345. *Polynuclear Heterocyclic Systems. Part VI.* Tetra-azabenzopentaphene and Related Compounds.*

By G. M. Badger and R. Pettit.

Unlike the linear compound (I), the tetra-azabenzopentaphene (VII) does not form a stable dihydride.

The supposed dihydride reported by Kehrmann (*Ber.*, 1923, **56**, 2390) has been shown to be 14-*o*-aminophenyl-13 : 14-dihydro-5 : 8 : 13 : 14-tetra-aza-6 : 7-benzopentaphene (XI). Some reactions of this compound have been investigated.

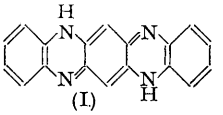
In Part IV of this series (Badger and Pettit, *J.*, 1951, 3211), it was pointed out that the linear pentacyclic compound "homofluorindine" (5 : 12-dihydro-5 : 7 : 12 : 14-tetra-aza-pentacene) must have the *p*-quinonoid type of structure (I). Its deep blue-purple colour and its absorption spectrum support such a formulation, and exclude the alternative structure (II) which could not have the observed spectrum or be so deeply coloured. The remarkable stability of this quinonoid dihydro-compound is of some theoretical importance.

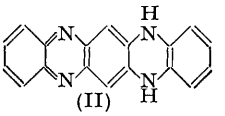
As we are investigating the relation between aromatic hydrocarbons and their heterocyclic analogues, we examined another compound which could exist in a similar quinonoid structure, *viz.*, the dihydro-derivative of 5 : 8 : 13 : 14-tetra-aza-6 : 7-benzopentaphene. Of the three possible structures for this, namely (III), (IV), and (V), the *p*-quinonoid structure (V) would be preferred by analogy with "homofluorindine" (I). Structure (V), involving complete conjugation through the molecule, would be more stable than the *o*-quinonoid structure (IV), or the alternative form (III) having two isolated conjugated systems.

A dihydro-derivative of tetra-azabenzopentaphene purporting to be (III) was reported by Kehrmann (*Ber.*, 1923, **56**, 2390); but further investigation shows that it does not have this structure (see below).

* Part V, preceding paper.

Many attempts have been made to obtain an authentic specimen of the dihydride (III, IV, or V). When 1 : 2-benzophenazine-3 : 4-quinone (VI) is condensed with *o*-phenylenediamine, it gives the parent aromatic substance, 5 : 8 : 13 : 14-tetra-aza-


(I)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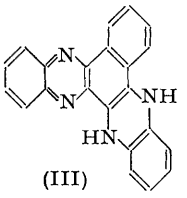
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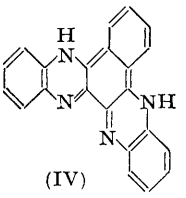
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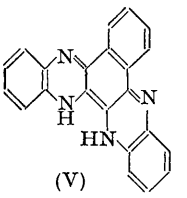
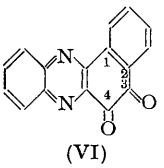
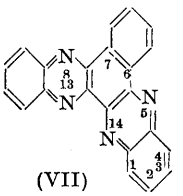

(V)

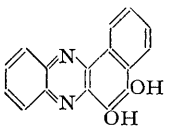
6 : 7-benzopentaphene (VII) (Zincke and Wiegand, *Annalen*, 1895, **286**, 58), and it was thought that similar condensation of 3 : 4-dihydroxy-1 : 2-benzophenazine (VIII) with *o*-phenylenediamine would give the desired dihydride. In fact, however, spontaneous oxidation occurred and only the aza-hydrocarbon (VII) was obtained.

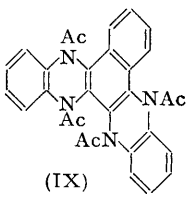
Attempts to obtain the dihydride by catalytic reduction of the aza-hydrocarbon (VII) were also unsuccessful. Hydrogen was absorbed, and a colourless solution was obtained; but on filtration to remove the catalyst, the solution rapidly became red, and later was oxidised to the original tetra-azabenzopentaphene.

Reductive acetylation of tetra-azabenzopentaphene proceeded normally, and a tetra-acetyl derivative (IX) was obtained. On hydrolysis with alcoholic potash or with sulphuric acid, however, this again reverted to the aza-hydrocarbon (VII). When the tetra-acetyl derivative was treated with sulphuric acid for 15 seconds and then immediately poured into water a red compound, probably (V), was obtained; but it was very unstable. It was very readily oxidised to tetra-azabenzopentaphene (VII) with nitric acid, and its


(VI)


(VII)

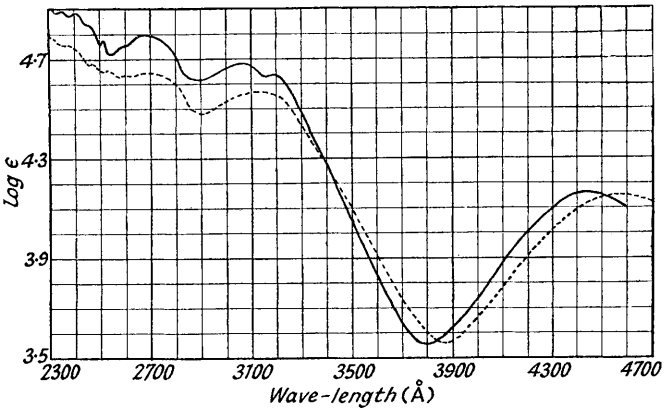

(VIII)


(IX)

alcoholic solutions were also rapidly oxidised in air. A completely pure specimen could not be obtained. It must be concluded, therefore, that although tetra-azabenzopentaphene does form a dihydride, this readily reverts to the more stable aromatic compound. This system is therefore not comparable with the remarkably stable "homofluorindine" (I). In this respect, it is also noteworthy that the angular compound 13 : 14-dihydro-5 : 8-diazapentaphene is also unstable, its solutions being rapidly oxidised in air (see Part V, *loc. cit.*).

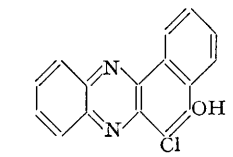
Kehrmann's supposed dihydride was prepared by condensation of 4-chloro-3-hydroxy-1 : 2-benzophenazine (X) with *o*-phenylenediamine in molten naphthalene. This reaction has now been shown to give three products. The first, also obtained by Kehrmann, was a dark blue-purple powder having no melting point. It was identified as "homofluorindine" (I) by reductive acetylation to 5 : 7 : 12 : 14-tetra-acetyl-5 : 7 : 12 : 14-tetrahydro-5 : 7 : 12 : 14-tetra-azapentacene and direct comparison with an authentic specimen. Its formation is due to atmospheric oxidation of the *o*-phenylenediamine (Badger and Pettit, *J.*, 1951, 3211). The second substance, which was not isolated by Kehrmann, crystallised from acetic acid in pale yellow needles, and was identified as 5 : 8 : 13 : 14-tetra-azapentaphene (VII). It is evidently formed by atmospheric oxidation of the dihydride (III), the expected product of the reaction. The third compound crystallised

from chloroform in yellow-orange plates, and was clearly identical with the substance isolated by Kehrmann and to which he assigned the structure (III). Repeated analyses, however, showed that it could not have this formula, and the structure (XI; R = H) is now proposed for it. It formed a stable dark red hydrochloride without difficulty, and was a moderately strong base. On oxidation with hydrogen peroxide, it gave tetra-aza-benzopentaphene (VII). It gave an alkali-soluble toluene-*p*-sulphonyl derivative (XI; R = $SO_2 \cdot C_6H_4Me$) which confirmed the presence of the primary amino-group, and, with

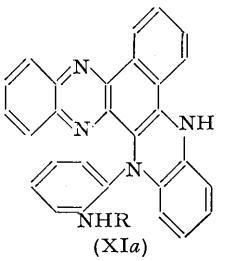


Absorption spectrum of 14 o-*aminophenyl*-13 : 14-*dihydro*-5 : 8 : 13 : 14-*tetra-aza*-6 : 7-*benzopentaphene* (XI) *in dioxan* (———) *and in* 50% *aqueous dioxan* (– – – –). *In the latter solvent, the long-wave-length absorption band is shifted nearly* 200 Å *to longer wave-lengths.*

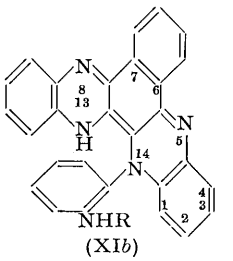
acetyl chloride, a monoacetyl derivative (XI; R = Ac). Attempted acetylation with acetic anhydride, however, gave a colourless oxygen-free compound, which seems to be (XIII). Such a compound could arise by acetylation of the imino-nitrogen atom to give the intermediate (XII), and subsequent transannular elimination of water.



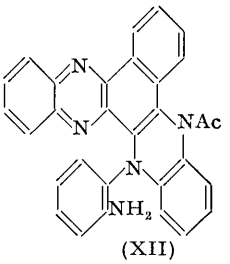
(X)



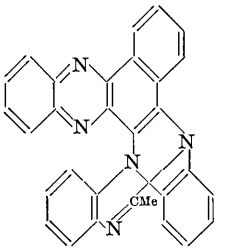
(XI*a*)



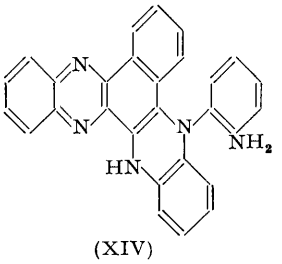
(XI*b*)



(XII)



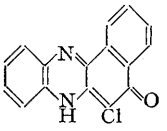
(XIII)



(XIV)

These reactions do not distinguish between structures (XI) and (XIV), but the former is preferred for spectrographic reasons. Solutions of the free base (XI; R = H), of the acetyl derivative (XI; R = Ac), and of the sulphonamido-derivative (XI; R = $SO_2 \cdot C_6H_4Me$), in pure dioxan, are all pale yellow; but on the addition of water there is a pronounced deepening of colour. This is illustrated by the two absorption curves of the free base (see figure). The increase in depth of colour with increase in the dielectric constant

of the solvent can only be associated with the tautomeric change (XI*a*) ⟶ (XI*b*), the quinonoid form being favoured by high dielectric constant. Similar tautomeric shifts are known to occur with 2-hydroxyacridine and 2-hydroxyphenazine (Albert and Short, *J.*, 1945, 760; Badger, Pearce, and Pettit, *J.*, 1951, 3204). Such changes do not occur with the 1-hydroxy-compounds, and a similar tautomeric shift would not be expected with structure (XIV).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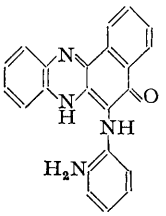
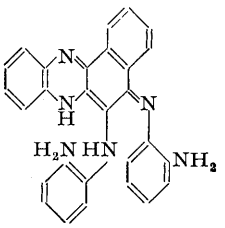

(XVI)


(XVII)

The mechanism of the reaction leading to Kehrmann's compound (XI) is also of interest. In this respect, it seems to be important that the intermediate 4-chloro-3-hydroxy-1 : 2-benzophenazine (X) must exist largely in the quinonoid form (XV), for it is a deep red compound (compare 4-chloro-3-methoxy-1 : 2-benzophenazine, which is yellow; see also Badger, Pearce, and Pettit, *loc. cit.*). It therefore seems likely that this compound will react as a chloroquinone, and that the chlorine atom will be very readily substituted by an amino-group to give the intermediate basic quinone (XVI). Such an intermediate could react in two ways. If the quinone group condenses with the second amino-group of the *o*-phenylenediamine moiety, the unstable dihydride (III) would be formed and would rapidly oxidise to the fully aromatic aza-hydrocarbon (VII) actually isolated from the reaction mixture. On the other hand, if the intermediate basic quinone (XVI) condenses with a second *o*-phenylenediamine molecule, the diamino-compound (XVII) would be formed, and at the high reaction temperature, this would be expected to eliminate ammonia and give (XI; R = H).

This scheme is supported by the fact that the pale yellow isomeric compound 3-chloro-4-hydroxy-1 : 2-benzophenazine, which does not exist in a quinoid form (cf. 1-hydroxyphenazine; Badger, Pearce, and Pettit, *loc. cit.*), condenses with *o*-phenylenediamine to give tetra-azabenzopentaphene (VII) alone. Kehrmann's compound (XI) could not be obtained from this reaction.

Experimental

5 : 8 : 13 : 14-*Tetra-aza*-6 : 7-*benzopentaphene*.—1 : 2-Benzophenazine was prepared from *o*-phenylenediamine and 1-nitroso-2-naphthol by Ullmann and Heisler's method (*Ber.*, 1909, **42**, 4263). Oxidation to the 3 : 4-quinone (VI) was achieved with chromic acid in acetic anhydride–acetic acid (Fischer and Schindler, *Ber.*, 1906, **39**, 2238). A solution of 1 : 2-benzophenazine-3 : 4-quinone (0·5 g.) in acetic acid (200 c.c.) was treated with *o*-phenylenediamine (1·0 g.) in a little alcohol, and the mixture boiled for 10 minutes. After cooling, the product (0·65 g.) was collected and recrystallised from glacial acetic acid. 5 : 8 : 13 : 14-Tetra-aza-6 : 7-benzopentaphene (VII) formed very pale yellow needles, m. p. 320—321° (Found: C, 79·2; H, 3·7. Calc. for $C_{22}H_{12}N_4$: C, 79·5; H, 3·6%). Zincke and Wiegand (*Annalen*, 1895, **286**, 58) report the m. p. as "above 275°." This substance electrifies very readily on being rubbed.

The same substance was also obtained when a mixture of 3 : 4-dihydroxy-1 : 2-benzophenazine (0·3 g.) (Badger, Pearce, and Pettit, *loc. cit.*) and *o*-phenylenediamine (1·0 g.) in ethyl acetate (20 c.c.) was boiled under reflux for 6 hours. The solution, which was initially blue, gradually became red-brown, and the pale yellow crystals of tetra-azabenzopentaphene separated in almost quantitative yield on cooling.

5 : 8 : 13 : 14-*Tetra-acetyl*-5 : 8 : 13 : 14-*tetra-aza*-5 : 8 : 13 : 14-*tetrahydro*-6 : 7-*benzopentaphene*.—The above tetra-azabenzopentaphene was boiled with zinc dust and acetic anhydride, containing a little anhydrous sodium acetate. The solution immediately became deep green, but became colourless on further heating. After 3 hours, the solution was filtered from the

excess of zinc and poured into water. The *tetra-acetyl* derivative (IX) formed small colourless prisms, m. p. 318° (Found : C, 71·1; H, 4·8. $C_{30}H_{24}O_4N_4$ requires C, 71·4; H, 4·8%).

Hydrolysis of this (0·5 g.) with boiling 5% alcoholic potash (50 c.c.) immediately gave a green solution. After 30 minutes, the solid was collected and identified as 5 : 8 : 13 : 14-tetra-aza-6 : 7-benzopentaphene by its m. p. and mixed m. p.

Hydrolysis with concentrated sulphuric acid for 5 minutes likewise gave the tetra-azabenzopentaphene. The crude dihydride (V) was obtained as follows. Finely powdered tetra-acetyl compound (IX) was quickly added to concentrated sulphuric acid, with vigorous stirring. After 15 seconds the mixture was poured into a large volume of water, and the precipitate collected. After being washed with a little water it was stirred into aqueous ammonia, and the resulting crude dihydride collected. This material always contained some tetra-azabenzopentaphene, and no purification could be effected by recrystallisation. Alcoholic solutions exposed to air rapidly oxidised completely to tetra-azabenzopentaphene, and immediate oxidation was also brought about by addition of a little nitric acid to an acetic acid solution. The crude red material gave blue solutions with sulphuric, hydrochloric, and acetic acids.

Preparation of Kehrmann's Compound (XI; R = H).—A mixture of 4-chloro-3-hydroxy-1 : 2-benzophenazine (12 g.), *o*-phenylenediamine (7·1 g.), and naphthalene (75 g.) was heated at 210—215° on a sand-bath for 20 minutes with continuous stirring. After removal of the naphthalene by steam-distillation, the residue was dried, powdered, and then heated under reflux for 30 minutes with chloroform (1000 c.c.). After filtration, the residue was similarly treated with a further quantity (300 c.c.) of chloroform. The dark blue-purple residue was identified as " homofluorindine " (I) by reductive acetylation. After recrystallisation from nitrobenzene, it formed colourless crystals, m. p. 375—376°, identical with 5 : 7 : 12 : 14-tetra-acetyl-5 : 7 : 12 : 14-tetrahydro-5 : 7 : 12 : 14-tetra-azapentacene (Badger and Pettit, *loc. cit.*).

The combined chloroform filtrates were concentrated to 350 c.c. and kept overnight. The material which separated (4·5 g.) was collected. After recrystallisation from chloroform, the 14-o-*aminophenyl*-13 : 14-*dihydro*-5 : 8 : 13 : 14-*tetra-aza*-6 : 7-*benzopentaphene* (XI; R = H) formed beautiful golden plates, m. p. 272° (Found : C, 78·6; H, 4·9; N, 16·15. $C_{28}H_{19}N_5$ requires C, 79·0; H, 4·5; N, 16·45%). It was also obtained in orange needles of the same m. p. by recrystallisation from alcohol–benzene. It dissolved in alcohol and in dioxan to give orange-yellow solutions, which became distinctly red on dilution. It gave a deep green solution in concentrated sulphuric acid, which became red on dilution. With concentrated hydrochloric acid, it gave the *dihydrochloride*. On recrystallisation from aqueous alcohol, this formed deep red glistening plates, m. p. 285—286° (Found : C, 64·9; H, 4·65. $C_{28}H_{19}N_5,2HCl,H_2O$ requires C, 65·1; H, 4·5%).

After removal of Kehrmann's compound, the chloroform liquors were concentrated to 100 c.c., and again set aside. After 12 hours, the 5 : 8 : 13 : 14-tetra-aza-6 : 7-benzopentaphene (4·2 g.) was collected. Recrystallisation from acetic acid gave pale yellow needles, m. p. and mixed m. p. 320°.

Acetylation of Kehrmann's Compound.—Acetylation of the above base (XI; R = H) was effected with acetyl chloride in pyridine. After recrystallisation from alcohol, the *acetyl* derivative (XI; R = Ac) formed fine yellow needles, m. p. 250—252° (slow heating) (Found : C, 73·8; H, 5·3; N, 13·0. $C_{30}H_{21}ON_5,1\frac{1}{2}C_2H_5{\cdot}OH$ requires C, 73·9; H, 5·6; N, 13·0%). It gave a yellow-orange solution in dioxan, becoming red on addition of water. With concentrated sulphuric acid, it gave a green solution, becoming red on dilution with water. It also gave a red solution with hydrochloric acid.

Action of Acetic Anhydride.—Brief boiling with acetic anhydride converted Kehrmann's compound (XI; R = H) into the substance (XIII). After recrystallisation from pyridine, this formed pale yellow plates, m. p. 266° (Found : C, 79·9; H, 4·2; N, 15·1. $C_{30}H_{19}N_5$ requires C, 80·2; H, 4·3; N, 15·6%).

*Formation of Toluene-*p*-sulphonyl Derivative.*—Treatment of Kehrmann's compound with toluene-*p*-sulphonyl chloride in dry pyridine gave the *toluene-*p*-sulphonyl* derivative (XI; R = $SO_2{\cdot}C_6H_4Me$). After recrystallisation from alcohol, it formed orange prisms, m. p. 228—229° (after slow heating to remove solvent of crystallisation) (Found, after drying at room temperature for several days : C, 69·8; H, 5·3; N, 10·2. $C_{35}H_{25}O_2N_5S,2C_2H_5{\cdot}OH$ requires C, 69·7; H, 5·5; N, 10·4%. Found, after drying at 110°/0·1 mm. for 8 hours : C, 70·8; H, 4·7; N, 11·25. $C_{35}H_{25}O_2N_5S,C_2H_5{\cdot}OH$ requires C, 71·0; H, 5·0; N, 11·2%).

Oxidation of Kehrmann's Compound with Hydrogen Peroxide.—A solution of Kehrmann's compound (XI; R = H) (0·1 g.) in acetic acid (10 c.c.) was treated with hydrogen peroxide (10 c.c.; 100-vol.), and the mixture kept for 2 days. After addition of water the product was

collected and recrystallised from acetic acid. The tetra-azabenzopentaphene formed pale yellow needles, m. p. and mixed m. p. 320°.

Preparation of Tetra-azabenzopentaphene from 3-*Chloro*-4-*hydroxy*-1 : 2-*benzophenazine.*—A mixture of the phenazine (10 g.) (Zincke, *Annalen*, 1891, **268**, 257; Zincke and Noak, *ibid.*, 1896, **295**, 6), *o*-phenylenediamine (8 g.), and naphthalene (60 g.) was heated on a sand-bath at 210—215° for 20 minutes. After removal of the naphthalene by steam-distillation and subsequent washing with light petroleum (200 c.c.), the dark brown residue (12 g.) was refluxed for 1 hour with chloroform (1300 c.c.), and then filtered off. The residue (5 g.) was identified as homofluorindine (I). Concentration of the liquors to 200 c.c. and storage overnight gave 5 : 8 : 13 : 14-tetra-aza-6 : 7-benzopentaphene (4·5 g.) as light yellow needles, m. p. and mixed m. p. 320°.

3-*Acetoxy*-4-*chloro*-1 : 2-*benzophenazine.*—This was prepared from the free hydroxy-compound (Kehrmann, *loc. cit.*) by 2 hours' boiling with excess of acetic anhydride. After recrystallisation from acetic acid, the *acetoxy*-compound formed yellow needles, m. p. 230—232°, after sintering (Found: C, 66·6; H, 3·4. $C_{18}H_{11}O_2N_2Cl$ requires C, 67·0; H, 3·4%).

4-*Chloro*-3-*methoxy*-1 : 2-*benzophenazine.*—This *methoxy*-compound was prepared in the usual way from the hydroxy-compound, with methyl sulphate. After recrystallisation from alcohol, it formed yellow needles, m. p. 177—178° (Found: C, 69·4; H, 3·7. $C_{17}H_{11}ON_2Cl$ requires C, 69·3; H, 3·8%).

Absorption Spectra.—These were determined with a Hilger Uvispek spectrophotometer.

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