237. *The Comparative Reactivity of the Carbonyl Groups in the Thionaphthenquinones. Part II. The Influence of Substituent Groups in the Thionaphthenquinones.*

By Charles E. Dalgliesh and Frederick G. Mann.

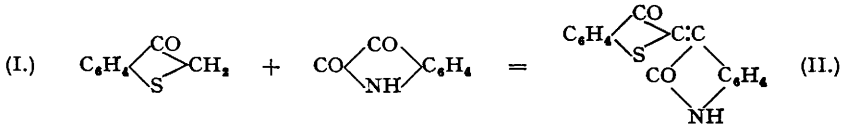
The work described in Part I has now been extended to include a comparison of the reactivities of the carbonyl groups in twelve thionaphthenquinones. These have been condensed with the corresponding thioindoxyls; condensation of the α-carbonyl group of the thioquinone with the methylene group of the thioindoxyl would thus produce a thioindigo, whereas similar condensation of the β-carbonyl group would produce a thioindirubin.

It is now shown, contrary to earlier evidence, that condensation of the thioquinones with the thioindoxyls may sometimes give rise to a mixture of a thioindigo and a thioindirubin; these products are not interconvertible under the conditions employed. Since the course of this condensation is now known to be influenced by the medium employed, a standard medium has been employed throughout, and the results summarised in Table I are thus strictly comparable.

The results confirm the earlier conclusions that the course of the condensation in these circumstances is determined primarily by the substituents in the thioquinone molecule and is rarely affected by those in the thioindoxyl molecule. A much wider basis is now available for the correlation of the position of the substituent with the type of resultant condensation, a further 99 pairs of dyes having been investigated in addition to the re-examination of many of the 42 such pairs previously studied.

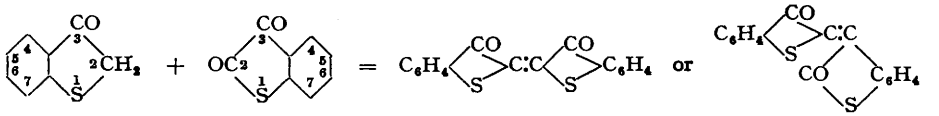
The significance of the extended evidence is discussed.

In Part I (Harley-Mason and Mann, *J.*, 1942, 404) it was pointed out that when thioindoxyl (I) condenses with isatin it is solely the β-carbonyl group of the latter which reacts, and the product (II) is consequently of the indirubin type; the non-reactivity of the α-carbonyl group of isatin was attributed to the fact that this compound acts predominantly in the enol or lactim form. Such tautomerism is impossible however in thionaphthenquinone (III), in which both carbonyl groups are consequently free for condensation with a reactive



(I.) (II.)

methylene group. Thioindoxyl (I) may therefore condense either with the α-carbonyl group of thionaphthenquinone to give thioindigo (IV) or with the β-carbonyl group to give thioindirubin (V). In order to ascertain

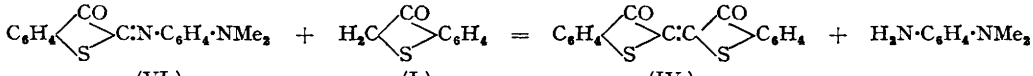


(I.) (III.) (IV.) (V.)

the fundamental factors that determine the comparative reactivity of the carbonyl groups in the thionaphthenquinone system, Harley-Mason and Mann (*loc. cit.*) condensed various substituted thioindoxyls with substituted

thionaphthenquinones, and then identified the nature of the product by comparison with an authentic sample of the corresponding thioindigo; clearly, if the condensation product proved to be identical with the thioindigo, the α-carbonyl group of the original quinone possessed the greater reactivity; if the condensation product was not identical, it was necessarily the thioindirubin, and therefore the β-carbonyl group of the quinone had been more reactive.

Authentic samples of the required thioindigos were prepared either by ferricyanide oxidation of the thioindoxyl or by condensation of the thioindoxyl (I) with the thioquinone-α-anil (VI) prepared from the thioindoxyl. The former method necessarily gave only symmetrically substituted thioindigos, whereas the second



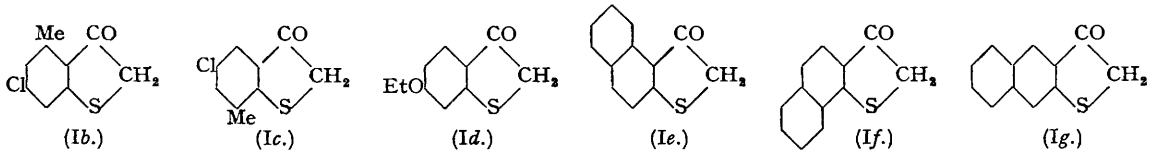
(VI.) (I.) (IV.)

method could, by the use of suitably substituted derivatives of (I) and (VI), provide thioindigos with substituents in any desired position.

To compare the above condensation products with the corresponding authentic thioindigos the chief method employed was reductive acetylation, the products being reduced by zinc dust in boiling acetic acid (Friedländer, *Monatsh.*, **1908**, **29**, 373), whereby diacetyldihydro-thioindigos (VII) and diacetyldihydro-thioindirubins (VIII) were obtained; these compounds were usually obtained as colourless crystals having sharp m. p.'s, and afforded a ready means of characterisation of the parent compounds.

(VII.) (VIII.)

The thioindoxyls used by Harley-Mason and Mann (*loc. cit.*) were: thioindoxyl (I); 6-chloro-4-methylthioindoxyl (I*b*); 5-chloro-7-methylthioindoxyl (I*c*); 6-ethoxythioindoxyl (I*d*); 4 : 5-benzthioindoxyl (I*e*); 6 : 7-benzthioindoxyl (I*f*); 5 : 6-benzthioindoxyl (I*g*).



(I*b*.) (I*c*.) (I*d*.) (I*e*.) (I*f*.) (I*g*.)

These compounds were converted into their 2-*p*-dimethylamino- or 2-*p*-hydroxy-anils, and the latter on hydrolysis furnished the corresponding thionaphthenquinones (III—III*g*).

These experiments indicated that the condensation of a thioindoxyl and a thioquinone apparently always

and (B) with the α-anil of the thioindoxyls (I—II) could now be studied. The product arising from (A) was compared with the authentic thioindigo obtained from (B) in order to determine whether the reaction (A) had involved the α- or β-carbonyl group of the quinone. The range of our original results has thus been more than trebled.

In the course of this extension of the original work, two novel factors have been detected, and ignorance of these factors invalidated certain of Harley-Mason and Mann's earlier conclusions.

In the first place, the condensation of certain thioindoxyls with the quinones is markedly affected by the nature of the solvent and catalyst used. This is discussed in Part III (p. 910) where it is shown that in general an increase in the acidic nature of the solvent or of the catalyst favours β-condensation. Furthermore, certain solvents, whilst promoting the condensation will at the same time react with the thioindoxyl, and the resulting dyestuff may consequently be contaminated with by-products. The majority of the condensations performed by Harley-Mason and Mann were carried out in glacial acetic acid containing a small quantity of zinc chloride; certain sluggish condensations were, however, accelerated by the addition of acetic anhydride, and in others the zinc chloride was replaced by hydrochloric acid. It is now recognised that the results were possibly not strictly comparable. Consequently we have repeated all the condensations of doubtful validity recorded in Part I, using throughout the standard condensation medium (acetic acid–zinc chloride) that we have employed for our new condensations. We can therefore claim that, in this respect, all our results are now strictly comparable.

Secondly, it is now apparent that some diacetyldihydro-thioindirubins form mixed crystals with the isomeric diacetyldihydro-thioindigos, and such mixed crystals often have a sharp m. p. In such cases, repeated recrystallisation will steadily change the m. p. until ultimately it becomes constant, *i.e.*, it becomes identical with that of a pure sample of one constituent. In Harley-Mason and Mann's earlier work, when a condensation product gave a diacetyldihydro-derivative which after recrystallisation was analytically pure and had a sharp m. p., and when moreover this m. p. differed decisively from that of the authentic diacetyldihydro-thioindigo, the original condensation product was deemed to be the pure thioindirubin, uncontaminated with any isomeric thioindigo. Obviously, these properties are not sufficient to identify the product as solely thioindirubin; for this purpose, the diacetyldihydro-derivative must have a m. p. which is both sharp and unaffected by further recrystallisation and which is either markedly different from that of the authentic isomeric diacetyldihydro-thioindigo or, if similar, causes a considerable depression in a mixed m. p. determination.

This factor does not enter, of course, into those condensations from which the product, on reductive acetylation, proved to be a pure thioindigo. In all other condensations—both those recorded in Part I and those encountered in our present extension—the diacetyldihydro-derivative has been very carefully investigated; in a few cases it proved to be the pure thioindirubin derivative, but in others it proved to be a mixture of the thioindigo and the thioindirubin derivatives. In the latter cases it was sometimes possible by fractional recrystallisation to isolate both the pure components; usually, however, only the least soluble component was isolated and identified, the presence of the other being proved by the fact that the m. p. of the original mixed components—which may have been sharp or extended over a range—changed markedly during the repeated recrystallisations, although the elementary analytical values remained unchanged. This improved technique has shown for the first time that both thioindigo and the isomeric thioindirubin may be produced simultaneously.

The identity of certain of our condensation products has again been independently determined by Dr. W. H. Taylor, assisted by Dr. D. L. Smare, Dr. I. G. Edmunds, and Dr. A. Hargreaves, at the Physics Department of the Manchester College of Technology. For this purpose, a direct comparison has been made between the *X*-ray " powder " photographs of the particular condensation product and of the corresponding authentic thioindigo (for details, see Harley-Mason and Mann, *loc. cit.*, p. 410). We are greatly indebted to Dr. Taylor and his staff for their very extensive and critical work on this subject. It is emphasised that their final conclusions have in no case been irreconcilable with those based on chemical evidence.

Our complete results, showing the identity of the products of the condensation of the twelve thioindoxyls and the corresponding thioquinones are summarised in Table I, the detailed evidence being collected in Tables II—XIII.

Before discussing these results, two other factors, which also might have invalidated our conclusions, must be briefly mentioned. It has already been stated (p. 894) that whereas authentic symmetrically substituted thioindigos were prepared by oxidation of the corresponding thioindoxyls, the authentic unsymmetrically substituted thioindigos could only be prepared by the condensation of one thioindoxyl with the anil of another (as VI). This assumes that the first thioindoxyl group directly replaces the *p*-dimethylamino-anil group and that the two thionaphthen nuclei become joined through the 2 : 2′-carbon atoms. The mechanism of this reaction may not, however, be so simple. It is conceivable that the first thioindoxyl molecule condenses with the β-carbonyl group of the anil, and the *p*-dimethylamino-anil group is then hydrolysed off and so replaced by an oxygen atom; the two thionaphthen nuclei would thus become linked through the 2 : 3′-carbon atoms, *i.e.*, a thioindirubin would result. The possibility of this mechanism receives some support from the work of Pummerer (*Ber.*, **1911**, **44**, 338), who showed that thioindoxyl (I) condensed with isatin-2-anil (IX) producing 2 : 3′-thionaphthen-indol-indigo-2′-anil (X), which he isolated in two tautomeric forms.

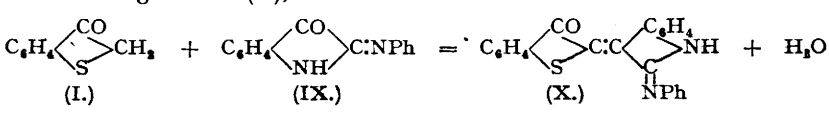


TABLE I.

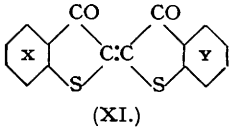
Thioindoxyls.	Thionaphthenquinones. Unsubstd. (III).	6-Cl-4-Me- (III*b*).	5-Cl-7-Me- (III*c*).	6-EtO- (III*d*).	4 : 5-Benz- (III*e*).	6 : 7-Benz- (III*f*).	5 : 6-Benz- (III*g*).	4-Me- (III*h*).	4-Cl- (III*i*).	5-Me- (III*j*).	7-Me- (III*k*).	7-Cl- (III*l*).
Unsubstd. (I)	$\underline{\alpha+\beta}$	α	α	$\underline{\alpha+\beta}$	α	α	$\alpha+\underline{\beta}$	α	α	α	$\underline{\alpha+\beta}$	α
6-Cl-4-Me- (I*b*)	$\alpha+\beta$	α	α	$\alpha+\beta$	α	α	$\underline{\alpha+\beta}$	α	α	α	$\underline{\alpha+\beta}$	$\alpha+\underline{\beta}$
5-Cl-7-Me (I*c*)	$\underline{\alpha+\beta}$	α	α	$\alpha+\beta$	α	α	$\alpha+\underline{\beta}$	α	α	α	α	α
6-EtO- (I*d*)	$\alpha+\beta$	α	α	$\alpha+\beta$	$\alpha(+\beta)$	$\underline{\alpha+\beta}$	$\underline{\alpha+\beta}$	α	α	$\alpha(+\beta)$	$\alpha(+\beta)$	α
4 : 5-Benz- (I*e*)	$\underline{\alpha+\beta}$	$\alpha+\beta$	α	$\alpha+\beta$	α	$\alpha+\underline{\beta}$	$\alpha+\beta$	α	α	α	β	α
6 : 7-Benz- (I*f*)	$\alpha+\beta$	α	$\underline{\alpha+\beta}$	$\underline{\alpha+\beta}$	α	α	$\alpha+\beta$	α	α	α	α	α
5 : 6-Benz- (I*g*)	$\underline{\alpha+\beta}$	α	α	$\underline{\alpha+\beta}$	α	α	$\alpha+\beta$			α	β	
4-Me- (I*h*)	α *	α	α	$\alpha(+\beta)$	α	α	$\alpha+\beta$	α	α	α	α	$\underline{\alpha}+\beta$
4-Cl- (I*i*)	α *	α	α	$\underline{\alpha+\beta}$	α	α	$\alpha+\beta$	α	α	β	β	β
5-Me- (I*j*)	$\underline{\alpha+\beta}$	α	α	$\alpha(+\beta)$	α	α	$\underline{\alpha+\beta}$	α	β	α	α	$\alpha+\beta$
7-Me- (I*k*)	α *	α	α	$\underline{\alpha+\beta}$	α	$\underline{\alpha+\beta}$	$\alpha+\underline{\beta}$	α	β	α	α	α
7-Cl- (I*l*)	$\underline{\alpha+\beta}$	α	α	$\underline{\alpha+\beta}$	α	α	$\alpha+\beta$	α	β	α	α	α

The entry "$\underline{\alpha+\beta}$" in the above Table indicates that both α- and β- condensation products were formed and have been separated, either as the dyes or as their diacetyl-dihydro derivatives. The entry "$\alpha+\beta$" indicates that both products were formed, but that their presence was determined chemically without actual separation; when, in such cases, one form occurred in much greater proportion than the other, its symbol is underlined, *e.g.* "$\underline{\alpha}+\beta$." Parentheses enclosing one symbol, *e.g.*, "$\alpha(+\beta)$," indicate that the presence of the form in parentheses was strongly suggested by *X*-ray analysis, but was not detected chemically.

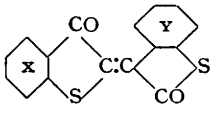
* In these condensations the mother-liquor from the reductive acetylation was not examined for the possible presence of the β-compound.

The following evidence shows, however, that the simpler mechanism applies to our anil condensation which, therefore, gives solely thioindigos. (*a*) We find that when a thioindoxyl is condensed with its own α-anil, the product is identical with that formed by ferricyanide oxidation of thioindoxyl alone, *i.e.*, it is a pure thioindigo. (*b*) We have attempted to prepare a compound similar to (X) by the condensation of thioindoxyl with thionaphthenquinone-2-*p*-dimethylamino-anil; for this purpose we have used both alkaline and acidic media, but all such attempts failed. Either the conditions were such that the reactants were isolated unchanged or the reaction proceeded normally with the production of thioindigo as the sole dyestuff. Furthermore, Pummerer's condensation was performed in an alkaline solution, whereas our standard condensations were all carried out in acid solutions.

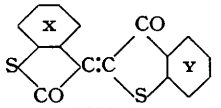
The second factor that might have invalidated our results would have been the existence of any interconversion, thioindigo $\rightleftarrows$ thioindirubin, under the conditions of our condensations. Clearly, if such interconversion occurred it would explain the formation of mixed dyestuffs in certain condensations which we have now detected; furthermore, in those condensations from which we have isolated only one dyestuff, this compound may have been merely the more stable of the two products initially formed. Such an interconversion is exceedingly improbable, however, on general chemical grounds. It is also disproved for the following reasons: (*a*) If an unsymmetrically substituted thioindigo (XI) were to undergo conversion to the thioindirubin, the latter could occur in two isomeric forms (XII) and (XIII). Similarly, if either of the unsymmetrically



(XI.)

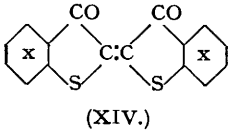


(XII.)

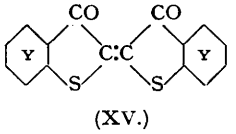


(XIII.)

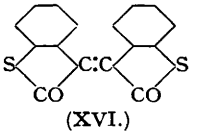
substituted thioindirubins (XII) or (XIII) were to undergo conversion to the thioindigo and, if this conversion entailed momentary formation of free radicals, the two symmetrically substituted thioindigos (XIV) and (XV) as well as (XI) and possibly even the thio-*iso*indigo (XVI), might be formed.



(XIV.)



(XV.)



(XVI.)

In all our numerous condensations, however, we have never detected the formation of isomeric thioindigos or of isomeric thioindirubins in any one experiment; the product has always been one thioindigo or one thio-

indirubin or a mixture of these two compounds. (*b*) The preparation of our authentic thioindigos by the condensation of the thioindoxyl and the anil was performed under conditions closely similar to those employed for the condensation of the thioindoxyl and the thioquinone; yet the former condensation always yielded solely the pure thioindigo. This is strong evidence against the above interconversion, unless it is assumed that the thioindigo is always considerably more stable than the thioindirubin. (*c*) In certain cases, however, condensation of the thioindoxyl with the thioquinone gave pure thioindirubin, whereas condensation of the thioindoxyl with the anil under almost identical conditions gave (as always) pure thioindigo. This shows that in these cases no interconversion occurred under our experimental conditions. (*d*) The possibility of the above interconversion is clearly greater when a mixture of thioindigo and thioindirubin does actually arise, *e.g.*, when thioindoxyl (I) and thionaphthenquinone (III) undergo condensation (Table II). We have therefore boiled pure thioindigo (IV) with acetic acid and zinc chloride, *i.e.*, under the conditions of our condensations, for four hours; it remained unchanged, however, and no thioindirubin could be detected. We have repeated other condensations that give rise to a mixture of a thioindigo and a thioindirubin, varying the time of boiling within wide limits. We have then determined the proportion of thioindigo and thioindirubin in the product by reductive acetylation followed by fractional crystallisation. This method for determining the proportion, admittedly, is not highly accurate, but we have been unable to detect any change in the proportion of the two products. The interconversion had therefore either not occurred or occurred with astonishing rapidity in the initial stages of the original condensations.

All the above evidence leaves no doubt that this interconversion does not occur under our conditions. Consequently, the results summarised in Table I can now be accepted as describing the authentic products of the various condensations performed under strictly comparable conditions.

Consideration of the collected results in Table I strongly confirms Harley-Mason and Mann's conclusion that, under comparable conditions, the nature of the condensation is determined primarily by the substituents in the thioquinone molecule and only to a small extent by those in the thioindoxyl molecule; individual members of several vertical columns are almost wholly identical, those of the horizontal columns never so. The following generalisations can be made: (i) and (iv) also strongly confirm the conclusions of Harley-Mason and Mann, but the others have been changed in view of our extended evidence. [A second benzene ring fused to the main ring is regarded as two separate substituents.] (i) A substituent in the 4-position in the thioquinone almost always gives solely α-condensation; of the 46 examples in Table I, 41 gave only thioindigos, 2 gave mixtures, and 3 gave only thioindirubins. (ii) A substituent in the 5-position in the thioquinone molecule also usually gives solely α-condensation; examples are the quinones (III*c*), where the 7-methyl group is ineffective (see below), (III*e*), where the 4- and 5-substituents reinforce one another, and (III*j*); in these 36 examples, 32 gave solely α-condensation, 3 gave mixtures containing mainly the thioindigo and 1 gave solely β-condensation. (iii) The absence of substituents, or a substituent in the 6-position in the thioquinone molecule, usually gives rise to both α- and β-condensation; the effect of the 6-substituent is well shown in (III*d*) and in (III*g*), where it apparently overrides the influence of the 5-substituent; in (III*b*) its influence is, as expected, completely suppressed by that of the powerful 4-substituent; in (III*f*) the joint effect of the 6- and 7-substituent is unpredictable. (iv) A substituent in the 7-position in the thioquinone is without apparent effect; in the absence of other substituents in the quinone, those in the thioindoxyl molecule determine the type of condensation; these are apparently the only conditions in which the thioindoxyl molecule exerts a dominant influence.

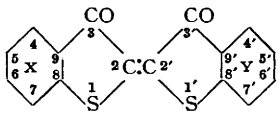
The theoretical interpretation of these results depends on many factors and must be exceedingly complex. The marked effect of a 4-substituent in the thioquinone molecule in suppressing thioindirubin formation may well be mainly steric and is discussed later. The effect of similar substituents in the 5-, 6-, and 7-positions cannot be steric and must be almost wholly electronic; this effect, in turn, must be intimately associated with the mechanism of the α- and β-condensation processes which are themselves unknown. Moreover, it is shown in Part III that the condensation medium, *i.e.*, the solvent with or without a catalyst, may have a marked effect on the type of condensation which occurs; this effect may be completely overridden by that of a favourably situated substituent in the thioquinone molecule (for example, III*b*) but when the substituents normally allow β-condensation the latter is promoted by an acidic and suppressed by a basic medium. The results collected in Table I must represent the resultant of these various influences.

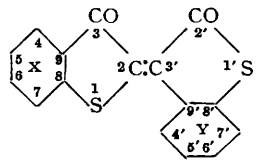
The probable structure of thioindigo and thioindirubin, and the possibility of steric hindrance in 4-substituted thioindirubins, deserve brief discussion. Harley-Mason and Mann (*loc. cit.*) have pointed out that thioindoxyl, thionaphthenquinone, thioindigo, and thioindirubin all exist as resonance hybrids; ignoring resonance in the benzene ring, thioindigo and thioindirubin may each exist in 6 canonical forms of one geometric configuration. Consequently we have no accurate knowledge of the inter-atomic distances and atomic sizes in the heterocyclic rings of these compounds; further, the geometric configuration of each of these compounds is unknown. Crystalline indigo has the *trans*-configuration (Reis and Schneider, *Z. Krist.*, 1928, **68**, 543), but there is chemical evidence that it may react in the *trans*- or *cis*-form (Posner, *Ber.*, 1926, **59**, 1799; van Alphen, *Ber.*, 1939, **72**, 525); it is highly probable that thioindigo also has the *trans*-configuration.

Considering the above properties, we have attempted to assess the probable dimensions of the thioindigo and thioindirubin molecules, numbered as in (XVII) and (XVIII) respectively. In (XVII), the C–C bond lengths in the benzene ring are taken as 1·39 A., the central C : C length as 1·33 A., and the radius of hydrogen joined to the benzene ring as 0·30 A. (*The Nature of the Chemical Bond*, Pauling, 2nd Edtn., 1940). The angles $S^1C^2C^3$ and $C^2C^3C^9$ are taken as 109° which is the C–C–C angle at the carbonyl group in benzoquinone (*Ann. Reports*,

1935, **32**, 223); the bond length C³–O is evaluated as 1·20 A., *i.e.*, the mean value for the C–O distance in benzoquinone (1·14 A.), urea (1·25 A.), and oxalic acid (1·25 A.) (*Ann. Reports, loc. cit.*). The bond length C^8S^1 and

(XVII.)





(XVIII.)

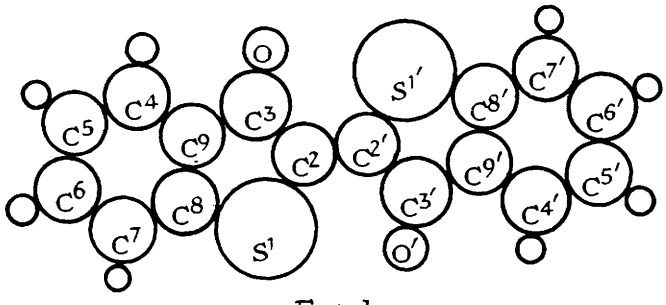


FIG. 1.

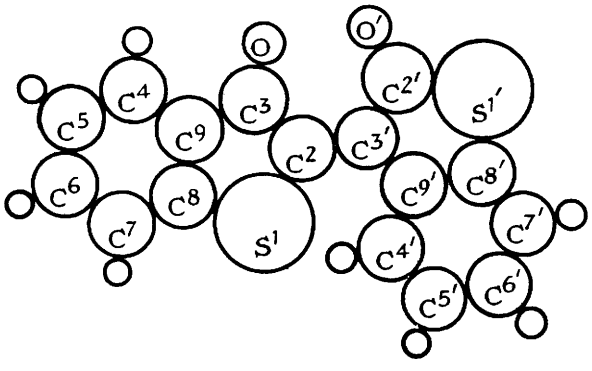


FIG. 2.

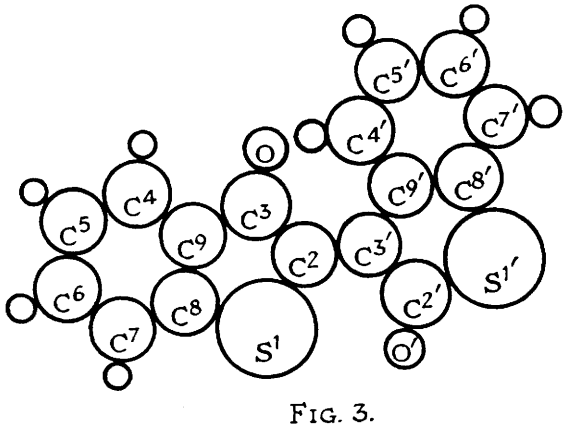
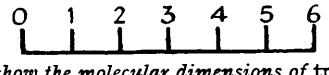


FIG. 3.



Figs. 1, 2, *and* 3 *show the molecular dimensions of* trans-*thioindigo*, cis-keto-*thioindirubin, and* trans-keto-*thioindirubin, respectively.*

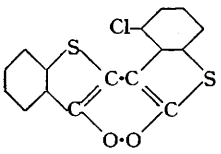
S^1C^2 are taken as 1·74 A.; the normal value for a C–S bond (1·81 A.) is reduced to 1·74 A. in thiophen (Pauling, *op. cit.*) and some allowance is thus made for resonance. Similarly, the bond lengths C^2–C^3 and C^3–C^9 have been reduced from the normal value of 1·54 A. to 1·48 A.; Robertson *et al.* (*J.*, 1938, 134; 1940, 36) have shown that the C–C distance in the pyrrole rings of phthalocyanine has been reduced to 1·47 A. and that the C–C bond joining the two rings in diphenyl is 1·48 A. No reliable data were available for the angle $C^8S^1C^2$, which has been taken as 98·5°. The mean value for the sulphur angle in various compounds is 103° (Pauling, *op. cit.*), but its value in a ring system has not been accurately determined; Schomaker and Pauling (*J. Amer. Chem. Soc.*, 1939, **61**, 1776) give the sulphur angle in thiophen as 91°±4°, whilst Robles (*Rec. trav. Chim.*, 1940, **59**, 184) has calculated the angle in tetrahydrothiophen to be 98·5°. Since in crystalline selenium the intervalency angle is 105° (Pauling, *op. cit.*) but is reduced to 96° in selenanthren (Wood and Williams, *Nature*, 1942, **150**, 321) our reduction for the sulphur angle appears justified.

In thioindirubin (XVIII), the bond $C^{3'}$–$C^{9'}$ (1·35 A.) is determined by the fact that $C^{3'}$ has a radius 0·665 A. due to the C:C bond, and C^9 has a radius 0·69 A., being part of the benzene ring; the bond $C^{2'}$–$C^{9'}$ is thus shorter than the corresponding bond C^3–C^9. The angles $C^{2'}C^{3'}C^{9'}$, $C^{3'}C^{2'}S$, and $C^{2'}SC^{8'}$, and the bond lengths S–$C^{8'}$ and S–$C^{2'}$ have the same values as the corresponding features in the other portion of the molecule. The bond length $C^{2'}$–$C^{3'}$ is necessarily slightly shortened.

On the basis of these data, we have constructed Figs. 1, 2, and 3, which show the molecular dimensions of *trans*-thioindigo, *cis-keto*-thioindirubin and *trans-keto*-thioindirubin. It is clear that a substituent (*e.g.*, a methyl group) in the 4'-position in thioindigo (Fig. 1) cannot cause steric hindrance, but, on the other hand, there is no room for such a group in this position in either form of thioindirubin (Figs. 2 and 3) unless considerable distortion of these normally planar molecules occurs. There is little doubt therefore that this steric factor does exist, and is probably the main reason why 4-substituted thioquinones almost invariably give solely thioindigos.*

* This conclusion is confirmed by the results which we have obtained in another investigation (to be published later), in which a reaction involving the >CO group in thioindoxyl is apparently completely suppressed by 4-substituents, but is unimpeded by substituents in the 5-, 6-, and 7-positions.

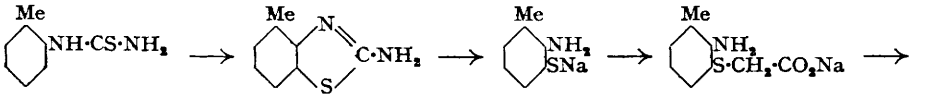
There are, however, three striking exceptions to this rule, for although 4-chlorothioquinone (III*i*) gives solely α-condensation with eight thioindoxyls (I—I*f*, I*h*, I*i*), it gives solely β-condensation with the remaining three (I*j*—I*l*). These three 4′-chloro-thioindirubins could presumably exist only if (*a*) the thiophen ring were considerably distorted, which is unlikely, or (*b*) the molecule were twisted about the C:C linkage, and so became no longer planar, or (*c*) the valency angles about the C:C bond were distorted, so that the two keto groups in Fig. 2 and the S^1 and $C^{2'}$ keto groups in Fig. 3 were brought nearer together, to give room for the 4′-chloro group. If this were to occur in the *cis-keto*-form, the two oxygen atoms might become sufficiently near to form a peroxide link, and the compound would be stabilised by resonance between the structure (XIX) and the normal thioindirubin structure. This explanation, however, should allow 4-chlorothioquinone (III*i*) to give thioindirubins with all the thioindoxyls studied; the influence of the 4-chloro-substituent is clearly anomalous and deserves further study.



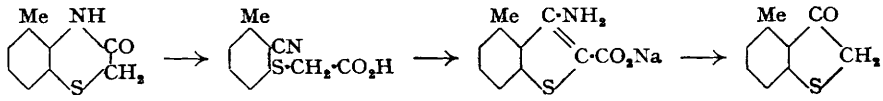
(XIX.)

A comprehensive discussion of the probable condensation mechanisms and of many other factors, summarised in Table I, requires more space than present conditions permit.

The preparation of the thioindoxyls (I*h*—I*l*) and their derivatives requires brief description. To prepare 4-methylthioindoxyl (I*h*), *o*-toluidine hydrochloride was converted by the action of sodium thiocyanate to *o*-tolylthiourea (XX), which by the action of bromine in chloroform was cyclised to 2-amino-4-methylbenzthiazole (XXI); this method of cyclisation, described by Erlenmeyer and Ueberwasser (*Helv. Chim. Acta*, 1942, **25**, 515) was preferable to the use of bromine and sulphuryl chloride in chlorobenzene (B.P. 379,341). The thiazole (XXI), when heated in an autoclave at 200° with 20% aqueous sodium hydroxide, gave the sodium salt of 2-amino-*m*-thiocresol (XXII), which condensed readily with sodium chloroacetate furnishing sodium 2-amino-3-methylphenylthioglycollate (XXIII); an aqueous solution of the latter on acidification

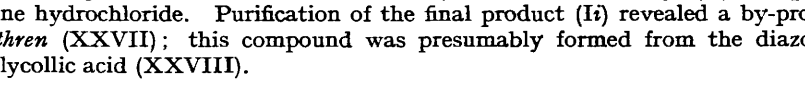


(XX.) (XXI.) (XXII.) (XXIII.)



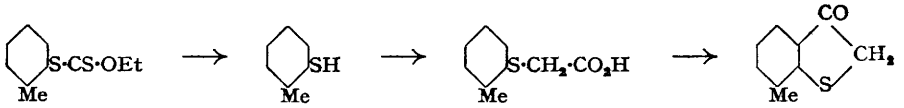
(XXIV.) (XXV.) (XXVI.) (I*k*.)

precipitated the lactam, 3-*keto*-5-*methyl*-3 : 4-*dihydro*-1 : 4-*benzothiazine* (XXIV). A solution of (XXIV) in sodium hydroxide, when diazotised and treated with cuprous cyanide, was converted into 2-cyano-3-methylphenylthioglycollic acid (XXV); this, when heated with sodium hydroxide, furnished sodium 3-amino-4-methylthionaphthen-2-carboxylate (XXVI) and this compound, on boiling with hydrochloric acid, underwent decarboxylation giving the required 4-methylthioindoxyl (I*h*). This compound has previously been prepared by the route: 3-nitro-*o*-toluidine ⟶ 2-cyano-*m*-toluidine ⟶ 2-carboxy-3-methylphenylthioglycollic acid (E.P. 279,489, cf. Guha, *J. Ind. Chem. Soc.*, 1938, **15**, 20). 4-*Chlorothioindoxyl* (I*i*) was prepared similarly from *o*-chloroaniline hydrochloride. Purification of the final product (I*i*) revealed a by-product, apparently 1 : 5-*dichlorothianthren* (XXVII); this compound was presumably formed from the diazotised 3-chloro-2-aminophenylthioglycollic acid (XXVIII).



5-Methylthioindoxyl (I*j*) was readily prepared by converting *p*-tolylthioglycollic acid into its chloride which, under the influence of aluminium chloride, readily cyclised to the thioindoxyl (I*j*). It has previously been prepared by the action of chloroacetyl chloride on *p*-tolyl methyl sulphide (Auwers and Arndt, *Ber.*, 1909, **42**, 541).

7-Methylthioindoxyl (I*k*) was prepared by a modification of Guha's method (*J. Ind. Chem. Soc.*, 1939, **16**, 219). *o*-Toluidine was diazotised and treated in alkaline solution with potassium xanthate; the *o*-tolyl xanthate (XXIX) so obtained, on alkaline hydrolysis, furnished *o*-thiocresol (XXX) which was converted to *o*-tolyl-



(XXIX.) (XXX.) (XXXI.) (I*k*.)

thioglycollic acid (XXXI). The latter was converted to the chloride which, in the presence of aluminium chloride, underwent cyclisation to 7-methylthioindoxyl (I*k*). 7-*Chlorothioindoxyl* (I*l*) was similarly prepared from *o*-chloroaniline.

We have critically examined the condensation of the thioindoxyls in alkaline solution with *p*-nitrosophenol and with *p*-nitrosodimethylaniline to give the 2-*p*-hydroxyanils and the 2-*p*-dimethylamino-anils respectively of the quinones. This preparation of the 2-*p*-hydroxyanils sometimes fails; Harley-Mason and Mann (*loc. cit.*) were able to condense only the thioindoxyls (I), (I*d*), and (I*f*) with *p*-nitrosophenol, and we have similarly failed in the cases of (I*b*), (I*c*), (I*e*), and (I*g*), although these anils can sometimes be obtained indirectly (see later). The condensation of a nitroso compound with a thioindoxyl is always accompanied by some oxidation of the latter to the thioindigo; since, however, the hydroxyanils form sodium salts which dissolve in hot water, the contaminating thioindigo can be readily removed, and these anils are in this respect of greater value than the dimethylamino-anils.

The method of preparation of the 2-*p*-dimethylamino-anils used by Mayer *et al.* (*Annalen*, 1931, **488**, 259) and by Harley-Mason and Mann (*loc. cit.*) has been advantageously modified; nevertheless, we found that in certain cases these anils readily underwent further hydrolysis to give dimethylamine, the 2-*p*-hydroxyanil and also the quinone. This reaction, noted originally by Mayer (*loc. cit.*), furnishes certain *p*-hydroxyanils, *e.g.*, those from (I*b*), (I*c*), and (I*e*), which could not be obtained by direct condensation.

Experimental.

Certain of the following compounds, whose preparation has been claimed in patent literature without proof of identity, are now recorded as new. The names of all new compounds are italicised as usual; where, to save space, the molecular formula and theoretical percentages are not given, these data have been given for isomeric substances earlier in the paper.

Preparation of Intermediates. Thioindoxyls.—*4-Methylthioindoxyl* (I*h*). (i) A dry mixture of *o*-toluidine hydrochloride (195 g.), sodium thiocyanate (119 g.), and chlorobenzene (880 c.c.) was refluxed for 6 hours and then allowed to cool. The solid was crushed, collected, and washed with methanol and water. The *o*-tolylthiourea (XX; 140 g., 62%) so obtained required no further purification. If the chlorobenzene filtrate was dried (calcium chloride) and used for the next preparation, the yield rose to 82%. The thiourea (XX), recrystallised from aqueous alcohol, had m. p. 155—156° (cf. F.P. 762,310).

(ii) A solution of bromine (37 c.c., 1 mol.) in chloroform (300 c.c.) was poured rapidly into a mixture of the dry powdered thiourea (120 g.) and chloroform (600 c.c.) contained in a 3-necked flask. Heat was evolved and the mixture rapidly gave a clear solution which was kept below 30° by external cooling. When the initial reaction had subsided the flask was fitted with a stirrer and condenser carrying a calcium chloride tube and the mixture refluxed until evolution of hydrogen bromide ceased (*ca.* 2 hours), the hydrobromide of the thiazole (XXI) crystallising out meanwhile. The mixture was set aside overnight, the liquid decanted and the residue boiled with fresh chloroform (300 c.c.). The cold mixture was filtered and the insoluble residue suspended in water and treated with sulphur dioxide until traces of free bromine had been removed (this was not always necessary). The mixture was again filtered and the residue suspended in warm water and made alkaline. The precipitated thiazole (XXI) was collected, washed with water, and dried (average yield, 106 g., 89%). This product (m. p. 130—135°) was sufficiently pure for the next stage. The thiazole (XXI) readily gave a *monopicrate*, yellow needles from acetone, m. p. 254° (decomp.) (Found: N, 17·7. $C_8H_8N_2S,C_6H_3O_7N_3$ requires N, 17·8%); it is sparingly soluble in alcohol.

(iii) A mixture of the thiazole (75 g.), sodium hydroxide (135 g.), and water (540 c.c.) was heated at 200° in a rotating autoclave for 5 hours. The mixture at 60° was poured into water (1100 c.c.); the temperature was raised to 80°, a solution of chloroacetic acid (50 g.) in 10% aqueous sodium hydroxide added and the temperature maintained at 80° for 30 minutes. The mixture whilst hot was filtered and acidified with hydrochloric acid, grey needles of the lactam (XXIV), *i.e.*, *3-keto-5-methyl-3 : 4-dihydro-1 : 4-benzothiazine* being immediately precipitated. When cold, these were collected, washed with water, and dried (average yield, 68 g., 83%). When recrystallised from alcohol, the compound had m. p. 125—127° (Found: C, 60·3; H, 5·2; N, 8·1. C_9H_9ONS requires C, 60·3; H, 5·0; N, 7·8%).

(iv) A mixture of the crude lactam (XXIV; 100 g.) and 10% aqueous sodium hydroxide was boiled for 3 hours and set aside overnight. A solution of sodium nitrite (45 g.) in water (70 c.c.) was added to the filtered mixture which was then added dropwise to a vigorously stirred mixture of ice (1200 g.) and concentrated hydrochloric acid (300 c.c.) maintained at 0—2° by external cooling. When the addition was complete the mixture was stirred for a further 15 minutes, made alkaline to Brilliant-Yellow with sodium carbonate and then slowly added to an agitated solution of cuprous cyanide (75 g.) and potassium cyanide (180 g.) in water (300 c.c.) maintained at 40°. Aqueous sodium hydroxide (33%; 150 c.c.) was added, and the temperature raised to 80° for 15 minutes to complete cyclisation to the sodium 3-amino-4-methyl-thionaphthen-2-carboxylate (XXVI), which was salted out by the addition of sodium chloride (600 g.). The sodium salt (XXVI) was collected, washed with 20% brine, added to 5% hydrochloric acid (1500 c.c.), and decarboxylation ensured by heating at 95° for 15 minutes. Filtration of the cold mixture gave the crude 4-methylthioindoxyl (I*h*) which was purified by washing with water followed by dissolution in boiling 10% aqueous sodium hydroxide; the solution was filtered directly on to ice and acidified with hydrochloric acid. The precipitated thioindoxyl (I*h*) was collected, washed with water and dried. It had m. p. 65—68° (highest yield obtained, 61 g.).

4-Chlorothioindoxyl (I*i*). The stages were strictly parallel to those above, and only quantities and yields are recorded.

(i) *o*-Chloraniline hydrochloride (460 g.), sodium thiocyanate (240 g.), and chlorobenzene (1750 c.c.) were heated together for 6 hours (initial yield of *o*-chlorophenylthiourea, 186 g., 35·5%; increase to 305 g., 58%, when saturated solvent was used again).

(ii) Bromine (40 c.c.) in chloroform (300 c.c.) and the thiourea (140 g.) in chloroform (600 c.c.) gave 4-chloro-2-aminobenzthiazole (126 g., 91%).

(iii) The thiazole (85 g.), sodium hydroxide (135 g.), and water (540 c.c.), heated at 200° for 3 hours and subsequently condensed with an alkaline solution of chloroacetic acid (55 g.), gave *5-chloro-3-keto-3 : 4-dihydro-1 : 4-benzothiazine* (72 g., 73·5%), white needles from alcohol, m. p. 153—154° (Found: C, 48·4; H, 2·8; N, 6·9. C_8H_6ONCIS requires C, 48·1; H, 3·0; N, 7·0%).

(iv) The lactam (101 g.) was dissolved in aqueous sodium hydroxide, diazotised with sodium nitrite (37·5 g.), and allowed to react with cuprous cyanide (62·5 g.) and potassium cyanide (150 g.). The mixture was cyclised by alkali as before, the sodium 4-chlorocarboxylate (as XXVI) salted out and decarboxylated to the crude *4-chlorothioindoxyl* (I*i*). The latter was purified by dissolution in boiling aqueous sodium hydroxide, filtering and reprecipitating with acid (maximum yield, 22·7 g., 26%). Further purification by distillation in steam gave (I*i*) as white needles, m. p. 116—118° (Found: C, 52·4; H, 3·1. C_6H_5OCIS requires C, 52·0; H, 2·7%). This compound rapidly oxidises in air.

On dissolving the crude compound (I*i*) in boiling aqueous sodium hydroxide an insoluble product remained; this was collected, dried, and extracted with boiling acetic acid. The brown crystals which separated from the filtered solution

were recrystallised from alcohol (charcoal) and then yielded colourless needles of 1 : 5-*dichlorothianthren* (XXVII), m. p. 174—175° (Found : C, 50·9; H, 2·4; Cl, 25·1; S, 23·1; *M*, cryoscopically in 1·106% ethylene dibromide solution, 306. $C_{12}H_6Cl_2S_2$ requires C, 50·5; H, 2·1; Cl, 24·9; S, 22·5%; *M*, 285).

5-*Methylthioindoxyl* (I*j*). Phosphorus trichloride (34·5 c.c., 1·35 mols.) was added to a mixture of *p*-tolylthioglycollic acid (54·6 g., 1 mol.) and chlorobenzene (300 c.c.); the mixture was vigorously stirred and heated on a water-bath for 2 hours. To the cold product, powdered aluminium chloride (44 g.) was added and, when the initial evolution of hydrogen chloride had subsided, the mixture was heated as before for 1½ hours. Ice (500 g.) was added and the mixture distilled with steam to remove chlorobenzene. The thioindoxyl (I*j*) could be steam distilled after the chlorobenzene but it was advantageous, when the chlorobenzene had passed over, to make the residue alkaline, filter the solution and precipitate the thioindoxyl (I*j*) by acidifying the filtrate (average yield, 37·7 g., 76·5%). The steam-distilled product had m. p. 94—98°; Auwers and Arndt (*loc. cit.*) give m. p. 102° (Found : C, 66·2; H, 4·9. Calc. for C_9H_8OS : C, 65·9; H, 4·9%).

7-*Methylthioindoxyl* (I*k*). (i) A solution of sodium nitrite (84 g.) in water (150 c.c.) was added dropwise during 1½ hours to a stirred mixture of *o*-toluidine (107 g.), concentrated hydrochloric acid (300 c.c.), and water (900 c.c.) maintained at 0—2°. The diazo-solution was then added in turn during 45 minutes to a stirred mixture of potassium xanthate (242 g.), anhydrous sodium carbonate (500 g.), and water (2 l.) maintained at 60—80°. After a further hour's stirring, the mixture was set aside overnight and then extracted with ether. Distillation of the ether left the crude yellow oily *o*-tolylxanthate (XXIX), which was boiled under reflux with a mixture of sodium hydroxide (215 g.), water (430 c.c.), and alcohol (1350 c.c.). A solution of chloroacetic acid (188 g.) in 10% aqueous sodium hydroxide (850 c.c.) was then cautiously added, and the boiling continued for a further 30 minutes. The alcohol was then distilled away, the solution added to ice (1 kg.), and the *o*-tolylthioglycollic acid (XXXI) precipitated with hydrochloric acid. The crude product was recrystallised from water (charcoal) : white plates, m. p. 106—107°. The average yield (85 g., 46·5%) was low owing to the large volume of water required in the recrystallisation to remove an oily impurity having a foul odour.

(ii) A mixture of the pure acid (XXXI; 18·2 g.), phosphorus trichloride (11·5 c.c., 1·33 mol.) and chlorobenzene (100 c.c.) was stirred and refluxed at 60—80° for 2 hours. Powdered aluminium chloride (14·7 g., 1·1 mols.) was cautiously added to the cold product. The temperature rose to 60°, and was maintained at this value for 1 hour. The cold mixture was added to ice (200 g.) and the chlorobenzene removed in steam.

The thioindoxyl (I*k*) was distilled in superheated steam and obtained in colourless needles (rapidly oxidising in air), m. p. 73—78°; average yield, 8·5 g., 51·5% calculated on compound (XXXI) used. Guha (*loc. cit.*) gives m. p. 68—69°.

7-Chlorothioindoxyl (I*l*) was prepared precisely as above (I*k*). (i) *o*-Chloraniline (105 c.c.), concentrated hydrochloric acid (270 c.c.) and ice (600 g.) were diazotised with sodium nitrite (84 g.) in water (200 c.c.). The solution was run into a mixture of potassium xanthate (240 g.), anhydrous sodium carbonate (500 g.), and water (2·5 l.) at 60—80°. The *o*-chlorophenyl xanthate, isolated as before, was hydrolysed with sodium hydroxide (214 g.), water (430 c.c.), and alcohol (1300 c.c.) for 5 hours, and then condensed with chloroacetic acid (188 g.) in 10% sodium hydroxide (800 c.c.). The *o*-chlorophenylthioglycollic acid, precipitated and recrystallised as compound (XXXI), was obtained in colourless leaflets, m. p. 117—118° (Found : C, 47·2; H, 3·8; Cl, 16·7. Calc. for C_8H_7OClS : C, 47·4; H, 3·5; Cl, 17·0%). The average yield, 67·5 g., 33·5%, was diminished by contamination of the crude product as in the former case. Friedländer, Chwala, and Slubek (*Monatsh.*, 1907, **28**, 272) give m. p. 112°.

(ii) Cyclisation to 7-*chlorothioindoxyl* (I*l*) was performed precisely as for (I*k*) above, using a mixture of the glycollic acid (20·2 g.), phosphorus trichloride (11·5 c.c.), and chlorobenzene (100 c.c.), and, later, aluminium chloride (14·7 g.). Steam-distillation ultimately removed the chlorobenzene and then furnished white needles of the thioindoxyl (I*l*), m. p. 103—106° (Found : C, 52·0; H, 3·1. C_8H_5OClS requires C, 52·0; H, 2·7%); the average yield was 9·0 g., 48·5%, based on the glycollic acid used.

The fact that the above pure thioindoxyls rarely possess sharp m. p.s may indicate a tautomeric equilibrium at or about the m. p.

Anils.—(*a*) The 2-*p*-hydroxy-anils were prepared by dissolving the thioindoxyl in boiling 5% aqueous sodium hydroxide, cooling to room temperature, and then rapidly adding, with vigorous stirring, a solution of *p*-nitrosophenol (1·1 mol.) in aqueous sodium carbonate. Salt was added until the solution contained *ca.* 20%, and the solution set aside for some hours. The sodium salt of the anil which had crystallised was collected, washed with 20% brine, suspended in water and acidified with hydrochloric acid. The precipitated anil was collected, washed with water, dried and, usually, recrystallised from amyl alcohol. Occasionally the anil was purified by reconversion to the sodium salt and reprecipitation. (*b*) The 2-*p*-dimethylamino-anils were prepared by dissolving the thioindoxyl in boiling 10% aqueous sodium hydroxide (*ca.* 10 c.c./1 g. thioindoxyl) and cooling to 60°; to this was added (during 5 minutes) with stirring a solution of *p*-nitrosodimethylaniline (1·1 mols.) in 5% hydrochloric acid (6 c.c./1 g. amine), also at 60°. The anil separated rapidly as the mixture was cooled. After some hours the anil was collected, and thoroughly washed successively with cold water, dilute hydrochloric acid, hot and cold water. The anils could be crystallised readily from benzene; they frequently separated with benzene of crystallisation, which was lost on heating at 80°/15 mm.

The yields of anils given below are based on the thioindoxyl used : 4-*methylthionaphthenquinone*-2-p-*hydroxyanil*, m. p. 234—236° (Found : C, 66·6; H, 4·4; N, 5·0. $C_{15}H_{11}O_2NS$ requires C, 66·9; H, 4·1; N, 5·2%), 25%; 4-*chlorothionaphthenquinone*-2-p-*hydroxyanil* (Found : C, 57·7; H, 2·9. $C_{14}H_8O_2NClS$ requires C, 58·0; H, 2·8%), 15%; 4-*chlorothionaphthenquinone*-2-p-*dimethylamino-anil*, m. p. 211—212° (Found : on sample dried in air, N, 7·9. $C_{16}H_{13}O_3N_2ClS,\frac{1}{4}C_6H_6$ requires N, 7·9%. On sample, heat-dried, C, 60·3; H, 4·3; N, 9·0. $C_{16}H_{13}O_3N_2ClS$ requires C, 60·6; H, 4·1; N, 8·9%); 5-methylthionaphthenquinone-2-*p*-hydroxyanil, 77%; 7-*methylthionaphthenquinone*-2-p-*hydroxyanil*, m. p. 248—250° (Found : C, 67·2; H, 4·0; N, 5·3. $C_{15}H_{11}O_2NS$ requires C, 66·9; H, 4·1; N, 5·2%; cf. B.P. 548,806), 67%; 7-*chlorothionaphthenquinone*-2-p-*hydroxyanil*, m. p. 272—273° (Found : C, 58·2; H, 3·1; N, 5·0. $C_{14}H_8O_2NClS$ requires C, 58·0; H, 2·8; N, 4·8%), 65%; 7-chlorothionaphthenquinone-2-*p*-dimethylamino-anil, 77%.

Thionaphthenquinones.—These were prepared by boiling a mixture of the anil and 15% hydrochloric acid (20 c.c./1 g. anil) for about 1 hour. The cold mixture was filtered, and the undissolved residue was washed with water and digested with an excess of boiling aqueous sodium carbonate for 20 minutes. The hot mixture was filtered on to ice, and the filtrate acidified to precipitate the crude quinone. The latter was collected, washed with water, and recrystallised from aqueous acetic acid. Steam distillation of the acetic acid mother-liquors sometimes furnished a further crop of the quinone. The following yields are calculated on the anil stated : 4-*methylthionaphthenquinone* (III*h*), m. p. 120—121° (Found : C, 60·5; H, 3·3. $C_9H_6O_2S$ requires C, 60·7; H, 3·4%), 66% on the hydroxyanil; 4-*chlorothionaphthenquinone* (III*i*), m. p. 138—139° (Found : C, 48·4; H, 1·9. $C_8H_3O_2ClS$ requires C, 48·4; H, 1·5%), 70% on amino-anil; 5-*methylthionaphthenquinone* (III*j*), m. p. 144—145° (Found : C, 61·1; H, 3·6. $C_9H_6O_2S$ requires C, 60·7; H, 3·4%), 74% on hydroxyanil; 7-*methylthionaphthenquinone* (III*k*), m. p. 126—127° (Found : C, 61·2; H, 3·7. $C_9H_6O_2S$ requires C, 60·7; H, 3·4%), 92% on hydroxyanil; 7-*chlorothionaphthenquinone* (III*l*), m. p. 149—150° (Found : C, 48·7; H, 1·7. $C_8H_3O_2ClS$ requires C, 48·4; H, 1·5%), 64% on the thioindoxyl (I*l*) *via* the amino-anil. Pummerer (*Ber.*, 1910, **42**, 1374) describes (III*j*) and (III*l*) without characterisation.

Condensation of anils with thioindoxyls. A mixture of the thioindoxyl (*ca.* 1 g.) and the anil (0·8 mol.) in acetic acid (*ca.* 25 c.c.) containing concentrated hydrochloric acid (0·3 c.c.) was refluxed for *ca.* 2 hours. The dye which

had crystallised from the cold product was collected, thoroughly washed with alcohol and water and dried. A portion was recrystallised from nitrobenzene for direct examination, and the remainder was subjected to reductive acetylation.

Condensation of thionaphthenquinones and thioindoxyls. The following standard method was adopted throughout. A mixture of the thioindoxyl (1 g.), the thionaphthenquinone (0·8 mol.), anhydrous zinc chloride (0·2 g.), and glacial acetic acid (25 c.c.) was refluxed gently for 2—3 hours. The mixture was set aside for some hours and the dye which had crystallised was then isolated as above, one portion being recrystallised and the remainder reductively acetylated.

Preparation of Diacetyldihydro-derivatives.—The following modification of Harley-Mason and Mann's method was always performed with the above unrecrystallised and therefore finely divided dyes. A mixture of the dye (*ca.* 1 g.), acetic acid (15 c.c.), acetic anhydride (15 c.c.), and zinc powder was refluxed for at least twice the time the solution required to become colourless, with a minimum of 2 hours even for the most rapid reductions; the speed of reduction appeared to depend primarily on the state of division rather than on the constitution of the dye. The product was filtered hot; the residue was extracted with boiling acetic acid (*ca.* 15 c.c.) and again filtered. The cold united filtrates were diluted with boiled water (*ca.* 100 c.c.) and set aside. The precipitated material was collected, washed with boiling water, drained and recrystallised from an acetic acid–acetic anhydride mixture, the proportion of the anhydride being increased for the less soluble products. Before analysis, the diacetyldihydro-derivatives were dried at 80°/15 mm. in a stream of dry air.

When the properties of the product so obtained indicated that it was a mixture of the diacetyldihydro-thioindigo and -thioindirubin, the separation of the components by fractional crystallisation was facilitated by the fact that not only was the thioindirubin derivative usually more soluble than the corresponding thioindigo derivative, but its separation from solution was often considerably delayed; this delay was apparently extended by the presence of the thioindigo derivative. Consequently, a solution of the two derivatives frequently gave on rapid, but undisturbed, cooling a first crop of material which was almost pure thioindigo derivative; the second crop, which frequently did not begin to separate for several hours, consisted, for the most part, of the thioindirubin derivative. In these circumstances, recrystallisation of each crop usually readily gave the main component in a state of purity.

The following Tables (II—XIII) give the detailed evidence upon which the final conclusions stated in Table I have been based. When in these Tables the diacetyldihydro-derivative of the condensation product of the thioquinone and the thioindoxyl is shown in two fractions, A(*a*) and A(*b*), these have been separated by fractional crystallisation. When the diacetyldihydro-derivative, B, of the condensation product of a thioindoxyl and an anil is quoted in brackets, its preparation was actually performed with the reverse thioindoxyl and anil, *e.g.*, in Table II, the diacetyldihydro-derivative of the authentic 5-methylthioindigo was prepared from the product obtained by condensing thioindoxyl (I) and the anil of 5-methylthionaphthenquinone (III*j*), this product necessarily being identical with that obtained by condensing 5-methylthioindoxyl (I*j*) and the anil of thionaphthenquinone (III). The authentic thioindigos were therefore prepared in only one of the two possible ways. The mixed m. p. values refer to the diacetyldihydro-derivatives in the previous column, *i.e.*, to mixtures of the product A or A(*a*) with B. The expressions "Id." and "Non-id." in the penultimate column indicate that the two dyes have been found by *X*-ray analysis to be identical or non-identical respectively. The names and analytical data of all new compounds are given immediately below each Table in the order in which they appear. Analyses are quoted for various mixtures of a diacetyldihydro-thioindigo and -thioindirubin to prove that the mixture before fractional crystallisation and separation contained only these two compounds. The thioindigos and thioindirubins are named according to (XVII) and (XVIII) respectively.

TABLE II.

Condensation of (A) *Thionaphthenquinone* (III) *and* (B) *its Anil with the Thioindoxyls.*

Thioindoxyl.		Diacetyldihydro-derivatives and m. p.	Mixed m. p.	*X*-Ray data.	Condensation.
Thioindoxyl (I)	A	(*a*) Colourless needles, 247—248° (*b*) Colourless plates, 132—133°	247—248°	—	$\alpha + \beta$
	B	Colourless needles, 247—248°			
6-Cl-4-Me- (I*b*)	A	Colourless crystals, 139—165°	—	—	$\alpha + \beta$
	B	(Colourless needles, 182—183°)			
5-Cl-7-Me- (I*c*)	A	(*a*) Colourless needles, 214—216° (*b*) Colourless crystals, 158—160°	214—216	—	$\alpha + \beta$
	B	(Colourless needles, 213—215°)			
6-EtO- (I*d*)	A	Colourless crystals, 158—167° (Colourless crystals, 173—174°)	—	—	$\alpha + \beta$
4 : 5-Benz- (I*e*)	A	(*a*) Pale yellow crystals, 214—216° (*b*) Pale yellow crystals, 166—169°	—	—	$\alpha + \beta$
	B	(Pale brown needles, 215—217°)			
6 : 7-Benz- (I*f*)	A	Colourless crystals, 245—251°	—	—	$\alpha + \beta$
	B	(Colourless needles, 254—256°)			
5 : 6-Benz (I*g*)	A	(*a*) Pale green needles, 256—258° (*b*) Pale green crystals, 162—163°	—	—	$\alpha + \beta$
	B	(Pale green crystals, 254—256°)			
4-Me- (I*h*)	A	Colourless needles, 214—216°	213—216	—	α †
	B	Colourless needles, 214—215°			
4-Cl- (I*i*)	A	Colourless needles, 204—206°	204—206	—	α †
	B	Colourless needles, 205—206°			
5-Me- (I*j*)	A	(*a*) Colourless needles, 208—210° (*b*) Colourless plates, 124—125°	208—210	Id.*	$\alpha + \beta$
	B	(Colourless needles, 208—210°)		Id.*	
7-Me- (I*k*)	A	Colourless needles, 229—230°	229—230	—	α †
	B	(Colourless needles, 229—230°)			
7-Cl- (I*l*)	A	(*a*) Colourless needles, 229—230° (*b*) Colourless plates, 131—132°	229—230	—	$\alpha + \beta$
	B	Colourless needles, 229—230°			

* *X*-Ray comparison showed also that the diacetyldihydro-derivatives of A(*a*) and B were identical.
† The filtrates were not examined for possible β-components in these cases.

Diacetyldihydrothioindirubin (Found: C, 62·9; H, 3·8. Calc. for $C_{20}H_{14}O_4S_2$: C, 62·8; H, 3·7%) crystallises with one molecule of acetic acid and this *complex* has m. p. 110—115° (Found: C, 59·7; H, 3·8. $C_{20}H_{14}O_4S_2,C_2H_4O_2$ requires

C, 59·7; H, 4·1%). Mixed diacetyldihydro-derivatives of 6-chloro-4-methylthioindigo and 6-chloro-4-methylthioindirubin (Found: C, 58·5; H, 3·7. Calc. for $C_{21}H_{15}O_4ClS_2$: C, 58·5; H, 3·5%). The dye from the condensation of (I*c*) and (III) (Found: C, 59·0; H, 2·9. Calc. for $C_{17}H_9O_2ClS_2$: C, 59·2; H, 2·6%) gave a diacetyldihydro-derivative, crystallisation of which furnished 5-chloro-7-methyldiacetyldihydrothioindigo (Found: C, 58·7; H, 4·0%) and *5-chloro-7-methyldiacetyldihydrothioindirubin* (Found: C, 58·8; H, 3·5%). Mixed diacetyldihydro-derivatives of 6-ethoxythioindigo and 6-ethoxythioindirubin (Found: C, 61·7; H, 4·3. Calc. for $C_{22}H_{18}O_5S_2$: C, 62·0; H, 4·2%). Diacetyldihydro-4 : 5-benzthioindigo (Found: C, 66·7; H, 4·0. Calc. for $C_{24}H_{16}O_4S_2$: C, 66·7; H, 3·7%). Diacetyldihydro-4 : 5-benzthioindirubin (Found: C, 66·3; H, 3·7%). Mixed diacetyldihydro-derivatives of 6 : 7-benzthioindigo and 6 : 7-benzthioindirubin (Found: C, 66·4; H, 3·9%). Diacetyldihydro-5 : 6-benzthioindigo (Found: C, 67·0; H, 4·0%); *diacetyldihydro-5 : 6-benzthioindirubin* (Found: C, 66·4; H, 3·8%). *4-Methylthioindigo* (Found: C, 66·0; H, 3·4. $C_{17}H_{10}O_2S_2$ requires C, 65·8; H, 3·2%); *diacetyldihydro-derivative* (Found: C, 63·4; H, 4·1. $C_{21}H_{16}O_4S_2$ requires C, 63·6; H, 4·0%). *4-Chlorothioindigo* (Found: C, 58·2; H, 2·2. $C_{16}H_7O_2ClS_2$ requires C, 58·1; H, 2·1%); *diacetyldihydro-derivative* (Found: C, 57·6; H, 3·4. $C_{20}H_{13}O_4ClS_2$ requires C, 57·6; H, 3·1%). *5-Methylthioindigo* (Found: C, 65·9; H, 3·6%) (G.P. 205,002); *diacetyldihydro-derivative* (Found: C, 63·8; H, 4·3%). *5-Methylthioindirubin* (Found: C, 66·2; H, 3·4%); *diacetyldihydro-derivative* (Found: C, 63·5; H, 4·3%). *7-Methylthioindigo* (Found: C, 65·8; H, 2·9%); *diacetyldihydro-derivative* (Found: C, 63·8; H, 4·2%). *7-Chlorothioindigo* (Found: C, 57·9; H, 2·2%); *diacetyldihydro-derivative* (Found: C, 57·7; H, 3·3%). *7-Chloro-thioindirubin* (Found: C, 57·8; H, 2·2%); *diacetyldihydro-derivative* (Found: C, 57·7; H, 3·1%).

TABLE III.

Condensation of (A) *6-Chloro-4-methylthionaphthenquinone* (III*b*), *and* (B) *its Anil, with the Thioindoxyls.*

Thioindoxyl.		Diacetyldihydro-derivatives and m. p.	Mixed m. p.	*X*-Ray data.	Condensation.
5-Cl-7-Me- (I*c*)	A	Colourless needles, 227—229°	228—230°	—	α
	B	Colourless needles, 228—229°			
4 : 5-Benz- (I*e*)	A	Pale yellow needles, 150—200°	—	—	α + β
	B	Pale cream needles, 234—235°			
4-Me- (I*h*)	A	Colourless needles, 230—233°	230—234	—	α
	B	(Colourless needles, 232—234°)			
4-Cl- (I*i*)	A	Pink needles, 240—242°	—	—	α
	B	Pink needles, 240—241°			
5-Me- (I*j*)	A	Pale pink needles, 213—214°	211—214	—	α
	B	(Colourless needles, 211—212°)			
7-Me- (I*k*)	A	Colourless needles, 190—193°	190—193	—	α
	B	(Colourless needles, 190—193°)			
7-Cl- (I*l*)	A	Pale pink needles, 191—192°	—	Id.	α
	B	(Colourless needles, 191—193°)		Id.	

5 : 6′-*Dichloro*-7 : 4′-*dimethylthioindigo* (Found: C, 54·9; H, 2·4. $C_{18}H_{10}Cl_2S_2$ requires C, 55·0; H, 2·5%); *diacetyldihydro-derivative* (Found: C, 55·0; H, 3·6. $C_{22}H_{16}O_4Cl_2S_2$ requires C, 55·1; H, 3·3%). *6′-Chloro-4′-methyl*-4 : 5-*benzthioindigo* (Found: C, 64·0; H, 3·0. $C_{21}H_{11}O_2ClS_2$ requires C, 63·9; H, 2·8%); diacetyldihydro-derivative (Found for specimen, m. p. 150—200° as above: C, 62·7; H, 3·7. $C_{25}H_{17}O_4ClS_2$ requires C, 62·4; H, 3·5%); after four recrystallisations, m. p. 223—226° (Found: C, 62·8; H, 3·6%). The original diacetyldihydro-derivative was therefore a mixture of the two isomers, the thioindigo being in greater proportion. *6′-Chloro*-4 : 4′-*dimethylthioindigo* (Found: C, 60·4; H, 3·4. $C_{18}H_{11}O_2ClS_2$ requires C, 60·2; H, 3·1%) (F.P. 648,861); *diacetyldihydro-derivative* (Found: C, 59·2; H, 4·1. $C_{22}H_{17}O_4ClS_2$ requires C, 59·4; H, 3·8%). 4 : 6′-*Dichloro-4′-methyl-thioindigo* (Found: C, 53·5; H, 2·2. $C_{17}H_8O_2Cl_2S_2$ requires C, 53·8; H, 2·1%) (E.P. 355,662); *diacetyldihydro-derivative* (Found: C, 54·2; H, 3·2. $C_{22}H_{14}O_4Cl_2S_2$ requires C, 54·2; H, 3·0%). *6′-Chloro*-5 : 4′-*dimethylthioindigo* (Found: C, 60·2; H, 2·8%); *diacetyldihydro-derivative* (Found: C, 59·3; H, 4·0%). *6′-Chloro*-7 : 4′-*dimethylthioindigo* (Found: C, 60·0; H, 3·2%); *diacetyldihydro-derivative* (Found: C, 59·8; H, 4·2%). 7 : 6′-*Dichloro-4′-methylthioindigo* (Found: C, 54·0; H, 2·2%); *diacetyldihydro-derivative* (Found: C, 54·2; H, 3·2%).

TABLE IV.

Condensation of (A) *5-Chloro-7-methylthionaphthenquinone* (III*c*), *and* (B) *its Anil, with the Thioindoxyls.*

Thioindoxyl.		Diacetyldihydro-derivatives and m. p.	Mixed m. p.	*X*-Ray data.	Condensation.
6-Cl-4-Me- (I*b*)	A	Colourless needles, 229—230°	—	—	α
	B	(Colourless needles, 228—229°)			
6 : 7-Benz- (I*f*)	A	(*a*) Colourless needles, 236—238°	—	—	α + β
		(*b*) Colourless plates, 171—173°			
	B	(Colourless needles, 235—238°)			
4-Me- (I*h*)	A	Fine colourless needles, 218—220°	218—220°	—	α
	B	(Fine colourless needles, 218—220°)			
4-Cl- (I*i*)	A	White fibres, 231—232°	—	—	α
	B	(White fibres, 230—231°)			
5-Me- (I*j*)	A	Colourless needles, 263—264°	263—264	—	α
	B	Colourless needles, 263—264°			
7-Me- (I*k*)	A	Colourless needles, 234—235°	234—235	—	α
	B	Colourless needles, 234—236°			
7-Cl- (I*l*)	A	Fibrous colourless needles, 245—246°	245—246	—	α
	B	Fibrous colourless needles, 245—246°			

The diacetyldihydro-derivative of the product from (I*f*) and (III*c*) gave a first crop, m. p. 236—238°, and a second crop, m. p. 169—174°, being raised to 171—173° on further recrystallisation (Found: C, 62·1; H, 3·6%). The original condensation product therefore contained both 5′-chloro-7′-methyl-6 : 7-benzthioindigo (50—60%) and 5′-chloro-7′-methyl-6 : 7-benzthioindirubin. *5′-Chloro*-4 : 7′-*dimethylthioindigo* (Found: C, 60·2; H, 3·0%); *diacetyldihydro-derivative* (Found: C, 59·6; H, 3·7%). 4 : 5′-*Dichloro-7′-methylthioindigo* (Found: C, 53·9; H, 2·1%); *diacetyldihydro-derivative* (Found: C, 54·5; H, 3·2%). *5′-Chloro*-5 : 7′-*dimethylthioindigo* (Found: C, 60·1; H, 3·1%); *diacetyldihydro-derivative* (Found: C, 59·6; H, 4·2%). *5′-Chloro*-7 : 7′-*dimethylthioindigo* (Found C, 60·3; H, 3·3%);

diacetyldihydro-derivative (Found: C, 59·5; H, 3·5%). 7 : 5′-*Dichloro*-7′-*methylthioindigo* (Found: C, 53·9; H, 2·3%); *diacetyldihydro-derivative* (Found: C, 54·3; H, 3·4%).

TABLE V.

Condensation of (A) 6-*Ethoxythionaphthenquinone* (III*d*), *and* (B) *its Anil, with the Thioindoxyls.*

Thioindoxyl.		Diacetyldihydro-derivatives and m. p.	Mixed m. p.	*X*-Ray data.	Condensation.
Thioindoxyl (I)	A	(*a*) Colourless crystals, 173—174°	—	—	$\alpha + \beta$
		(*b*) Colourless crystals, 132—133°			
	B	Colourless crystals, 173—174°			
6-Cl-4-Me- (I*b*)	A	Pale pink crystals, 180—198°	—	—	$\alpha + \beta$
	B	(Pale pink needles, 186—188°)			
5-Cl-7-Me- (I*c*)	A	Colourless crystals, 159—177°	—	—	$\alpha + \beta$
	B	(Colourless needles, 213—215°)			
6-EtO- (I*d*)	A	(*a*) Colourless crystals, 228—230°	—	—	$\alpha + \beta$
		(*b*) Colourless crystals, 175—190°			
	B	(Pale brown crystals, 230—232°)			
4 : 5-Benz- (I*e*)	A	Acetylation unsatisfactory	—	Mainly α	$\alpha + \beta$
	B	(Pale yellow plates, 223—225°)		Some β	
6 : 7-Benz- (I*f*)	A	(*a*) Colourless needles, 215—217°	—	—	$\alpha + \beta$
		(*b*) Colourless plates, 165—166°			
5 : 6-Benz- (I*g*)	A	(*a*) Pale green needles, 224—226°	—	—	$\alpha + \beta$
		(*b*) Pale green plates, 167—169°			
	B	(Pale yellow crystals, 224—225°)			
4-Me- (I*h*)	A	Pale pink needles, 157—161°	158—161°	Mixture	$\alpha + \beta$
	B	Colourless needles, 160—161°			
4-Cl- (I*i*)	A	(*a*) Colourless needles, 170—171°	170—171	—	$\alpha + \beta$
		(*b*) Colourless plates, 152—153°			
	B	Cream needles, 170—171°			
5-Me- (I*j*)	A	Fibrous colourless needles, 180—182°	180—184	Mixture	$\alpha + \beta$
	B	Fibrous pink needles, 184—186°			
7-Me- (I*k*)	A	Pale pink needles, 159—161°	158—161	Mixture	$\alpha + \beta$
	B	Pale pink needles, 160—161°			
7-Chloro- (I*l*)	A	(*a*) Colourless needles, 181—182°	181—183		$\alpha + \beta$
		(*b*) Colourless plates, 158—159°			
	B	(Pale pink needles, 181—183°)			

The original diacetyldihydro-derivative of the condensation product of (I) and (III*d*) had m. p. 127—165°; after separation, α-component (Found: C, 62·0; H, 4·5%); β-component (Found: C, 62·0; H, 4·0%). The original diacetyldihydro-derivative from the product of (I*b*) and (III*d*), m. p. 180—198° (Found: C, 58·4; H, 4·1. Calc. for $C_{23}H_{19}O_5ClS_2$: C, 58·2; H, 4·0%), had m. p. 184—211° after one further recrystallisation. The original diacetyldihydro-derivative from the product of (I*c*) and (III*d*) of m. p. 159—177° (Found: C, 57·9; H, 4·0%) changed to m. p. 155—170° after one recrystallisation. The diacetyldihydro-derivative from the product of (I*d*) and (III*d*) gave a first crop, m. p. 228—230°, and a second crop, m. p. 175—190° softening above 130° (Found: C, 61·0; H, 4·9%. Calc. for $C_{24}H_{20}O_6S_2$: C, 61·3; H, 4·7%). 6′-*Ethoxy*-4 : 5-*benzthioindirubin* (Found: C, 67·4; H, 4·0. $C_{22}H_{14}O_3S_2$ requires C, 67·7; H, 3·6%). The original diacetyldihydro-derivative from the product of (I*f*) and (III*d*) had m. p. 162—174°; crystallisation gave α-component (Found: C, 65·2; H, 4·4%. Calc. for $C_{26}H_{20}O_5S_2$: C, 65·5; H, 4·2%) and 6′-*ethoxydiacetyldihydro*-4 : 5-*benzthioindirubin* (Found: C, 65·2; H, 4·5%). 6′-*Ethoxydiacetyldihydro*-5 : 6-*benzthioindirubin* (Found: C, 65·6; H, 4·4%). 6′-*Ethoxy*-4-*methylthioindigo* (Found: C, 64·3; H, 3·8. $C_{19}H_{14}O_3S_2$ requires C, 64·4; H, 3·9%); *diacetyldihydro-derivative* (Found: C, 62·4; H, 4·4. $C_{23}H_{20}O_5S_2$ requires C, 62·7; H, 4·5%). 4-*Chloro*-6′-*ethoxythioindigo* (Found: C, 57·6; H, 3·0. $C_{18}H_{11}O_3ClS_2$ requires C, 57·7; H, 2·9%); *diacetyldihydro-derivative* (Found: C, 57·4; H, 3·9. $C_{22}H_{17}O_5ClS_2$ requires C, 57·3; H, 3·7%). This diacetyldihydro-derivative also crystallises with one molecule of acetic acid of recrystallisation, and this *complex* has m. p. 135° (Found: C, 55·7; H, 4·4. $C_{22}H_{12}O_5ClS_2,C_2H_4O_2$ requires C, 55·4; H, 4·0%); drying at 80°/15 mm. in CO_2 causes loss of acetic acid, and the m. p. rises to 170—171°. The addition of alcohol to the nitrobenzene mother liquor from the recrystallisation of this thioindigo precipitated darker crystals of 4-*chloro*-6′-*ethoxythioindirubin*, which were then recrystallised from nitrobenzene (Found: C, 57·8; H, 3·2%); *diacetyldihydro-derivative* (Found: C, 57·0; H, 3·9%). 6′-*Ethoxy*-5-*methylthioindigo* (Found: C, 64·3; H, 4·2%); *diacetyldihydro-derivative* (Found: C, 62·6; H, 4·4%). 6′-*Ethoxy*-7-*methylthioindigo* (Found: C, 64·1; H, 4·0%); *diacetyldihydro-derivative* (Found: C, 63·0; H, 4·7%). 7-*Chloro*-6′-*ethoxy-thioindigo* (Found: C, 57·7; H, 3·0%); *diacetyldihydro-derivative* (Found: C, 57·4; H, 3·9%). Addition of alcohol to the nitrobenzene mother-liquor precipitated darker crystals of 7-*chloro*-6′-*ethoxythioindirubin* which were recrystallised from nitrobenzene (Found: C, 57·6; H, 3·0%); *diacetyldihydro-derivative* (Found: C, 57·0; H, 3·8%).

TABLE VI.

Condensation of (A) 4 : 5-*Benzthionaphthenquinone* (III*e*), *and* (B) *its Anil, with the Thioindoxyls.*

Thioindoxyl.		Diacetyldihydro-derivatives and m. p.	Mixed m. p.	*X*-Ray data.	Condensation.
4-Me- (I*h*)	A	Yellow needles, 201—202°	201—202°	—	α
	B	(Pale green needles, 201—202°)			
4-Cl- (I*i*)	A	Pale brown needles, 237—238°	—	—	α
	B	(Pale green needles, 235—236°)			
5-Me- (I*j*)	A	Yellow needles, 244—246°	244—246	—	α
	B	Pale brown needles, 244—246°			
7-Me- (I*k*)	A	Pale pink needles, 209—211°	208—211	Id.	α
	B	Pale pink needles, 204—206°		Id.	
7-Cl- (I*l*)	A	Yellow needles, 216—217°	215—217	—	α
	B	(Pale green needles, 215—216°)			

4-Methyl-4′ : 5′-benzthioindigo (Found : C, 70·0; H, 3·6. $C_{21}H_{12}O_2S_2$ requires C, 70·0; H, 3·3%); *diacetyldihydro-derivative* (Found : C, 67·6; H, 4·5. $C_{25}H_{16}O_4S_2$ requires C, 67·3; H, 4·0%). *4-Chloro-4′ : 5′-benzthioindigo* (Found : C, 63·2; H, 2·3. $C_{20}H_9O_2ClS_2$ requires C, 63·1; H, 2·4%) (F.P. 593,560); *diacetyldihydro-derivative* (Found : C, 61·4; H, 3·4. $C_{24}H_{15}O_4ClS_2$ requires C, 61·1; H, 3·2%). *5-Methyl-4′ : 5′-benzthioindigo* (Found : C, 70·1; H, 3·3%); *diacetyldihydro-derivative* (Found : C, 66·9; H, 3·8%). *7-Methyl-4′ : 5′-benzthioindigo* (Found : C, 70·1; H, 3·5%); *diacetyldihydro-derivative* (Found : C, 67·6; H, 3·9%). *7-Chloro-4′ : 5′-benzthioindigo* (Found : C, 62·9; H, 2·3%); *diacetyldihydro-derivative* (Found : C, 61·1; H, 3·5%).

TABLE VII.

Condensation of (A) 6 : 7-*Benzthionaphthenquinone* (III*f*), *and* (B) *its Anil, with the Thioindoxyls.*

Thioindoxyl.		Diacetyldihydro-derivatives and m. p.	Mixed m. p.	*X*-Ray data.	Condensation.
4-Me-6-Cl- (I*b*)	A	Colourless needles, 246—248°	246—249°	—	α
	B	(Pale brown needles, 252—253°)			
6-EtO- (I*d*)	A	(*a*) Colourless needles, 206—209°	—	—	α + β
		(*b*) Colourless crystals, 175—176°			
	B	(Pale pink needles, 205—208°)			
4 : 5-Benz- (I*e*)	A	Pale brown needles, 216—220°	—	—	α + β
	B	Pale brown needles, 255—257°))			
4-Me- (I*h*)	A	Fibrous colourless needles, 235—237°	235—237	—	α
	B	(Fibrous colourless needles, 235—237°)			
4-Cl- (I*i*)	A	Colourless needles, 230—231°	230—231	—	α
	B	(Colourless needles, 230—231°)			
5-Me- (I*j*)	A	Fibrous colourless needles, 245—247°	245—247	—	α
	B	Fibrous colourless needles, 245—247°			
7-Me- (I*k*)	A	(*a*) Colourless needles, 253—254°	—	—	α + β
		(*b*) Colourless plates, 180—181°			
	B	Colourless needles, 249—250°			
7-Cl- (I*l*)	A	Colourless needles, 251—252°	250—252	—	α
	B	(Pale green needles, 250—251°)			

The original diacetyldihydro-derivative from the product (I*d*) and (III*f*) separated as two crops, m. p.'s 200—206° and 162—176°, which were recrystallised to constant m. p. : α-component (Found : C, 65·3; H, 4·3%); β-component (Found : C, 65·3; H, 4·5%). The diacetyldihydro-derivative from the product of (I*e*) and (III*f*), m. p. 216—220° (Found : C, 69·8; H, 3·7%) raised to m. p. 219—220° by recrystallisation, was predominantly β-derivative, containing some α-. *4-Methyl-6′ : 7′-benzthioindigo* (Found : C, 70·0; H, 3·3%); *diacetyldihydro-derivative* (Found : C, 67·2; H, 4·4%). *4-Chloro-6′ : 7′-benzthioindigo* (Found : C, 63·1; H, 2·6%); *diacetyldihydro-derivative* (Found : C, 61·3; H, 3·5%). *5-Methyl-6′ : 7′-benzthioindigo* (Found : C, 70·3; H, 3·4%); *diacetyldihydro-derivative* (Found : C, 67·4; H, 3·8%). *7-Methyl-6′ : 7′-benzthioindigo* (Found : C, 69·8; H, 3·4%); the crude dyestuff from preparation A gave a diacetyldihydro-derivative, m. p. 175—225° (Found : C, 66·8; H, 4·0%), and the latter was therefore a mixture of the two isomeric diacetyldihydro-derivatives only. This mixture was fractionally crystallised to give the two components of constant m. p. : *7-Methyl-diacetyldihydro-6′ : 7′-benzthioindigo* (m. p. 253—254°) (Found : C, 66·9; H, 4·2%); *7-methyl-diacetyldihydro-6′ : 7′-benzthioindirubin* (m. p. 180—181°) (Found : C, 66·9; H, 4·0. $C_{25}H_{18}O_4S_2$ requires C, 67·3; H, 4·0%). *7-Chloro-6′ : 7′-benzthioindigo* (Found : C, 63·2; H, 2·6%); *diacetyldihydro-derivative* (Found : C, 61·2; H, 3·5%).

TABLE VIII.

Condensation of (A) 5 : 6-*Benzthionaphthenquinone* (III*g*), *and* (B) *its Anil, with the Thioindoxyls.*

Thioindoxyl.		Diacetyldihydro-derivatives and m. p.	Mixed m. p.	*X*-Ray data.	Condensation.
Thioindoxyl (I)	A	Pale green crystals, 183—184°	—	—	α + β
	B	(Pale green plates, 254—256°)			
6-Cl-4-Me- (I*b*)	A	(*a*) Pale green needles, 261—263°	—	—	α + β
		(*b*) Pale brown crystals, 186—188°			
	B	(Pale green needles, 261—263°)			
5-Cl-7-Me- (I*c*)	A	Pale green crystals, 130—165°	—	—	α + β
	B	(Pale green needles, 258—260°)			
6-EtO- (I*d*)	A	(*a*) Pale green crystals, 224—245°	—	—	α + β
		(*b*) Pale yellow crystals, 166—167°			
	B	(Pale yellow crystals, 224—225°)			
4 : 5-Benz- (I*e*)	A	Pale yellow crystals, 178—187°	—	—	α + β
	B	(Green-yellow needles, 263—265°)			
6 : 7-Benz- (I*f*)	A	Pale yellow needles, 177—186°	—	—	α + β
	B	(Greenish brown plates, 251—253°			
5 : 6-Benz- (I*g*)	A	Pale green crystals, 227—235°	—	—	α + β
	B	(Pale green needles, 297—300°)			
4-Me- (I*h*)	A	Pale green crystals, 222—224°	—	—	α + β
	B	Not acetylated (see below)			
4-Cl- (I*i*)	A	Pale yellow crystals, 202—203°	—	Non-id.	α + β
	B	Not acetylated			
5-Me- (I*j*)	A	(*a*) Pale green needles, 267—269° } (*b*) Pale green plates, 198—199° }	—	{Mixture	α + β
	B	Not acetylated			
7-Me- (I*k*)	A	Pale yellow crystals, 198—210°	—	—	α + β
	B	Pale green crystals, 250—253°			
7-Cl- (I*l*)	A	Pale green plates, 147—148°	—	—	α + β
	B	Not acetylated			

The original diacetyldihydro-derivative from the product of (I) and (III*g*) had m. p. 173—190° and was fractionally recrystallised into its components; *diacetyldihydro-5′ : 6′-benzthioindirubin* (Found : C, 66·4; H, 4·0%). The product of (I*b*) and (III*g*) was separated into its two components: diacetyldihydro-4-methyl-6-chloro-5′ : 6′-benzthioindigo (Found : C, 62·8; H, 3·9%). *6-Chloro-4-methyl-5′ : 6′-benzthioindirubin* (Found : C, 63·7; H, 3·1%); *diacetyldihydro-derivative* (Found : C, 62·3; H, 3·4%). The diacetyldihydro-derivative, m. p. 130—165°, from the product of (I*c*) and (III*g*) (Found : C, 62·0; H, 3·8%), after recrystallisation had m. p. 140—155°. The diacetyldihydro-derivative from the product of (I*d*) and (III*g*) had m. p. 118—155° and was separated by fractional recrystallisation; *6-ethoxydiacetyldihydro-5′ : 6′-benzthioindirubin* (m. p. 166—167°) (Found : C, 65·1; H, 4·3%). The diacetyldihydro-derivative from the product of (I*e*) and (III*g*) had m. p. 178—187°, raised to 185—195° by one recrystallisation (Found : C, 70·2; H, 4·2%); that derived from the product of (I*f*) and (III*g*) had m. p. 177—186° (Found : C, 69·5; H, 4·0%). The diacetyldihydro-derivative from the condensation of (I*g*) and (III*g*) had m. p. 227—235° (Found : C, 69·8; H, 4·2%) changing to 225—232° after one recrystallisation. *4-Methyl-5′ : 6′-benzthioindigo* (Found : C, 69·7; H, 3·3%); the diacetyldihydro-derivative of the product from (I*h*) and (III*g*) had m. p. 185—215° (Found : C, 67·7; H, 4·5%) and was therefore a mixture of the two isomeric diacetyldihydro-thioindigo and -thioindirubin only. The above *diacetyldihydro-derivative*, m. p. 222—224°, was isolated by repeated recrystallisation (Found : C, 67·5; H, 4·5%) (sufficient quantity of the authentic thioindigo not being available prevented its complete identification). *4-Chloro-5′ : 6′-benzthioindigo* (Found : C, 63·1; H, 2·6%). The diacetyldihydro-derivative of the product from (I*i*) and (III*g*) had m. p. 166—174° (Found : C, 61·2; H, 3·6%) and therefore was a mixture of the two possible isomers only; repeated recrystallisation gave a *diacetyldihydro-derivative*, m. p. 202—203° (Found : C, 61·2; H, 3·2%), but insufficient material again made its complete identification uncertain. *5-Methyl-5′ : 6′-benzthioindigo* (Found : C, 69·8; H, 3·4%). The diacetyldihydro-derivative of the product from (I*j*) and (III*g*) had m. p. 197—215° (Found : C, 67·0; H, 4·0%) and therefore it was a mixture of the two possible isomers only; it was separated into two components by fractional crystallisation from acetic acid and these were recrystallised to a constant m. p., giving *5-methyldiacetyldihydro-5′ : 6′-benzthioindigo* (the less soluble fraction, m. p. 267—269°. Found : C, 67·1; H, 4·2%) and *5-methyldiacetyldihydro-5′ : 6′-benzthioindirubin*, m. p. 198—199° (Found : C, 66·9; H, 4·2%). *7-Methyl-5′ : 6′-benzthioindigo* (Found : C, 69·7; H, 3·4%); *diacetyldihydro-derivative* (Found : C, 67·3; H, 4·3%). The diacetyldihydro-derivative of the product from (I*k*) and (III*g*) had m. p. 198—210° (Found : C, 67·6; H, 4·5%) and was therefore a mixture of the two isomeric α- and β-condensation products only; repeated recrystallisation gave the pure α-form. *7-Chloro-5′ : 6′-benzthioindigo* (Found : C, 62·9; H, 2·7%). The diacetyldihydro-derivative of the product from (I*l*) and (III*g*) was separated by fractional crystallisation from acetic acid into a very small fraction, m. p. 240—248° (pale green needles, probably diacetyldihydro-7-chloro-5′ : 6′-benzthioindigo), and a large fraction which on recrystallisation gave *7-chlorodiacetyldihydro-5′ : 6′-benzthioindirubin*, m. p. 147—148° (Found : C, 61·5; H, 3·4. $C_{24}H_{15}O_4ClS_2$ requires C, 61·1; H, 3·2%); sufficient quantity of the authentic thioindigo not being available, its complete identification was indeterminate.

The failure, previously recorded, to reduce thioindirubins containing the 5 : 6-benzthionaphthen group was apparently due to the presence of impurities produced by the use of acetic anhydride in the original condensation; we find that reduction to the diacetyldihydro-derivatives proceeds smoothly if the condensation has been performed in our standard medium.

TABLE IX.

Condensation of (A) *4-Methylthionapthenquinone* (III*h*), *and* (B) *its Anil, with the Thioindoxyls.*

Thioindoxyl.		Diacetyldihydro-derivatives and m. p.	Mixed m. p.	*X*-Ray data.	Condensation.
Thioindoxyl (I)	A	Colourless needles, 214—215°	214—215°	—	α
	B	(Colourless needles, 214—215°)			
6-Cl-4-Me- (I*b*)	A	Fibrous pale pink needles, 233—234°	232—234	—	α
	B	Fibrous colourless needles, 232—234°			
5-Cl-7-Me- (I*c*)	A	Fibrous colourless needles, 216—218°	217—219	—	α
	B	Fibrous colourless needles, 218—220			
6-EtO- (I*d*)	A	Pale pink needles, 156—160°	157—161	Id.	α
	B	(Colourless needles, 160—161°			
4 : 5-Benz- (I*e*)	A	Pale brown needles, 198—202°	—	—	α
	B	Pale green needles, 201—202°			
6 : 7-Benz- (I*f*)	A	Fibrous colourless needles, 236—237°	235—237	—	α
	B	Fibrous colourless needles, 235—237°			
4-Me- (I*h*)	A	Pale pink needles, 247—248°	—	—	α
	B	Pale pink needles, 247—249° *			
4-Cl- (I*i*)	A	Pale pink needles, 244—246°	—	—	α
	B	Pale pink needles, 246—247°			
5-Me- (I*j*)	A	Colourless needles, 194—195°	194—195	—	α
	B	Pale pink needles, 194—195°			
7-Me- (I*k*)	A	Colourless needles, 200—201°	—	—	α
	B	(Colourless needles, 200—201°)			
7-Cl- (I*l*)	A	Colourless needles, 219—220°	219—220	—	α
	B	Colourless needles, 219—220°			

* The authentic 4 : 4′-dimethylthioindigo was prepared by oxidation of 4-methylthioindoxyl, and not from the anil.

4 : 4′-Dimethylthioindigo (Found : C, 67·0; H, 3·8%) (E.P. 279,489); *diacetyldihydro-derivative* (Found : C, 65·0; H, 5·1%). *4-Chloro-4′-methylthioindigo* (Found : C, 59·5; H, 2·7%) (E.P. 365,662); *diacetyldihydro-derivative* (Found : C, 58·2; H, 3·7%). *5 : 4′-Dimethylthioindigo* (Found : C, 66·8; H, 3·9. $C_{18}H_{12}O_2S_2$ requires C, 66·7; H, 3·7%); *diacetyldihydro-derivative* (Found : C, 64·6; H, 4·7. $C_{22}H_{18}O_4S_2$ requires C, 64·4; H, 4·4%). *7 : 4′-Dimethylthioindigo* (Found : C, 66·9; H, 3·8%); *diacetyldihydro-derivative* (Found : C, 64·7; H, 4·4%). *7-Chloro-4′-methylthioindigo* (Found : C, 59·4; H, 2·9%); *diacetyldihydro-derivative* (Found : C, 58·7; H, 3·7%).

TABLE X.

Condensation of (A) *4-Chlorothionaphthenquinone* (III*i*), *and* (B) *its Anil, with the Thioindoxyls.*

Thioindoxyl.		Diacetyldihydro-derivatives and m. p.	Mixed m. p.	*X*-Ray data.	Condensation.
Thioindoxyl (I)	A	Colourless needles, 200—201°	200—204°	—	α
	B	(Colourless needles, 205—206°)			
6-Cl-4-Me- (I*b*)	A	Pink needles, 241—243°	240—243	—	α
	B	(Pink needles, 240—241°)			
5-Cl-7-Me- (I*c*)	A	Colourless needles, 231—232°	229—232	—	α
	B	Colourless needles, 230—231°			
6-EtO- (I*d*)	A	Fibrous cream needles, 171—172° *	170—172	—	α
	B	(Fibrous cream needles, 170—171°) *			
4 : 5-Benz- (I*e*)	A	Pale green needles, 234—235°	235—236	—	α
	B	Pale green needles, 235—236°			
6 : 7-Benz- (I*f*)	A	Pale brown needles, 229—231°	229—231	—	α
	B	Colourless needles, 230—231°			
4-Me- (I*h*)	A	Pink needles, 246—247°	—	—	α
	B	(Pink needles, 246—247°)			
4-Cl- (I*i*)	A	Pink needles, 275—277°	275—277	—	α
	B	Pink needles, 273—275° †			
5-Me- (I*j*)	A	Colourless needles, 207—208°	—	—	β
	B	(White needles, 149—151°)			
7-Me- (I*k*)	A	Colourless needles, 183—184°	—	—	β
	B	(Colourless needles, 165—167°)			
7-Cl- (I*l*)	A	Colourless plates, 231—232°	—	—	β
	B	(Colourless needles, 162—164°)			

* M. p. of diacetyldihydro-derivative after drying in CO_2.
† The authentic 4 : 4′-dichlorothioindigo was prepared by oxidation of 4-chlorothioindoxyl, and not from the anil.

4 : 4′-*Dichlorothioindigo* (Found : C, 52·7; H, 1·8. $C_{16}H_6O_2Cl_2S_2$ requires C, 52·6; H, 1·6%) (B.P. 355,661); *diacetyldihydro-derivative* (Found : C, 53·2; H, 2·7. $C_{20}H_{12}O_4Cl_2S_2$ requires C, 53·2; H, 2·7%). 4′-*Chloro*-5-*methylthioindigo* (Found : C, 59·1; H, 2·8%); *diacetyldihydro-derivative* (Found : C, 58·2; H, 3·6%). 4′-*Chloro*-5-*methylthioindirubin* (Found : C, 59·5; H, 2·8. $C_{17}H_9O_2ClS_2$ requires C, 59·2; H, 2·6%); *diacetyldihydro-derivative* (Found : C, 58·3; H, 3·6. $C_{21}H_{15}O_4ClS_2$ requires C, 58·5; H, 2·8%). 4′-*Chloro*-7-*methylthioindigo* (Found : C, 59·4; H, 2·8%); *diacetyldihydro-derivative* (Found : C, 58·4; H, 3·6%). 4′-*Chloro*-7-*methylthioindirubin* (Found : C, 59·5; H, 3·0%); *diacetyldihydro-derivative* (Found : C, 58·3; H, 3·7%). 7 : 4′-*Dichlorothioindigo* (Found : C, 52·8; H, 2·0%); *diacetyldihydro-derivative* (Found : C, 53·5; H, 3·1%). 7 : 4′-*Dichlorothioindirubin* (Found : C, 52·3; H, 1·9. $C_{16}H_6O_2Cl_2S_2$ requires C, 52·6; H, 1·6%); *diacetyldihydro-derivative* (Found : C, 53·0; H, 2·7. $C_{20}H_{12}O_4Cl_2S_2$ requires C, 53·2; H, 2·7%).

TABLE XI.

Condensation of (A) *5-Methylthionaphthenquinone* (III*j*), *and* (B) *its Anil, with the Thioindoxyls.*

Thioindoxyl.		Diacetyldihydro-derivatives and m. p.	Mixed m. p.	*X*-Ray data.	Condensation.
Thioindoxyl (I)	A	Colourless needles, 206—207°	206—208°	—	α
	B	(Colourless needles, 208—210°)			
6-Cl-4-Me- (I*b*)	A	Colourless needles, 211—212°	211—212	—	α
	B	Colourless needles, 211—212°			
5-Cl-7-Me- (I*c*)	A	Colourless needles, 263—264°	263—264	—	α
	B	(Colourless needles, 263—264°)			
6-EtO- (I*d*)	A	Pink fibres, 183—186°	183—186	—	α
	B	(Pink fibres, 183—186°)			
4 : 5-Benz- (I*e*)	A	Pale green crystals, 244—246°	244—246	—	α
	B	(Pale brown crystals, 244—246°)			
6 : 7-Benz- (I*f*)	A	Fibrous colourless needles, 244—246°	244—246	—	α
	B	(Fibrous colourless needles, 245—247°)			
5 : 6-Benz- (I*g*)	A		—	Id.	α
	B				
4-Me- (I*h*)	A	Pale pink needles, 194—195°	194—195	—	α
	B	(Pale pink needles, 194—195°)			
4-Cl- (I*i*)	A	Colourless needles, 202—204°	—	Non-id.	β
	B	Colourless needles, 149—151°			
5-Me- (I*j*)	A	Colourless needles, 253—255°	—	—	α
	B	Colourless needles, 252—254° *			
7-Me- (I*k*)	A	Colourless needles, 193—194°	192—194	—	α
	B	(Colourless needles, 192—194°)			
7-Cl- (I*l*)	A	Colourless needles, 207—208°	207—208	—	α
	B	Colourless needles, 207—208°			

* The authentic 5 : 5′-dimethylthioindigo was prepared by oxidation of 5-methylthioindoxyl, and not from the anil.

4-*Chloro*-5′-*methylthioindirubin* (Found : C, 59·1; H, 2·2%); *diacetyldihydro-derivative* (Found : C, 58·8; H, 3·7%). 5 : 5′-*Dimethylthioindigo* (Found : C, 66·4; H, 3·9%) (G.P. 241,910; 243,087); *diacetyldihydro-derivative* (Found : C, 64·4; H, 4·8%). 7 : 5′-*Dimethylthioindigo* (Found : C, 66·5; H, 4·0%); *diacetyldihydro-derivative* (Found : C, 64·4; H, 4·6%). 7-*Chloro*-5′-*methylthioindigo* (Found : C, 59·0; H, 2·7%); *diacetyldihydro-derivative* (Found : Cl, 8·2. $C_{21}H_{15}O_4ClS_2$ requires Cl, 8·2%).

TABLE XII.

Condensation of (A) *7-Methylthionaphthenquinone* (III*k*), *and* (B) *its Anil, with the Thioindoxyls.*

Thioindoxyls.		Diacetyldihydro-derivative and m. p.	Mixed m. p.	*X*-Ray data.	Condensation.
Thioindoxyl (I)	A	(*a*) Colourless needles, 229—230° (*b*) Colourless crystals, 144—146°	—	—	α + β
	B	(Colourless needles, 229—230°)			
6-Cl-4-Me- (I*b*)	A	(*a*) Colourless needles, 192—194° (*b*) Pale pink crystals, 285—287°	—	—	α + β
	B	Colourless needles, 194—195°			
5-Cl-7-Me- (I*c*)	A	Colourless needles, 234—236°	234—236°	—	α
	B	(Colourless needles, 234—236°)			
6-EtO- (I*d*)	A	Pink needles, 158—161°	—	Mainly α Some β	α + β
	B	(Pink needles, 160—161°)			
4 : 5-Benz (I*e*)	A	Pale brown needles, 256—258°	203—205	Non-id.	β
	B	(Pale pink needles, 204—206°)			
6 : 7-Benz- (I*f*)	A	Colourless needles, 249—251°	249—251	—	α
	B	(Colourless needles, 249—250°)			
5 : 6-Benz- (I*g*)	A	Not acetylated	—	Non-id.	β
	B	(Pale green crystals, 250—253°)			
4-Me- (I*h*)	A	Colourless needles, 200—201°	200—202	—	α
	B	Colourless needles, 200—201°			
4-Cl- (I*i*)	A	Colourless needles, 187—188°	166—173	—	β
	B	Colourless needles, 165—167°			
5-Me- (I*j*)	A	Colourless needles, 190—193°	190—194	—	α
	B	Colourless needles, 192—194°			
7-Me- (I*k*)	A	Colourless needles, 244—246°	244—246	—	α
	B	Colourless needles, 244—246° *			
7-Cl- (I*l*)	A	Fibrous colourless needles, 243—244°	243—244	—	α
	B	Fibrous colourless needles, 243—244°			

* The authentic 7 : 7′-dimethylthioindigo was prepared by oxidation of 7-methylthioindoxyl, and not from the anil.

7′-*Methylthioindirubin* (Found: C, 65·4; H, 3·4. $C_{17}H_{10}O_2S_2$ requires C, 65·8; H, 3·2%). The original diacetyldihydro-derivative, m. p. 163—167°, was separated into two fractions, which were recrystallised to constant m. p. (*a*) White needles (α-component), m. p. 229—230°, (*b*) 7′-*methyldiacetyldihydro-thioindirubin* (Found: C, 63·3; H, 3·1%), m. p. 144—146°. The diacetyldihydro-derivative of the product from (I*b*) and (III*k*) had m. p. 163—171° (Found: C, 59·4; H, 4·3%) and was therefore a mixture of the two possible isomers only; it was separated into two fractions which were recrystallised to constant m. p., giving the diacetyldihydro-thioindigo and also 6-*chloro*-4 : 7′-*dimethyldiacetyldihydrothioindirubin* (Found: C, 59·6; H, 3·4%). 7′-*Methyl*-4 : 5-*benzthioindirubin* (Found: C, 70·3; H, 3·3. $C_{21}H_{12}O_2S_2$ requires C, 70·0; H, 3·3%). 7′-*Methyl*-5 : 6-*benzthioindirubin* (Found: C, 70·0; H, 3·2%). 4-*Chloro*-7′-*methylthioindirubin* (Found: C, 59·5; H, 2·9%); *diacetyldihydro-derivative* (Found: C, 58·6; H, 3·5%). 7 : 7′-Dimethylthioindigo (Found: C, 66·7; H, 3·7%) (Guha, *J. Ind. Chem. Soc.*, 1943, **20**, 37); *diacetyldihydro-derivative* (Found: C, 64·7; H, 4·1%). 7-*Chloro*-7′-*methylthioindigo* (Found: C, 59·2; H, 2·8%); *diacetyldihydro-derivative* (Found: C, 58·4; H, 3·4%).

TABLE XIII.

Condensation of (A) *7-Chlorothionaphthenquinone* (III*l*), *and* (B) *its Anil, with the Thioindoxyls.*

Thioindoxyl.		Diacetyldihydro-derivatives and m. p.	Mixed m. p.	*X*-Ray data.	Condensation.
Thioindoxyl (I)	A	Colourless needles, 229—230°	229—230°	—	α
	B	(Colourless needles, 229—230°)			
6-Cl-4-Me- (I*b*)	A	Colourless needles, 195—215°	—	—	α + β
	B	Colourless needles, 191—193°)			
5-Cl-7-Me- (I*c*)	A.	Fibrous colourless needles, 245—246°	245—246	—	α
	B	(Fibrous colourless needles, 245—246°)			
6-EtO- (I*d*)	A	Pink needles, 180—182°	180—183	—	α
	B	Pink needles, 181—183°			
4 : 5-Benz- (I*e*)	A	Pale green needles, 211—213°	211—214	—	α
	B	Pale green needles, 215—216°			
6 : 7-Benz- (I*f*)	A	Pale yellow needles, 251—252°	250—252	—	α
	B	Pale green needles, 250—251°			
4-Me- (I*h*)	A	Pale pink needles, 197—200°	—	—	α + β
	B	(Colourless needles, 219—220°)			
4-Cl- (I*i*)	A	Colourless needles, 222—223°	—	—	β
	B	Colourless needles, 162—164°			
5-Me- (I*j*)	A	Fibrous colourless needles, 190—202°	—	—	α + β
	B	(Colourless needles, 207—208°)			
7-Me- (I*k*)	A	Pale orange needles, 242—244°	242—244	—	α
	B	Fibrous colourless needles, 243—244°)			
7-Cl- (I*l*)	A	Fibrous colourless needles, 280—281°	280—281	—	α
	B	Fibrous colourless needles, 283—284° *			

* The authentic 7 : 7′-dichlorothioindigo was prepared by oxidation of 7-chlorothioindoxyl, and not from the anil.

The diacetyldihydro-derivative of the product from (I*b*) and (III*l*) had m. p. 195—215° (Found: C, 54·5; H, 3·1%) and therefore was a mixture of the two possible isomers only; further recrystallisation of this mixture steadily raised the

m. p., and after four recrystallisations the m. p. was 218—253° (Found: Cl, 15·3. Calc. for $C_{31}H_{14}O_4Cl_2S_3$: Cl, 15·3%). Recrystallisation therefore resulted in the isolation of 6 : 7′-dichloro-4-methyldiacetyldihydrothioindirubin; the isolation could not be completed owing to lack of material. 4 : 7′-*Dichlorothioindirubin* (Found: C, 52·3; H, 1·6%); *diacetyldihydro-derivative* (Found: C, 52·9; H, 2·7%). The diacetyldihydro-derivative of the product from (I*j*) and (III*l*) had m. p. 190—202° (Found: C, 58·6; H, 3·4%) and was therefore a mixture of the two possible isomers only; recrystallisation furnished ultimately 7′-chloro-5-methyldiacetyldihydrothioindigo. 7 : 7′-*Dichlorothioindigo* (Found: C, 52·6; H, 1·9%); *diacetyldihydro-derivative* (Found: Cl, 15·3. $C_{20}H_{12}O_4Cl_2S_2$ requires Cl, 15·7%).

Table XIV contains for rapid reference the collected m. p.s of the pure diacetyldihydro-derivatives of the thioindigos and thioindirubins, which are named according to (XVII) and (XVIII) respectively. Almost all the values given by Harley-Mason and Mann (*loc. cit.*) have been confirmed or corrected and are therefore included; a few of their values for the thioindirubins have not been checked and are omitted, as these products may be mixtures (p. 895).

TABLE XIV.

M. p.'s of Diacetyldihydro-derivatives of Thioindigos and Thioindirubins.

Substitution.		Thioindigo derivative.	Thioindirubin derivative.	Substitution.		Thioindigo derivative.	Thioindirubin derivative.
X.	Y.			X.	Y.		
—	—	247—248°	132—133°	4 : 5-Benz-	4 : 5-Benz-	>315°	—
6-Cl-4-Me-	—	183—184	— *	6 : 7-Benz-	,,	255—257	—
5-Cl-7-Me-	—	214—216	158—160	5 : 6-Benz-	,,	263—265	— †
6-EtO-	—	173—174	— *	4-Me-	,,	201—202	—
4 : 5-Benz-	—	215—217	166—169	4-Cl-	,,	237—238	—
6 : 7-Benz-	—	254—256	— *	5-Me-	,,	244—246	—
5 : 6-Benz-	—	256—258	162—163	7-Me-	,,	209—211	—
4-Me-	—	214—215	—	7-Cl-	,,	216—217	—
4-Cl-	—	205—206	—	6-EtO-	6 : 7-Benz-	(215—217)	175—176°
5-Me-	—	208—210	124—125	4 : 5-Benz-	,,	(255—257)	219—220
7-Me-	—	229—230	—	6 : 7-Benz-	,,	>315	—
7-Cl-	—	229—230	131—132	5 : 6-Benz-	,,	252—253	— †
6-Cl-4-Me	6-Cl-4-Me	290—292	—	4-Me-	,,	235—237	—
5-Cl-7-Me-	,,	229—230	—	4-Cl-	,,	230—231	—
6-EtO-	,,	186—188	— †	5-Me-	,,	245—247	—
4 : 5-Benz-	,,	234—235	— *	7-Me-	,,	253—254	180—181
6 : 7-Benz-	,,	252—253	— †	7-Cl-	,,	251—252	—
5 : 6-Benz-	,,	261—263	—	—	5 : 6-Benz-	(256—258)	183—184
4-Me-	,,	232—234	—	6-Cl-4-Me-	,,	(261—263)	186—188
4-Cl-	,,	240—241	—	6-EtO-	,,	(224—226)	166—167
5-Me-	,,	213—214	—	5 : 6-Benz-	,,	297—300	— *
7-Me-	,,	194—195	—	5-Me-	,,	267—269	198—199
7-Cl-	,,	191—193	— †	7-Me-	,,	250—253	— *†
5-Cl-7-Me-	5-Cl-7-Me-	308—310	—	4-Me-	4-Me-	247—249	—
6-EtO-	,,	214—216	— †	4-Cl-	,,	246—247	—
4 : 5-Benz-	,,	274—276	—	5-Me-	,,	194—195	—
6 : 7-Benz-	,,	236—238	171—173	7-Me-	,,	200—201	—
5 : 6-Benz-	,,	258—260	— †	7-Cl-	,,	219—220	— †
4-Me-	,,	218—220	—	4-Cl-	4-Cl-	275—277	—
4-Cl-	,,	231—232	—	5-Me-	,,	149—151	207—208
5-Me-	,,	263—264	—	7-Me-	,,	165—167	183—184
7-Me-	,,	234—236	—	7-Cl-	,,	162—164	231—232
7-Cl-	,,	245—246	—	4-Cl-	5-Me-	(149—151)	202—204
—	6-EtO-	(173—174)	132—133	5-Me-	,,	253—255	—
6-EtO-	,,	230—232	— *	7-Me-	,,	193—194	—
4 : 5-Benz-	,,	223—225	— *	7-Cl-	,,	207—208	— †
6 : 7-Benz-	,,	215—217	165—166	—	7-Me-	(229—230)	144—146
5 : 6-Benz-	,,	224—226	167—169	6-Cl-4-Me-	,,	(194—195)	285—287
4-Me-	,,	160—161	— *	4 : 5-Benz-	,,	(209—211)	256—258
4-Cl-	,,	170—171	152—153	4-Cl-	,,	(165—167)	187—188
5-Me-	,,	184—186	— *	7-Me-	,,	244—246	—
7-Me-	,,	160—161	— *	7-Cl-	,,	243—244	—
7-Cl-	,,	181—183	158—159	7-Cl-	7-Cl-	283—284	—

* The thioindirubin has been shown to exist but was not isolated in the pure state.

† The isomeric thioindirubin (*i.e.*, with substituents in X and Y reversed) has been shown to exist, but was not isolated in the pure state.

Brackets ( ) indicate that the m. p. has already been quoted earlier in the Table.

Erratum. In Part I, p. 410, line 15 from bottom, *for* " (I*g*) " *read* " (I*f*)."

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