Synthesis, Structure and Semiconductivity of a *p*-Terphenoquinone

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3,3′,5,5′-Tetra-*tert*-butyl-*p*-terphenoquinone **5**, the first terphenoquinone, has been obtained as metallic blue–green crystals showing anisotropic semiconductivity; the crystal structure of **5** shows that the nearly-planar molecules form slipped stacks along the needle axis.

Stable terphenoquinones have apparently not previously been reported, although an attempt to prepare a tetraphenyl *p*-terphenoquinone was recorded by Dimroth in 1963.[1] The unstable product exhibited a very strong ESR signal, attributed to the biradical. Here we report the synthesis of *p*-terphenoquinone **5**, by reactions outlined in Scheme 1.† Stable extended quinonoid molecules with structures related to that of **5** include the diquinoethylene[3] and a recently reported series of *p*-quinones extended by thiophenylidene units.[4]

Compound **5** may be crystallised as large needle-like prisms, up to 2 cm in length, by slow evaporation of diethyl ether solutions. The air-stable crystals are metallic bluish green in colour, reflecting gold from end facets. Solutions of **5** are purple in colour; the electronic spectrum is shown in Fig. 1. No ESR signal was detected for **5** either in solution or as a solid.

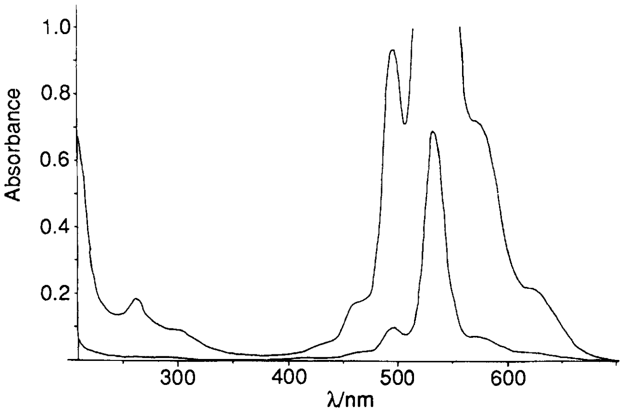

Fig. 1 Electronic spectrum of terphenoquinone **5** in diethyl ether

The crystal structure of **5**, determined by X-ray diffraction,‡ is shown in Fig. 2. The lengths of C–C ring bonds and C=O bonds are similar to those for the related 2,2′, 6,6′-tetra-*tert*-butyl-*p*-benzoquinone.[6] The C=C bonds between the rings are quite long for a double bond, 141.7 pm, and there is a 12.5° twist between the outer rings and the central ring.

The single-crystal conductivity was measured using a direct-current four-probe technique on crystals about 0.2 × 0.2 × 5 mm. After exhaustive (10×) recrystallization from diethyl ether, conductivity was recorded as $1 \times 10^{-8}\ \Omega^{-1}\ \mathrm{cm}^{-1}$,

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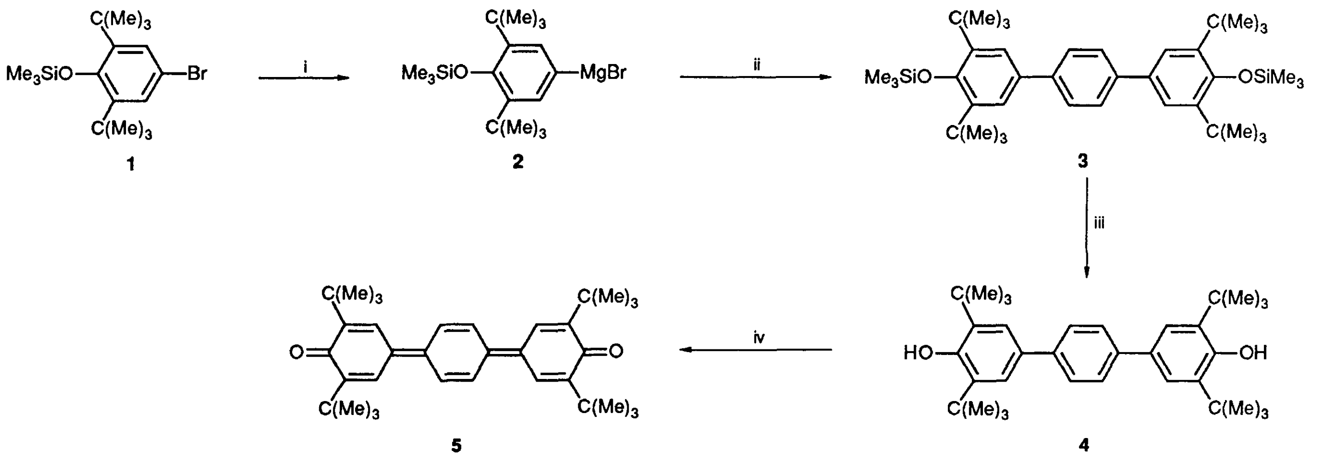
† Coupling of the Grignard reagent from 2,6-di-*tert*-butyl-4-bromo-1-trimethylsiloxybenzene[2] with *p*-dibromobenzene in benzene–tetrahydrofuran (THF), in the presence of catalytic $\mathrm{Ni(acac)_2}$ (Hacac = pentane-2,4-dione), gave after workup 78% of **3** as white crystals, m.p. 262–263 °C, ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.44 (s, 18H), 1.50 (s, 36H), 7.53 (s, 4H), 7.62 (s, 4H); IR ν/cm^{-1} ($\mathrm{CCl_4}$) 2960m, 1420s, 1232s, 1120s, broad, 930s, 865s, 630s; UV (THF) 296 nm, log ε 4.53; MS calcd. *m/z* 630.42883, found 630.42771. A solution of **3** in diethyl ether–methanol was hydrolysed with *tert*-BuOH, then acidified with HCl to produce a white precipitate of **4** (95%), m.p. >295 °C, ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.50 (s, 36H), 5.21 (s, 2H), 7.45 (s, 4H), 7.59 (s, 4H); IR ν/cm^{-1} ($\mathrm{CCl_4}$) 3645s, 2960s, 1430s, 1230s, 1118s, 835m, 630m; UV (THF) λ_{max} 294 nm, log ε 4.50; MS calcd. *m/z* 486.34928, found 486.34827. To a solution of 0.49 g of **4** in 50 ml benzene was added 1.3 g of $\mathrm{K_3Fe(CN)_6}$ in 20 ml of 0.5 mol dm^{-3} KOH. The solution was stirred rapidly for 2 h; the purple organic layer was separated and washed with water, then the benzene was removed under vacuum and the product was crystallised from diethyl ether yielding 0.34 g (81%) of **5**, m.p. 226–227 °C. ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.53 (s, 36H), 7.37 (s, 4H), 7.63 (s, 4H); IR ν/cm^{-1} (KBr) 2960m, 1630w, 1575s, 1452m, 1359m, 1254m, 1092m, 1042m, 895m, 869m, 827m; UV–VIS ($\mathrm{Et_2O}$) λ_{max} (log ε) 631 sh (3.87), 583 sh (4.37), 534 (5.40), 496 (4.53), 458 sh (3.78), 435 sh (3.25), 305 sh (3.51), 262 (3.81). Satisfactory elemental analyses were obtained for all compounds.

‡ *Crystal data* for **1**: $\mathrm{C_{34}H_{44}O_2}$, $M = 484.72$, tetragonal, $P4_2/n$ [$C_{4h}{}^4$, No. 86] (Origin at $\bar{1}$) $a = b = 2196.3(1.5)$, $c = 623.2(2)$ pm, $U = 3006.5(2.9)$ Å^3, $Z = 4$, $D_c = 1.07$ g cm^{-3}. Data were measured on a Syntex P1 diffractometer with Mo-Kα radiation (graphite monochromator) using θ–2θ scans. The structure was solved by direct methods (MULTAN)[5] with hydrogen atoms included as fixed atom contributions in idealised positions, and refined by a blocked diagonal least-squares method using absorption corrected data to give $R = 0.043$, $R_w = 0.055$ for 2660 independently observed reflections.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1 *Reagents and conditions*: i, Mg, THF; ii, 1,4-dibromobenzene, Ni(acac)$_2$; iii, RO$^-$, then H$^+$; iv, PbO$_2$ or K$_3$Fe(CN)$_6$

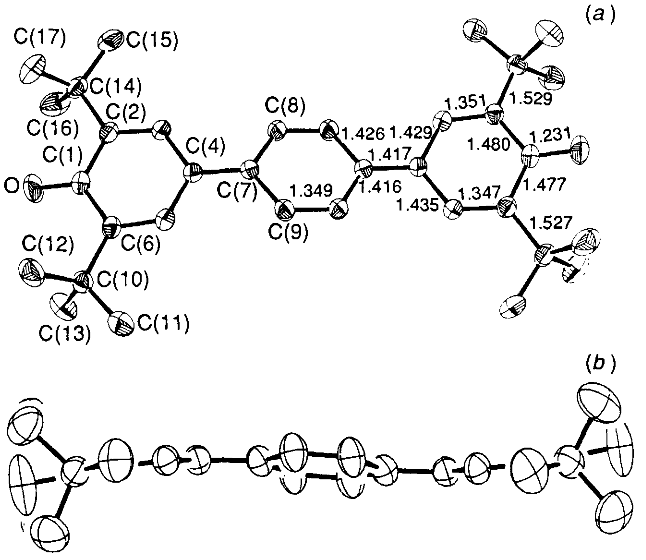


Fig. 2 ORTEP drawings showing two views of **5**. Thermal ellipsoids are 30% probability contours. Atom labels and important bond lengths (Å) for the centric molecule are shown in (a).

along the needle axis. The bulk conductivity of a compressed pellet prepared from finely-ground **5** was measured as $<1 \times 10^{-11}\ \Omega^{-1}\ \text{cm}^{-1}$, so the anisotropy of conductivity is quite large ($>10^3$). Analytically pure crystals of **5** at earlier stages of purification showed conductivities of $2\text{–}9 \times 10^{-5}\ \Omega^{-1}\ \text{cm}^{-1}$, indicating that the conductivity is probably extrinsic. Over the temperature range 273–373 K, the conductivity conformed to the expression $\sigma = \sigma_0\ e^{(-E_a/KT)}$ with an activation energy for conduction of 0.51 eV (E = 1.02 eV). This value is also consistent with extrinsic semiconductivity. A measurement of the sign of the thermoelectric power indicated that electrons are the majority carriers.

The packing arrangement for **5** shows that the molecules form slipped stacks, with the electron-deficient quinone rings above the relatively electron-rich central rings. Although the intermolecular distances are rather large, *ca.* 400 pm, this arrangement may possibly facilitate electron mobility.

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