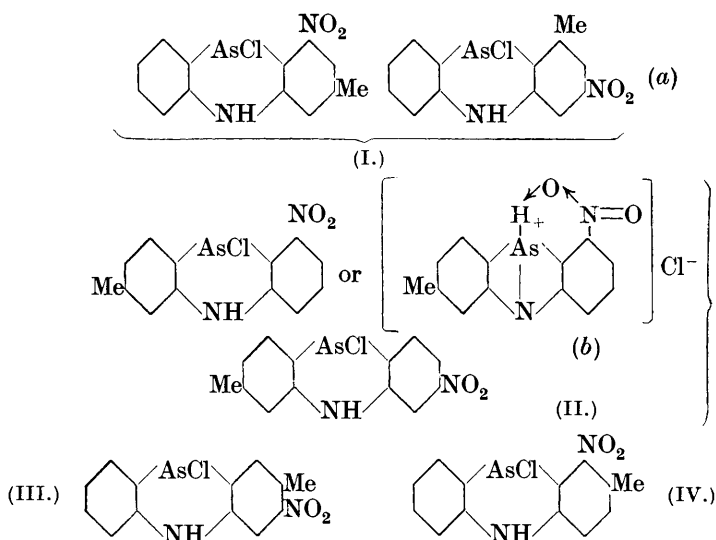


CCXII.—10-Chloro-5 : 10-dihydrophenarsazine and its
Derivatives. Part XIII. Absorption Spectra.

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It was emphasised in Part IX (Gibson and Johnson, J., 1929, 1229) that the visible colour of some simple nitromethyl derivatives of 10-chloro-5 : 10-dihydrophenarsazine varied according to the position of the nitro-group. This variation of visible colour seemed to be capable of correlation with other properties of the compounds (particularly melting points or decomposition points and solubilities), account being taken of analogous properties of the parent substance and of other related substances, which have been previously described, especially of those nitro-derivatives in which the position of the nitro-group was definitely known. It thus seemed possible to draw tentative conclusions as to the constitution, for example, of compound (I), the homogeneous product derived from 5-nitro-3-methyldiphenylamine-6'-arsinic acid, of compound (II), the homogeneous product derived from 3-nitro-3'-methyldiphenylamine-6'-arsinic acid, and of the two compounds (III and IV) derived simultaneously from 3-nitro-4-methyldiphenylamine-6'-arsinic acid. In compound (I), which is orange-yellow, decomposes at 245—247°, and is insoluble in the ordinary solvents, it was concluded that, in all probability, the nitro-group is in the 3-position (formula *a*); in compound (II), which is deep red, has m. p. 253—255° (decomp.), and is very sparingly soluble in the ordinary solvents, it was concluded that the nitro-group was in the 1-position (formula *b*). Similarly, in the light of our increased knowledge, we would now conclude that the homogeneous product derived from 3-nitrodiphenylamine-6'-arsinic acid, *viz.*, the so-called 10-chloro-1(or 3)-nitro-5 : 10-dihydrophenarsazine (J., 1927, 2514), has the nitro-group probably in the 1-position because the compound is deep red and has m. p. 258—259° (decomp.). Of the two isolated compounds (III and IV), it was concluded that the one which is bright red, decomposes at 225—226°, and is sparingly

soluble has the nitro-group in the 1-position (IV) and that the other, which is orange-yellow, decomposes at 257—258°, and is also sparingly soluble, has the nitro-group in the 3-position (III).

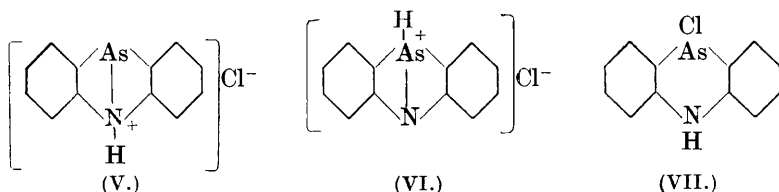


It seemed desirable to try to supplement what may be termed visual evidence by exact physical measurements. The present communication describes the results which have been obtained in investigating the absorption spectra of a series of these related compounds in the ultra-violet and the visible parts of the spectrum.

A Hilger C-type quartz spectrograph and a Hilger sector photometer were used, with an iron-nickel arc as a source of radiation. A concentration of $M/10,000$ in optically pure ethyl alcohol gave the best results in the ultra-violet region for 1 cm. length of tube, but in certain cases it was necessary to supplement the results so obtained by using a concentration of $M/4000$ in order to follow the absorption band more fully.

The colours of 10-chloro-5:10-dihydrophenarsazine and of its methyl, nitro-, and nitromethyl derivatives are very intense. The parent substance and its methyl derivatives in the solid state have a brilliant yellow colour, but the colours of the nitro-derivatives depend on the position occupied by the nitro-group. Our previous knowledge of the visible colour and known constitution of some of the latter compounds indicated that those possessing a deep crimson colour have the nitro-group in the 1- or 4-position, whereas those which are yellow have the nitro-group in the 2- or 3-position in the

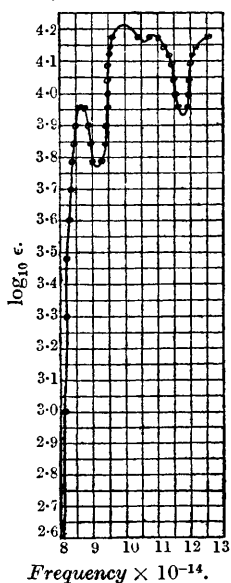
phenarsazine nucleus.* Although the exact relationships between chemical constitution and the absorption spectra of substances in solution are far from being understood, it is shown in the present discussion that in this series of closely related compounds the absorption spectra can be correlated with the position of the nitro-group in the molecule.



(A) Evidence has been brought forward (J., 1929, 1238) to indicate that the constitution of 10-chloro-5:10-dihydrophenarsazine is more adequately represented by either formula (V) or (VI) rather than by (VII); since, apart from other properties, the *N*-substituted derivatives are colourless and they cannot possess a transannular bond.

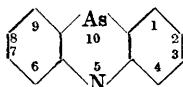
FIG. 1.

10-Chloro-5:10-dihydrophenarsazine.

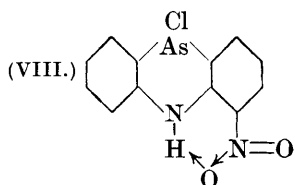


Further, the *As*-alkyl derivatives are also colourless (Aeschlimann, J., 1927, 413; Seide and Gorski, *Ber.*, 1929, **62**, 2186) and those compounds do not possess salt-like properties. It appears reasonable to assume, therefore, that any absorption in the visible and near ultra-violet spectrum of the parent substance may be associated with this transannular bond. Fig. 1, giving the absorption curve of 10-chloro-5:10-dihydrophenarsazine, shows a strong absorption band in the near ultra-violet, the centre of the band being at a frequency of 8.65×10^{14} , while the general trend of the curve indicates marked absorption in the extreme violet. A strong double-branched absorption band occurs further in the ultra-violet, with two maxima at frequencies of 10.0×10^{14} and 10.8×10^{14} .

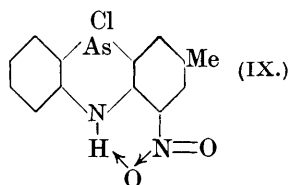
* On account of the confusion in nomenclature in different journals, it is again desirable to indicate that we prefer to number the atoms in the phenarsazine nucleus thus :



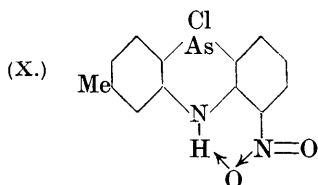
(B) The deep crimson colour, greater solubility, and lower melting points of the 4-nitro-derivatives of 10-chloro-5 : 10-dihydrophenarsazine as compared with the 2- and 3-nitro-derivatives were ascribed to the presence in the former of a chelate ring as indicated : *



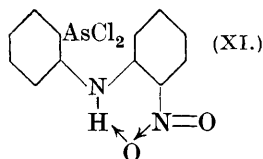
10-Chloro-4-nitro-5 : 10-dihydrophenarsazine.



10-Chloro-4-nitro-2-methyl-5 : 10-dihydrophenarsazine.



10-Chloro-4-nitro-7-methyl-5 : 10-dihydrophenarsazine.



2-Nitrodiphenylamine-6'-dichloroarsine.

According to this view, no transannular bond is possible in compounds of this type, and, if the absorption band at frequency 8.65×10^{14} is ascribed to the presence of the transannular bond in the parent substance, it should be absent from the absorption spectra of these 4-nitro-compounds (VIII, IX, X, and XI). Further, it would be expected that a new absorption band might appear to correspond with the new ring system present.

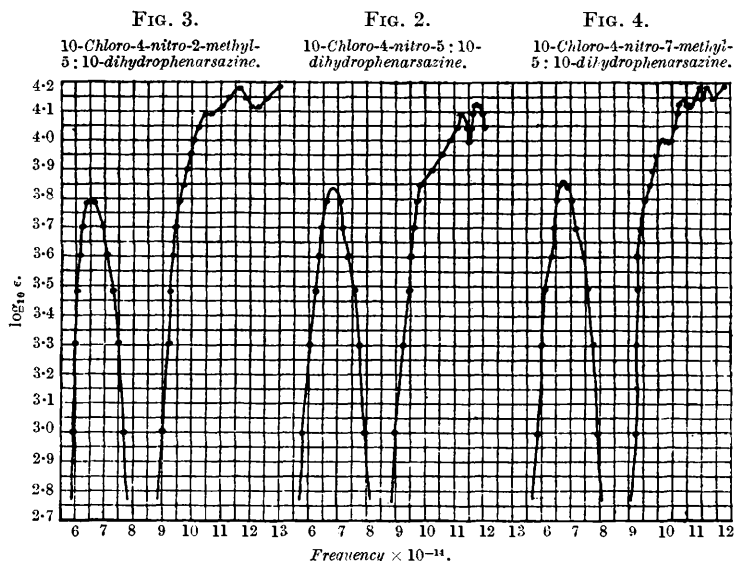
Figs. 2, 3, and 4, giving the absorption curves of compounds (VIII, IX, and X) in which the nitro-group is in the 4-position, appear to indicate that these predictions are justified. It will be seen that the absorption band having its maximum at frequency 8.65×10^{14} is absent and that a new band appears, the position and intensity of which are the same in the three cases, the maximum being at a frequency of 6.7×10^{14} . The peaks of the curves are in the visible region and there is a considerable absorption in the green region at the low concentration employed. The absorption band

* These conclusions regarding the constitution of 10-chloro-5 : 10-dihydrophenarsazine and its derivatives find analogies in the anthracene series. For example, the effect of chlorine atoms in the 4- and/or 5-positions in 10-hydroxyanthranones and in 10-phenylanthranones in preventing the formation of anthracene derivatives containing the transannular (transannellar) bond has recently been ascribed by Barnett and Wiltshire (*Ber.*, 1930, **63**, 1114) to chelation or co-ordination between the chlorine and the hydrogen atom in the 10-position.

common to all three substances is obviously responsible for the deep crimson colour.

In addition to this, strong absorption takes place in the ultra-violet region at frequencies greater than $\nu = 9 \times 10^{14}$ at the concentration used, and this band is resolved into subsidiary maxima. We have not been able to correlate the positions of the subsidiary maxima with any variation in constitution.

It was shown (*loc. cit.*) that the 4-nitro-derivatives are produced by cyclisation of the corresponding 2-nitrodiphenylamine-6'-dichloroarsines by boiling in acetic acid solution. The latter substances are orange or orange-yellow, and in explanation of their



stability it was suggested (p. 1290) that a chelate ring was present whereby the freedom of the hydrogen atom of the NH group was restricted. The same chelate ring being present in these nitrodichloroarsines and the corresponding 4-nitro-compounds, the 2-nitrodichloroarsines should show an absorption band the maximum of which is at frequency 6.7×10^{14} . One such case has been examined (compound XI), and a strong absorption band having a maximum at frequency 7.2×10^{14} (Fig. 5) occurs. The character of this band in intensity and frequency recalls very strongly that of the 4-nitro-derivative of 10-chloro-5:10-dihydrophenarsazine, the slightly greater frequency being consistent with a faster vibrating centre as would be expected from the absence of the As-N ring.

(C) The 2-nitro-derivatives of 10-chloro-5:10-dihydrophen-

arsazine in the crystalline state have a deep yellow colour. The absorption spectra (Figs. 6 and 7) of two of these compounds (XII and XIII) show the presence of a strong band having its maximum

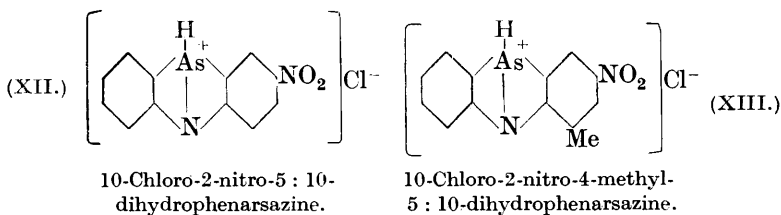
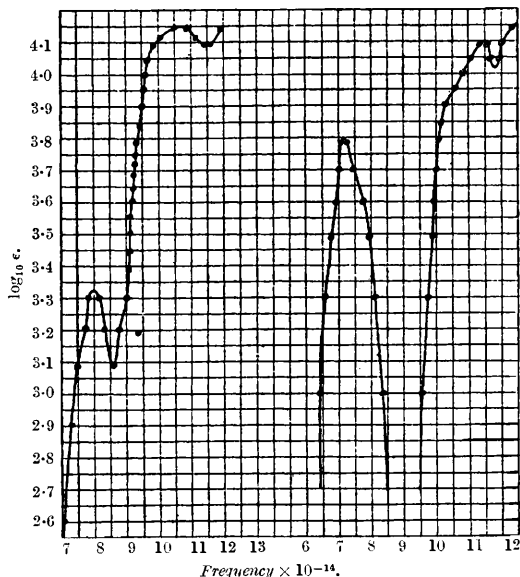


FIG. 13.

5-Nitro-2-methyldiphenylamine-6'-dichloroarsine.

FIG. 5.

2-Nitrodiphenylamine-6'-dichloroarsine.



at a frequency of 7.6×10^{14} , the persistence of the band being almost the same for the two substances. It would thus appear that this band is the one responsible for the deep yellow colour of the two substances.* The identity of these two absorption curves

* Wieland and Rheinheimer (*Annalen*, 1921, **423**, 1) showed that 2-nitrophenarsazinic acid forms two sodium salts, the monosodium salt being yellow and the disodium salt deep red. Neither of these compounds can be formulated as having a transannular bond and, in comparing the behaviour of salts of 2-nitrophenarsazinic acid with those of *pp'*-dinitrophenylhydroxylamine derivatives, which also yield *aci*-salts (*Ber.*, 1920, **53**, 213), the above authors

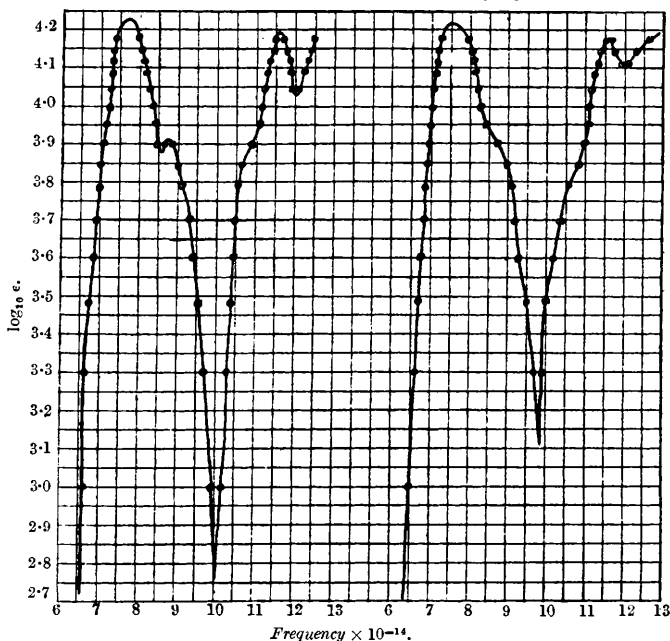
is all the more apparent in view of the fact that the subsidiary band occurring at frequency 8.8×10^{14} is present in both, indicated in Fig. 6 by a change in direction.

FIG. 7.

10-Chloro-2-nitro-4-methyl-5:10-dihydrophenarsazine.

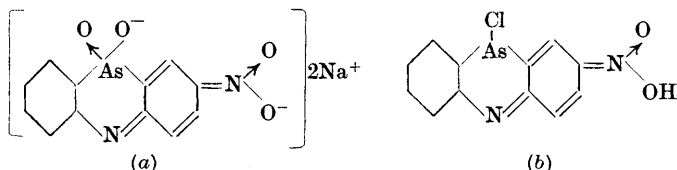
FIG. 6.

10-Chloro-2-nitro-5:10-dihydrophenarsazine.



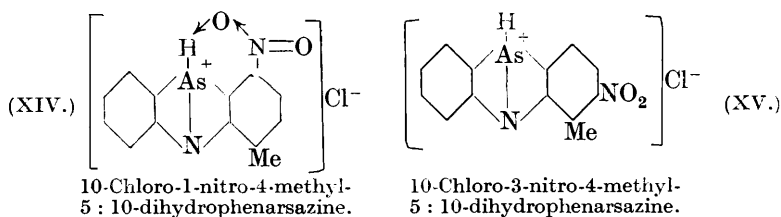
(D) As pointed out above and in previous papers (J., 1927, 2499; 1928, 2204; 1929, 767, 1229), the cyclisation of diphenyl-

concluded that the disodium salt has a *p*-quinonoid structure which may be represented by (a).



This implies a tendency for the hydrogen of the :NH group to migrate to the NO_2 group in the para-position to itself. In view of this, it might be suggested that the 2-nitro-derivatives of 10-chloro-5:10-dihydrophenarsazine might possess a *p*-quinonoid structure as indicated by (b). The one serious objection to this is that the compound is yellow and quite different in this respect from that of the above-mentioned *aci*-salts.

amine-6'-arsinic acids substituted in the 3-position may lead to two isomeric cyclic products. The products derived in this way from 3-nitrodiphenylamine-6'-arsinic acids are sometimes red and sometimes yellow or orange-yellow (J., 1929, 1239), for example, compounds (II) and (I) respectively, and the so-called 10-chloro-1(or 3)-nitro-5 : 10-dihydrophenarsazine referred to above is red. In one case the two theoretically possible reduction products were isolated, one being red (assumed for the present to be compound IV) and the other orange-yellow (compound III). Now a compound having the nitro-group in the 1-position (compound XIV) was synthesised and found to be red, and a compound having the nitro-group in the 3-position (compound XV) was also synthesised



and proved to be yellow. On these grounds, the constitutions already indicated were assigned to the compounds (I, II, III, and IV), and it was of interest to see how far information which might be derived from absorption spectra measurements agreed with the previous conclusions.

The absorption curves of the rationally synthesised compounds (XIV and XV) are shown in Figs. 9 and 8 respectively. These absorption curves are distinctive: the band of the red compound (XIV) with a frequency of 7.5×10^{14} has considerable persistence, and in this compound we are of opinion that a chelate group is present; while in the yellow compound (XV) the band is of little persistence and is definitely displaced towards the violet, as would be expected from a band arising from a molecule with less restraint, *i.e.*, without the chelate ring.

There is a remarkable resemblance between the absorption curves shown in Figs. 9 and 10. Fig. 10 is the absorption curve of the red compound previously described as 10-chloro-1(or 3)-nitro-5 : 10-dihydrophenarsazine and it appears that this compound should have an analogous constitution to that whose absorption curve is represented in Fig. 9, *i.e.*, 10-chloro-1-nitro-4-methyl-5 : 10-dihydrophenarsazine. We therefore advance the view that the compound whose constitution has so far remained doubtful is 10-chloro-1-nitro-5 : 10-dihydrophenarsazine, and that our previous deduction that it might be the 3-nitro-compound, which was based

on the work of other authors who investigated analogous compounds, must now be revised.

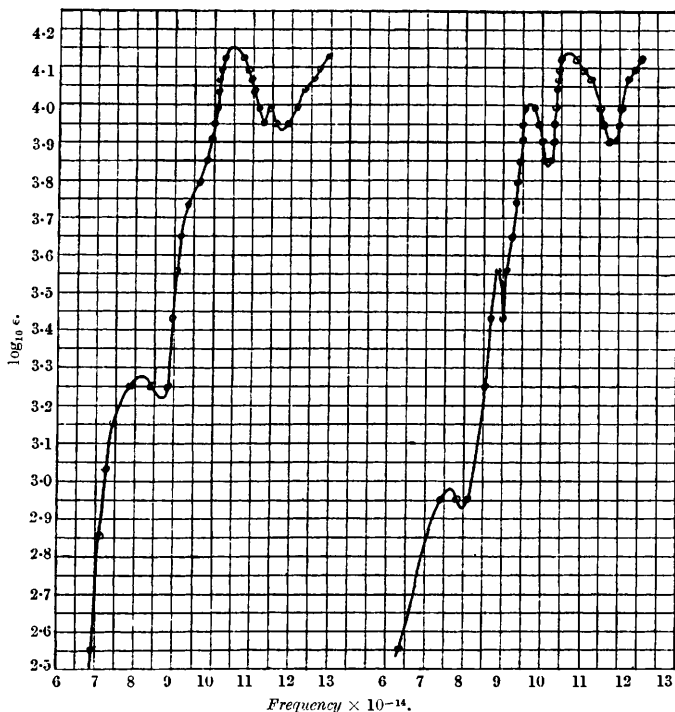
Of the two isomeric compounds, 10-chloro-3-nitro-2-methyl-5 : 10-dihydrophenarsazine and 10-chloro-1-nitro-2-methyl-5 : 10-dihydrophenarsazine, produced simultaneously from 3-nitro-4-methyl-diphenylamine-6'-arsinic acid, one is red and the other is yellow. The absorption curve of the red compound is shown in Fig. 11 and that of the yellow compound in Fig. 12.

FIG. 8.

10-Chloro-3-nitro-4-methyl-5 : 10-dihydrophenarsazine.

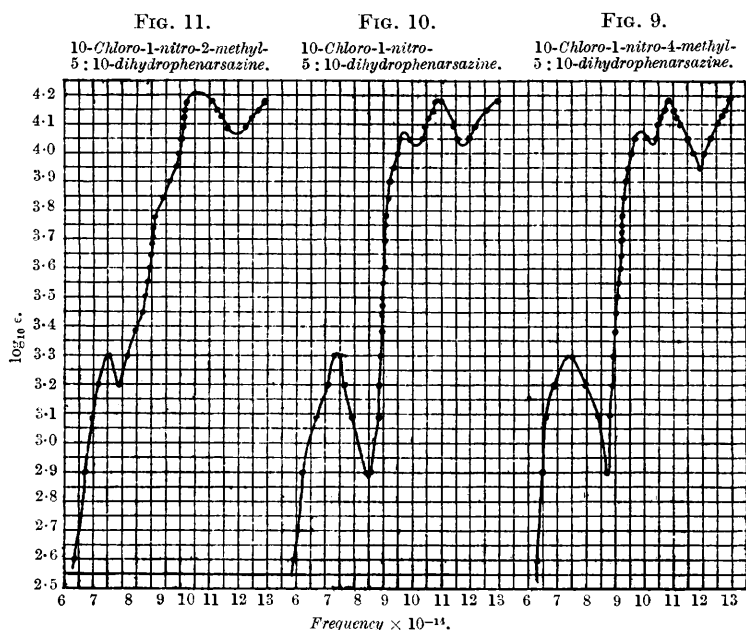
FIG. 12.

10-Chloro-3-nitro-2-methyl-5 : 10-dihydrophenarsazine.



The band of lower frequency of the red compound of Fig. 11 at 7.5×10^{14} is in practically the same position as that of the red compound of Fig. 9, pointing strongly to the 1-nitro-position; this would lead to the isomeric yellow compound having the nitro-group in the 3-position. One of the compounds being yellow, its absorption curve might be expected to follow that shown in Fig. 8 in having a band of higher frequency, while the other being red, its absorption curve should simulate that shown in Fig. 9, as, in fact, is seen to be the case.

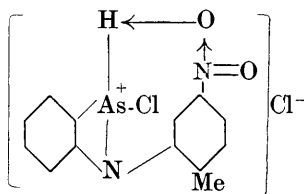
The absorption curves of Figs. 8 and 12 show certain resemblances inasmuch as both substances have bands of slight persistence in the same region about $7.5-9 \times 10^{14}$, the differences in the curves shown being accounted for by the steepness of the absorption curves rendering it difficult to trace the structure of the band readily. Now the yellow compound, 10-chloro-3-nitro-4-methyl-5 : 10-dihydrophenarsazine, whose absorption spectrum is represented by Fig. 8 has been synthesised (*loc. cit.*), so all these considerations are in favour of the isomeric yellow compound represented by Fig. 12 being 10-chloro-3-nitro-2-methyl-5 : 10-dihydrophenarsazine.



The absorption curve shown in Fig. 11 indicates only a change of direction at a frequency of about 8.5×10^{14} , and this change in direction is represented in Figs. 8 and 12 by clearly marked bands. This change in direction, however, gives the curve the same general features as those of Figs. 8 and 12. In this connexion, attention may be directed to the fact that the three compounds whose absorption curves are given in Figs. 8, 11, and 12 all have a methyl group and a nitro-group in the *o*-position to each other and it is not without significance that their absorption curves are similar. While there is little evidence for assuming the possibility of any chelate ring formation between neighbouring methyl and nitro-groups, it seems not unreasonable to suppose that, while

in the 1-nitro-compounds of this series a chelate ring is indicated (formulae IIb and XIV), this chelate ring may be absent or may not be stable in the 1-nitro-compounds which have a methyl group in the 2-position.

These views receive some confirmation from a consideration of the absorption curve (Fig. 13) of 5-nitro-2-methyldiphenylamine-6'-dichloroarsine, which is the only case we have encountered of the actual isolation of a dichloroarsine during the reduction of the corresponding arsenic acid when the latter does not contain a nitro-group in the *o*-position to the .NH group of the substituted diphenylamine. This dichloroarsine is bright yellow and has m. p. 173°—unusually high for a dichloroarsine—these properties suggesting the presence of a transannular bond and a salt-like character. For the reasons previously set forth (Part IX, J., 1929, 1241—2), to this compound should be ascribed the formula



indicating the presence of chelation. The absorption curve (Fig. 13) of this dichloroarsine shows the presence of the characteristic band having its maximum at a frequency of 8.0×10^{14} , and this band has a persistence comparable with that indicated in Fig. 9, which is the absorption curve of a compound in which we have arrived at the conclusion that the chelate ring is present.

In conclusion, it can be stated that the hypothesis previously developed in Part IX to correlate the visible colour with the constitution of nitro-derivatives of 10-chloro-5 : 10-dihydrophenarsazine has received substantial confirmation by the more accurate study of the absorption spectra in the ultra-violet and visible regions.

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