Tetranaphthocyclo-octatetraene Tetra-oxide, a Cyclisation Product from α-Naphthoquinone

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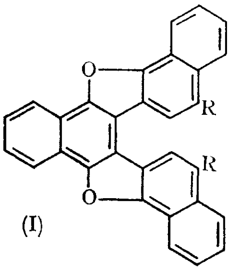
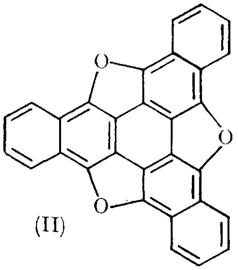
In 1881 Knapp and Schultz[1] reported that α-naphthoquinone, when treated with concentrated hydrochloric acid, is transformed into an amorphous insoluble product. Some thirty-five years ago one of us re-investigated this material.[2] The product was acetylated and the resulting product found to contain two main components. One, assigned structure (I; R = OAc), was soluble in boiling quinoline but the other was insoluble in all solvents tried and was assigned structure (II). The latter compound has lately been obtained in excellent yield from α-naphthoquinone by the action of aluminium chloride in nitrobenzene or chlorobenzene solution (Marschalk,[3] Riegelbauer[4]).

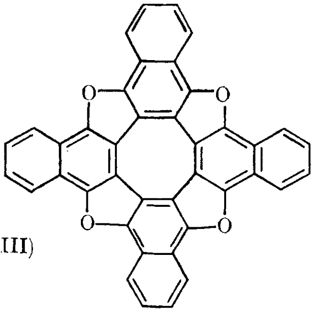
Structure (II) has been accepted[3–5] but we have long considered it to be improbable because such a compound would be highly strained. The compound can be purified by sublimation (400°/10^{-3} mm.) or by recrystallisation from boiling dibenzofuran, forming long yellowish-white needles. The mass spectrum confirmed our suspicion as to its structure [$M^+ = 560{\cdot}1079$, base peak, corresponding to $C_{40}H_{16}O_4$. Other peaks were at $M = 280$ (M^{2+}) and $M = 186{\cdot}7$ (M^{3+}). No other large peaks were present.] Furthermore the substance was obtained from a mixture of bis-α-naphthoquinone and the corresponding hydroquinone (1 : 1) with aluminium chloride in nitrobenzene.



(I)



(II)



(III)

The non-phenolic polymerisation product of α-naphthoquinone is obviously the tetranaphthocyclo-octatetraene tetra-oxide (III). The molecule is probably planar; X-ray investigation will settle this point. The i.r. spectrum (KBr disc) showed strong peaks at 665, 760, 920, 1030, 1060, 1110, 1350, and 1425 cm.$^{-1}$. Owing to the insolubility of the compound a good u.v. spectrum has not yet been obtained.

On distillation with zinc dust (I; R = OH) gives (I; R = H) as needles, m.p. 416—418°, solidifying and remelting at 435—436°. The mass spectrum showed $M^+ = 408{\cdot}1167$, corresponding to $C_{30}H_{16}O_2$. The i.r. spectrum (KBr disc) showed strong peaks at 670, 735, 760, 800, 920, 1070, 1210, 1360, 1375, and 1410 cm.$^{-1}$. The u.v. spectrum in $CHCl_3$ showed λ_{max}: 284 (log ε 4·88), 316 (4·49), 330·5 (4·44), 338 (4·42), and 347·5 nm. (4·40).

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