

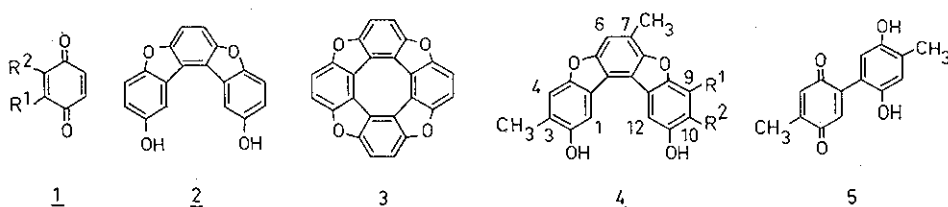
THE STRUCTURE OF A TERMOLICULAR CONDENSATION PRODUCT OBTAINED
BY THE ACTION OF STRONG ACIDS ON TOLUQUINONE*

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When treated with sulfuric acid in acetic acid, toluquinone 1 ($R^1 = \text{CH}_3$, $R^2 = \text{H}$) gives the termolecular compound 4 ($R^1 = \text{H}$, $R^2 = \text{CH}_3$) as the major product.

As reported in several earlier papers, many quinones undergo condensation reactions in strongly acidic solution. Thus p-benzoquinone, 1 ($R^1 = R^2 = \text{H}$), possessing four reactive CH groups, gives large amounts of black polymers and, among other products, a relatively small amount of a termolecular compound,^{1,2} 2, and a minute amount of the circulene 3.³ For an X-ray study of the latter compound, see ref. 4.



Disubstituted benzoquinones such as 1 ($R^1 = R^2 = \text{CH}_3$ or C_3H_7), possessing two reactive CH groups situated in o-positions to each other, give large amounts

*Dedicated to Professor S. Sugawara in remembrance of the happy years we spent together in Sir Robert Robinson's laboratories in the early thirties.
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of the corresponding alkylated compounds of types 2 and 3.^{3,5,6} Under special conditions α -naphthoquinone furnishes a cyclic analogue of type 3 in over 90 % yield.^{1,7-9}

Toluquinone 1 ($R^1 = \text{CH}_3$, $R^2 = \text{H}$), possessing three reactive methine groups, differs from *p*-benzoquinone in giving less polymers. A fair yield of a compound of type 2 has been isolated from the reaction mixture.¹ An improved method of preparation is given below.

Based on slender evidence, the structure 4 ($R^1 = \text{CH}_3$, $R^2 = \text{H}$) was suggested for this compound in 1933, when it was first described.¹

The work on quinone oligomerisation was continued by the senior author with, *inter alia*, Nils E. Stjernström.¹⁰ The structure of compound 2 was strictly proved.²

The dimethyl ether of the termolecular analogue of compound 2 obtained from ethyl-*p*-benzoquinone could be oxidised to a tricarboxylic acid which on decarboxylation furnished a compound identical with the dimethyl ether of the *p*-benzoquinone trimer 2.² Hence there is no doubt that, like compound 2, the ethylquinone product and, by analogy, the toluquinone product, are derivatives of 1,2-diphenylbenzene.

It was deemed probable that two of the methyl (ethyl) groups were situated in positions 3 and 7 because in the early stages of the reaction the toluquinone dimer 5 was formed.¹ Later on this compound disappeared and the termolecular product appeared. The dimer 5 is thus probably an intermediate in the trimerisation process. The position of the third methyl group, however, remained unknown. There were some indications that it might occupy the 9-position, but they were by no means convincing.

Since a knowledge of the orientation of this methyl group is of considerable importance in relation to the mechanism of quinone oligomerisation, a problem to which we intend to return in a forthcoming publication, we tried to settle this point by an NMR study. The diacetate and the dimethyl ether of the tolu-

quinone product already described¹ proved to be too sparingly soluble in the common solvents. For this reason the divalerate was prepared from the crude toluquinone product. Hydrolysis of the ester followed by methylation furnished the above-mentioned dimethyl ether.

The 60 MHz NMR spectrum (CDCl_3) of the divalerate appeared to suggest a structural analogue of 4 with hydrogen atoms at carbon atoms 1, 3, 6, 10 and 12 and hence methyl groups at carbon atoms 4, 7 and 9. However, decoupling experiments gave ambiguous results and a 270 MHz NMR spectrum was therefore recorded.¹¹ This spectrum displayed five singlets at $\delta = 7.45, 7.48, 7.53, 7.83$ and 7.86 ppm ($\text{H}_1, \text{H}_4, \text{H}_6, \text{H}_9$ and H_{12}). There were three singlets corresponding to the Ar-CH_3 groups at $\delta = 2.36, 2.37$ and 2.71 ppm (methyl groups in positions 3, 10 and 7, respectively) as well as signals due to the valeroyl groups at $\delta = 1.04$ (6 H, triplet), 1.54 (4 H, sextet), 1.84 (4 H, quintet) and 2.70 ppm (4 H, triplet), $J = 7.5$ Hz for all protons of the valeroyl groups. This is in full accord with the structure 4 ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CH}_3$, $\text{C}_4\text{H}_9\text{COO-}$ instead of HO-). Obviously the asymmetry of the molecule is great enough to induce the small shift differences observed for the, pairwise, very similar protons H_4 and H_9 , H_1 and H_{12} and those of the 3- and 10-methyl groups. The absence of any observable coupling between the protons attached to the terminal rings clearly shows that they must be situated in para positions to each other. This rules out all the theoretically possible structures except that of the divalerate of 4 ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CH}_3$).

Compound 4 ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CH}_3$): To a solution of toluquinone (4 g) in acetic acid (20 ml) was added a solution of toluhydroquinone (4 g), acetic acid (20 ml) and conc. H_2SO_4 (0.8 ml). The mixture turned brown and after a few minutes a precipitate began to separate. After 24 h the precipitate was collected by filtration and washed with water containing NaHSO_3 and then with pure water and dried. Yield 3.0 g.

Valeroylation: The above product (1.5 g) was heated with valeric anhydride containing a few drops of pyridine. On cooling the crude divalerate separated. It was collected by filtration and recrystallized from dimethylformamide, acetic acid or acetonitrile. It formed cotton wool-like needles which on rubbing became electrified and which gave a violet-red colour reaction with conc. H_2SO_4 . M.p. 188-190 °C. (Found: C 74.1, H 6.4. Calc. for $\text{C}_{31}\text{H}_{32}\text{O}_6$: C 74.4, H 6.4).

Hydrolysis and methylation: The divalerate was heated with acetic acid containing sulfuric acid. A solution was obtained which was poured into water. The solid which formed was collected and methylated with dimethyl sulfate and sodium hydroxide. The methyl ether melted at 234-236 °C. The m.p. was undepressed by admixture with the methyl ether described in ref. 1.

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- 11 We thank Dr. O. Wennerström for recording this spectrum.

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