution added dropwise to a well-stirred solution of potassium dichromate (8 g.) in water (250 c.c.) at room temperature. After the addition was completed, the fine microcrystalline yellow product (0·44 g.) was collected, washed with water, and dried. 5 : 7 : 12 : 14-*Tetra-azapentacene*-6 : 13-*quinone* (XII) was very sparingly soluble in alcohol, benzene, and chloroform, but slightly more soluble in pyridine. After recrystallisation from nitrobenzene, it formed bright golden-yellow plates, m. p. above 400°, and for analysis was further purified by sublimation at 320°/0·1 mm. (Found: C, 69·3; H, 2·6. $C_{18}H_8O_2N_4$ requires C, 69·2; H, 2·6%).

6 : 13-*Diacetoxy*-5 : 7 : 12 : 14-*tetra-acetyl*-5 : 7 : 12 : 14-*tetrahydro*-5 : 7 : 12 : 14-*tetra-azapentacene*.—A mixture of the above quinone (1·0 g.), zinc dust (1·0 g.), anhydrous sodium acetate (0·4 g.), and acetic anhydride (30 c.c.) was boiled under reflux. The solution immediately became greenish-blue, slowly changed to red, and finally, after 1 hour, became colourless. After cooling, the mixture was poured into water, and the suspension stirred for 1 hour to complete hydrolysis of the excess of acetic anhydride. The product was decanted from the excess of zinc dust, washed with water, and dried. The 6 : 13-*diacetoxy*-5 : 7 : 12 : 14-*tetra-acetyl*-5 : 7 : 12 : 14-*tetrahydro*-5 : 7 : 12 : 14-*tetra-azapentacene* (1·3 g.) obtained was practically insoluble in ethanol, chloroform, and benzene. After recrystallisation from nitrobenzene, it formed small colourless plates, which decomposed gradually above 350° in a sealed capillary tube (Found: C, 63·5; H, 5·0. $C_{30}H_{26}O_8N_4$ requires C, 63·2; H, 4·6%).

Microanalyses were carried out by the C.S.I.R.O. Microanalytical Laboratory, Melbourne. We are grateful to Mr. R. S. Pearce for the absorption spectrum.

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