1,3,5-Tris[(2-hydroxy-3,5-diphenyl)phenyl]benzene and its Phenoxyl Radicals

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Keywords: [2+2+2] Cycloadditions / ESR spectroscopy / Solid-state radicals / Triphenoxybenzenes

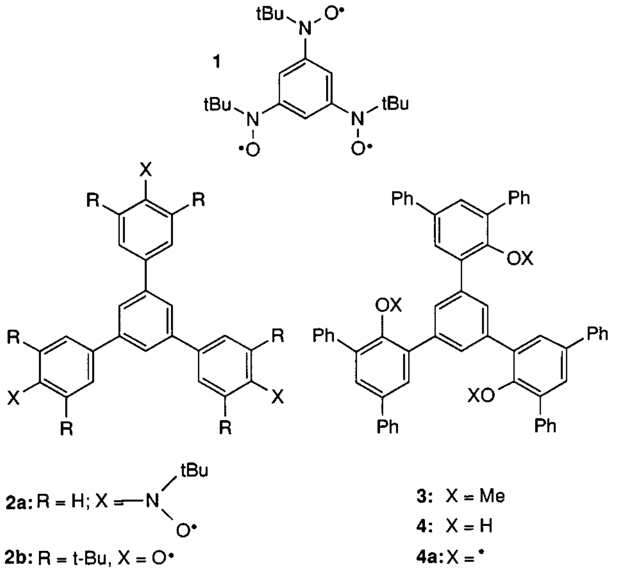
The title compound **4** was synthesized, starting from 4-hydroxybiphenyl (**6**), in a search for organic ferromagnets. Electrochemical and chemical oxidation of **4** resulted in a dark green, insoluble solid with the properties of a monoradical rather than the expected trisradical **4a**.

Organic polyradicals have received considerable interest as basic materials for organic magnets. For this purpose, the unpaired electrons have to be placed in close proximity to each other and in such positions as will permit intra- and intermolecular spin interactions without collapse to closed shell systems. For ferromagnetic interactions the spin alignment must be parallel.[3,4,5,7,10]

One successful approach exploits radical centers attached to a benzene ring (as a ferromagnetic coupler). The chosen *meta* substitution pattern should furthermore stabilize the "open-shell" state. A 1,3,5-substitution pattern at the phenyl center is still more valuable, since a higher radical concentration can be obtained.[6,11,18]

Following this strategy, various substituents with unpaired electrons have been employed, among them phenylcarbenes,[7,10] diaryl methyl radicals,[7,9] diphenylamine cation radicals,[13] nitroxides,[8] nitrenes,[14,15] and *p*-phenoxyl radicals.[11,12,16] The effect of the distance between the parallel spins is demonstrated by the tris-nitroxide radicals **1** and **2a**: Whereas **1** shows definite ferromagnetic interactions, the tris-phenyl analogue **2a** displays only weak antiferromagnetic coupling.[18]

Therefore, the tris-phenoxyl radical **2b**,[16,17] for which no investigations of magnetic properties have been reported, is expected to behave like **2a**.



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2a: R = H; X =

2b: R = t-Bu, X = O•

3: X = Me

4: X = H

4a: X = •

Consequently, we synthesized the trisphenol **4**, in which the oxygen functionality on the phenolic substituents is shifted to the *ortho* position. From the geometrical point of view, the arrangement of spins in **4a** might be sufficient for (ferro)magnetic interactions in the hypothetical trisradical. Trisradical **4a** relies on the stabilizing effect of phenyl groups in phenoxyl radicals.[19] Although 1,3,5-trisphenyl phenoxyl exists exclusively as a dimer in the solid state,[20,21] dimerization of the 1,3,5-trisphenylphenoxy moieties should be precluded thanks to steric hindrance. In addition, high thermal persistencies have been reported for related *ortho* diphenylphenoxyls (cf. **12**).

Preliminary experiments to characterize the radicals obtained from **4** are reported. However, these did not support the anticipated trisradical **4a**.

1,3,5-Tris[(2-methoxy-3,5-diphenyl)phenyl]benzene (3)

The key step in our route to **3** and **4** consists of the construction of the central benzene ring by trimerization of suitable substituted acetylenes. The crucial intermediate is therefore represented by compound **11**, which was successfully synthesized in six steps as outlined in Scheme 1.

Starting from 4-hydroxybiphenyl (**5**), the long known bromination to **6**[52] was easily achieved, as was the *O*-methylation to **7**, providing a protected hydroxyl group compatible with all subsequent reactions. Of several possible metal-assisted aryl couplings[23,24,25] we selected the

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[‡‡] See ref.[2]

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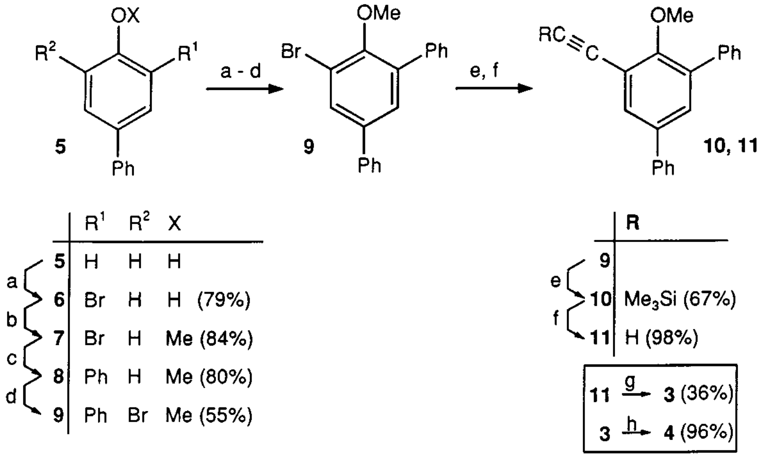


a) Br_2, $CHCl_3$, Δ, 16 h; b) Me_2SO_4, 2.5 N NaOH, Δ, 6 h; c) PhMgBr, $NidppCl_2$, Et_2O, Δ, 48 h; d) $Br_2/CHCl_3$, Δ, 20 h; e) $HC{=}CSiMe_3$, Pd $(PPh_3)_2Cl_2$, CuI, NEt_3, 100%, 24 h; f) $KF{\cdot}H_2O$, DMF, [18]crown-6, 3 h; g) $CpCo(CO)_2$, o-xylene, Δ, 18 h; h) BBr_3, CH_2Cl_2, -78 °C

Scheme 1

well developed nickel route using haloaromatics and aromatic Grignard reagents (cf. ref.[26−29]). In this fashion, 2,4-diphenylanisol **8** was obtained from **7** and phenylmagnesium bromide under mild conditions, with $NidppCl_2$ employed as the most active catalyst.[26]

Unlike the bromination **5** → **6**, the yield of **9** could not be raised over 55%. More modern bromination methods, such as the use of hexamethylene tribromide,[30] or tetraalkylammonium tribromides,[31−33] or even the iron-catalyzed bromination of sterically crowded anisoles[34] were still less efficient. The yield of **9** is depressed mainly by the formation of a side product, which contains both bromine and all the substituents, but which has not yet been identified.

Of the different variant techniques for the palladium-catalyzed *ipso*-substitution of bromoarenes by monoprotected acetylenes,[35−40] we chose the most versatile procedure.[35,36] Compound **9** was transformed into **10** by trimethylsilylacetylene in the presence of the triphenyl phosphinane complex with palladium(II) chloride and copper iodide in 67% yield. However, refluxing at 100° C for 24 h was necessary, rather than ambient temperature conditions.[35]

Desilylation of **10** by potassium hydroxide in methanol[35] was not observed. Instead, formation of **11** proceeded very smoothly when potassium fluoride in the presence of equivalent amounts of [18]crown-6 was used.[41]

The well documented cobalt-catalyzed [2+2+2] cycloaddition[42] was applied for the trimerization of **11** in boiling *o*-xylene. After 18 h (TLC monitoring), the expected 1,3,5-substituted product **3** was found as the only isomer formed (36% yield), with none of the possible 1,2,4-isomers present. In the latter compounds, the three methoxy groups would be characterized by three singlets (^{1}H NMR) and three quadruplets (^{13}C NMR). However, the isolated product displayed only two closely spaced singlets, δ = 3.80 (s, 3 H) and δ = 3.84 (s, 6 H), together with only one ^{13}C signal [δ = 55.72 (q, OCH_3)]. Demethylation of the methoxy groups in **3** by the common boron tribromide route[43,44] afforded **4** in almost quantitative yield. The clean demethylation is remarkable, since the isomeric 1,3,5-tris[(4-methoxy-3,5-diphenyl)phenyl]benzene is reported not to be deprotected either by boron tribromide or pyridine hydrochloride.[45]

In the construction of a benzene ring from three C_2-units, the cycloaddition of acetylenes can be replaced by aldol condensation of acetyl groups (in acetophenone, for example) in the presence of hydrochloric acid/orthoformic ester[46] or just silicon tetrachloride.[47] This attractive route had to be abandoned, though, due to very low yields.

Friedel−Crafts acetylation of **8** with acetic anhydride failed, despite various attempts with different catalysts and the forcing conditions which were necessary. Use of aluminium chloride/nitrobenzene at 100 °C for 2 days produced only 2% of 6-acetyl-1-methoxy-2,4-diphenylbenzene (m.p. 98−99 °C), while an appreciable amount of the starting material **8** was demethylated. This side reaction has also been observed in, for example, the alkylation of 1,3-dimethoxy-2-nitrobenzene with *tert*-butyl chloride.[48]

Phenoxy Radicals from Trisphenol 4

Cyclic voltammetry of **4** was expected to demonstrate at least quasireversible redox behavior. In sharp contrast to these expectations, no reasonable anodic peak potential of **4** could be found in various solvents (CH_2Cl_2, MeCN, PhCN, DMF), even with a high scan rate (500 mV/s). In all cases, the platinum electrode was already blocked at the first scan, indicating very rapid subsequent reactions of the first oxidation product.

The versatile oxidation of phenols with basic hexacyanoferrate(III)[45] was performed with **4** in a two-phase system with diethyl ether.[49] A dark green solid, $\mathbf{4}_{OX}$, was formed rapidly and quantitatively; it could not be dissolved without decomposition, thus precluding measurement of its UV/Vis spectrum. Heating above 200 °C decolorized this oxidation product. Since, in contrast to **4**, the green compound produced gave no relevant mass spectral signals, a polymeric state seems probable.

The clean ESR spectrum of $\mathbf{4}_{\mathrm{OX}}$ clearly indicates a monoradical, as the typical pattern of biradicals in the solid state with $\Delta m = 2$ in the range of the half-field is missing. The g-factor $g = 2.0039$, is suitably located within the range of 1.99 to 2.0052 for phenoxyl radicals and close to $g = 2.0023$ for the free electron.[19]

In the IR spectrum of $\mathbf{4}_{\mathrm{OX}}$, a sharp OH band ($\tilde{\nu}$ = 3520−3500 cm^{-1}) indicates that not all the phenolic groups have been oxidized. The absence of a carbonyl absorption rules out dimers of the type known from the 1,3,5-triphenylphenoxy radical.[20]

The temperature-dependent magnetic susceptibility (Figure 1) clearly indicates exclusively paramagnetic interactions.

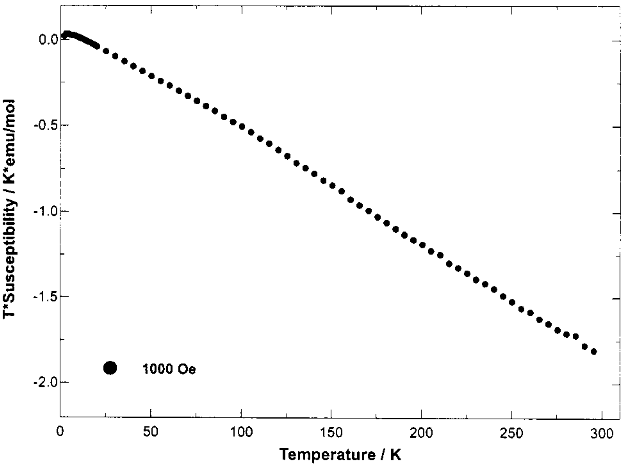
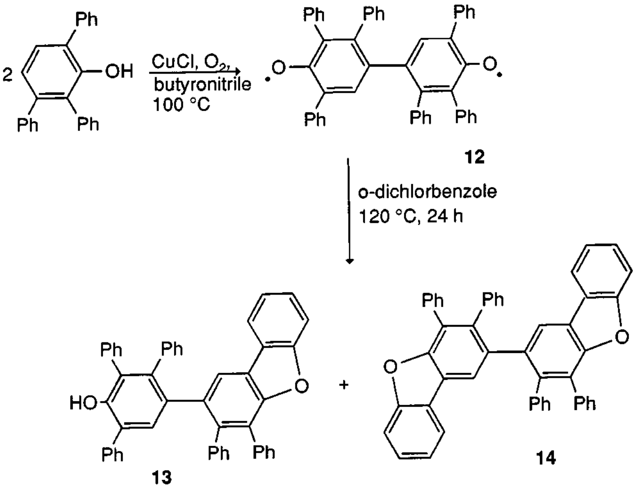
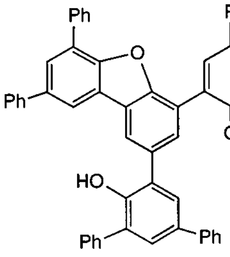


Figure 1. Correlation of $\chi \cdot T$ versus T not corrected

In the light of the persistence of the isomeric trisphenoxy radical **2b**, the instability of radical states of **4a** was not expected. Even the biradical **12** needs high temperatures and long reaction times to form the subsequent products **13** and **14**.[50]



Therefore, a phenoxyl radical[51] formed from **4** is less likely to attack the unsubstituted phenyl ring in the *ortho* position. One must rather assume that the trisubstituted (activated?) central benzene ring is involved. A possible structure for the oxidative transformation product may be **15**, containing both the identified radical moiety and a hydroxyl group. However, further *inter*molecular coupling of **15** is difficult to imagine, due to the steric hindrance involved. Thus, this piece of research, which we cannot follow up further, is left as an open question.



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Conclusions

Tris(hydroxyphenyl)benzene **4** has been synthesized by a route including formation of the benzene nucleus from acetylenic precursors as one of the final steps. This approach may serve as a model for similar compounds.

In sharp contrast to our expectations based on the highly persistent phenoxy radical **12**, the anticipated trisradical **4a** could be obtained neither by electrochemical nor by chemical oxidation. Instead, the insoluble material formed could be characterized only as a persistent monoradical, of unknown composition and which may contain structural elements of **15**. Since the phenyl groups *ortho* to the oxygen radical center are very probably involved in the observed transformation, a trisradical of type **4a**, but with the phenyl groups replaced by *tert*-butyl groups, may be more likely to be achievable.

Experimental Section

Melting points: Kofler microscope (Fa. Reichert) corrected. − IR: Perkin−Elmer 1420. UV/Vis: Perkin−Elmer 330. − NMR: Bruker AV 250 (250.1 MHz or 62.9 MHz). − MS: Finnigan MAT 8200 and MAT 90. ESR: Bruker ESP 300. − Cyclic voltammetry: AMEL 553 and Wg&G PARC 175. Working electrode Pt (ϕ 1.0 mm) versus Ag/AgCl. − Susceptibilities: SQUID-Susceptometer. − Solvents were purified according to standard procedures. − Flash chromatography with silica gel 0.0032−0.063 mm. Petroleum ether (PE) boiling range 30−75 °C.

2-Bromo-4-phenylphenol (6): Preparation according to ref.[52] Yield 79%, m.p. 93−94 °C (ref.:[38] 80% yield, m.p. 95−96 °C; no analytic data given). − IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1} (OH), 3040−3020 (CH), 1600−1540 (C=C). − UV (CH$_3$CN): $\lambda_{\max}$ (lg ε) = 259 nm (4.24). − ^{1}H NMR (250 MHz, CDCl$_3$): δ = 5.52 (s, 1 H, OH), 7.09 (d, J_o = 8.5 Hz, 1 H, 6-H), 7.29−7.50 (m, 6 H, aromat. H), 7.69 (d, J_m = 2.14 Hz, 1 H, 3-H). − ^{13}C NMR (63 MHz, CDCl$_3$): δ =

110.6 (s, C-7), 116.3, 126.7, 127.3, 127.9, 128.9, 130.4 (6 d, C-H), 135.4 (s, C-4), 139.4 (s, C-2), 151.6 (s, C-1). − $C_{12}H_9BrO$ (249.1): calcd. C 57.86, H 3.64; found C 58.06, H 3.54.

3-Bromo-4-methoxybiphenyl (7): In an adaptation of a procedure from ref.[22], compound **6** (50.0 g, 202 mmol) in NaOH (2.5 N, 150 mL) was treated slowly, at ca. −10 °C, with dimethylsulfate (25.1 g, 202 mmol). The viscous mixture was refluxed until **6** had been consumed (6 h, TLC: PE/EE 2:1). Excess Me_2SO_4 was quenched with ammonia, and after cooling the solid product was separated and washed with water. Recrystallization from PE (30−75 °C) yielded shiny, colorless crystals of **7** (44.6 g, 84%), m.p. 73−75 °C. − IR (KBr): $\tilde{\nu}$ = 3040−3020 cm^{-1}, 2960−2940 (CH), 1600 (C=C), 1050, 1010 (OMe). − UV (CH_3CN): λ_{max} (lg ε) = 240 nm (4.27). − ^1H NMR (250 MHz, $CDCl_3$): δ = 3.91 (s, 3 H, CH_3), 6.97 (d, J_o = 8.55 Hz, 1 H, 6-H), 7.30−7.55 (m, 6 H, aromat. H), 7.79 (d, J_m = 2.44 Hz, 1 H, 3-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 56.34 (q, CH_3), 112.1, 126.7, 127.0, 127.2, 128.8, 131.9 (6 d, C-H), 135.2, 139.4 (2 s, C-2, -4), 155.3 (s, C-1). The signal for C-7 was not detected. − $C_{13}H_{11}BrO$ (263.1): calcd. C 59.34, H 4.21; found C 59.56, H 4.20.

1-Methoxy-2,4-diphenylbenzene (8): In an adaptation of a procedure from ref.[27], magnesium turnings (3.42 g, 140 mmol) were treated in DE with bromobenzene (22.5 g, 140 mmol) under nitrogen. The solution of phenylmagnesium bromide was added at 0−10 °C to a solution of **7** (22.4 g, 85.2 mmol) and $NidpppCl_2$[16] (0.48 g, 0.90 mmol) in dry DE (65 mL). After warming to ambient temperature, the mixture was refluxed for 48 h (TLC monitoring, PE/EE 8:1). After cooling with ice, HCl (2 N, 100 mL) was added and the yellow ether phase separated. Extraction of the water phase, treatment of the organic fraction with a solution of Na_2CO_3, drying with $CaCl_2$, and evaporation yielded an orange oil, which crystallized on addition of PE. Recrystallization from methanol afforded colorless needles of **8** (17.8 g, 80%), m.p. 93−94 °C. − IR (KBr): $\tilde{\nu}$ = 3050−3020 cm^{-1}, 2960−2900, 2830 (CH), 1600 (C=C), 1055, 1025 (OMe). − UV (CH_3CN): λ_{max} (lg ε) = 242 nm (4.47). − ^1H NMR (200 MHz, $CDCl_3$): δ = 3.84 (s, 3 H, CH_3), 7.04 (d, J_o = 8.54 Hz, 1 H, 6-H), 7.27−7.46 (m, aromat. H), 7.53−7.61 (m, 6 H, aromat. H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.74 (q, CH_3), 111.1, 126.8, 127.1, 128.0, 128.7, 129.6, 129.7 (7 d, C-H), 131.0, 133.8, 138.4 (3 s, C-4, -7, -8), 140.66 (s, C-2), 156.01 (s, C-1). − $C_{19}H_{16}O$ (260.3): calcd. C 87.66, H 6.19; found C 87.52, H 5.96.

6-Bromo-1-methoxy-2,4-diphenylbenzene (9): The conditions for **5** → **6** were adapted, using **8** (10.0 g, 38.5 mmol) and bromine (6.15 g, 38.5 mmol) in 65 mL of $CHCl_3$, at reflux (19 h, TLC: PE/EE 6:1, two spots for products). The crude product (oil) was heated in methanol. On cooling, a solid separated; this was recrystallized from methanol, yielding colorless microcrystals of **9** (6.82 g, 55%), m.p. 111−113 °C. From the mother liquor, 2 g of a second product, m.p. 73−75 °C was isolated (faster running TLC spot) but not identified. − IR (KBr): $\tilde{\nu}$ = 3040−3010 cm^{-1}, 2950−2900, 2830 (CH), 1600 (C=C), 1020 (OMe). − UV (CH_3CN): λ_{max} (lg ε) = 250 nm (4.48), 270 (4.38). − ^1H NMR (250 MHz, $CDCl_3$): δ = 3.85 (s, 3 H, CH_3), 7.03−7.06 (m, 1 H, aromat. H), 7.32−7.58 (m, 11 H, aromat. H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.77 (q, CH_3), 111.6 (d, C-H), 120.9 (s, C-), 126.9, 127.2, 128.1, 128.3, 129.5 (5 d, C-H), 131.2 (s, C-), 131.8 (d, C-H), 132.6 (s, C-), 138.2 (s, C-2), 139.6 (s, C-6), 156.3 (s, C-1). − $C_{19}H_{15}BrO$ (339.2): calcd. C 67.27, H 4.46; found C 66.93, H 4.26.

1-Methoxy-2,4-diphenyl-6-(trimethylsilylethynyl)benzene (10): In an adaptation of a procedure from ref.[35,36], compound **9** (10.0 g, 29.4 mmol) and trimethylsilylacetylene (6.20 mL, 51.0 mmol) in dry NEt_3 (60 mL), together with $Pd(PPh_3)_2Cl_2$ (502 mg, 0.58 mmol) and CuI (29.4 mg, 0.30 mmol), were refluxed for 24 h (TLC: PE/EE 6:1) under nitrogen atmosphere. After removal of the solvent, the residue was dissolved in dichloromethane and washed with water, HCl (5%), and water. After drying with $MgSO_4$, the brown solution was filtered through ALOX (activity 1) and eluted with dichloromethane. On evaporation a solid remained. Pale yellow crystals of **10** (7.00 g, 67%) were obtained from methanol, m.p. 122−123 °C. − IR (KBr): $\tilde{\nu}$ = 3040−3020 cm^{-1}, 2940−2900, 2830 (CH), 2150 (C≡C), 1600 (C=C), 1050, 1020−1005 (OMe). − UV (CH_3CN): λ_{max} (lg ε) = 220 nm (4.34), 265 (4.38), 295 (4.56). −^1H NMR (250 MHz, $CDCl_3$): δ = 0.26 (s, 9 H, $SiCH_3$), 3.85 (s, 3 H, CH_3), 7.02−7.05 (m, 1 H, aromat. H), 7.31−7.57 (m, 11 H, aromat.H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 0.00 (q, $SiMe_3$), 55.72 (q, CH_3), 94.63, 105.1 (2 s, C-9, -10), 111.6 (d, C-H), 121.4 (s, C-), 126.4, 127.0, 127.1, 128.1, 129.5 (5 d, C-H), 131.2 (s, C-), 132.4 (d, C-H), 132.9 (s, C-4), 138.3, 140.6 (2 s, C-2, -6), 156.3 (s, C-1). − $C_{24}H_{24}OSi$ (356.5): calcd. C 80.85, H 6.78; found C 80.52, H 7.09.

6-Ethynyl-1-methoxy-2,4-diphenylbenzene (11): In an adaptation of a procedure from ref.[41], compound **10** (5.50 g, 15.4 mmol) in DME (20 mL) was stirred with $KF{\cdot}H_2O$ (1.29 g, 16.9 mmol) and [18]crown-6 (4.06 g, 15.4 mmol) for 3 h at ambient temperature (TLC monitoring, PE/EE 6:1). After addition of dichloromethane (50 mL), the organic phase was extracted several times with water. Removal of the solvent yielded a crude product, which afforded colorless leaflets of **11** (4.30 g, 98%) from methanol. m.p. 131−132 °C. − IR (KBr): $\tilde{\nu}$= 3270 cm^{-1} (C≡*CH*), 3000−2900, 2840 (CH), 2100 (C≡C), 1600 (C=C), 1050, 1020 (OMe). − UV (CH_3CN): λ_{max} (lg ε) = 220 nm (4.32), 255 (4.39), 287 (4.46). − ^1H NMR (250 MHz, $CDCl_3$): δ = 3.11 (s, 1 H, C≡C-H), 3.85 (s, 3H, CH_3), 7.03−7.07 (m, 1 H, aromat. H), 7.31−7.46 (m, 3 H, aromat. H), 7.52−7.58 (m, 8 H, aromat. H). − ^{13}C NMR (63 MHz, $[D_6]DMSO$): δ = 55.71 (q, CH_3), 81.28 (s, C-9), 83.51 (d, C-10), 112.4 (d, C-H), 120.1 (s, C-), 126.4, 127.1, 128.1, 128.7, 129.4 (5 d, C-H), 130.4, 131.7 (2 s, C-4,8), 132.27 (d, C-H), 137.9, 140.1 (2 s, C-2, -6), 156.19 (s, C-1). − $C_{21}H_{16}O$ (284.4): calcd. C 88.70, H 5.67; found C 88.09, H 6.30.

1,3,5-Tris[(2-methoxy-3,5-diphenyl)phenyl]benzene (3): In an adaptation of a procedure from ref.[41,42], compound **11** (1.69 g, 5.95 mmol) and $CpCo(CO)_2$ (0.03 mL) in degassed dry *o*-xylene (25 mL) was refluxed (Ar) for 18 h (TLC, CH_2Cl_2/PE 1:1). After removal of the solvent, the brownish residue was purified by flash chromatography (SiO_2/CH_2Cl_2/PE, 1:1), affording a yellow crude product (1.00 g, 59%). Recrystallization from acetonitrile provided colorless crystals (0.60 g, 36%), m.p. 181−182 °C. − IR (KBr): $\tilde{\nu}$ = 3010 cm^{-1}, 2920, 2820 (CH), 1600 (C=C), 1020−1005 (OMe). − UV (CH_3CN): λ_{max} (lg ε) = 250 nm (4.08), 290 (3.99). − ^1H NMR (250 MHz, $CDCl_3$): δ = 3.80 (s, 3 H, CH_3), 3.84 (s, 6 H, CH_3), 6.96−7.08 (m, 3 H, aromat. H), 7.27−7.78 (m, 33 H, aromat. H), 7.84 (s, 3 H, aromat. H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.72 (q, CH_3), 111.5, 111.6 (2 d, C-H), 126.2, 126.3, 126.9, 127.0, 127.1, 127.2, 127.4, 127.7, 128.0, 128.1, 129.5, 129.6, 130.2, 130.3, 131.0 (d, s, C-H, C-, assignment not possible), 133.2, 133.2, 138.4, 139.9 (4 s, C-), 156.02, 156.17 (2 s, C-OMe). − $C_{63}H_{48}O_3$ (852.1): calcd. C 88.70, H 5.67; found C 88.36, H 5.64.

1,3,5-Tris[(2-hydroxy-3,5-diphenyl)phenyl]benzene (4): In an adaptation of a procedure from ref.[43], compound **3** (0.50 g, 0.59 mmol) in dichloromethane was treated under nitrogen at −72 °C with BBr_3 (0.48 g, 1.94 mmol) in dichloromethane (1 mL). The mixture was allowed to warm to room temperature over 16 h and hydrolyzed with water (30 mL). The aqueous layer was extracted with dichloromethane and the organic phase evaporated, yielding 0.6 g of a greenish solid. The solid was dissolved in hot toluene and PE added. On cooling, colorless crystals of **4** separated (0.45 g, 95%), m.p. 149−150 °C. − IR (KBr): $\tilde{\nu}$ = 3510−3200 cm^{-1} (OH), 3040−3020 (CH), 1600 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 250 nm (4.78), 290 (4.64). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 5.25, 5.30 (2 s, 3 H, OH), 7.01−7.79 (m, 36 H, aromat. H), 7.86 (s, 3 H, aromat. H$_a$). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 116.2, 116.3 (2 d, C-H), 126.2, 126.2, 127.2, 127.5, 127.6,. 127.7, 128.0, 128.1, 128.4, 128.7, 129.1, 129.3, 129.4 (d, s, C-H, C-, assignment not possible), 130.3, 130.3 (2 d, C-H), 133.4, 137.0, 139.9 (3 s, C-), 152.0, 152.1, 152.2 (3 s, COH). − MS/DCI (isobutane), *m/z* (%) = 812.5 [M$^+$ + 2] (64), 811.5 [M$^+$ + 1] (100). − $C_{60}H_{42}O_3$ (810.9): calcd. C 88.86, H 5.22; found C 88.60, H 5.33.

Oxidation of 4 to a Radical Species: In an adaptation of a procedure from ref.[49], compound **4** (70.0 mg, 0.09 mmol) in degassed diethyl ether (15 mL) was slowly added $K_3[Fe(CN)_6]$ (3.30 g, 58.9 mmol) and KOH (0.6 g, 10.0 mmol)] in degassed water (35 mL) at room temperature. A dark green solid was immediately precipitated. After 30 min, all **4** had been consumed (TLC: acetone/PE 1:1.5). The suspension was treated with ultrasound for better filtering and washing (water) of the solid, which was finally treated with some acetone and ether and dried in vacuum. Yield 70 mg (100%), decoloration >200 °C. − IR (KBr): $\tilde{\nu}$ = 3530−3500 cm^{-1} (OH), 3050−3020 (CH), 1590 (C=C). − ESR (solid): center field. 3478.9 G ($\tilde{\nu}$ = 9.756972 GHz), g = 2.0039. − Measurement of the susceptibility identified paramagnetism. Proposed polymer unit: Spin concentration ca. 25.7%. C = 0.0963 emu K mol^{-1}. − $C_{60}H_{41}O_3$ (809.98): calcd. C 88.97, H 5.10; found C 88.12, H 5.13.

Acknowledgments

Financial support by the Fonds der Chemischen Industrie, Frankfurt/Main, and the Stiftung Volkswagenwerk, Hannover, is gratefully acknowledged.

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Received October 19, 2000
[O00530]