

MAGNETIC COUPLING BETWEEN TWO PHENOXYL RADICALS ATTACHED TO THE PHENYL RINGS OF *CIS*- AND *TRANS*-STILBENES

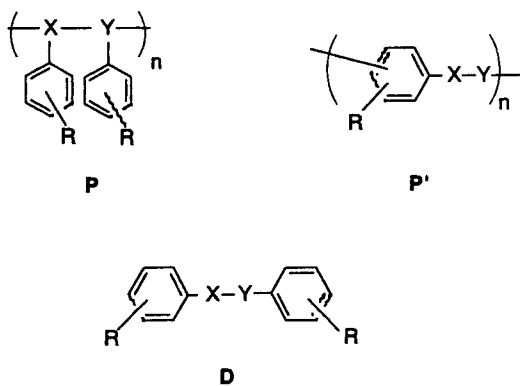
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Magnetic coupling between two sterically protected phenoxy radicals through the *cis*- and *trans*-stilbene chromophores was studied by means of their EPR fine structures. While the zero-field splitting parameters D , which are governed by the magnitude of dipolar coupling, were dependent on the geometrical isomerism, the sign of exchange coupling was independent of it and dictated by the topology of the π -conjugated systems: ferromagnetic in *o,m*-isomers and antiferromagnetic in *m,m'*-isomers.

INTRODUCTION

One of the promising structures leading to organic molecules with very high-spin ground states is a π -conjugated polymer having open shell centres as pendants in the side-chains.¹ In order to predict the magnetic properties of such polymers, it is necessary to understand how two open shell centres would couple through a magnetic coupler in a model diradical possessing a partial structure of the polymer chain. Dimer structures **D** would serve as prototypes for judging the sign and magnitude of the intramolecular coupling in polyradicals **P** and **P'**. Poly(phenylenevinylene)s **P'** ($X-Y = CH=CH$) were considered in this study as



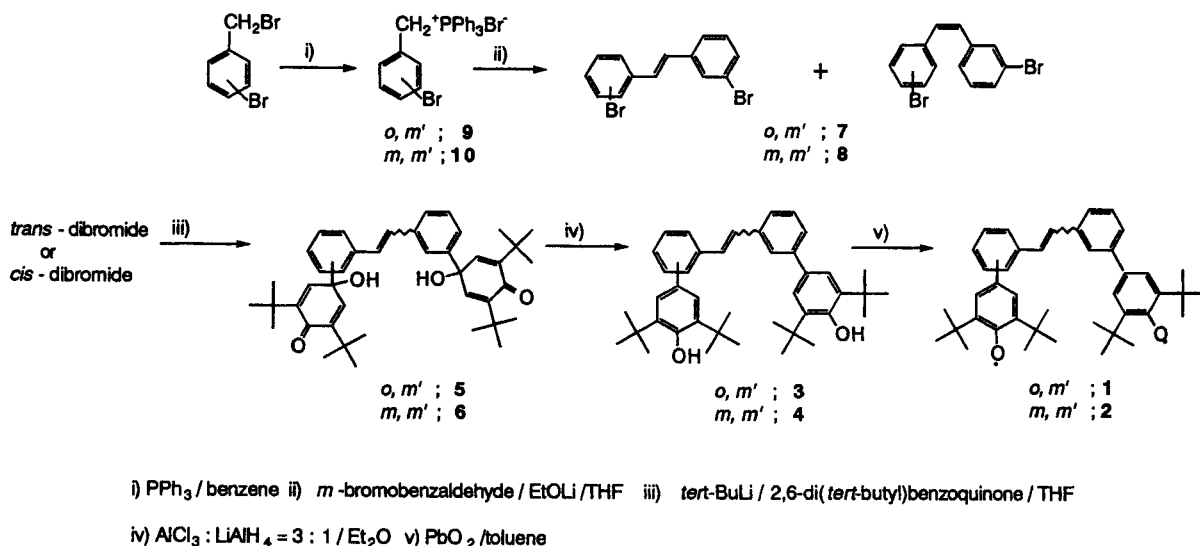
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versatile polymer main chains for making potentially high-spin organic polymers.² Sterically protected 2,6-di-*tert*-butylphenoxy radicals were chosen as spin-carrying centres R, since the phenoxy was presumed to be reasonably persistent³ and the interaction between the two radical centres through the π -conjugated framework was expected to be stronger than that of nitroxides. We report here regioselectivity in the exchange coupling between the two phenoxy units in various stilbenediyl units as studied by EPR spectroscopy.

RESULTS AND DISCUSSION

The *cis*- and *trans*-isomers of 3-(3,5-di-*tert*-butyl-4-oxyphenyl)-2'- and 3'-(3,5-di-*tert*-butyl-4-oxyphenyl)-stilbenes **1** and **2** were prepared by the sequence of reactions summarized in Scheme 1. Isomeric stilbene dibromides were prepared by the Wittig reaction, which gave a *cis*-rich mixture (*cis*:*trans* = 6:4), from which *cis*- and *trans*-isomers were separated and purified by fractional recrystallization from *n*-hexane. When the *trans*-isomer was desired, the *cis*-*trans* mixture was refluxed in nitrobenzene in the presence of iodine to afford *trans*-rich stilbene. The bromide moieties of each conformer were converted into 3,5-di-*tert*-butyl-4-hydroxyphenyls, followed by oxidation with lead dioxide to give the bisphenoxy radicals.

The diradicals thus obtained were unstable in the descending order *cis*-1 > *cis*-2 > *trans*-2 > *trans*-1, even under a nitrogen atmosphere at room temperature, but reasonably stable below -50°C . The EPR signal intensities of *trans*-1 in degassed toluene solution, for



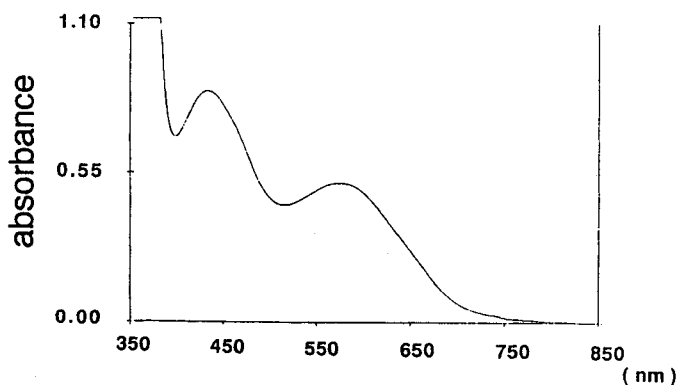
Scheme 1

example, decreased to one third in 3 h at room temperature but showed no significant change at -50°C . Therefore, radicals were used for UV-visible and EPR measurements immediately after oxidation (and filtration for UV-visible measurement) at room temperature without isolation.

UV-visible spectra of both geometrical isomers of 3, 4, 1 and 2 in diethyl ether were taken at -50°C . *trans*-3 and -4 had absorption maxima at 269 and 315(sh) nm and 277 and 310(sh) nm, respectively, and the corresponding radicals after oxidation showed characteristic absorptions for phenoxyl radicals⁴ at 435 and 584 nm and 431 and 572 nm, respectively. The UV-visible spectrum of *trans*-1 at -50°C is shown in Figure 1. While *cis*-3 and -4 had absorptions at 268 and 271 nm, respectively, no sample of *cis*-1 and -2 could be obtained in a

state pure enough to take UV-visible spectra, as decomposition of the radicals was very fast under the ambient oxidation conditions.

The oxidation of phenols 3 and 4 in toluene solution in the presence of lead dioxide was followed by means of EPR spectrometry. As the oxidation proceeded, sharp twelve lines due to hyperfine coupling with the hydrogen of the two phenyl rings appeared first and were replaced gradually with a broad single line with $\Delta H_{\text{pp}} = 2.8 \text{ G}$ and $g_{\text{iso}} = 2.0044$. The spectral change of *trans*-3 is shown in Figure 2(a), (c) and (d). The initial spectrum is ascribed to the formation of the monophenoxyl radical and the assignment was confirmed by a computer simulation as shown in Figure 2(b). The optimized parameters are $g = 2.0046$ and hyperfine splitting (hfs) constants $a_{\text{H}} = 1.74, 0.7$ and

Figure 1. UV-visible spectrum of a solution of *trans*-1 in diethyl ether at -50°C

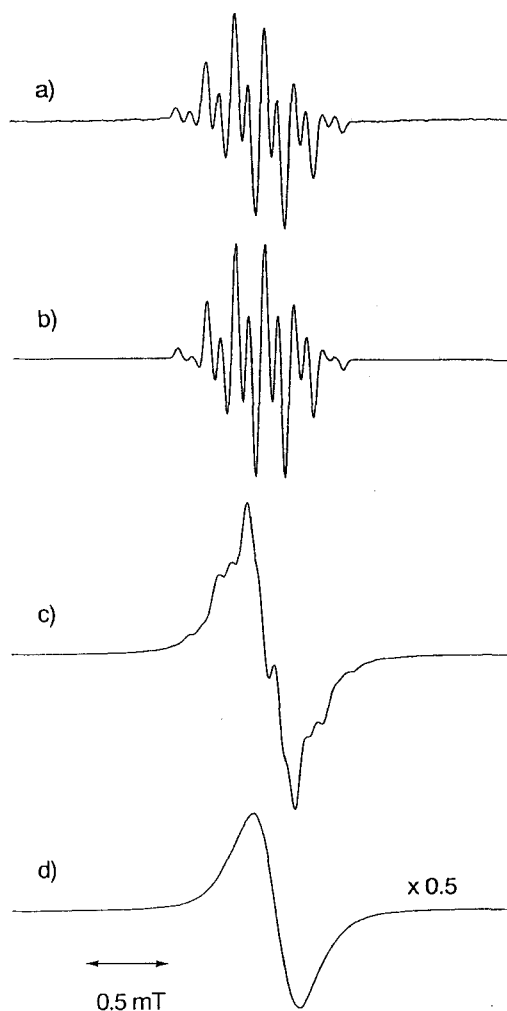


Figure 2. X-band ($\nu = 9.394$ GHz) EPR spectra of a solution of *trans*-3 in toluene at 20°C after being shaken with lead dioxide for (a) 5, (c) 10 and (d) 15 s. (b) Simulation of EPR spectrum of (a) for monophenoxyl radical with $a_{\text{H}} = 1.7, 0.7$ and 0.3 G for five, one and one proton, respectively, and $g = 2.0046$

0.3 G for five magnetically equivalent ring protons ($\text{H}_3, \text{H}_5, \text{H}_2', \text{H}_4',$ and H_6'), one ring proton (H_5'), and one vinyl proton, respectively. Without 0.3 G for one vinyl proton, symmetrical pairs of six lines were obtained in the calculated spectrum, which is significantly different in appearance from the observed spectrum. These hfs and g values are in good agreement with those of analogous phenoxyl radicals reported in the literature.⁵ The spectra of monoradicals observed at an early stage of the oxidation of 3 and 4 were very similar to each other, indicating that the hydroxy

moiety at the *meta* position was more readily oxidized than that in the *ortho* position in 3.

Toluene solutions of oxidised 3 and 4, which showed broad single lines at room temperature, were frozen at 10 K in an EPR cavity. Characteristic fine structures corresponding to randomly oriented triplet species were observed together with half-field resonance at 167.8 and 167.5 mT, respectively, due to $\Delta m_s = 2$ transitions, demonstrating that the expected diphenoxyl radicals were formed at the later stage of the oxidation. The EPR spectra of *trans*-1 and -2 thus obtained are shown in Figure 3.

From both the outermost signals ($-H_z$ and H_z) in the $\Delta m_s = 1$ transitions of the EPR spectra, zero-field splitting parameters $|D/hc|$ were determined to be 0.0022 and 0.0014 cm^{-1} for *trans*-1 and -2, respectively. Similarly, in the EPR spectra of *cis*-1 and -2 under similar conditions, triplet signals were observed with $|D/hc| = 0.0035$ and 0.0036 cm^{-1} in $\Delta m_s = 1$ and at 167.3 and 167.4 mT in $\Delta m_s = 2$ transitions, respectively, in addition to the signal at $g = 2.0046$ due to monoradicals. Attempts to obtain E parameters by simulation of the observed fine structures due to the

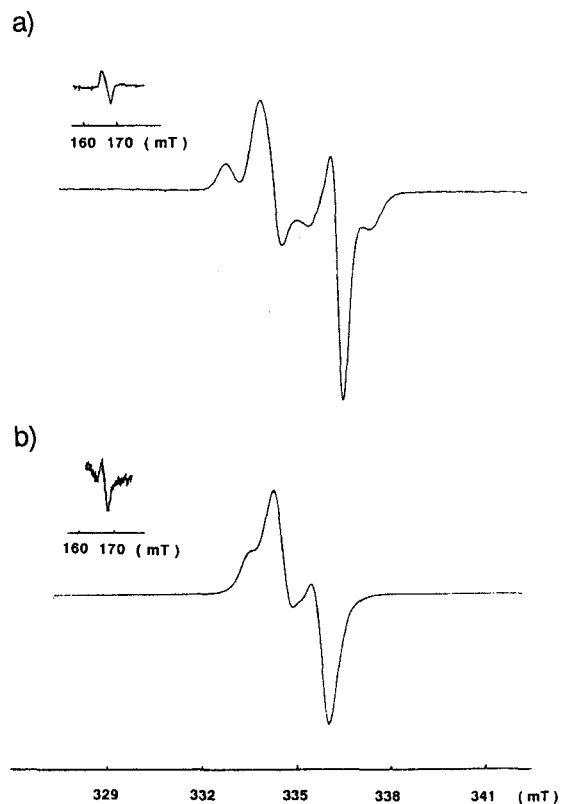


Figure 3. X-band ($\nu = 9.401$ GHz) EPR spectra in toluene glass at 10 K of (a) *trans*-1 and (b) *trans*-2

triplet species were unsuccessful, probably owing to the g anisotropy and the presence of more than one conformer. The observed differences in $|D/hc|$ values in the four phenoxy biradicals are explained in terms of a point dipole approximation:⁶

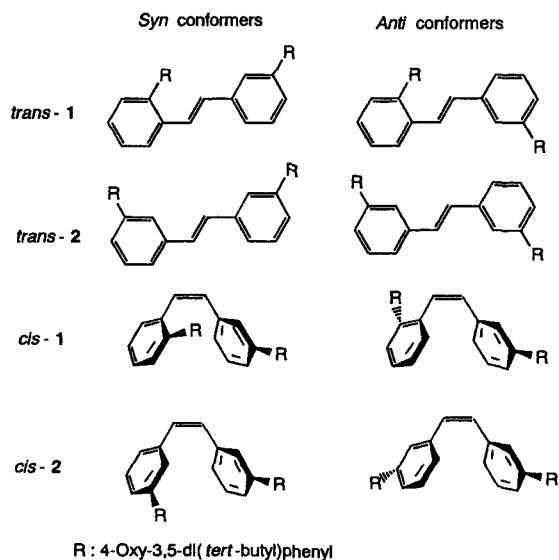
$$D(G) = 27810/r^3 \quad (1)$$

from which distances r between the two radical centres were estimated using the observed D values to be 10.6, 11.5, 9.09, and 8.99 Å for *trans*-1, and -2 and *cis*-1 and -2, respectively. These r values correspond well with those between the centres of the phenyl ring of the phenoxy radicals in *syn* conformers as depicted in Scheme 2, indicating that the *syn* rather than *anti* conformers are predominant in these rigid glass media.

The triplet signal intensities for *trans*- and *cis*-1 obeyed the Curie law in the temperature range 10–110 K (Figure 4), whereas those for *trans*- and *cis*-2 deviated from the Curie law below 25 K, indicating that the phenoxy radicals 1 were with triplet ground state and 2 were with singlet ground states having low-lying excited triplet states. A Bleaney–Bowers-type equation:⁷

$$I = \frac{C}{T[3 + \exp(-2J/kT)]} \quad (2)$$

where I and C are EPR signal intensity and proportionality constant, respectively, and the other symbols have their usual meanings, was applied to the observed temperature dependence of the signal intensities for *trans*- and *cis*-2. The singlet–triplet energy gaps ($\Delta E_{S-T} = 2J$) were estimated to be $0 > \Delta E_{S-T} > -35 \text{ cal mol}^{-1}$ (1 cal = 4.184 J) for both geometrical isomers.



Scheme 2

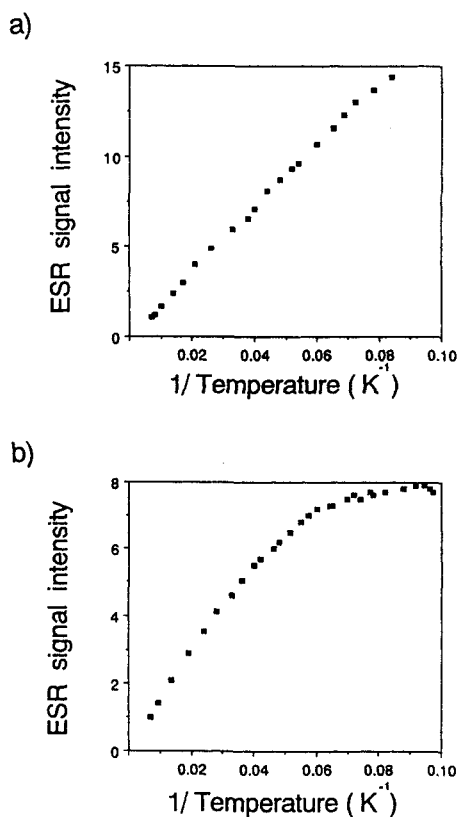


Figure 4. Temperature dependence of the triplet signals (a) at 333.4 mT for *trans*-1 and (b) at 334.2 mT for *trans*-2 in EPR spectra

CONCLUSIONS

EPR spectra of isomeric *cis*- and *trans*-1 and 2 revealed characteristic signals due to randomly oriented triplet species. The zero-field D parameters were determined and found to depend not only on the regiochemistry but also on the geometrical isomerism. The magnitude was in harmony with the distance dependence of dipolar coupling of the electron spins. While the temperature dependence of the signal intensities due to triplet 1 followed the Curie law, that of 2 deviated from this law below 25 K. It is concluded that the two phenoxy radicals interacted with each other ferro- and antiferromagnetically in 1 and 2, respectively. The singlet–triplet energy gaps of $0 > \Delta E_{S-T} = 2J > -35 \text{ cal mol}^{-1}$ for both the geometrical isomers are very similar to $\Delta E_{S-T} = -37 \text{ cal mol}^{-1}$ for *trans*-1,2-bis{3-(*N*-oxy-*N*-*tert*-butylamino)phenyl}ethene,⁸ indicating that the 2,6-di-*tert*-butylphenoxy moiety is magnetically nearly equivalent to *N*-oxy-*N*-*tert*-butyl group. When two carbene⁹ or two nitrene centres¹⁰ are placed at the

m,p'-positions of a stilbene skeleton, they couple strongly in a ferromagnetic fashion. In the *m,m'*-isomer of the former, a preliminary result placed a quintet state higher in energy by $6J = 200 \text{ cal mol}^{-1}$ than a singlet.⁹

According to the current theory of spin polarization in non-Kekulé hydrocarbons¹¹ and their heteroatom analogues, those related by connectivity to trimethylenemethane on the one hand and tetramethyleneethane and pentamethylene propane on the other have high- and low-spin ground states, respectively.¹² Compounds **1** and **2** are therefore predicted to have triplet and singlet ground states, respectively. The observations made in this study not only substantiated these theoretical predictions but also showed that the signs of the exchange coupling did not depend on the geometrical isomerism. Connectivity is more important than geometrical shape in controlling the spin states of the conjugated diradical molecules.

Another important message of these studies is that polymers **P'** ($X-Y = \text{CH}=\text{CH}$) should become super-high-spin if all the radical centres are introduced in the same position of the repeating monomer units. In other words, ferromagnetic coupling between the neighbouring radical centres will be obtained in homopolymers. Some of the efficient methods currently available for poly(phenylenevinylene)s cannot distinguish between the head and tail of the monomer unit. It is strongly suggested that we have to employ polymerization/condensation reactions, e.g. Wittig reactions, which take place regiospecifically.

EXPERIMENTAL

General methods. Infrared spectra were recorded on a Hitachi I-5040 Fourier transform spectrometer. ¹H NMR spectra were measured on a JEOL GX-270 Fourier transform spectrometer using CDCl₃ or CD₂Cl₂ as solvent and referenced to TMS. UV-visible absorption spectra were measured on a JASCO UVIDEC-610C spectrometer. EPR spectra were obtained on a Bruker ESP 300 X band spectrometer equipped with an Air Products LTD-3-110 liquid helium transfer system. Melting points were recorded on a MEL-TEMP. Elemental analyses were performed in the Analytical Centre of this Department.

Materials. Unless stated otherwise, the preparative reactions were carried out under a dry, high-purity nitrogen atmosphere. Diethyl ether, benzene, toluene and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Ethanol was distilled over magnesium wire. Starting materials, 2-bromobenzyl bromide and 3-bromobenzaldehyde, were purchased from Tokyo Kasei. Reaction mixtures were worked up by diluting with diethyl ether, if necessary, washing the

organic layer with aqueous ammonium chloride, drying over magnesium sulphate and evaporation of the solvent under reduced pressure using a rotary evaporator.

(2-Bromobenzyl)triphenylphosphonium bromide (9). A solution of 2-bromobenzyl bromide (10.0 g, 40.0 mmol) and triphenylphosphine (11.5 g, 43.8 mmol) in benzene (100 ml) was refluxed for 16 h. After cooling to room temperature, the resulting precipitates were collected by filtration to give a white powder (20.5 g) in quantitative yield, m.p. 171–174 °C; ¹H NMR (270 MHz, CDCl₃), δ 5.66 (d, 2H, $J = 14.3 \text{ Hz}$), 7.1–7.9 (m, 19H).

(3-Bromobenzyl)triphenylphosphonium bromide (10). This was prepared in a manner similar to that employed for **9** by using 3-bromobenzyl bromide in place of the 2-bromo compound. The bromide was obtained in a quantitative yield, m.p. 181–185 °C; ¹H NMR (270 MHz, CDCl₃), δ 5.57 (d, 2H, $J = 14.7 \text{ Hz}$), 6.97–7.05 (m, 2H), 7.28–7.37 (m, 2H), 7.59–7.68 (m, 6H), 7.73–7.85 (m, 9H).

1-(2-Bromophenyl)-2-(3-bromophenyl)ethene (trans-7). To (2-bromobenzyl)triphenylphosphonium bromide (15.0 g, 29.3 mmol) and 3-bromobenzaldehyde (5.42 g, 29.3 mmol) dissolved in THF (500 ml) was added dropwise a solution of lithium ethoxide prepared from lithium (0.21 g, 30.3 mmol) and ethanol (20 ml). After being stirred for 15 h at room temperature, the solution was concentrated to less than half its volume on a rotary evaporator. Quenching with 1 M HCl (200 ml), the usual work-up and addition of *n*-hexane to the yellow oil gave a white precipitate, which was removed by filtration. The filtrate was concentrated to dryness. A *trans*- and *cis*-dibromide mixture (8.05 g) was obtained as a colourless oil after purification by chromatography on silica gel. For separating the *trans*- and *cis*-isomers, the mixture was chromatographed on silica gel with *n*-hexane as eluent to give *trans*-**7** (3.6 g) and *cis*-**7** (2.4 g) as a white powder and a colourless oil, respectively. For converting the *cis* into the *trans* form, a solution of the mixture in nitrobenzene was refluxed in the presence of a catalytic amount of iodine for 15 min. After evaporating the solvent to dryness under reduced pressure, the brown oil was chromatographed on silica with *n*-hexane to afford *trans*-**7** (1.5 g) as a white solid, m.p. 40–42 °C; IR (KBr), 960 cm^{-1} ; ¹H NMR (270 MHz, CDCl₃), δ 7.18 (dd, 2H, $J = 16.1, 140 \text{ Hz}$), 7.12 (dt, 1H, $J = 1.1$ and 8.0 Hz), 7.22 (t, 1H, $J = 8.0 \text{ Hz}$), 7.30 (tq, 1H, $J = 0.7$ and 7.3 Hz), 7.35–7.50 (m, 2H), 7.57 (dd, 1H, $J = 1.1$ and 8.1 Hz), 7.62 (dd, 1H, $J = 1.6$ and 7.7 Hz), 7.66 (t, 1H, $J = 1.8 \text{ Hz}$). Analysis: calculated for C₁₄H₁₀Br₂, C 49.74, H 3.14, Br 47.27; found, C 49.57, H 3.14, Br 47.71%. *cis*-**7**: ¹H NMR (270 MHz, CDCl₃), δ 6.63

(dd, 2H, $J = 22.7$ and 10.1 Hz), 7.04 – 7.14 (m, 5H), 7.24 – 7.30 (m, 2H), 7.57 – 7.63 (m, 1H). HRMS: m/z , found, 339.9108 (100%), calculated for $C_{14}H_{10}OBr_2$, 339.9108 .

1,2-Bis(3-bromophenyl)ethene (**8**). This was prepared by using 3-bromo-**10** in place of **9** in a manner similar to **7**. Separation of *trans* and *cis* forms was also performed by chromatography on silica gel with *n*-hexane as eluent. *trans*-**8**: m.p. 90 – 92 °C; IR (KBr), 970 cm^{-1} ; 1H NMR (270 MHz, $CDCl_3$), δ 7.02 (s, 2H), 7.22 (t, 2H, $J = 7.9$ Hz), 7.38 – 7.41 (m, 4H), 7.64 (t, 2H, $J = 1.4$ Hz). Analysis: calculated for $C_{14}H_{10}Br_2$, C 49.74, H 2.98, Br 47.27; found, C 49.74, H 3.12, Br 47.64%. *cis*-**8**: 1H NMR (270 MHz, $CDCl_3$), δ 6.52 (s, 2H), 7.05 (t, 2H $J = 7.7$ Hz), 7.02 – 7.16 (m, 4H), 7.29 – 7.38 (m, 4H). HRMS: m/z , found, 339.9108 (49.6%); calculated for $C_{14}H_{10}Br_2$, 339.9122 .

trans-1-[2-(3,5-Di-*tert*-butyl-1-hydroxy-4-oxocyclohexa-2,5-dienyl)phenyl]-2-[3-(3,5-di-*tert*-butyl-1-hydroxy-4-oxocyclohexa-2,5-dienyl)phenyl] ethene (*trans*-**5**). To a solution of *trans*-**7** (2.44 g, 7.27 mmol) in THF (150 ml) were added dropwise 18.7 ml (31.8 mmol) of a 1.7 M solution of *tert*-butyllithium in *n*-pentane at -78 °C under a nitrogen atmosphere. After stirring for 2 h, a solution of 3,5-di-*tert*-butyl-*p*-benzoquinone (3.55 g, 16.6 mmol) in THF (20 ml) was added dropwise and the solution was stirred for another 3 h. The mixture was allowed to warm to room temperature by removal of the cooling bath. After the usual work-up, the orange oil obtained was chromatographed on silica gel with hexane– CH_2Cl_2 (2:1) as the eluent and crystallized from *n*-hexane to give 0.85 g (29%) of *trans*-**5** as a white solid, m.p. (decomp.) 225 °C; IR (KBr), 962 , 1643 , 1664 cm^{-1} ; 1H NMR (270 MHz, CD_2Cl_2), δ 1.24 (s, 18H), 1.15 (s, 18H), 6.58 (s, 2H), 6.62 (s, 2H), 7.03 (dd, 2H, $J = 149$ and 16.2 Hz), 7.04 – 7.10 (m, 1H), 7.20 – 7.40 (m, 4H), 7.47 – 7.52 (m, 2H), 7.71 – 7.86 (m, 1H). HRMS: m/z , found, 620.3846 (6.7%); calculated for $C_{42}H_{52}O_4$, 620.3866 .

trans-1,2-Bis[3-(3,5-di-*tert*-butyl-1-hydroxy-4-oxocyclohexa-2,5-dienyl)phenyl] ethene (*trans*-**6**). This was prepared in a similar manner to *trans*-**5** by using *trans*-**8** in place of *trans*-**7**. Crystallization from *n*-hexane gave white solid *trans*-**6** in 50% yield, m.p. (decomp.) 240 °C; IR (KBr), 962 , 1631 , 1660 cm^{-1} ; 1H NMR (270 MHz, CD_2Cl_2), δ 1.25 (s, 36H), 6.59 (s, 4H), 7.10 (s, 2H), 7.33 (t, 2H, $J = 7.5$ Hz), 7.22 – 7.45 (m, 4H), 7.61 – 7.65 (m, 2H). Analysis: calculated for $C_{42}H_{52}O_4$, C 81.25, H 8.44; found, C 80.95, H 8.43%.

cis-1-[2-(3,5-Di-*tert*-butyl-1-hydroxy-4-oxocyclohexa-2,5-dienyl)phenyl]-2-[3-(3,5-di-*tert*-butyl-1-hydroxy-4-oxocyclohexa-2,5-dienyl)phenyl] ethene (*cis*-**5**). This was prepared by using *cis*-**8** in place of

trans-**7** in a manner similar to that for *trans*-**5**. Crystallization from *n*-hexane gave a white solid in 50% yield. IR (KBr), 1645 , 1660 cm^{-1} ; 1H NMR (270 MHz, CD_2Cl_2), δ 1.14 (s, 18H), 1.20 (s, 18H), 6.41 (s, 1H), 6.59 (s, 1H), 6.51 (dd, 2H, $J = 82.8$ and 6.0 Hz), 6.78 – 6.83 (m, 1H), 7.02 – 7.18 (m, 7H), 7.35 (t, 1H, $J = 7.33$ Hz), 7.90 (d 1H, $J = 8.1$ Hz). HRMS: m/z , found, 620.3871 (9.6%); calculated for $C_{42}H_{52}O_4$, 620.3866 .

cis-1,2-Bis[3-(3,5-di-*tert*-butyl-1-hydroxy-4-oxocyclohexa-2,5-dienyl)phenyl] ethene (*cis*-**6**). This was prepared by using *cis*-**8** in place of *trans*-**7** in a manner similar to the preparation of *trans*-**5**. Crystallization from *n*-hexane gave a white solid in 70% yield, m.p. 80 – 85 °C; IR (KBr), 1633 , 1645 , 1667 cm^{-1} ; 1H NMR (270 MHz, CD_2Cl_2), δ 1.19 (s, 36H), 6.51 (s, 4H), 6.58 (s, 2H), 7.14 – 7.20 (m, 6H), 7.47 – 7.50 (m, 2H). HRMS: m/z , found, 620.3880 (16.5%); calculated for $C_{42}H_{52}O_4$, 620.3866 .

trans-1-[2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)phenyl]-2-[3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)phenyl] ethene (*trans*-**3**). To a suspension of $LiAlH_4$ (0.135 g) in dry diethyl ether (50 ml) was added finely crushed anhydrous aluminium chloride in small portions under a nitrogen atmosphere. The mixture was stirred and became clear after 2.5 h. A 5 ml volume of a diethyl ether solution of *trans*-**5** (0.1 g) was added dropwise at -40 °C and the reaction mixture was stirred at room temperature. After the usual work-up, the pale yellow oil obtained was chromatographed on silica gel with *n*-hexane– CH_2Cl_2 (9:1) as the eluent to give 0.04 g (40%) of *trans*-**3** as a white solid, m.p. 170 – 175 °C; IR (KBr) 972 , 3634 cm^{-1} ; 1H NMR (270 MHz, CD_2Cl_2), δ 1.37 (s, 18H), 1.43 (s, 18H), 7.12 (dd, 2H, $J = 40.7$ and 16.1 Hz), 7.17 (s, 2H), 7.31 (s, 2H), 7.26 – 7.37 (m, 6H), 7.45 – 7.49 (m, 1H), 7.70 – 7.76 (m, 1H). HRMS: m/z , found, 588.3949 (100%); calculated for $C_{42}H_{52}O_2$, 588.3949 .

trans-1,2-Bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)phenyl] ethene (*trans*-**4**). This was prepared by using *trans*-**6** in place of *trans*-**5** in a manner similar to the synthesis of *trans*-**3**. Purification by chromatography on silica gel with *n*-hexane– CH_2Cl_2 (9:1) as the eluent gave white solid *trans*-**4** in 85% yield, m.p. 275 – 277 °C; IR (KBr) 960 , 3638 cm^{-1} ; 1H NMR (270 MHz, CD_2Cl_2), δ 1.41 (s, 36H), 7.21 (s, 2H), 7.36 – 7.49 (m, 10H), 7.62 – 7.65 (m, 2H). HRMS: m/z , found, 588.3985 (51.9%); calculated for $C_{42}H_{52}O_2$, 588.3967 .

cis-1-[2-(3',5'-Di-*tert*-butyl-4'-hydroxyphenyl)phenyl]-2-[3-(3',5'-di-*tert*-butyl-4'-hydroxyphenyl)phenyl] ethene (*cis*-**3**). This was prepared by using *cis*-**5** in place of *trans*-**5** in a manner similar to the preparation of *trans*-**3**. Purification by chromatography on

silica gel with *n*-hexane-CH₂Cl₂ (9:1) as the eluent gave white solid *cis*-3 in 60% yield, m.p. 178–180 °C; IR (KBr), 3616 cm⁻¹; ¹H NMR (270 MHz, CD₂Cl₂), δ 1.43 (s, 18H), 1.44 (s, 18H), 6.53 (dd, 2H, *J* = 22.4 and 12.1 Hz), 7.21 (s, 1H), 7.31 (s, 1H), 7.10–7.42 (m, 9H), 7.49–7.51 (m, 1H). HRMS: *m/z*, found, 588.3946 (100%); calculated for C₄₂H₅₂O₂, 588.3967.

cis-1,2-Bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-phenyl] ethene (*cis*-4). This was prepared by using *cis*-6 in place of *trans*-5 in a manner similar to the synthesis of *trans*-3. Chromatography on silica gel with *n*-hexane-CH₂Cl₂ as the eluent gave white solid *cis*-4 in 70% yield, m.p. 218–220 °C, IR (KBr) 3615, 3638 cm⁻¹; ¹H NMR (270 MHz, CD₂Cl₂), δ 1.42 (s, 36H), 6.68 (s, 2H), 7.23 (s, 4H), 7.24–7.40 (m, 6H), 7.48–7.50 (m, 2H). HRMS: *m/z*, found, 588.3937 (26.9%); calculated for C₄₂H₅₂O₂, 588.3967

Generation of biphenoxyl radicals and EPR measurements. A 5 mm o.d. quartz tube with a reaction vessel attached as a side-arm was prepared for EPR measurements. A toluene solution of 3 or 4 and lead dioxide powder were separately placed in a quartz tube and a reaction vessel, respectively, degassed by three freeze-thaw cycles and sealed. Oxidation was performed by transferring the toluene solution into the reaction vessel, shaking the mixture for 1 s and returning the solution back to the quartz tube by decantation. EPR spectra were measured below -50 °C. By repeating this cycle, the degree of oxidation was controlled.

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