which could not occur in precisely the same way with a different substance unless the coincidence was due to some as yet unrecognized general relation, and not to accident.

CHICAGO, December 20, 1909.

THE CONDENSATION PRODUCTS OF MELLITIC ACID WITH META-AMINO PHENOL AND THEIR BEARING ON THE RELATIONSHIP OF COLOR AND FLUORESCENCE TO CONSTITUTION.

BY OSWALD SILBERRAD AND CHARLES SMART ROY.

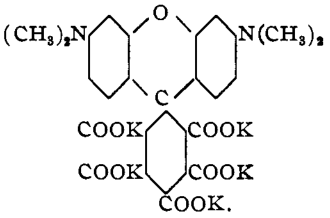
Received November 27, 1909.

In a previous paper by one of the authors on the condensation products of mellitic[1] and pyromellitic acids with resorcinol,[2] much evidence was brought to show that color and fluorescence are not necessarily dependent on quinoidal structure.

The present work deals with the corresponding rhodamines, and fully confirms the conclusions arrived at in the previous paper. Coupled with, and to some extent interdependent on these results is the possibility of ascribing fluorescence to oscillatory tautomerism. As will be shown below it is illogical and impractical to formulate all the compounds dealt with in this paper on the quinone system, and since they are without exception intensely colored and strongly fluorescent, it becomes evident that a quinoidal grouping is not a necessarily integral part of a colored and fluorescent compound.

The compounds dealt with in this paper may be divided into three groups, namely:

1. *Monoxanthyl Derivatives*, of which tetramethyldiaminoxanthylbenzenepentacarboxylic acid may be taken as typical—formula I represents the potassium salt,



I.

2. *Dixanthyl Derivatives*.—These exist in two modifications according to whether the xanthyl groups are para or meta to one another. They behave as tetrabasic acids:

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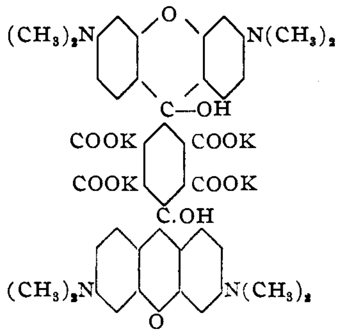
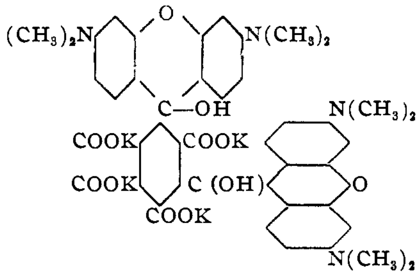
[1] The mellitic acid required for this investigation was manufactured from charcoal according to British Patent No. 24,662, '07.

[2] Silberrad, *J. Chem. Soc.*, **89**, 1789 (1906).



II.



III.

The potassium salt of

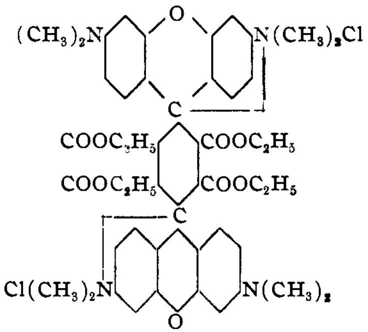
II. Octamethyltetraminodihydroxyparadixanthylbenzenetetracarboxylic acid

and of

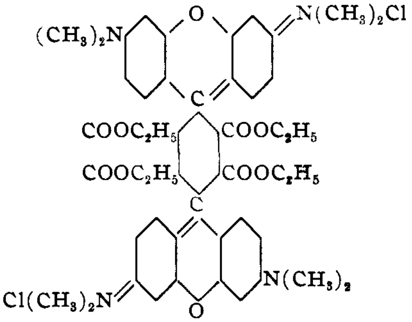
III. Octamethyltetraminodihydroxymetadixanthylbenzenetetracarboxylic acid.

3. *Trixanthyl Derivatives*, of which hydrated dodecamethylhexaminotrihydroxysymtrixanthylbenzenetricarboxylactone may be regarded as typical (formula VI). This is a well-defined base which gives rise to a readily soluble hydrochloride.

All these compounds form anisolines which may with equal readiness be formulated either as carbinol (IV) or quinone derivatives (V).



IV.



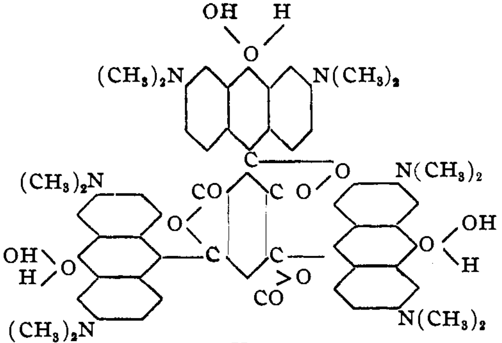
V.

Octamethyltetraminodihydroxyparadixanthylbenzenetetracarboxylic ethyl ester dichloride.

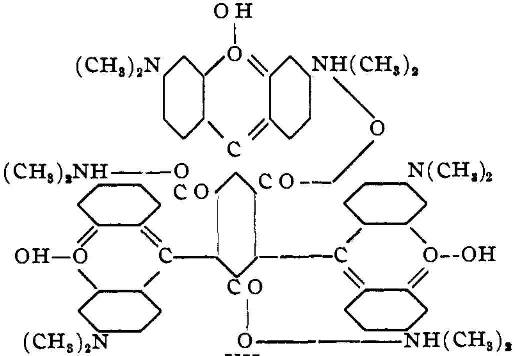
Of the two formulas, the balance of evidence is clearly in favor of a non-quinoidal structure, for there is no reason for assuming the anisolines to differ from the parent acids, the constitutions of which are fairly definitely settled below.

Constitution of the Rhodamines of Mellitic Acid.—In dealing with this subject it will be found simplest to consider the trixanthyl derivatives in the first place.

Hydrated dodecamethylhexaminotrihydroxytrixanthylbenzenetricarboxylactone may be regarded as typical. Of the many configurations it is possible to suggest on paper, we need seriously consider only two (VI and VII). The others will be found either to represent carboxylic acids, which may be rejected at once as the compound is a strong base, insoluble in caustic potash, or else, less satisfactory modifications of VI and VII.



VI.

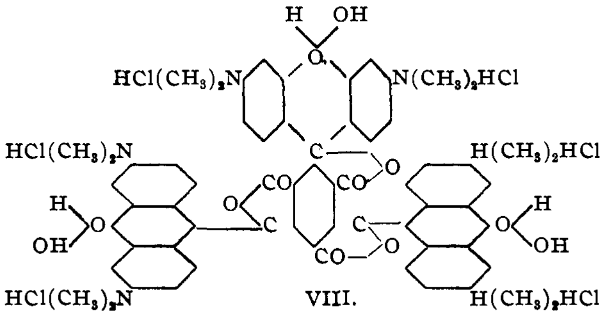


VII.

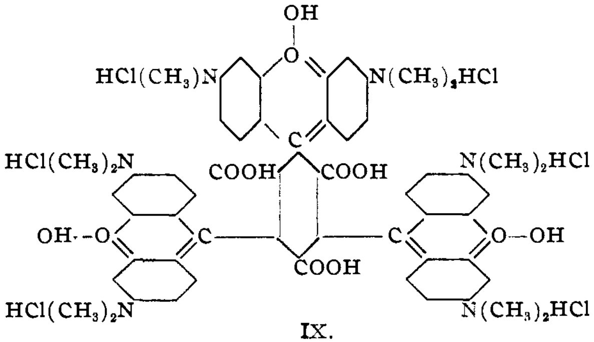
Hydrated dodecamethylhexaminotrihydroxytrixanthylbenzenetricarboxylactone.

The problem thus resolves itself into the question, Is this coloring matter a quinone or a lactone?

The compound is readily soluble in hydrochloric acid with formation of a hexahydrochloride without loss of water: formulating this salt on the two systems they assume the configurations represented by VIII and IX.



VIII.



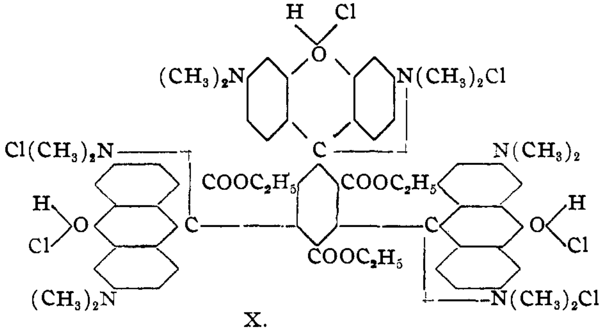
IX.

Hexahydrochloride of hydrated dodecamethylhexaminotrihydroxytrixanthylbenzenetricarboxylactone.

Of these two formula VIII is far the more probable. A free tricarboxylic acid such as represented by formula IX would scarcely form a hexahydrochloride; compare for instance the strongly acid character of the monoxanthyl derivatives which form pentabasic salts (I).

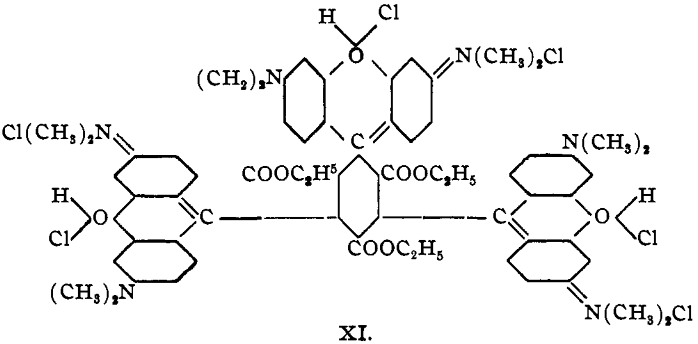
Further, anisolation can only be effected with extreme difficulty, whereas the dixanthyl derivatives, which are proved below to exist as inner salts, form anisolines with great readiness. This property must therefore be regarded as strong evidence in favor of the lactonic formula.

The anisoline chlorides combine with three molecules of hydrochloric acid forming trihydrochlorides of the trichlorides. These compounds can be formulated with equal readiness as lactones or quinones, X, XI.



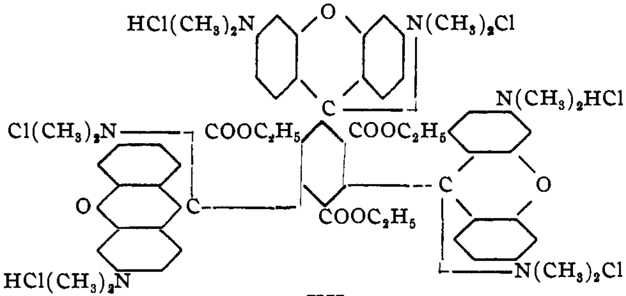
X.

Of the two formulas X is to be preferred, for although in this case the treatment required for anisolation is so drastic that the constitution may well have suffered alteration in the process, yet in the case of the dixanthyl compounds anisolation proceeds with the utmost ease: for this reason also the formula X is preferred to XII as well as to XI for the hydrochloride of the anisoline chloride; it is more strictly parallel with the most probable formula of the dixanthyl anisolines.



XI.

Trihydrochloride of anhydrododecamethylhexaminotrihydroxytrixanthylbenzenetricarboxylic ethyl ester trichloride.



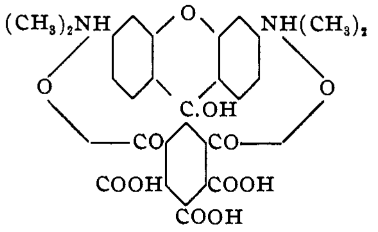
XII.

Hence this again must be regarded as an argument in favor of the lactonic formula.

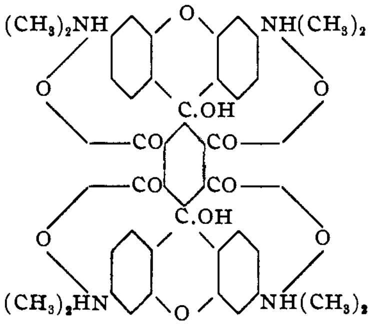
Action of Caustic Potash.—As already stated the compound is insoluble in caustic potash; heated with this reagent it slowly decomposes with evolution of dimethylamine. Such behavior is fairly conclusive evidence for the lactone formula. Indeed the possibility of an inner salt as represented by formula VII–IX withstanding the action of caustic potash in this manner is almost out of the question, especially when it is recollected that inner salts of the dixanthyl derivatives exhibit no such tendency, but dissolve immediately, forming tetrabasic salts (II and III).

It becomes evident therefore that the formula VI represents the constitution of hydrated dodecamethylhexaminotrihydroxytrixanthylbenzenetricarboxylactone, its hexahydrochloride being represented by formula VIII; while formula X most probably represents the constitution of the hydrochloride of the corresponding anisoline chloride.

Constitution of the Mono- and Dixanthyl Derivatives.—On carefully considering the properties of these derivatives in the light of the above arguments, it will become fairly evident that the parent compounds—for instance tetramethyldiaminohydroxyxanthylbenzenepentacarboxylic acid and octamethyltetraminodihydroxyparadixanthylbenzenetetracarboxylic acid—are to be regarded, not as hydrated lactones, but as inner salts, XIII and XIV.



XIII.



XIV.

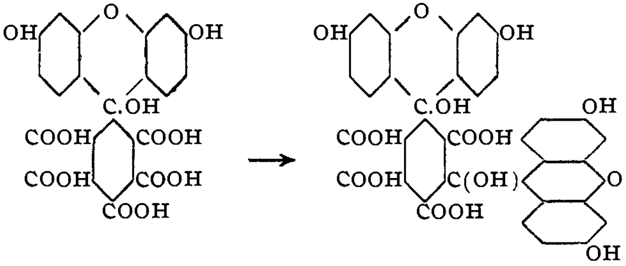
XIII. **Tetramethyldiaminohydroxyxanthylbenzenepentacarboxylic acid.**

XIV. Octamethyltetraminodihydroxyparadixanthylbenzenetetracarboxylic acid.

Anisolation, Action of Alkalies, Etc.—Unlike the trixanthyl derivatives these compounds anisolate with the greatest ease and dissolve at once in potash or ammonia, forming penta- and tetrabasic salts respectively (I and II). They can hardly therefore be regarded as hydrated lactones analogous to the trixanthyl compound which is insoluble in alkalies and readily dissolved in acids, but must be inner salts of true carboxylic acids.

The Formation of Dixanthyl Derivatives affords, perhaps, the most conclusive proof that the parent compounds are true inner salts.

When mellitic acid is heated with four molecular proportions of resorcinol it was shown by one of the authors[1] that the monoxanthyl derivative first formed passed exclusively to the meta compound thus:



When, however, dimethylmetaaminophenol is substituted for resorcinol the para derivative is the sole product:

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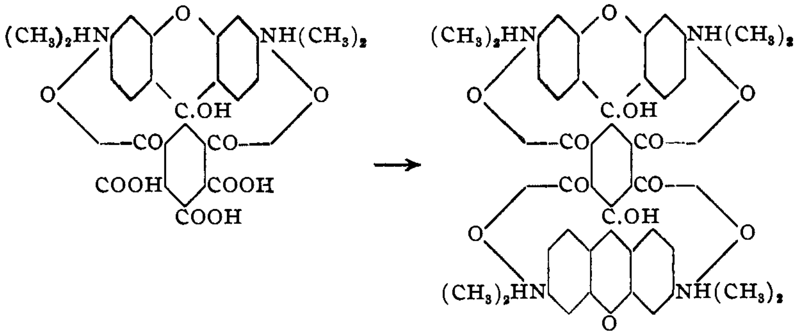
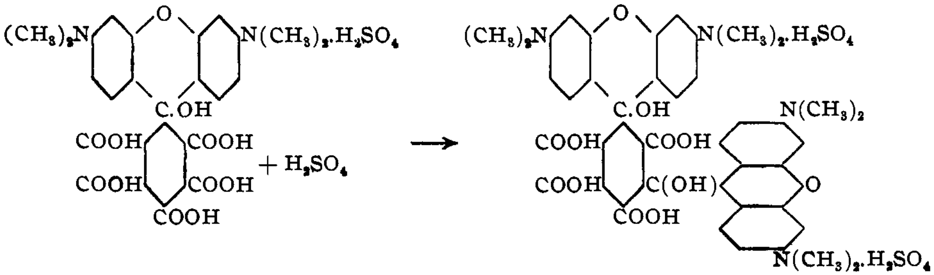
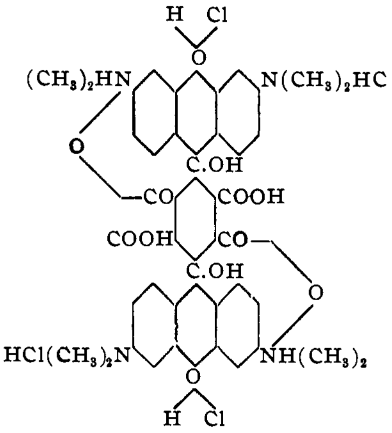
[1] *Loc cit.*



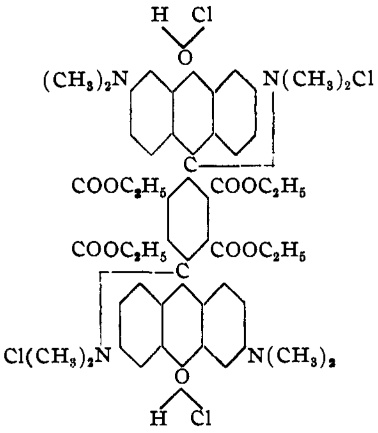
If, however, a small quantity of sulphuric acid be added the inner salt is broken up and the condensation proceeds in the normal manner with formation of the meta compound, the yield being almost theoretical:



From this it may be reasonably concluded that the parent compound exists as an inner salt.



XV.



XVI.

XV. Tetrahydrochloride of octamethyltetraminodihydroxydixanthylbenzenetetracarboxylic acid.

XVI. Dihydrochloride of anhydro-octamethyltetraminodihydroxydixanthylbenzenetetracarboxylic ethyl ester dichloride.

The formation of a tetrahydrochloride of the acid (XV) and also the higher hydrochlorides of the anisolines (XVI) thus becomes a function of the latent property of the pyrone oxygen to become tetravalent.[1]

Lactones Isomeric but Not Tautomeric with Compounds of Quinonoid Structure.—In the previous work by one of the authors already referred to[2] indications were obtained that the lactone ring in these complex phthaleins shows much greater stability than has usually been attributed to it in compounds of this group. The present work has afforded additional evidence of this, for the trixanthyl derivatives, which must, as shown above, be regarded as lactones, are insoluble in alkalies but dissolve as lactones in acids (compare formulas VI and VIII), yielding solutions almost as strongly fluorescent as their corresponding anisolines, which, as has also been shown above, can be formulated with equal readiness either as quinonoid or carbinol derivatives (compare formulas X and XI). This has an important bearing on the theory of fluorescence of the phthalein group, which has generally been attributed to an oscillatory tautomerism between the lactone and quinonoid structures, inasmuch as it shows that no such oscillatory tautomerism can exist or account for the fluorescence of those compounds.

Orientation of the Xanthyl Groups in Aminodixanthyl Derivatives of Mellitic Acid.—As in the previous study of the resorcinol derivatives[2] the problem presented itself as to the relative positions of the xanthyl groups in the dixanthyl derivatives. As before, the method used for differentiating between the meta and the para position was to ascertain whether a third xanthyl group could be introduced.

Two isomeric dixanthyl derivatives are formed when mellitic acid is heated with dimethylmetaaminophenol, according as sulphuric acid is present or not. It is found that the compound prepared in presence of sulphuric acid is capable of taking up a third xanthyl group on heating with excess of dimethylmetaaminophenol, the resultant compound having the formula VI. Hence the dixanthyl compound from which this was prepared must have been a meta derivative, a salt of which is represented by formula III. When, however, mellitic acid and dimethylmetaaminophenol are heated together in absence of sulphuric acid, the product refuses to take up a third xanthyl group and is therefore the para compound, a salt of which is shown in formula II.

Since the para compound still contains two pairs of carboxylic groups ortho to one another, the non-formation of a trixanthyl derivative must be directly attributed to stearic hindrance, of which this thus forms one of the clearest examples on record.

Apart from this property the meta and para isomerides differ in other

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[1] Compare Silberrad, *Proc. Chem. Soc.*, 24, 209 (1908).

[2] *Loc cit.*

respects. Thus the octamethyltetraminodihydroxymetadixanthylbenzenetetracarboxylic acid is more readily anisolated than the para compound. In color also the two isomers show a marked difference.

Conclusions.

1. That, although it is conceivable that certain of these compounds—notably the anisolines—may possess a quinonoid structure, to represent them all as quinones, involves an absolute disregard for their properties and an indiscriminate introduction of the tetravalent oxygen irrespective of whether the presence of this element exercises a basic or acidic influence on the molecule.

2. That it may be regarded as fairly proved that *the presence of quinoidal grouping is not an essential integral part of a colored or fluorescent compound.*

Experimental Part.

In preparing the desired compounds the reacting ingredients were mixed in approximately molecular proportions and heated under widely varying conditions and the product from each experiment roughly purified and analyzed. A large quantity of the material was then prepared by that method which gave rise to the purest product. Final purification was, in most cases, effected by systematic fractional precipitation, samples being taken from time to time and analyzed; the fractionation was then again proceeded with until the analytical results became constant. In the execution of this work over four hundred analyses, the majority being nitrogen estimations, were carried out.

Monoxanthyl Derivatives.

3,6-Diamino-9-hydroxyxanthylbenzene-2-carboxylactone 3,4,5,6-Tetracarboxylic Acid (2 molecules metaaminophenol + 1 molecule mellitic acid), $C_{24}H_{14}O_{11}N_2$.

Preparation.—A finely powdered mixture of 6.84 parts mellitic acid and 4.32 parts metaaminophenol is heated to 160° for 8 hours. The resulting mass is ground and extracted with dilute aqueous caustic potash, the solution obtained filtered and the condensation product precipitated by acidification. The precipitate is filtered off, washed with boiling water, and then with alcohol, until the alcoholic washings are only slightly colored. The residue is purified by repeated fractional precipitation from an alkaline solution by the addition of dilute hydrochloric acid. The precipitate is finally boiled with a large volume of water, filtered and dried on a porous tile at 100°.

Calculated for $C_{24}H_{14}O_{11}N_2$:	N, 5.53.
Found (three different preparations):	N, 5.39, 5.55, 5.38.

Properties.—Light brown, amorphous powder, decomposing without melting above 300°. Insoluble in water, concentrated hydrochloric acid and nearly all organic solvents. Readily soluble in dilute alkalies giving a deep brown solution having a green fluorescence, precipitated from its solution on acidulation. Readily soluble in concentrated sulphuric acid, giving a brownish black solution, from which, on dilution, the acid is again precipitated. Fairly soluble in glacial acetic acid, giving a dark brown solution, from which the compound is precipitated on dilution.

Potassium Salt.—This is prepared by boiling an excess of the acid with dilute caustic potash, filtering off the excess and evaporating the neutral solution thus obtained to dryness. The salt separates out as a dark brown powder with a very dark bronzy metallic reflex; readily soluble in water, giving a deep brown solution.

Silver Salt, $C_{24}H_{10}O_{11}N_2Ag_4$.—This is precipitated as a dark brown powder on adding silver nitrate to a solution of the potassium salt. It is fairly stable to heat and light; is decomposed by dilute nitric and glacial acetic acids, the free acid being precipitated. It dissolves instantly in ammonia.

Calculated for $C_{24}H_{10}O_{11}N_2Ag_4$: Ag, 46.25.
Found (two different preparations): Ag, 46.35, 46.38.

The copper, barium, lead, ferrous and chromium salts form brown precipitates, while the cobalt, mercuric and ferric salts are reddish brown in color. The compound forms no definite hydrochloride.

Tetramethyl-3,6-diamino-9-hydroxyxanthylbenzenepentacarboxylic Acid (2 mols. dimethylmetaaminophenol + 1 mol. mellitic acid), $C_{28}H_{24}O_{12}N_2$.

Preparation.—A finely ground mixture of 6.2 parts mellitic acid and 5 parts dimethylmetaaminophenol is heated to 170° for 8 hours. During heating the mixture gradually solidifies, and on cooling forms a hard bronzy mass. This is powdered, boiled with water and then with alcohol to remove any unchanged acid or phenol. The condensation product is dissolved in dilute aqueous caustic potash, filtered and fractionally precipitated by the addition of hydrochloric acid. This treatment will be found insufficient to remove the impurities present. (The purest fraction from the fifteenth precipitation gave N = 5.17; $C_{28}H_{24}O_{12}N_2$ requires 4.84 per cent.) In order to obtain the pure compound, protracted extraction with alcohol followed by repeated fractional precipitation from its solution in dilute alkali by the addition of acid is necessary. In this way a pure compound is ultimately obtained.

Calculated for $C_{28}H_{24}O_{12}N_2$: C, 57.90; H, 4.17; N, 4.84.
Found (three different preparations): C, 57.68, 57.72; H, 4.24, 4.22; N, 4.94, 4.91, 4.95.

Properties.—Amorphous heliotrope-colored powder which decomposes, without melting, above 300°. Dyes silk and wool a silvery violet-pink. Insoluble in water, alcohol, chloroform, ether and ethyl acetate and only very slightly soluble in aniline and phenol. Slightly soluble in glacial acetic acid from which solution it is precipitated on dilution with water. Soluble in concentrated hydrochloric and sulphuric acids giving brown solutions; on dilution the pink color returns and the acid is for the most part precipitated unaltered. Readily soluble in dilute caustic potash and ammonia, giving dark red solutions having a brown fluorescence; from these solutions the compound is precipitated on acidulation.

The Potassium Salt is prepared by boiling an excess of the acid with dilute alkali, filtering off the excess and evaporating the neutral solution to dryness. The salt forms a dark violet-red powder having a dark violet reflex. It is very soluble in water and its solution fluoresces strongly.

The Silver Salt $C_{28}H_{19}O_{12}N_2Ag_5$ is precipitated as a dark blood-red precipitate, which when dry has a dark reddish brown color and is remarkably stable to light. Dissolves instantly in ammonia. Dilute nitric and glacial acetic acids dissolve the salt and precipitate out the acid.

Calculated for $C_{28}H_{19}O_{12}N_2Ag_5$: Ag, 48.43.
Found (two different preparations): Ag, 48.67, 48.59.

The copper, cobalt, ferric and ferrous salts are precipitated as reddish brown powders, while the barium and chromium salts are blood-red precipitates. The compound forms no definite hydrochloride. On evaporating its solution in concentrated hydrochloric acid the residue retains only traces of chlorine, which it slowly loses over quicklime.

Tetramethyl-3,6-diamino-9-hydroxyxanthylbenzenepentacarboxylic Ethyl Ester Chloride, $C_{38}H_{43}O_{11}N_2Cl$.

Preparation. — Tetramethyl-1,3,6-diamino-9-hydroxyxanthylbenzene pentacarboxylic acid is suspended in absolute alcohol and dry hydrochloric acid gas passed through the liquid, until nearly all the acid has gone into solution. The mixture is evaporated to dryness on the water bath and the residue extracted with alcohol. The unchanged acid is filtered off and the filtrate evaporated to dryness, and finally purified by repeated fractional precipitation.

Calculated for $C_{38}H_{43}O_{11}N_2Cl$: N, 3.79; Cl, 4.80.
Found (three different preparations): N, 3.96, 3.67, 3.65; Cl, 5.16, 4.98, 4.61.

Properties. — Dark violet-red, amorphous powder, having a bronzy metallic reflex. Dyes silk and wool a violet-red. Insoluble in ether, benzene and chloroform. Very slightly soluble in water, acetone, ethyl acetate and concentrated hydrochloric acid, giving fine deep pink solutions. Readily soluble in phenol, aniline, glacial acetic acid and alcohol in which last it gives a deep violet-red solution having an intense brown fluorescence. Readily soluble in concentrated sulphuric acid, giving a brown solution which on dilution becomes red. In strong, cold, caustic potash and ammonia it is slightly soluble, giving deep violet-red solutions having a brown fluorescence.

Hydrochloride of Tetramethyldiaminohydroxyxanthylbenzenepentacarboxylic Ethyl Ester Chloride, $C_{38}H_{44}O_{11}N_2Cl_2$.

Preparation.—On evaporating the pure anisoline chloride described above with hydrochloric acid the ester takes up another molecule of hydrochloric acid. The compound is purified by exposure over quicklime until it becomes constant in weight.

Calculated for $C_{38}H_{44}O_{11}N_2Cl_2$:	Cl, 9.03.
Found:	Cl, 8.5.

Properties.—Dark reddish powder possessing a bronzy reflex. On treatment with water it loses one molecule of hydrochloric acid with formation of the anisoline chloride.

Tetraethyl-3,6-diamino-9-hydroxyxanthylbenzenepentacarboxylic Acid (2 mols. diethylmetaaminophenol + 1 mol. mellitic acid), $C_{32}H_{32}O_{12}N_2$.

Preparation.—A finely ground mixture of six parts mellitic acid and 5 parts diethylmetaaminophenol is heated to 170° for 5 hours. The mass on cooling is dissolved in dilute caustic potash, filtered, and the condensation product precipitated by means of hydrochloric acid, filtered off, washed with boiling water, then with alcohol, and purified by repeated fractional precipitation of its alkaline solution by the addition of acid. The compound is then freed from salt which it tenaciously retains, by extraction with water.

Calculated for $C_{32}H_{32}O_{12}N_2$:	N, 4.41.
Found (two different preparations):	N, 4.48, 4.39.

Properties.—Dull red heliotrope, amorphous powder, which decomposes without melting above 300°. Dyes silk and wool a silver gray pink. In its solubility and other properties, it is practically identical with the tetramethyl compound.

Octamethyl-3,3′,6,6′-tetramino-9,9′-dihydroxy-m-dixanthylbenzene-2,4,5,6-tetracarboxylic Acid (4 mols. dimethylmetaaminophenol + 1 mol. mellitic acid), $C_{44}H_{42}O_{12}N_4$.

Preparation.—6.84 parts of mellitic acid and 11 parts dimethylmetaaminophenol are finely ground together and heated to 165–170° with 4 parts concentrated sulphuric acid for 6 hours. The mixture gradually solidifies. On cooling, the mass is ground, boiled out thoroughly with water and the residue dissolved in dilute alkali. The solution is filtered and the condensation product precipitated by means of acid. The product is then well washed with boiling water, then with alcohol to remove unchanged dimethylaminophenol, and purified by repeated fractional precipitation from its potassium salt by means of acid.

Calculated for $C_{44}H_{42}O_{12}N_4$:	C, 64.50; H, 5.17; N, 6.86.
Found (three different preparations):	C, 64.34, 64.42, 64.36; H, 5.16, 5.31, 5.17; N, 6.76, 6.85, 6.72.

Properties.—Bright violet-red, amorphous powder, much brighter than the para isomeride. Decomposes without melting above 300°. Dyes silk and wool a violet-red; is insoluble in water, alcohol, chloroform, ethyl acetate, ether and acetone. Fairly soluble in phenol and aniline. Readily soluble in concentrated sulphuric, hydrochloric and acetic acids, from which solutions it is precipitated on being largely diluted. Very soluble in dilute caustic potash and ammonia, giving a deep violet-red solution, having a brown fluorescence; precipitated on acidification.

Salts.—The potassium and lithium salts are dark brownish violet powders with a bronze metallic reflex. Very soluble in water, forming deep bright violet-red solutions having an intense brown fluorescence.

Silver Salt, $C_{44}H_{38}O_{12}N_4Ag_4$.—Is a dark violet-red powder, with a dark violet-red reflex. Is extremely stable to light and heat and dissolves instantly in ammonia. Dilute nitric and acetic acids dissolve the salt but precipitate out the acid.

Calculated for $C_{44}H_{38}O_{12}N_4Ag_4$: Ag, 34.65.
Found (two different preparations): Ag, 34.51, 34.66.

The copper, barium, cobalt, ferric, ferrous, chromium and mercuric salts are formed as bright violet-red precipitates, the copper and barium salts being unaltered by ammonia.

Tetrahydrochloride of Octamethyl-3,3′,6,6′-tetramino-9,9′-dihydroxymetadixanthylbenzene-2,4,5,6-tetracarboxylic Acid, $C_{44}H_{46}O_{12}N_4Cl_4$.

Preparation.—The aforementioned acid is dissolved in concentrated hydrochloric acid and the solution evaporated to dryness on the water bath and allowed to stand over quicklime until a constant weight is reached.

Calculated for $C_{44}H_{45}O_{12}N_4Cl_4$: Cl, 14.73.
Found (three different preparations): Cl, 15.00, 14.97, 14.95.

Properties.—Dark reddish powder possessing a metallic reflex, which when dissolved in water suffers hydrolysis, the acid being precipitated practically free from chlorine. Under no conditions could a compound containing two molecules of hydrochloric acid be obtained.

Octamethyl-3,3′,6,6′-tetramino-9,9′-dihydroxymetadixanthylbenzene-2,4,5-6-tetracarboxylic Ethyl Ester Dichloride, $C_{52}H_{56}O_{10}N_4Cl_2$.

Preparation.—The foregoing acid is suspended in alcohol and dry hydrochloric acid gas passed through the mixture. The acid rapidly passes into solution with evolution of heat. In order to obtain the pure compound it is advisable to stop the current of gas just before all the acid is esterified. The mixture is then evaporated to dryness, the residue extracted with alcohol and the alcoholic extract precipitated by the addition of water.

Calculated for $C_{52}H_{56}O_{10}N_4Cl_2$: N, 5.73; Cl, 7.27.
Found (two different preparations): N, 5.98, 5.81; Cl, 7.27, 7.43.

Properties.—Dark violet-red amorphous powder having a bright bronzy reflex. On rapid heating it softens at 169–170°. Dyes silk and wool a reddish violet. Insoluble in ether, water, acetone, benzene, chloroform and ethyl acetate. Readily soluble in phenol, glacial acetic acid and aniline, giving bright violet-red solutions. Readily soluble in concentrated sulphuric and hydrochloric acids, giving brown solutions which turn red on dilution. Readily soluble in alcohol and precipitated therefrom on dilution with water.

Dihydrochloride of Octamethyl-3,3′,6,6′-tetraminometadixanthylbenzene-2,4,5,6-tetracarboxylic Ethyl Ester Dichloride, $C_{52}H_{58}O_{10}N_4Cl_4$.

Preparation.—An alcoholic solution of the aforementioned anisoline is saturated with hydrochloric acid, evaporated to dryness and exposed over quicklime until the weight becomes constant.

Calculated for $C_{52}H_{58}O_{10}N_4Cl_4$: Cl, 13.65.
Found (two different preparations): Cl, 13.80, 13.88.

Properties.—Dark reddish powder possessing a bronzy reflex. On treatment with water it at once loses 2 molecules of hydrochloric acid with the formation of the anisoline dichloride.

Octamethyl-3,3′,6,6′-tetramino-9,9′-dihydroxymetadixanthylbenzene-2,4,5,6 tetracarboxylic Benzyl Ester, $C_{72}H_{66}O_{12}N_4$.

Preparation.—The potassium salt of octamethyltetraminodihydroxy-*m*-dixanthylbenzene-2,4,5,6-tetracarboxylic acid is suspended in alcohol, excess of benzyl iodide added, and the mixture heated to 130° for 8 hours. The colored solution is filtered, the residue washed thoroughly with boiling absolute alcohol, and the filtrate and washings evaporated to dryness on the water bath. The ester is purified by redissolving in alcohol, evaporating to dryness, and warming to 100° *in vacuo* to remove the excess of benzyl iodide; it is then again dissolved in alcohol and fractionally precipitated by the addition of water.

Calculated for $C_{72}H_{66}O_{12}N_4$: N, 4.76.
Found (two different preparations): N, 4.89, 4.65.

Properties.—The benzyl ester is a bright reddish violet, amorphous powder, having a dark violet-red metallic reflex. On rapid heating it melts and froths up at 147°. Dyes silk and wool a fine reddish mauve color. Insoluble in water, ether, benzene, caustic potash and ammonia. Slightly soluble in ethyl acetate and chloroform. Readily soluble in alcohol, aniline, acetone, phenol, and glacial acetic acid, the last giving a deep red colored solution having an intense brown fluorescence. Readily soluble in concentrated sulphuric acid with a reddish brown coloration which turns much redder on dilution.

Octamethyl - 3,3′,6,6′ - tetramino - 9,9′ - dihydroxyparadixanthylbenzene - 2,3,5,6-tetracarboxylic Acid (4 mols. dimethylmetaaminophenol + 1 mol. mellitic acid), $C_{44}H_{42}O_{12}N_4$.

Preparation.—10.25 parts mellitic acid and 19.4 parts of dimethylmetaaminophenol are finely ground together and heated to 160° for 8 hours. On commencing the heating the phenol melts but subsequently the whole gradually solidifies and the reaction is completed in about 8 hours.

When cold the mass, which has a bronzy metallic glance, is powdered and the condensation product together with the unchanged phenol is extracted with dilute aqueous caustic potash. The solution is filtered and the products are precipitated by acidifying with hydrochloric acid. The precipitate is filtered off, washed very thoroughly with boiling water, then with alcohol till the washings are scarcely colored, and finally purified by repeated fractional precipitation of its potassium salt by means of dilute acid. This it will be found is insufficient to produce a pure product, it being necessary subsequently to extract for at least 2 hours with alcohol and then dry at 80° on a porous tile.

Calculated for $C_{44}H_{42}O_{12}N_4$:	C, 64.50; H, 5.17; N, 6.86.
Found (two different preparations):	C, 64.35, 64.64; H, 5.05, 5.00; N, 6.83, 6.93.

Properties.—Dark reddish violet, amorphous powder. Decomposes without melting above 300°. Dyes silk and wool a silvery pink. Insoluble in water, alcohol, chloroform, ethyl acetate and ether. Slightly soluble in aniline, phenol, glacial acetic acid from which last solution it is precipitated on dilution with water. Very soluble in dilute alkalies, precipitated on acidification. In concentrated hydrochloric and sulphuric acids it is readily soluble without decomposition, and is precipitated on addition of water.

Salts.—The potassium and lithium salts are dark violet-red powders, having a dark violet-red reflex. They dissolve readily in water, giving fine violet-red solutions which show a marked brown fluorescence in concentrated solution.

Silver Salt, $C_{44}H_{38}O_{12}N_4Ag_4$, is precipitated as a dull red precipitate which is very stable to light and heat. It is readily soluble in ammonia. Dilute nitric and acetic acids dissolve the salt with precipitation of the free acid.

Calculated for $C_{44}H_{38}O_{12}N_4Ag_4$:	Ag, 34.65.
Found (four different preparations):	Ag, 34.67, 34.79, 34.52, 34.48.

The copper, cobalt, lead, ferrous and chromium salts are precipitated as deep red powders, while the barium salt is a blood-red precipitate.

The ferric salt is as a reddish brown, gelatinous precipitate.

Tetrahydrochloride of Octamethyl-3,3′,6,6′-tetramino-9,9′-dihydroxypara-dixanthylbenzene-2,3,5,6-tetracarboxylic Acid, $C_{44}H_{46}O_{12}N_4Cl_4$.

Preparation.—A solution of the acid in strong hydrochloric acid is evaporated just to dryness on the water bath, and then exposed over quicklime until its weight becomes constant.

Calculated for $C_{44}H_{46}O_{12}N_4Cl_4$: Cl, 14.73.
Found (two different preparations): Cl, 14.51, 14.55.

Properties.—Dark reddish powder possessing a metallic reflex, which, when dissolved in water, evidently suffers hydrolysis, the acid being reprecipitated practically free from chlorine. Under no circumstances could a compound containing 2 HCl be obtained.

Octamethyl - 3,3,'6,6' - tetramino - 9,9' - dihydroxyparadixanthylbenzene - 2,3,5,6-tetracarboxylic Ethyl Ester Dichloride, $C_{52}H_{56}O_{10}N_4Cl_2$.

Preparation.—The corresponding acid is suspended in alcohol and dry hydrochloric acid gas passed slowly through the solution. During this process the temperature rises; the gas is passed through the mixture until solution is almost complete. The product is then evaporated to dryness, the residue extracted with alcohol, and the alcoholic extract evaporated on the water bath and purified by fractional precipitation.

Calculated for $C_{52}H_{56}O_{10}N_4Cl_2$: N, 5.73; Cl, 7.27.
Found (two different preparations): N, 5.62, 5.90, 5.84; Cl, 7.46, 7.52.

Properties.—Dark reddish violet, amorphous powder, having a bronzy metallic reflex. On rapid heating the substance begins to froth up at 138°. Dyes silk and wool a violet-red. Insoluble in ether, benzene, chloroform and ethyl acetate. Very slightly soluble in water and acetone. Readily soluble in phenol, aniline, glacial acetic acid and alcohol, giving deep violet-red solutions having an intense brown fluorescence. Readily soluble in concentrated sulphuric acid and hydrochloric acid, giving a brown solution from which the compound is precipitated on dilution with water.

Dihydrochloride of Octamethyl-3,3',6,6'-tetraminoparadixanthylbenzene-2,4,5,6-tetracarboxylic Ethyl Ester Dichloride, $C_{52}H_{58}O_{10}N_4Cl_4$.

Preparation.—An alcoholic solution of the corresponding anisoline is saturated with hydrochloric acid gas, evaporated to dryness and exposed over quicklime until the weight becomes constant.

Calculated for $C_{52}H_{58}O_{10}N_4Cl_4$: Cl, 13.65.
Found (two different preparations): AgCl, 13.29, 15.69.

Properties.—Dark reddish powder possessing a bronzy reflex. On treatment with water it at once loses two molecules of hydrochloric acid with formation of the anisoline dichloride.

Octaethyl - 3,3',6,6' - tetramino - 9,9' - dihydroxyparadixanthylbenzene - 2,3,5,6-tetracarboxylic Acid (4 mols. diethylmetaaminophenol + 1 mol. mellitic acid), $C_{52}H_{58}O_{12}N_4$.

Preparation.—This is prepared by heating 8 parts diethylmetaaminophenol with 6 parts mellitic acid to 160° for 6 hours. The unaltered diethylmetaaminophenol is dissolved out by means of alcohol, and the condensation product purified by repeated fractional precipitation from its potassium salt by the addition of dilute acid.

Calculated for $C_{52}H_{58}O_{12}N_4$: N, 6.03.
Found (two different preparations): N, 6.00, 6.17.

Properties.—Light violet-red, amorphous powder. Decomposes without melting above 300°. Dyes silk and wool a silvery violet-red. General properties similar to those of the octamethylparadixanthyl compound.

Tetramethyl - 3,6 - diaminotetraethyl - 3′,6′ - diamino-9,9′ - dihydroxymeta - dixanthylbenzene-2,4,5,6-tetracarboxylic Acid (2 mols. diethylmetaaminophenol + 2 mols. diethylmetaaminophenol + 1 mol. mellitic acid), $C_{48}H_{50}O_{12}N_4$,

Preparation.—This is prepared by heating a mixture of tetraethyldiaminohydroxyxanthylbenzenepentacarboxylic acid and dimethylmetaaminophenol in the proportion of 1 molecule of the former to two of the latter with sulphuric acid to 170° for 6 hours. Water is then added to the mixture and the condensation product filtered off and purified in the usual manner.

Calculated for $C_{48}H_{50}O_{12}N_4$: N, 6.42.
Found (two different preparations): N, 6.49, 6.33.

Properties.—Dark violet-red, amorphous powder decomposing above 300° without melting. Dyes silk and wool a violet-red color. In its general properties it closely resembles the octamethylmetadixanthyl compound.

Orientation of the Two Isomeric Dixanthyl Derivatives.—In order to determine the relative position of the two xanthyl groups the two octamethyl isomers were further heated with excess of dimethylmetaaminophenol to 200°. In the case of the para compound (prepared in the absence of sulphuric acid) no trixanthyl derivative was formed. The result was similar when this compound was heated for 12 hours to 170° with dimethylmetaaminophenol and concentrated sulphuric acid, 80 per cent. of the original dixanthyl compound being recovered in a pure state and the residue was proved to be free from trixanthyl derivatives. The xanthyl groups therefore occupy para positions in the compound produced by heating mellitic acid with 4 or more molecular proportions of dimethylmetaaminophenol in the absence of sulphuric acid. This, it is interesting to note, is contrary to the behavior of the hydroxyxanthyl derivatives dealt with in a previous paper (*J.Chem.Soc.*(*London*), **89**, 1760).

The compound above described as octamethyltetraminometadixanthylbenzenetetracarboxylic acid, produced by condensing mellitic acid with dimethylmetaminophenol in the presence of sulphuric acid, readily combines with another molecular proportion of the aminophenol with production of the trixanthyl derivatives described below.

Dodecamethyl - 3,3′,3′′,6,6′,6′′ - hexamino - 9,9′,9′′ - trihydroxy - sym - tri - xanthylbenzene-2,4,6-tricarboxylactone (6 mols. dimethylmetaaminophenol + 1 mol. mellitic acid), $C_{60}H_{60}O_{12}N_6$.

Preparation.—All early attempts to obtain this compound were fruitless owing to the fact that unlike the resorcinol compounds previously studied[1] direct heating of the mixture of aminophenol and mellitic acid leads to the production of the para dixanthyl derivatives. Thus varying excesses of aminophenol were heated with mellitic acid to temperatures ranging from 160 to 200° for times varying from 8 to 18 hours, both alone and subsequently in the presence of small quantities of sulphuric acid; in the latter instances small quantities of a trixanthyl compound were obtained which ultimately led to the following method of preparation.

Twenty-five parts mellitic acid were finely ground up with 62 parts dimethylmetaaminophenol, 100 parts concentrated sulphuric acid added and the whole gradually heated up to 180° and maintained at that temperature for 8 hours. After cooling, water is added to the black mixture and the whole warmed till the product is almost all dissolved. The solution is then filtered and the filtrate precipitated by the addition of a slight excess of alkali. The precipitate is then repeatedly washed, but owing to the impervious and slime-like nature great difficulty is experienced in purifying the compound. At this stage, after drying at 100°, one preparation gave on analysis 8.6 per cent. N (required by $C_{60}H_{60}O_{12}N_6$ 7.95); after extraction with alcohol for several days in a Soxhlet it was found to contain 8.25 per cent. The product was therefore repeatedly boiled for several hours with large quantities of water, allowed to settle over night and the aqueous liquor decanted off. This treatment was then repeated with alcohol until the supernatant liquor is but faintly colored, after which the residue was finally filtered off and dried at 90°.

Calculated for $C_{60}H_{60}O_{12}N_6$: C, 68.18; H, 5.68; N, 7.95.
Found (three different preparations): C, 68.30, 67.95, 68.00; H, 5.53, 5.75, 5.53; N, 7.97, 7.88, 8.04, 7.97.

Properties.—Dark violet-brown, amorphous powder, which decomposes without melting above 300°. Dyes silk and wool a pale silver pink. Insoluble in water, alcohol, chloroform, acetone, ether, benzene, ethyl acetate and ammonia. Slightly soluble in glacial acetic acid, readily soluble in phenol giving a deep red solution. Readily soluble in concentrated sulphuric and hydrochloric acids, giving a brownish red solution which on dilution becomes red. The compound is insoluble in caustic potash; boiling with a 40 per cent. solution causes slight decomposition with evolution of dimethylamine.

Hexahydrochloride of Dodecamethyl-3,3',3'',6,6',6''-hexamino-9,9'9''-trihydroxy-sym-trixanthylbenzene-2,4,6-tricarboxylactone, $C_{60}H_{66}O_{12}N_6Cl_6$.

Preparation.—The above lactone is dissolved in concentrated hydrochloric acid, and the solution evaporated to dryness on the water bath; the residue is then exposed over quicklime until a constant weight is reached.

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[1] *Loc. cit.*

Calculated for $C_{60}H_{66}O_{12}N_6Cl_6$: Cl, 16.70.
Found (two different preparations): Cl, 16.96, 16 90, 16.34, 16.47.

Properties.—Dark bronzy powder. Soluble in water with gradual precipitation of the base; boiling accelerates the hydrolysis. The precipitated base is practically free from chlorine; the compound shows no tendency to produce a trichloride.

Dodecamethyl-3,3′,3′′,6,6′,6′′-hexamino-9,9′,9′′-trihydroxy-sym-trixanthylbenzene-2,4,6-tricarboxylic Ethyl Ester Trichloride, $C_{66}H_{69}O_9N_6Cl_3$.

Preparation.—This is prepared by dissolving the foregoing acid in concentrated hydrochloric acid, precipitating the hydrochloride by means of absolute alcohol and then heating the finely divided hydrochloride thus obtained in a sealed tube with excess of alcoholic hydrochloric acid to 140°. The residue is filtered off and the alcoholic solution evaporated to dryness on the water bath, the residue being purified by repeated fractional precipitation of its alcoholic solution by means of water.

Calculated for $C_{66}H_{69}O_9N_6Cl_3$: N, 7.02.
Found (two different preparations): N, 7.11, 7.11.

Properties.—Dark violet-brown, amorphous powder having a dark metallic reflex. Decomposes without melting above 300°. Dyes silk and wool a pinkish mauve. Insoluble in chloroform, acetone, ether, benzene, ethyl acetate, glacial acetic acid, aqueous alkalies and water. Fairly soluble in alcohol, giving a deep red solution having a brown fluorescence. Readily soluble in phenol and aniline, giving red-brown solutions. Readily soluble in concentrated sulphuric and hydrochloric acids, giving red-brown solutions which on dilution assume a fine red; and from which the ester is precipitated by alkalies.

Trihydrochloride of Dodecamethyl-3,3′,3′′,6,6′,6′′-hexamino-9,9′,9′′-trihydroxy-sym-trixanthylbenzene-2,4,6-tricarboxylic Ethyl Ester Trichloride, $C_{66}H_{72}O_9N_6Cl_6$.

Preparation.—An alcoholic solution of the corresponding anisoline is saturated with hydrochloric acid evaporated to dryness and exposed over quicklime until the weight becomes constant.

Calculated for $C_{66}H_{72}O_9N_6Cl_6$: Cl, 16.32.
Found (two different preparations): Cl, 16.00, 16.08.

Properties. — Dark reddish powder possessing a violet-bronzy reflex soluble in alcohol from which solution water precipitates the trichloride.

In conclusion we desire to express our gratitude to Messrs. Read Holliday & Sons of Huddersfield, England and Brooklyn, U. S. A., for permission to publish this work and also for supplying much of the *mellitic acid* required in its execution.

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