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Calorimetric and Computational Study of the Thermochemistry of Phenoxyphenols

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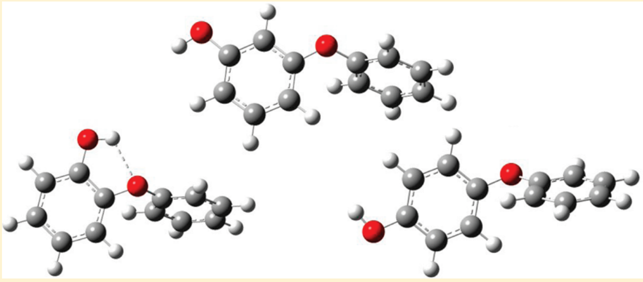
Supporting Information



ABSTRACT: Thermodynamic properties of 3- and 4-phenoxyphenol have been determined by using a combination of calorimetric and effusion techniques as well as by high-level ab initio molecular orbital calculations. The standard (p° = 0.1 MPa) molar enthalpies of formation in the condensed and gas states, $\Delta_f H_m^\circ$(cr or l) and $\Delta_f H_m^\circ$(g), at T = 298.15 K, of 3- and 4-phenoxyphenol were derived from their energies of combustion in oxygen, measured by a static bomb calorimeter, and from the enthalpies of vaporization or sublimation derived respectively by Calvet microcalorimetry for the 3-phenoxyphenol and by Knudsen effusion technique for the 4-phenoxyphenol. The theoretically estimated gas-phase enthalpies of formation were calculated from high-level ab initio molecular orbital calculations at the G3(MP2)//B3LYP level of theory. Furthermore, this composite approach was also used to obtain information about the gas-phase acidities, gas-phase basicities, proton and electron affinities, adiabatic ionization enthalpies, and, finally, O−H bond dissociation enthalpies. The good agreement between the G3MP2B3-derived values and the experimental gas-phase enthalpies of formation for the 3- and 4-phenoxyphenol gives confidence to the estimate concerning the 2-phenoxyphenol isomer, which was not experimentally studied, and to the estimates concerning the radical and the anion. Additionally, the experimental values of gas-phase enthalpies of formation were also compared with estimates based on the empirical scheme developed by Cox.

INTRODUCTION

The chemistry of phenols has attracted continuing interest in the last two centuries. Phenol and phenolic derivatives have achieved considerable importance as the starting material for numerous intermediates and final products, which have several indispensable applications in our daily life. Phenolic derivatives constitute, among others, an important class of antioxidants that inhibit or reduce the rate of the oxidative degradation of organic materials including a large number of biological aerobic organisms and commercial products. This antioxidant property can be related to the ability of phenols to trap the peroxyl radicals via the hydrogen transfer reaction. Hence, calculations of the hydrogen−oxygen bond strengths and ionization energies of the phenolic hydroxyl groups on various phenols allow for predictions of their potential as antioxidants.[1−4]

In addition, phenol and phenolic derivatives are widely used in the manufacture of phenolic resins, epoxy resins, plastics, plasticizers, polycarbonates, antioxidants, lube oil additives, nylon, caprolactam, aniline insecticides, explosives, surface active agents, dyes and synthetic detergents, polyurethanes, wood preservatives, herbicides, fungicides (for wood preparation), gasoline additives, inhibitors, pesticides, and as raw material for producing drugs like aspirin.[1,5−9] Phenolic compounds are also known to suppress the lipid peroxidation in living organisms, and are also used as additives in food technology.[1]

It is well-known that phenols are precursors of dioxins. The formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans mainly produced in thermal processes, especially incineration and by photocyclization, is of significant concern,[10−12] as well as by condensation of polychlorinated phenoxyphenol.[13]

The phenoxyphenols are widely used in the production of polymers, conducting polymers,[14−17] and cell fuels,[18] and they also appear in the environment as degradation products of materials such as triclosan (2,4,4′-trichloro-2′-hydroxydiphenyl ether),[19−21] first used in 1972 as a component of surgical scrub for aseptic hospital procedures. Since then this material has been widely used as a broad-spectrum antimicrobial or antibacterial agent in a number of common household products, including cosmetics, deodorants, mouthwashes, soaps, and toothpastes, and it is infused in consumer items such as bedding, kitchen utensils, socks, toys, and trash bags.

The 4-phenoxyphenoxy skeleton and other closely related structures have been employed as starting materials of drugs used as antiproliferative agents against *Trypanosoma cruzi*, the etiologic agent of American trypanosomiasis (Chagas disease),[22−24] considered by the World Health Organization to be one of the most important tropical parasitic diseases worldwide along with

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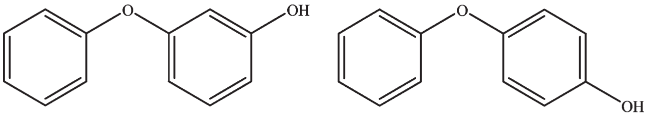
malaria and schistosomiasis. Phenoxyphenols have also been tested in the development of novel Tuberculosis (TB) chemotherapeutic agents,[25] and of a potent and selective inhibitor of human *gelatinases*, enzymes implicated in a number of pathological conditions, including cancer growth, tumor metastasis and angiogenesis, arthritis, connective tissue diseases, inflammation, and cardiovascular, neurological, and autoimmune diseases.[26,27]

To contribute to a better understanding of the relative reactivity and the relationship between the energetics and structural properties of this class of compounds, we have examined the thermochemical properties of 3- and 4-phenoxyphenol, both essential technological and pharmaceutical applications.

This paper reports a detailed experimental and computational thermochemical study of 3- and 4-phenoxyphenol, whose structural formulas are depicted in Figure 1. The standard (p° = 0.1 MPa) molar enthalpies of formation in the condensed phase at T = 298.15 K of the two compounds were determined by means of static bomb combustion calorimetry. High-temperature Calvet microcalorimetry allowed the determination of the standard molar enthalpy of vaporization at T = 298.15 K of the 3-phenoxyphenol. Vapor pressure measurements at different temperatures, using the Knudsen mass loss effusion technique, enabled the determination of the enthalpy, entropy, and Gibbs energy of sublimation, at T = 298.15 K, of 4-phenoxyphenol.



3-Phenoxyphenol 4-Phenoxyphenol

Figure 1. Structural formulas of the compounds studied in this work.

Table 1. Individual Values of the Standard (p° = 0.1 MPa) Massic Energies of Combustion $\Delta_c u^\circ$, for the 3- and 4-Phenoxyphenol, at T = 298.15 K

3-phenoxyphenol	4-phenoxyphenol
$-\Delta_c u^\circ$/J·g^{-1}	
31862.24	31727.20
31872.36	31716.98
31856.92	31732.51
31855.11	31736.28
31864.75	31726.43
31865.47	31734.03
	31722.50
$-\langle\Delta_c u^\circ\rangle$/J·g^{-1})[a]	
31862.8 ± 2.6	31728.0 ± 2.6

[a] Mean value and standard deviation of the mean. (ε(calor) = (15906.6 ± 1.9) J·g^{-1}).

The experimental values yield the standard molar enthalpies of formation in the gaseous phase at T = 298.15 K. The results were analyzed and interpreted in terms of the enthalpic increments associated with molecular structure, and were also compared with the ones estimated by the Cox[28] empirical method.

Additionally, the gas-phase standard molar enthalpies of formation of these two compounds were estimated computationally, along with the gas-phase acidities, gas-phase basicities, proton and electron affinities, adiabatic ionization enthalpies, and, finally, O−H bond dissociation enthalpies.

This study is part of a broad research project that is being carried out in the University of Porto Chemical Research Center on the systematic study of the energetics of phenol derivatives such as 4-nitrosophenol,[29] *tert*-butyl- and di-*tert*-butylphenols,[30,31] catechol and alkylsubstituted catechols,[32] cyanophenols,[33] mono-, di-, and trimethoxyphenols,[34,35] methoxynitrophenols,[36] hydroxymethylphenols,[37] and methylbenzenediols.[38] Thermochemical parameters for halogenated phenols have been reported for pentafluorophenol,[39] pentachlorophenol,[40] chloronitrophenol isomers,[41] cyanophenol and cyanothiophenol isomers,[42] as well as for the mono- and dichlorophenol isomers,[43,44] mono- and difluorophenol isomers,[45,46] and mono- and dibromophenols.[47,48]

RESULTS AND DISCUSSION

Combustion Calorimetry Results. For each compound, the individual values of the standard (p° = 0.1 MPa) massic energies of combustion, $\Delta_c u^\circ$, together with the mean values, $\langle\Delta_c u^\circ\rangle$, are given in Table 1, where the indicated uncertainty represents the standard deviation of the mean. The values of $\Delta_c u^\circ$ refer to the combustion reaction described by the following equation:

$$C_{12}H_{10}O_2(\text{cr or l}) + 13.5O_2(g) \rightarrow 12CO_2(g) + 5H_2O(l) \quad (1)$$

Table 2 lists, for each compound, the derived standard molar values for the energy, $\Delta_c U^\circ_m$(cr or l), and enthalpy, $\Delta_c H^\circ_m$(cr or l), of combustion reaction, at T = 298.15 K, measured in a static combustion bomb, under oxygen at p = 3.04 MPa, in the presence of 1.00 cm^3 of liquid water, yielding $CO_2(g)$ and $H_2O(l)$. The uncertainties of the standard molar energies and enthalpies of combustion are twice the overall standard deviation of the mean and include the uncertainties in calibration as well as the respective uncertainties of the auxiliary compounds used.[49,50] To derived $\Delta_f H^\circ_m$(cr or l) from $\Delta_c H^\circ_m$(cr or l) the standard molar enthalpies of formation of $CO_2(g)$ and $H_2O(l)$, at T = 298.15 K, −(393.51 ± 0.13) kJ·mol^{-1}[51] and −(285.830 ± 0.040) kJ·mol^{-1},[51] respectively, were used.

Knudsen Effusion Results. The standard molar enthalpies of sublimation, at the mean temperature of the experimental range, were derived by fitting data of vapor pressures at several temperatures to the integrated form of the Clausius−Clapeyron equation, $\ln(p/\text{Pa}) = a - b(\text{K}/T)$, where a is a constant and $b = \Delta^g_{cr}H^\circ_m(\langle T\rangle)/R$. The experimental results obtained from each

Table 2. Derived Standard (p° = 0.1 MPa) Molar Energies, $\Delta_c U^\circ_m$(cr or l), and Enthalpies, $\Delta_c H^\circ_m$(cr or l), of Combustion and Standard Molar Enthalpies of Formation, $\Delta_f H^\circ_m$(cr or l), in the Condensed Phase, for the 3- and 4-Phenoxyphenol, at T = 298.15 K

compd	$-\Delta_c U^\circ_m$(cr or l)/kJ·mol^{-1}	$-\Delta_c H^\circ_m$(cr or l)/kJ·mol^{-1}	$\Delta_f H^\circ_m$(cr or l)/kJ·mol^{-1}
3-phenoxyphenol (l)	5933.1 ± 2.3	5936.8 ± 2.3	214.5 ± 2.8
4-phenoxyphenol (cr)	5908.0 ± 1.8	5911.7 ± 1.8	239.6 ± 2.4

Table 3. Knudsen Effusion Results for the 4-Phenoxyphenol[a]

T/K	t/s	orifices	p^b/Pa			$10^2\ \Delta\ln(p/\text{Pa})^c$		
			small	medium	large	small	medium	large
				4-phenoxyphenol				
325.17	22137	A3−B6−C9	0.121	0.118	0.116	0.9	−1.3	0.1
327.20	22137	A2−B5−C8	0.155	0.156	0.152	0.8	1.1	1.0
329.13	22137	A1−B4−C7	0.199	0.204	0.196	2.0	3.3	2.4
331.16	20780	A3−B6−C9	0.246	0.251	0.240	−1.2	−1.2	−2.6
333.19	20780	A2−B5−C8	0.312	0.316	0.309	−1.8	−2.9	−2.1
335.13	20780	A1−B4−C7	0.390	0.413	0.400	−2.7	0.1	0.3
337.12	10852	A1−B4−C7	0.497	0.526	0.509	−1.8	0.4	0.6
339.16	11683	A3−B6−C9	0.644	0.673	0.632	0.6	0.9	−1.8
341.18	11683	A2−B5−C8	0.825	0.821	0.815	2.3	−2.9	0.2
343.12	11683	A1−B4−C7	1.013	1.085	1.037	0.9	2.5	1.8

[a] Detailed data of the effusion orifices (diameter and Clausing factors) of the Knudsen effusion apparatus are presented in Table S1 in the Supporting Information. [b] The uncertainty associated with each calculated individual vapor pressure measurement is estimated to be less than 0.01 Pa. [c] The deviations of the experimental results from those given by the Clausius−Clapeyron equations are denoted by $\Delta\ln(p/\text{Pa})$.

Table 4. Experimental Results for 4-Phenoxyphenol, Where a and b Are from the Clausius−Clapeyron Equation, $\ln(p/\text{Pa}) = a - b\cdot(\text{K}/T)$ and $b = \Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}(\langle T\rangle)/R$, Where $R = 8.314472\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

orifices	a	b	$\langle T\rangle$/K	$p(\langle T\rangle)$/Pa	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}(\langle T\rangle)/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}(\langle T\rangle,p(\langle T\rangle))/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
			4-phenoxyphenol			
A1−A2−A3	38.58 ± 0.34	13235 ± 114			110.0 ± 0.9	
B4−B5−B6	39.62 ± 0.41	13578 ± 136			112.9 ± 1.1	
C7−C8−C9	39.34 ± 0.33	13493 ± 109			112.9 ± 0.9	
global results	39.18 ± 0.26	13435 ± 87	334.15	0.358	111.7 ± 0.7	334.3 ± 2.1

effusion cell from the Knudsen effusion experiments are summarized in Table 3. In this table, $10^2\ \Delta\ln(p/\text{Pa})$ are the residuals of the Clausius−Clapeyron equation, derived from least-squares adjustments.

Table 4 presents, for each orifice used and for the global treatment of all the (p,T) points obtained for 4-phenoxyphenol, the detailed parameters of the Clausius−Clapeyron equation, together with the calculated standard deviations and the standard molar enthalpies of sublimation at the mean temperature of the experiments, $T = \langle T\rangle$, as well as the equilibrium vapor pressure at this temperature $p(\langle T\rangle)$ and the entropies of sublimation, at equilibrium conditions, $\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}(\langle T\rangle,p(\langle T\rangle))$, calculated as $\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}(\langle T\rangle,p(\langle T\rangle)) = \Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}(\langle T\rangle)/\langle T\rangle$. The calculated enthalpies of sublimation obtained from each individual orifice are in consonance within the associated experimental uncertainties.

Figure 2 shows the plots of $\ln p = f(1/T)$ for the global results obtained for the 4-phenoxyphenol, a straight line with a correlation coefficient $R^2 = 0.9988$.

The standard molar enthalpies of sublimation, at $T = 298.15$ K, were derived from the sublimation enthalpies calculated at the mean temperature $\langle T\rangle$ using the relation

$$\Delta_{\text{g}}^{\text{cr}}H_{\text{m}}^{\text{o}}(298.15\ \text{K}) = \Delta_{\text{g}}^{\text{cr}}H_{\text{m}}^{\text{o}}(\langle T\rangle) + \Delta_{\text{g}}^{\text{cr}}C_{p,\text{m}}^{\text{o}}(298.15\ \text{K} - \langle T\rangle) \tag{2}$$

where $\Delta_{\text{cr}}^{\text{g}}C_{p,\text{m}}^{\text{o}} = C_{p,\text{m}}^{\text{o}}(\text{g}) - C_{p,\text{m}}^{\text{o}}(\text{cr})$. For 4-phenoxyphenol, $C_{p,\text{m}}^{\text{o}}(\text{cr}) = 225.0\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, was derived from data of Domalski and Hearing[52] and using a second-order group additivity approach developed by Benson and co-workers,[53] considering the following expression:

$$C_{p,\text{m}}^{\text{o}}(\text{4-phenoxyphenol, cr}) = \{(9 \times [\mathbf{C_B}\text{-(H)(C}_\text{B})_2]) + [\mathbf{O}\text{-(C}_\text{B})_2]_{\text{cr}} + 3 \times [\mathbf{C_B}\text{-(O)(C}_\text{B})_2]_{\text{cr}} + [\mathbf{O}\text{-(H)(C}_\text{B})]_{\text{cr}}\} \tag{3}$$

and using the group contribution values derived by Domalski and Hearing:[52] $[\mathbf{C_B}\text{-(H)(C}_\text{B})_2]_{\text{cr}} = 20.13\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$; $[\mathbf{O}\text{-(C}_\text{B})_2]_{\text{cr}} = 15.9\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$; $[\mathbf{C_B}\text{-(O)(C}_\text{B})_2]_{\text{cr}} = -0.29\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$; $[\mathbf{O}\text{-(H)(C}_\text{B})]_{\text{cr}} = 29.25\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Due to the absence of the parameter $[\mathbf{O}\text{-(C}_\text{B})_2]_{\text{g}}$ in the method described by Domalski,[52] the gas-phase heat capacity of the isomers was determined computationally by means of DFT calculations, using the B3LYP functional and the 6-31+G(d) basis set, as $194.62\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Hence, the heat capacity difference, $\Delta_{\text{cr}}^{\text{g}}C_{p,m}^{\text{o}}$, used for the calculation of the sublimation enthalpy and entropy of 4-phenoxyphenol was $-(30.4 \pm 11)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. This value was confirmed by using the eq 4 derived by Chickos et al.,[54] which gives a value of $-(35. \pm 12)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

$$\Delta_{\text{cr}}^{\text{o}}C_{p,\text{m}}^{\text{o}} = -\{0.75 \pm 0.15C_{p,\text{m}}^{\text{o}}(\text{cr})\} \tag{4}$$

The standard molar entropies of sublimation were calculated by eq 5, where $p^{\text{o}} = 0.1$ MPa, and the standard molar Gibbs energies of sublimation were calculated by using eq 6, where all thermodynamic parameters are referenced to the temperature of 298.15 K.

$$\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}^{\text{o}}(T = 298.15\ \text{K}) = \Delta_{\text{cr}}^{\text{g}}S_{\text{m}}^{\text{o}}\{\langle T\rangle, p(\langle T\rangle)\} + \Delta_{\text{cr}}^{\text{g}}C_{p,\text{m}}^{\text{o}}\ln(298.15\ \text{K}/\langle T\rangle) - R\ln\{p^{\text{o}}/p(\langle T\rangle)\} \tag{5}$$

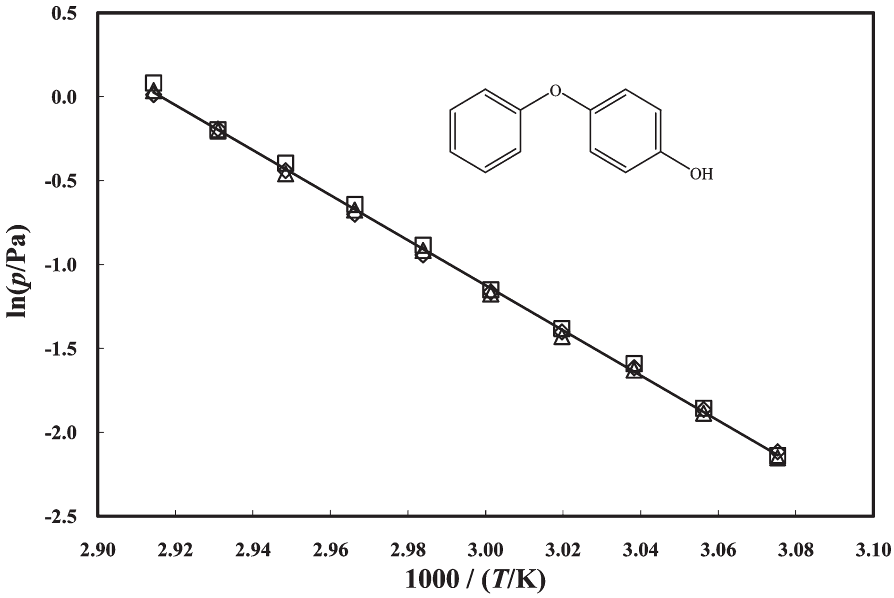


Figure 2. Plots of $\ln(p/\mathrm{Pa}) = f(1/T)$ for 4-phenoxyphenol: ◇, small orifices; □, medium orifices; □, large orifices.

Table 5. Derived Standard (p^o = 0.1 MPa) Molar Enthalpy, $\Delta_{cr}^{g}H_m^o$, Entropy, $\Delta_{cr}^{g}S_m^o$, and Gibbs Energy, $\Delta_{cr}^{g}G_m^o$, of Sublimation, of 4-Phenoxyphenol, at T = 298.15 K

compd	$\Delta_{cr}^{g}H_m^o/\mathrm{kJ \cdot mol^{-1}}$	$\Delta_{cr}^{g}S_m^o/\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\Delta_{cr}^{g}G_m^o/\mathrm{kJ \cdot mol^{-1}}$	p/Pa
4-phenoxyphenol (cr)	112.8 ± 0.4	235.8 ± 2.1	43.2 ± 0.7	$(2.7 \pm 0.8) \times 10^{-3}$

Table 6. Standard (p^o = 0.1 MPa) Molar Enthalpies of Vaporization, $\Delta_l^g H_m^o$, at T = 298.15 K, of 3-Phenoxyphenol

compd	no. of expts	T/K	$\Delta_{l,\ 298.15K}^{g,T}H_m^o/\mathrm{kJ \cdot mol^{-1}}$	$\Delta_{298.15K}^{T}H_m^o(\mathrm{g})/\mathrm{kJ \cdot mol^{-1}}$	$\Delta_l^g H_m^o(298.15\mathrm{K})/\mathrm{kJ \cdot mol^{-1}}$
3-phenoxyphenol (l)	6	385.5	109.9 ± 0.4	19.5	90.4 ± 2.3

$$\Delta_{cr}^{g}G_m^o = \Delta_{cr}^{g}H_m^o - 298.15\Delta_{cr}^{g}S_m^o \qquad (6)$$

The values of the standard molar enthalpies, entropies, and Gibbs energies of sublimation, at T = 298.15 K, together with the calculated vapor pressure of the pure compound at the same reference temperature, are presented in Table 5.

Microcalorimetry Results. Results of the microcalorimetric determination of the enthalpies of vaporization of 3-phenoxyphenol are given in Table 6. The enthalpy of vaporization at the temperature T corresponds to the mean value of six individual experiments. The quoted uncertainty of the standard molar enthalpy of vaporization, at T = 298.15 K, is twice the overall standard deviation of the mean and includes the uncertainties in calibration with *n*-undecane.[49,50]

Experimental Enthalpies of Formation. The standard molar enthalpies of formation, in the gaseous phase, at T = 298.15 K, derived from the experimental values of the standard molar enthalpies of formation, in the condensed phase (Table 2), and from the values of the standard molar enthalpies of sublimation or vaporization (Tables 5 and 6, respectively) are summarized in Table 7. From the experimental values presented in this table, the insertion of a hydroxyl group in the aromatic ring of diphenyl ether in either the para- or meta-position produces a similar enthalpic stabilization, within the associated uncertainties. No other experimental data for the enthalpies of combustion and formation of the title compounds have been found in the literature for comparison with our results.

Enthalpies of Formation Estimated with the Cox Scheme. The values of $\Delta_f H_m^o(\mathrm{g})$ are compared (Table 7) with values estimated by using the Cox scheme.[28] This empirical scheme is based on the transferability of enthalpic group contributions in benzene derivatives, assuming that each group, when bound to the benzene ring, produces a characteristic enthalpic increment in the enthalpy of formation in the gaseous phase. The addition of a correction term of $+4\ \mathrm{kJ \cdot mol^{-1}}$ is necessary whenever a pair of substituents are bound on the aromatic ring in ortho positions. Using the methodology developed by Cox, it is possible to estimate $\Delta_f H_m^o(\mathrm{g})$ for the phenoxyphenol isomers according to the approach, presented in Figure 3, taking into account the following literature values of the gas phase standard molar enthalpies of formation: $\Delta_f H_m^o(\text{benzene, g}) = (82.6 \pm 0.7)\ \mathrm{kJ \cdot mol^{-1}}$,[55] $\Delta_f H_m^o(\text{phenol, g}) = -(96.4 \pm 0.9)\ \mathrm{kJ \cdot mol^{-1}}$,[55] and $\Delta_f H_m^o(\text{diphenyl ether, g}) = (52.0 \pm 1.8)\ \mathrm{kJ \cdot mol^{-1}}$,[55] at T = 298.15 K.

The estimated value of $\Delta_f H_m^o(\mathrm{g})$ derived from the application of the Cox scheme[28] to *o*-phenoxyphenol is $-(123.0 \pm 2.1)\ \mathrm{kJ \cdot mol^{-1}}$, while the estimated value for both the meta and para isomers is $-(127.0 \pm 2.1)\ \mathrm{kJ \cdot mol^{-1}}$. These values are listed in Table 7 along with the experimental results and the deviation between them. For the meta and para isomers, the estimated

Table 7. Experimental and Computed Enthalpies of Formation, $\Delta_f H_m^o(g)$, in the Gas Phase, for the 3- and 4-Phenoxyphenol, at T = 298.15 K[a]

	$-\Delta_f H_m^o(g)$/kJ·mol^{-1}				
			G3MP2B3		
compd	exptl	Cox scheme	atomization (eq 10)	eq 11	eq 12
2-phenoxyphenol		123.0 ± 2.1	126.5	132.7	132.6
3-phenoxyphenol	124.1 ± 3.6	127.0 ± 2.1 (2.9 ± 4.2)	121.0(−3.1)	127.2(+3.1)	127.1(+3.0)
4-phenoxyphenol	126.8 ± 2.4	127.0 ± 2.1 (0.2 ± 3.2)	116.6(−10.2)	122.8(−4.0)	122.6(−4.2)

[a] The values between brackets are the differences between experimental and estimated values of $\Delta_f H_m^o(g)$.

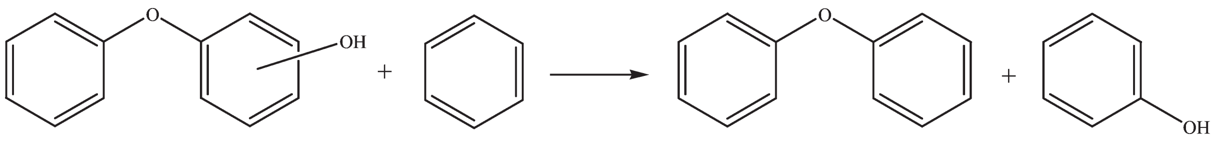


Figure 3. Empirical scheme for the estimation of $\Delta_f H_m^o(g)$ by the Cox scheme.

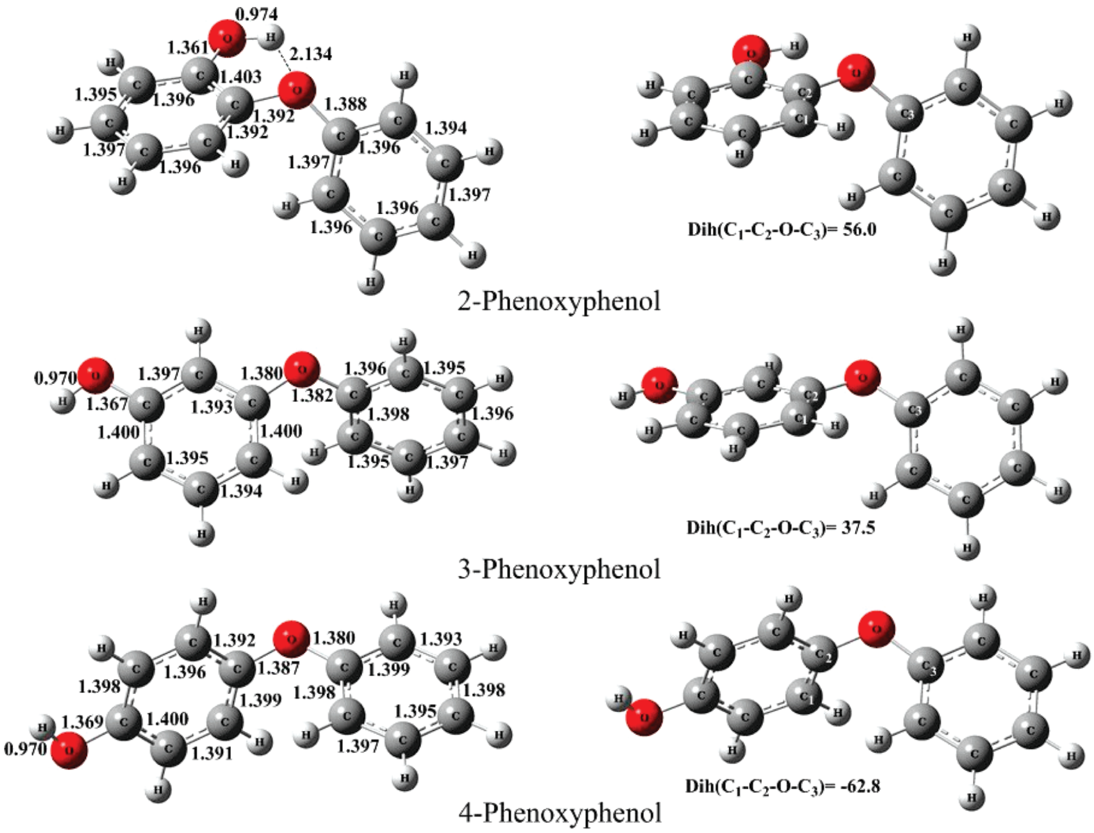


Figure 4. Front and side views of the B3LYP/6-31G(d) optimized geometries of the three different isomers of phenoxyphenol. Distances are given in Å and angles in deg.

values are in very good agreement with the experimental ones, with calculated deviations of (2.9 ± 4.2) kJ·mol^{-1} and (0.2 ± 3.2) kJ·mol^{-1}, respectively. The results are well within the limit of acceptance of ±10 kJ·mol^{-1} for agreement between experimental and estimated values indicated by Cox for his scheme.[28] This methodology fails completely to differentiate between the 3- and 4-phenoxyphenol isomers, since the same value is predicted for both. The Cox scheme[28] does not provide any correction to differentiate substitutions at aromatic ring positions meta or para resulting from different resonance/inductive effects depending on substituent. This method also predicts that the 2-phenoxyphenol isomer is the least stable compound as a result of the steric interaction between the hydroxyl group and the oxygen of phenoxyl group. The method does not take into account the possible stabilization due to the formation of a hydrogen bond between the oxygen of the phenoxyl group and the hydrogen of the hydroxyl group. Cox[28] also suggested that whenever the two ortho substituents were $-CH_3$ groups, or $-OH$ and $-COOH$ groups, no correction term of $+4$ kJ·mol^{-1} should be applied. Cox[28] concluded that in these specific situations, the enthalpic destabilizing steric interactions are negligible, and also mentioned that due to the lack of experimental values, it was not possible to make predictions as in the case mentioned above. In previous work developed in our research group[45−57] it has been reported that whenever the ortho substituents are halogen atoms (in particular, Cl and Br) and a $-NH_2$ or $-OH$ group, no correction of $+4$ kJ·mol^{-1} should be applied. This suggests that a reparametrization of the Cox method is needed in order to ensure reliable results in the cases where it is possible to incur an enthalpic stabilizing effect due to the formation of a hydrogen bond between two ortho substituents.

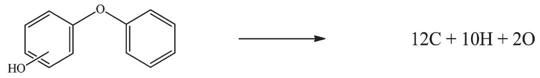
To substantiate the existence of this stabilizing enthalpic interaction for 2-phenoxyphenol, computational thermochemistry calculations were performed for the three phenoxyphenol isomers.

Gas-Phase Molecular Structures. Figure 4 presents the optimized geometries of the three different isomers of phenoxyphenol calculated at the B3LYP/6-31G(d) level of theory. This is the level of theory at which the geometry optimization is carried out within the G3MP2B3 theory. Bond distances and angles are included.

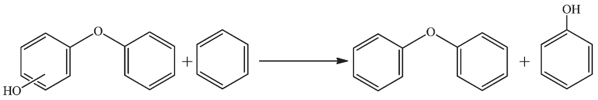
The dihedral angle between the two rings is 56.0°, 37.5°, and −62.8° for the 2-, 3-, and 4-phenoxyphenol, respectively. The ortho isomer is the one with the shortest C−OH distance, which is not surprising due to the inductive effect. Additionally, there is a hydrogen bond between the H(OH) and the O(PhCOCPh) that makes this isomer the most stable one.

Platz et al.[58] obtained the 4-phenoxyphenol structure at the PW91 level of theory using a double-ζ Slater-type basis set. Comparing this structure with our prediction results are in very good agreement. The most significant difference between the two calculations is the dihedral angle between the two cycles. At the PW91 level of theory the angle is predicted to be −46.7° while at the B3LYP level it is −62.8°. For the other isomers no theoretical data have been found in the literature for comparison.

Calculated Enthalpies of Formation. The gas-phase enthalpies of formation of the three isomers studied were estimated by using the reactions described by eqs 7−9, using the experimental enthalpies of formation in the gaseous phase of the other atoms and molecules involved: carbon, 716.7 kJ·mol^{-1};[59] hydrogen, 218.0 kJ·mol^{-1};[59] oxygen, 249.2 kJ·mol^{-1};[59] benzene, 82.6 kJ·mol^{-1};[55] diphenyl ether, 52.0 kJ·mol^{-1};[55] phenol, −96.4 kJ·mol^{-1};[55] ethene, 52.5 kJ·mol^{-1};[55] and phenyl vinyl ether, 22.7 kJ·mol^{-1}.[55]



(7)



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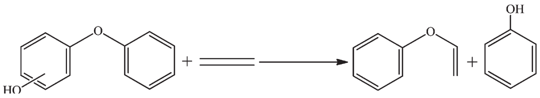

(9)

Table 8. G3MP2B3 Computed Gas-Phase Acidities, $\Delta H_{acidity}$, Gas-Phase Basicities, $\Delta G_{basicity}$, Proton (*PA*) and Electron Affinities (*EA*), Adiabatic Ionization Enthalpies (*IE*), and O−H Bond Dissociation Enthalpies, $\Delta_{O-H}H$ at T = 298.15 K, for All the Phenoxyphenol Isomers[a]

compd	$\Delta H_{acidity}$	$\Delta G_{basicity}$	*PA*	*EA*	*IE*	$\Delta_{O-H}H$
2-phenoxyphenol	1431.5	757.0 (O) 768.3 (OH)	754.5 (O) 764.8 (OH)	−125.4	776.1	379.5
3-phenoxyphenol	1425.5	783.5 (O) 753.4 (OH)	781.3 (O) 749.4 (OH)	−63.9	801.3	378.8
4-phenoxyphenol	1432.7	786.1 (O) 757.4 (OH)	784.7 (O) 754.7 (OH)	−52.2	755.6	365.8

[a] All values are given in kJ·mol^{-1}.

Table 7 reports the calculated enthalpies of formation along with the experimental ones. The table shows that the agreement between the experimental and the G3MP2B3 calculated values is good, with the maximum deviation from the experimental result corresponding to the bond additivity corrected atomization reaction of 4-phenoxyphenol, −10.2 kJ·mol^{-1}.

At the G3MP2B3 level, the most stable isomer is the 2-phenoxyphenol followed by the 3-phenoxyphenol, which lies 5.5 kJ·mol^{-1} higher. Finally, the less stable one is the 4-phenoxyphenol, which lies 9.9 kJ mol^{-1} higher. The higher stability of 2-phenoxyphenol is due to, as was mentioned before, the hydrogen bond present between the H(OH) and the O(Ph−O−Ph). Between 3- and 4-phenoxyphenol, the 3-phenoxyphenol is more stable because the π-delocalization energy is larger than in 4-phenoxyphenol, so that the dihedral angle in the case of the 3-isomer is closer to 0° than in the case of 4-phenoxyphenol. The π-delocalization is larger as the dihedral angle between the two cycles approximates 0° or 180°.

Other Gas-Phase Thermodynamic Properties. Other thermodynamic properties for all the isomers of phenoxyphenol using the G3(MP2)//B3LYP approach were also computed. The calculated values of gas-phase acidity (ΔH_{acid}), gas-phase basicity ($\Delta G_{basicity}$), proton (*PA*) and electron affinities (*EA*), adiabatic ionization enthalpies, and O−H dissociation enthalpies $\Delta_{O-H}H$ are reported in Table 8.

From these values it can be concluded that the most acidic species is 3-phenoxyphenol followed by the 2- and 4-isomers, both having similar acidity. Concerning the gas-phase basicities, the ether oxygen (Ph−O−Ph) is the most basic center in 3- and 4-phenoxyphenol while in the case of the 2-phenoxyphenol the most basic center is the oxygen of the OH group. The calculated gas-phase basicities allow us to propose the following order: 4-phenoxyphenol ≈ 3-phenoxyphenol > 2-phenoxyphenol. Proton affinities follow the same pattern. No experimental or computational data have been found in the literature for comparison with our results on gas-phase acidity, basicity, and proton affinity.

From Table 8, it can be seen that the electron affinities are all negative, with 2-phenoxyphenol the most destabilized with respect to the incoming electron. This is due to the fact that the incoming electron is occupying an antibonding orbital. With respect to the ionization enthalpies, removing an electron is easiest for 4-phenoxyphenol. Finally, while all the O−H bond dissociation enthalpies are very similar, 2-phenoxyphenol has the strongest OH bond. No computational or experimental values regarding these properties have been found in the literature.

Table 9. Standard (p^o = 0.1 MPa) Massic Energy of Combustion of 3-Phenoxyphenol, at T = 298.15 K

	experiment no.					
	1	2	3	4	5	6
$m(CO_2, total)$/g	1.88071	1.96242	1.91290		1.89153	
$m'(cpd)$/g	0.63030	0.65339	0.63089	0.64678	0.63030	0.69271
$m''(fuse)$/g	0.00289	0.00272	0.00260	0.00302	0.00295	0.00268
$m'''(Melinex)$/g	0.03896	0.04618	0.05250	0.03958	0.04112	0.04090
T_i/K	298.1503	298.1509	298.1508	298.1512	298.1515	298.1503
T_f/K	299.5731	299.6273	299.5926	299.6068	299.5753	299.6955
ΔT_{ad}/K	1.32121	1.37814	1.34144	1.35497	1.32450	1.44889
ε_i/J·K^{-1}	14.72	14.45	14.45	14.73	14.67	14.69
ε_f/J·K^{-1}	16.09	15.88	15.83	16.13	16.04	16.19
$\varepsilon(calor)_{corr}$/J·K^{-1}	15906.6	15906.6	15906.6	15906.6	15906.6	15907.0
$\Delta m(H_2O)$/g	0.0	0.0	0.0	0.0	0.0	0.1
$-\Delta U(IBP)^a$/J	21036.26	21942.22	21357.99	21573.79	21088.62	23070.08
$\Delta U(fuse)$/J	46.93	44.17	42.22	49.04	47.91	43.52
$\Delta U(Melinex)$/J	892.32	1057.71	1202.32	906.48	941.66	936.63
$\Delta U(HNO_3)$/J	0.68	1.02	1.37	1.07	1.08	1.37
$\Delta U(ign)$/J	0.96	1.20	1.01	1.05	0.94	0.88
ΔU_Σ/J	13.56	14.24	13.87	13.95	13.62	15.03
$-\Delta_c u^o$/J·g^{-1}	31862.24	31872.36	31856.92	31855.11	31864.75	31865.47
	$-\langle\Delta_c u^o\rangle$ = (31862.8 ± 2.6) J·g^{-1}					

[a] $\Delta U(IBP)$ includes $\Delta U(ign)$.

■ CONCLUSIONS

A combined experimental and computational study was performed, and the standard molar enthalpies of formation, in the gaseous phase, $\Delta_f H^o_m(g)$ at T = 298.15 K, for 2- and 3-phenoxyphenols were obtained. Experimentally, these values were derived from the standard molar enthalpies of combustion and of vaporization or sublimation, at T = 298.15 K, measured by static bomb combustion calorimetry and Calvet microcalorimetry or Knudsen effusion experiments. The experimental $\Delta_f H^o_m(g)$ values are −(124.1 ± 3.6) kJ·mol^{-1} and −(126.8 ± 2.4) kJ·mol^{-1} for 3- and 4-phenoxyphenols, respectively. The G3(MP2)//B3LYP approach was used to estimate the gas-phase enthalpies of formation of the title compounds at T = 298.15 K by considering several appropriate working reactions. Computed values could be compared with the experimental data for 3- and 4-phenoxyphenol; agreement is good, which allows us to rely on the calculations for 2-phenoxyphenol. Other thermodynamic properties of the three phenoxyphenol isomers were also calculated by means of this composite method. The Cox scheme[28] was found to reproduce the experimental enthalpies of formation in the gas phase for 3- and 4-phenoxyphenol, but the scheme should be applied with some caution in the case of the 2-phenoxyphenol due to the presence of a hydrogen bond between the oxygen atom [O(PhCOCPh))] and the hydrogen of the hydroxyl group [H(OH].

■ EXPERIMENTAL SECTION

Materials and Purity Control. The 3-phenoxyphenol [CAS Registy No. 713-68-8] and 4-phenoxyphenol [CAS Registy No. 831-82-3] were obtained commercially, with assessed minimum massic fraction purities of 0.98 and 0.99, respectively.

The liquid 3-phenoxyphenol was purified by successive fractional distillations under reduced pressure and stored under nitrogen atmosphere. The crystalline 4-phenoxyphenol was purified by repeated vacuum sublimations. The final purity of each phenoxyphenol isomer was checked by gas chromatography, using a column, cross-linked, 5% diphenyl and 95% dimethylpolysiloxane (15 m × 0.530 mm i.d. × 1.5 μm film thickness), and with nitrogen as carrier gas. The temperature of the injector was set at 473 K and the oven temperature was programmed as follows: 323 K (1 min), ramp at 10 K·min^{-1}, 473 K (10 min). No impurities greater than 10^{-3} in mass fraction could be detected in the samples of the two isomers used for the calorimetric and vapor pressure measurements.

The purities were also checked from the consistent results obtained on the combustion experiments, as well as by the closeness to unity of the carbon dioxide recovery ratios. The average ratios of the mass of carbon dioxide recovered after combustion to that calculated from the mass of samples used in each experiment were (0.99972 ± 0.00012) for the 3-phenoxyphenol and (1.00008 ± 0.00016) for the 4-phenoxyphenol, where the uncertainties are twice the standard deviations of the means.

The specific density used to calculate the true mass from the apparent mass in air of 3-phenoxyphenol was taken as 1.159 g·cm^{-3},[60] and (1.175 ± 0.001) g·cm^{-3} for 4-phenoxyphenol, determined from the ratio mass/volume of a pellet of the compound (made in vacuum, with an applied pressure of 10^5 kg·cm^{-2}).

The relative atomic masses used in the calculation of all molar quantities throughout this paper were those recommended by the IUPAC Commission in 2007;[61] using those values, the molar mass for the two isomers is 186.2077 g·mol^{-1}.

Procedure for Combustion Measurements. The combustion experiments were performed with a static bomb calorimeter, with a twin valve combustion bomb made of stainless steel, with an internal volume of 0.340 dm^3; the apparatus and technique have been previously described.[32,62] The energy equivalent, ε(calor), of the calorimeter was

Table 10. Standard (p^o = 0.1 MPa) Massic Energy of Combustion of 4-Phenoxyphenol, at T = 298.15 K

	experiment no.						
	1	2	3	4	5	6	7
$m(CO_2, \text{total})$/g		1.35550		2.06932	1.52097	1.79909	
$m'(\text{cpd})$/g	0.54303	0.47632	0.48820	0.72798	0.53460	0.63245	0.57139
$m''(\text{fuse})$/g	0.00300	0.00282	0.00303	0.00287	0.00293	0.00331	0.00335
T_i/K	298.1504	298.1513	298.1505	298.1511	298.1503	298.1504	298.1506
T_f/K	299.3482	299.2209	299.2428	299.7036	299.3311	299.5188	299.4018
ΔT_{ad}/K	1.08587	0.95241	0.97678	1.45489	1.06901	1.26475	1.14261
$\varepsilon_i/\text{J}\cdot\text{K}^{-1}$	15.13	15.06	15.07	15.35	15.07	15.24	15.11
$\varepsilon_f/\text{J}\cdot\text{K}^{-1}$	15.81	15.64	15.67	16.26	15.73	16.03	15.82
$\varepsilon(\text{calor})_{corr}/\text{J}\cdot\text{K}^{-1}$	15906.6	15906.6	15906.6	15906.6	15906.6	15906.6	15906.6
$\Delta m(H_2O)$/g	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$-\Delta U(\text{IBP})^a$/J	17288.65	15163.40	15551.55	23165.06	17020.15	20137.02	18192.07
$\Delta U(\text{fuse})$/J	48.72	45.80	49.21	46.61	47.58	53.75	54.40
$\Delta U(HNO_3)$/J	0.31	0.81	0.91	0.12	1.00	0.29	0.32
$\Delta U(\text{ign})$/J	1.02	1.12	1.01	0.97	0.98	1.13	1.06
ΔU_Σ/J	10.80	9.36	9.62	14.95	10.62	12.79	11.43
$-\Delta_c u^o/\text{J}\cdot\text{g}^{-1}$	31727.20	31716.98	31732.51	31736.28	31726.43	31734.03	31722.50

$-\langle\Delta_c u^o\rangle = (31728.0 \pm 2.6)\ \text{J}\cdot\text{g}^{-1}$

[a] ΔU(IBP) includes ΔU(ign).

determined from the combustion of benzoic acid (NIST Standard Reference Material 39j), having a massic energy of combustion under bomb conditions of $-(26434 \pm 3)\ \text{J}\cdot\text{g}^{-1}$.[63] The calibration results were corrected to give the ε(calor) corresponding to the average mass of water added to the calorimeter: 3119.6 g. From eight calibration experiments, performed according to the procedure suggest by Coops et al.,[64] $\varepsilon(\text{calor}) = (15906.6 \pm 1.9)\ \text{J}\cdot\text{K}^{-1}$, where the quoted uncertainty refers to the standard deviation of the mean.

For all combustion experiments of the two phenoxyphenols, samples were ignited at $T = (298.150 \pm 0.001)$ K in oxygen at a pressure of 3.04 MPa, with a volume of 1.00 cm^3 of deionized water added to the bomb. The electrical energy for ignition was determined from the change in potential difference across a capacitor (1400 μF) when discharged through the platinum ignition wire (ϕ = 0.05 mm, mass fraction 0.9999). The calorimeter temperatures were measured to $\pm 10^{-4}$ K, at time intervals of 10 s, with a quartz crystal thermometer, interfaced to a PC programmed to compute the adiabatic temperature change. At least 100 temperature readings were taken for the main period and for both the fore and after periods. Data acquisition, control of the calorimeter temperature, and calculation of the adiabatic temperature change was performed with the program LABTERMO.[65]

The liquid 3-phenoxyphenol was burnt enclosed in sealed polyester bags made of Melinex, 0.025 mm thick, $\Delta_c u^o = -(22902 \pm 5)\ \text{J}\cdot\text{g}^{-1}$,[66] a value previously confirmed in our laboratory, using the technique described by Skinner and Snelson,[66] while the crystalline 4-phenoxyphenol was burnt in pellet form. The mass of Melinex used in each experiment was corrected for the mass fraction of water (w = 0.0032), and the mass of CO_2 produced from it was calculated by using a factor previously reported.[66]

All the necessary weights for the combustion experiments were made with a precision of $\pm 10^{-5}$ g and corrections from apparent mass to true mass were introduced. The gases of combustion were analyzed to recover the carbon dioxide resulting from the combustion experiments. The amount of compound, m'(cpd), used in each experiment and on which the energy of combustion was based, was determined from the total mass of carbon dioxide produced, determined from the CO_2 recoveries, taking into account that formed from the combustion of the cotton thread fuse and of the auxiliary materials (Melinex). For the cotton thread fuse, empirical formula $CH_{1.686}O_{0.843}$, $\Delta_c u^o = -16240\ \text{J}\cdot\text{g}^{-1}$,[67] a value that has been previously confirmed in our laboratory. Corrections for the nitric acid formed were based on $\Delta_f U^o_m(HNO_3, \text{aq}, 0.1\ \text{mol}\cdot\text{dm}^{-3}) = -59.7\ \text{kJ}\cdot\text{mol}^{-1}$,[68] from $^1/_2N_2(g)$, $^5/_4O_2(g)$, and $^1/_2H_2O(l)$. An estimated pressure coefficient of massic energy—$(\partial u/\partial p)_T = -0.2\ \text{J}\cdot\text{g}^{-1}\cdot\text{MPa}^{-1}$, at T = 298.15 K, a typical value for most organic compounds[69]—was used for the two studied compounds. For each compound, the correction to standard state, ΔU_Σ, and the calculation of $\Delta_c u^o$ were made as described by Hubbard et al.[70]

Detailed results for each combustion experiment performed for 3- and 4-phenoxyphenol are given in Tables 9 and 10. In the last row of these tables are presented the mean values of the standard (p^o = 0.1 MPa) massic energies of combustion, $\langle\Delta_c u^o\rangle$, where the indicated uncertainty represents the standard deviation of the mean. The symbols presented in Tables 9 and 10 have the following meaning: $m(CO_2, \text{total})$ is the mass of CO_2 recovered in each combustion; m'(cpd) is the mass of compound burnt in each experiment; m''(fuse) is the mass of fuse (cotton) used in each experiment; m'''(Melinex) is the mass of Melinex used in each experiment; ΔT_{ad} is the corrected temperature rise; ε_i is the energy equivalent of the contents in the initial state; ε_f is the energy equivalent of the contents in the final state; $\Delta m(H_2O)$ is the deviation of mass of water added to the calorimeter from 3119.6 g; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions and includes ΔU(ignition), $\Delta U(\text{IBP}) = -\{\varepsilon(\text{calor}) + c_p(H_2O,l)\cdot\Delta m(H_2O,l) + \varepsilon_f\}\cdot\Delta T_{ad} + \Delta U(\text{ign})$; ΔU(fuse) is the energy of combustion of the fuse (cotton); ΔU(Melinex) is the energy of combustion of Melinex; $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; ΔU(ign) is the electric energy for the ignition; ΔU_Σ is the standard state correction; and $\Delta_c u^o$ is the standard massic energy of combustion.

Procedure for Knudsen Effusion. The vapor pressures of the 4-phenoxyphenol were measured as a function of temperature, through the mass-loss Knudsen effusion method, using an apparatus that enables the simultaneous operation of nine aluminum effusion cells, which are placed in cylindrical holes inside three aluminum blocks, each one with three cells. Each block is maintained at a constant temperature, different from the other two blocks. There are three different groups of effusion cells according to their different areas of effusion orifices: series A (small orifice; $A_o \approx 0.5$ mm^2), series B (medium orifice; $B_o \approx 0.8$ mm^2), and series C (large orifice; $C_o \approx 1.0$ mm^2). The exact areas and the transmission probability factors (Clausing factors) of each effusion orifice, made in platinum foil of 0.0125 mm thickness, are presented in the Supporting Information. The apparatus, as well as the measuring procedure and technique have been previously described.[71]

The measurements were extended through a selected temperature interval of ca. 20 K, chosen to correspond to measured vapor pressures in the range 0.1 to 1.0 Pa.

The vapor pressure, p, of each compound in an effusion experiment is calculated by means of eq 10, knowing the mass of sublimed compound, m (determined by weighing the effusion cells to $\pm 10^{-5}$ g, before and after each effusion experiment), during a convenient effusion time period, t, at the temperature T of the experiment, in a system evacuated to a pressure near 1×10^{-4} Pa. The uncertainty of the temperature measurements is estimated to be less than $\pm(1 \times 10^{-2})$ K, and the uncertainty of the calculated vapor pressures is estimated to be less than 0.01 Pa.

$$p = (m/A_o w_o t)(2\pi RT/M)^{1/2}, \tag{10}$$

where M represents the molar mass of the effusing vapor, R is the gas constant ($R = 8.314472$ J·K^{-1}·mol^{-1}), A_o is the area of the effusion hole, and w_o is the transmission probability factor (Clausing factor) calculated by means of the following eq 11:

$$w_o = \{1 + (3l/8r)\}^{-1}. \tag{11}$$

Procedure for Calvet Microcalorimetry Experiments. The standard molar enthalpy of vaporization of the 3-phenoxyphenol was measured in a high-temperature Calvet microcalorimeter, using a similar technique[72] to that described by Skinner and co-workers[73] for the sublimation of solid compounds. The measuring procedures, as well as the detailed description of the apparatus, have been recently reported.[74] The calibration of the calorimeter was made with n-undecane, 99+, by the same experimental procedure as with the 3-phenoxyphenol, and using the reported standard molar enthalpy of vaporization of n-undecane (mass fraction purity >0.99), $\Delta_l^g H_m^o(T = 298.15\ \mathrm{K}) = (56.58 \pm 0.57)$ kJ·mol^{-1}.[75] From five independent experiments, the calibration constant, k, of the calorimeter at experimental temperature was found to be $k(T = 385.5\ \mathrm{K}) = (0.9945 \pm 0.0064)$ for the vaporization experiments of the 3-phenoxyphenol; the quoted uncertainty is the standard deviation of the mean.

In a typical experiment, the liquid samples with a mass of 6 to 9 mg were placed into small glass capillary tubes sealed at one end, and weighed with a precision of $\pm 10^{-6}$ g on an analytical balance. The sample and reference capillaries were simultaneously dropped at room temperature into the hot reaction cells, held at $T = 385.5$ K. After dropping, an endothermic peak due to the heating of the sample from room temperature to the temperature of the calorimeter was first observed. Following the stabilization period, when the signal returned to the baseline, the sample and reference cells were simultaneously evacuated and the curve corresponding to the vaporization of the compound was acquired. The thermal corrections for the glass capillary tubes were determined in separate experiments[74] and were evaluated and minimized in each experiment by dropping glass capillary tubes of near equal mass into both measuring cells. The observed values of the vaporization enthalpies, at the temperature of the experiments, $\Delta_{l,298.15\mathrm{K}}^{g,T} H_m^o(T)$, have been corrected to $T = 298.15$ K using the corrective term $\Delta_{298.15\mathrm{K}}^{T} H_m^o(g) = \int_{298.15\mathrm{K}}^{T} C_{p,m}^o(\mathrm{g})\, \mathrm{d}T$, where T is the temperature of the hot reaction vessel and $C_{p,m}^o(\mathrm{g})$ is the molar heat capacity of the compounds in the gas phase, obtained by means of DFT calculations with the B3LYP functional and the 6-31+G(d) basis set, yielding the following adjustment: $\Delta_{298.15\mathrm{K}}^{T} H_m^o(\mathrm{g}) = 19.5$ kJ·mol^{-1}.

$$C_{p,m}^o(\text{4-PhOPhOH, g})/\mathrm{J \cdot mol^{-1} \cdot K^{-1}} = (2.97 \times 10^{-7})(T/\mathrm{K})^3 - (6.81 \times 10^{-4})(T/\mathrm{K})^2 + (6.87 \times 10^{-1})(T/\mathrm{K}) + 1.95 \times 10^2 \tag{12}$$

Computational Details. Standard ab initio molecular orbital calculations were performed with the Gaussian 03 series of programs.[76] The G3MP2B3 composite method was used throughout this work.[77] This is a variation of the G3MP2 theory,[78] which uses the B3LYP density functional method[79,80] for geometries and zero-point energies. The B3LYP functional uses a combination of the hybrid three-parameter Becke's functional, first proposed by Becke,[79] together with the Lee–Yang–Parr nonlocal correlation functional.[81] The computations carried out with the G3MP2B3 composite approach use the B3LYP method and the 6-31G(d) basis set for both the optimization of geometry and calculation of frequencies. Introduction of high-order corrections to the B3LYP/6-31G(d) enthalpy is done in a manner that follows the Gaussian-3 philosophy, albeit using a second-order Møller–Plesset perturbation instead of MP4, as in the original G3 method.[82]

The enthalpy of formation of the phenoxyphenol isomers was estimated after the consideration of the gas-phase working reactions represented by eqs 7–79. These reactions have been chosen on the basis of the available experimental thermochemical data.

The energies computed at $T = 0$ K were thermally corrected to $T = 298.15$ K by introducing the vibrational, translational, rotational, and the pV terms. The vibrational term is based on the vibrational frequencies calculated at the B3LYP/6-31G(d) level. The same computational approach was used to calculate also the ionization enthalpies, proton and electron affinities, gas-phase acidities and basicities, and O–H bond dissociation enthalpies. For that purpose, the G3MP2B3 computations were also extended to cationic, anionic, and radicalar species of phenoxyphenol isomers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Detailed description of the effusion orifices (diameter and Clausing factors) of the Knudsen effusion apparatus, Cartesian coordinates of the optimized structures for 2-, 3-, and 4-phenoxyphenol, and G3MP2B3 computed enthalpies for all species involved in the isodesmic reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Rappoport, Z. *The Chemistry of Phenols*; John Wiley & Sons, Ltd.: Chichester, England, 2003.

(2) Santos, R. M. B.; Simões, J. A. M. *J. Phys. Chem. Ref. Data* **1998**, *27*, 707–741.

(3) Pantelidis, G. E.; Vasilakakis, M.; Manganaris, G. A.; Diamantidis, G. *Food Chem.* **2007**, *102*, 777–783.

(4) Zheng, W.; Wang, S. Y. *J. Agric. Food Chem.* **2001**, *49*, 5165–5170.

(5) Glaser, R. *J. Org. Chem.* **2001**, *66*, 771–779.

(6) Kałedkowska, B.; Hetper, J. *Polymer* **2000**, *41*, 1679–1684.

(7) Higuchi, M.; Urakawa, T.; Morita, M. *Polymer* **2001**, *42*, 4563–4567.

(8) Sprung, M. M.; Gladstone, M. T. *J. Am. Chem. Soc.* **1949**, *71*, 2907–2913.

(9) Hart, M. C.; Hirschfelder, A. D. *J. Am. Chem. Soc.* **1921**, *43*, 1688–1693.

(10) Wiater, I.; Born, J. G. P.; Louw, R. *Eur. J. Org. Chem.* **2000**, 921–928.

(11) Freeman, P. K.; Jonas, V. *J. Agric. Food Chem.* **1984**, *32*, 1307–1313.

(12) Minna Laine, M.; Ahtiainen, J.; Wågman, N.; Öberg, L. G.; Jørgensen, K. S. *Environ. Sci. Technol.* **1997**, *31*, 3244–3250.

(13) Macdonald, R. W.; Ikonomou, M. G .; Paton, D. W. *Environ. Sci. Technol.* **1998**, *32*, 331–337.

(14) Shibasaki, Y.; Kamimori, T.; Kadokawa, J.; Hatano, B.; Tagaya, H. *Polym. Degrad. Stab.* **2004**, *83*, 481–485.

(15) Higashimura, H.; Fujisawa, K.; Moro-oka, Y.; Kubota, M.; Shiga, A.; Terahara, A.; Uyama, H.; Kobayashi, S. *J. Am. Chem. Soc.* **1998**, *120*, 8529–8530.

(16) Kobayashi, S.; Higashimura, H. *Prog. Polym. Sci.* **2003**, *28*, 1015–1048.

(17) Kobayashi, S.; Makino, A. *Chem. Rev.* **2009**, *109*, 5288–5353.

(18) Matsumoto, K.; Higashihara, T.; Ueda, M. *Macromolecules* **2008**, *41*, 7560–7565.

(19) Bokare, V.; Murugesan, K.; Kim, Y.-M.; Jeon, J.-R.; Kim, E.-J.; Chang, Y. S. *Bioresour. Technol.* **2010**, *101*, 6354–6360.

(20) Chau, W. C.; Wu, J.; Cai, Z. *Chemosphere* **2008**, *73*, 13–17.

(21) Knust, K. N.; Foley, M. P.; Mubarak, M. S.; Skljarevski, S.; Raghavachari, K.; Peters, D. G. *J. Anal. Chem.* **2010**, *638*, 100–108.

(22) Cinque, G. M.; Szajnman, S. H.; Zhong, L.; Docampo, R.; Schvartzapel, A. J.; Rodriguez, J. B.; Gros, E. G. *J. Med. Chem.* **1998**, *41*, 1540–1554.

(23) Szajnman, S. H.; Yan, W.; Bailey, B. N.; Docampo, R.; Elhalem, E.; Rodriguez, J. B. *J. Med. Chem.* **2000**, *43*, 1826–1840.

(24) Elhalem, E.; Bailey, B. N.; Docampo, R.; Ujváry, I.; Szajnman, S. H.; Rodriguez, J. B. *J. Med. Chem.* **2002**, *45*, 3984–3999.

(25) Ende, C. W.; Knudson, S. E.; Liu, N.; Childs, J.; Sullivan, T. J.; Boyne, M.; Xu, H.; Gegina, Y.; Knudson, D. L.; Johnson, F.; Peloquin, C. A.; Slayden, R. A.; Tonge, P. J. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 3029–3033.

(26) Brown, S.; Margarida Bernardo, M.; Li., Z.-H.; Kotra, L. P.; Tanaka, Y.; Fridman, R.; Mobashery, S. *J. Am. Chem. Soc.* **2000**, *122*, 6799–6800.

(27) Lim, I. T.; Brown, S.; Mobashery, S. *J. Org. Chem.* **2004**, *69*, 3572–3573.

(28) Cox, J. D. *A Method for Estimating the Enthalpies of Formation of Benzene Derivatives in the Gas State*; NPL Report CHEM *83*, June 1978.

(29) Ribeiro da Silva, M. D. M. C.; Matos, M. A. R.; Ferrão, M. L. C. C. H.; Amaral, L. M. P. F.; Miranda, M. S.; Acree, W. E., Jr.; Pilcher, G. *J. Chem. Thermodyn.* **1999**, *31*, 1551–1559.

(30) Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Morais, V. M. F.; Miranda, M. S. *J. Org. Chem.* **1999**, *64*, 8816–8820.

(31) Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Miranda, M. S.; Sousa, M. H. F. A.; Santos, R. M. B.; Bizarro, M. M.; Simões, J. A. M. *Struct. Chem.* **2001**, *12*, 171–181.

(32) Ribeiro da Silva, M. A. V.; Ribeiro da Silva, M. D. M. C.; Pilcher, G. *J. Chem. Thermodyn.* **1984**, *16*, 1149–1155.

(33) Matos, M. A. R.; Miranda, M. S.; Morais, V. M. F. *Struct. Chem.* **2004**, *15*, 103–116.

(34) Matos, M. A. R.; Miranda, M. S.; Morais, V. M. F. *J. Chem. Eng. Data* **2003**, *48*, 669–679.

(35) Matos, M. A. R.; Miranda, M. S.; Morais, V. M. F. *J. Chem. Thermodyn.* **2008**, *40*, 625–631.

(36) Miranda, M. S.; Morais, V. M. F.; Matos, M. A. R. *J. Chem. Thermodyn.* **2004**, *36*, 431–436.

(37) Ribeiro da Silva, M. A. V.; Lobo Ferreira, A. I. M. C. *J. Therm. Anal. Calorim.* **2010**, *100*, 447–455.

(38) Ribeiro da Silva, M. A. V.; Lobo Ferreira, A. I. M. C. *J. Chem. Thermodyn.* **2009**, *41*, 1096–1103.

(39) Cox, J. D.; Gundry, H. A.; Harrop, D.; Head, A. J. *J. Chem. Thermodyn.* **1969**, *1*, 77–87.

(40) Sinke, G. C.; Stull, D. R. *J. Phys. Chem.* **1958**, *62*, 397–401.

(41) Morais, V. M. F.; Miranda, M. S.; Matos, M. A. R. *J. Chem. Eng. Data* **2007**, *52*, 627–634.

(42) Gomes, J. R. B.; Liebman, J. F.; Ribeiro da Silva, M. A. V. *Struct. Chem.* **2007**, *18*, 15–23.

(43) Ribeiro da Silva, M. A. V.; Ferrão, M. L. C. C. H.; Jiye, F. *J. Chem. Thermodyn.* **1994**, *26*, 839–846.

(44) Gomes, J. R. B.; Ribeiro da Silva, M. A. V. *J. Phys. Chem. A* **2003**, *107*, 869–874.

(45) Ribeiro da Silva, M. A. V.; Lobo Ferreira, A. I. M. C. *J. Chem. Eng. Data* **2009**, *54*, 2517–2526.

(46) Ribeiro da Silva, M. A. V.; Lobo Ferreira, A. I. M. C. *J. Chem. Thermodyn.* **2010**, *42*, 182–188.

(47) Ribeiro da Silva, M. A. V.; Lobo Ferreira, A. I. M. C. *J. Chem. Thermodyn.* **2009**, *41*, 1104–1110.

(48) Lobo Ferreira, A. I. M. C.; Ribeiro da Silva, M. A. V. *J. Chem. Thermodyn.* **2009**, *41*, 1096–1103.

(49) Rossini, F. D. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1Chapter 14.

(50) Olofsson, G. In *Combustion Calorimetry*; Sunner, S., Månsson, M., Eds.; Pergamon: Oxford, UK, 1979; Chapter 6.

(51) Cox, J.D.; Wagman, D.D.; Medvedev, V.A., Eds., *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989.

(52) Domalski, E. S.; Hearing, E. D. *J. Phys. Chem. Ref. Data* **1993**, *22*, 805–1159.

(53) Benson, S. W.; Buss, J. H. *J. Chem. Phys.* **1958**, *29*, 546–572.

(54) Chickos, J. S.; Hosseini, S.; Hesse, D. G.; Liebman, J. F. *Struct. Chem.* **1993**, *4*, 271–278.

(55) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; Thermodynamics Research Center: College Station, Texas, 1994.

(56) Ribeiro da Silva, M. A. V.; Lobo Ferreira, A. I. M. C.; Gomes, J. R. B. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1852–1859.

(57) Ribeiro da Silva, M. A. V.; Lobo Ferreira, A. I. M. C.; Gomes, J. R. B. *J. Phys. Chem. B* **2005**, *109*, 13356–13362.

(58) Platz, J.; Nielsen, J. *J. Phys. Chem. A* **1998**, *102*, 7964–7974.

(59) Chase, M. W., Jr. NIST-JANAF Thermochemical Tables, Fourth Edition, Monograph 9. *J. Phys. Chem. Ref. Data* **1998**, 1–1951.

(60) *Catalogue Handbook of Fine Chemicals and Laboratory Equipment*; The Sigma-Aldrich Chemical Co.: España, Portugal, 2009−2010.

(61) Wieser, M. E.; Berglund, M. Atomic Weights of the Elements 2005 (IUPAC Technical Report). *Pure Appl. Chem.* **2009**, *81*, 2131–2156.

(62) Ribeiro da Silva, M. A. V.; Ribeiro da Silva, M. D. M. C.; Pilcher, G. *Rev. Port. Quim.* **1984**, *26*, 163–172.

(63) Certificate of Analysis, Standard Reference Material 39j, Benzoic Acid Calorimetric Standard, NIST, Gaithersburg,1995.

(64) Coops, J.; Jessup, R. S.; Van Nes, K. *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, Chapter 3.

(65) Santos, L. M. N. B. F. Ph.D. Thesis, University of Porto, 1995.

(66) Skinner, H. A.; Snelson, A. *Trans. Faraday Soc.* **1960**, *56*, 1776–1783.

(67) Hubbard, W. N.; Scott, D. W.; Waddington, G. *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol .1, Chapter 3.

(68) The NBS Tables of Chemical Thermodynamic Properties. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. No. 2.

(69) Washburn, E. W. *J. Res. Natl. Bur. Stand. (U.S.)* **1933**, *10*, 525–558.

(70) Hubbard, W. N.; Scott, D. W.; Waddington, G. *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, Chapter 5.

(71) Ribeiro da Silva, M. A. V.; Monte, M. J. S.; Santos, L. M. N. B. *J. Chem. Thermodyn.* **2006**, *38*, 778–787.

(72) Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Amaral, L. M. P. F. *J. Chem. Thermodyn.* **1995**, *27*, 565–574.

(73) Adedeji, F. A.; Brown, D. L. S.; Connor, J. A.; Leung, W. L.; Paz-Andrade, I. M.; Skinner, H. A. *J. Organomet. Chem.* **1975**, *97*, 221–228.

(74) Santos, L. M. N. B. F.; Schröder, B.; Fernandes, O. O. P.; Ribeiro da Silva, M. A. V. *Thermochim. Acta* **2004**, *415*, 15–20.

(75) Chickos, J. S.; Acree, W. E., Jr. *J. Phys. Chem. Ref. Data* **2003**, *32*, 519–878.

(76) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A., *Gaussian03*, Revision C.01; Gaussian, Inc., Wallingford, CT, 2004.

(77) Baboul, A. G.; Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **1999**, *110*, 7650–7657.

(78) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703–4709.

(79) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(80) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623–11627.

(81) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1998**, *37*, 785–789.

(82) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764–7776.