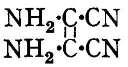
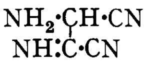
NOTES.

The Constitution of the Tetrapolymer of Hydrogen Cyanide. A Reply. By L. E. HINKEL.

GRYSZKIEWICZ-TROCHIMOWSKI in his reply (J., 1938, 1466) to the paper of Hinkel, Richards, and Thomas (J., 1937, 1432) offers no further experimental evidence in support of his claim that the tetrapolymer is diaminomaleinitrile (I). These authors have already pointed out that no evidence of tautomerism for the polymer had been obtained. It is therefore still considered that the imino-formula (II) is alone capable of explaining all the reactions of the compound. The authors have also shown that the reaction between glyoxal and the polymer does, in fact, proceed stepwise as postulated by Gryszkiewicz-Trochimowski for formula (II).

(I.) 

$$\begin{array}{c}NH_2\cdot C\cdot CN\\ \| \\ NH_2\cdot C\cdot CN\end{array}$$

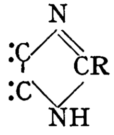
 (II.)

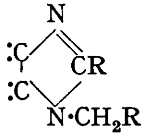
$$\begin{array}{c}NH_2\cdot CH\cdot CN\\ | \\ NH{:}C\cdot CN\end{array}$$

That Gryszkiewicz-Trochimowski did not isolate this intermediate compound is probably due to his employing impure materials, since he states (*Rocz. Chem.*, 1928, **8**, 165) that he obtained a *dark crystalline mass* by mixing hot aqueous solutions of the reactants. He did not, however, examine or analyse this mass, but crystallised it from hot water, a process which in presence of the small quantity of acid associated with ordinary glyoxal is sufficient to convert any of the *bright red amorphous* intermediate compound into the colourless dicyanopyrazine.

The behaviour of the polymer as a mono-acid base lends further support for the structure (II), since it has been shown (compare, *inter alia*, Jay and Curtius, *Ber.*, 1894, **27**, 60) that the cyano-group does not inhibit the basic property of the amino-group; *e.g.*, aminoacetonitrile readily yields a sparingly soluble hydrochloride, $CN\cdot CH_2\cdot NH_2,HCl$, with cold concentrated hydrochloric acid in a manner similar to the polymer.

Gryszkiewicz-Trochimowski states that many other diamines (*e.g.*, *o*-phenylenediamines) react with only *one* molecule of an aldehyde, forming iminazole derivatives. This statement cannot be accepted without new facts to support it, since it has been shown (Ladenburg, *Ber.*, 1878, **11**, 590, 1648; Hinsberg, *Ber.*, 1887, **20**, 1585; Pinnow and Wiskott, *Ber.*, 1899, **32**, 898) that *o*-diamines react with aldehydes, giving rise to the substituted iminazoles (III) and (IV), of which (IV) predominate.


(III.)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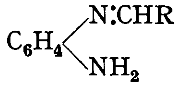
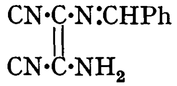

(V.)



$$\begin{array}{l} CN\cdot C\cdot N{:}CHPh \\ \quad\ \| \\ CN\cdot C\cdot NH_2 \end{array}$$

(VI.)

Furthermore, in those isolated cases where *o*-diamines react with only one molecule of an aldehyde, compounds of type (V) result, and these compounds react with a second molecule of an aldehyde to give the iminazole derivative (III).

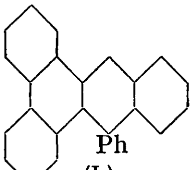
A benzylidene compound (VI) based on the diamine formula does not account for the non-basic properties of the compound or for its inactivity towards nitrous acid.

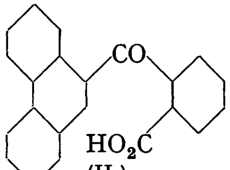
Gryszkiewicz-Trochimowski's criticisms have in no way weakened the original conclusions of the authors.—UNIVERSITY COLLEGE, SWANSEA. [*Received, February* 4*th*, 1939.]

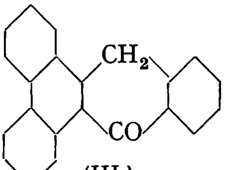
9-Phenyl-1 : 2 : 3 : *4-dibenzanthracene*. By ERNST BERGMANN and T. BERLIN.

WHEN lithium is substituted for the hydrogen atom in position 4 of 1 : 2 : 3-triphenylnaphthalene and the metal atom is then removed by treatment with iodine or mercury, a hydrocarbon, $C_{28}H_{18}$, m. p. 227°, is formed. On the basis of oxidative degradation experiments, this had been formulated as 9-phenyl-1 : 2 : 3 : 4-dibenzanthracene (I) by Bergmann and Zwecker (*Annalen*, 1931, **487**, 155). We have been able to support the existing evidence from the synthetic side. *o*-9-Phenanthroylbenzoic acid (II) (Weizmann and co-workers, J., 1935, 1367) on reduction, by Clemmensen's method, gave *o-9-phenanthrylmethylbenzoic acid*: this was cyclised to 1 : 2 : 3 : *4-dibenz-9-anthrone* (III), which was treated with phenyl-lithium, and the resulting carbinol dehydrated to yield (I).

Fieser and co-workers (*J. Amer. Chem. Soc.*, 1937, **59**, 128; 1938, **60**, 170) found appreciable difficulty in introducing methyl radicals *via* their magnesium derivative into various anthrones similar to (III). Whether this difference in behaviour is due to the use of a phenyl compound or to the use, in our case, of lithium instead of magnesium, is not clear.


(I.)


(II.)


(III.)

o-9-*Phenanthrylmethylbenzoic Acid.*—*o*-9-Phenanthroylbenzoic acid (I) (15 g.) was reduced with amalgamated zinc-wool (150 g.) and hydrochloric acid by Clemmensen's method. The reduced *acid* separated spontaneously and was recrystallised from 80% acetic acid, forming clusters of needles (12 g.), m. p. 197° (Found: C, 84·2, 84·3; H, 5·4, 5·3. $C_{22}H_{16}O_2$ requires C, 84·6; H, 5·1%).

1 : 2 : 3 : *4-Dibenz-9-anthrone* (III).—The foregoing acid (9 g.) was boiled for 3 hours with thionyl chloride (40 c.c.), the excess of the latter distilled off, and the residual acid chloride dissolved in carbon disulphide (100 c.c.) (which caused partial crystallisation) and treated at 0° with powdered aluminium chloride (4·4 g.). After standing at room temperature for 12 hours, the mass was poured into ice-cold concentrated hydrochloric acid, and the solid, together with the product remaining after evaporation of the carbon disulphide solution, was extracted

with boiling glacial acetic acid. The crystalline precipitate obtained from the acetic acid solution gave, on recrystallisation from ethyl malonate or nitrobenzene, the desired *ketone* (2 g.), m. p. 286° (Found : C, 89·3; H, 4·7. $C_{22}H_{14}O$ requires C, 89·7; H, 4·7%).

9-*Phenyl*-1 : 2 : 3 : 4-*dibenzanthracene* (I).—Powdered 1 : 2 : 3 : 4-dibenz-9-anthrone (1 g.) was shaken with ethereal phenyl-lithium solution (from 5 c.c. of bromobenzene and 6 g. of lithium; 10 mols.) in a Schlenk tube (nitrogen atmosphere) for 2 days. The solution was decomposed with dilute sulphuric acid and the crystalline 9-hydroxy-9-phenyl-9 : 10-dihydro-1 : 2 : 3 : 4-dibenzanthracene remaining after evaporation of the ethereal layer was collected after trituration with alcohol. It had m. p. 250° (decomp.). As it underwent only partial dehydration on heating with butyl alcohol (from which it formed lancet-shaped leaflets), it was converted into (I) by crystallisation from butyl alcohol containing some concentrated hydrochloric acid. (I) formed broad colourless needles, m. p. 227°, which were identified by the method of mixed m. p. with a sample of 9-phenyl-1 : 2 : 3 : 4-dibenzanthracene prepared by Bergmann and Zwecker (*loc. cit.*).—THE DANIEL SIEFF RESEARCH INSTITUTE, REHOVOTH, PALESTINE. [*Received, November* 29*th*, 1938.]

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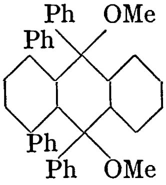
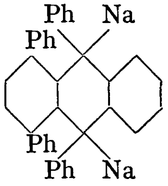
1 : 4 : 9 : 10-*Tetraphenylanthracene*. By CH. WEIZMANN and ERNST BERGMANN.

THE *dimethyl* ether (I), easily accessible by the action of methyl-alcoholic sulphuric acid on 9 : 10-dihydroxy-1 : 4 : 9 : 10-tetraphenyl-9 : 10-dihydroanthracene, is treated with sodium powder in ethereal suspension, whereby the disodium compound (II) is formed (Schlenk and Bergmann, *Annalen*, 1928, **463**, 159). On treatment with an excess of mercury, the sodium atoms are eliminated (*idem, ibid.*, p. 6), leaving the desired 1 : 4 : 9 : 10-tetraphenylanthracene in a pure state. When these experiments had been completed, Bachmann and Chemerda (*J. Amer. Chem. Soc.*, 1938, **60**, 1023) described a somewhat similar process for the preparation of 9 : 10-dimethyl-1 : 2-benzanthracene; they hydrolysed the disodium compound, and dehydrogenated the 9 : 10-dihydro-derivative by means of sulphur.

(I.)





(II.)

9 : 10-*Dimethoxy*-1 : 4 : 9 : 10-*tetraphenyl*-9 : 10-*dihydroanthracene* (I).—The dihydroxy-compound (Weizmann, Bergmann, and Haskelberg, this vol., p. 397) (2 g.) was suspended in hot methyl alcohol (50 c.c.), and a solution of concentrated sulphuric acid (3 c.c.) in methyl alcohol (50 c.c.) added (methylation apparently occurs even in absence of sulphuric acid : the diol dissolves in the methyl alcohol, but crystallisation quickly sets in); the mixture was then heated for 3 hours at the b. p. The product was collected, washed with methyl alcohol, and recrystallised from butyl acetate, forming prisms, m. p. 309°, in quantitative yield (Found : C, 88·1, 87·9; H, 6·2, 5·9. $C_{40}H_{32}O_2$ requires C, 88·2; H, 5·9%).

1 : 4 : 9 : 10-*Tetraphenylanthracene*.—The foregoing *dimethyl* ether (1 g.) was shaken in ethereal suspension (about 250 c.c.) with sodium powder during 24 hours; a dark violet solution was obtained in which most of the sodium compound (II) was suspended as a brown-violet powder. The solution and powder were decanted from the excess of metal in a nitrogen atmosphere and shaken with mercury (15 c.c.) for 24 hours. The yellowish mass was poured into water, and the ethereal layer dried and evaporated. The residue (0·7 g.) crystallised spontaneously; its m. p. (204°) was not depressed by authentic 1 : 4 : 9 : 10-tetraphenylanthracene.

1 : 4 : 9 : 10-*Tetraphenyl*-9 : 10-*dihydroanthracene*.—The easy accessibility of the above-mentioned disodium compound led us to study its hydrolysis in the usual way, by adding alcohol. The ethereal solution, on evaporation, left a crystalline cake, which was recrystallised from glacial acetic acid containing some acetic anhydride; the mixture of white leaflets and stout yellowish prisms thus obtained was separated mechanically. The leaflets crystallised from butyl alcohol in long broad needles, m. p. 217° (Found : C, 93·8; H, 6·1. $C_{38}H_{28}$ requires C, 94·2; H, 5·8%). The prisms were fractionated from glacial acetic acid, giving a further crop of the substance, m. p. 217°, and yellowish prisms, m. p. 205°, after several recrystallisations (Found : C, 93·9; H, 6·3%). These substances represent, according to the analytical figures,

the stereoisomeric forms of 1 : 4 : 9 : 10-*tetraphenyl*-9 : 10-*dihydroanthracene*. [The lower-melting substance is not a molecular compound of 1 : 4 : 9 : 10-tetraphenylanthracene and its dihydro-derivative, m. p. 217° (compare Haack, *Ber.*, 1929, **62**, 1771). The two substances do not combine, but crystallise separately from their mixed solutions.] Usually (Schlenk and Bergmann, *Annalen*, 1928, **463**, 149, 155) only one form is obtained in reactions of this type, but a similar observation has been made recently by Bachmann and Pence (*J. Amer. Chem. Soc.*, 1937, **59**, 2339) in the case of 1 : 2 : 6 : 7-dibenzanthracene.—THE DANIEL SIEFF RESEARCH INSTITUTE, REHOVOTH, PALESTINE. [*Received, November 29th*, 1938.]