THE CONSTITUTION OF THE DIHYDROXY-DERIVATIVE OF DIPHENYLENE OXIDE OBTAINED FROM RESORCINOL.

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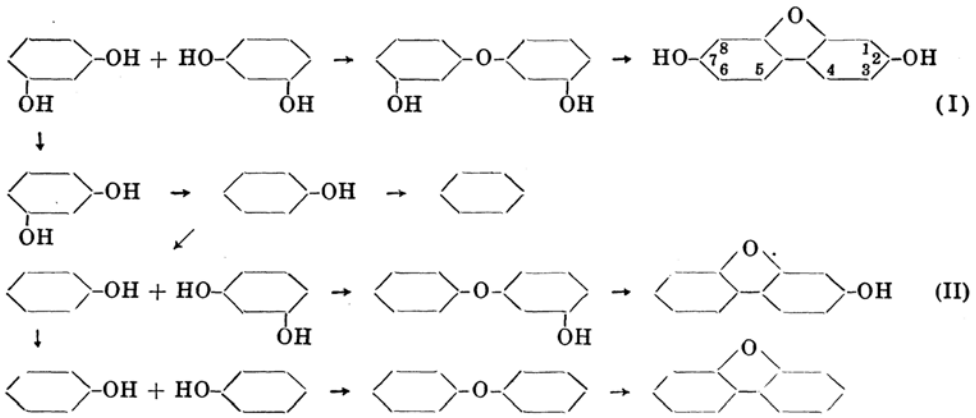
It was previously reported[1] that resorcinol vapour, being passed over the blue oxide of tungsten at 500–550°, undergoes a certain reduction and condensation, and gives two substances besides benzene, phenol

(1) B. Kubota, Y. Fujimura, and K. Akashi, *Sci. Pap. Inst. Phys. Chem. Research, Japan*, **2** (1925), 185; Y. Tsuzuki, *ibid.*, **6** (1927), 301.

and diphenylene oxide. These two substances, one melting at 138–138.5° and the other at 241–242°, were supposed to be monohydroxy- and dihydroxy-derivatives of diphenylene oxide respectively. In the preceding report,[2] we decided that the substance melting at 138–138.5° is 2-hydroxy-diphenylene oxide(II) by synthesizing it from 2-amino-diphenylene oxide, and considered that the substance melting at 241–242° is most probably 2,7-dihydroxy-diphenylene oxide(I). The mechanism of the reactions giving these compounds by the catalytic action of the blue oxide of tungsten, was assumed to be represented by the scheme shown below:



With the view of ascertaining the constitution of the substance melting at 241–242° we have synthesized 2,7-dihydroxy-diphenylene oxide from *p*-anisidine, and compared it with dihydroxy-diphenylene oxide obtained from resorcinol by the catalytic reaction.

The 2,7-dihydroxy-diphenylene oxide obtained from *p*-anisidine melts at 241–241.5°, and when it is mixed with the substance melting at 241–242° obtained from resorcinol, no depression of melting point can be recognized. The melting points of dimethyl derivatives of these compounds, one obtained by synthesis and the other by catalytic reaction, also coincide with each other. The melting points of these compounds are compared in Table 1.

It can be consequently decided that the substance melting at 241–242°, obtained from resorcinol, is nothing but 2,7-dihydroxy-diphenylene oxide, and that, as we have expected, the reaction follows the process represented by the scheme shown above to produce (I).

(2) K. Tatematsu and B. Kubota, This Bulletin, **9** (1934), 448.

Table 1. Comparison of the Melting Points.

Substance	From resorcinol	From *p*-anisidine	Mixed m.p.
Dihydroxy-diphenylene oxide	241–242°	241–241.5°	241–242°
Dimethoxy-diphenylene oxide	150°[3]	150°	—

Moreover, the ferric chloride reaction and the absorption curve of the synthesized 2,7-dihydroxy-diphenylene oxide quite coincide with those of the dihydroxy-diphenylene oxide obtained from resorcinol, indicating that these two substances are undoubtedly identical.

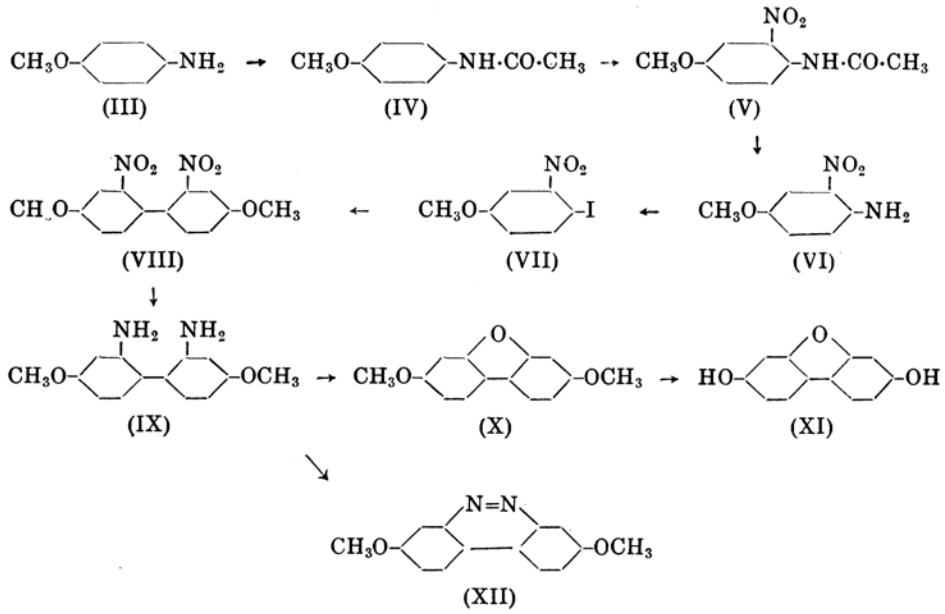
The absorption curve of 2,7-dihydroxy-diphenylene oxide, as shown by the figure in the experimental part, has a remarkable resemblance in form to those of diphenylene oxide and previously synthesized 2-hydroxy-diphenylene oxide. Further, the hydroxyl-groups having bathochromic influence on the absorption spectra, the absorption band is transferred to long wave in proportion to the number of substituted hydroxyl groups.

From these facts we can assert that the dihydroxy-diphenylene oxide melting at 241–242° obtained by the catalytic dehydration and condensation from resorcinol, has the constitution of (I) in the scheme shown above.

2,7-Dihydroxy-diphenylene oxide was synthesized as follows: *p*-anisidine (III) was changed into *p*-acetanisidide (IV) by acetylation, and after a nitro-group was introduced with nitric acid, nitro-*p*-anisidine was obtained by deacetylation,[4] which was already confirmed by H. Hähle[5] to be *o*-nitro-*p*-anisidine (VI). It was converted into *m*-nitro-*p*-iodo-anisol (VII) by the diazo-reaction, which was condensed to 2,2′-dinitro-4,4′-dimethoxy-diphenyl (VIII) with copper bronze by means of F. Ullmann's method.[6] Then it was reduced with stannous chloride and hydrochloric acid to 2,2′-diamino-4,4′-dimethoxy-diphenyl (IX). Applying E. Täuber's method of diphenylene oxide synthesis,[7] this amine was diazotized and the resulted diazonium solution was dropped into boiling copper sulphate solution, when a condensation took place giving

(3) Y. Tsuzuki, *Sci. Pap. Inst. Phys. Chem. Research, Japan*, **6** (1927), 305.
(4) F. Reverdin, *Ber.*, **29** (1896), 2595.
(5) H. Hähle, *J. prakt. Chem.* [2], **43** (1891), 66, 67.
(6) F. Ullmann and J. Bielecki, *Ber.*, **34** (1901), 2174.
(7) E. Täuber and E. Halberstadt, *Ber.*, **25** (1892), 2745.

2,7-dimethoxy-diphenylene oxide(X). Now, by the action of hydroiodic acid, the methyl groups were removed and 2,7-dihydroxy-diphenylene oxide(XI) was obtained.

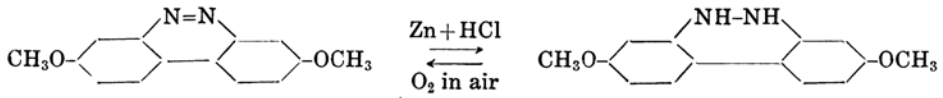


On cooling the mother liquor, from which 2,7-dimethoxy-diphenylene oxide was distilled off with steam, a new substance melting at 197° was obtained. By the investigation of its properties it was found to be 2,7-dimethoxy-phenazone(XII).

This substance separated out in dark yellow needles from water. It turned reddish brown with dilute acid, and again dark yellow when the solution was made alkaline. These colour changes were probably due to the formation and hydrolysis of phenazone salt, phenazone being a weak base. 2,7-Dimethoxy-phenazone was heated with 8% hydrochloric acid to an orange-red solution. On adding zinc dust, the solution immediately turned pale yellow, and subsequently almost colourless; it was supposed that 2,7-dimethoxy-phenazone was reduced to 2,7-dimethoxy-9,10-dihydrophenazone, similarly as phenazone was to dihydrophenazone,[8] and that the elimination of the azo group led to the decoloration. The dihydro-compound, however, was so unstable that, by removing the reducing agent, the decolourized solution soon became yellow; that is, 2,7-

(8) E. Täuber, *Ber.*, **24** (1891), 3086.

dimethoxy-phenazone was supposed to be reproduced by oxidation with air.



Now, J. J. Dobbie and his co-workers[9] reported that, main products of the reaction between the diazonium bromide of 2,2′-diamino-diphenyl and cuprous bromide, were phenazone and carbazole, while only trace of 2,2′-dibromo-diphenyl was obtained. Thereupon, it can be affirmed by this that the above-mentioned substance, melting at 197°, is 2,7-dimethoxy-phenazone. Further, it can be assumed that the black resinous matter which remained in the flask after the steam distillation, presumably contains some 2,7-dimethoxy-carbazole, but an attempt to extract this carbazole derivative was not especially made.

Experimental.

(1) **o-Nitro-p-anisidine.** (i) *p-Acetanisidide* (IV). *p*-Anisidine (25 g.) was warmed with water (30 c.c.) to form an emulsion, and acetic anhydride (20 c.c.) was added with stirring. The reaction took place at once with considerable heat evolution. After cooling, the yielded crystals were collected, and recrystallized from hot water, when colourless plates melting at 127.0–127.5° were obtained. (Yield 28 g.).

(ii) *o-Ntiro-p-acetanisidide* (V). According to F. Reverdin,[10] *p*-acetanisidide (38 g.) was mixed with 150 c.c. of 11% nitric acid, and the mixture was gradually heated to boiling. Heating was interrupted when the mixture about began to boil, and boiling continued for a while by the reaction heat. When the reaction mixture was left to cool, brown oil separated out which solidified to crystalline mass after cooling, and at the same time, some yellow needles separated out in the liquid. These were collected together, and recrystallized from water over again, yellow needles melting at 117°. (Yield 19 g.).

(iii) *o-Nitro-p-anisidine* (VI). *o*-Nitro-*p*-acetanisidide (19 g.) was heated with alcoholic potash (110 c.c.) on the water-bath under a reflux condenser. The saponification was completed after one hour. Then the solution was concentrated to about 30 c.c. and a sufficient quantity of water (50 c.c.) was added. Brilliant red crystals separated out at once, these were collected after cooling, and recrystallized from dilute alcohol to obtain red plates melting at 122.5–123.0° (Yield 14.5 g.).

(2) **m-Nitro-p-iodo-anisol** (VII). *o*-Nitro-*p*-anisidine (13.5 g.) was converted into its sulphate by heating with dilute sulphuric acid (200 c.c. of water and 9.2 c.c. of conc. sulphuric acid). Some insoluble matter was filtered off while still hot, and much quantity of sulphate separated out from the filtrate after cooling. The sulphate

(9) J. J. Dobbie, J. J. Fox, and A. J. Hoffmeister Gauge, *J. Chem. Soc.*, **99** (1911), 1615.

(10) F. Reverdin, *loc. cit.*

was collected, and the mother liquor was boiled with the previous insoluble matter to obtain more sulphate. This procedure was repeated again and again, and all the amine was converted into its sulphate. Then the sulphate was cooled below 10° together with the last mother liquor, and the solution of sodium nitrite (6.5 g. in 20 c.c. of water) was added drop by drop. Being kept for two hours, all the sulphate was diazotized to form yellow solution. It was cooled below 10°, and the potassium iodide solution (20 g. potassium iodide dissolved in 20 c.c. of water) was added drop by drop, when at once nitrogen gas was evolved vigorously, the reaction liquid turning deep black and giving iodine odour. After a while black oil separated out which solidified to a crystalline mass as it was cooled. It was allowed to stand overnight at ordinary temperature, then the black crystals were collected and washed with sodium thiosulphate solution again and again, when the black colour of iodine was easily removed and yellow crystals were obtained. After washed with 5% caustic soda solution and water, they were recrystallized from alcohol, yellow prisms[11] melting at 62°. (Yield 17.5 g.).

(3) **2,2′-Dinitro-4,4′-dimethoxy-diphenyl** (VIII). *m*-Nitro-*p*-iodo-anisol (9 g.) was thoroughly mixed with copper bronze (6 g.) in a large test tube, and heated in an oil-bath with incessant stirring. When the bath-temperature reached 130°, the viscosity of the reaction liquid suddenly increased, and copper lost its lustre to turn green-tinged white, owing to the formation of copper iodide. After being kept at 130–140° for half an hour, the temperature was raised to 160–170°, and the condensation was completed by keeping at this temperature for another half an hour. After cooling the reaction product was extracted with benzene over and over again, till benzene was no more tinged yellow. All the extracts were combined and the solvent was distilled off, when yellow crystals were obtained. They were recrystallized from benzene, yellow plates[12] melting at 136–137°. (Yield 4.0 g. Found: C, 55.70, 55.14; H, 4.32, 4.24; N, 9.28%; Mol. wt. (K. Rast), 305. Calc. for $C_{14}H_{12}N_2O_6$: C, 55.24; H, 3.98; N, 9.21%; Mol. wt., 304.)

(4) **2,2′-Diamino-4,4′-dimethoxy-diphenyl** (IX). 2,2′-Dinitro-4,4′-dimethoxy-diphenyl (5.7 g.) was dissolved in a solution of stannous chloride (60 g.) in glacial acetic acid (200 c.c.) saturated with hydrogen chloride, and after being allowed to stand overnight at room temperature, this solution was heated on the water-bath for an hour. By adding an excess (2000 c.c.) of 10% caustic soda solution, the amino compound separated out in fine crystals. It was collected and dissolved in dilute hydrochlorid acid, and purified by reprecipitation with 5% caustic soda solution after insoluble impurities were filtered off. Further, it was recrystallized from dilute alcohol when it separated out in colourless plates melting at 110.5–111.0°. (Yield 3.0 g. Found: C, 68.87; H, 6.90; N, 11.32%; Mol. wt. (K. Rast), 246. Calc. for $C_{14}H_{16}N_2O_2$: C, 68.81; H, 6.60; N, 11.48%; Mol. wt., 244.)

(5) **2,7-Dimethoxy-diphenylene oxide** (X). 2,2′-Diamino-4,4′-dimethoxy-diphenyl (1.2 g.) was dissolved in dilute hydrochloric acid (100 c.c. of water and 5 c.c. of conc. hydrochloric acid) to obtain its hydrochloride. The solution was cooled with ice,

(11) F. Reverdin described *m*-nitro-*p*-iodo-anisol as red needles melting at 62°, recrystallized from benzine or alcohol (*Ber.*, **29** (1896), 2595).

(12) This substance turns orange-yellow, when it is exposed to light for a long time.

and was diazotized by dropping sodium nitrite solution (0.7 g. sodium nitrite in 5 c.c. of water) with stirring. After being kept for two hours below 5°, the diazonium solution was gradually added drop by drop to a boiling 50% copper sulphate solution (60 g. copper sulphate in 60 c.c. of water), the latter being distilled during the addition so as to keep the volume of the solution in the flask constant.[13] Together with the distilled water, colourless crystals separated out in the condenser and receiver. After all the diazonium solution was added, the distillation was continued with the addition of water, still keeping the concentration of copper sulphate constant, until no more crystals distilled. The crystalline substance in the receiver was collected, and the condenser was washed with alcohol. After the alcoholic solution was evaporated to a small volume, a white crystalline precipitate was obtained by adding water. The products were together recrystallized from dilute alcohol, when the substance separated out in small white plates melting at 150°. (Yield 0.05 g. Found: C, 73.89; H, 5. 58%; Mol. wt. (K. Rast), 230. Calc. for $C_{14}H_{12}O_3$: C, 73.65; H, 5.30%; Mol. wt., 228.).

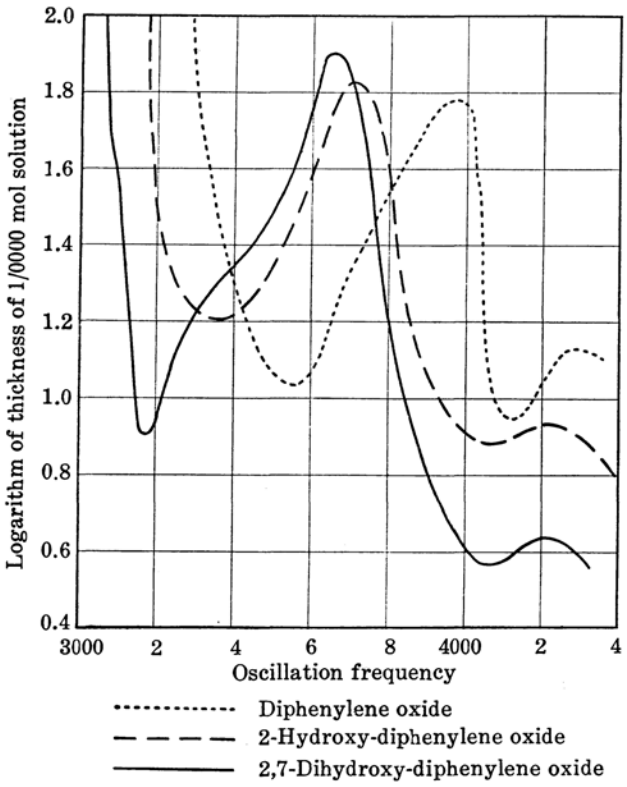
(6) **2,7-Dimethoxy-phenazone** (XII). After 2,7-dimethoxy-diphenylene oxide was thoroughly distilled off with steam, much quantity of black resinous matter in the flask was filtered off from the mother liquor while still hot. From the filtrate reddish brown needles separated out when it was cooled. It was dissolved in hot water, treated with animal charcoal, twice recrystallized from water, and dark yellow needles melting at 197° were obtained. (Yield 0.3 g. Found: N, 11.46%; Mol. wt. (K. Rast), 245. Calc. for $C_{14}H_{12}N_2O_2$: N, 11.67%; Mol. wt., 240.).

(7) **2,7-Dihydroxy-diphenylene oxide** (XI). 2,7-Dimethoxy-diphenylene oxide (50 mg.) was heated with 5 c.c. of hydroiodic acid (d = 1.7) in a sulphuric acid bath under a reflux condenser. After boiling for an hour and a half, it was left to cool after adding 10 c.c. of water, when white crystals separated out. They were collected and dissolved in dilute caustic potash solution, and reprecipitated with hydrochloric acid. Then the substance was recrystallized from hot water, some animal charcoal being used, colourless prisms melting at 241–241.5°. (Yield 12 mg.). On being dehydrated in Abderhalden's desiccating apparatus over P_2O_5 at 100° under a diminished pressure, 5.770 mg. of the substance lost 0.246 mg. of water. (Found: H_2O, 4.26. Calc. for $C_{12}H_8O_3 \cdot \frac{1}{2}H_2O$: H_2O, 4.31%.) Analysis and molecular weight determination were made with the anhydrous substance. (Found: C, 72.04; H, 4.35%; Mol. wt. (K. Rast), 204. Calc. for $C_{12}H_8O_3$: C, 71.98; H, 4.03%; Mol. wt., 200.)

2,7-Dihydroxy-diphenylene oxide thus obtained is soluble in alcohol, ether, and hot water, but scarcely soluble in cold water. When it is recrystallized from hot water, it separates out in white prisms, but being exposed to light for a long time it is gradually tinged with faint brown colour. On being heated it becomes almost colourless at 100° and melts at 241–241.5°. On adding a drop of ferric chloride solution to a solution of the substance, made by dissolving it in a very small quantity of alcohol and then adding water till the solution just begins to become turbid, it gives a green colour turning to a light brown on the addition of sodium carbonate solution.

These properties of 2,7-dihydroxy-diphenylene oxide obtained from *p*-anisidine, are perfectly coincident with those of dihydroxy-diphenylene oxide obtained from

(13) D. R. P., 167211.



resorcinol.[14] Moreover, no depression was observed in the mixed melting point of these two substances, indicating the identity of them.

Absorption curves. The absorption curve of 2,7-dihydroxy-diphenylene oxide obtained from *p*-anisidine was observed, and at the same time those of dihydroxy-diphenylene oxide obtained from resorcinol and 2-hydroxy-diphenylene oxide obtained from 2-amino-diphenylene oxide were also observed afresh. The results of their comparative study are shown in the figure, where the absorption curve of dihydroxy-diphenylene oxide obtained from resorcinol is not especially drawn as it is superposed on that of 2,7-dihydroxy-diphenylene oxide obtained from *p*-anisidine. All the observations of absorption spectra were made in a 1/10000 mol alcoholic solution.

As already pointed out, these curves strikingly resemble in form to that of diphenylene oxide,[15] suggesting that the substances melting at 138–138.5° and 241–242° obtained from resorcinol are derivatives of diphenylene oxide. It is remarkable that the absorption band removes to long wave with the increase of substituted hydroxyl groups, which have a bathochromic effect upon the absorption spectra.

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(14) Y. Tsuzuki, *Sci. Pap. Inst. Phys. Chem. Research, Japan,* **6** (1927), 304. 304.

(15) Y. Tsuzuki, *loc. cit.* K. Tatematsu and B. Kubota, *loc. cit.*