116. Synthesis and Structure of a *p*-Terphenoquinone and Paramagnetic Species Derived Therefrom[1])

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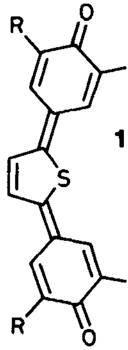
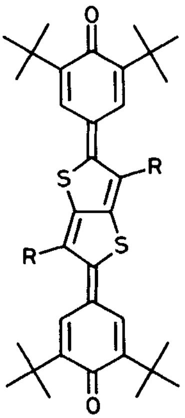
3,5,3″,5″-Tetra(*tert*-butyl)-*p*-terphenoquinone (**12b**) was synthesized and characterized by its spectroscopic and X-ray structural data. The ground state of **12b** is singlet with a strong contribution of a biradical structure. Paramagnetic derivatives of **12b**, such as the semiquinone radical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

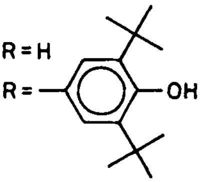
Introduction. – In the last few years, there has been an increasing interest in 'extended quinones', in view of their technical applications, *e.g.*, in the search for organic semiconductors (2,7-pyrenequinones [2] [3]) or for electron acceptors in xerography (3,5,3′,5′-tetraalkyldiphenoquinones [4]). 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].



1a R = H
b R = Me
c R = *t*-Bu



2a R = H
b R =



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

p-Terphenoquinone (= 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 calculations[2]), a planar *p*-terphenoquinone should have a singlet ground state. To verify this prediction, we have synthesized 3,5,3″,5″-tetra(*tert*-butyl)-*p*-terphenoquinone (**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 $FeCl_3$ in Ac_2O to yield **7**. Conversion of **7** into its BF_4^- salt **8** and reaction with $MeNO_2$ 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 $K_3[Fe(CN)_6]$ 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 $FeCl_3$ in Ac_2O (42%) or directly to **8b** with Ph_3CBF_4 (79%). Unfortunately, nitration of **8b** to give **9b** did not succeed, even using various bases such as *t*-BuOK, EtOK, and Et_3N. 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 $LiAlH_4$ [14] to **11b**. Oxidation of **11b** with $K_3[Fe(CN)_6]$ 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 O_2) 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 ($\log \varepsilon = 5.314$). The final product has been identified as 3,5,3″,5″-tetra(*tert*-butyl)-*p*-terphenoquinone (**12b**) in a singlet ground state.

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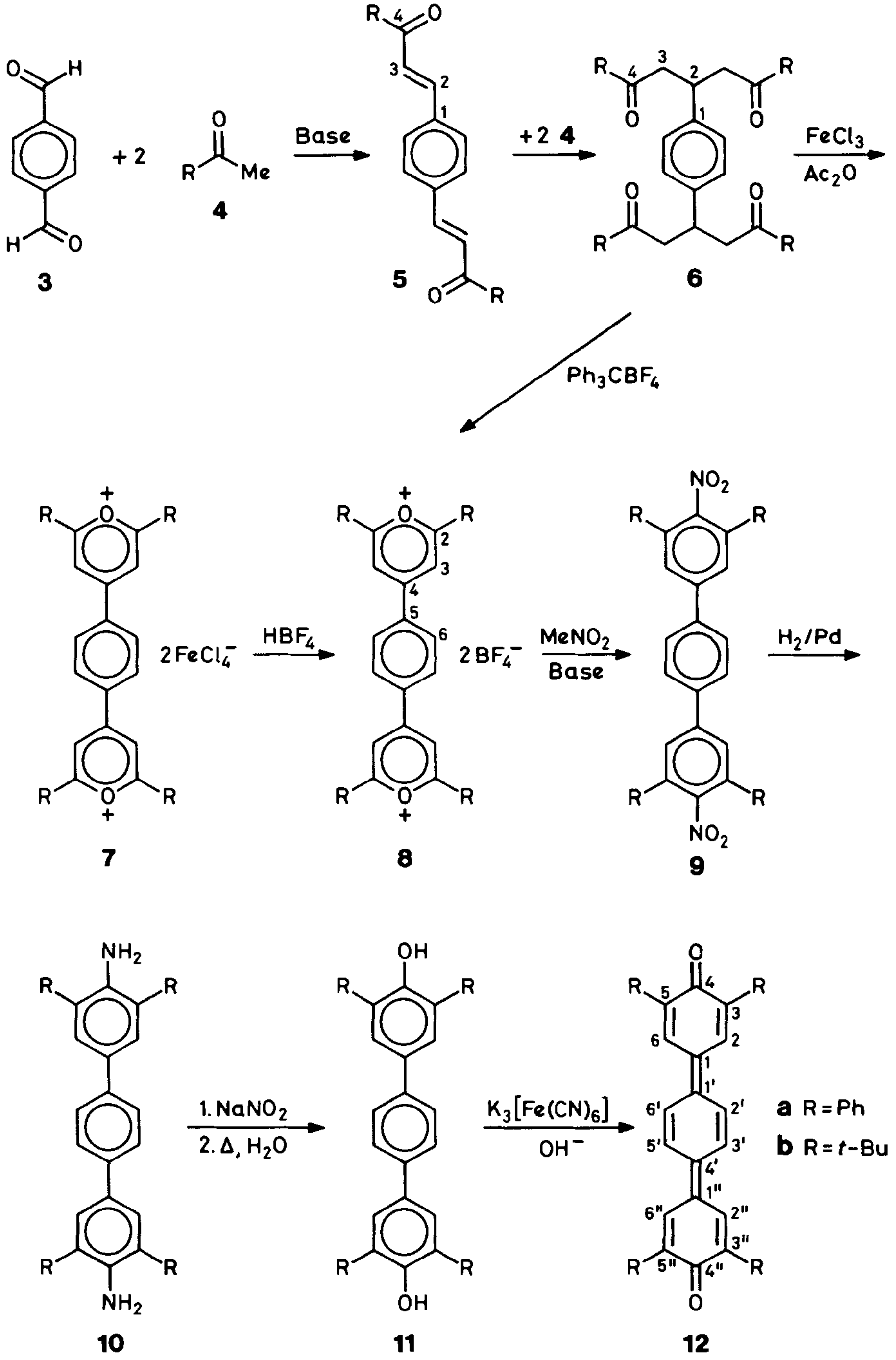
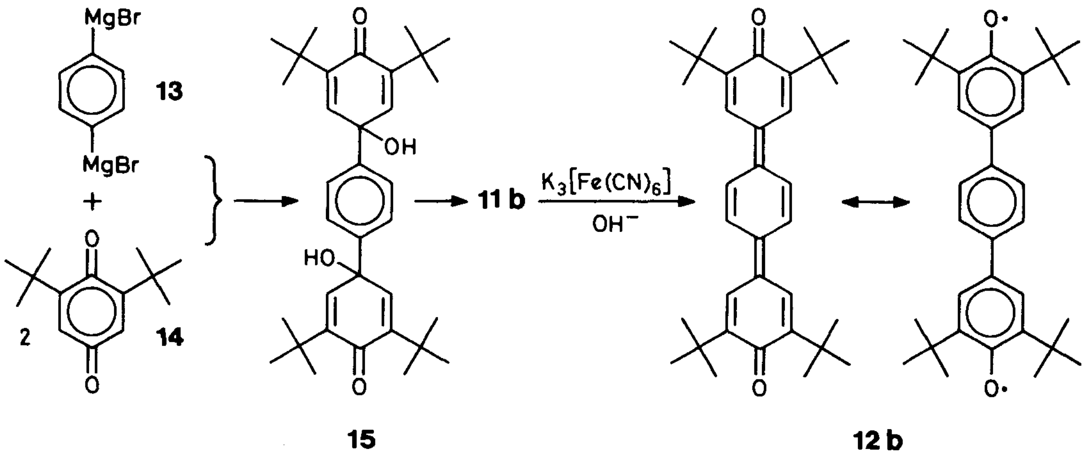
[2]) Performed using MNDOC parametrization (MNDO procedure with CI) as described in [11]. For details, see [9].

Scheme 1

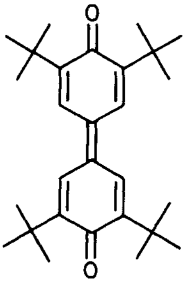


3
+ 2
4
Base
5
+ 2 4
6
FeCl$_3$
Ac$_2$O
Ph$_3$CBF$_4$
7
2 FeCl$_4^-$
HBF$_4$
8
2 BF$_4^-$
MeNO$_2$
Base
9
H$_2$/Pd
10
1. NaNO$_2$
2. Δ, H$_2$O
11
K$_3$[Fe(CN)$_6$]
OH$^-$
12
a R = Ph
b R = t-Bu

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*-diphenoquinone (**16**) → **12b**. IR (KBr): ν(CO) = 1655 → 1599 → 1575 cm^{-1}; UV/VIS: $\lambda_{\max}$ (logε) = 255 (4.525) → 421 (4.115) → 538 nm (5.314); ^{1}H-NMR: δ(ring-H) = 6.51 → 7.64 → 7.70, 7.81; ^{13}C-NMR: δ(C(O)) = 187.77, 189.02 → 185.45 → 186.10. Apart



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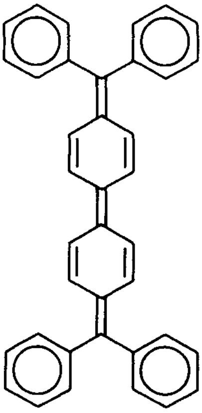

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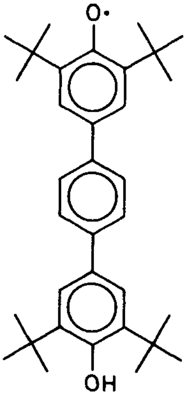

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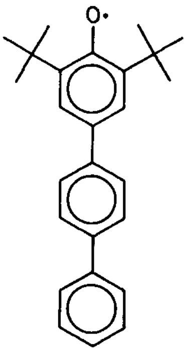

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from the M^+ peak at m/z 484 (56%), the MS exhibits a $[M+2]^+$ peak at 486 (100%) typical of quinones. Some biradical 'character' of **12b** is indicated by the low frequency of ν(CO) (1575 cm^{-1}) which approaches that of phenoxy radicals (1560 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 C(1)–C(4) and C(1″)–C(4″) is 22°. The C=C bonds between the rings are rather long for formal double bonds: 141.8–142.8 pm.

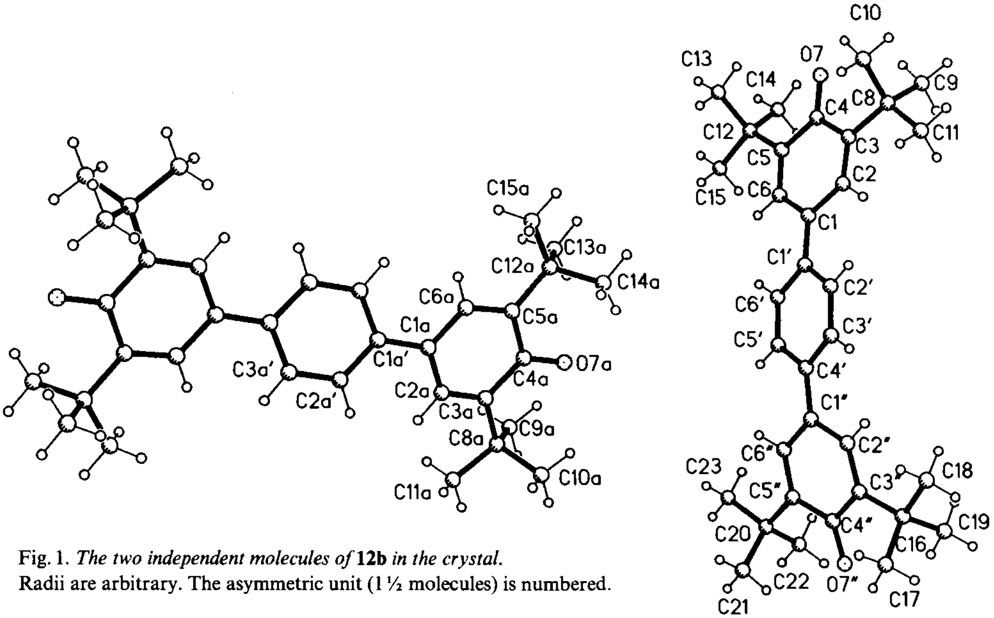


Fig. 1. *The two independent molecules of* **12b** *in the crystal.* Radii are arbitrary. The asymmetric unit (1 ½ molecules) is numbered.

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 C=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 semiquinone 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**$^{\cdot-}$.

The *semiquinone anion* **12b**$^{\cdot-}$ 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**$^{\cdot-}$ are indicated in the *Table*.

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

Position	**12b**$^{\cdot-}$	**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′	– 0.074 (4 H)	– 0.182 (2 H)	0.184 (2 H)
3′,5′		+ 0.073 (2 H)	0.058 (2 H)
3,5-*t*-Bu	+ 0.004 (36 H)	< 0.010 (18 H)	b)
3″,5″-*t*-Bu		< 0.010 (18 H)	b)
O	–	< 0.010 (1 H)	–
g	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**$^{\cdot-}$. The relatively intense satellites at the peripheries of the ESR spectrum (*Fig. 2*) may be attributed to ^{13}C nuclei in the two outer O-bearing rings of **12b**$^{\cdot-}$, as the observed ^{13}C 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**$^{\cdot-}$, a ^{13}C-coupling constant was derived from the intense satellites at the peripheries of the ESR

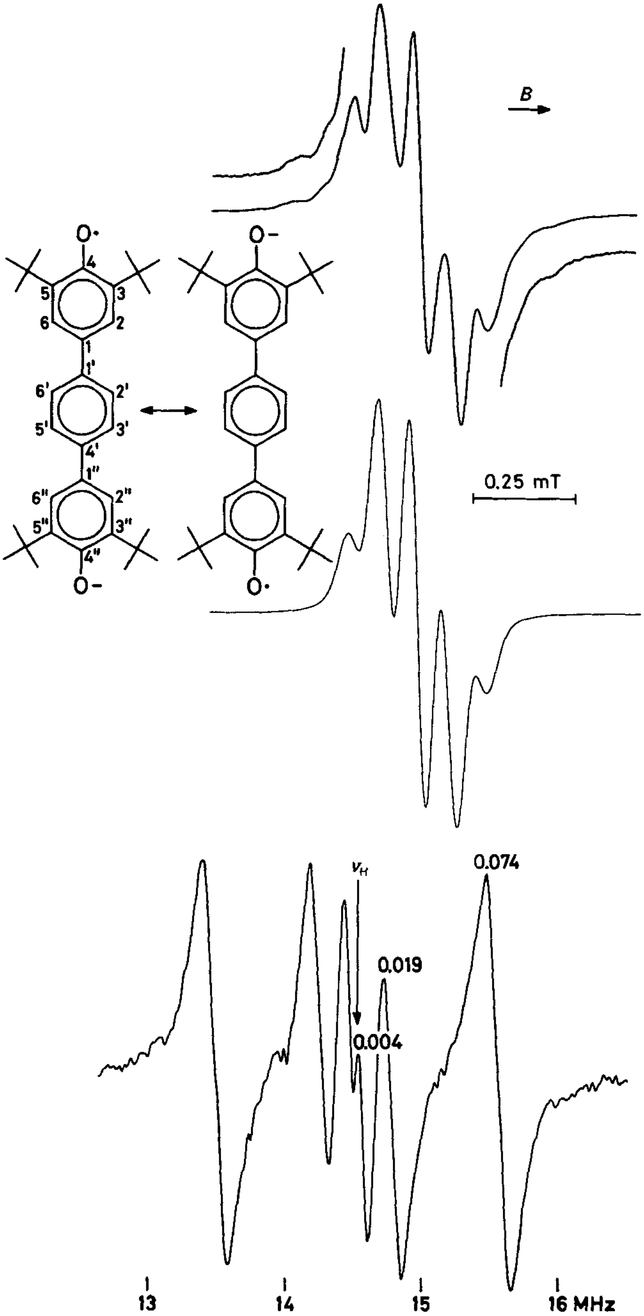


Fig. 2. Top: *ESR spectrum of* **12b**$^{-}$. Solvent: DME; counterion: K^+; temp.: 243 K. Center: *simulation of the ESR spectrum.* Coupling constants as given in the text and in the *Table*; line-shape: *Lorentz*ian; line-width: 0.035 mT. The simulation does not account for the ^{13}C-hyperfine splittings.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

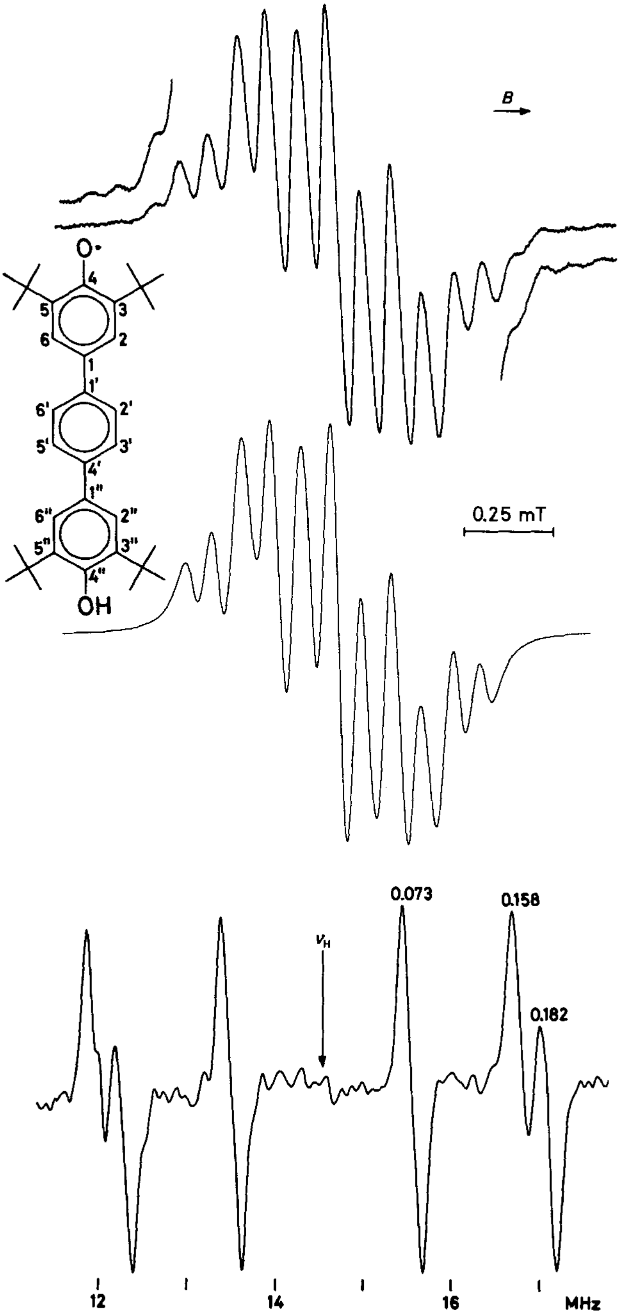
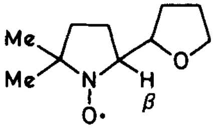


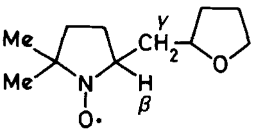
Fig. 3. Top: *ESR spectrum of* **18**. Solvent: MTHF; temp.: 293 K. Center: *simulation of the ESR spectrum*. Coupling constants as given in the text and in the *Table*; line-shape: *Lorentz*ian; line-width: 0.085 mT. The simulation does not account for the ^{13}C-hyperfine splittings. Bottom: *corresponding 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



S(THF)
$a_N = 1.40$ mT
$a_{H_\beta} = 1.78$ mT



S(MTHF)
$a_N = 1.41$ mT
$a_{H_\beta} = 1.85$ mT
$a_{H_\gamma (axial)} = 0.20$ mT

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:

$$\mathbf{12b} + \mathbf{11b} \rightleftharpoons 2 \times \mathbf{18} \qquad (1)$$

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 phenoxy radical **18** was obtained by use of various oxidizing agents such as *i)* DDQ in toluene, benzene, MTHF, or $CHCl_3$, and *ii)* $(p\text{-}BrC_6H_4)_3N\ SbCl_6$ 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.

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Experimental Part

General. TLC: SiO_2-coated sheets (0.25 mm, *Polygram SIL G/UV*$_{254}$) or Al_2O_3-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 Al_2O_3 (*Alumina N, 2222 Superl, ICN Biomedicals*). M.p.: not corrected. UV/VIS: *UV 5230* (*Beckman Instruments*). IR (KBr): *Acculab 4* (*Beckman Instruments*) or *Perkin-Elmer 1420*. NMR ($CDCl_3$, if not otherwise stated): *Bruker AC 200* (^{1}H: 200 MHz; ^{13}C: 50.3 MHz), *Bruker AM 400* (^{1}H: 400 MHz; ^{13}C: 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 H_2O (15 ml). After heating to 35–40°, 2N NaOH (10 ml) was added dropwise. The yellow precipitate was washed with H_2O and EtOH and dried: **5b** (24.4 g, 0.08 mol, 82%). Faint-yellow crystals. M.p. 201–202°. IR: 3010*w* (arom. CH), 2970*m*, 2955*m* (aliph. CH), 1680v*s* (C=O), 1610v*s* (C=C, alkene), 1585*m*, 1465*m*, 1330*m*, 1080*s*, 1010*m*, 985*s*, 820*m*, 740*m*. H-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)). ^{13}C-NMR: 26.29 (*q*, 6 Me); 43.30 (*s*, 2 Me_3*C*); 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 $C_{20}H_{26}O_2$ (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 H_2SO_4 (30 ml) was added. The residue was filtered, washed with H_2O, and recrystallized from EtOH: **6b** (12.8 g, 25.7 mmol, 77%). Colorless crystals. M.p. 210°. IR: 2970*s* (aliph. CH), 1705v*s* (C=O), 1475*m*, 1470*m*, 1425*m*, 1365*m*, 1075*m*, 1000*m*, 825*w*. ^{1}H-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). ^{13}C-NMR: 26.12 (*q*, 12 Me); 35.60 (*d*, 2 C, C(2)); 42.49 (*t*, 4 C, C(3)); 44.03 (*s*, 4 Me_3*C*); 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 $C_{32}H_{50}O_4$ (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. $FeCl_3$ (5.0 g, 30.8 mmol) was added in small portions to a suspension of **6b** (4.0 g, 8.0 mmol) in Ac_2O (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 Et_2O and dried: **7b** (2.9 g, 3.4 mmol, 42%). Brownish-red powder. M.p. 300–310° (dec.). IR: 3020*w* (arom. CH), 2965*m* (aliph. CH), 1610v*s* (C=O, pyrylium), 1515*s* (C=C, arom.), 1450*m*, 1365*m*, 1325*m*, 1230*m*, 1125*m*, 840*m*, 825*m*. 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**. HBF_4 (7 ml, 54% in Et_2O) was added dropwise to a boiling soln. of **7b** (2.9 g, 3.39 mmol) in AcOH (80 ml) and H_2O (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 Et_2O and recrystallized from AcOH/H_2O: **8b** (1.6 g, 2.52 mmol, 74%). Colorless crystals. M.p. 270–272° (dec.). UV/VIS (MeCN): λ_{max} ($\log\varepsilon$) = 353 (4.607), 317 (sh, 4.429), 196 (sh, 4.577), 194 (4.585). IR: 2975*m* (aliph. CH), 1620v*s* (C=O, pyrylium), 1530*s* (C=C, arom.), 1470*m*, 1370*m*, 1245*m*, 1140*m* (sh), 1095*s*, 1050v*s*, 1035*s*, 850*m*, 835*m*. ^{1}H-NMR (CF_3COOD): 1.72 (*s*, 4 *t*-Bu); 8.32, 8.37 (*s*, 4 H, H–C(3), 4 H, H–C(6)). ^{13}C-NMR (CF_3COOD): 28.99 (*q*, 12 Me); 41.61 (*s*, 4 Me_3*C*); 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 $C_{32}H_{44}O_2B_2F_8$ (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 Ph_3CBF_4 (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 Et_2O (addition of Et_2O 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 $MeNO_2$ (4 ml). After refluxing for 45 min, the precipitated KBF_4 was removed by filtration and the hot filtrate diluted with warm H_2O. 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, CH_2Cl_2) 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 $MeNO_2$ (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, H_2O (30 ml) was added. The precipitate and the filtrate were analyzed as described above with a similarly disappointing result.

c) *With Et_3N as Base.* In a procedure analogous to that by *Dimroth et al.* [26], Et_3N (1.16 ml, 8.34 mmol) was added to a suspension of **8b** (0.5 g, 0.79 mmol) in $MeNO_2$ (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. H_2SO_4. The org. phase was filtered on Al_2O_3 and evaporated. Red oily residue consisting of several compounds (DC, CH_2Cl_2) 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 $MeNO_2$ (120 ml). After refluxing for 1 h and filtrating at high temp., H_2O (4 ml) was added to the filtrate at r.t. The precipitate was washed with H_2O, EtOH, and Et_2O, and dried: **9a** (1.10 g, 1.76 mmol, 63%). Brownish-yellow powder. M.p. 345–350° ([12]: 342–344°). IR: 3060*w*, 3035*w* (arom. CH), 1592*m*, 1530*vs* (C=C, arom.), 1495*m*, 1370*s*, 860*m*, 835*m*, 775*m*, 760*m*, 700*s*. ^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 H_2 pressure), until no more **9a** could be detected (DC, CH_2Cl_2, 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: 3450*m* (NH), 3365*m* (NH), 3025*m* (arom. CH), 1610*s*, 1460*s*, 1425*s*, 1245*m*, 840*m*, 780*m*, 770*m*, 725*m*, 700*s*, 635*m*. ^1H-NMR (CF_3COOD): 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 N_2 in AcOH (7.8 ml) and conc. H_2SO_4 (2.4 ml) at 70°, was added dropwise below 5° a soln. of $NaNO_2$ (0.20 g, 2.90 mmol) in H_2O (1.1 ml). After stirring for 1 h at 0°, icy H_2O (7.8 ml) was added, and the excess of $NaNO_2$ was destroyed with HSO_3NH_2. The cooled yellow suspension of the diazonium salt was slowly added to a boiling soln. of conc. H_2SO_4 (3.9 ml) in H_2O (15.7 ml). The mixture was stirred for 45 min, stored for 12 h at 4°, and filtered. The residue was washed with H_2O, 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: 3525*s* (OH), 3055*m* (arom. CH), 3030*m*, 1600*w*, 1495*m*, 1465*s*, 1425*s*, 1320*m*, 1225*s*, 1120*m*, 835*m*, 780*m*, 725*s*, 700*s*. 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 Ac_2O and catalytical amounts of pyridine. **11a**-Diacetate: M.p. 265° (from EtOH; [12]: 268–270°). IR: 3055*w* (arom. CH), 1760*s* (C=O, ester), 1210*s*, 1185*vs*, 700*m*. ^1H-NMR: 1.82 (*s*, 2 Ac); 7.35–7.54 (*m*, 20 H–C(Ph)); 7.65, 7.71 (2*s*, 8 H–C(terphenyl)). ^{13}C-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 Et_2O (100 ml) was added dropwise under N_2 $BrCH_2CH_2Br$ (7.3 ml, 84.7 mmol) in dry Et_2O (100 ml) for 20 h. The *Grignard* reagent, *1,4-bis(bromomagnesium)benzene* (**13**), prepared in this way, was added dropwise under N_2 to a soln. of *2,6-bis(*tert*-butyl)-1,4-benzoquinone* (**14**) (10.0 g, 45.4 mmol) [28] in dry Et_2O (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. NH_4Cl (50 ml). The mixture was extracted with Et_2O and the solvent evaporated. The residue was digested several times with CH_2Cl_2, washed with Et_2O, and recrystallized from $CHCl_3$: **15** (4.3 g, 8.3 mmol, 37%). Colorless crystals. M.p. 268°. R_f 0.09 (CH_2Cl_2/CCl_4 3:1). UV/VIS (MeCN): λ_{max} (log ε) = 277 (sh, 3.776), 253 (sh, 4.138), 233 (4.411), 199 (4.570). IR: 3510*s* (OH), 2960*vs* (aliph. CH), 2915*m*, 1660*s* (C=O), 1630*s* (C=O), 1485*m*, 1460*m*, 1400*m*, 1365*s*, 1335*m*, 1165*m*, 1150*m*, 1010*m*, 955*s*. ^1H-NMR ((D_6)acetone): 1.22 (*s*, 4 *t*-Bu); 6.62 (*s*, H–C(2,6,2″,6″)); 7.44 (*s*, 4 H–C(Ph)). ^{13}C-NMR ((D_6)acetone): 29.67 (*q*, 12 Me); 35.11 (*s*, 4 Me_3C); 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, NH, positive): 536 (8, $[M + 1 + NH]^+$), 519 (8, $[M + 1]^+$), 504 (6), 503 (14), 502 (38), 501 (100). HR-MS: 518.3396 ($C_{34}H_{46}O_4$); calc. 518.3396.

*3,3″,5,5″-Tetra(*tert*-butyl)-1,1′:4′,1″-terphenyl-4,4″-diol* (**11b**). To a boiling soln. of $LiAlH_4$ (0.50 g, 13.2 mmol) in dry Et_2O (250 ml) was added dropwise under N_2 a soln. of **15** (5.2 g, 10.0 mmol) in Et_2O (200 ml). The mixture was boiled until no more **15** was detectable (TLC, CH_2Cl_2/CCl_4, 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} ($\log \varepsilon$) = 293 (4.492), 208 (4.697). IR: 3635*s* (OH), 2960*s* (aliph. CH), 2915*m*, 2875*m*, 1465*w*, 1430*s*, 1395*w*, 1365*w*, 1310*w*, 1235*s*, 1155*m*, 835*m*. ^{1}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}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 $C_{34}H_{46}O_2$ (486.74): C 83.90, H 9.53; found: C 82.91, H 9.41[3]. 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 (CH_2Cl_2/CCl_4 3:1). IR: 3005*w* (arom. CH), 2965*m* (aliph. CH), 2915*w*, 1760*s* (C=O), 1425*m*, 1215*s*, 1205*s*, 1190*s*, 1110*m*, 835*w*. ^{1}H-NMR: 1.41 (*s*, 12 Me); 2.38 (*s*, 2 Ac); 7.55, 7.62 (2 *s*, 8 H–C(terphenyl)). ^{13}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 $C_{39}H_{50}O_4$ (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 $K_3Fe(CN)_6$.* 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 $K_3Fe(CN)_6$ (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} ($\log \varepsilon$) = 636 (4.056), 570 (sh, 4.508), 538 (5.314), 500 (4.480), 470 (3.781), 266 (3.919), 199 (4.564). IR: 2955*s* (aliph. CH), 2915*m*, 2880*m*, 2865*m*, 1575*vs* (C=O), 1485*m*, 1455*m*, 1360*s*, 1335*m*, 1255*m*, 1095*s*, 1040*s*, 870*s*, 830*s*. ^{1}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}H-NMR ((D_6)benzene): 1.53 (*s*, 4 *t*-Bu); 7.36, 7.63 (2*s*, H–C(2,6,2″,6″), H–C(2′,3′,5′,6′)). ^{13}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 $C_{34}H_{44}O_2$ (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 $Na_2S_2O_3$. 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: $C_{34}H_{44}O_2 \cdot 1/3(C_3H_6O)$, $M = 504.1$, triclinic, space group $P\bar{1}$, $a = 1018.3(4)$, $b = 1540.1(6)$, $c = 1561.0(6)$ pm, $\alpha = 103.03(3)$, $\beta = 90.90(3)$, $\gamma = 105.79(3)$°, $U = 2287.2$ nm^3, $Z = 3$, $D_x = 1.098$ Mg m^{-3}, $\lambda(MoK_\alpha) = 71.069$ pm, $\mu = 0.07$ mm^{-1}, $F(000) = 824$, $T = -95$°.

Data Collection and Reduction. A crystal of *ca.* 0.6 × 0.4 × 0.4 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 $2\theta_{max}$ 50°, of which 8026 were independent (R_{int} 0.018) and 4718 significant ($> 3\sigma(F)$). Cell constants were refined from diffractometer angles of 50 reflections in the 2θ range 20–23°.

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.

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[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_ϱ 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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