The formula given on p. 2297 in the November number of THIS JOURNAL in the paper entitled "Solubility and Internal Pressure" should have been written

$$\log N = \frac{-L(T_m - T)}{4.58TT_m}.$$

The correct form was used in the calculation of the data used in the paper.

The value N for anthracene in Table I on p. 2298 should be 0.0107.

JOEL H. HILDEBRAND.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

PHTHALIC ACID DERIVATIVES; CONSTITUTION AND COLOR, V.[1] SOME DERIVATIVES OF TETRACHLORO- AND TETRAIODO PHTHALIMIDES.

BY DAVID S. PRATT AND GRANVILLE A. PERKINS.

Received October 17, 1917.

One of the most interesting sections in the vast field of investigation attempting more or less successfully to correlate constitution and color is the study of substances related to phthalic acid. Since the primary interest of such study, in the beginning if not now, was connected with visible color, investigations have dealt chiefly with the more complex members of the group, such as the phthaleins and related compounds. Such work was sufficient to establish certain theories of chromophores, auxochromes, etc., which must, however, be considered mere approximations. The *exact* correlation of absorption and constitution even in the simplest known substances seems at present such a complex affair that in the opinion of the authors it is not logical to expect to improve much on the present theories of color by a study confined to complicated substances such as the phthaleins or indeed any colored compounds. Our present knowledge indicates that while the physicist is approaching the problem of chemical affinity and its relation to radiant energy from the standpoint of molecular dynamics, the corresponding task of the organic chemist is to trace the relations between the absorption spectra of large numbers of closely related substances, thus linking the complex with the simple.

The already large literature dealing with absorption spectra unfortunately has the fault of being so detached in all but a few marked exceptions that it is generally impossible to trace accurately the connections between spectra even of substances in the same class. Information is lacking as a rule concerning the progressive changes brought

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[1] For previous papers on simpler derivatives such as the anhydride, imide, oxime and anil see *Am. Chem. J.*, 47, 89 (1912); *Phil. J. Sci.*, (*A*) 8, 165, 399 (1913); *Ibid.*, 9, 105 (1914).

about by various steps leading from simple to complex derivatives. Thus, while it was a great step in advance several decades ago to connect the deep color of phenolphthalein salts with a quinoid arrangement of the molecule, neither this idea alone nor its amplifications have gone very far since then in correlating the absorption bands shown by various compounds related to the phthaleins, or towards ascribing to each a definite origin in the structure of the molecule. On the one hand, the quinoid rearrangement in itself seems insufficient to cause a deep purple color; on the other hand, deeply colored compounds are known, such as the salts of phthaloxime, where no quinoid arrangement seems possible.

It is the purpose, then, of this series of investigations to study the absorption spectra of a large number of compounds related to phthalic acid, each differing from its neighbors by minute steps only. It is hoped that the result will be a clearer insight into the relations between the absorption bands shown by different members of the same family and a more exact knowledge of the origin of each band.

The possible substitutions in the phthalic anhydride molecule fall naturally into three classes according to the position taken by the entering group. One or more hydrogens in the ring may be replaced, as in tetrachlorophthalic anhydride; oxygen in a carbonyl group may be substituted by a divalent radical or two monovalent atoms or radicals, and finally the anhydride oxygen may be replaced.

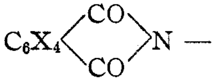
The present paper deals with the preparation of examples of the first and third types. Interesting molecular compounds were also encountered which do not come under the above classification since they are not substitution products. The absorption spectra of the various derivatives will be reported on at a later date since war conditions have made it impossible for the firm of Adam Hilger, London, to supply certain essential pieces of new apparatus ordered two years ago.

The replacement of hydrogen by halogen in the ring of phthalic acid was taken as the simplest example of this type of substitution. Here the effect of the change is known to be in general an increase in the period of vibration of whatever causes the main absorption bands, and a consequent shift toward the longer wave lengths. This fact is utilized commercially, tetrachloro- and 3,6-dichlorophthalic acids being well-known dye intermediates although the isomeric 3,4- and 4,5-dichloro acids have not been used so extensively. Studies of the imide derivatives of these partially chlorinated and a number of partially iodinated phthalic acids will appear in succeeding articles. Meanwhile the bromine series is being extensively studied.

Aside from being a series of preparations preliminary to spectroscopic study the investigation here reported brought to light an interesting type of molecular addition product; a new type of diphenyl amine derivative resulting from the introduction of an anilino group into the phthalic acid nucleus; and an interesting connection between dimorphism and "solvent of crystallization."

Preparation of the Imide Derivatives.

In passing spectroscopically from the halogen substituted anhydride to some other types such as the anil, oxime and phenylhydrazone, the imide was taken to serve as a connecting link. We have found it very convenient to convert various phthalic anhydrides into corresponding imides by gently warming them with formamide. The yields are excellent and contaminating products are not formed to any appreciable extent. Prolonged heating of tetrachlorophthalimide with formamide, however, carries the reaction further. While we have not succeeded in isolating any pure product from this second reaction, our analyses indicate a replacement of chlorine by an amino group.

The anils or phenylimides for the most part represented by  $C_6X_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle N — C_6H_4R$ were readily prepared from the anhydride and amine. Generally acetic acid or nitrobenzene was used as a solvent. Difficulties experienced by previous investigators in preparing pure samples of halogenated phthalanils were mostly due to the effect of the amine upon the halogen. This reaction will be discussed after a consideration of the manner in which the amine breaks the anhydride ring.

The Action of Amines on the Anhydride Ring.

A fact which seems to have escaped notice hitherto is that certain amines give deeply colored unstable products with many substituted phthalic anhydrides. In some cases it is possible to isolate the addition products, in others the reaction, if it may be so called, is evidenced only by the color produced. Tetrachlorophthalic anhydride, for example, gives with dimethylaniline a 1 : 1 molecular addition product which crystallizes in intensely red prisms. That this reaction does not depend on the chlorine is shown by a similar crystalline product prepared[1] from 3-nitrophthalic anhydride, and colors produced with a number of other substituted phthalic anhydrides. The unsubstituted anhydride gives an orange color when dissolved in dimethyl aniline. In fact, sufficient examples of this reaction have been tried besides those directly within the scope of this article to warrant the conclusion that aromatic amines, perhaps all amines, form as a *first* step in their reactions with phthalic anhydride and its nuclear substituted derivatives a molecular addition product.

The structural formula to be assigned such a compound is doubtful as in all such cases. Chemists are wont to pick out the main or primary

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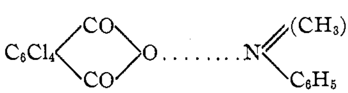
[1] By A. B. Coleman.

forces which hold atoms together, represent them by "bonds," and consider the secondary forces relatively unimportant. Taking into account, however, their undoubted relations to the absorption of light by the molecule, a knowledge of the secondary forces is essential from the point of view of the spectroscopic study in hand. What, then, can we say of the forces which unite a tetrachlorophthalic anhydride molecule to a dimethylaniline molecule with the production of a deep red color? The most reasonable point of attachment on the amine molecule would seem to be the nitrogen, known to have "residual valency." In the other molecule the anhydride ring is evidently responsible for the union, which may accordingly be expressed



Perhaps the uniting forces engage the carbonyl groups more directly than is here indicated; the dotted line merely shows approximately what we consider the points of attachment.

The production of a deep color by such an unstable union is a phenomenon often observed. Accepting for the sake of definiteness the view that visible absorption is caused primarily by the vibration of valence electrons,[1] it is probable that here the union or conjugation through secondary atomic forces has caused a remarkable weakening of one or more valence fields. In other words, it has greatly lowered the potential gradients surrounding one or more valence electrons, thus allowing them to vibrate in periods corresponding to the frequency of visible light instead of the ultraviolet rays which they formerly absorbed. Another possibility is that certain "residuary" valence electrons, not recognized in Stark's hypothesis, have had their surrounding fields strengthened so that their absorption is shifted into the visible from the infra red. A decision between these two possibilities can probably be arrived at by a spectroscopic study of sufficient related complexes to trace the main visible absorption from its origin in the ultraviolet or infra red. The first-mentioned alternative is certainly the most usual effect of conjugation.

Considering, then, that certain force fields are weakened the next step in the reaction seems quite natural. With tertiary amines, indeed, no further step is possible, but in case the amine is secondary a rearrangement quickly takes place, while with primary amines three steps may be observed. For example, aniline added to a benzene solution of tetrachlorophthalic anhydride gives first a transitory yellow color (I), immediately followed by a white precipitate of aniline tetrachlorophthalanilate (II), which when warmed gives off aniline and water forming the anil (III).

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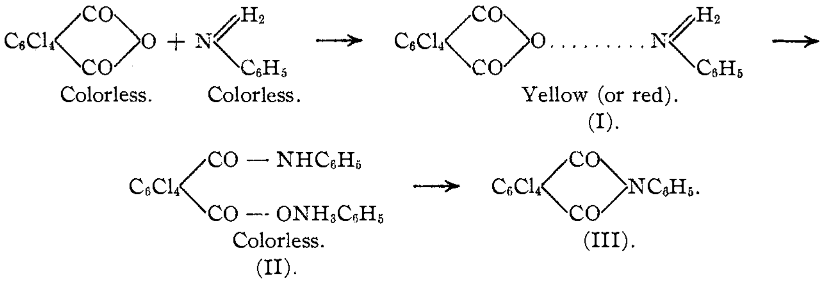
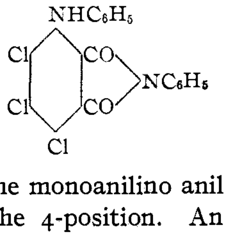
[1] J. Stark, "Die Electrizitat im chemischen Atom," Leipzig, 1915.



It seems probable that primary amines in general react with phthalic anhydrides in the three steps illustrated above giving imides, anils, oximes, or hydrazones according to the nature of the amine. Although most amines give little or no color as a result of the first step, a few produce a deep red (*e. g.*, α-naphthylamine and tetrachlorophthalic anhydride). The second step might perhaps better be represented as a simple rearrangement to the amic acid which would then react with another molecule of amine forming the salt shown in (II). The precipitate actually obtained, however, was the salt, not the amic acid. The third step, *i. e.*, the closing of the imide ring, has been studied from a theoretical standpoint by Tingle.[1] Our interest in this reaction was more from a practical point of view. Almost the only difficulty experienced in the preparation of halogenated phthalanils was due to the further effect of amines upon them.

The Action of Aniline upon Halogen in the Nucleus.

After an amine has reacted completely with the anhydride ring of the halogenated phthalic molecule it shows a tendency to attack the halogen. Long boiling with aniline converts tetrachlorophthalanil, for example, into a tarry mixture from which a monoanilino and a dianilino product were isolated. The structure



seems a probable one for the monoanilino anil but it is also possible that the anilino group takes the 4-position. An attempt to establish the structure of the dianilino product will be described in the seventh paper of this series. Attempting to prepare some dianilino-dichlorophthalanils from diiododichlorophthalanils of known structure, we have so far succeeded in obtaining only one, the 3,6-dianilino-4,5-dichloro derivative. This was found to be different from the product from tetrachlorophthalanil, but

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[1] This Journal, **32**, 1319 (1910).

since we were unable to purify it too much reliance should not be placed on the difference.

The monoanilino product from tetrachlorophthalanil is orange, the dianilino derivative red. This new class of compounds has such possibilities from the standpoint of color that we have continued its investigation. The next paper of this series will be devoted to the anilino products from some dichlorophthalanils. These give better yields and a better opportunity for determination of structure.

Dimorphism in the Anils.

Tetrachlorophthal-*p*-tolil was found to exhibit dimorphism in that it was obtained both as colorless, hexagonal leaflets and as long, hair-like, yellow needles. Either form can be converted easily into the other without change in weight, and so readily that actual structural isomerism is improbable. The colorless form is stable at ordinary temperatures, does not combine with solvent of crystallization and melts at 207° (corr.). The yellow form is unstable except above 118°, combines with many solvents, and melts at 214–214.5° (corr.).

Dimorphic forms of anils have been reported by Chattaway[1] who recorded a few similar cases but without giving different melting points for the two forms or any tendency of one to add solvent of crystallization. The unstable form must possess more free energy below its transition point than the colorless modification. The corresponding greater unsaturation in its valency fields is evidenced by the tendency to form coördination products by conjugation with solvents such as benzene *m*-xylene, nitrobenzene and dimethylaniline. For the reason given above this difference in valency fields is not to be attributed to actual isomerism, but to the different intermolecular effect caused by differing crystal structure.

The addition products with solvents do not show a molecular ratio of one to one; our results with different solvents vary from 1 : 3 to 1 : 5. One molecule of dimethylaniline, for example, apparently combines with five molecules of the *p*-tolil. This is so different from its action with tetrachlorophthalic anhydride that the two cases are hardly comparable; both products, however, have a deep red color.

Dimorphism was found to be very common among phthalimide derivatives. The cases of 3,4-dichlorophthalanil, 3-anilino-6-chloro-phthalanil, and 4,5-diiodophthalanil will be considered in the two succeeding papers of this series.

Experimental.

Tetrachlorophthalic Acid.—The tetrachlorophthalic acid used for a part of this work was the commercial product purified by Delbridge's[2] method. We found it necessary, however, to use twice as much sodium hydroxide

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[1] *J. Chem. Soc.*, 109, 89 (1916).

[2] *Am. Chem. J.*, 41, 414 (1909).

as he recommends. The acid was conveniently changed to anhydride by recrystallization from acetic acid.

After the commercial supply had been cut off tetrachlorophthalic anhydride was prepared from phthalic anhydride.[1]

500 g. of phthalic anhydride, 2 kg. of 50% fuming sulfuric acid, and 10 g. of iodine were the proportions we used. The mixture was heated in an oil bath to 70° and a stream of chlorine passed through for about 40 hours. During the first few hours the temperature was increased to about 100°, and there maintained until the last few hours, when it was raised to 180°. The mixture was transferred to a porcelain dish, allowed to cool, and treated slowly with water. The tetrachlorophthalic anhydride, which separated in well-formed crystals, was freed from sulfuric acid by digestion with water at 100°. It melted at 255–256.5° (corr.) without further purification. Delbridge gives 255–257° (corr.) for the pure substance.

Addition Product with Dimethylaniline.—Tetrachlorophthalic anhydride is very soluble in warm dimethylaniline, giving an intensely red solution which deposits large red prisms on cooling. These crystals readily effloresce on exposure to air or on washing with organic solvents, giving off dimethylaniline and leaving the anhydride as a somewhat contaminated light yellow powder.

Exact analysis was prevented by the difficulty of freeing the crystals entirely from mother liquor without efflorescence taking place. A close approximation, however, was not found difficult. Sample No. I was prepared by drying fresh crystals on paper as well as possible without much crushing and then exposing to the air overnight. Six hours at 100° sufficed to drive off the solvent of crystallization. Sample No. II was prepared by leaving fresh crystals 10 days in a desiccator containing tetrachlorophthalic anhydride to absorb excess of solvent.

Subst. (I) 2.9718, (II) 0.2906.
Loss (6 hours at 100°): (I) 0.8900, (II) 0.0844.
Calc. for $C_8O_3Cl_4.C_6H_5N(CH_3)_2$: loss, 29.8%. Found: (I) 30.0, (II) 29.0.

Addition Product with Dimethyl-*p*-toluidine.—Tetrachlorophthalic anhydride combines with dimethyl-*p*-toluidine just as with dimethylaniline, but the product has a deeper, almost purple color. The crystals obtained were contaminated with a small amount of a colorless substance, probably the salt. Sample No. I was prepared by allowing the crystals to stand exposed until a very slight efflorescence was observed. This required 23 hours. The loss was determined as before. Sample No. II was prepared by drying fresh crystals 10 days in a desiccator containing excess anhydride.

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[1] Juvalta, D. R. P. 50,177; *Fortschr. Teerfarb.-fabrik.*, **2**, 93 (1889).

Subst. (I) 0.9520, (II) 0.2475.
Loss (6 hours at 100°): (I) 0.2897, (II) 0.0696.
Calc. for $C_8O_3Cl_4.C_7H_7N(CH_3)_2$: loss, 32.4%. Found: (I) 30.4, (II) 28.1.

Action of Other Tertiary Amines.—Tetrachlorophthalic anhydride gives a red color with diethylamine but crystallizes out unchanged. Pyridine gives no color. Triethylamine gives little or no color.

Action of Secondary Amines.—Monomethylaniline gives a deep red with tetrachlorophthalic anhydride. The anhydride slowly dissolves, the color fades, and disappears. In xylene solution the same fading color is produced. No precipitate is formed. Diphenylamine in xylene solution gives an orange color.

Action of Primary Amines.—α-Naphthylamine in xylene solution gives a deep red color and a white precipitate when added to a xylene solution of tetrachlorophthalic anhydride. The color persists for some hours in the cold, but disappears on long standing or warming. β-Naphthylamine in xylene solution gives an orange-red color, which quickly fades leaving a white, gelatinous precipitate. Aniline gives a transient yellow color, immediately forming white aniline tetrachlorophthalanilate.

Tetrachlorophthalimide.—Graebe[1] prepared this substance by the action of ammonia gas on the melted anhydride and stated that it melts "near the boiling point of mercury." We preferred the following method: Ten grams of powdered tetrachlorophthalic anhydride were dissolved by warming with 100 g. of formamide. Soon the imide began to precipitate, and after five minutes' gentle heating it was filtered off without cooling, and washed with alcohol. Ten grams of anhydride were added to the filtrate and the process repeated. The combined yield, about 90% of theoretical, was 18 g. of colorless blades, which melted at 338–339° (corr.) after recrystallization from acetic acid. Very slow heating gives a slightly lower melting point. This forms an exceptionally good method for making imides of halogenated phthalic anhydrides.

The imide was analyzed for chlorine by the lime combustion method.

Subst. (I) 0.2615, (II) 0.4308; cc. 0.1 *N* $AgNO_3$, (I) 36.82, (II) 60.46.
Calc. for $C_8HO_2NCl_4$: Cl, 49.79. Found: (I) 49.93, (II) 49.77.

One gram of the imide dissolves in 100 cc. of boiling acetic acid. It is more soluble in nitrobenzene and readily dissolved by pyridine. The alkali salts are colorless and insoluble in water.

Action of Formamide on Tetrachlorophthalimide.—The light yellow-colored formamide filtrate from the preparation of tetrachlorophthalimide was treated with 10 g. more of anhydride, then heated 45 minutes to dissolve the imide formed, and finally boiled briskly for 10 minutes. The solution, which was deep red with a strong green fluorescence, gave

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[1] *Ann.*, **238**, 332 (1887).

no deposit on standing overnight, showing that the imide had practically disappeared. About 5 g. of an impure green product were obtained by boiling with water, cooling and filtering. This melted at about 313° (corr.) after two recrystallizations from alcohol.

Subst. 0.0851; cc. 0.1 *N* $AgNO_3$, 11.16.
Calc. for $C_8HO_2NCl_4$: Cl, 49.79.
Calc. for $C_8H_3O_2N_2Cl_3$: Cl, 40.07. Found: 45.98.

The chlorine analysis indicates that some of the chlorine had been removed from the imide, but not sufficient to represent the replacement of one atom by an amino group. A Kjeldahl analysis was made.

Subst. 0.0812; cc. 0.1 *N* HCl, 3.61.
Calc. for $C_8HO_2NCl_4$: N, 4.92.
Calc. for $C_8H_3O_2N_2Cl_3$: N, 10.55. Found: 6.23.

This analysis indicates that the chlorine missing in the previous analysis has been replaced by the amino group. Further experiments were made, including the use of acetamide which seems to act like formamide except more slowly, but no pure product was obtained.

Aniline Tetrachlorophthalanilate.—Six grams of tetrachlorophthalic anhydride were dissolved in hot benzene and a solution of two grams of aniline in benzene slowly added. The first addition gave a yellow color quickly followed by a white precipitate, but precipitation was still incomplete after addition of all the aniline. Since slightly over one molecular equivalent had been added the precipitate must have contained more than one mol of amine per mol of anhydride. A further addition of 2 g. of aniline in benzene completed the precipitation. The product was filtered off and recrystallized from alcohol. The mixture was boiled with benzene to remove some anil formed in the reaction.

Analysis:[1]

Subst. (I) 0.2520, (II) 0.1879; cc. 0.1 *N* HCl, (I) 9.90, (II) 7.50.
Calc. for $C_{20}H_{14}O_3N_2Cl_4$: N, 5.94. Found: (I) 5.50, (II) 5.59.

Since the benzene had apparently removed a little aniline from the salt, it was boiled with benzene containing a small amount of aniline.

Subst. (I) 0.1490, (II) 0.1639; cc. 0.1 *N* HCl, (I) 6.26, (II) 6.91.
Calc. for $C_{20}H_{14}O_3N_2Cl_4$: N, 5.94. Found: (I) 5.89, (II) 5.91.

Subst. (I) 0.2322, (II) 0.2871; cc. 0.1 *N* $AgNO_3$, (I) 19.68, (II) 24.36.
Calc. for $C_{20}H_{14}O_3N_2Cl_4$: Cl, 30.05. Found: (I) 30.05, (II) 30.09.

Aniline tetrachlorophthalanilate dissolves in about ten parts of boiling alcohol from which it separates on cooling in a white crystalline powder mixed with leaflets of the anil. It is insoluble in benzene, but very

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[1] Kjeldahl determinations of nitrogen required the modifications suggested in *Z. anal. Chem.*, 31, 525 (1892); Conn. Agr. Exp. Sta., *Rep.* 190 (1898) and long-continued boiling, otherwise the results were invariably low. This method was used in all the nitrogen analyses reported in this paper.

soluble in acetic acid, quickly forming the anil. The purified salt melted at 271–273° (corr.) on rapid heating.

Tetrachlorophthalanil.—This substance was prepared by Graebe's[1] method, by the method of Tingle and Bates,[2] and also by heating the anhydride in aniline. None of these methods, however, was as satisfactory as adding aniline to a boiling solution of the anhydride in acetic acid. The resulting product is nearly pure, and forms leaflets of rhombic outline. These are almost colorless, but have, especially when the crystals are large, a pale yellow cast not removed by several recrystallizations.

Subst. (I) 0.1566, (II) 0.1409; cc. 0.1 *N* $AgNO_3$, (I) 17.33, (II) 15.59.
Calc. for $C_{14}H_5O_2NCl_4$: Cl, 39.30. Found: (I) 39.24, (II) 39.24.
Subst. (I) 0.3113, (II) 0.2607; cc. 0.1 *N* HCl, (I) 8.34, (II) 7.21.
Calc. for $C_{14}H_5O_2NCl_4$: N, 3.88. Found: (I) 3.75, (II) 3.87.

Tetrachlorophthalanil was found to melt at 274–275° (corr.). (Graebe and Buenzod record 268–269°.) It is soluble in ethyl acetate, acetone, benzene and acetic acid, very slightly in ether or alcohol, insoluble in petroleum ether.

No addition products of the anil with solvents were isolated. It gives a deep red color with dimethylaniline or dimethyl-*p*-toluidine, and a lighter red with dimethyl-*o*-toluidine, but crystallizes from these solvents in the original colorless form.

3-Anilino-4,5,6-trichlorophthalanil (4,3,5,6,?). — One part of tetrachlorophthalic anhydride was boiled gently for three hours in four parts of aniline. It was found advisable to avoid oxidation of the aniline by using an inactive atmosphere such as natural gas. Acetic acid was added to the product and the mixture poured into dilute hydrochloric acid. The precipitate was filtered off and recrystallized, using boneblack, once from acetic acid and several times from alcohol. Orange blades were obtained melting at 179.5–180.5° (corr.).

Subst. (I) 0.2869, (II) 0.2612; cc. 0.1 *N* $AgNO_3$, (I) 20.56, (II) 18.82.
Calc. for $C_{20}H_{11}O_2N_2Cl_3$: Cl, 25.48. Found: (I) 25.41, (II) 25.55.
Subst. (I) 0.2294, (II) 0.2396; cc. 0.1 *N* HCl, (I) 11.02, (II) 11.50.
Calc. for $C_{20}H_{11}O_2N_2Cl_3$: N, 6.71. Found: (I) 6.73, (II) 6.72.

One gram of the anilino anil dissolves in 5 cc. of boiling acetic acid or in 100 cc. of boiling alcohol.

Dianilino-dichlorophthalanil.—A small quantity of this substance was isolated from the mother liquors of the monoanilino product. More was obtained by increasing the time of boiling with aniline to 24 hours. The product, after purification as described for the monoanilino anil, was a very small yield of bright scarlet blades melting at 182.5–183.5° (corr.). It is somewhat more soluble than the monoanilino derivative.

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[1] *Ber.*, **32**, 1994 (1899).

[2] THIS JOURNAL, **32**, 1325 (1910).

Subst. (I) 0.1463, (II) 0.0969, (III) 0.1571; cc. 0.1 *N* $AgNO_3$, (I) 6.31, (II) 4.18, (III) 6.72.

Calc. for $C_{26}H_{17}O_2N_3Cl_2$: Cl, 14.96. Found: (I) 15.28, (II) 15.30, (III) 15.17.

Subst. 0.1835; cc. 0.1 *N* HCl, 11.12.

Calc. for $C_{26}H_{17}O_2N_3Cl_2$: N, 8.87. Found: 8.49.

Tetrachlorophthal-*o*-tolil.—Ten grams of the anhydride were boiled with 50 cc. of acetic acid, 20 g. of freshly distilled *o*-toluidine added, and the boiling continued a few seconds. The product was filtered off after cooling and recrystallized twice from acetic acid using boneblack. About 8 g. of colorless rhombic leaflets were thus obtained, having a melting point of 232–236.5° (corr.) unchanged by recrystallization.

Subst. (I) 0.2093, (II) 0.2164; cc. 0.1 *N* $AgNO_3$, (I) 22.46, (II) 23.26.

Calc. for $C_{15}H_7O_2NCl_4$: Cl, 37.83. Found: (I) 38.05, (II) 38.11.

The *o*-tolil has about the same solubilities as the anil. One gram dissolves in 40 cc. of boiling acetic acid.

Tetrachlorophthal-*m*-tolil.—Ten grams of powdered anhydride were boiled with 30 cc. of acetic acid and 20 g. of freshly distilled *m*-toluidine added. The procedure was continued as with the *o*-tolil, resulting in 8 g. of colorless rhombic leaflets of constant melting point 245.5–246.5° (corr.). One gram dissolves in 80 cc. of boiling acetic acid.

Subst. (I) 0.3122, (II) 0.2727; cc. 0.1 *N* $AgNO_3$, (I) 33.41, (II) 29.23.

Calc. for $C_{15}H_7O_2NCl_4$: Cl, 37.83. Found: (I) 37.95, (II) 38.01.

Tetrachlorophthal-*p*-tolil.—Twenty grams of tetrachlorophthalic anhydride were dissolved in 250 cc. of boiling acetic acid, 20 g. of recrystallized *p*-toluidine acetate added, and the boiling continued a few minutes. The product was filtered off after cooling and recrystallized from acetic acid.

Subst. (I) 0.1815, (II) 0.1483; cc. 0.1 *N* $AgNO_3$, (I) 19.39, (II) 15.82.

Calc. for $C_{15}H_7O_2NCl_4$: Cl, 37.83. Found: (I) 37.88, (II) 37.83.

Subst. (I) 0.2876, (II) 0.3176; cc. 0.1 *N* HCl, (I) 7.73, (II) 8.47.

Calc. for $C_{15}H_7O_2NCl_4$: N, 3.74. Found: (I) 3.77, (II) 3.74.

Dimorphism.

Tetrachlorophthal-*p*-tolil usually crystallizes from acetic acid or alcohol in colorless hexagonal leaflets. This modification is stable at ordinary temperatures and even at the boiling point of acetic acid, but when heated to 207° (corr.), it softens and turns yellow, giving a second modification, which is stable at that temperature, and melts at 214–214.5° (corr.). The melting point of the colorless modification was determined by dipping successive samples contained in capillary tubes into the melting point bath at various known temperatures. At 206° (corr.) no change could be observed. At 207° the sample melted to a cloudy liquid, immediately turning yellow. At 210° a fresh sample melted to a clear liquid, which did not immediately solidify, but when removed from the bath immediately changed to a yellow solid that did not melt on returning to the bath at 210°.

It is evident that tetrachlorophthal-*p*-tolil has a transition point between 118° and 207°. The rate of transformation is so slow even at high temperatures, that the colorless form may be heated slowly to its melting point without changing to the yellow form. Just as it begins to melt, at 207° (corr.), transformation rapidly sets in, and the fact that the yellow form is much more stable at this temperature is shown by the difference of 7° between the melting points.

The yellow form of tetrachlorophthal-*p*-tolil may sometimes be obtained by dissolving the leaflets in acetic acid or alcohol and allowing the warm solution to stand undisturbed. Seeding with the yellow form insures the result. Long hair-like needles appear which spread through the solution so much faster than the more stable leaflets that almost the entire quantity may be obtained in the unstable modification. This may be kept a few days in the dry condition, but in contact with solvent soon changes to colorless leaflets. The transformation takes place without change in weight, showing that no solvent of crystallization is involved.

Addition Products with Solvents.

Tetrachlorophthal-*p*-tolil forms colored addition products with solvents such as benzene, xylene, nitrobenzene, dimethylaniline, etc. The colorless modification, however, does not appear to react with the vapors of these substances. A sample of this form was powdered and exposed to air nearly saturated with benzene vapor for several days. The powder did not increase in weight or change color even after a small spot was moistened with benzene. The spot remained yellow, but did not spread, which shows the inability of the colorless modification to take up benzene. In contact with liquid benzene, however, it immediately forms the yellow addition product. In fact, none of the above-named solvents have been observed to deposit the *p*-tolil except as an addition product (cf. acetic acid and alcohol).

The action of dimethylaniline vapor is prettily shown by melting some *p*-tolil on a watch-glass and cooling in such a manner that part remains yellow and part becomes white, seeding with the colorless form if necessary. On exposure to the vapor of dimethylaniline in a desiccator, the yellow part quickly becomes a deep red while the white remains unaffected.

Addition Product with Benzene.—The *p*-tolil separates from benzene solution in long hair-like yellow crystals. If not broken up these are fairly stable in air. In the first determination the sample taken was some of the pure *p*-tolil which was then left in a desiccator with benzene. Here the air was saturated with benzene vapor, so that the sample became moist and formed the addition product. After several hours the excess benzene was allowed to evaporate in the open air, requiring about 8 hours for practically constant weight. The percentage was calculated not on the weight of sample but on the weight of addition product, to correspond with the following determinations: Sample No. 2 was composed of well-formed crystals from benzene, air-dried to constant weight (12 hours). The sample rapidly lost weight on being ground by a small pestle, included in the tare, and came to constant weight in 3 hours at 100°. Sample No. 3 had been kept six months, and showed decomposition only by a slight dullness of the crystals. The benzene was removed by adding alcohol and heating to 100°, repeating to constant weight. Sample No. 4 was prepared by allowing fresh crystals to stand in a desiccator containing some yellow *p*-tolil to absorb the excess benzene. The benzene of crystallization was removed from this and the following samples by adding ethyl acetate and heating to 100°. This was found to be the quickest method. Sample No. 5 was dried 30 minutes in air and 15 minutes *in vacuo*. Samples No. 6 and No. 7 were dried 5 minutes in air and 10 minutes *in vacuo*.

Subst. (I) 0.7173, (II) 0.4926, (III) 0.5964, (IV) 0.5466, (V) 1.0337, (VI) 0.8319, (VII) 1.0591. Loss: (I) 0.0423, (gain): (II) 0.0315, (III) 0.0326, (IV) 0.0310, (V) 0.0561, (VI) 0.0472, (VII) 0.0602.

Calc. for $(C_{15}H_7O_2NCl_4)_3.C_6H_6$: loss, 6.49%. For $(C_{15}H_7O_2NCl_4)_4.C_6H_6$: loss, 4.95%. Found: (I) 5.57, (II) 6.39, (III) 5.47, (IV) 5.67, (V) 5.43, (VI) 5.67, (VII) 5.68.

Apparently the ratio of *p*-tolil molecules to benzene molecules was between 3 and 4.

Addition Product with *m*-Xylene.—Sample No. I was crystallized from *m*-xylene and exposed to the air 12 hours. Sample No. II was dried in air 1 hour after which it lost practically no weight during 15 minutes *in vacuo*. Both samples were decomposed by ethyl acetate and heated to 100°.

Subst. (I) 0.4167, (II) 1.0001; loss, (I) 0.0263, (II) 0.0633.

Calc. for $(C_{15}H_7O_2NCl_4)_4.C_8H_{10}$: loss, 6.61. Found: (I) 6.31, (II) 6.33.

Addition Product with Nitrobenzene.—Sample No. I was crystallized from nitrobenzene, washed rapidly with petroleum ether, and exposed 30 minutes to the air, after which it lost no more weight *in vacuo* during 15 minutes. The solvent of crystallization was driven off by adding acetic acid and heating to 110°. A repetition of this treatment caused no further loss in weight. Sample No. II was treated in practically the same manner.

Subst. (I) 0.7423, (II) 1.0922; loss, (I) 0.0539, (II) 0.0851.

Calc. for $(C_{15}H_7O_2NCl_4)_4.C_6H_5O_2N$: loss, 7.58. Found: (I) 7.26, (II) 7.79.

The product is yellow like that from benzene, but has more the appearance of blades.

Addition Product with Dimethylaniline.—Tetrachlorophthal-*p*-tolil is quite soluble in dimethylaniline and crystallizes out in scarlet needles.

The fresh crystals were washed with petroleum ether. Almost no loss in weight was observed when the first sample was dried in air one hour, and the second *in vacuo* ten minutes. Ethyl acetate was employed as before to remove the solvent of crystallization.

Subst. (I) 0.7486, (II) 1.3563; loss, (I) 0.0498, (II) 0.0880.
Calc. for $(C_{15}H_7O_2NCl_4)_4.C_8H_9N$: loss, 7.47.
Calc. for $(C_{15}H_7O_2NCl_4)_5.C_8H_9N$: loss, 6.07. Found: (I) 6.65, (II) 6.49.

The observed loss represents a molecular ratio of nearly 5 to 1.

Tetrachlorophthal-*o*-nitroanil.—Twenty grams of the anhydride and 10 g. of *o*-nitraniline were boiled one-half hour in 200 cc. of acetic acid. The crystals were filtered off on cooling and the filtrate evaporated to one-third to recover more of the product. The total yield, about 70% of the theoretical, was 20 g. of colorless leaflets. These, after crystallization from benzene using boneblack, showed a melting point of 272–273° (corr.) unchanged by recrystallization from xylene.

Subst. (I) 0.2475, (II) 0.1432; cc. 0.1 *N* $AgNO_3$, (I) 24.66, (II) 14.26.
Calc. for $C_{14}H_4O_4N_2Cl_4$: Cl, 34.94. Found: (I) 35.33, (II) 35.31.

One gram of the *o*-nitroanil dissolves in 40 cc. of boiling benzene or 12 cc. of boiling xylene. It is quite soluble in acetic acid, slightly in ethyl acetate, almost insoluble in alcohol.

Tetrachlorophthal-*m*-nitroanil.—Twenty grams of the anhydride in 600 cc. of acetic acid were boiled one-half hour with 10 g. of *m*-nitraniline. The product after cooling was filtered off and recrystallized from acetic acid and xylene, giving almost colorless blades of melting point 300–301.5° (corr.) unchanged by recrystallization from xylene. The final product weighed 14 g.

Subst. (I) 0.2459, (II) 0.1752; cc. 0.1 *N* $AgNO_3$, (I) 24.37, (II) 17.44.
Calc. for $C_{14}H_4O_4N_2Cl_4$: Cl, 34.94. Found: (I) 35.14, (II) 35.30.

One gram of the *m*-nitroanil dissolves in 150 cc. of boiling acetic acid or 50 cc. boiling xylene.

Tetrachlorophthal-*p*-nitroanil.—Fifteen grams of *p*-nitraniline were added to a boiling solution of 30 g. of tetrachlorophthalic anhydride in 400 cc. of acetic acid. The mixture was boiled 15 minutes and then heated an hour in a water bath. The fine, colorless needles obtained were recrystallized from benzene using boneblack. The product then had a melting point of 292–297° (corr.), unchanged by repeating the treatment. One gram of the substance dissolves in 100 cc. of boiling benzene.

Subst. (I) 0.1545, (II) 0.2035; cc. 0.1 *N* $AgNO_3$, (I) 15.27, (II) 20.09.
Calc. for $C_{14}H_4O_4N_2Cl_4$: Cl, 34.94. Found: (I) 35.05, (II) 35.01.

Tetrachlorophthal-*p*-hydroxyanil. — Twenty grams of tetrachlorophthalic acid were dissolved in 100 cc. of acetic acid and boiled to form the anhydride. Ten grams of *p*-aminophenol were then added and the boiling continued 5 minutes. Twenty-two grams, an 89% yield, of bright yellow needles were filtered off after cooling. On recrystallization from acetic acid the melting point was 305–307° (corr.) unchanged by recrystallization from xylene.

Subst. (I) 0.2142, (II) 0.2970; cc. 0.1 *N* $AgNO_3$, (I) 22.73, (II) 31.37.
Calc. for $C_{14}H_5O_3NCl_4$: Cl, 37.63. Found: (I) 37.63, (II) 37.45.

One gram of the *p*-hydroxyanil dissolves in 100 cc. of boiling acetic acid or about 120 cc. of boiling xylene.

Tetrachlorophthal-*p*-acetylaminoanil.—*p*-Amino acetanilide was prepared by reducing the nitro compound following Nietzki's directions.[1]

Twenty grams of tetrachlorophthalic acid were boiled in 800 cc. of acetic acid, forming the anhydride. A solution of 10 g. of *p*-amino acetanilide in 200 cc. of acetic acid was added and the boiling continued 10 minutes. Twenty-five grams of product, an 86% yield, were filtered off after cooling. This was recrystallized twice from acetic acid, using boneblack.

Subst. (I) 0.2165, (II) 0.2181; cc. 0.1 *N* $AgNO_3$, (I) 20.79, (II) 20.84.
Calc. for $C_{16}H_8O_3N_2Cl_4$: Cl, 33.93. Found: (I) 34.05, (II) 33.88.

The *p*-acetylaminoanil melts with decomposition at about 339° (corr.). One gram dissolves in 100 cc. of boiling acetic acid, from which it crystallizes in a mixture of pale yellow warts and very small, colorless needles. It is readily dissolved by pyridine.

Tetraiodophthalimide.—Fifty grams of tetraiodophthalic anhydride[2] in 150 cc. of nitrobenzene were treated with 50 g. of formamide and boiled one-half hour. The yield was 30 g., about 60%, a part of which was recrystallized twice from nitrobenzene.

Subst. (I) 0.5222, (II) 0.3366; cc. 0.1 *N* $AgNO_3$, (I) 32.40, (II) 20.97.
Calc. for $C_8HO_2NI_4$: I, 78.02. Found: (I) 78.57, (II) 79.07.

One gram of the imide dissolves in 70 cc. of boiling nitrobenzene, from which it crystallizes in fine, yellow needles melting at about 370–380° (corr.) with decomposition. It is moderately soluble in aniline, phenol and pyridine but not in the ordinary solvents.

Tetraiodophthalanil.—Twenty grams of the anhydride were dissolved in 100 cc. of boiling nitrobenzene and 10 cc. of aniline added. A yield of 18 g., 82%, was obtained. This was recrystallized twice from xylene and twice from nitrobenzene. Its melting point of 314–315° (corr.) was unchanged by the last crystallization.

Subst. (I) 0.3619, (II) 0.2469; cc. 0.1 *N* $AgNO_3$, (I) 20.08, (II) 13.80.
Calc. for $C_{14}H_5O_2NI_4$: I, 69.85. Found: (I) 70.42, (II) 70.94.

One gram of the anil dissolves in 8 cc. of boiling nitrobenzene from which it separates in yellow blades. It is about one-half as soluble in xylene, and nearly insoluble in acetic acid.

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[1] *Ber.*, 17, 343 (1884); 33, 191 (1900).

[2] Detailed directions for preparing the tetraiodophthalic anhydride will appear in a later article by Pratt and Shupp on phenoltetraiodophthalein.

Tetraiodophthal-*o*-tolil.—Thirty grams of the anhydride were dissolved in 80 cc. of boiling nitrobenzene and 7 g. of *o*-toluidine added. The mixture was boiled a minute and allowed to cool. A yield of 27 g., 79%, was obtained. This was recrystallized from xylene using boneblack, having then a melting point of 314–315° (corr.) unchanged by recrystallization.

Subst. (I) 0.3687, (II) 0.3303; cc. 0. 1 *N* $AgNO_3$, (I) 20.21, (II) 18.10.
Calc. for $C_{15}H_7O_2NI_4$: I, 68.53. Found: (I) 69.57, (II) 69.55.

One gram of the *o*-tolil is dissolved by 30 cc. of boiling xylene, from which it separates in minute, yellow crystals.

Tetraiodophthal-*m*-tolil.—The preparation and yield of the *m*-tolil were the same as given for the *o*-tolil. The product melted at 325–326° (corr.) after three recrystallizations from xylene using boneblack. One gram dissolves in 30 cc. boiling xylene and crystallizes in fine, yellow blades.

Subst. (I) 0.2877, (II) 0.2678; cc. 0.1 *N* $AgNO_3$, (I) 15.66, (II) 14.56.
Calc. for $C_{15}H_7O_2NI_4$: I, 68.53. Found: (I) 69.08, (II) 69.01.

Tetraiodophthal-*p*-tolil.—Fifty grams of the anhydride were dissolved in 200 cc. of boiling nitrobenzene, 15 g. of *p*-toluidine added, and the boiling continued one minute. The product melted at 317–318° (corr.) after two recrystallizations from xylene using boneblack. One gram of the *p*-tolil is dissolved by 40 cc. of boiling xylene. It crystallizes in yellow blades.

Subst. (I) 0.2320, (II) 0.3743; cc. 0.1 *N* $AgNO_3$, (I) 12.78, (II) 20.39.
Calc. for $C_{15}H_7O_2NI_4$: I, 68.53. Found: (I) 69.91, (II) 69.14.

Tetraiodophthal-*m*-nitroanil.—This was prepared like the *o*-tolil. The yield was 29 g., 82%. A part of this was recrystallized twice from acetic acid, after which its melting point of 318–319° (corr.) was unchanged by another recrystallization.

Subst. (I) 0.2433, (II) 0.2504; cc. 0.1 *N* $AgNO_3$, (I) 12.69, (II) 13.10.
Calc. for $C_{14}H_4O_4N_2I_4$: I, 65.78. Found: (I) 66.20, (II) 65.95.

The *m*-nitroanil is soluble in about 1000 parts of boiling acetic acid from which it crystallizes in fine, yellow, matted needles. It is much more soluble in xylene and nitrobenzene but does not crystallize well from these solvents.

Under the conditions mentioned above, even on boiling considerably longer, *p*-nitraniline does not appear to react with tetraiodophthalic anhydride. The latter crystallizes out unchanged. *o*-Nitraniline acts only very slowly.

Tetraiodophthal-*p*-hydroxyanil.—This substance is decomposed by boiling nitrobenzene, so the following method was adopted: A boiling solution of 12 g. *p*-aminophenol in 1200 cc. of xylene was added to a boiling solution of 30 g. of the anhydride in 800 cc. of xylene. The purplish gray precipitate was filtered off, added to a liter of boiling acetic acid, boiled one minute, cooled and filtered. A portion melted at

330–336° (corr.) (with decomposition), after recrystallization from about 4000 parts of acetic acid. It crystallizes in very fine, yellow needles almost insoluble in xylene, excessively soluble in pyridine.

Subst. (I) 0.2837, (II) 0.5972; cc. 0.1 *N* $AgNO_3$, (I) 15.14, (II) 31.94.
Calc. for $C_{14}H_5O_3NI_4$: I 66.79. Found: (I) 67.73, (II) 67.88.

Tetraiodophthal-*p*-acetylaminoanil.—Fifteen grams of *p*-aminoacetanilide were added to a boiling solution of 50 g. of the anhydride in 200 cc. of nitrobenzene. A part of the product was crystallized from nitrobenzene in minute, yellow blades of melting point 339° (corr.) (with decomposition), unchanged by a recrystallization from nitrobenzene.

Subst. (I) 0.4612, (II) 0.4873; cc. 0.1 *N* $AgNO_3$, (I) 22.79, (II) 24.19.
Calc. for $C_{16}H_8O_3N_2I_4$: I 64.77. Found: (I) 62.72, (II) 63.01.

The product is practically insoluble in xylene and acetic acid, somewhat soluble in phenol and pyridine. One gram dissolves in 400 cc. of boiling nitrobenzene.

Summary.

(1) The systematic study of phthalic acid derivatives from the standpoint of constitution and color has been continued by the preparation of a large number of derivatives of tetrachloro- and tetraiodophthalimides. New methods have been used for the preparation of these compounds which are improvements upon methods previously used for similar preparations.

(2) A study of the action of various amines on nuclear substituted phthalic anhydrides indicates that the first stage of this type of reaction is a molecular addition involving secondary valency forces only, and often resulting in the production of a deep red color. Tertiary amines show no further action on the anhydride ring; primary and secondary amines rapidly break it, forming the colorless amic acid or its salts.

(3) A new type of phthalic acid derivative has been prepared by replacing chlorine in the nucleus by anilino groups.

(4) The dimorphic modifications of tetrachlorophthal-*p*-tolil show a difference in color, melting point, and ability to combine with solvents.

(5) The spectroscopic study of halogenated phthalimide derivatives will be reported in a later paper.

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PHTHALIC ACID DERIVATIVES; CONSTITUTION AND COLOR, VI. THE ACTION OF AMINES UPON DICHLOROPHTHALIC ANHYDRIDES.

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The action of amines on halogenated phthalimides and their derivatives first came to the authors' attention in connection with preparing tetra-