at 5°. Fraction VB (8.2 g.) had m.p. 127.5–128.5° and $[\alpha]^{25}_{D}$ +98.8 (1.00% in $CHCl_3$). The crystals of this fraction were long orange colored needles which did not tend to form rosettes. They were indistinguishable from vitamin D_3 dinitrobenzoate crystals obtained from crystallization from benzene-methanol. The extinction coefficient of Fraction VB was identical with that of Fraction VA (cf. Table I).

Fraction IVA (15.5 g.) was dissolved in 80 ml. of methyl ethyl ketone and allowed to stand overnight at 5°. The small crop of crystals which formed was discarded, and an equal volume of methanol was added. Crystallization at 5° yielded 14.7 g. of vitamin Dm dinitrobenzoate (I) as Fraction VIA. This fraction had m.p. 128.5–129° and $[\alpha]^{25}_{D}$ (+91.2 1.00% in $CHCl_3$). Mixed melting point with authentic vitamin D_3 dinitrobenzoate showed a marked lowering, a wide range of melting and a high clearing point, it being 127–131–137°. The extinction coefficient given in Table I for this fraction is identical with that described above for (I).

Anal. Found: N, 5.00, 4.87.

Biological efficacy of vitamin Dm. Since vitamin Dm (III) has not yet been obtained in crystalline form as the free alcohol, the biological efficacy of the vitamin was determined by using a resin obtained from highly purified dinitrobenzoate (I), or by using the vitamin in solution obtained from a given amount of highly purified ester and calculating the efficacy on the basis of the ester.

The dinitrobenzoate I (0.600 g.) was saponified according to the procedure of Petering and Waddell[12] with the exception of the use of hexane instead of benzene. The hexane solution, containing the free vitamin Dm, was concentrated under nitrogen and reduced pressure until a resin resulted. The resin was then subjected to alternate periods of dry ice bath temperature and warming to 25° while being evacuated under high vacuum. In the end a brittle resin free of all solvent, which could be weighed readily, was obtained.

This resin (0.1000 g.) was dissolved in hexane (250 ml.) and an aliquot of 2.50 ml. was transferred to 100.0 g. of corn oil. The corn oil mixture was evacuated under nitrogen at 50° to remove the hexane. This sample was then used for biological assays.

The corn oil solution, containing 10.00 γ of vitamin Dm resin per g., was tested against Standard U.S.P. Reference Cod Liver Oil in the accepted U.S.P. assay for rat activity and A.O.A.C. test for chick vitamin D activity. It was found that the oil contained 335 U.S.P. units per g. and 300 A.O.A.C. units per g. These data indicate that the resin itself then has a biological efficacy of 33,000,000 U.S.P. units per g. and 30,000,000 A.O.A.C. units per g. This indicates a rat-chick ratio of activity of about 1.0, which identifies the vitamin as of the D_3-type.

In another experiment in which the resin was not isolated, it was found that the ester (I) contains 22,500,000 U.S.P. units per g. and 19,500,000 A.O.A.C. units per g., which agrees well with the above data. If one assumes a molecular weight of 425 for the free vitamin Dm, which is indicated by the spectroscopic and specific rotation data, then the values obtained above for free resin and (I) are self-consistent.

On the other hand, although vitamin Dm is of the D_3-type insofar as its physiological function is concerned, yet a comparison of the efficacy of vitamin D_3, which has an activity of about 45,000,000 USP or AOAC units per gram, with vitamin Dm, which contains about 30,000,000 units per gram, indicates that the latter is a less active compound. The lower efficacy of vitamin Dm over that of vitamin D_3 cannot be explained on the basis of the higher molecular weight of the former compound. These facts indicate the need for careful work with purified compounds rather than the reliance only on comparative biological assay for the determination of structural relationships in the area of the vitamins D.

Acknowledgment. It is a pleasure to thank J. Waddell for helpful advice, and E. L. Rohdenberg, G. H. Kennedy, and J. P. Marvel for assistance in obtaining the biological assays used in this report. A. Bratcher gave me valuable aid in obtaining the physical data reported here.

KALAMAZOO, MICH.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

On the Color of Diaminopyromellitic Esters and Related Compounds*

LEE IRVIN SMITH AND ROGER L. ABLER[1]

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The tetramethyl and tetraethyl esters of diaminopyromellitic acid (I, II) are inherently colored compounds, and the colors do not arise from the presence of diimino compounds or from molecular compounds (quinhydrones) formed from diimino and diamino compounds. Several other diaminobenzenecarboxylic acids and their derivatives have been reported in the literature as being colored, and the color of these substances is discussed in terms of resonance among the functional groups present. The principal frequencies in the ultraviolet, visible, and infrared spectra of compounds I, II, XII, XIII and XIV are given in tabular form.

Many years ago, it was reported by Nef that tetramethyl diaminopyromellitate (I) and the corresponding ethyl ester (II) were colored orange-red and red, respectively.[1–3] These are not the only diaminobenzenepolycarboxylic acids that show color of themselves or in their derivatives. 3,6-Diaminophthalic acid (III) forms brown needles which become black when heated above 200°;[4] 4,6-diaminoisophthalic acid (IV) and its ethyl ester (V) are colored pink and yellow, respectively;[5] diethyl 2,5-diaminoterephthalate (VI) is

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(*) Abstracted from a thesis by Roger L. Abler, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the M.S. degree, April 1956.

(1) J. U. Nef, *Ann.*, **258**, 261 (1890).

(2) J. U. Nef, *Ann.*, **237**, 1 (1887).

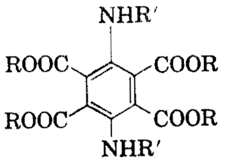
(3) J. U. Nef, *J. Chem. Soc.*, **53**, 428 (1888).

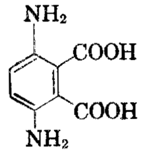
(4) V. Merz and W. Weith, *Ber.*, **15**, 2708 (1882).

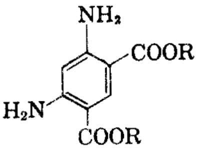
(5) M. T. Bogert and A. H. Kropft, *J. Am. Chem. Soc.*, **31**, 841 (1909).

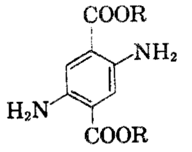
orange-red whereas the acid (VII) is yellowish-green. Often the ester VI forms light yellow crystals which, upon recrystallization, are transformed into the orange-red form.[6] Dimethyl 2,6-diaminoterephthalate (VIII) is yellow.[7] The only definitely characterized diaminobenzenepolycarboxylic acid (or derivative) which is not colored is 3,5-diaminophthalic acid (IX).[4] 2,6-Diaminobenzoic acid (X) is not known, but 6-acetylaminoanthranilic acid (XI) forms brown crystals which do not melt below 300°.[8] Nef[9] reported that the diamino ester II was converted into the orange-yellow quinone diimide (XII) by the action of bromine in chloroform, and that XII was converted back to II by action of zinc dust and acetic acid.

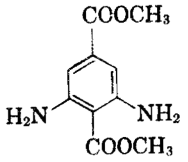
The color of these compounds is difficult to explain on the basis of the structures assigned to them. On the other hand, if the diamino esters (I, II) were really the diimino esters (XII, XIV) or a quinhydrone of the diamino- and diimino-compounds, the color would be expected, and such changes would cause but slight differences in the analytical values. Nef's preparation of the quinone imide (XII) could well have led to a quinhydrone, and aside from Nef's work, only Smith and Byrkit[10] have prepared II and no work was done by these authors to investigate the structure of II or to explain its color. Moreover, at the time of this work the modern physical tools for investigating structure of organic compounds were unknown. It appeared worthwhile, therefore, to repeat Nef's preparation of I and II and in larger quantities, to purify these compounds carefully, to obtain accurate analytical values, to determine their absorption curves in the infrared and ultraviolet, and to determine whether or not a quinhydrone type of compound could be formed from I and XII.

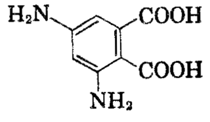

I, $R = CH_3$; $R' = H$ (orange-red)
II, $R = C_2H_5$; $R' = H$ (red)
XIII, $R = CH_3$; $R' = COC_6H_5$

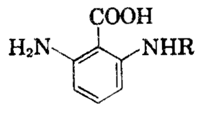

III, (brown → black) 200°)

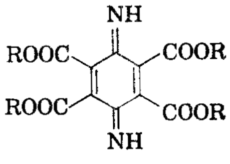

IV, $R = H$ (pink)
V, $R = C_2H_5$ (yellow)

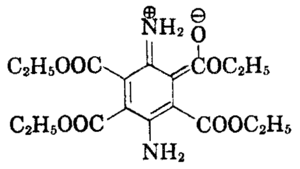

VI, $R = C_2H_5$ (orange-red / dimorph lt yellow)
VII, $R = H$ (yellowish-green)


VIII, (yellow)


IX, (colorless)


X, $R = H$ (not known)
XI, $R = Ac$ (brown, m.p.) 300°)


XII, $R = CH_3$
XIV, $R = C_2H_5$


XV

Dinitropyromellitic acid was prepared from 5-acetopseudocumene[11] via durylic acid,[12] and dinitrodurylic acid,[2,3] which was purified according to Gissman.[13] Oxidation of this produced dinitropyromellitic acid,[2,3] which was converted into the tetramethyl and tetraethyl esters by action of diazomethane and diazoethane, respectively. These esters required several recrystallizations to remove the yellow polymers of the diazohydrocarbons, particularly of diazomethane. Reduction of the tetramethyl and tetraethyl esters by action of zinc dust and acetic acid led to the diamino esters I and II, respectively.

The tetramethyl ester I, crystallized several times from methanol, formed orange needles melting at 149.4–151° which gave excellent analytical values in agreement with formula I. This material was chromatographed from chloroform onto alumina, and the column was developed and eluted with petroleum ether (C)-chloroform mixtures. Three eluates were taken: from the first, I

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(6) M. T. Bogert and A. W. Dox, *J. Am. Chem. Soc.*, **27**, 1127 (1905).

(7) H. Kaufmann and L. Weisel, *Ann.*, **393**, 1 (1912).

(8) T. S. Moore, M. T. Marrack, and A. K. Proud, *J. Chem. Soc.*, **119**, 1786 (1921).

(9) J. U. Nef, *Am. Chem. J.*, **11**, 1 (1889).

(10) L. I. Smith and G. D. Byrkit, *J. Am. Chem. Soc.*, **55**, 4305 (1933).

(11) R. Wegler, *J. prakt. Chem.*, **148**, 135 (1937).

(12) W. H. Mills, *J. Chem. Soc.*, **101**, 2191 (1912).

(13) R. Gissman, *Ann.*, **216**, 200 (1883).

was recovered as orange needles melting at 149.6–150.6°. From the second and third eluates I was recovered as orange needles, but mixed with these was a very small amount of brick-red needles. The two types of crystals were separated mechanically; the red material, at 120–130°, became orange and then melted at 149–150°. The orange needles melted, after crystallization from methanol, at 150–151°. No other material was recovered from the column, and it can be concluded that the red and orange forms of I are polymorphs. The significant bands in the infrared spectrum of I are shown in Table II. The ultraviolet and visible spectra of I are given in Table I.

TABLE I

Absorption Spectra in Ultraviolet and Visible Light (in 95% Ethanol)

Compound	Ultraviolet λ_{max} mμ	Ultraviolet $\epsilon_{max} \times 10^{-4}$	Visible λ_{max} mμ	Visible $\epsilon_{max} \times 10^{-4}$
I	215	1.34	445	0.503
	252	0.975		
II	217	2.83	440	0.582
	252	0.985		
XII	245	1.56	375	1.92
	376	2.16	450	0.902
XIV	246	1.19	376	1.75
	375	1.70	453	0.855
XIII	232	3.82		
	272	1.67		

TABLE II

Infrared Frequencies

Compound	Phase[a]	ν(cm.$^{-1}$)
I	A	NH: 3450, 3420 (doublet); 3380, 3340 (doublet); 1613. C=O: 1726
	B	NH: 3480, 3380, 1590. C=O: 1713
	C	NH: 3450, 3360. C=O: 1715
II	A	NH: 3490, 3400, 1600. C=O: 1721
	B	NH: 3490, 3390, 1589. C=O: 1706
Monobenzoyl I	A	NH: 3430, 3320, 1599, 1542. C=O: 1741, 1702, 1667
XIII	A	NH: 3400, 1520. C=O: 1727, 1700, 1684
XII	A	NH: 3480, 3360, 1595 (NH?). C=O: 1752, 1730, 1718, 1696
	B	NH: 3440, 3340, 1592 (NH?) C=O: 1713
XIV	A	NH: 3490, 3450 (doublet); 3390, 3350 (doublet), 1588. C=O: 1729, 1704
	B	NH: 3470, 3360, 1591 (NH,?) C=O: 1709

[a] A = Nujol mull; B = solution in chloroform; C = solution in carbon tetrachloride.

The ester I was converted into a white hydrochloride when dry hydrogen chloride was passed through the chloroform solution of I. This white salt decomposed in air with regeneration of I. The ester I was converted into a monobenzoyl derivative (yellow, melting at 194.5–195.5°) and a dibenzoyl derivative (XIII) melting at 264–266° which was only slightly yellow. Several attempts were made to oxidize XIII to a dibenzoylquinone imide by action of lead tetraacetate, but the reagent was essentially without action and unchanged XIII was recovered.

Oxidation of I by action of lead tetraacetate[14] gave the quinone diimide XII as orange-red prisms melting at 260–261°. The same result was achieved when bromine was used as the oxidizing agent, as described by Nef.[9] The significant bands in the infrared spectrum of XII are shown in Table II. The ultraviolet and visible spectra of XII are given in Table I.

Attempts were made to prepare a quinhydrone of I and XII by recrystallizing solutions of equimolar amounts of the two compounds in acetic acid or benzene. When these solutions were cooled, a mixture of I and XII separated. Finally, a melting point diagram of mixtures of I and XII was constructed. This (Figure 1) definitely shows that no compound of I and XII is formed.

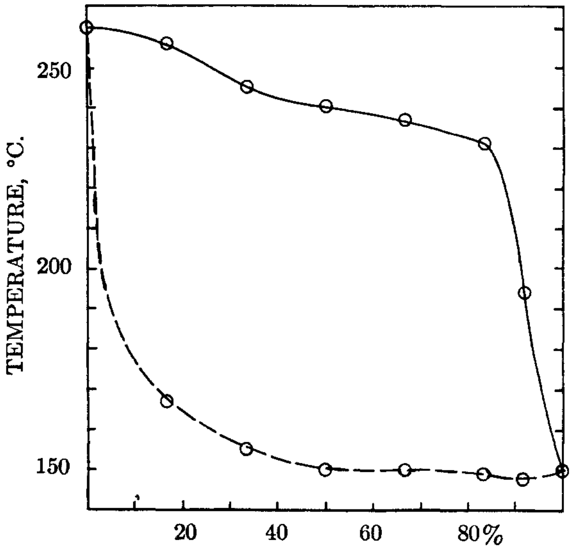

Fig. 1. Melting-Point Diagram for Mixtures of I and XII. Dotted line, beginning of melting; solid line, complete liquefaction.

Reduction of dinitropyromellitic acid in slightly acidic medium gave a red solution. Ether extracts of this solution were red, and showed a marked yellowish-red fluorescence. The ester I also shows this fluorescence in ultraviolet light. Although the diamino acid was not isolated, the experiment showed that it also was a colored substance.

The ethyl ester II, after crystallization several times from ethanol, formed brick-red prisms

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(14) R. Adams and A. S. Nagarkatti, *J. Am. Chem. Soc.*, **72**, 4603 (1952).

melting at 138–138.7°, giving excellent analytical values for formula II. The significant bands in the infrared spectrum of II are shown in Table II. The ultraviolet and visible spectra of II are given in Table I. The ester showed a reddish-orange fluorescence in ultraviolet light. Considering the red color of crystalline II and the orange color of crystalline I, a larger difference in λ_{max} might have been expected. However, I was also obtained as a red polymorphic form; two forms of II were not obtained.

Oxidation of II by action of bromine in chloroform gave the quinone diimide XIV as orange yellow needles melting at 159–160°. The significant bands in the infrared spectrum of XIV are shown in Table II. The ultraviolet and visible spectra of XIV are given in Table I. There was a marked difference in the color of the two crystalline quinone diimides XII (orange-red) and XIV (orange-yellow). The values of λ_{max} and ϵ in the visible spectra of the two compounds are, however, almost identical. The difference in visible color might possibly be explained by polymorphism, that is, one form of XII and the other form of XIV were in hand, but no experimental evidence was accumulated to verify this supposition.

DISCUSSION

On the basis of the facts presented above and in the experimental section, it can be concluded that the pure diamino esters I and II, and the dibenzoyl compound XIII are colored, that they possess the structures assigned to them, and that the color does not arise from the presence of any impurities or from the presence of any quinhydrones formed from the diamino and diimino compounds. Assuming that compounds III, IV, V, VI, VII, VIII, and XI, as reported in the literature, also have the structures assigned to them and are colored, whereas compound IX is colorless, the question arises as to the cause of the striking and often deep color of these compounds. The color must involve some interaction between the nitrogen atom(s) with the lone pair(s) of electrons, and the carboxyl or ester groups. The number of possible resonance forms involving such interactions in these compounds, such as XV etc. for II, (exclusive of those involving hydrogen bonding) together with the color of the compounds, is shown in Table III.

TABLE III

NUMBER OF RESONANCE FORMS

Esters	Number of Resonance Forms	Color of Solid
I	8	Orange-red
II	8	Red
V	5	Yellow
VI	3	Orange-red, dimorph yellow
VIII	2	Yellow
Acids		
III	3	Brown, → black > 200°
IV	5	Pink
VII	3	Greenish-yellow
IX	2	Colorless
X	2	Unknown
XI (Monoacetyl X)	2	Brown

From the table it appears that for color, at least three resonance forms of this sort must be possible, and in general, the more resonance forms possible, the deeper the color. If the esters I, II, V, VI, and VIII are considered as one group, and the acids III, IV, VII, IX, X, and XI are considered as another group, the change in color with increasing number of resonance forms is shown clearly by each group.

That the ability of the nitrogen atom to function as an electron donor is connected with the color is shown by the fact that the hydrochloride of I is colorless, and is also indicated by a consideration of the oxygen analogs of these compounds, many of which have been described in the literature. Oxygen is not as powerful a donor atom as is nitrogen, therefore it would be expected that the oxygen analogs would be less deeply colored, and this is, indeed, the case. The hydroquinones corresponding to I and II are known;[2,15–17] that corresponding to I is light yellow and melts at 207° (this is also the melting point reported for the quinone); that corresponding to II is reported to crystallize in two forms: "yellowish-green needles" and "bright yellow grains". The needles "change" at 111–115°, then melt at 133.2–133.6°; the "grains" change at 64°, begin to melt at 123–124°, then partially solidify and finally melt at 128.5°. The quinone corresponding to II melts at 148–149°. The monomethyl ether of the hydroquinone corresponding to II[9,18] forms a sodium salt which is yellow with a green fluorescence. All the other dervatives of these hydroquinones—dimethyl ether, diacetate, dibenzoate—are colorless. Hydroquinone tetracarboxylic acid crystallizes with water of crystallization and forms yellow needles which decompose at 150°.[19] None of these compounds shows the deep orange and red colors of I and II. The acids in Table III are not as deeply colored as the esters; this would be expected because ionization of the carbonyl group(s) would make more difficult any type of resonance in which the carbonyl oxygen atom acts as an acceptor.

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(15) H. v. Pechmann and L. Wolmann, *Ber.*, **30,** 2570 (1897).

(16) J. U. Nef and W. Muthmann, *J. Chem. Soc.*, **53,** 449 (1888).

(17) J. U Nef, *Ann.*, **258,** 318 (1890).

(18) J. U. Nef, *Ann.*, **258,** 289 (1890).

(19) J. U. Nef, *Ann.*, **237,** 33 (1887).

EXPERIMENTAL[20]

Dinitropyromellitic acid. A solution of potassium carbonate (65.6 g., 0.475 mole) and dinitrodurylic acid (30 g., 0.118 mole) in water (3 l.) was heated on a steam bath while potassium permanganate (117.5 g., 0.744 mole) was added with stirring. Heating was continued for 8 days. Manganese dioxide was removed by filtration and the yellow filtrate was concentrated to a volume of 500 cc. and acidified strongly with hydrochloric and sulfuric acids. The solution was then extracted with six 100-cc. portions of ether, the extracts were combined and evaporated, leaving the white crystalline acid. This was dissolved in water (200 cc.) and converted into the calcium salt by addition of calcium carbonate until there was no further reaction. Ethanol (250 cc.) was added, whereupon the yellow calcium salt (A) separated. This was removed and set aside and the filtrate was evaporated to obtain the calcium salts of tribasic and other acids (B). The salts B were dissolved in water, the solution was strongly acidified and extracted with ether. Removal of the ether left 8 g. of light yellow material, which was again oxidized as described above by action of permanganate (10 g.) in water (200 cc.) containing potassium carbonate (10 g.). This reaction mixture was processed as above and the calcium salt of the tetrabasic acid was combined with A. The combined calcium salts were partially dissolved in water (400 cc.), reprecipitated by addition of ethanol, again partially dissolved in water (250 cc.) and this mixture was strongly acidified and extracted with five 100-cc. portions of ether. The product, obtained by evaporation of the ether, weighed 30.4 g. (74.7%) and melted at 225–230° (dec.).

Tetramethyl ester. Diazomethane was prepared from nitrosomethylurea, according to Arndt.[21] The above acid (20 g.) was added to an ethereal solution of excess diazomethane and the reaction mixture was allowed to stand for 2 hr. The solvent and excess reagent were removed, and the slightly yellow residue was triturated with methanol (50 cc.) and filtered. The crude ester (20.2 g., 90%) melted at 176–178°. Three recrystallizations from methanol-acetone gave a material (14 g.) melting at 179–180°. The analytical sample, recrystallized four times from methanol, melted at 181.8–182.8°.

Anal. Calcd. for $C_{14}H_{12}O_{12}N_2$: C, 42.01; H, 3.02; N, 7.00. Found: C, 42.20; H, 3.30; N, 6.84.

The infrared spectrum of this ester showed absorption bands consistent with the structure assigned to it.

Tetraethyl ester. Diazoethane was prepared from nitrosoethylurethane according to Wilds and Mender.[22] Excess ethereal diazoethane was added to the solid acid (3 g.) and the mixture was allowed to stand overnight at room temperature. The solution was then extracted once with aqueous sodium bicarbonate (100 cc., 2%) and the ether was removed. The residue of ester (2.66 g., 66%) melted at 134.5–135.5°. The analytical sample, crystallized twice from ethanol, melted at 135.5–136°.

Anal. Calcd. for $C_{18}H_{20}O_{12}N_2$: C, 47.37; H, 4.42; N, 6.14. Found: C, 47.56; H, 4.70; N, 6.10.

The infrared spectrum of this ester showed absorption bands consistent with the structure assigned to it.

Reduction of dinitropyromellitic acid. Iron filings (0.5 g., 20 mesh, degreased), water, and acetic acid (0.1 cc.) were heated on the steam bath and a solution of the acid (0.5 g.) in water (10 cc.) was added. The mixture became red immediately; it was heated for 20 min., filtered, and the filtrate was extracted several times with ether. Removal of the ether left only a small amount of red material; the red diaminopyromellitic acid was not isolated from the aqueous layer.

Tetramethyl diaminopyromellitate (I). The tetramethyl dinitro ester (3.134 g., 0.008 mole) was dissolved in acetic acid (30 cc.) and water (0.5 cc.). To the hot solution (steam bath), zinc dust (9.8 g.) was added in small portions over 20 min. The mixture was heated for 10 min., then filtered hot. The insoluble material was washed with three 5-cc. portions of hot acetic acid, and the combined filtrate and washings were poured into water (90 cc.). The product (1.5 g., 56%) was removed; it melted at 148–149°. After three recrystallizations from methanol, the ester melted at 149.4–151°. A column (1.5 × 20 cm.) was packed with alumina (45 g.) wet with petroleum ether (redistilled, b.p. 80–100°), and a solution of I (0.307 g.) in chloroform (30 cc.) was poured into the tube. The column was developed and eluted with petroleum ether–chloroform mixtures, increasing in chloroform content from 5 to 45% (volume). The eluate was separated into three fractions in order A, B, C. A yielded I (0.075 g.) as orange needles melting at 149.6–150.6° after one crystallization from methanol. B and C likewise yielded I (0.128 g.), but along with the orange form melting at 150–151°, there was obtained a small amount of the red form (separated mechanically) which was converted to the orange form at 120–130° and then melted at 149–150°. The sample melting at 150–151° was analyzed.

Anal. Calcd. for $C_{14}H_{16}O_8N_2$: C, 49.41; H, 4.74; N, 8.23. Found: C, 49.55; H, 4.72; N, 8.30.

The significant bands in the infrared spectrum of this material are given in Table II; the ultraviolet and visible spectra are given in Table I. A solution of the ester I in chloroform, when subjected to action of hydrogen chloride gas, deposited a white hydrochloride. When the white solid was removed by filtration, it was immediately transformed into the orange I on contact with the air.

Tetramethyl N,N'-dibenzoyldiaminopyromellitate (XIII). The ester I (1.6 g.) was suspended in aqueous sodium hydroxide (30 cc., 10%) containing benzoyl chloride (4 cc.). The mixture was stirred and heated (steam bath) for 15 min. The cooled mixture was filtered, and a small amount of ether (2 cc.) was poured over the precipitate on the filter. The remaining yellow solid melted at 185–190° and was the monobenzoyl compound. This, when benzoylated again, gave the dibenzoyl derivative XIII. Both compounds were recrystallized several times from dimethylformamide. The dibenzoyl derivative XIII formed slightly yellow needles melting at 264–266° (dec.).

Anal. Calcd. for $C_{28}H_{26}O_{10}N_2$: C, 61.09; H, 4.76; N, 5.09. Found: C, 61.11; H, 4.41; N, 5.14.

The significant bands in the infrared spectrum of XIII, and the monobenzoyl derivative, are given in Table II; the ultraviolet absorption spectrum of XIII is given in Table I.

Several attempts to oxidize XIII to a dibenzoylquinone diimide by action of lead tetraacetate in acetic acid, as described below for preparation of XII led only to recovered XIII.

The monobenzoyl derivative, crystallized several times from dimethylformamide, melted at 194.5–195.5° and formed greenish-yellow needles.

Anal. Calcd. for $C_{21}H_{20}O_9N_2$: C, 56.75; H, 4.54; N, 6.30. Found: C, 57.18; H, 4.94; N, 6.39.

Tetracarbomethoxy-p-quinonediïmide (XII). (A) The diaminoester I (0.19 g., 0.00056 mole), lead tetraacetate (0.375 g., 0.00085 mole) and acetic acid (10 cc.) were placed in a pear-shaped flask fitted with a stirrer and a reflux condenser protected by a calcium chloride drying tube. The mixture was stirred and heated at 130° for 45 min. The deep red mixture was filtered and the filtrate was poured into water (30 cc.). The product (0.05 g., 26%) was removed, dried, and crystallized three times from dimethylformamide, when it formed orange-red prisms melting at 260–261°.

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(20) All melting points were determined on a Kofler micro hot-stage apparatus, and are therefore corrected. Boiling points are uncorrected. Microanalyses by J. H. Cooley, C. B. Koons, and R. L. Lange. Spectrographs by the spectrophotometric laboratory of the School of Chemistry of the University of Minnesota.

(21) F. Arndt, *Org. Syntheses*, **15**, 3, 48 (1935).

(22) A. L. Wilds and A. L. Mender, Jr., *J. Org. Chem.*, **13**, 768 (1948).

(B) The diaminoester I (0.2 g., 0.0006 mole) was dissolved in chloroform, and bromine (0.2 g.) was added. Insoluble material separated at once; the mixture was allowed to stand overnight in an open beaker, when there remained a mixture of red and yellow solids melting at 146–151°. This material was washed with water (30 cc.), dried, again taken up in chloroform (15 cc.) and treated with bromine 0.4 g.). The reaction mixture was allowed to stand for two days, and the solid residue was washed with water (30 cc.) and hot methanol (15 cc.), and then extracted with hot dimethylformamide (10 cc.). The extract was diluted with water and centrifuged. The solid, crystallized four times from dimethyl formamide-water, formed orange-red crystals, weighed 0.05 g. (24%) and melted at 260–261°, alone or when mixed with the product from A above.

Anal. Calcd. for $C_{14}H_{14}O_8N_2$: C, 49.71; H, 4.17; N, 8.28. Found: C, 49.63; H, 4.34; N, 7.50, 8.14.

The significant bands in the infrared spectrum of XII are given in Table II; the ultraviolet and visible spectra are given in Table I.

Equimolar quantities of I and XII were dissolved in hot acetic acid. When the solution was cooled, it deposited two types of crystals, and the mixture melted at 155–258°. In another experiment, but with benzene as the solvent, the same result was obtained. Six mixtures of I and XII, from 92% I and 8% XII to 16% I and 84% XII were studied as to melting point behavior on a Kofler micro hot-stage apparatus. The melting point diagram, given in Figure 1, shows that no compound is formed when mixtures of I and XII are melted. In the figure, the points on the dotted line represent the temperatures at which melting began; those on the solid line represent the temperatures at which melting was complete.

Tetraethyl diaminopyromellitate (II) (1.033 g., 60.5%) was prepared by reduction of the dinitro ester (0.96 g.) in acetic acid (20 cc.) by action of zinc dust (6.02 g.), essentially as described for the preparation of I. The product, crystallized three times from ethanol, formed red prisms melting at 138–138.5°. The analytical sample, crystallized three times again from ethanol, melted at 138.0–138.5°.

Anal. Calcd. for $C_{18}H_{24}O_8N_2$: C, 54.54; H, 6.10; N, 7.07. Found: C, 54.56; H, 6.14; N, 7.08.

The significant bands in the infrared spectrum of II are given in Table II; the ultraviolet and visible spectra are given in Table I.

Tetracarbethoxy-p-quinonediimide (XIV) (0.094 g., 46.5%) was prepared from II (0.203 g.) in chloroform (10 cc.) by action of bromine (0.4 g.) essentially as described for the preparation of XII (B) above, including retreatment of the crude product with bromine. The product was crystallized five times from ethanol, and then formed orange-yellow needles melting at 159–160°.

Anal. Calcd. for $C_{18}H_{22}O_8N_2$: C, 54.82; H, 5.62; N, 7.10. Found: C, 54.52; H, 5.66; N, 7.23.

The significant bands in the infrared spectrum of XIV are given in Table II; the ultraviolet and visible spectra are given in Table I.

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