

116. Synthesis and Structure of a *p*-Terphenoquinone and Paramagnetic Species Derived Therefrom¹⁾

by **Peter Boldt*** and **Detlev Bruhnke**

Institut für Organische Chemie der Technischen Universität Braunschweig, Hagenring 30, D-3300 Braunschweig

and **Fabian Gerson*** and **Markus Scholz**

Institut für Physikalische Chemie der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

and **Peter G. Jones**

Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig, Hagenring 30, D-3300 Braunschweig

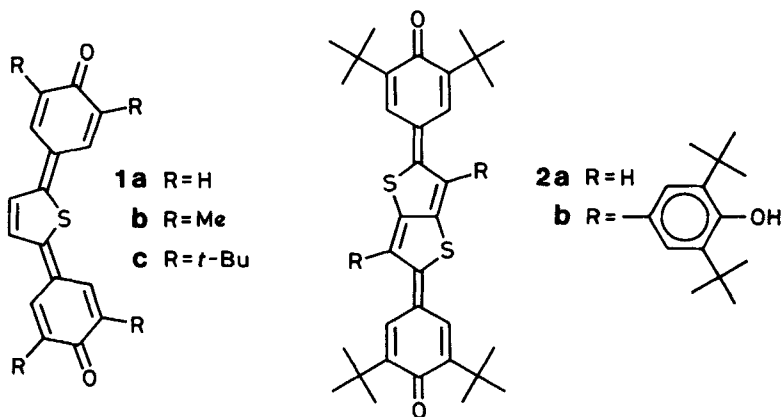
and **Friedrich Bär**

Fachbereich Chemie der Universität Marburg, Hans-Meerwein-Strasse, D-3550 Marburg

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3,5,3',5'-Tetra(*tert*-butyl)-*p*-terphenoquinone (**12b**) was synthesized and characterized by its spectroscopic and X-ray structural data. The ground state of **12b** is singlet with a strong contribution of a biradical structure. Paramagnetic derivatives of **12b**, such as the semiquinone radical anion (**12b^{•-}**) and its *O*-protonated form, the phenoxo radical (**18**), were studied by ESR and ENDOR spectroscopy.

Introduction. – In the last few years, there has been an increasing interest in 'extended quinones', in view of their technical applications, *e.g.*, in the search for organic semiconductors (2,7-pyrenequinones [2] [3]) or for electron acceptors in xerography (3,5,3',5'-tetraalkyldiphenobenzoquinones [4]). Analogues of *p*-terphenoquinone with a central thiophene or thienothiophene system (**1a–c** and **2a, b**) were recently synthesized and studied with regard to their special redox properties [5–7].



¹⁾ Part 12 of 'Quinones'. Part 11: [1].

p-Terphenyloquinone (= 1,1':4',1''-terphenyl-4,4''-dione; **12**, R = H) itself has not yet been characterized, presumably because of its high reactivity. Dimroth *et al.* [8] dehydrogenated the hydroquinone **11a** (R = Ph) and obtained a product which exhibited a 'very strong ESR signal' and was, therefore, assigned a diradical structure. However, an analysis of this signal was not carried out. According to our calculations²), a planar *p*-terphenyloquinone should have a singlet ground state. To verify this prediction, we have synthesized 3,5,3'',5''-tetra(*tert*-butyl)-*p*-terphenyloquinone (**12b**, R = *t*-Bu), in which the four bulky alkyl substituents served to enhance the kinetic stability. After this synthesis was completed [9], preparation of **12b** by a different route was reported [10].

Results and Discussion. – *Synthesis of 12b.* To begin with, an attempt was made to follow the route for the preparation of the tetraphenyl derivative **12a**, as described by Dimroth *et al.* [8] (*Scheme 1*). This route involves the bispyrylium salt **7** which is obtained starting from terephthalaldehyde **3**. Base-catalyzed aldol condensation of **3** with the ketone **4** gives the diketone **5** which, subsequently, reacts with further two molecules of **4** and with FeCl₃ in Ac₂O to yield **7**. Conversion of **7** into its BF₄⁻ salt **8** and reaction with MeNO₂ results in the dinitro derivative **9** which is reduced to the diamino compound **10**. This is transformed into the hydroquinone **11** by diazotation and boiling. Finally, oxidation of **11** with K₃[Fe(CN)₆] should yield **12**.

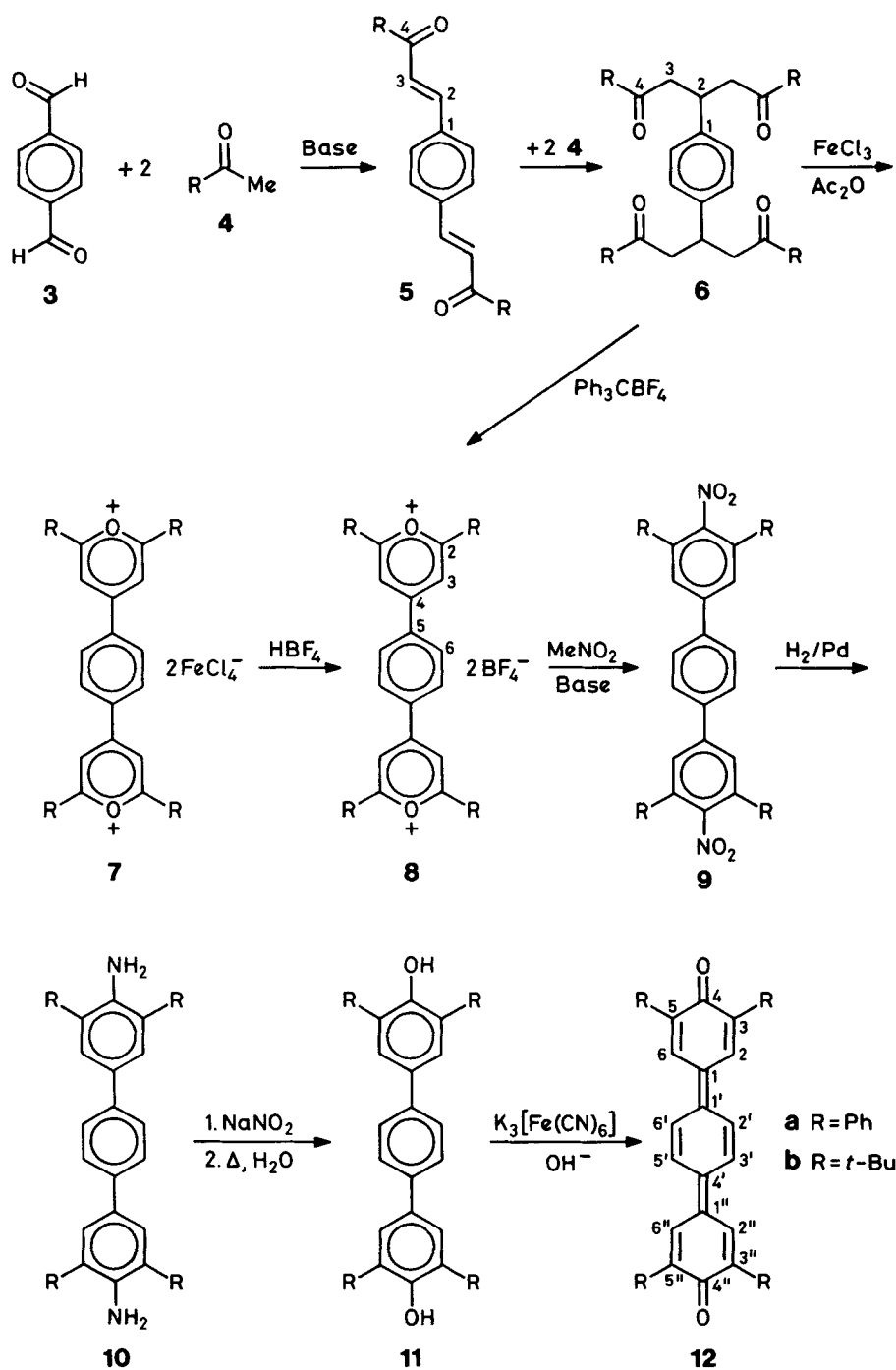
This synthetic procedure was carried out for both **12b** (R = *t*-Bu) and **12a** (R = Ph), because no experimental details were reported for **8a** and the following steps, and because no spectroscopic data were available for **9a**–**11a** [8] [12].

The diketone **5b**, obtained by condensation of **3** with **4b** (82%), did not react further according to *Scheme 1*, in contrast to **5a** which yielded **7a** under these conditions. The failure to obtain **7b** is presumably due to the steric hindrance in the *Michael* addition of **4b** to **5b** which should give **6b** as an intermediate undergoing ring closure to **7b**. The two steps of the reaction **5b** → **7b** were, therefore, carried out separately. Firstly, catalysis of the *Michael* addition by *t*-BuOK led to **6b** with 77% yield and, secondly, **6b** was converted to **7b** with FeCl₃ in Ac₂O (42%) or directly to **8b** with Ph₃CBF₄ (79%). Unfortunately, nitration of **8b** to give **9b** did not succeed, even using various bases such as *t*-BuOK, EtOK, and Et₃N. Again, steric hindrance is considered to be responsible for this failure. In contrast, **11a** could be prepared from **8a** via **9a** and **10a** (*Scheme 1*), albeit with lower yield than reported previously [8] [12].

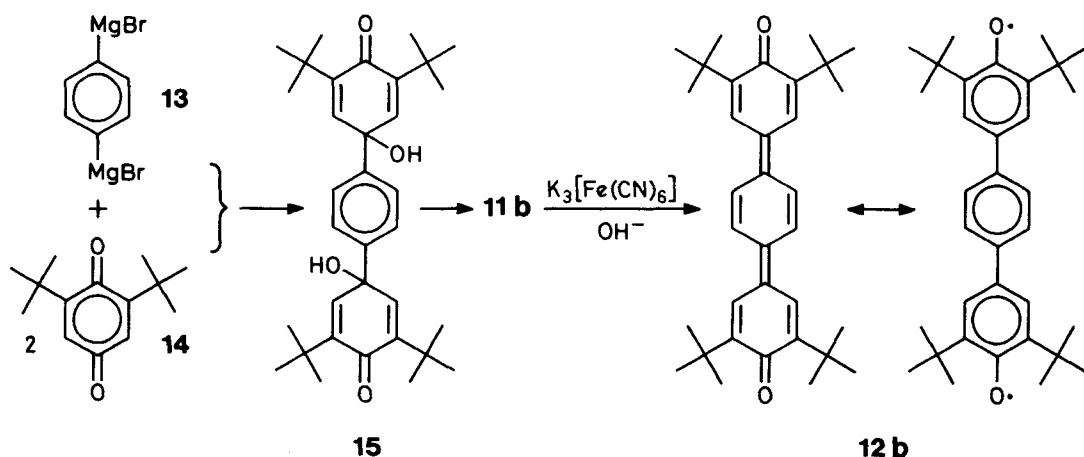
Because the attempted synthesis of **12b** following *Scheme 1* did not proceed beyond **8b**, an alternative route had to be found. As indicated in *Scheme 2*, this route started with **13** prepared from 1,4-dibromobenzene and Mg [13]. Reaction of **13** with two molecules of the quinone **14** yielded the bisquinole **15** (37%) which was reduced with LiAlH₄ [14] to **11b**. Oxidation of **11b** with K₃[Fe(CN)₆] afforded green-yellow crystals of metallic lustre (85% yield; m.p. 214° (dec.)) which were indefinitely stable at –20° either as solid (even in presence of O₂) or in solution. A striking feature of the solutions was their intense blue-violet color, due to an unusually sharp absorption maximum at 538 nm (width at half-height, *ca.* 25 nm) with a high extinction coefficient (log ϵ = 5.314). The final product has been identified as 3,5,3'',5''-tetra(*tert*-butyl)-*p*-terphenyloquinone (**12b**) in a singlet ground state.

²) Performed using MNDOC parametrization (MNDO procedure with CI) as described in [11]. For details, see [9].

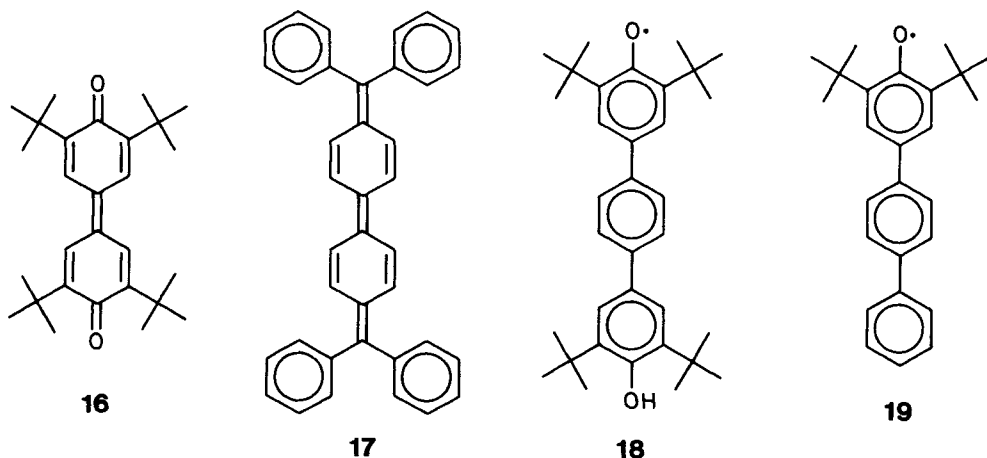
Scheme 1



Scheme 2



Characterization of 12b. As stated in [10], ESR studies of **12b** give no evidence for a triplet ground state, neither did such studies indicate a low-lying excited triplet state of the compound. This is because glassy solutions of **12b** in 2-methyltetrahydrofuran (MTHF) are ESR-silent, and they remain so upon irradiation in the absorption band at 538 nm. The diamagnetism of **12b** is also consistent with the observation of sharp NMR signals. The values determined from the UV/VIS, NMR, and IR spectra (see *Exper. Part*) lie in the region expected by extrapolation in the series **14** → 3,5,3',5'-tetra(*tert*-butyl)-*p*-diphenylquinone (**16**) → **12b**. IR (KBr): $\nu(\text{CO}) = 1655 \rightarrow 1599 \rightarrow 1575 \text{ cm}^{-1}$; UV/VIS: λ_{max} ($\log \epsilon$) = 255 (4.525) → 421 (4.115) → 538 nm (5.314); $^1\text{H-NMR}$: $\delta(\text{ring-H}) = 6.51 \rightarrow 7.64 \rightarrow 7.70, 7.81$; $^{13}\text{C-NMR}$: $\delta(\text{C(O)}) = 187.77, 189.02 \rightarrow 185.45 \rightarrow 186.10$. Apart



from the M^+ peak at m/z 484 (56%), the MS exhibits a $[M + 2]^+$ peak at 486 (100%) typical of quinones. Some biradical 'character' of **12b** is indicated by the low frequency of $\nu(\text{CO})$ (1575 cm^{-1}) which approaches that of phenoxy radicals (1560 cm^{-1}) [15].

X-Ray structure analysis shows that two independent molecules are present in the unit cell: one lies in a general position, while the other displays crystallographic inversion symmetry (Fig. 1). The three rings, in which the bond lengths exhibit the quinone pattern, are approximately coplanar, the dihedral angles being *ca.* 10° between adjacent rings in both molecules. These deviations lead to a slightly domed form of the molecule in the general position, as the angle between the vectors $\text{C}(1)–\text{C}(4)$ and $\text{C}(1'')–\text{C}(4'')$ is 22° . The $\text{C}=\text{C}$ bonds between the rings are rather long for formal double bonds: $141.8–142.8\text{ pm}$.

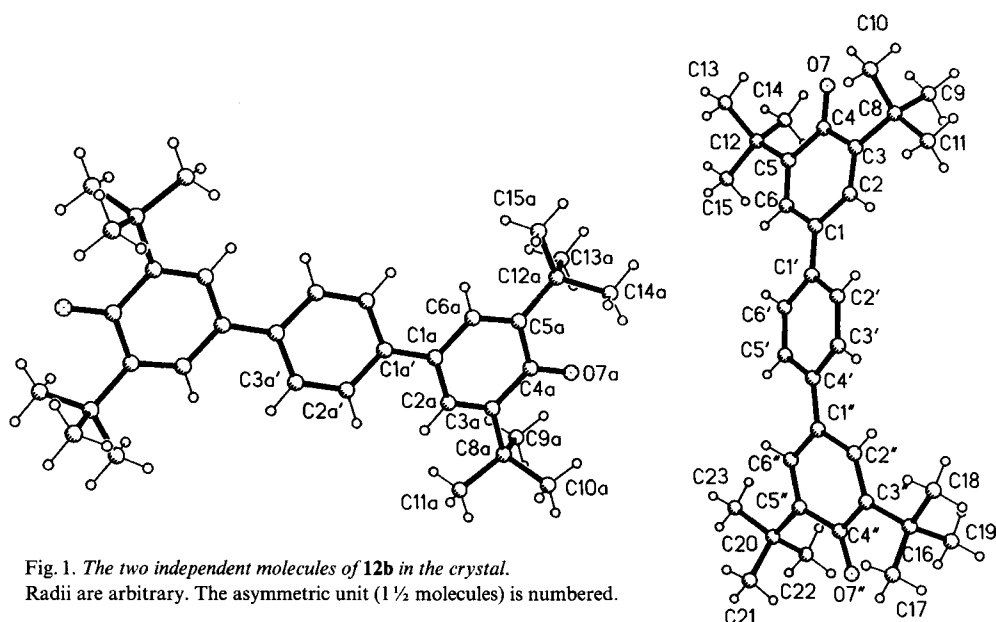


Fig. 1. The two independent molecules of **12b** in the crystal. Radii are arbitrary. The asymmetric unit ($1\frac{1}{2}$ molecules) is numbered.

A very similar value (141.7 pm) was reported for a different modification of **12b**, which crystallized tetragonally without solvent; the molecule displayed inversion symmetry [10]. Analogous bond lengths are 135.5 and 139.1 pm in **1c** [5] and 140.1 pm in **2b** [16]; the dihedral angles between the central and the outer rings in these quinones are 10 and 13° , respectively. A still more pronounced lengthening of the $\text{C}=\text{C}$ bonds between the rings (141.5 and 144.8 pm) was found in the *Chichibabin's* hydrocarbon **17** [17] which presumably exists in a singlet ground state with a strong admixture of biradical character (triplet energy of *ca.* 23 kJ/mol) [18]. Similarly, the spectroscopic properties and the X-ray data of **12b** are consistent with a singlet ground state having significant contribution of biradical structure (see mesomeric formulas in Scheme 2).

Doublet-State Radicals Derived from 12b. Paramagnetic species in a doublet ground state were readily generated from **12b** by the uptake of an extra electron to form the semi-quinone anion **12b $^{\cdot-}$** or by the addition of an H-atom to one of the O-atoms to yield the

p-substituted phenoxy radical **18** which may be considered as an *O*-protonated radical anion **12b^{•-}**.

The *semiquinone anion 12b^{•-}* was produced by reduction of **12b** with K in 1,2-dimethoxyethane (DME), and it gave rise to an intense but incompletely resolved ESR spectrum shown in *Fig. 2*. The hyperfine pattern of this spectrum is due to four protons having a coupling constant of 0.074 mT. More information was provided by the corresponding ENDOR spectrum also presented in *Fig. 2*. In addition to 0.074 mT, two smaller proton-coupling constants of 0.019 and 0.004 mT were revealed by the ENDOR signals. According to a general-TRIPLE resonance experiment [19], the sign of these two values is opposite to that of 0.074 mT. Absolute signs and assignments of all three coupling constants to protons in individual positions of **12b^{•-}** are indicated in the *Table*.

Table. Proton-Coupling Constants [mT] for **12b^{•-}**, **18**, and **19**

Position	12b^{•-}	18	19^{a)}
2,6	} + 0.019 (4 H)	+ 0.158 (2 H)	0.184 (2 H)
2'',6''		< 0.010 (2 H)	^{b)}
2',6'		- 0.182 (2 H)	0.184 (2 H)
3',5'	} - 0.074 (4 H)	+ 0.073 (2 H)	0.058 (2 H)
3,5- <i>t</i> -Bu		< 0.010 (18 H)	^{b)}
3'',5''- <i>t</i> -Bu		< 0.010 (18 H)	^{b)}
O	-	< 0.010 (1 H)	-
<i>g</i>	2.0037	2.0039	^{c)}

^{a)} [21]; signs of the coupling constants undetermined. ^{b)} Hyperfine splitting unresolved. ^{c)} Not indicated in [21].

They have been based on HMO-*McLachlan* calculations with the use of standard parameters [20a], and they are consistent with the π -spin population being evenly distributed over the whole π -system of **12b^{•-}**. The relatively intense satellites at the peripheries of the ESR spectrum (*Fig. 2*) may be attributed to ¹³C nuclei in the two outer O-bearing rings of **12b^{•-}**, as the observed ¹³C coupling constant of *ca.* 0.2 mT is comparable to values predicted for such nuclei in the 1,3,5,1'',3'',5''- and 2,4,6,2'',4'',6''-positions (with a positive sign in the former and a negative one in the latter positions [20b]).

The *phenoxy radical 18* was obtained by irradiating solutions of **12b** in MTHF or THF at 313 nm, *i.e.*, outside the absorption region of the quinone **12b**. From the ESR and ENDOR spectra of **18**, displayed in *Fig. 3*, the coupling constants of 0.182, 0.158, and 0.073 mT were determined, each for a pair of equivalent protons. General-TRIPLE resonance experiments indicated that the largest value differs in sign from the two smaller ones. In the *Table*, the three coupling constants observed for **18** are compared with the hyperfine data reported for the phenoxy radical **19** [21]. The similarities in the values for protons in corresponding positions of the two radicals point to an almost identical π -spin distribution. Thus, in **18** also, the π -spin population does not essentially extend beyond the phenoxy moiety and the adjacent ring, so that the coupling constants of the protons at the OH-substituted ring are too small to be detected. Such a spin distribution is also confirmed by HMO-*McLachlan* calculations [20a] which lead to the assignments and absolute signs of the coupling constants in the *Table*. As in the case of **12b^{•-}**, a ¹³C-coupling constant was derived from the intense satellites at the peripheries of the ESR

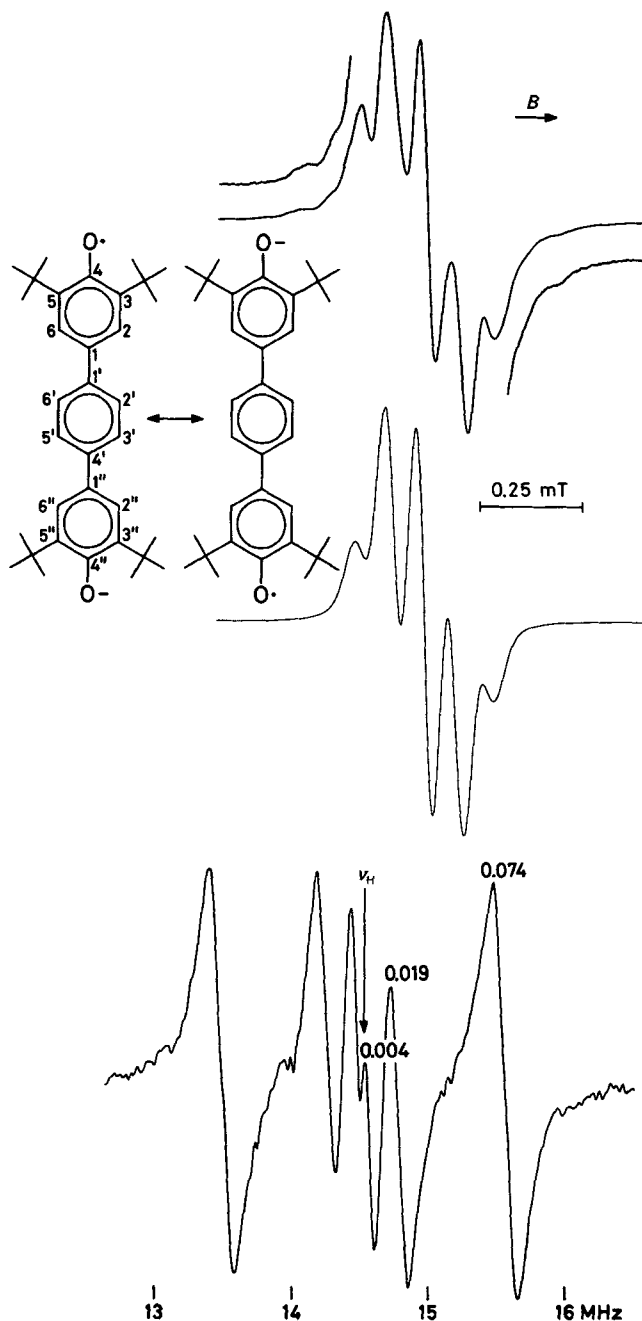


Fig. 2. Top: ESR spectrum of $12b^{\bullet-}$. Solvent: DME; counterion: K^+ ; temp.: 243 K. Center: simulation of the ESR spectrum. Coupling constants as given in the text and in the Table; line-shape: Lorentzian; line-width: 0.035 mT. The simulation does not account for the ^{13}C -hyperfine splittings. Bottom: corresponding proton-ENDOR spectrum. The numbers are the coupling constants [mT] associated with the signals.

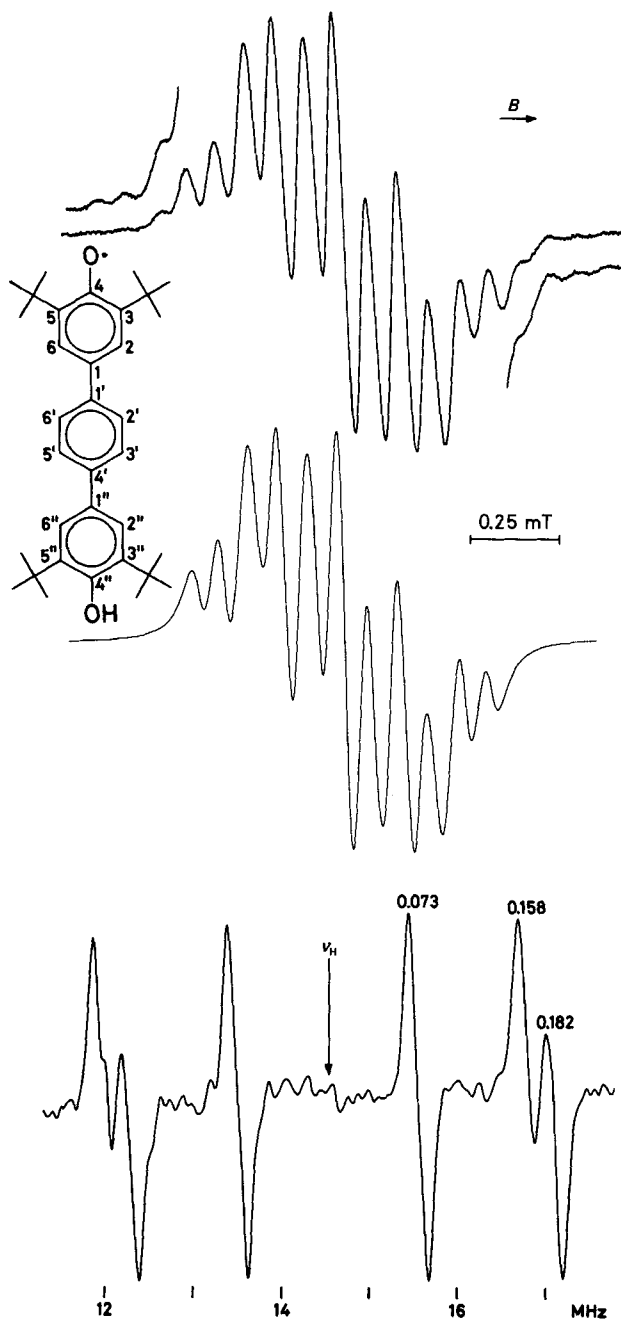
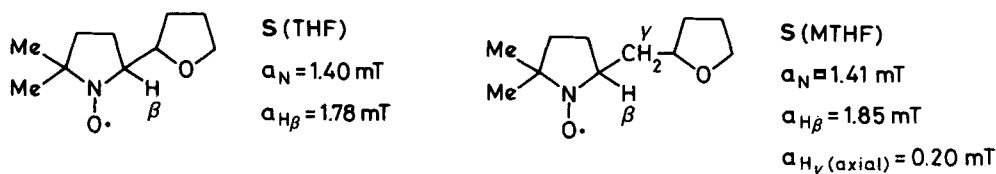


Fig. 3. Top: *ESR spectrum of 18*. Solvent: MTHF; temp.: 293 K. Center: *simulation of the ESR spectrum*. Coupling constants as given in the text and in the Table; line-shape: *Lorentzian*; line-width: 0.085 mT. The simulation does not account for the ^{13}C -hyperfine splittings. Bottom: *corresponding proton-ENDOR spectrum*. The numbers are the coupling constants [mT] associated with the signals.

spectrum (Fig. 3). The observed value of 0.85 mT seems appropriate for ^{13}C nuclei in the 1,3,5- and 2,4,6-positions (again a positive sign is required for this value in the former, and a negative one in the latter positions) [20b].

The H-atom of the OH group in **18** stems from the UV-irradiated solvent, THF or MTHF. Occurrence of an excited triplet state of **12b** as the H-abstracting agent seems improbable because of the wavelength of the applied irradiation (see above). Loss of an H-atom from THF and MTHF generated the tetrahydrofuran-2-yl and 2-tetrahydrofuranylmethyl radicals, respectively, which were trapped by 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) to yield the spin adducts S(THF) and S(MTHF). When only DMPO



was present in the UV-irradiated THF or MTHF, solely the ESR spectra of the spin adducts S(THF) or S(MTHF) appeared. (Contrary to the previous reports [22], addition of a sensitizer was not required.) With both DMPO and **12b** dissolved, the observed ESR spectrum was a superposition of those of **18** and S(THF) or S(MTHF). Obviously, while the H-atom is attached to one of the O-atoms of **12b**, the radicals formed by an H-abstraction from THF and MTHF are trapped by DMPO.

Interestingly, **18** was also produced by a variety of other procedures. When equimolar solutions of the quinone **12b** and the hydroquinone **11b** were dissolved in THF or MTHF, an ESR spectrum of **18** of weak intensity was observed, due to comproportionation:



UV-irradiation shifted the equilibrium strongly to the right by enhancing the rate of the H-atom transfer from **11b** to **12b**, as evidenced by the fourfold increase in the intensity of the ESR spectrum of **18**.

Starting from hydroquinone **11b** alone, the phenoxyl radical **18** was obtained by use of various oxidizing agents such as *i*) DDQ in toluene, benzene, MTHF, or CHCl_3 , and *ii*) (*p*- BrC_6H_4)₃N SbCl_6 in toluene or CHCl_3 with 4-(dimethylamino)pyridine as a base. The intensity of the ESR spectrum of **18** was roughly proportional to the amounts of the substrate **11b** and the oxidizing agent; thereby the concentration of the radical **18** did not exceed a few percent of that of the diamagnetic molecules **11b** and **12b**, as estimated by comparing the intensities of the ESR signals from **18** and those of the reference DPPH. Again, the ESR spectrum of **18** was enhanced by simultaneous irradiation at 313 nm. The experimental findings, thus, speak against **18** being an intermediate between **11b** and **12b**, but are readily rationalized in terms of the *Equilibrium 1* between the three species.

Experimental Part

General. TLC: SiO₂-coated sheets (0.25 mm, *Polygram SIL G/UV₂₅₄*) or Al₂O₃-coated sheets (*Alox/N*), *Macherey & Nagel*. Prep. TLC: silica gel (1.5 mm, 60 PF, *Merck*). CC: silica gel (60, 70–230 mesh, *Merck*) or Al₂O₃ (*Alumina N*, 2222 *Super1*, *ICN Biomedicals*). M.p.: not corrected. UV/VIS: *UV 5230* (*Beckman Instruments*). IR (KBr): *Acculab 4* (*Beckman Instruments*) or *Perkin-Elmer 1420*. NMR (CDCl₃, if not otherwise stated): *Bruker AC 200* (¹H: 200 MHz; ¹³C: 50.3 MHz), *Bruker AM 400* (¹H: 400 MHz; ¹³C: 100.6 MHz). Shifts refer to TMS as internal standard. ESR: *Varian-E9*. ENDOR/TRIPLE resonance: *Bruker-ESP-300*. MS (70 eV): *Finnigan MAT 8430* (EI measurements, 70 eV).

5,5'-(1,4-Phenylene)bis(2,2-dimethylpent-4-en-3-one) (5b). Terephthalaldehyde (**3**, 13.4 g, 0.10 mol) was added to a stirred mixture of pinacolone (**4b**; 50 ml, 0.40 mol), EtOH (50 ml), and H₂O (15 ml). After heating to 35–40°, 2N NaOH (10 ml) was added dropwise. The yellow precipitate was washed with H₂O and EtOH and dried: **5b** (24.4 g, 0.08 mol, 82%). Faint-yellow crystals. M.p. 201–202°. IR: 3010w (arom. CH), 2970m, 2955m (aliph. CH), 1680vs (C=O), 1610vs (C=C, alkene), 1585m, 1465m, 1330m, 1080s, 1010m, 985s, 820m, 740m. ¹H-NMR: 1.24 (s, 2 t-Bu); 7.16 (d, *J* = 16, 2 H, H–C(3)); 7.59 (s, 4 arom. H); 7.66 (d, *J* = 16, 2 H, H–C(2)). ¹³C-NMR: 26.29 (*q*, 6 Me); 43.30 (*s*, 2 Me₃C); 136.64 (*s*, 2 C, C(1)); 121.56, 128.72, 141.80 (*d*, 2C, C(2), 2C, C(3), 4 C(arom.)); 204.03 (*s*, 2 CO). MS: 298 (6, *M*⁺), 241 (100), 213 (6), 184 (14), 156 (18), 128 (26), 57 (70). Anal. calc. for C₂₀H₂₆O₂ (298.45): C 80.50, H 8.78; found: C 80.69, H 8.91.

5,5'-(1,4-Phenylene)bis(2,2,8,8-tetramethylnonane-3,7-dione) (6b). To a soln. of K (0.26 g, 6.70 mmol) in dry *t*-BuOH (25 ml) were added **5b** (10.0 g, 33.5 mmol) and **4b** (10.8 ml, 134.0 mmol). After refluxing for 14 h, 2N H₂SO₄ (30 ml) was added. The residue was filtered, washed with H₂O, and recrystallized from EtOH: **6b** (12.8 g, 25.7 mmol, 77%). Colorless crystals. M.p. 210°. IR: 2970s (aliph. CH), 1705vs (C=O), 1475m, 1470m, 1425m, 1365m, 1075m, 1000m, 825w. ¹H-NMR: 0.99 (*s*, 4 *t*-Bu); 2.79 (*ABX*, *J* = 17.2, 8 H, H–C(3)); 3.69 (*quint.*, *J* = 7.0, 2 H, H–C(2)); 7.09 (*s*, 4 arom. H). ¹³C-NMR: 26.12 (*q*, 12 Me); 35.60 (*d*, 2 C, C(2)); 42.49 (*t*, 4 C, C(3)); 44.03 (*s*, 4 Me₃C); 127.52 (*d*, 4 C(arom.)); 142.42 (*s*, 2 C, C(1)); 213.85 (*s*, 4 CO). MS: 498 (12, *M*⁺), 441 (20), 399 (22), 341 (62), 313 (23), 257 (20), 85 (33), 57 (100). Anal. calc. for C₃₂H₅₀O₄ (498.75): C 77.06, H 10.11; found: C 76.71, H 10.07.

4,4'-(1,4-Phenylene)bis[2,6-bis(tert-butyl)pyrylium]Bis(tetrachloroferrate(III)) (7b). Following a procedure of *Dilthey* [23], anh. FeCl₃ (5.0 g, 30.8 mmol) was added in small portions to a suspension of **6b** (4.0 g, 8.0 mmol) in Ac₂O (20 ml). The mixture was stirred for 2 h at 100°, cooled for 24 h at 4°, and filtered. The residue was washed with EtOH and Et₂O and dried: **7b** (2.9 g, 3.4 mmol, 42%). Brownish-red powder. M.p. 300–310° (dec.). IR: 3020w (arom. CH), 2965m (aliph. CH), 1610vs (C=O, pyrylium), 1515s (C=C, arom.), 1450m, 1365m, 1325m, 1230m, 1125m, 840m, 825m. MS: 461 (36, [*M* + 1]⁺), 460 (100, *M*⁺), 445 (58), 185 (28), 57 (74), 43 (80). The poor solubility of **7b** prevented the measurement of the NMR spectra and further purification.

4,4'-(1,4-Phenylene)bis[2,6-bis(tert-butyl)pyrylium] Bis(tetrafluoroborate) (8b). a) From **7b**. HBF₄ (7 ml, 54% in Et₂O) was added dropwise to a boiling soln. of **7b** (2.9 g, 3.39 mmol) in AcOH (80 ml) and H₂O (175 ml). The yellow precipitate was dissolved by addition of further AcOH, and the hot soln. was filtered. On cooling, a yellow solid precipitated; it was washed with Et₂O and recrystallized from AcOH/H₂O: **8b** (1.6 g, 2.52 mmol, 74%). Colorless crystals. M.p. 270–272° (dec.). UV/VIS (MeCN): λ_{max} (log ε) = 353 (4.607), 317 (sh, 4.429), 196 (sh, 4.577), 194 (4.585). IR: 2975m (aliph. CH), 1620vs (C=O, pyrylium), 1530s (C=C, arom.), 1470m, 1370m, 1245m, 1140m (sh), 1095s, 1050vs, 1035s, 850m, 835m. ¹H-NMR (CF₃COOD): 1.72 (*s*, 4 *t*-Bu); 8.32, 8.37 (*s*, 4 H, H–C(3), 4 H, H–C(6)). ¹³C-NMR (CF₃COOD): 28.99 (*q*, 12 Me); 41.61 (*s*, 4 Me₃C); 118.23, 132.62 (*d*, 4 C, C(3), 4 C, C(6)); 140.54, 169.85 (*s*, 2 C, C(4), 2 C, C(5)); 191.48 (*s*, 4 C, C(2)). MS: 461 (37, [*M* + 1]⁺), 460 (100, *M*⁺), 445 (52), 57 (31). FAB-MS (70 eV, matrix: NBA, positiv): 479 (36, [*M* + 1 + OH]⁺), 461 (46, [*M* + 1]⁺), 460 (100, *M*⁺). Anal. calc. for C₃₂H₄₄O₂B₂F₈ (634.31): C 60.59, H 6.99; found: C 60.48, H 7.16.

b) From **6b**. According to a procedure of *Maroni-Barnaud et al.* [24], a soln. of **6b** (1.0 g, 2.01 mmol) and Ph₃CBF₄ (1.5 g, 4.41 mmol) in AcOH (15 ml) was refluxed for 1 h. After cooling to r.t., the mixture was filtered and the residue washed with Et₂O (addition of Et₂O and standing for 12 h afforded more substance): **8b** (1.0 g, 1.58 mmol, 79%).

Attempts to Prepare 4,4''-Dinitro-3,3'',5,5''-tetra(tert-butyl)-1,1',4',1''-terphenyl (9b). a) With *t*-BuOK as Base. In analogy to a procedure described by *Dimroth et al.* [25], K (0.13 g, 3.32 mmol), dissolved in *t*-BuOH (6.3 ml), was added dropwise at 50° to a soln. of **8b** (0.5 g, 0.79 mmol) in freshly distilled MeNO₂ (4 ml). After refluxing for 45 min, the precipitated KBF₄ was removed by filtration and the hot filtrate diluted with warm H₂O. No precipitate was formed upon cooling. The yellow residue (0.2 g) remaining after evaporation of the org. phase contained at least 8 compounds (DC, CH₂Cl₂) and was discarded.

b) *With EtONa as Base*. A suspension of EtONa, prepared from Na (0.08 g, 3.49 mmol) and EtOH (3.5 ml) in MeNO₂ (22 ml), was added dropwise to a soln. of **8b** (0.5 g, 0.79 mmol) in EtOH (58 ml). After heating for 10 min, H₂O (30 ml) was added. The precipitate and the filtrate were analyzed as described above with a similarly disappointing result.

c) *With Et₃N as Base*. In a procedure analogous to that by Dimroth *et al.* [26], Et₃N (1.16 ml, 8.34 mmol) was added to a suspension of **8b** (0.5 g, 0.79 mmol) in MeNO₂ (0.10 ml, 1.86 mmol) and anh. EtOH (2.2 ml). After refluxing for 3.5 h, benzene was added, and the mixture was washed with dil. H₂SO₄. The org. phase was filtered on Al₂O₃ and evaporated. Red oily residue consisting of several compounds (DC, CH₂Cl₂) was discarded.

4,4'-Dinitro-3,3',5,5'-tetraphenyl-1,1':4',1''-terphenyl (9a). K (0.60 g, 15.35 mmol) dissolved in *t*-BuOH (30 ml) was added dropwise at 40° to a suspension of **8a** (2.00 g, 2.80 mmol) [12] [27] in freshly distilled MeNO₂ (120 ml). After refluxing for 1 h and filtrating at high temp., H₂O (4 ml) was added to the filtrate at r.t. The precipitate was washed with H₂O, EtOH, and Et₂O, and dried: **9a** (1.10 g, 1.76 mmol, 63%). Brownish-yellow powder. M.p. 345–350° ([12]: 342–344°). IR: 3060w, 3035w (arom. CH), 1592m, 1530vs (C=C, arom.), 1495m, 1370s, 860m, 835m, 775m, 760m, 700s. ¹H-NMR: 7.43–7.47 (m, 20 H–C(Ph)); 7.67, 7.75 (s, 8 H–C(terphenyl)). MS: 625 (45, [M + 1]⁺), 624 (100, M⁺), 607 (16), 543 (20).

3,3',5,5'-Tetraphenyl-1,1':4',1''-terphenyl-4,4'-diamine (10a). Hydrogenation of **9a** (1.00 g, 1.60 mmol) was carried out with Pd (0.2 g, 5% on active C) in anh. DMF (300 ml, 3.5-bar H₂ pressure), until no more **9a** could be detected (DC, CH₂Cl₂, R_f(**9a**) 0.80, R_f(**10a**) 0.64). After workup: **10a** (0.68 g, 1.09 mmol, 68%). Colorless crystals. M.p. 314–317° (from AcOH; [12]: 308–309°). IR: 3450m (NH), 3365m (NH), 3025m (arom. CH), 1610s, 1460s, 1425s, 1245m, 840m, 780m, 770m, 725m, 700s, 635m. ¹H-NMR (CF₃COOD): 7.53–7.60 (m, 20 H–C(Ph)); 7.81 (s, H–C(terphenyl)). MS: 566 (10, [M + 2]⁺), 565 (44, [M + 1]⁺), 564 (100, M⁺), 282 (22).

3,3',5,5'-Tetraphenyl-1,1':4',1''-terphenyl-4,4'-diol (11a). To **10a** (0.64 g, 1.13 mmol), dissolved under N₂ in AcOH (7.8 ml) and conc. H₂SO₄ (2.4 ml) at 70°, was added dropwise below 5° a soln. of NaNO₂ (0.20 g, 2.90 mmol) in H₂O (1.1 ml). After stirring for 1 h at 0°, icy H₂O (7.8 ml) was added, and the excess of NaNO₂ was destroyed with HSO₃NH₂. The cooled yellow suspension of the diazonium salt was slowly added to a boiling soln. of conc. H₂SO₄ (3.9 ml) in H₂O (15.7 ml). The mixture was stirred for 45 min, stored for 12 h at 4°, and filtered. The residue was washed with H₂O, dissolved in benzene and filtrated on silica gel. Evaporation of the solvent and purification by thick layer chromatography (toluene: R_f 0.37): **11a** (70 mg, 0.124 mmol, 11%). M.p. 249–251° (from AcOH/toluene; [12]: 247–248°). UV/VIS (MeCN): λ_{max} (log ε) = 297 (4.639), 248 (4.748), 203 (4.929). IR: 3525s (OH), 3055m (arom. CH), 3030m, 1600w, 1495m, 1465s, 1425s, 1320m, 1225s, 1120m, 835m, 780m, 725s, 700s. MS: 568 (10, [M + 2]⁺), 567 (46, [M + 1]⁺), 566 (100, M⁺), 283 (16).

The diacetate of **11a** was prepared in the usual way by heating of **11a** with Ac₂O and catalytical amounts of pyridine. **11a**-Diacetate: M.p. 265° (from EtOH; [12]: 268–270°). IR: 3055w (arom. CH), 1760s (C=O, ester), 1210s, 1185vs, 700m. ¹H-NMR: 1.82 (s, 2 Ac); 7.35–7.54 (m, 20 H–C(Ph)); 7.65, 7.71 (2s, 8 H–C(terphenyl)). ¹³C-NMR: 21.42 (q, 2 Me); 128.52, 129.23, 129.59, 129.88 (d, 28 C (arom.)); 137.12, 138.68, 139.83, 140.19, 145.50 (s, 14 C (arom.)); 169.98 (s, 2 CO). MS: 650 (20, M⁺), 608 (34), 566 (100).

4,4'-(1,4-Phenylene)bis[2,6-bis(tert-butyl)-4-hydroxycyclohexa-2,5-diene-1-one] (15). To a boiling mixture of 1,4-dibromobenzene (10.0 g, 42.4 mmol) and Mg borings (4.3 g, 176.9 mmol) in dry Et₂O (100 ml) was added dropwise under N₂ BrCH₂CH₂Br (7.3 ml, 84.7 mmol) in dry Et₂O (100 ml) for 20 h. The Grignard reagent, 1,4-bis(bromomagnesium)benzene (**13**), prepared in this way, was added dropwise under N₂ to a soln. of 2,6-bis(tert-butyl)-1,4-benzoquinone (**14**) (10.0 g, 45.4 mmol) [28] in dry Et₂O (100 ml). After refluxing for 1 h and standing overnight, the mixture was filtered with the use of a Büchner funnel, and the residue was hydrolyzed by stirring for 1 h with sat. aq. NH₄Cl (50 ml). The mixture was extracted with Et₂O and the solvent evaporated. The residue was digested several times with CH₂Cl₂, washed with Et₂O, and recrystallized from CHCl₃: **15** (4.3 g, 8.3 mmol, 37%). Colorless crystals. M.p. 268°. R_f 0.09 (CH₂Cl₂/CCl₄ 3:1). UV/VIS (MeCN): λ_{max} (log ε) = 277 (sh, 3.776), 253 (sh, 4.138), 233 (4.411), 199 (4.570). IR: 3510s (OH), 2960vs (aliph. CH), 2915m, 1660s (C=O), 1630s (C=O), 1485m, 1460m, 1400m, 1365s, 1335m, 1165m, 1150m, 1010m, 955s. ¹H-NMR ((D₆)acetone): 1.22 (s, 4 *t*-Bu); 6.62 (s, H–C(2,6,2'',6'')); 7.44 (s, 4 H–C(Ph)). ¹³C-NMR ((D₆)acetone): 29.67 (q, 12 Me); 35.11 (s, 4 Me₃C); 71.20 (s, C(1,1'')); 126.45 (d, 4 C(Ph)); 142.26 (s, C(1',4'')); 144.40 (d, C(2,6,2'',6'')); 144.63 (s, C(3,5,3'',5'')); 187.63 (s, C(4,4'')) [29]. MS: 518 (4, M⁺), 502 (5), 486 (6), 462 (53), 406 (98), 405 (100), 57 (56). CI-MS (70 eV, NH₃, positive): 536 (8, [M + 1 + NH]⁺), 519 (8, [M + 1]⁺), 504 (6), 503 (14), 502 (38), 501 (100). HR-MS: 518.3396 (C₃₄H₄₆O₄); calc. 518.3396.

3,3',5,5'-Tetra(tert-butyl)-1,1':4',1''-terphenyl-4,4'-diol (11b). To a boiling soln. of LiAlH₄ (0.50 g, 13.2 mmol) in dry Et₂O (250 ml) was added dropwise under N₂ a soln. of **15** (5.2 g, 10.0 mmol) in Et₂O (200 ml). The mixture was boiled until no more **15** was detectable (TLC, CH₂Cl₂/CCl₄ 3:1, R_f(**15**) 0.09; R_f(**11b**) 0.77). The excess

of LiAlH_4 was destroyed with MeOH and the mixture acidified with H_2SO_4 . The aq. phase was extracted twice with Et_2O and the combined org. phase dried. After evaporation of the solvent and recrystallization from toluene: **11b** (3.7 g, 7.5 mmol, 75%). Colorless needles. M.p. 292° . UV/VIS (MeCN): λ_{max} ($\log \epsilon$) = 293 (4.492), 208 (4.697). IR: 3635s (OH), 2960s (aliph. CH), 2915m, 2875m, 1465w, 1430s, 1395w, 1365w, 1310w, 1235s, 1155m, 835m. $^1\text{H-NMR}$: 1.51 (s, 12 Me); 5.26 (s, 2 OH); 7.44, 7.59 (s, H-C(2,6,2'',6''), H-C(2',3',5',6')). $^{13}\text{C-NMR}$: 30.37 (q, 12 Me); 34.50 (s, 4 Me_3C); 123.93 (d, C(2,6,2'',6'')); 127.21 (d, C(2',3',5',6'')); 132.27 (s, C(1,1'')); 136.20 (s, C(3,5,3'',5'')); 140.32 (s, C(1',4'')); 153.46 (s, C(4,4'')). MS: 487 (36, $[M + 1]^+$), 486 (100, M^+), 471 (26), 57 (28). Anal. calc. for $\text{C}_{34}\text{H}_{46}\text{O}_2$ (486.74): C 83.90, H 9.53; found: C 82.91, H 9.41³⁾. HR-MS: 486.3497; calc. 486.3497.

The diacetate of **11b** was prepared in the usual way by heating **11b** for 2 d with Ac_2O and catalytical amounts of AcONa . **11b-Diacetate**: M.p. 289° (from EtOH). Colorless microcrystals. R_f 0.46 ($\text{CH}_2\text{Cl}_2/\text{CCl}_4$ 3:1). IR: 3005w (arom. CH), 2965m (aliph. CH), 2915w, 1760s (C=O), 1425m, 1215s, 1205s, 1190s, 1110m, 835w. $^1\text{H-NMR}$: 1.41 (s, 12 Me); 2.38 (s, 2 Ac); 7.55, 7.62 (2 s, 8 H-C(terphenyl)). $^{13}\text{C-NMR}$: 22.27 (q, 2 Me); 31.07 (q, 12 Me); 35.13 (s, 4 Me_3C); 124.93 (d, C(2,6,2'',6'')); 127.15 (d, C(2',3',5',6'')); 137.44 (s, C(1,1'')); 139.93 (s, C(1',4'')); 142.23 (s, C(3,5,3'',5'')); 147.11 (s, C(4,4'')); 170.71 (s, 2 CO). MS: 570 (14, M^+), 528 (38), 486 (66), 57 (100, C_4H_9^+). Anal. calc. for $\text{C}_{39}\text{H}_{50}\text{O}_4$ (570.81): C 79.96, H 8.83; found: C 79.92, H 8.85.

3,3'',5,5''-Tetra(tert-butyl)-1,1':4',1''-terphenyl-4,4''-dione (**12b**). a) With $\text{K}_3\text{Fe}(\text{CN})_6$. To a soln. of **11b** (0.50 g, 1.0 mmol) in benzene (50 ml) was added under exclusion of O_2 and vigorous stirring a soln. of KOH (2.50 g, 44.6 mmol) and $\text{K}_3\text{Fe}(\text{CN})_6$ (3.00 g, 9.0 mmol) in H_2O (20 ml). The stirring was continued for 15 min. The org. layer was washed thoroughly with H_2O and dried (Na_2SO_4). Benzene was evaporated slowly *i.v.* at -15° : **12b** (0.41 g, 0.85 mmol, 85%). Large yellow-green crystals with metallic lustre. M.p. 214° (dec.).

b) With PbO_2 . Freshly precipitated PbO_2 (3.90 g, 16.3 mmol) [30] was added to a soln. of **11b** (0.20 g, 0.40 mmol) in benzene (20 ml). After vigorous stirring for 2 h, the mixture was filtrated, the residue thoroughly washed with benzene. Benzene was evaporated from the combined solns.: **12b** (0.20 g, 0.40 mmol, 100%). Titration of a sample which had been stored for 10 d at -15° with KI/thiosulfate showed an oxidation equivalent of 95%. Solns. of **12b** are stable at -10° for several weeks. R_f 0.53 (toluene). UV/VIS (MeCN): λ_{max} ($\log \epsilon$) = 636 (4.056), 570 (sh, 4.508), 538 (5.314), 500 (4.480), 470 (3.781), 266 (3.919), 199 (4.564). IR: 2955s (aliph. CH), 2915m, 2880m, 2865m, 1575vs (C=O), 1485m, 1455m, 1360s, 1335m, 1255m, 1095s, 1040s, 870s, 830s. $^1\text{H-NMR}$: 1.38 (s, 4 *t*-Bu); 7.70, 7.81 (2 s, H-C(2,6,2'',6''), H-C(2',3',5',6'')). $^1\text{H-NMR}$ (D_6 benzene): 1.53 (s, 4 *t*-Bu); 7.36, 7.63 (2s, H-C(2,6,2'',6''), H-C(2',3',5',6'')). $^{13}\text{C-NMR}$: 29.86 (q, 12 Me); 36.19 (s, 4 Me_3C); 125.69, 127.52 (d, C(2,6,2',3',5',6',2'',6'')); 134.52, 139.16, 149.69 (s, C(1,3,5,1',4',1'',3'',5'')); 186.10 (s, C(4,4'')). MS: 486 (100, $[M + 2]^+$), 484 (56, M^+), 471 (24), 470 (23), 443 (6), 442 (10), 428 (12), 427 (11), 57 (65). Anal. calc. for $\text{C}_{34}\text{H}_{44}\text{O}_2$ (484.72): C 84.25, H 9.15; found: C 83.69, H 9.14.

Iodometric Titration of 12b. A soln. of **12b** (1.0 mmol) in benzene (20 ml) was added quickly to a freshly prepared soln. of KI (*p.a.*, 1.0 g, 6.0 mmol) in AcOH (50 ml) and H_2O (100 ml). After short stirring and standing for 5 min, the evolved I_2 was titrated with 0.1N $\text{Na}_2\text{S}_2\text{O}_3$. As could be shown by TLC only **11b** was formed upon reduction with iodide.

Crystallographic Structure Analysis of 12b (1/3 Acetone Solvate). Crystal data: $\text{C}_{34}\text{H}_{44}\text{O}_2 \cdot 1/3(\text{C}_3\text{H}_6\text{O})$, $M = 504.1$, triclinic, space group $P\bar{1}$, $a = 1018.3(4)$, $b = 1540.1(6)$, $c = 1561.0(6)$ pm, $\alpha = 103.03(3)$, $\beta = 90.90(3)$, $\gamma = 105.79(3)^\circ$, $U = 2287.2 \text{ nm}^3$, $Z = 3$, $D_x = 1.098 \text{ Mg m}^{-3}$, $\lambda(\text{MoK}\alpha) = 71.069 \text{ pm}$, $\mu = 0.07 \text{ mm}^{-1}$, $F(000) = 824$, $T = -95^\circ$.

Data Collection and Reduction. A crystal of ca. $0.6 \times 0.4 \times 0.4 \text{ mm}$ was mounted on a glass fibre with inert oil and transferred to the cold gas stream of the diffractometer (Siemens R3 with LT-2 low-temp. attachment). 8519 Intensities were registered to $2\theta_{\text{max}} 50^\circ$, of which 8026 were independent ($R_{\text{int}} 0.018$) and 4718 significant ($> 3\sigma(F)$). Cell constants were refined from diffractometer angles of 50 reflections in the 2θ range $20\text{--}23^\circ$.

Structure Solution and Refinement. The program system Siemens SHELXTL PLUS was used. The structure was solved with direct methods and refined anisotropically. H-Atoms were included using a riding model. An acetone molecule, disordered over a symmetry centre, was refined isotropically. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0004F^2$. The final R value was 0.058, with wR 0.061. 499 Parameters; S 1.6; max. Δ/σ 0.008; max.

³⁾ It was not possible to remove entirely the solvent by drying in high vacuum at 150° . Therefore, a HR-MS spectrum of **11b** was recorded and the elemental analysis of the diacetate of **11b** was carried out in order to characterize **11b**.

D_e 0.6×10^{-6} e pm⁻³ in the region of the acetone molecule. Details of the structure determination (atomic coordinates, complete bond lengths and angles, H-atom coordinates, structure factors, temp. factors) have been deposited at the *Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH*, D-7514 Eggenstein-Leopoldshafen 2. Any request for this material should quote a full literature citation and the reference number CSD 57322.

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