

Thermochemical and Kinetic Studies of a Bisphenol Antioxidant

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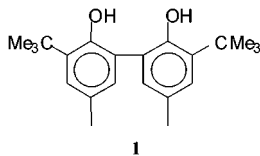
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The results of a thermodynamic and kinetic investigation on the homolytic reactivity of 3,3'-*tert*-butyl-5,5'-dimethyl(1,1'-biphenyl)-2,2'-diol (**1**) are reported. EPR studies of the equilibration between **1**, 2,4,6-trimethylphenol, and the corresponding radicals obtained by abstraction of a hydroxylic hydrogen allowed us to determine the OH bond dissociation energy (BDE) of investigated bisphenol as 83.10 kcal/mol. This value is considerably larger than that reported for the structurally related 2,6-di-*tert*-butyl-4-methylphenol (BHT), i.e., 81.02 kcal/mol. Absolute rate constants for the reaction of **1** with alkyl, alkoxy, and peroxy radicals, at or nearly to room temperature, were also determined by competition kinetics in the first two cases and by autoxidation studies under controlled conditions in the last one. The experimental data indicate that this bisphenol is a moderately efficient antioxidant and polymerization inhibitor.

Introduction

In a recent paper,¹ some of us reported a simple and cheap procedure for the synthesis of the bisphenol **1** by reacting *tert*-butyl hydroperoxide, Me₃COOH, with *p*-cresol, MeC₆H₄OH, in the presence of FeCl₃ as catalyst. The structure of **1** closely resembles that of the widely used antioxidant 2,6-di-*tert*-butyl-4-methylphenol (BHT) although with some features, such as higher molecular weight and lower volatility, making this bisphenol potentially more suitable than BHT for some applications, especially in view of the low cost by which **1** can be obtained with the above reaction. Although substituted phenols have been extensively studied as antioxidants,² bisphenols having structures similar to **1** have not received much attention. We have, therefore, undertaken a thorough investigation aiming to assess the thermochemistry of **1** as well as its reactivity toward peroxy, alkyl, and alkoxy radicals.



Results and Discussion

When the bisphenol **1** was reacted with photolytically produced alkoxy radicals in deoxygenated benzene solutions inside the cavity of an EPR spectrometer, a strong spectrum of the corresponding phenoxyl radical **2** ob-

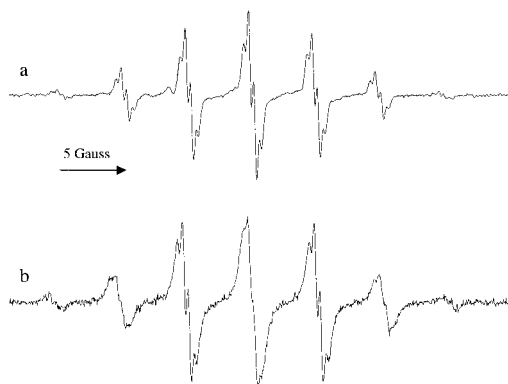


Figure 1. EPR spectra of the radical obtained by photolyzing solutions of the bisphenol **1** (0.1 M) and di-*tert*-butyl peroxide (10% v/v) in (a) benzene at room temperature and (b) cyclopropane at -122 °C.

tained by hydrogen abstraction from one of the two OH groups was observed, similar to that reported in the literature.³

The EPR spectrum (Figure 1a) is interpreted in terms of the coupling of the unpaired electron with the six equivalent protons (5.12 G) of the two methyl groups in positions 5 and 5' and by the additional coupling (0.40 G) with three equivalent protons.

These were identified as two of the four aromatic protons meta to the hydroxyl groups (either the 4 and 4' or the 6 and 6') and the remaining hydroxyl proton, which accidentally show identical hyperfine splitting constants. This assignment was confirmed by hydrogen–deuterium exchange, which led to the disappearance of the latter splitting. Actually, when adding a drop of deuterated methanol to the solution, the 0.4 G quartet was replaced

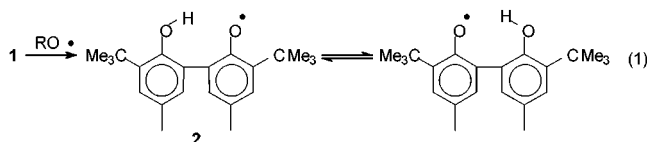
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by a 1:2:1 triplet. The line width (0.31 G) was larger than usual in phenoxyl radicals due to unresolved coupling with the *tert*-butyl protons.

The coupling constants at the *p*-methyl and at the aromatic protons are approximately half those observed in radicals from related monophenols (for instance, these splittings are 11.20 and 1.67 G,⁴ respectively, in the 2,6-di-*tert*-butyl-4-methylphenoxy radical), this indicating that the unpaired electron is uniformly distributed over the two aromatic rings. The apparent equivalence of the aryl groups observed at room temperature might arise by fast exchange of the residual hydroxyl proton between the two oxygens (eq 1); an additional possibility is that the hydroxyl proton is equally shared by the two oxygen atoms.^{3,5} In the former case, by lowering the temperature one should be able to freeze, in the EPR time scale, the intramolecular migration of the OH proton, this being revealed by selective line broadening effects and eventually by different proton splitting constants at the two rings. No temperature dependence of the EPR spectrum should instead be observed if a symmetric structure is adopted by the radical.



To decide between these two possibilities, we recorded the EPR spectrum of **2** at lower temperatures in dimethyl ether or cyclopropane. Only at $-122\text{ }^{\circ}\text{C}$ in cyclopropane did the spectrum start to show some alternating line width effect (see Figure 1b) with the even lines of the main septet getting broader than the odd ones. This is what is expected if intramolecular hydrogen migration takes place, as exemplified in eq 1. Freezing the solution prevented the possibility of recording EPR spectra at lower temperatures. By analyzing the spectrum⁶ recorded at $-122\text{ }^{\circ}\text{C}$, under the assumption that the unpaired electron is forced to stay on one ring at once, i.e., the exchanging proton splittings were taken equal to twice the experimental values on one aromatic ring and equal to zero on the other ring, the rate constant for the intramolecular hydrogen exchange k_1 was estimated as $1.0 \times 10^9\text{ s}^{-1}$.

Bond Dissociation Energy (BDE) of the O–H Bond. The BDE value of the O–H bond was determined by a previously described method^{4,7} based on the measure of the equilibrium constant for the hydrogen atom transfer reaction (eq 5) between two phenols and the corresponding phenoxyl radicals by means of EPR spectroscopy.

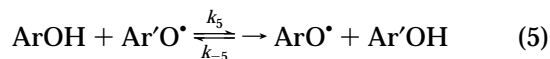


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As a reference compound, Ar'OH, we chose 2,4,6-trimethylphenol, whose O–H BDE value in benzene is 82.73 kcal/mol.⁴ The two equilibrating radicals were generated, within the cavity of an EPR spectrometer, by continuous photolysis of deoxygenated benzene solutions of the two phenols, containing a small amount of the radical photoinitiator di-*tert*-butyl peroxide. The overall reaction scheme is shown in eqs 2–8.

The molar ratio of the two equilibrating radicals [ArO•]/[Ar'O•] was obtained from the EPR spectra by comparison with computer simulations. The equilibrium constant, K_5 , was determined by introducing in eq 9 the initial concentrations of the two phenols [ArOH]₀ and [Ar'OH]₀, and to ensure that at the time of measurement no significant depletion of the reactants has occurred, high concentrations (ca. 0.1 M) were used.

$$K_5 = \frac{[\text{ArO}^{\bullet}][\text{Ar}'\text{OH}]_0}{[\text{Ar}'\text{O}^{\bullet}][\text{ArOH}]_0} \quad (9)$$

To check that the hydrogen transfer reaction of eq 5 takes place rapidly relative to the decay of the phenoxyl radicals,⁴ measurements were done at different initial concentrations of the reactants and of the peroxide initiator or by partially cutting off the light. The BDEs were calculated from the equilibrium constants by means of eq 10 obtained assuming that the entropy change for the hydrogen-transfer reaction is negligible.

$$\text{BDE}(\text{ArO} - \text{H}) = \text{BDE}(\text{Ar}'\text{O} - \text{H}) - RT \ln K_5 \quad (10)$$

The accuracy of this assumption was verified by measuring K_5 at several temperatures in the range 25–70 °C. By reporting the data in a Van't Hoff plot, a ΔS° value of 0 ± 0.2 , was obtained, this justifying the neglect of the entropy contribution to reaction 5. The results of these measurements provided a BDE(ArO–H) value for **1** in benzene of 83.1 ± 0.2 kcal/mol, obtained by multiplying the bisphenol concentration by the statistical factor of 2, to account for the presence of two equivalent hydroxyl groups in **1** (vide infra). No dependence on solvent⁸ of the bond dissociation energy of **1** was investigated.

Reactivity toward Alkyl Radicals. The rate of hydrogen abstraction by primary alkyl radicals in benzene was measured at 298 K by the radical clock method based on competition kinetics between the bimolecular reaction to be timed and a known monomolecular process.⁹ This was either the neophyl radical rearrangement ($k_r = 1.1 \times 10^3\text{ s}^{-1}$ at 298 K)^{10,11} or the similar 1,2-aryl migration of 2-methyl-2-(2-naphthyl)-1-propyl radical

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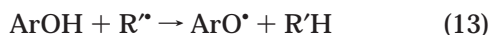
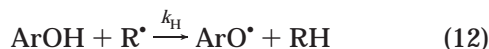
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Table 1. Absolute Rate Constants for the Abstraction of the O–H Hydrogen Atom from the Bisphenol 1 by Primary Alkyl Radicals (R•) and *tert*-Butoxyl Radical (Me₃CO•) at 298 K in Benzene Solution

clock	$k_{\text{H}} (\text{M}^{-1} \text{s}^{-1}) (\text{R}^\bullet)$	competitor	$k_{\text{H}} (\text{M}^{-1} \text{s}^{-1}) (\text{Me}_3\text{CO}^\bullet)$
neophyl	9.7×10^4	Et ₃ SiH	7.0×10^7
MNP1 ^a	8.6×10^4	Bu ₃ SnH	4.1×10^7

^a MNP1 = 2-methyl-2-(2-naphthyl)-1-propyl radical.

(MNP1) ($k_{\text{r}} = 1.4 \times 10^4 \text{ s}^{-1}$ at 298 K) which has been recently calibrated in our laboratory.¹²



The alkyl radicals were generated by photolyzing oxygen-free solutions of the corresponding bromides in the presence of hexabutyldistannane as photoinitiator and were allowed to react with the bisphenol (eqs 11–13). Experimental conditions were chosen so to avoid significant consumption of the diol during the reaction. The reaction products RH and R'H were analyzed by means of gaschromatography (GC), and the rate constants for hydrogen abstraction, k_{H} , were obtained by a least-squares fitting of the experimental data to eq 14.

$$k_{\text{H}}[\text{ArOH}] = k_{\text{r}} \frac{[\text{RH}]}{[\text{R}'\text{H}]} \quad (14)$$

The measured k_{H} values obtained with the two clocks are in reasonable agreement with each other (see Table 1), and thus, we may take the average value of $9.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for the rate constant for hydrogen atom abstraction from bisphenol 1 by primary alkyl radicals. This value, divided by the statistical factor 2, should be compared with those for BHT ($4.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) and for 2,4,6-trimethylphenol in benzene ($6.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$).¹³

Reactivity toward Alkoxy and Peroxyl Radicals.

The rate of hydrogen abstraction from the bisphenol 1 by alkoxy radicals has been studied by competition kinetics using as reference the hydrogen abstraction from triethylsilane, Et₃SiH, and tributyltin hydride, Bu₃SnH, for which the room-temperature rate constants for the reaction with *tert*-butoxyl radicals has been reported as $5.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $1.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively.¹⁴ The *tert*-butoxyl radicals were generated by UV irradiation, at 298 K, of the reaction mixture containing di-*tert*-butyl peroxide, an internal standard, and different amounts of the silane or stannane and of 1. The mixture was analyzed by GC and CG–MS before and after irradiation and the desired rate constants were obtained from the loss of the starting hydrogen donors.¹⁵ The results, reported in Table 1, indicate that this molecule

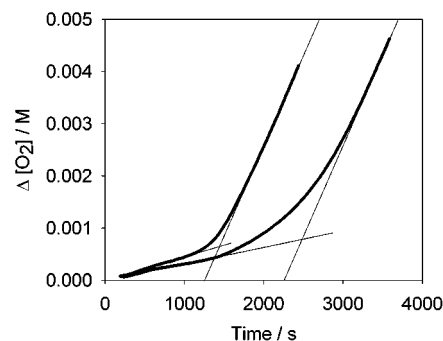


Figure 2. Oxygen consumption observed during the AIBN (0.0068)-initiated autoxidation at 50 °C of cumene (5.46 M) in benzene in the presence of either BHT the bisphenol 1 or at the same concentration ($1.0 \times 10^{-4} \text{ M}$).

is characterized by a reactivity toward butoxyl radicals similar to those observed for structurally related monophenols.

The rate constant for the reaction of 1 with peroxy radicals was obtained by studying the thermally initiated autoxidation of either cumene or styrene in the presence of the bisphenol. The autoxidation was followed by monitoring the oxygen consumption with an automatic recording gas absorption apparatus, built in our laboratory, using a commercial differential pressure transducer. The reactions (initiated by AIBN) were carried out under controlled conditions at 50 °C in air-saturated solutions of the oxidizable substrate in benzene containing various amounts of the bisphenol or of BHT, which was used as the reference chain-breaking antioxidant.

Figure 2 shows the plot of the oxygen uptake during the initiated autoxidation of cumene in the presence of the same concentration of either 1 or BHT. From these plots, it appears that, with both antioxidants, the oxygen consumption was strongly inhibited during the initial period; then, the slope of the oxygen uptake trace increased suddenly when BHT was used as inhibitor, while in the presence of 1 the autoxidation was still somewhat retarded for an approximately equivalent period. By knowing the rate of radical chain initiation by AIBN, R_i , determined in previous experiments where α -tocopherol was the autoxidation inhibitor,¹⁶ we could obtain from the lengths of the inhibition periods, τ , the value of the stoichiometric factor n of the antioxidant, i.e., the number of peroxy radicals trapped by one molecule of antioxidant, as 2 and ca. 4 with BHT and 1, respectively. With the latter compound, both induction periods where the autoxidation was strongly and weakly inhibited, respectively, were characterized by a stoichiometric factor of approximately 2.

The absolute rate constant for inhibition during the first period, k_{inh} , was determined from the slopes of the experimental plots of $\Delta[\text{O}_2]_t$ versus $-\ln(1 - t/\tau)$ (see eq 15)¹⁷ and from the value of rate constant for the propagation of the autoxidative chain reaction, k_{p} , for cumene ($0.75 \text{ M}^{-1} \text{ s}^{-1}$) recently determined by some of us under identical experimental conditions.¹⁸

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$$\Delta[\text{O}_2]_t = k_p/k_{\text{inh}}[\text{RH}]\ln(1 - t/\tau) \quad (15)$$

The average of three independent determinations, carried out under experimental conditions where the length of the chain reaction is at least 5, was $(3.2 \pm 0.4) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. This value should be divided by 2 to compare the antioxidant activity of **1** with that of simple phenols, due to the presence in **1** of two hydroxyl groups. Thus, after correction for the statistical factor k_{inh} is $1.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, i.e., a value slightly lower than that of $2.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ obtained for BHT at the same temperature.

We also determined the second inhibition rate constant, i.e., that one referring to the second part of the oxidation trace recorded in the presence of **1**, where the autoxidation of cumene is weakly inhibited. Treatment of the experimental data similar to that described above afforded (see Table 2) a value ($5.7 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) considerably lower than that obtained from the initial period of inhibition.

The first inhibition rate constant of the bisphenol **1** was also determined by studying the autoxidation of styrene. Due to the larger value of $2k_t$ of the latter compound as compared to that of cumene, the oxygen uptake plots recorded in the presence of **1** did not show a definite induction period but only a retarding of the autoxidation. This is due to the fact that, under these conditions, not all the peroxy radicals are quenched by the antioxidant but some of them decay by self-termination. As a consequence, eq 15, which has been obtained under the assumption that self-termination is negligible, does not hold anymore. The value of k_{inh} was therefore determined by making measurements at different bisphenol concentrations and analyzing the data using the method proposed by Darley–Usmar et al.,¹⁹ which provides a composite rate constant k_{AH} given by eq 16.

$$k_{\text{AH}} = \frac{k_{\text{inh}}}{\sqrt{2k_t R_i}} \quad (16)$$

To calculate k_{inh} for **1**, the rate of initiation R_i was measured as described above while the value of the rate constant of self-termination for the styrylperoxy radicals was obtained by studying the BHT-inhibited autoxidation of styrene at 50 °C, using different concentrations of this phenol. From the resulting k_{AH} value, for which k_{inh} was previously determined as $2.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ (see Table 2), we calculated $2k_t$ at 50 °C as $1.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, by means of eq 16. This value, although somewhat larger than that one reported in the literature,²⁰ gives an inhibition rate constant for **1**, $3.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, almost identical to that determined using cumene as oxidizable substrate. No attempts were made to measure the second inhibition constant of **1** from the inhibited oxidation of styrene.

Product Studies

To investigate the nature of the products formed from the bisphenol **1** during their reaction with peroxy radicals, we reacted a 0.03 M solution of **1** in ACN containing a large excess of azoisobutyronitrile (AIBN)

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Table 2. Stoichiometric Factors, n , and Rate Constants for Hydrogen Atom Transfer to Peroxy Radicals, k_{inh} , of **1 and BHT at 50 °C in Mixtures of Benzene and Either Cumene or Styrene**

phenol	substrate	n	$k_{\text{inh}}/\text{M}^{-1} \text{ s}^{-1}$
1	cumene	2 (~ 2) ^a	3.2×10^4 (5.7×10^3) ^a
1	styrene	—	3.3×10^{4b}
BHT	cumene	2	2.6×10^4

^a The value in parentheses refers to the second inhibition period observed during the AIBN initiated autoxidation of cumene.

^b Determined from the slope of the inhibited autoxidation by using the method of ref 18.

at 50 °C in an open atmosphere for ca. 30 min. Since the reaction of phenols with peroxy radicals usually leads to peroxides whose identification is tedious and time-consuming using conventional approaches, the crude reaction mixture was analyzed by mass spectrometry using two different “soft” ionization techniques: ionspray ionization (ISI-MS)²¹ and coordination (Ag^+) ionspray ionization (Ag^+ -CIS-MS).²² This last technique has been recently developed to overcome the problems encountered with the analysis of those compounds which, due to the low basicity/acidity, are poorly accessible by the more conventional electrospray (ESI)²³ and ionspray (ISI)²¹ ionization, and has been shown to be a very effective method to perform mass spectrometry of hydroperoxides and other extremely labile products of autoxidation.²⁴

Figure 3A represents the ISI-MS spectrum obtained by direct liquid injection of the reaction mixture. Besides the pseudomolecular ion $[\mathbf{1} + \text{H}]^+$ that is still visible at $m/z = 327$, a very intense signal is present at $m/z = 426$, which we attribute to the $[\mathbf{4} + \text{H}]^+$ ion from the monoadduct of $\text{Me}_2\text{C}(\text{CN})\text{OO}^\bullet$ to the phenoxyl radical **2** (see Scheme 1). Further oxidation of **4** would bring to the diadduct **5** whose $[\mathbf{5} + \text{H}]^+$ ion was found at $m/z = 525$. A rather intense signal is also seen at $m/z = 341$ which we attribute to a product arising from the decomposition of **4** by loss of $\text{Me}_2\text{C}(\text{CN})\text{OH}$. On the contrary only a very weak signal could be observed at $m/z = 325$, which would correspond to the $[\mathbf{3} + \text{H}]^+$ ion from the dione **3**.

Similar results were obtained by CSI-MS analysis of the reaction mixture after the addition of 100 μM AgNO_3 (Figure 3B). The weak peaks at $m/z = 433$ and 435 can be attributed to the adducts $[\mathbf{1} + \text{Ag}]^+$ formed from ¹⁰⁷Ag and ¹⁰⁹Ag isotopes present in a $\sim 1:1$ ratio. The most intense signals are found at $m/z = 532$ and 534 corresponding to the $[\mathbf{4} + \text{Ag}]^+$ adduct, while the peaks expected for $[\mathbf{5} + \text{Ag}]^+$ can be found at $m/z = 631$ and 633. Signals at $m/z = 447$ and 449, on the other hand, can be attributed to the silver adduct of its decomposition product giving the peak at $m/z = 341$ in the ISI-MS spectrum. No peaks are instead observed at $m/z = 431/433$ which would be due to $[\mathbf{3} + \text{Ag}]^+$.

Discussion

The OH bond dissociation energy of the bisphenol **1** measured in benzene as 83.10 kcal/mol is larger by ca. 2

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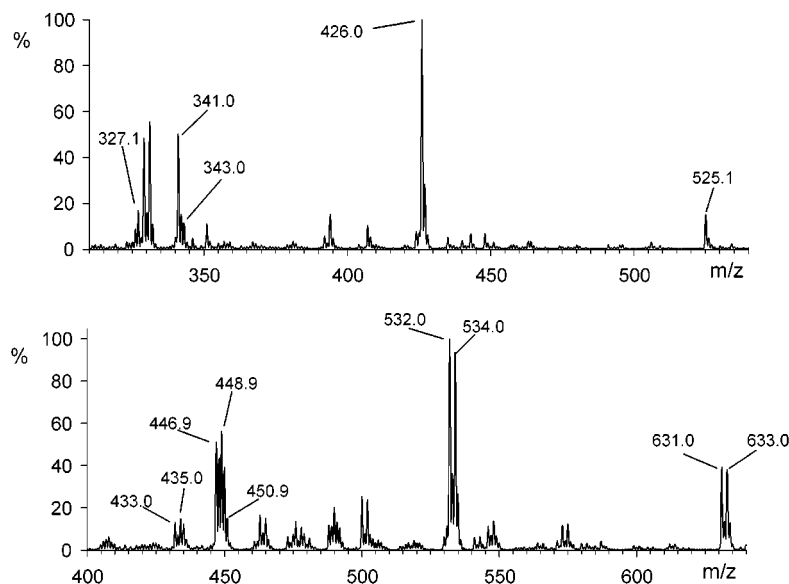
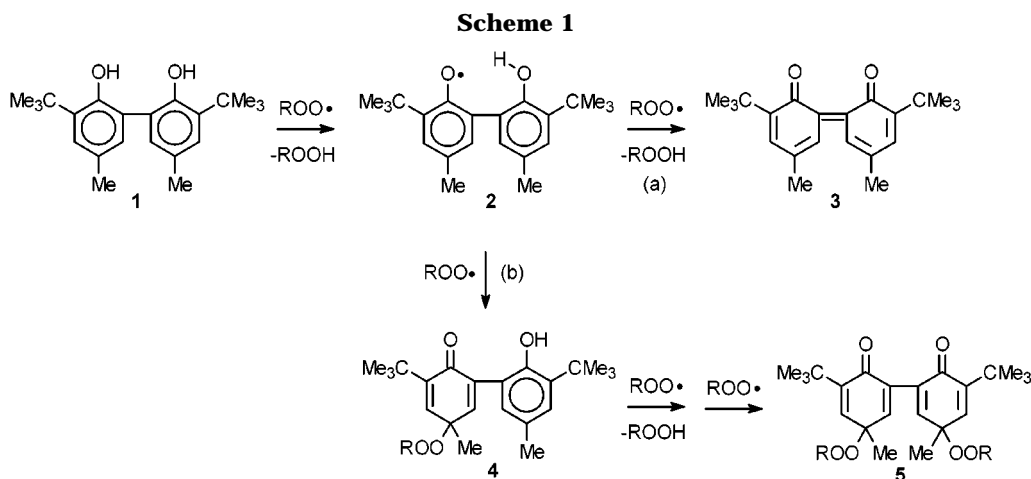


Figure 3. Ionspray ionization (ISI-MS, top) and coordination (Ag^+ , bottom) ionspray ionization mass spectra of the products formed in the reaction of the bisphenol **1** with AIBN under air.



kcal/mol than that of the related 2,6-di-*tert*-butyl-4-methylphenol (BHT), 81.02 kcal/mol.⁴ To compare these values and to discuss the various factors exerting a stabilization or a destabilization of the bisphenol and of the corresponding aroxyl radical, we need to know the geometry of these species. The EPR data indicate that in the radical **2** formed by abstraction of one hydroxyl hydrogen from **1**, the unpaired electron is jumping very fast between the two aromatic rings. This process is driven by the intramolecular 1,6-hydrogen migration between the two oxygen atoms, occurring with a rate constant of $1.0 \times 10^9 \text{ s}^{-1}$ at -122°C . By assuming for this reaction a log *A* of 13,²⁵ the activation energy is calculated as 2.76 kcal/mol. This very low value of E_a is in agreement with an oxygen to oxygen transfer of the hydrogen atom, since also intermolecular H-atom transfers between two oxygen atoms are characterized by very low activation energies.²⁶ The very large value of k_1 ($1.0 \times 10^9 \text{ s}^{-1}$) observed in this case suggests that hydrogen transfer occurs without any significant structural changes, i.e., that radical **2** adopts a geometry where the oxygen

atoms are on the same side of the C–C bond joining the two rings with the hydroxyl proton bonded to the second oxygen atom.

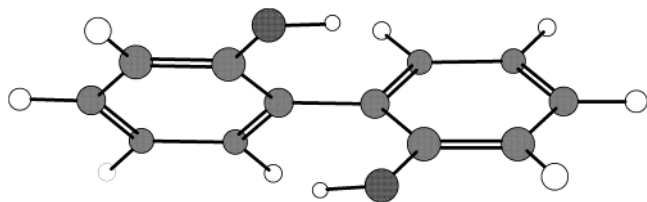
As far the bisphenol **1** is concerned, indication about its preferred geometry is provided by the FT-IR spectrum recorded in diluted CCl_4 solutions (see the Experimental Section), which in the region between 3100 and 4000 cm^{-1} shows only an absorption at 3531 cm^{-1} from a hydrogen-bonded species. Both the sharpness of the peak and the independence of the IR spectral shape on the concentration of the bisphenol indicate that hydrogen bonding is intramolecular. Actually, semiempirical AM1 calculations carried out on the 2,2'-dihydroxybiphenyl, as well as on **1**, confirm that this is really the case since the lowest energy conformation is predicted to be that one shown in Scheme 2 where the two aromatic rings make a dihedral angle of 55° and the two hydroxyl groups are in a *cisoid* geometry. These calculations also predict hydrogen–oxygen distances of 2.5 Å, which is in agreement with expectations for the formation of hydrogen bonding between the two OH groups.

According to these considerations, the higher BDE value for the O–H bond observed in **1** with respect to BHT is likely due to the fact that both hydroxyl protons are hydrogen bonded intramolecularly, this resulting in

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Scheme 2



an additional stabilization of the bisphenol, which gives rise to an increase of the O–H BDE value.^{3,27–31}

Despite the larger O–H bond strength, **1** shows a reactivity toward alkyl, alkoxy, and peroxy radical higher or comparable to that of BHT. It is likely that the expected decrease in reactivity due to the lower exothermicity of the hydrogen transfer reaction does not occur because of the reduced steric crowding around the hydroxyl group in the bisphenol **1**.

Another interesting observation concerns the behavior of the bisphenol **1** when used as inhibitor of the AIBN-induced autoxidation of cumene. The oxygen uptake plots are characterized by a first part where the diol is able to interrupt two radical chains with a relatively large inhibition rate constant (ca $3.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$) followed by a second part where two more radical chains are stopped, although with a lower k_{inh} ($5.7 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$). An explanation of this effect can be given on the basis of the products formed in the thermal reaction of **1** with AIBN in the presence of oxygen (see Scheme 1). The mass spectra of the reaction mixtures indicate that, after the initial abstraction from **1** of an OH hydrogen atom, the resulting aroxyl radical **2** reacts with an other peroxy radical by combination to afford the peroxide adduct **4** (route b) rather than by transfer of the second hydroxylic hydrogen to give the dione **3** (route a). Compound **4**, being a phenol, also behaves as an antioxidant by trapping two more peroxy radicals to afford eventually **5**. The decreased antioxidant power of the second hydroxyl group is likely due to the formation in **4** of an intramolecular hydrogen bond between the hydroxyl proton and the carbonyl group which, being a better hydrogen bond acceptor than an OH group, reduces the availability of the phenolic hydrogen for the reaction with peroxy radicals.

In conclusion, the bisphenol **1** behaves as a moderately efficient antioxidant having, as compared to simple phenols, the advantage of a higher molecular weight and hence of a lower mobility inside solid matrixes. A drawback for this application is the formation, by reaction with peroxy radicals, of yellow-brown products determining color changes of the host matrix.

Experimental Section

Materials. Bisphenol **1** was prepared as described in a previous paper.¹ Solvents were of the highest purity grade commercially available and were used as received.

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Kinetic Measurements. Alkyl Radicals. In a typical experiment, 200 μL of a solution of the bisphenol (0.1–1 M) containing either neophyl bromide or 6-bromo-1-hexene (0.005–0.01 M) and hexa-*n*-butylditin (0.01 M) were sealed in a quartz tube after being deoxygenated by bubbling nitrogen. The reaction mixtures were then irradiated for 30–120 min at the desired temperature in a thermostated photoreactor, built in our laboratories, equipped with a 125 W high-pressure mercury lamp, and the products were analyzed by gas chromatography. For each bromide, five measurements were made at different concentrations of **1** and the reaction products ratio $[\text{UH}]/[\text{RH}]$ was plotted versus the diol concentration to obtain the $k_{\text{H}}/k_{\text{r}}$ ratio by linear regression of the experimental data.

Alkoxy Radicals. For measuring the kinetic parameters for the reaction of *tert*-butoxy radical with the bisphenol, solutions of di-*tert*-butyl peroxide (0.2–0.4 M), the diol (ca 0.1 M), triethylsilane, or tributyltin hydride as reference hydrogen donor and *tert*-butylbenzene as internal GC standard, in benzene, were degassed and sealed under nitrogen in quartz ampules. The reaction mixture was photolyzed at 298 K for 15–30 min in a thermostated photoreactor equipped with a 125 W high-pressure mercury lamp, and the disappearance of the products was analyzed by GC and GC–MS. For each compound the results were averaged over three to five measurements with different bisphenol concentrations.

Determination of the BDE Values. Deoxygenated benzene solutions containing the bisphenol (0.2–0.3 M), 2,4,6-trimethylphenol (0.1 M), and di-*tert*-butyl peroxide (0.1 M) was sealed under nitrogen in a Suprasil quartz EPR tube sitting inside the thermostated cavity of an EPR spectrometer. Photolysis was carried out by focusing the unfiltered light from a 500 W high-pressure mercury lamp on the EPR cavity. The temperature was controlled with a standard variable temperature accessory and was monitored before and after each run with a copper–constantan thermocouple.

The molar ratio of the two equilibrating radicals was obtained from the EPR spectra and used to determine the equilibrium constant, K , by introducing in the eq 5 the initial concentrations of the two reactants. Initial concentrations were chosen so to avoid significative consumption during the course of the experiment.

Relative radical concentrations were determined by comparison of the digitized experimental spectra with computer simulated ones. In these cases an iterative least-squares fitting procedure based on the systematic application of the Monte Carlo method was performed in order to obtain the experimental spectral parameters of the two species including their relative intensities.⁷

The EPR spectra were recorded on a Bruker ESP 300 spectrometer equipped with a Hewlett-Packard 5350B microwave frequency counter for the determination of the g -factors, which were corrected with respect to that of perylene radical cation in concentrated H_2SO_4 ($g = 2.00258$).

Autoxidation. Autoxidation experiments were performed in a two channels oxygen uptake apparatus, built in our laboratories, similar to that developed by Barclay and co-workers but optimized for low volume samples. The apparatus is based on a Validyne DP 15 differential pressure transducer interfaced to a Pentium II 200 MHz personal computer through a fast response (50 kHz) 14bit A/D converter card (Validyne UPC card). Each channel of the transducer (sample and reference channels) is connected to a handmade calibrated 1–5 mL round-bottom flask, equipped with a 3-way glass connector, through HPLC stainless steel low dead volume junctions and 1/16 in. HPLC peek tubing (Varian). Equilibration between the two channels and between each channel and the outer atmosphere is ruled by a Varian HPLC 3-way valve. Direct access to the sample and reference flasks is possible by means of a Hamilton syringe through the three-way glass connectors. The entire apparatus is set to have a total dead volume of ca. 5–8 mL (depending on the flasks employed) for each channel, under operative conditions. Sample and reference flasks were equipped with two magnetic microstirrers (H+P, Variomag) whose speeds were synchronized by a digital control unit. The entire apparatus was immersed in a ther-

mostated bath (Haake DC1-W18), which ensured a constant temperature within ± 0.02 °C.

In a typical experiment, an air-saturated benzene solution of cumene (or styrene) containing the phenolic antioxidant (5×10^{-6} – 1×10^{-4} M) was equilibrated with the reference solution containing only an excess of α -tocopherol (1×10^{-3} – 1×10^{-2} M) in the same solvent at 50 °C. After equilibration, a concentrated benzene solution of AIBN (final concentration $(1-10) \times 10^{-2}$ M) was injected in both the reference and sample flasks and the oxygen consumption in the sample was measured, after calibration of the apparatus, from the differential pressure recorded with time between the two channels. Initiation rates, R_i , were determined for each conditions in preliminary experiments by the inhibitor method using α -tocopherol as reference antioxidant: $R_i = 2[\alpha\text{-tocopherol}]/\tau$.³²

FT-IR measurements. The FT-IR spectra were measured from 4000 to 3000 cm^{-1} using a Nicolet Protégé 460 spectrometer having a resolution 0.4 cm^{-1} . Tetrachloromethane solutions of the bisphenol **1** in the concentration range 0.01–0.5 M were examined in a sealed KBr cell with 0.1 mm optical path.

MS Analysis. 1 mmol of bisphenyldiol was stirred in air-bubbled acetonitrile (~50 mL) at 323 K for 60 min in the presence of 0.5 mol of α, α' -azoisobutyronitrile (AIBN). Reaction time was chosen on the basis of inhibited autoxidation experiments so as to correspond approximately to the second half of the inhibition period. The crude reaction mixture was then

analyzed by mass spectrometry by direct liquid injection (DLI) at flow rates of 5–20 $\mu\text{L}/\text{min}$. The instrument employed was a Micromass ZMD spectrometer equipped with single quadrupole analyzer and a Z-spray ionspray source outfitted with a 50 μm deactivated fused Si capillary connected to a Harvard Apparatus pump 11 for sample injection. Data acquisition and spectral analysis were conducted with Masslynx 3.3 software running on a Digital Equipment Corp. personal computer. Nitrogen was used both as desolvation and nebulizer gas. For ionspray ionization experiments (ISI-MS), desolvation temperature was set at 200 °C and capillary voltage at 4.1 kV. Cone and Hexapole extractor voltages were optimized to obtain the highest ion current at m/z corresponding to $[\text{M} + \text{H}]^+$ and were determined to be 8 and 3 V, respectively. For complex ion spray ionization (CSI-MS), the sample was added of 100 μM AgNO_3 prior to injection and desolvation temperature was set at 120 °C to decrease decomposition of adduct ions. Since the source is not optimized for CSI appropriate experimental settings were be find to maximize ion current. Capillary voltage was decreased to 3.0 kV to minimize other competing mechanism of ionization and optimal cone and extractor voltages we determined to be 34 and 3 V respectively.

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