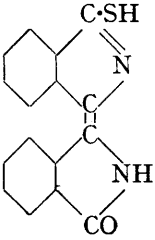
115. *Dithio-β*-iso*indigo. Part III. Further Members of the Series.*

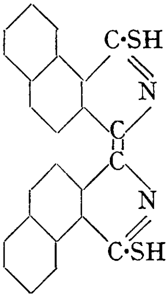
By H. D. K. Drew and D. B. Kelly.

Some further examples are described of the production, from *o*-dinitriles and ammonium hydrosulphide, of compounds of the dithio-β-*iso*indigo series, tending to show that the method is general. The question of the structure of the blue complex compound produced from β-*iso*indigodihydrazone by the action of organic acids is discussed. *Monothio*-β-iso*indigo* has been prepared, and a new method of changing phthalonitrile into phthalocyanine is given.

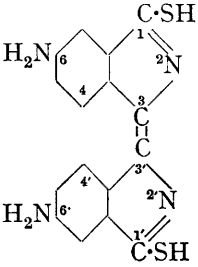
Monothio-β-iso*indigo* (I) was obtained by the action of alcoholic ammonia and hydrogen sulphide on the residues from the purification of phthalonitrile. Its structure was established by showing that (*a*) its methyl and ethyl derivatives were identical with those prepared by the partial hydrolysis of *SS'*-dimethyl- and *SS'*-diethyl-dithio-β-*iso*indigo (Drew and Kelly, preceding paper) and (*b*) (I) was identical with the product of hydrolysis of *S*-monomethyldithio-β-*iso*indigo (*loc. cit.*, p. 633). (I) occurred as brown needles, but was otherwise similar to dithio-β-*iso*indigo in physical character. β-iso*Indigomonophenylhydrazone*, prepared from (I), was red-brown, and, like the corresponding thio-compound (*loc. cit.*, p. 633), dissolved to intensely blue solutions in aqueous-alcoholic alkalis.



(I.)



(II.)



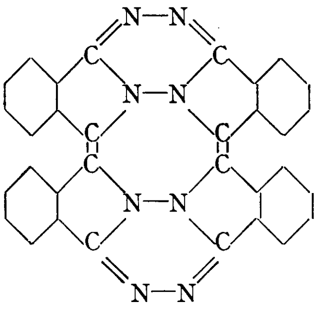
(III.)

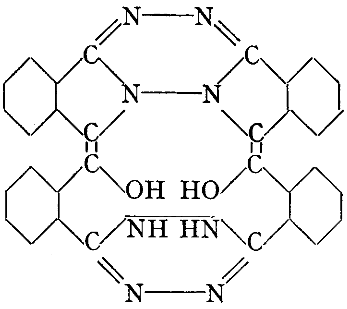
From naphthalene-1 : 2-dinitrile and ammonium hydrosulphide was prepared 6 : 7 : 6' : 7'-*dibenzdithio*-β-iso*indigo* (II), which formed dark green crystals, purple by transmitted light. It might, theoretically, occur in two *cis*- and three *trans*-forms, one of the last of which might be expected to show interference displacement due to overlapping of the groupings; but no isomerism was observed. Its *dimethyl* derivative was bright red; hydrolysis of it removed first one methylthio-group, giving orange-yellow S-*methyl*-6 : 7 : 6' : 7'-*dibenzthio*-β-iso*indigo*, and then the second, giving yellow 6 : 7 : 6' : 7'-*dibenz*-β-iso*indigo*.

4-*Nitrophthalonitrile* has been mentioned in the patents literature (B.P. 410,814) but not described. Prepared from 4-nitrophthalodiamide and acetic anhydride, it consisted of colourless crystals, which reacted with alcoholic ammonia and hydrogen sulphide with generation of a dithio-β-*iso*indigo derivative, obtained as small dark crystals, deep red by transmitted light. Analysis showed that the nitro-group of the nitrile had been reduced to an amino-group, so that the above substance was *diaminodithio*-β-iso*indigo*. Whether or not reduction of the nitro-group occurred before or after one of the stages of condensation was uncertain, but on theoretical grounds it is probable that the substance obtained was the 6 : 6′-diamino-isomeride (III). Only a preliminary study was made of the preparation of 4-aminophthalonitrile and its direct condensation to a dithio-β-*iso*indigo derivative (see experimental section). Under other conditions, 4-nitrophthalonitrile is converted by ammonium sulphide into 6-nitro-6′-aminodithio-β-*iso*indigo (Drew, Kelly, and Imperial Chemical Industries Limited, B.P. 516,342).

The action of hot aqueous acetic acid upon the dihydrazone of β-*iso*indigo, prepared from dithio-β-*iso*indigo, gave an insoluble, intensely blue substance of great stability to acids and alkalis. Further study of this somewhat intractable substance led to the provisional suggestions as to its structure set out below. Its production from the dihydrazone occurred also with butyric, phenylacetic, or chloroacetic acid, but in every case the presence of water was necessary. The organic acid employed was evidently not incorporated in the structure of the blue compound. Ammonia, but not hydrazine, was liberated in the reaction forming it, and its oxidation afforded a high yield of phthalimide. The purified *substance* was a dark blue powder with brassy reflex, decomposing vigorously near 300° ; when dried, it was hygroscopic, and it evolved its nitrogen only slowly during analysis by the micro-Dumas method. Consideration of the analytical data and of the facts mentioned above suggested that the compound was a hexahydrated form of a tetrapolymeride of phthalonitrile (IV), which retained at least two molecules of water on desiccation in a stream of dry air at 130°. It is possible that the " dihydrated " substance has the formula (IV*A*).

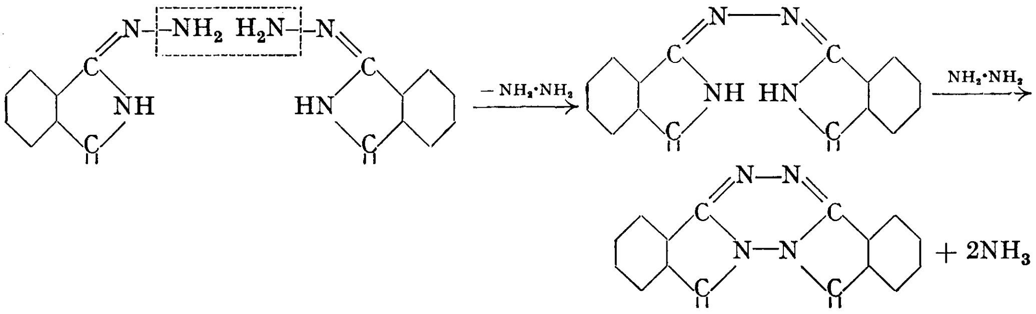
(IV.)





(IV*A*.)

The formation of substances of this type is readily accounted for by assuming the displacement of two hydrazine molecules between two molecules of the dihydrazone, followed by the replacement of the pairs of imino-groups by hydrazino-groups, as shown below (for the halves of two molecules of the dihydrazone) :



The elimination of ammonia, and not hydrazine, is thus explained.

Crystalline phthalocyanine resulted (*a*) from molten phthalonitrile alone, when treated with dry hydrogen sulphide during about 1 hour, as the temperature of the melt was raised slowly from 150° to 170°, and (*b*) from a mixture of phthalonitrile and aniline, at 180°, in a stream of hydrogen sulphide (1½ hours). In case (*a*) the yield of pure product exceeded 50% of the theoretical, only a primitive method of stirring being used. These reactions demonstrate in a simple manner that hydrogen is taken up in the change of the nitrile into phthalocyanine. No chemical change occurred when phthalonitrile was fused with sulphur, and therefore it is clear that hydrogen sulphide acted as a reducing agent in the above reactions.

EXPERIMENTAL.

Monothio-β-iso*indigo* (I).—Crude phthalonitrile (1 part), recovered from the impure fractions of preparative experiments, was suspended in boiling alcohol (2 parts) and treated with ammonia and excess of hydrogen sulphide for 3 hours; the solid product was filtered off, washed with boiling water and alcohol, and extracted with boiling nitrobenzene (1 part). The residue was a mass of very small, brown needles of (I), darkening at about 355° (Found: C, 68·8; H, 3·7. $C_{16}H_{10}ON_2S$ requires C, 69·0; H, 3·6%); it coloured pyridine orange-brown and dissolved in aqueous or alcoholic alkalis to reddish-brown solutions; its stability to concentrated acids and its solubility in organic solvents were of the same order as those of dithio-β-*iso*indigo. Its mono-*S*-methyl and mono-*S*-ethyl derivatives were prepared by the action of the respective alkyl iodide on a solution of (I) in aqueous-alcoholic sodium hydroxide; each was shown to be identical with the first hydrolysis product of the corresponding *SS'*-dialkyldithio-β-*iso*indigo.

(I) was prepared also by heating *S*-methyldithio-β-*iso*indigo for 6 hours with concentrated hydrochloric acid, methylthiol being set free; its identity with the product from the former method of preparation was shown by preparing the methyl and ethyl derivatives and taking mixed melting points with the former samples.

β-iso*Indigomonophenylhydrazone* was prepared by heating (I) for 3 hours with a large excess of phenylhydrazine; the product which separated on cooling was repeatedly crystallised from pyridine and obtained in bright reddish-brown needles, m. p. 273° (slight decomp.) (Found: C, 74·5; H, 4·2; N, 16·5. $C_{22}H_{16}ON_4$ requires C, 75·0; H, 4·5; N, 15·9%); it dissolved in aqueous-alcoholic sodium hydroxide to an intensely blue solution.

6 : 7 : 6' : 7'-*Dibenzdithio*-β-iso*indigo* (II).—Naphthalene-1 : 2-dicarboxynitrile (3 g.) was suspended in a mixture of alcohol (50 c.c.) and aqueous ammonia (5 c.c.; *d* 0·88), and the liquid was saturated with hydrogen sulphide and then boiled under reflux in a slow stream of the gas for 1½ hours. The tough grey precipitate was washed with boiling alcohol and extracted with carbon disulphide to remove sulphur; the yield of residue was 2·9 g. (calc., 3·3 g.). For analysis, (II) was crystallised from boiling nitrobenzene or α-chloronaphthalene; it formed small needles with dark green reflex but purple by transmitted light; it did not melt up to 350° (Found: C, 72·95; H, 4·0; S, 15·9. $C_{24}H_{14}N_2S_2$ requires C, 73·1; H, 3·6; S, 16·3%); it was very sparingly soluble in organic solvents (solutions intensely purple), but readily soluble in aqueous-alcoholic caustic alkalis.

SS'-*Dimethyl*-6 : 7 : 6' : 7'-*dibenzdithio*-β-iso*indigo* was obtained from (II) and methyl iodide in aqueous-alcoholic sodium hydroxide; it formed bright red needles, m. p. 321°, from pyridine (Found: C, 74·2; H, 4·6. $C_{26}H_{18}N_2S_2$ requires C, 73·9; H, 4·3%); it was insoluble in alcohol but gave an orange solution in aqueous-alcoholic hydrogen chloride. It evolved methylthiol when boiled with alcohol and concentrated hydrochloric acid, forming S-*methyl*-6 : 7 : 6' : 7'-*dibenzthio*-β-iso*indigo*, which crystallised from nitrobenzene in orange-yellow, asbestos-like needles, not melted up to 350° (Found: C, 76·8; H, 4·1. $C_{25}H_{16}ON_2S$ requires C, 76·5; H, 4·1%).

6 : 7 : 6' : 7'-*Dibenz*-β-iso*indigo* was obtained by boiling the above *SS'*-dimethyl derivative of (II) with 50% sulphuric acid (10 hours) and then heating the product with the concentrated acid at 180° (12 hours). The final product was precipitated by adding water and was extracted with pyridine and nitrobenzene, and the residue crystallised from a considerable volume of a hot mixture of phenol and *p*-cresol; it was a yellow powder, unmelted at 350° (Found: N, 8·0. $C_{22}H_{14}O_2N_2$ requires N, 7·7%); it dissolved only in concentrated solutions of aqueous caustic alkalis (solutions orange).

4-*Nitrophthalonitrile*.—A mixture of 4-nitrophthalodiamide (5 g.) and pure acetic anhydride (20 c.c.) was refluxed for 6 hours, the clear liquid rapidly poured, whilst boiling, into boiling water (50 c.c.), and the whole cooled in a freezing mixture with addition of ice. The *nitrile* was filtered off, dried, dissolved in benzene, and recovered (yield, 2·1 g.); it formed colourless crystals from alcohol or water, m. p. 142° (Found : C, 55·9; H, 1·9. $C_8H_3O_2N_3$ requires C, 55·5; H, 1·75%). When reduced with sodium hydrosulphite, it gave colourless crystals, m. p. 160—170°, of a substance containing a diazotisable amino-group, which was probably 4-aminophthalonitrile; this substance gave with acetic anhydride small colourless plates, m. p. 188°, of 4-acetamidophthalonitrile. The latter was prepared also from 4-aminophthalimide as follows: the imide (2 g.) was shaken with aqueous ammonia (30 c.c.; *d* 0·88), and the mixture kept overnight; the white leaflets of 4-*aminophthalodiamide* obtained began to decompose near 250° and melted between 280° and 290° (Found : C, 54·6; H, 5·3; N, 24·2. $C_8H_9O_2N_3$ requires C, 53·6; H, 5·1; N, 23·5%). Although the diamide was not pure, its identity was established from the fact that treatment with warm water decomposed it quantitatively into ammonia and 4-aminophthalimide. On being boiled with acetic anhydride for 6 hours, the diamide gave 4-*acetamidophthalonitrile*, which formed colourless plates (from water), m. p. 194° (Found : C, 65·7; H, 4·2. $C_{10}H_7ON_3$ requires C, 64·8; H, 5·1%). This substance, although not obtained pure, gave a dithio-β-*iso*indigo derivative when treated with ammonium hydrosulphide, this being a dark red powder which yielded a yellow methyl derivative.

Diaminodithio-β-iso*indigo* (III).—4-Nitrophthalonitrile (1 part) was suspended in alcohol (35 parts), and dry ammonia passed in for 10 minutes and then hydrogen sulphide for 1 hour; the liquid turned dark red and deposited part of the thio-compound; the reaction was completed by 2 hours' boiling under reflux, with occasional passage of small amounts of ammonia and hydrogen sulphide. When the ammonia was finally driven off, the whole of the dithio-derivative separated; it was freed from sulphur in the usual manner and then purified by extraction with boiling nitrobenzene and α-chloronaphthalene, the residue (yield, 73%) consisting of small needles, deep red by transmitted light, of (III) (Found : C, 58·8; H, 3·95; S, 19·5. $C_{16}H_{12}N_4S_2$ requires C, 59·2; H, 3·7; S, 19·8%). It was practically insoluble in organic solvents.

The Blue Substance obtained by the Action of Aqueous Acids upon β-iso*Indigodihydrazone*.—The dihydrazone (5 g.) was dissolved, by warming, in a mixture of water (50 c.c.) and glacial acetic acid (20 c.c.), and the dark brown solution filtered and boiled on an oil-bath under reflux for 6 hours. A dark blue powder with metallic lustre was deposited. It was best purified by extracting it under reflux several times with glacial acetic acid (oil-bath), to remove soluble impurities, washing the residue with boiling water, and then extracting the moist solid several times with boiling pyridine (50 c.c.) for 1 hour : a considerable proportion of the substance dissolved in the pyridine in these circumstances, although the dry substance is only very sparingly soluble. The blue compound was obtained from the pyridine solution on addition of water (10 c.c.) and keeping for some days, or on addition of benzene. The product melted between 295° and 310°, with decomposition, and was very sparingly soluble in the common solvents; boiling nitrobenzene, α-chloronaphthalene, or quinoline gradually decomposed it. The same substance was prepared from the dihydrazone, aqueous butyric, chloroacetic, or phenylacetic acid being used, instead of acetic acid; but anhydrous acetic, chloroacetic, or phenylacetic acid did not yield any blue substance on prolonged fusion with the dihydrazone. The blue substance was also obtained when a filtered solution of the dihydrazone (5%) in cold glacial acetic acid, containing a little water, was kept for a month at room temperature.

The considerable variations observed at first in analyses of the blue substance were later found to be due to the facts (*a*) that the material dried over calcium chloride or potash was somewhat hygroscopic, and (*b*) that the conditions of the preparation and preliminary purification produced variations in the content of the combined water (*i.e.*, that not removable by means of the common desiccating agents). An average of analyses of six earlier specimens, prepared and purified in various ways and dried over calcium chloride, gave C, 65·9; H, 4·7; N, 19·8; whereas $C_{32}H_{16}N_8,4H_2O$ requires C, 65·75; H, 4·1; N, 19·2%. Later, a specially pure sample was prepared, by the method given first above, and was purified by precipitation from pyridine with benzene; it was allowed to become fully hydrated in the air, giving then C, 62·0; H, 4·7; N, 18·3 ($C_{32}H_{16}N_8,6H_2O$ requires C, 61·95; H, 4·5; N, 18·1%); on now being heated in a stream of dry air for 4 hours at 130°, it lost 8·6% of water (calc. for the loss of $3H_2O$ in above formula, 8·7%) : thus, allowing for the water of hydration ($3H_2O$), the dried substance had C, 67·8; H, 4·1; N, 20·0, and may thus have been (IV) combined internally with three molecular proportions of water ($C_{32}H_{16}N_8,3H_2O$ requires C, 67·85; H, 3·9; N, 19·8%). When the blue compound was prepared by the prolonged action of concentrated acetic acid on the dihydrazone in the cold, it appeared to consist of (IV*A*) in a tetrahydrated condition, the material dried at 130° having C, 70·4; H, 3·7; N, 21·2 ($C_{32}H_{16}N_8,2H_2O$ requires C, 70·05; H, 3·65; N, 20·45%). Oxidation of the blue compound was carried out in boiling glacial acetic acid, to which chromic acid was added slowly until the suspended solid had dissolved; the liquid, when diluted with water and cooled in ice, gave pure phthalimide (0·55 g. from 1 g. of the blue compound). For comparison, phthalaz-1 : 4-dione was oxidised in the same manner: no phthalimide resulted, indicating that the blue compound did not possess a *cyclo*hydrazide structure. Phthalaz-1 : 4-dithione gave no blue compound when heated with phthalimidine at 200°, this result pointing in the same direction.

Action of Hydrogen Sulphide on Phthalonitrile.—(*a*) Pure phthalonitrile (5 g.) was heated in a glass tube on an oil-bath at 150°, a vigorous stream of hydrogen sulphide (dried over phosphoric oxide) being passed through the molten mass by means of a wide delivery tube which was kept in rotation to act as a stirrer. The temperature was gradually raised to 160°, the melt solidifying after about ¾ hour. The solid was powdered and treated with a slow stream of the gas at 180° for ½ hour; it was then extracted with boiling pyridine (two portions of 50 c.c. each) to remove tarry matter, washed with hot alcohol, and dried at 110°. The residue of phthalocyanine weighed 2·6 g. (52% yield).

(*b*) A mixture of phthalonitrile (2 parts) and aniline (1·46 parts; 1 mol.) was treated with a stream of hydrogen sulphide while being heated in an oil-bath at 180° for 1½ hours. A stiff paste of greenish-blue needles with bronze lustre was obtained. This was submitted to filtration, and the crystals washed with boiling alcohol and pyridine. The product (yield, 0·55 part), which was free from sulphur, was identified as phthalocyanine by its properties and analysis (Found: C, 75·0; H, 3·6. Calc. for $C_{32}H_{18}N_8$: C, 74·7; H, 3·5%).

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