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The Addition Product of 4,4′-Dimethoxydiquinone and Hydrogen Chloride

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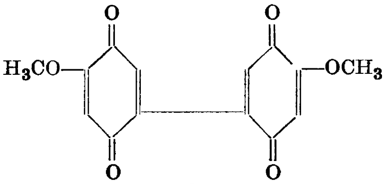
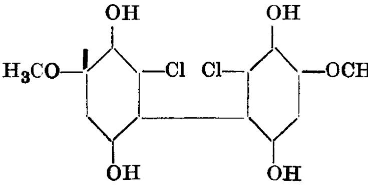
By the addition of hydrogen chloride to 4,4′-dimethoxydiquinone (I) Erdtman[1] obtained a substance possessing the expected composition (*i. e.*, addition of two moles of hydrogen chloride occurred) but very unexpected properties. On attempted recrystallization it decomposed into the original quinone and hydrogen chloride. On acetylation the addition product yielded a diacetate, not a tetraacetate as would be expected if it were dichloro-4,4′-dimethoxydiquinol (II).

Erdtman considered that the chlorine atoms entered the 6,6′-positions, an assumption which, although originally based on an analogy that was later shown to be invalid[2], is nevertheless supported by the Thiele acetylation of 4,4′-dimethoxydiquinone[3].



I



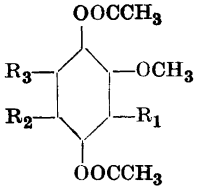
II

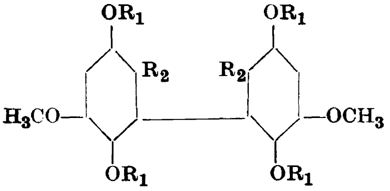
The addition product has now been methylated with diazomethane, and, by this reaction also, only two hydroxyl groups could be detected.

The instability of the addition product is not inconsistent with the diquinol structure (II), since Asp and Lindberg[4] have shown that another quinol, monobromo-2,6-dimethoxyquinol is very unstable and easily decomposes into 2,6-dimethoxyquinone and hydrogen bromide. The fact that only two hydroxyl groups can be acetylated or methylated, however, is not easily understandable on the basis of this structure.

ULTRAVIOLET ABSORPTION DETERMINATIONS

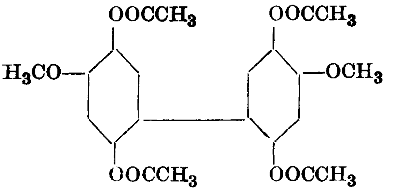
In order to investigate the structure of the addition product, the ultraviolet absorption spectra of this substance and a number of potentially related phenyl and diphenyl derivatives have been examined. The results are summarized in Table 1 and four typical absorption curves are given in Fig. 1.





III $R_1 = R_2 = R_3 = H$
IV $R_1 = Cl, R_2 = R_3 = H$
V $R_2 = Cl, R_1 = R_3 = H$
VI $R_3 = Cl, R_1 = R_2 = H$

VII $R_1 = CH_3, R_2 = H$
VIII $R_1 = OCCH_3, R_2 = H$
IX $R_1 = CH_3$ $R_2 = Br$



X

XI Diacetate of addition product

XII Dimethyl ether of addition product

Table 1. Ultraviolet absorption spectra. All determinations in absolute ethanol solution.

Substance	Maximum	Inflexion	Minimum
III	272 mμ		247 mμ
IV	270		248
V	280		250
VI	275		250
VII	286		263
VIII	278		261
IX	292		263
X	246	273 mμ	234
XI	234, 288	248, 315	223, 274
XII	237, 295	253, 320	225, 275

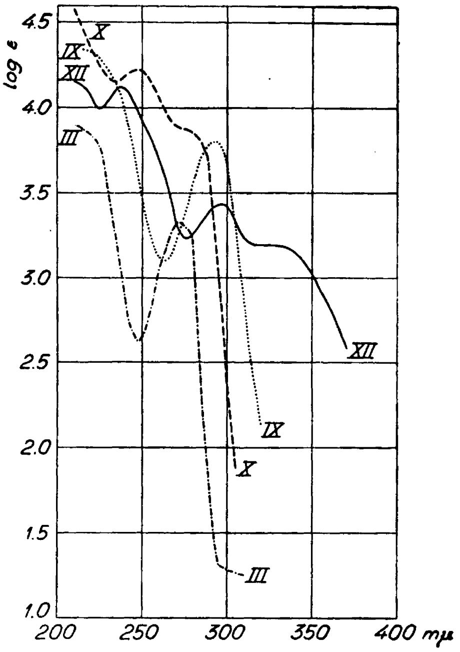


Fig. 1. Ultraviolet absorption spectra for methoxyquinol diacetate (III), 2.2′ di. bromo 3,5,6,3′,5′,6′,hexamethoxydiphenyl (IX), 4,4′-dimethoxydiquinol tetraacetate (X) and the dimethyl ether of the addition product (XII). All determinations in absolute ethanol.

The spectra of III, IV, V and VI are very similar and only that of III is given in Fig. 1. For the same reason, IX has been chosen as representative for VII, VIII and IX, and XII for XI and XII.

Both from Table 1 and Fig. 1 it is evident that the substances XI and XII cannot be aromatic. The spectra do not correspond at all with those of the diphenyls (VII—X), in particular the high absorption at longer wavelengths (log $\varepsilon = 3$ at 350 mμ) has no counterpart at all in the latter.

INFRARED ABSORPTION DETERMINATIONS

In order to confirm the foregoing evidence of the non-aromatic nature of the addition product, the infrared absorption spectrum of its dimethyl ether has been determined (Fig. 2). No hydroxyl band (3400—3800 cm^{-1}) was found but a strong band at 1683 cm^{-1} was present. The region 1660—1830 cm^{-1} is typical for the C = O group absorption band and no other groups are known to appear in this region [5]. For ketones the C = O absorption band lies between 1670 and 1720 cm^{-1}. As the diquinol structure involves two hydroxyl groups but no C = O groups, the infrared spectrum furnishes conclusive evidence against it.

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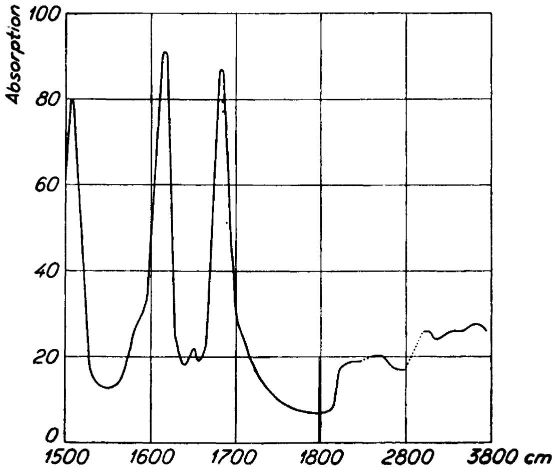
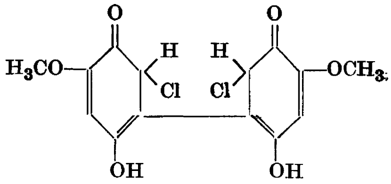


Fig. 2. Infrared absorption spectrum of the dimethyl ether of the addition product.

DISCUSSION

The ultraviolet and infrared absorption spectra show that the product obtained when hydrogen chloride is added to 4,4'-dimethoxydiquinone, or at least the diacetate and the dimethyl ether of this addition product, is non-aromatic and contains carbonyl groups. Different formulas can be suggested fulfilling these requirements, of which structure II' seems to be the most probable. The six conjugated double bonds will render this structure stable compared with the other non-aromatic isomers. A hydrogen shift would transform this substance into the diquinol (II) which, by analogy with the previously mentioned monobromo-2,6-dimethoxyquinol, would probably not be stable in the presence of acids. The non-aromatic substance (II'), on the other hand, is stable towards acids but very unstable towards bases, as the structure requires.



II'

EXPERIMENTAL

The addition product and its diacetate were prepared according to Erdtman [1]. The preparation of the substances III—VI has been described elsewhere [6]. The substances VII—X were Erdtman's original specimens.

Dimethyl ether of the addition product

To the addition product (2 g) in a solution of acetone (300 ml) was added diazomethane, prepared from nitrosomethylurea (10 g), in ether (150 ml). After 24 hours a yellow material which had separated was removed by filtration and the solution then concentrated to dryness under reduced pressure. The residue was dissolved in ether (500 ml) and the solution washed with 10 % potassium hydroxide (3 × 50 ml), which as a result turned dark red in colour. The ether solution was then washed three times with water, dried over calcium chloride and concentrated to a small volume (30 ml). Slightly yellow crystals of m. p. 210—211° (uncorr.) were precipitated during the concentration. After one recrystallization from acetic acid-water, 1 : 1, these crystals were almost colorless and had m. p. 214—215°. Yield, 350 mg. For analysis and spectrophotometric determinations the substance was recrystallized four times further from the same solvent. The melting point was unchanged by these recrystallizations.

$C_{16}H_{16}O_6Cl_2$ (375.2)	Calc.	C 51.2	H 4.30	Cl 18.9	OCH_3 33.1
	Found	» 51.2	» 4.44	» 19.0	» 33.2

The ultraviolet absorption determinations were carried out with a Beckman Model DU spectrophotometer. All determinations were made in absolute ethanol.

The infrared absorption determinations were carried out with a Perkin Elmer infrared spectrometer, Model 12 B, with a 60° rock salt prism, using the paraffin oil paste method.

SUMMARY

The dimethyl ether of the addition product of hydrogen chloride and 4,4'-dimethoxydiquinone has been prepared. The ultraviolet spectra of this substance, the corresponding diacetate and a number of related benzene and diphenyl derivatives have been investigated. The infrared spectrum of the dimethyl ether has also been investigated. On the basis of these experiments, a non-aromatic structure for the addition product has been suggested.

The author wishes to thank Professor H. Erdtman of this Institute for suggesting this work and for valuable discussions. His thanks are also due to Professor H. Theorell, Medicinska Nobelinstitutet, Stockholm, for placing facilities for the infrared absorption determination at his disposal and to Dr. K-G. Paul of the same Institute, for a discussion concerning the infrared spectrum.

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