

XXXVI.—*Carboxyl-derivatives of Benzoquinone.*

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CHLORO-, bromo-, hydroxy-, nitro-, and amido-derivatives of benzoquinone have long been known, but attempts to obtain carboxyl-derivatives have hitherto been unsuccessful.

The following experiments, undertaken with the intention of filling up this gap, were carried out at the suggestion of Prof. v. Baeyer, and it is an especial pleasure to the author to have this opportunity of expressing his gratitude to Prof. v. Baeyer for the kindness and interest shown him during his stay in Munich.

Durene was chosen as the starting-point for the experiments, on account of the especial interest attaching to the production of quinone-tetracarboxylic acid, $C_{10}H_4O_{10} = C_6O_2(COOH)_4$, which has the same percentage composition as croconic acid, $C_8H_2O_8$, one of the products obtained by Gmelin (*Gmelin, Handbuch*, 4 Aufl., 5, 478) from the explosive bye-product formerly obtained in the preparation of potassium.

The Russian chemist, Basaroff (*Dict. de Chemie par Würtz*, 2, 1363), expressed the opinion that croconic acid and quinone-tetracarboxylic acid were identical, but very recently Nietzki and Benckiser (*Ber.*, 19, 293, 772), by a series of remarkable experiments, have shown that croconic acid has the formula $C_8H_2O_8$, thus rendering it impossible that it can be identical with a derivative of benzene. The following synthesis of ethylic quinonetetracarboxylate confirms the conclusion that the two compounds are totally different.

A close investigation of ethylic quinonetetracarboxylate has led to the discovery of a series of compounds which stand in a remarkably close relation to ethylic succinosuccinate and its derivatives. A study of durylic-acid-quinone, $C_6O_2(CH_3)_3 \cdot COOH$, has shown that carboxylated quinones are very unstable substances, and that the carboxyl-group, which is usually so stable in benzene-derivatives, can easily be displaced by other groups; the nitro-group, for example. On the whole, however, they exhibit the general chemical reactions characterising other quinone-derivatives. On reduction, they take up two atoms of hydrogen, forming colourless quinols, which on oxidation yield the original quinone.

A very noteworthy fact is the existence of many carboxyl-paradihydroxy-derivatives of benzene, which cannot under any conditions be oxidised to the corresponding quinones. The oxidation to a

* Compare *Annalen*, 237, 1.

quinone can only be accomplished in the case of hexa-substituted benzene-derivatives, which in this respect exhibit a much greater stability than other incompletely substituted derivatives of benzene.

The durenene used was obtained from the chemical factory of Langfeld and Reuter, Bramow, near Rostock, and was made from monobromopseudocumene, $C_6H_2(CH_3)_3Br$ [1 : 2 : 4 : 5] (m. p. 71°), by Fittig's method. It was not pure, as the boiling point ranged from 185° to 220° , and contained, moreover, a liquid boiling at about 170° , and a solid compound melting at 100° , and boiling at 240° .

Durylic acid was prepared from pseudocumidine, $C_6H_2(CH_3)_3 \cdot NH_2$ [1 : 2 : 4 : 5], by Sandmeyer's method of displacing the amido- by the cyanogen-group (Haller, *Ber.*, **18**, 93). Although the yield of duronitrile is poor (10—15 per cent.), and the preparation of the acid therefore wearisome, this is by far the best method of making durylic acid, and the product obtained is pure (m. p. 149°). As pseudocumidine is now much used in the colour industry in making azo-dyes, and, therefore, easily procurable, I have recently tried to better the yield of duronitrile by modifying Sandmeyer's method somewhat. Cuprous cyanide was used, the solution in potassic cyanide being kept boiling over a flame, while the diazo-pseudocumene solution was added. After extracting with ether, washing the ethereal solution with dilute sodic hydrate and sulphuric acid, and distilling off the ether, the nitrile was distilled over with steam. It was thus obtained pure, fusing at 57.5° . It can be saponified quantitatively by heating it with concentrated hydrochloric acid (1.18) in a sealed tube at 160 — 170° . The yield thus obtained was about 50 per cent., which is far better than that afforded by the usual method.

The course pursued in the investigation was the following:—The durenene was converted by the usual methods into duroquinone, $C_6O_2(CH_3)_4$. As attempts to oxidise the methyl-groups to carboxyl-groups were unsuccessful, the durenene was used solely to make durylic acid which on nitration gives dinitrodurylic acid; this acid was then converted into durylic-acid-quinone and pyromellithic-acid-quinone.

I. Duroquinone from Durenene.

Dinitro-durenene was made according to Jannasch and Fittig's method (*Zeit. f. Chem.*, 1870, 161). The durenene (5 grams) was added slowly to pure fuming nitric acid (1.49), 40 c.c., kept at a temperature below 0° . The substance rotates rapidly, and then dissolves with a passing deep-brown coloration. After allowing the mixture to remain for two hours, it is poured on to ice, when the dinitro-durenene separates out as a white flocculent precipitate. By crystallisation from alcohol, it can be separated from an oily by-product,

and obtained in colourless prisms melting at 205° . It has all the properties ascribed to it by Jannasch and Fittig; it dissolves easily in benzene and ether, sparingly in hot, and very little in cold alcohol. It sublimes without decomposition in needles, and volatilises with steam. It is unusually stable in the presence of oxidising agents; dilute nitric acid, or a mixture of 1 vol. glacial acetic acid, 1 vol. concentrated nitric acid, and 1 vol. of water (in which the substance dissolves), not having the slightest action on it.

Dinitrodurel is best reduced as follows:—A hot solution of the substance in acetic acid is treated with zinc-dust until it no longer gives any turbidity on addition of water. The zinc is then precipitated from the diluted solution with sulphuretted hydrogen, and the filtrate concentrated. On addition of sodic hydrate, diamidodurene is precipitated in colourless pearly plates; this was not analysed, but converted directly into duroquinone. It is easily soluble in chloroform and alcohol; less so in ether. When exposed to the air in solution, or in a moist condition, it turns green. The hydrochloride of the base is sparingly soluble in concentrated hydrochloric acid. An aqueous solution thereof treated in the cold with ferric chloride, platonic chloride, or sodic nitrite is oxidised to duroquinone. In the case of platonic chloride, the addition of alcohol precipitates ammonium platinochloride, whilst duroquinone remains in solution, $C_6(CH_3)_4(NH_2Cl)_2 + H_2PtCl_6 + 2H_2O + O = C_6(CH_3)_4O_2 + (NH_4)_2PtCl_6 + 2HCl + H_2O$. A similar easy elimination of the amido-groups with formation of a quinone was also observed in the case of diamidodurylic acid.

The duroquinone was made by treating a solution of diamidodurene in hydrochloric acid with an excess of ferric chloride in the cold. A temporary deep-green coloration is noticed, and then the solution becomes yellow and the quinone crystallises out in yellow needles. The yield is almost quantitative and the product obtained is pure. If the diamidodurene is not isolated after the reduction with zinc-dust, and the ferric chloride is added directly to the acetic acid solution (from which the zinc has been removed), the quinone is obtained in small quantity as a very dark-coloured impure product.

Duroquinone was obtained by crystallisation from light petroleum in beautiful, long, yellow needles, melting at 111° .

0.1220 gram substance dried in a vacuum gave 0.3259 gram CO_2 and 0.0815 H_2O .

	Calculated for $C_6(CH_3)_4O_2$.	Found.
C	73.18	72.86
H	7.32	7.42

The quinone is volatile with steam, and sublimes at 100° in needles,

which possess a feeble but distinct odour characteristic of quinone. It is very easily soluble in alcohol, ether, chloroform, and in hot light petroleum; insoluble in water or alkalis. It was not possible under any condition to oxidise the methylated side-chains to carboxyl; oxidising agents in alkaline, neutral, or acid solution, decomposed the benzene ring completely. Worthy of note is the great stability of duroquinone in the presence of concentrated nitric acid (1.4), in which it dissolves with ease, but even after long heating on a water-bath remains in great part unchanged.

Treated with zinc-dust and acetic acid, the quinone is reduced, and on adding water, a colourless substance melting at about 210° is precipitated. Oxidising agents, such as ferric chloride or nitric acid, oxidise it again to duroquinone. It is probable that the substance is dihydroxydurene, but want of material has prevented me from obtaining the product in amount sufficient for an analysis.

II. Dinitrodurylic Acid out of Durol.

Durylic Acid, $C_6H_2(CH_3)_3COOH$.—Jannasch (*Zeit. f. Chem.*, 1870, 449, and 1871, 33) has shown that durene heated for a long time with dilute nitric acid, yields, in about equal amount, two acids, one of which, durylic acid, $C_6H_2(CH_3)_3COOH$, is volatile with steam; the other, cumidic acid,* $C_6H_2(CH_3)_2(COOH)_2$, is not volatile with steam. In my experiments, however, the great object was to obtain as much of the durylic acid as possible. When durene is heated with dilute nitric acid for three or four hours only, and the acid formed is then separated from unchanged durene, I find that durylic acid alone is formed. Durylic acid is also the sole oxidation-product obtained on treating a solution of durene in acetic acid with the calculated amount of chromic acid also dissolved in acetic acid. The yield in this case is, however, not so good as when the following method is employed.

20 grams durene is heated for three to four hours, with 500 c.c. dilute nitric acid (1 vol. concentrated nitric acid, sp. gr. 1.4, to 3 vols. water), taking care to add a few pieces of porous porcelain to prevent bumping. After filtering from the nitric acid, the product is treated with dilute sodium carbonate solution and the unchanged durene heated again with nitric acid as above. After the second and third treatment with sodium carbonate an insoluble yellowish oil remains which can easily be separated from the soda solution by means of ether. On distilling off the ether, an oil is left which contains nitrogen and undergoes little change on further heating with nitric acid.†

* This has recently been shown to consist of two isomeric acids (Schnapauff, *Ber.*, 19, 2510).

† The oil has a peculiar camphor-like odour, and is very easily soluble in ether.

On adding hydrochloric acid to the mixed sodium carbonate solution, impure durylic acid separates as a flocculent precipitate. It is first treated in acetic acid solution with zinc-dust, to get rid of the nitro-products possibly formed, and then distilled with steam. As the whole is volatile with steam, there can be no bibasic cumidic acid formed. The durylic acid thus driven over with steam is pure, melting at 149° , and has all the properties assigned to it by Jannasch (*Zeit. f. Chem.*, 1870, 449).

It is very sparingly soluble even in boiling water and volatilises with steam without melting. The yield obtained by the above method was 15–20 grams of impure durylic acid and 20–22 grams of oily bye-product from 40 grams of durenene. In the further experiments, the impure durylic acid, obtained on adding hydrochloric acid to the soda solutions, was used.

(2.) *Dinitrodurylic Acid*, $C_6(NO_2)_2(CH_3)_3COOH$.—The nitration of durylic acid, according to Gissmann's method, was not found advantageous, as the reaction is too violent. The following process gives a quantitative yield:—20 grams finely pulverised durylic acid (dried at 100°) is dissolved in pure concentrated sulphuric acid, and the solution cooled down to -10° or -15° by means of a freezing mixture. A solution of 28 grams potassic nitrate in concentrated sulphuric acid is now added as quickly as possible—taking care to stir well, and to keep the temperature below 5° .

A deep brown colour appears at first which changes finally to light yellow, while dinitrodurylic acid partly separates. After allowing the mixture to remain at the ordinary temperature for four or five hours, or over night, the solution is poured carefully on to ice. The nitro-acid separates out as a flocculent, yellowish precipitate which is collected and well washed. If pure durylic acid is used, the product thus obtained is sufficiently pure; if, however, the impure acid is employed, the nitro-derivative must be purified by means of its calcium salt. (Gissmann, *Annalen*, **216**, 208.)

The crude product is heated with water and finely pulverised marble until the reaction is neutral; on filtering and concentrating, the calcium salt crystallises out in colourless, radiating needles. When heated on platinum-foil, it explodes violently.

An analysis of the oil, as well as of a solid product obtained therefrom by cooling below 0° and pressing between filter-paper (melting point $35-40^{\circ}$), gave figures agreeing with those required by mononitrodurenene. The oil, however, does not yield dinitrodurenene on treatment with fuming nitric acid, and it is therefore more probable that the oil is a nitrate of a trimethylated benzyl alcohol. This is the more probable as, by oxidation with potassium permanganate in soda solution, acids are obtained which contain no nitrogen. In this way I succeeded in isolating an acid possessing all the properties of pyromellitic acid, and the analysis of the silver salt gave figures which are exactly those required by $C_6H_2(COOAg)_4$.

0.3155 gram substance dried at 180° gave 0.0760 gram $\text{CaSO}_4 = 7.10$ per cent. calcium; calculated, 7.32 per cent.

The free acid, obtained by the addition of hydrochloric acid to the purified calcium salt, is a yellowish, amorphous powder melting at about 205° . It has all the properties mentioned by Gissmann (*loc. cit.*).

The potassium salt is sparingly soluble in cold water, and crystallises in colourless, lustrous needles.

III. Durylic Acid Quinone from Dinitrodurylic Acid.

(1.) *Diamidodurylic Acid*, $\text{C}_6(\text{NH}_2)_2(\text{CH}_3)_3\text{COOH}$.—A solution of dinitrodurylic acid in acetic acid (50 per cent.) is treated with zinc-dust in small portions; a violent reaction takes place at first, and finally the solution becomes colourless. After filtering hot from the excess of zinc-dust, the solution is diluted with about 4 volumes of water and allowed to cool, when the diamidodurylic acid crystallises out almost completely in colourless, silky needles. The small portion remaining in solution is recovered by precipitating the zinc, concentrating the ammoniacal solution, and adding dilute acetic acid. The yield is almost quantitative.

For analysis, the substance was crystallised from water several times, and then dried carefully at 110° .

0.1642 gram anhydrous substance gave 0.1105 gram H_2O and 0.371 gram CO_2 .

0.0950 gram anhydrous substance gave 12 c.c. nitrogen at 15° and 723 mm.

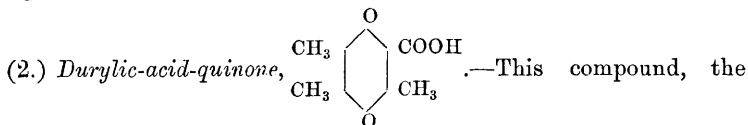
	Calculated for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2$.	Found.
C	61.85	61.62
H	7.22	7.48
N	14.42	14.10

The figures obtained for carbon were at first always about 1 per cent. too low, because the substance sticks together on heating, and it is difficult to remove the last trace of water of crystallisation.

Diamidodurylic acid forms salts with bases and with mineral acids. The compounds with hydrochloric acid and with sulphuric acid are easily soluble in water. On adding platinic chloride to a solution of the hydrochloride in the cold, ammonium platinochloride separates and durylic-acid-quinone is formed. The oxidation to the quinone also takes place with equal ease on treatment with ferric chloride or sodic nitrite.

Diamidodurylic acid is sparingly soluble in cold alcohol or water; much more soluble in hot; it is insoluble in ether. It melts at 221°

with decomposition. When heated with acetic anhydride for several hours at 140° , an acetyl-derivative was formed. After getting rid of the acetic anhydride, the substance was dissolved in ammonia, and precipitated therefrom by hydrochloric acid; in this way, it was precipitated in colourless quadratic plates melting at about 275° . When heated in a test-tube, the substance loses carbonic anhydride, and a compound sublimes in colourless needles; it is insoluble in alkalis.



first carboxylated quinone-derivative known, is formed quantitatively on adding an excess of ferric chloride to a solution of pure diamido-durylic acid in hydrochloric acid, and allowing the mixture to remain for about half an hour. No colour reactions are noticed, but the yellow solution has a faint but distinct quinone-like odour. If the solution is sufficiently concentrated, part of the acid crystallises out in yellow rhombohedrons. The solution is extracted three or four times with ether, and the ether dried with calcium chloride; after distilling off part of the ether and allowing the remainder to evaporate spontaneously, the quinone acid remains as a dark-yellow, crystalline substance having a distinct quinone odour.

If the above directions are carefully followed, it is only necessary to wash away the traces of adhering ferric chloride with a little water in order to obtain a perfectly pure product. On heating with ferric chloride, or on trying to convert dinitrodurylic acid directly into the quinone without isolating the diamido-compound, a very impure yellow, oily product is obtained.

The crystals obtained from the ethereal solution are radiating flat needles of a deep yellow colour. Heated in a capillary tube, they become red at $127\text{--}129^{\circ}$, and decompose at 130° with brisk evolution of gas.

- I. 0.1340 gram substance dried in a vacuum gave 0.3038 gram CO_2 and 0.065 gram H_2O .
- II. 0.1540 gram substance dried in a vacuum gave 0.346 gram CO_2 and 0.076 gram H_2O .

		Found.	
		I.	II.
Calculated for			
$\text{C}_6\text{O}_2(\text{CH}_3)_3\cdot\text{COOH}$.			
C	61.85	61.83	61.68
H	5.15	5.40	5.52

Durylic-acid-quinone dissolves easily in alcohol and in other organic solvents, except light petroleum. It is sparingly soluble in cold

water, more soluble in hot water (the quinone odour is then especially noticeable), but does not crystallise out well on cooling. It dissolves in benzene in the cold unchanged, but, on heating, the yellow solution changes to an intense dark red. Durylic-acid-quinone differs from other quinones in being non-volatile and easily decomposed. Being an acid it decomposes soluble carbonates in the cold, and dissolves in alkalis and in ammonia with a deep yellow colour. The alkaline solutions can be partly evaporated without change. In other respects, the quinone acid resembles the other paraquinone compounds of benzene; thus, for example, it can be reduced in alkaline or acid solution to the corresponding quinol or paradihydroxy-compound which on oxidation yields the original quinone compound again.

An intermediate compound corresponding to quinhydrone was not noticed. Like quinone itself, the above quinone acid reacts with phenol and resorcinol, forming dark-red compounds.

On allowing a dilute alcoholic solution of the quinone acid to stand for two days with an excess of hydroxylamine hydrochloride, a yellow unstable compound containing nitrogen is formed; this is probably the quinoneoxime.

Of the salts of durylic-acid-quinone, the silver salt was prepared by adding silver nitrate to a concentrated solution of the neutral ammonium salt. It was thus obtained in yellow needles, little soluble in cold water, more so in hot. It is unstable towards heat and light, and explodes when heated quickly on platinum foil.

0.146 gram substance dried in a vacuum gave 0.041 gram H_2O , 0.2125 gram CO_2 , and 0.0525 gram Ag.

	Calculated for $C_6O_2(CH_3)_3 \cdot COOAg$.	Found.
C.....	39.87	39.70
H	2.99	3.12
Ag	35.88	35.96

A concentrated solution of the ammonium salt of durylic-acid-quinone treated with *lead acetate* gives the lead salt as an insoluble yellow amorphous precipitate. *Baric chloride* gives the barium salt as a yellow crystalline precipitate, dissolving on heating. *Copper sulphate* gives the copper salt as a pale-yellow, sparingly soluble granular precipitate.

(3.) *Dihydroxydurylic Acid*, $C_6(OH)_2(CH_3)_3 \cdot COOH$.—Durylic-acid-quinone can be reduced quantitatively in alkaline or acid solution to dihydroxydurylic acid. In my first experiments, I used zinc-dust and sodic hydrate. A dilute solution of the substance in sodic hydrate was treated in the cold with zinc-dust added in small portions at a

time. The solution turns green, then violet, and finally becomes colourless; it is then acidified with concentrated hydrochloric acid, and extracted with ether. On distilling off the ether, a white amorphous mass remains, having a characteristic sweet smell. This method of reduction is uncertain on account of the instability of dihydroxydurylic acid in alkaline solution, and it is much better to reduce with sulphurous acid, which at once gives a pure product. On adding a concentrated cold aqueous solution of sulphurous acid to finely pulverised durylic-acid-quinone and shaking, the whole mass is converted into dihydroxydurylic acid without dissolving; in order to obtain a colourless product, the mixture is heated in a sealed tube at 100° for two to three hours, and then repeatedly crystallised out of water containing sulphurous acid. Dihydroxydurylic acid is thus obtained in colourless spheres, made up of very fine radiating needles; it melts at 210° with decomposition.

I. 0.1432 gram substance dried at 110° gave 0.3208 gram CO_2 and 0.084 gram H_2O .

II. 0.1556 gram substance dried at 110° gave 0.3485 gram CO_2 and 0.089 gram H_2O .

	Calculated for $\text{C}_6(\text{OH})_2(\text{CH}_3)_3\text{COOH}$.	Found.	
		I.	II.
C.....	61.27	61.10	61.08
H	6.13	6.52	6.36

This quinol dissolves easily in alcohol and ether, sparingly in benzene and chloroform. Ferric chloride added to a dilute alcoholic solution oxidises it, with passing green coloration, to the quinone. The colourless alkaline solution of the acid is unstable when exposed to the air, changing quickly to a yellow, red, red-violet, and finally to a deep violet. An ammoniacal solution of the acid reduces silver nitrate in the cold. Lead acetate, added to a solution of the ammonium salt, gives a colourless amorphous precipitate.

(4.) *Ethyl quinonedurylate*, $\text{C}_6\text{O}_2(\text{CH}_3)_3\text{COOC}_2\text{H}_5$, was made by allowing the silver salt of durylic-acid-quinone to stand for 24 hours with a dry ethereal solution of ethyl iodide. The ethereal solution, filtered from the silver iodide, was washed with sodic carbonate, and dried by means of calcic chloride. After distilling off the ether, a yellow oil remained, which, on rubbing with a glass rod, solidified readily to yellow radiating needles. On recrystallisation from hot light petroleum, it was obtained in long yellow needles melting at 51° .

0.1225 gram substance dried in a vacuum gave 0.0706 gram H_2O and 0.2902 gram CO_2 .

	Calculated for $C_6O_2(CH_3)_3COOC_2H_5$.	Found.
C.....	64.86	64.61
H	6.31	6.40

The ethereal salt, unlike the free acid, is odourless. Like other quinones, it sublimes with ease, and without decomposition. It is easily soluble in alcohol and ether; insoluble in water or alkalis. It is saponified when heated with sodic hydrate.

(5.) *Ethyl Dihydroxydurylate*, $C_6(OH)_2(CH_3)_3COOC_2H_5$.—On heating ethyl quinonedurylate with a concentrated aqueous solution of sulphurous acid it is reduced, and on cooling ethyl dihydroxydurylate crystallises out in needles. The substance may be purified by dissolving it in alcohol and adding water containing sulphurous acid to the hot alcoholic solution. It is thus obtained in colourless, broad needles melting at 109° , and having a characteristic sweet smell.

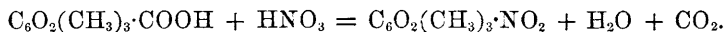
0.0935 gram substance dried in a vacuum gave 0.2185 gram CO_2 and 0.06 gram H_2O .

	Calculated for $C_6(OH)_2(CH_3)_3COOC_2H_5$.	Found.
C.....	64.29	63.73
H	7.14	7.13

The ethereal salt is soluble in alcohol and other organic solvents except light petroleum. It is somewhat soluble in cold water; much more so in hot. It dissolves in sodic hydrate, forming a colourless solution; on heating, however, hydrolysis occurs and the colour of the solution changes to deep violet.

In alcoholic solution, ferric chloride oxidises it to the quinone with passing green coloration. Nitric acid (sp. gr. 1.4) also oxidises it to the quinone. An intermediate product corresponding to quinhydrone was not noticed.

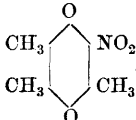
(6.) *Action of Concentrated Nitric Acid on Durylic-acid-quinone*.—Durylic-acid-quinone dissolves without change in nitric acid (sp. gr. 1.4) in the cold. On heating on a water-bath, however, a strong evolution of gas is observed. The addition of water now precipitates a beautiful, yellow, crystalline substance which is insoluble in alkalis, and therefore no longer an acid. Further investigation has shown that the carboxyl-group of durylic-acid-quinone has been displaced, and, in fact, quantitatively, by a nitro-group, according to the reaction:—



The resulting compound, nitropseudocumoinone, is one of the most stable of quinone compounds.

By heating durylic-acid-quinone with alcoholic ammonia in a sealed tube at 100°, the elements of carbon dioxide are removed, and a deep-red solution is obtained. Want of material has prevented me thus far from investigating the product more closely.

These observations are in harmony with those of Hermann (*Annalen*, **211**, 343) in the case of paradihydroxyterephthalic acid. The latter when treated with concentrated nitric acid gives no terephthalic-acid-quinone, but 2 mols. CO₂ are eliminated in the cold with formation of nitranilic acid. All these facts go to show that the carboxyl-group in carboxylated quinone-compounds is very loosely bound.

Nitropseudocumolquinone, , is formed quantitatively on

heating durylic-acid-quinone on a water-bath for about half an hour with nitric acid (sp. gr. 1·4) until the evolution of carbonic anhydride ceases. On adding water, the quinone separates out completely and crystallises in yellow plates melting at 113°.

0·1485 gram substance dried in a vacuum gave 0·3023 gram CO₂ and 0·0655 gram H₂O.

0·230 gram substance dried in a vacuum gave 15 c.c. nitrogen at 16° and 710 mm.

	Calculated for C ₆ O ₂ (CH ₃) ₃ ·NO ₂ .	Found.
C.....	55·38	55·52
H.....	4·62	4·9
N.....	7·18	7·09

This substance is very stable. It sublimes easily and without decomposition. Heated on a water-bath for hours with concentrated nitric acid, it remains in great part unchanged. On crystallisation from nitric acid, light petroleum, or especially from dilute alcohol, it is obtained in yellow plates, melting at 113°, and possessing a faint but distinct quinone-like odour.

(7.) *Nitropseudocumolquinol*, C₆(OH)₂(CH₃)₃·NO₂.—This was obtained by treating nitropseudocumolquinone in a sealed tube at 100° with a concentrated solution of sulphurous acid in 25 per cent. alcohol. On cooling, the tube is filled with long, broad, yellow needles, which are quite pure, and remain unchanged on repeated treatment with sulphurous acid solutions. For analysis, the substance was crystallised from ether, when it was obtained in flat, yellow needles, melting at 106°.

0.1797 gram substance dried in a vacuum gave 0.3592 gram CO_2 , and 0.0902 gram H_2O .

	Calculated for $\text{C}_6(\text{OH})_2(\text{CH}_3)_3\cdot\text{NO}_2$.	Found.
C.....	54.82	54.52
H	5.58	5.58

Nitropseudocumolquinol is easily soluble in chloroform, ether, and alcohol. It is somewhat soluble in hot water, crystallising therefrom in flat needles. Sodid hydrate colours it bluish-violet, and it then dissolves with a pale greenish-yellow colour. Ferric chloride or concentrated nitric acid oxidises it to the corresponding quinone.

On treating a solution of the quinone or of the quinol in acetic acid with zinc-dust, reduction takes place, and finally a colourless solution is obtained, which on exposure to the air soon becomes deep red-violet. On neutralising with sodic carbonate, after precipitation of the zinc as zinc sulphide, ether extracts a deep red substance, which with hydrochloric acid forms a colourless hydrochloride, crystallising in needles, and sparingly soluble.

IV. *Conversion of Dinitrodurylic Acid into Ethyl Quinonetetracarboxylate.*

(1.) *Dinitropyromellitic Acid*, $\text{C}_6(\text{NO}_2)_2(\text{COOH})_4^*$.—The oxidation of the three methyl side-chains in dinitrodurylic acid to carboxyl was carried out by means of potassium permanganate, and gave an almost quantitative yield.

20 grams of dinitrodurylic acid (dried at 100°) and 50 grams of anhydrous potassic carbonate were dissolved in 2 litres of water, and heated on a water-bath. To this, a solution of 72 grams of potassic permanganate was slowly added. At first oxidation takes place rapidly, but towards the end very slowly, and is finished after four or five days. The manganese dioxide formed was filtered off, and the filtrate concentrated. After acidifying with concentrated hydrochloric acid and dilute sulphuric acid, the solution was extracted four times with ether; on distilling off the ether, a white mass remained behind, consisting of a mixture of the tribasic and the tetrabasic acid. After many trials, the following method of separation was found to be exceedingly sharp. The mixture was dissolved in water and heated

* The direct nitration of pyromellitic acid seems to be impossible. This acid can be heated with a mixture of concentrated sulphuric acid and potassic nitrate for 10 hours in a sealed tube at 150° without the slightest change. The application of Burkhardt's method, by which, as is well known, terephthalic acid has been nitrated (*Berichte*, 10, 145) was, in this case, entirely fruitless.

on a water-bath with finely pulverised marble until the reaction was neutral, and alcohol (about 2 volumes) was then added to the concentrated filtrate, until no further precipitation took place. In this way the calcium salt of the tetrabasic acid is precipitated completely in pale-yellow needles, while the calcium salt of the tribasic acid remains in solution, and in fact cannot be precipitated at all by addition of more alcohol. The tribasic acid was then converted into the tetrabasic acid by renewed treatment with potassic permanganate. The last methyl-group in the tribasic acid is attacked by oxidising agents with great difficulty, so that it takes from four to five days to oxidise 10 grams. The yield was excellent; 20 grams of dinitrodurylic acid gave from 20 to 23 grams of pure anhydrous dinitropyromellitic acid.

The abovementioned calcium salt of dinitropyromellitic acid was purified by dissolving it in water and precipitating by addition of alcohol. It crystallises in pale-yellow needles. When heated in an air-bath at 180° , it loses its water of crystallisation, and becomes deep golden-yellow.

I. 0.1260 gram salt dried at 180° gave 0.0802 gram CaSO_4 .

II. 0.1602 " " " 0.1022 " "

	Calculated for $\text{C}_6(\text{NO}_2)_2(\text{COO})_4\text{Ca}_2$.	Found.	
		I.	II.
Ca.....	19.05	18.73	18.76

To obtain the acid, the purified calcium salt was dissolved in water, and the strongly acidified solution extracted three or four times with pure ether. On distilling off the ether and drying at 100° , pure dinitropyromellitic acid is left. The acid is colourless, has a very strong acid smell, and decomposes marble in the cold with violent evolution of carbonic anhydride. It crystallises from ether or water in long, silky needles. It is easily soluble in cold water, still more so in hot water, and deliquesces in ether vapour. It is also readily soluble in alcohol and acetic acid, but insoluble in chloroform, benzene, and light petroleum.

With the exception of the silver, lead, and barium salts, the salts of this acid are easily soluble in water, and most of them are precipitated from their aqueous solutions by alcohol. The barium salt is easily soluble in hot water, much less so in cold water. A separation of the tribasic and tetrabasic acids can also be accomplished by means of their barium salts, as the salt of the tribasic acid is much more easily soluble.

When heated in a capillary tube, dinitropyromellitic acid loses water (100 — 160°) and becomes slightly yellow. Above 160° , it

becomes gradually deeper and deeper yellow, and decomposes with violent evolution of gas, between 208° and 225° , according as the temperature rises slowly or quickly. If heated in an air-bath at 140° for several hours, the acid decomposes, and is converted into a deep-yellow substance.

When dried at 100° , the acid is colourless and anhydrous, as was deduced from the precipitation and analysis of the silver salt.

I. 10.2 grams acid gave 22.5 grams silver salt.

Calculated: 22.88 " "

II. 21.3 grams acid gave 47.6 " "

Calculated: 47.77 " "

The silver salt was prepared by adding a neutral solution of the ammonium salt of the acid to a hot solution of silver nitrate. It forms a stable, amorphous, yellow precipitate, quite insoluble in water. For analysis, it was dried at 100° , and as it explodes on heating, it was carefully mixed with the copper oxide.

I. 0.3954 gram substance gave 0.2278 gram CO_2 and 0.0210 H_2O .

II. 0.4115 gram substance gave 0.2340 gram CO_2 and 0.0120 H_2O .

0.223 gram substance gave 0.1650 gram AgCl or 0.1242 Ag .

0.5668 gram substance gave 18.75 c.c. nitrogen at 7° and 714 mm.

	Calculated for $\text{C}_6(\text{NO}_2)_2(\text{COOAg})_4$	Found.	
		I.	II.
C	15.55	15.71	15.51
H	—	0.59	0.32
Ag.....	55.96	55.70	—
N	3.63	3.73	—

It is not possible to convert dinitropyromellitic acid into the normal ethereal salt by the ordinary methods. An alcoholic solution saturated with gaseous hydrogen chloride and allowed to stand for two days did not yield it, and the acid heated with alcohol and a few drops of concentrated sulphuric acid for two days on a water-bath remained in great part unchanged.

With reducing agents, the acid shows a very characteristic reaction; all reducing agents whether applied in neutral, acid, or alkaline solution produce a deep red coloration. Ether extracts from acid solutions a red substance; the deep red ethereal solution has a very marked yellowish-red fluorescence. The red substance remains unchanged even when heated with reducing agents for a long time; it is undoubtedly, as will be seen below from results obtained with the ethereal salt, free diamidopyromellitic acid. The reduction takes a

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different course when granulated zinc and dilute sulphuric acid are used in the cold. In this case, a yellow solution is produced, from which ether extracts a yellow substance. The yellow ethereal solution has a marked green fluorescence.

The tribasic acid, methylparadinitrotrimellitic acid,



which is obtained along with dinitropyromellitic acid on oxidising dinitrodurylic acid, forms a deliquescent calcium salt. With basic lead acetate, it gives a fine yellow basic lead salt. The silver salt comes down after long heating with silver nitrate in sparingly soluble yellow plates.

The acid itself is easily soluble in hot water; much less so in cold. It dissolves with the greatest ease in alcohol and ether. It is obtained in long, colourless needles by crystallisation from water containing hydrochloric acid.

(2.) *Ethyl Dinitropyromellitate*, $\text{C}_6(\text{NO}_2)_2(\text{COOC}_2\text{H}_5)_4$.—The ethyl salt of dinitropyromellitic acid was prepared in considerable quantity by treating the silver salt with ethyl iodide. The neutral silver salt can be precipitated quantitatively as follows:—A solution of 20 grams of dinitropyromellitic acid, carefully neutralised with ammonium hydrate, is added slowly to a warm (50°) solution of 50 grams of silver nitrate. The silver salt was dried at 100° , and then allowed to stand over night with ethyl iodide ($1\frac{1}{2}$ times the calculated amount) and dry ether; to complete the reaction, the mixture was heated for five or six hours on a water-bath. The ethereal solution was now filtered from the silver iodide, washed with dilute sodic carbonate, and then dried with calcic chloride; after distilling off the ether, the solid ethyl salt was left sufficiently pure for farther work. For analysis, it was crystallised twice from alcohol, when it formed long, colourless needles melting at 130° .

0.1155 gram substance gave 0.2006 gram CO_2 and 0.0465 gram H_2O .

	Calculated for $\text{C}_6(\text{NO}_2)_2(\text{COOC}_2\text{H}_5)_4$.	Found.
C.	47.37	47.38
H.	4.39	4.47

It is easily soluble in benzene, chloroform, acetic acid, and acetone; less so in ether. By crystallisation from hot alcohol or light petroleum, it is obtained in beautiful needles. It dissolves in alcoholic ammonia with a fugitive red colour. The yield was seldom over 60 per cent. of the theoretical.

(3.) *Ethyl Diamidopyromellitate*, $\text{C}_6(\text{NH}_2)_2(\text{COOC}_2\text{H}_5)_4$.—Ethyl di-

nitropyromellitate, on reduction with zinc-dust and acetic acid, gives a beautiful red compound, which I long regarded as ethyl azopyromellitate. It was found impossible, in spite of repeated efforts, to reduce this substance further with elimination of the nitrogen. I thought therefore that it might possibly be an inner azo-compound, as it sublimes without decomposition like a quinone. I tried to ascertain its molecular weight by means of a vapour-density determination, using Victor Meyer's method, but without success.

Nevertheless the analytical figures obtained did not agree sharply; the hydrogen especially was always too high. Later, when I had larger quantities of the substance in my hands, and analysed a product purified with especial care, I obtained figures agreeing exactly with those required by ethyl diamidopyromellitate. Finally the formation and isolation of a colourless diacetyl-derivative by treating it with acetic anhydride, is a convincing proof that the red substance is actually a diamido-compound.

The deep red colour of the diamido-compound is now no longer remarkable, as v. Baeyer (*Ber.*, **19**, 430) has recently shown that ethyl paradiamidoterephthalate has the colour of potassic dichromate.

For reducing ethyl dinitropyromellitate, the following method was found most advantageous, and gave an almost quantitative yield. The substance was first dissolved in acetic acid, and to the hot solution a little water, and then zinc-dust in small portions at a time were added. When the addition of more zinc-dust no longer produced a violent reaction, and the red colour had changed to yellow, the solution was filtered hot from the zinc-dust, and poured slowly (stirring well) into a dish containing water. The diamido-compound then separated completely in yellow flakes, which soon changed to a red crystalline precipitate. For purification, the substance was dissolved in ether, washed with dilute sodic carbonate, and the ethereal solution, dried with calcic chloride, was then allowed to evaporate over sulphuric acid; the diamido-compound crystallised out in beautiful deep red four-sided prisms.

For analysis, the large crystals were mechanically picked out and dried at 100°. They melted at 134°, and sublimed without decomposition and without leaving any residue. When melted and allowed to solidify again, the substance has exactly the appearance of sealing-wax.

- I. 0.1231 gram substance gave 0.2447 gram CO₂ and 0.0675 gram H₂O.
- II. 0.1774 gram substance gave 0.3554 gram CO₂ and 0.1044 gram H₂O.

III. 0.1842 gram substance gave 0.3681 gram CO_2 and 0.1036 gram H_2O .

0.2970 gram substance gave 20.3 c.c. nitrogen at 19° and 723 mm.

	Theory for $\text{C}_6(\text{NH}_2)_2(\text{COOC}_2\text{H}_5)_4$.	Found.		
		I.	II.	III.
C	54.55	54.20	54.64	54.50
H	6.06	6.09	6.54	6.25
N	7.07	7.47	—	—

Ethyl Diamidopyromellitate.

Dr. W. Muthmann examined the above crystals of ethyl diamidopyromellithate in the mineralogical laboratory of P. Groth in Munich, and reports as follows:—

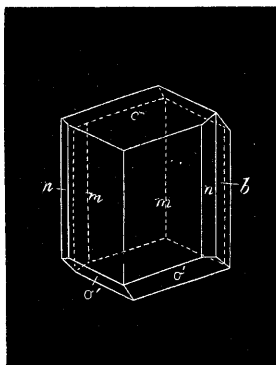
Monoclinic system: β $61^\circ 17'$.

$$a : b : c = 0.66964 : 1 : 0.62686.$$

Planes: $m = (110) = \infty\text{P}$.

$c = (001) = 0\text{P}$; $0 = (\bar{1}11) = +\text{P}$.

$b = (010) = \infty\text{P}\infty$; $n = (110) = \infty\text{P}2$.



The majority of the crystals showed only the crystal faces m , c , and b .

	Found.	Calculated.
$(110) : (1\bar{1}0) = *60^\circ$	50'	— —
$(110) : (001) = *65$	31	— —
$(010) : (\bar{1}11) = *60$	55	— —
$(\bar{1}10) : (\bar{1}11) = 53$	39	53° 35'
$(110) : (120) = 19$	7	19 10
$(010) : (001) = 90$	3	90 —

Colour: reddish-orange (Radde's International colour scale). The plane of the optic axes is parallel to the plane of symmetry.

One bisectrix lies in the acute angle of the crystallographic axes and forms with the vertical one an angle of $15\frac{1}{2}^\circ$. An optical axis comes out very nearly perpendicular to (001). From these data, the axial angle is found to be approximately $85-90^\circ$.

The crystals are very soft, and possess a remarkably perfect cleavage in the direction (001).

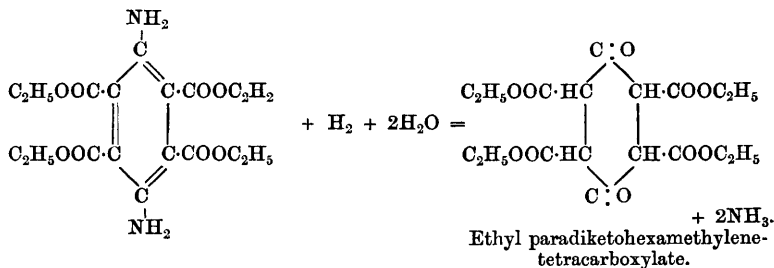
Ethyl diamidopyromellitate has feeble basic properties. On adding to it concentrated hydrochloric acid, it becomes colourless; and on diluting with an equal volume of water and heating, the colourless salt dissolves, and crystallises out again in needles on cooling. More water decomposes the salt, and the free base separates out in beautiful rhombic plates. The diamido-compound dissolves in concentrated sulphuric acid with a pale-yellow colour; water precipitates the free base again unchanged.

The substance dissolves easily in alcohol, ether, and acetic acid. The ethereal solution is red, and shows a very marked yellowish-red fluorescence. On saponification with alcoholic potash, and acidifying, ether extracts from the solution a red substance identical with that obtained by the reduction of dinitropyromellitic acid.

On treating a hot alcoholic solution of the ethereal salt of the diamido-compound with sulphuric acid (1 H_2SO_4 to 1 of water) and zinc-dust, it is easily reduced, and on adding water a colourless substance crystallising in needles separates out. This was found to contain no nitrogen, and it was therefore supposed to be ethyl pyromellitate. A close study, however, of the substance, after v. Baeyer had observed that ethyl paradiamidoterephthalate is converted by reduction into ethyl succinosuccinate, has shown that it is identical with ethyl paradiketohexamethylenetetracarboxylate, described below.

On converting this product into ethyl quinoltetracarboxylate and into ethyl quinonetetracarboxylate, the last doubt about the complete identity of the two substances vanished.

Ethyl diamidopyromellitate is therefore reduced by means of zinc-dust and sulphuric acid according to the following reaction:—



Oxidising agents such as ferric chloride, platinic chloride, or sodic nitrite in acid solution, do not convert the ethereal salt of the diamido-compound into the corresponding quinone, chromic acid in acetic acid solution as well as potassic dichromate and sulphuric acid decompose it entirely. Concentrated nitric acid, however, oxidises it to the quinone.

(4.) *Ethyl Diacetyldiamidopyromellitate*.—This was obtained by heating the diamido-compound with excess of acetic anhydride at 140° for four or five hours; on adding alcohol, the new compound was in great part precipitated. After getting rid of the excess of acetic anhydride, the substance was purified by crystallisation from alcohol; it forms colourless, lustrous rhombic plates melting at 149° .

0.1161 gram substance gave 0.2342 gram CO_2 and 0.0614 gram H_2O .

	Theory for $\text{C}_6(\text{COOC}_2\text{H}_5)_4(\text{NHAc})_2$.	Found.
C	55.00	55.01
H	5.83	5.88

The acetyl-derivative dissolves easily in acetone, chloroform, and in warm alcohol. It cannot be again resolved into its components by treating with sodium hydrate or hydrochloric acid. The same is true of many other acetyl-derivatives of amido-acids.

(5.) *Ethyl Quinonetetracarboxylate or Ethyl Quinonepyromellitate*.—On heating ethyl diamidopyromellitate with concentrated nitric acid, or with sulphuric acid and potassic nitrate, it is oxidised to the corresponding quinone. The presence of nitrous acid is detrimental, giving rise to oily bye-products. The best yield (50—55 per cent.) was obtained by the following method: 5 grams of the substance were dissolved in 40 c.c. pure concentrated nitric acid (sp. gr. 1.4) and allowed to stand in the cold for two hours. The substance dissolves at first with yellow colour and without change; soon, however, the solution becomes much darker, and the quinone begins to crystallise out in yellow needles. A slow and constant evolution of gas is noticed after the end of the first hour. It is therefore well to stir from time to time. On pouring into water, the quinone separates out completely in yellow needles. For analysis, it was crystallised twice from alcohol, when it was obtained in long, yellow needles, melting at $148\text{--}149^{\circ}$.

The results of the analysis agreed with the formula $\text{C}_6\text{O}_2(\text{COOC}_2\text{H}_5)_6$.

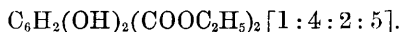
0.1375 gram substance gave 0.2756 gram CO_2 and 0.0662 gram H_2O .

	Theory.	Found.
C	54.55	54.66
H	5.15	5.35

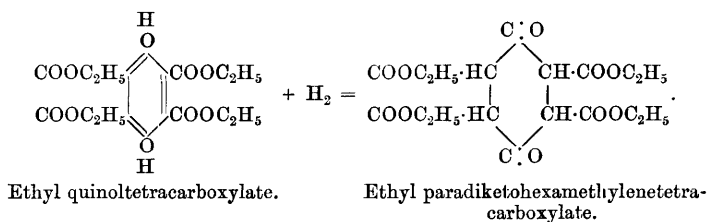
The substance is of quinone-yellow colour; it is odourless; it sublimes readily without decomposition, and unquestionably belongs to the class of true (para) quinone compounds. It is very stable in the presence of concentrated nitric acid, in which it easily dissolves. The solution, even when heated a long time, undergoes little change, and the quinone separates again completely on adding water. It is but little soluble in cold alcohol or ether; much more so in warm.

Hydroxylamine hydrochloride in neutral or acid solution reduces it almost immediately to the quinol compound. It is insoluble in cold potassic hydrate; on heating gently, however, it liquefies, turns dark-red, and then goes into solution. By using the calculated amount of potassic hydrate, it was saponified, and, strangely enough, the product obtained was dihydroxypyromellitic acid. On saponifying in acid solution with acetic acid and concentrated sulphuric acid, dihydroxypyromellitic acid also was obtained, and not as was expected pyromellitic-acid-quinone.

(6.) *Ethyl Dihydroxypyromellitate or Ethyl Quinoltricarboxylate*.—On treating ethyl quinonetetracarboxylate with zinc-dust and acetic acid, it is reduced with great ease to the corresponding quinol-compound, $C_6(OH)_2(COOC_2H_5)_4$ [1:4:2:3:5:6]. This, as will become evident from what follows, has a most remarkable resemblance, in chemical as well as physical properties, to Herrmann's (*Annalen*, **211**, 327) so-called ethyl quinonedihydrodicarboxylate; the latter, according to recent results obtained by v. Baeyer (*Ber.*, **19**, 428), is to be regarded as ethyl quinolparadicarboxylate,



Of especial interest, moreover, is the action of reducing agents on ethyl quinoltetracarboxylate. It is converted in a manner analogous to the conversion of ethyl quinoldicarboxylate to ethyl succinosuccinate—to a hexamethylene-derivative or hexahydrated derivative of benzene—that is, from a tertiary to a secondary bound ring (v. Baeyer, "*Ueber Nomenclatur*," *Ber.*, **19**, 160).



The resulting compound, ethyl paradiketohexamethylenetetra-carboxylate (*Ber.*, **19**, 160) has a remarkably deceptive resemblance in all respects to ethyl succinosuccinate. By means of bromine in carbon

bisulphide solution, it can be reconverted to ethyl quinonetetracarboxylate.

In order to reduce ethyl quinonetetracarboxylate, it is dissolved in acetic acid and zinc-dust added in small portions. The yellow solution immediately become colourless with a beautiful blue fluorescence. On adding water, the quinol compound separates out in almost colourless needles having a marked bluish tinge. For purification, it is dissolved in acetic acid and precipitated again by addition of water.

I. 0.1280 gram substance gave 0.2564 gram CO_2 and 0.0676 gram H_2O .

II. 0.1475 gram substance gave 0.2934 gram CO_2 and 0.0752 gram H_2O .

		Found.	
		I.	II.
Theory for $\text{C}_6(\text{OH})_2(\text{COOC}_2\text{H}_5)_4$.			
C	54.27	54.62	54.25
H	5.53	5.86	5.66

Ethyl quinoltetracarboxylate crystallises in pale-yellow needles having a bluish tinge. It has no sharp melting point, $127-129^\circ$. When carefully heated between two watch-glasses, it sublimes without decomposition. It dissolves easily in alcohol, ether, and acetic acid, and the solutions show a very marked, beautiful blue fluorescence. On adding a drop of ferric chloride to an alcoholic solution of the substance, a bluish-green coloration is produced.

If heated with concentrated nitric acid, it dissolves and is oxidised quantitatively to the quinone. It remains unchanged when exposed to an atmosphere of bromine for several days. It dissolves unchanged with yellow colour in dilute sodic hydrate or sodic carbonate. Concentrated sodic hydrate precipitates a deep cinabar-red sodium salt, which is also obtained on adding sodic ethylate to a dry ethereal solution of the quinone. On heating the sodium hydrate solution, hydrolysis takes place, and the sparingly soluble sodium salt of dihydroxypyromellitic acid separates out in yellowish prisms.

Ethyl quinoneparadicarboxylate also forms a similar coloured sodium salt, and gives bluish-green coloration with ferric chloride. The solution of the substance in ether also shows the same marked blue fluorescence.

An investigation of the physical properties of ethyl quinoltetracarboxylate has shown still further the remarkable resemblance existing between these two compounds. The study of the physical properties of this substance—which certainly is one of the most

remarkable substances physically in chemistry—was begun during the last Easter vacation in the new chemical crystallographical laboratory of Professor P. Groth.

Dr. W. Muthmann reports thereon as follows:—

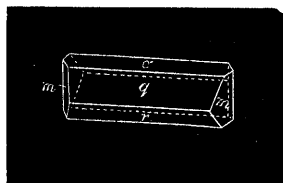
Ethyl Quinoltetracarboxylate.

Modification I.

Monoclinic system: $\beta = 64^\circ 36'$.

$$a : b : c = 2.3875 : 1 : 3.0601.$$

Planes: $c = (001) = 0P$. $r = (\bar{1}01) = +P_\infty$.
 $q = (101) = -P_\infty$. $m = (110) = \infty P$.



Elongation in the direction of the axis b ; often in thin needles. The base never predominates but always appears as a small plane.

	Found.	Calculated.
$(110) : (\bar{1}10)$	$*49^\circ 45'$	— —
$(001) : (101)$	$*36 46$	— —
$(001) : (\bar{1}01)$	$*68 45$	— —
$(110) : (101)$	$68 10$	$68^\circ 29'$
$(\bar{1}10) : (\bar{1}01)$	$73 13$	$73 27$

Colour, greenish-yellow. The plane of the optic axes lies in the plane of symmetry. An optical axis appears very nearly perpendicular to $(\bar{1}01)$ and as a consequence no total reflection is noticeable on this face.

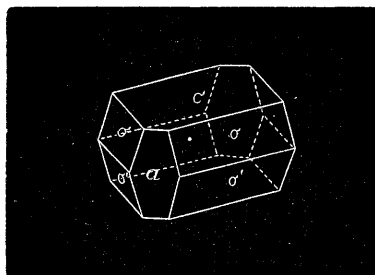
In (101) pretty strong dichroism—dark-yellow and light-yellow—noticeable; this was not perceptible in $(\bar{1}01)$.

Modification II.

Monoclinic system: $\beta = 81^\circ 53'$.

$$a : b : c = 1.7896 : 1 : 3.3206.$$

Planes: $c = (001) = 0P$. $0 = (111) = -P$.
 $a = (100) = \infty P_\infty$. $0' = (\bar{1}11) = +P$.



Thick plates in direction (001). In many of the crystals the corresponding opposite planes were not quite parallel owing to disturbances in their growth.

The angles used in the calculation of the axial ratios, &c., are the mean of 20—25 angle measurements on eight of the best crystals.

	Found.	Calculated.
(111) : ($\bar{1}\bar{1}1$)	56° 43'	— —
(111) : ($1\bar{1}1$)	111 44	— —
($\bar{1}\bar{1}1$) : ($1\bar{1}1$)	117 53	— —
(100) : (001)	81 57	81° 53'
(001) : (111)	71 25	71 28
(001) : ($\bar{1}\bar{1}1$)	78 45	78 55
(100) : (111)	59 40	59 49
($\bar{1}00$) : ($\bar{1}\bar{1}1$)	63 21	63 28

Colour, pale-yellow. Dichroism—colourless and bright-yellow—noticeable in (001). The total reflection in (001) exactly diagonal.

In the summer, transparent crystals of the first modification alone were obtained from carbon bisulphide solution. These on heating become turbid and seem to undergo a transformation. The change begins at 111° and is complete at 115°. The product then melts, on higher heating sharply, at 133·2—133·6°.

In the colder months (April), at a temperature of about —5°, crystals of the second modification were obtained side by side with the first modification from a solution in carbon bisulphide. Modification II becomes transformed at 63·5—64° into a different modification. On cooling, this does not change back to the original again. The modification thus obtained at 64° shows a peculiar fusing point. It begins to melt at 123—124°, and thereupon a part of the substance becomes solid again and the whole melts entirely at 128·5°. On cooling and reheating, the same phenomena again appear.

Besides these two modifications, a third was observed to crystallise from the carbon bisulphide solution at very low temperatures. The

amount of material on hand has up to the present time been insufficient for the closer study of this peculiar modification.

The modifications I and II described are undoubtedly totally different from one another, and it is *not* possible by heating or fusing to convert either one into the other. There is first of all a remarkable difference in colour: I is green; II, pale-yellow. On fusing and cooling, I appears dark-yellow; II, bright-yellow. One modification crystallises in needles, the other in plates, so that it is an easy matter to separate them mechanically. When either modification thus sharply separated is dissolved in carbon bisulphide, the mixture of the two modifications side by side, like two substances totally distinct from one another, is again obtained. If these are carefully separated mechanically and the operation repeated, the same result is invariably obtained, showing a mixture of the two modifications side by side.

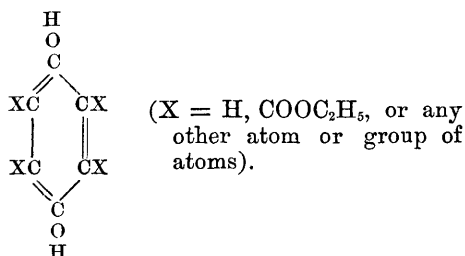
The substance, therefore, on being dissolved in carbon bisulphide (the same result is obtained on using pure dry ether) must undergo some transformation. The molecules of the substance must either possess a very peculiar tendency to arrange themselves always in two definite states of equilibrium corresponding to the two totally different crystalline forms, or, what is equally probable, certain atoms of the molecule of the substance itself must be in a perpetual unstable equilibrium, and the two modifications observed would then correspond each to a different molecular structure. Certain it is the solutions of the two modifications have exactly the same colour. The absorption-spectrum of each modification dissolved in dilute sodium carbonate solution was quantitatively determined for all parts of the spectrum, and found in both cases to be exactly the same. The data, &c., will be given later in connection with a study of the absorption-spectra of various other closely allied substances. On oxidation with concentrated nitric acid, both modifications I and II give the same perfectly homogeneous substance, the quinone melting sharply at 149°, whilst on treatment with zinc-dust and hydrochloric acid in alcoholic solution, both give the same *colourless* and perfectly homogeneous substance—the diketone compound melting at 144°.

It is worthy of note that quinol and many other derivatives of quinol or paradihydroxybenzene, as well as *paradiamido*-derivatives of benzene are dimorphous. It may be noted now that Dr. Muthmann has discovered two entirely distinct modifications of ethyl paradiamidoterephthalate (*Ber.*, 19, 430), and measured the crystals of both forms, only one modification has as yet been found of the very closely allied ethyl paradiamidopyromellitate.

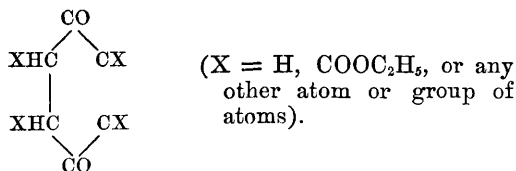
The fact that so many of the paradihydroxy-derivatives of benzene are dimorphous naturally leads one to suspect that this dimorphism

may be due to a difference in the molecular constitution of these substances.

It might be supposed that one modification corresponds to the real paradihydroxy-derivative of benzene, *e.g.*,



and that the other modification corresponds to the pseudo- or ketone form, *e.g.*,



The transference of the hydrogen-atoms to adjacent carbon-atoms which is assumed here, is analogous, for instance, to what takes place in the case of carbostyryl, isatin, pyridone, and phloroglucin (*Ber.*, **19**, 159). In all these instances, the chemical behaviour of these substances necessitates the assumption of pseudo-forms or of the migration of the hydrogen-atom to an adjacent carbon- or nitrogen-atom. These compounds, however, have never been obtained in two different physical modifications.

If the dimorphism of the quinol compounds is due to a difference in chemical constitution, it must be possible to prove this by chemical means; the experiments thus far carried out, however, have been insufficient to settle this question.

A short time ago Nietzki and Kehrman (*Ber.*, **20**, 613) found that quinol reacts with hydroxylamine, giving a compound $\text{C}_6\text{H}_6\text{N}_2\text{O}_2$. If the above theory is correct, this compound ought to have the formula $\text{C}_6\text{H}_8\text{N}_2\text{O}_2$ (that is, contain two more hydrogen-atoms). These experiments were repeated, but the analysis of the substance confirmed the formula given by Nietzki and Kehrman, which seems to show that quinol is first oxidised to quinone, and then acted on by the hydroxylamine.

The study of the action of hydroxylamine on ethyl quinoltetracar-

boxylate, as well as on tetrachloroquinol, has not as yet given any positive results.

Dr. Muthmann and myself have joined to make a combined chemical and physical study of this subject. We have decided to publish here the results thus far obtained, because Hantzsch and his pupils (Hantzsch and Zeckendorf, *Ber.*, **20**, 1308, 2796; Hantzsch and Hermann, *Ber.*, **20**, 2801) in their study of ethyl quinolparadicarboxylate and its derivatives have found the same peculiar dimorphism to exist.

Hantzsch has gone further, and puts especial stress on the colour of the modifications. If the modification is colourless, he says, this corresponds to the *true* paradihydroxy-compound of benzene, as all *true* compounds of benzene must be colourless (?). If the modification is coloured, it corresponds to the ketone or quinone form, because all ketones or quinones are coloured (?).

The question of colour is, it seems to us, purely arbitrary, and does not prove anything whatever. More has hitherto been considered necessary in settling the constitution of a chemical compound.

It is very difficult to see, for instance, why ethyl quinolparadicarboxylate, which according to Hantzsch is a ketone in its *two* most stable modifications, does not under any circumstances act chemically like a ketone, but invariably like a dihydroxy-compound of benzene.

Hermann's argument (*Ber.*, **19**, 2229, 2235) that ethyl quinolparadicarboxylate forms isomorphous mixtures with ethyl succinosuccinate seems a much more powerful argument for its ketone form. On the other hand, it must be remembered that ethyl succinosuccinate acts like a dihydroxy-compound as well as like a diketone, so that it is more logical to conclude that in the isomorphous mixtures the dihydroxy modification of ethyl succinosuccinate is present.

(7.) *Dihydroxypyromellitic Acid, or Quinoltricarboxylic Acid.*—On heating ethyl quinoltricarboxylate with potassic hydrate, it is easily saponified; the product, dihydroxypyromellitic acid, resembles very closely paradihydroxyterephthalic acid (*Annalen*, **211**, 335).

2 grams of the ethereal salt were heated with twice the calculated amount of potassic hydrate (4 grams) on a water-bath; a dark-yellow solution with a green fluorescence was obtained. After neutralising with acetic acid, the lead salt was precipitated by means of lead acetate; the precipitate was collected, carefully washed, and then decomposed with sulphuretted hydrogen. After filtering hot from the lead sulphide and concentrating the yellowish solution, a pale-yellow substance crystallised out almost completely on cooling in four- and six-sided prisms. The substance purified by recrystallisation from water was found not to be free from ash. On adding concentrated hydrochloric acid to a hot concentrated solution, pure

dihydroxypyromellitic acid separates out almost completely in pale-yellow, broad, flat needles.

The acid, dried on an air-bath at 100° , was found to contain $1\frac{1}{2}$ mols. H_2O .

0.1227 gram substance gave 0.1706 gram CO_2 and 0.0339 gram H_2O .

	Theory for $C_6(OH)_2(COOH)_4 + 1\frac{1}{2}H_2O$.	Found.
C	38.34	37.92
H	2.87	3.07

Heated to a higher temperature (150°), the substance not only lost its water of crystallisation, but was further changed.

Dihydroxypyromellitic acid dried at 100° is of a pale-yellow colour, and dissolves sparingly in most solvents. The yellow solutions show a characteristic green fluorescence. It dissolves easily in hot water, and is precipitated therefrom by mineral acids. The aqueous solution is coloured deep blue on the addition of a few drops of ferric chloride. The colour remains unchanged for days, even when a great excess of ferric chloride is added.

When heated in a test-tube, it melts at a very high temperature, losing water, and then sublimes without leaving any residue, the sublimate, which is probably the dianhydride of the acid, crystallising in yellow, flat needles. It dissolves in dilute alcohol with yellowish-red colour and reddish-yellow fluorescence. On shaking the solution with air, a peculiar violet tinge is noticed on the sides of the test-tube. On standing, or more quickly on heating, the colour of the solution changes to the yellow tint and green fluorescence of dihydroxypyromellitic acid again.

The salts of this acid are yellow, and in solution exhibit a characteristic green fluorescence. The silver salt was more closely studied and analysed. It was obtained by adding a solution of the neutral ammonium salt to a neutral solution of silver nitrate in the cold. It separates out as a lemon-yellow flocculent precipitate. When dry, it is stable at ordinary temperature. Heated quickly on platinum foil it explodes; if heated slowly, a volatile, yellow substance sublimes.

0.2283 gram substance dried over sulphuric acid in a vacuum gave

0.1394 gram CO_2 and 0.0114 gram H_2O .

0.0562 gram substance gave 0.0338 gram silver.

	Theory for $C_6(OH)_2(COOAg)_4$.	Found.
C	16.80	16.65
H	0.28	0.55
Ag	60.51	60.14

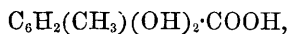
Lead acetate throws down the lead salt as a light-yellow, flocculent precipitate; baric chloride gives the barium salt as a granular, pale-yellow precipitate. The sodium salt is especially characteristic. On heating the free acid with sodium hydrate, the sodium salt separates out in pale-yellow prisms, which are very sparingly soluble even in boiling sodium hydrate.

The oxidation of dihydroxypyromellitic acid to pyromellitic acid-quinone, $C_6O_2(COOH)_4$, presented unexpected difficulties. Concentrated nitric acid has, in the cold, no effect on dihydroxypyromellitic acid; on heating, gently, however, the substance dissolves with a violent evolution of carbonic anhydride, and, as it would seem, is completely decomposed.

When heated gently with a solution of chromic acid, a violent evolution of gas is noticed. Potassium permanganate oxidises the acid in neutral or acid solution in the cold, but although as much as three times the calculated amount of the oxidising agent was used, much unchanged dihydroxypyromellitic acid was the only product obtained. A solution of the acid allowed to stand in the cold for days with a great excess of ferric chloride, retained the beautiful blue coloration unchanged, and much unchanged acid was found to be present. It may be mentioned here again that ethyl quinonetetracarboxylate on hydrolysis in acid or in alkaline solution invariably gives dihydroxypyromellitic acid and not the quinone.

A similar resistance towards the formation of the quinone from a paradioxy-compound was observed in the case of paradihydroxybenzoic acid $C_6H_3(OH)_2COOH$, and its ethyl salt. Repeated attempts were made to oxidise these substances to quinones, varying the conditions in every conceivable way. Paradihydroxybenzoic acid was found to evolve carbonic anhydride even on heating gently with such a mild oxidising agent as ferric chloride. Ethyl paradihydroxybenzoate, when treated with oxidising agents, either remained unchanged or was entirely decomposed.

Similar negative results were obtained by Brunner (*Monats. Chem.*, 1881, 464) in the case of toluquinolcarboxylic acid,



and its ethyl salt.

Hantzsch and Loewy (*Ber.*, 19, 26) could not convert ethyl quinolparadicarboxylate into the corresponding quinoneterephthalate, although they succeeded in obtaining another oxidation product.

(8.) *Ethyl Paradiketohexamethylenetetracarboxylate*.—The conversion of ethyl quinoltetracarboxylate into a derivative of hexahydrobenzene or hexamethylene—that is, from a tertiary to a secondary chain of six carbon-atoms—can readily be accomplished by v. Baeyer's

method (*Ber.*, **19**, 432). To a very concentrated hot alcoholic solution of the substance (2 grams), zinc-dust (10 grams) was added, and then concentrated hydrochloric acid. The change takes place almost instantly and quantitatively. On adding water to the filtrate, a colourless substance separates out in needles: this, when purified by dissolving in a little alcohol and precipitating with water, was obtained in long, colourless needles.

The substance contains water of crystallisation, and melts therein at 94° . Heated in an air-bath at 110° , it loses its water of crystallisation, and a hard, granular mass remains, fusing at 144° .

0.1312 gram substance dried at 110° gave 0.2590 gram CO_2 and 0.0720 gram H_2O .

	Theory for $\text{C}_{18}\text{H}_{24}\text{O}_{10}$.	Found.
C	54.00	53.84
H	6.00	6.10

The anhydrous substance is very sparingly soluble in alcohol, ether, and carbon bisulphide. It separates from hot carbon bisulphide solution in beautiful, colourless needles. The solutions show a very faint but distinct blue fluorescence. The substance containing water of crystallisation, on the other hand, is easily soluble in alcohol and ether.

On adding sodium ethylate to a dry ethereal solution of the diketone compound, a colourless salt separates out at first, but on adding more sodium ethylate, this changes to a rose-coloured salt. Ethyl succinosuccinate gives exactly the same reaction.

Potassic hydrate colours the substance yellow; on diluting with water, it dissolves, forming a yellow solution, from which the substance is precipitated unchanged on the addition of an acid.

A drop of ferric chloride added to an alcoholic solution produces a cherry-red coloration. By treatment with bromine in carbon bisulphide solution, the substance is reconverted quantitatively into ethyl quinoltetracarboxylate.

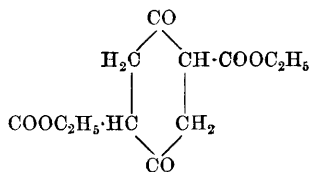
That the compound has free ketone-groups is proved by the ease with which it reacts with phenylhydrazine, hydroxylamine, and ammoniac acetate. Heated over a flame with ammoniac acetate, a yellow substance is obtained which dissolves in ether with a marked green fluorescence. It contains nitrogen, and melts between 115° and 120° . It is not, however, converted by treatment with bromine and concentrated sulphuric acid into ethyl diamidopyromellitate, as might be expected, from a di-imido-derivative (*Ber.*, **19**, 429). On further treatment with ammoniac acetate, products melting at higher temperatures (180 – 200°) were obtained; these also could not be converted

into ethyl diamidopyromellitate. It was therefore considered probable that the ethylated carboxyl-groups, as well as the ketone-groups, were attacked by the ammoniac acetate.

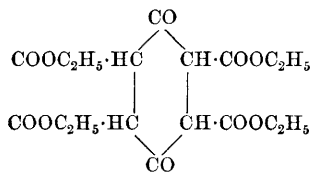
On heating an alcoholic solution of ethyl paradiketohexamethylenetetracarboxylate with phenylhydrazine (twice the calculated amount) for 10 hours at a temperature of 110—120°, in small amount, a substance crystallising in red needles is formed; as it is quite insoluble in alcohol, it is readily obtained pure. The chief products of the reaction are soluble in alcohol, and form a red, granular mixture; want of material has thus far prevented me from obtaining them in quantity sufficient to purify them for analysis. They all contain nitrogen.

The red product insoluble in alcohol shows all the properties of diphenyldipyrzohexahydrobenzene (*Ber.*, **17**, 551, 2055), a compound which Knorr obtained by the action of phenylhydrazine on ethyl succinosuccinate. It dissolves in alkalis with purple-red colour; also in concentrated mineral acids, but is precipitated in yellow flakes on the addition of water. On treatment with sodium nitrite in acetic acid solution, a blue insoluble dye is formed. The same blue compound is produced on adding sodium nitrite to an alkaline solution, and then acidifying with dilute sulphuric acid.

The above facts suffice to show the very great resemblance between ethyl paradiketohexamethylenetetracarboxylate and ethyl succinosuccinate. This is not surprising when one reflects that the former compound is simply the ethereal salt of a dicarboxylated derivative of succinosuccinic acid.



Ethyl succinosuccinate.



Ethyl paradiketohexamethylene-tetracarboxylate.

To show the great resemblance between the derivatives obtained from ethyl succinosuccinate and those obtained from ethyl diamidopyromellitate, the following tables (pp. 458, 459) are added, showing the chief reactions of the different compounds.

The experiments on durylic-acid-quinone and pyromellitic-acid-quinone will be continued.

Name.	Properties.	Solutions.	Ferric chloride.	Sodium ethylate.	Bromine in CS ₂ solution.
Ethyl succinosuccinate	colourless needles, m. p. 126—127°	faint blue fluorescence	cherry - red coloration	colourless, then rose-coloured salt	Ethyl paradihydroxyterephthalate.
Ethyl paradiketohexamethylenetetra-carboxylate	colourless needles, m. p. 144°	faint blue fluorescence	cherry - red coloration	colourless, then rose-coloured salt	Ethyl dihydroxypyromellitate.

Name.	Properties.	Solutions.	Ferric chloride.	Sodium ethylate.	Zn and HCl in alcoholic solution.	Nitric acid.
Ethyl paradihydroxyterephthalate	light yellow needles or prisms, m. p. 133°	marked blue fluorescence	bluish-green coloration	deep red-coloured salt	Ethyl succinosuccinate	no ethyl quinone-terephthalate.
Ethyl dihydroxypyromellitate	greenish-yellow needles, m. p. 133.5°; light-yellow plates, m. p. 128.5°	marked blue fluorescence	bluish-green coloration	deep red-coloured salt	Ethyl paradiketohexamethylenetetra-carboxylate	Ethyl quinone-pyromellitate.
Paradihydroxyterephthalic acid	yellow plates	yellowish - green, with green fluorescence	intense blue coloration			CO ₂ split off. Nitro-anilic acid formed.
Dihydroxypyromellitic acid	light-yellow flat needles	yellow, with green fluorescence	intense blue coloration			CO ₂ split off. Decomposition.

Name.	Properties.	Solutions.	Ferric chloride.	Sodium ethylate.	Zn and HCl or H ₂ SO ₄ in alcoholic solution.	Nitric acid.
Ethyl paradiamidoterephthalate	gold-yellow needles, m. p. 168°, strong base	brown, with gold-yellow fluorescence			Ethyl succinosuccinate	<i>no</i> ethyl quinone-terephthalate
Ethyl diamidopyromellitate	fire-red prisms, m. p. 134°, weak base	red, with yellowish-red fluorescence			Ethyl paradiketohexamethylenetetetracarboxylate	Ethyl quinonopyromellitate