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Theoretical Study on the Stability of Formylphenol and Formylaniline Compounds and Corresponding Radicals: O−H or N−H vs C−H Bond Dissociation

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The composite G3(MP2)//B3LYP approach was considered for the calculation of the gas-phase standard molar enthalpies of formation, at T = 298.15 K, of 2-, 3-, and 4-formylphenols and of *N*-, 2-, 3- and 4-formylanilines. The calculated results for the 2- and 4-formylphenols are in excellent agreement with the experimental results available in the literature with differences lower than 5 kJ/mol, supporting the computational strategy considered. Based on available experimental data for 2-formylphenol, a new value ($\Delta_f H_m^o(g) = -241.2 \pm 2.8$ kJ/mol) is suggested. The same approach was used in the calculation of enthalpies of isomerization of the formylphenols to several compounds, namely, benzoic acid, 1,3-benzodioxole, phenylformate, 2-furanacrolein, and tropolone and also in the calculation of C−H, N−H, and O−H bond dissociation enthalpies, enthalpies of deprotonation of the C−H, N−H, and O−H bonds, and ionization enthalpies. It was found that the C−H bond is the easiest to cleave in all compounds. Finally, the introduction of the formyl substituent in phenol and aniline is found to decrease the calculated enthalpies of deprotonation in the parent compounds, and the ionization enthalpies have values between those calculated for phenol or aniline and benzaldehyde. The calculated data for these properties are in very good agreement with experimental results.

1. Introduction

The thermodynamic properties of the derivatives of phenol and aniline (benzamine) are of relevant importance due to their impact as air pollutants and also due to their numerous industrial and biological applications. These compounds are widely used as antioxidants being their radicals important in many reactions. Furthermore, the derivatives of phenol and aniline are also important synthetic organic materials and used also in the synthesis of Schiff bases.

The present research work is devoted to the formyl derivatives of phenol and aniline,[1] a class of compounds for which thermodynamic data is scarce. In fact, only very recently, appeared in the literature two works[2,3] dealing with the energetics of 2-formylphenol,[2,3] and 4-formylphenol[3] (named 2- and 4-hydroxybenzaldehydes in ref 3; the ortho compound is also known as salicylaldehyde). Bernardes and Minas da Piedade[3] combined combustion and Calvet calorimetries and Knudsen effusion techniques to determine the enthalpies of formation in the condensed phase and the vaporization or sublimation enthalpies of 2- and 4-formylphenols (2-formylphenol is a liquid whereas the 4-isomer is a solid).[4] From these quantities, these authors derived the gas-phase enthalpies of formation showing that the 2-formylphenol ($\Delta_f H_m^o(g) = -238.3 \pm 2.5$ kJ/mol) is more stable than the 4-isomer ($\Delta_f H_m^o(g) = -220.3 \pm 2.0$ kJ/mol) by ~20 kJ/mol.[3] In parallel, the same authors complemented their work with a very complete computational thermochemical study obtaining estimates of the enthalpies of formation in the gas-phase and also O−H bond dissociation enthalpies (BDEs). From a very recent review of BDE values for several compounds,[5] it seems that BDEs for the formylphenols were not available before. The B3LYP/6-311++G(d,p) O−H ΔBDEs (relative to the BDE computed for phenol) reported by Bernardes and Minas da Piedade for 2- and 4-formylphenols are 36.7 and 9.9 kJ/mol, respectively.[3] Finally, they correlated the thermodynamic quantities obtained with a series of parameters such as interatomic distances, internal angles, electron densities at the bond critical point and Hammett constants. Unfortunately, these authors neglected completely the possible occurrence of C−H bond cleavage in these compounds. As we will see later on, C−H bond scission is energetically more favorable than O−H bond break in some compounds, as for example in 2-formylphenol. Ribeiro da Silva and Araújo,[2] employed similar experimental techniques and obtained a more negative gas-phase enthalpy of formation for 2-hydroxybenzaldehyde ($\Delta_f H_m^o(g) = -245.6 \pm 2.2$ kJ/mol). The difference between the experimental numbers available for 2-formylphenol is 7.3 kJ/mol which is due to a difference of 2.9 kJ/mol in the enthalpies of vaporization and 4.4 kJ/mol in the enthalpies of formation in the liquid state. Even this is not a quite large difference, it is large enough to cause problems when we are interested in the calibration of a computational approach for the estimation of thermochemical data or in the estimation by computational methods of enthalpies of formation for other compounds anchored on available experimental gas-phase enthalpies of formation of related molecules. As we have found very recently, the use of several reactions and computational approaches may help in the selection of experimental results available in the literature.[6] Thus, in the present work, we will try to suggest one $\Delta_f H_m^o(g)$ value for 2-formylphenol. Important for this discussion is the earlier work due to Stull,[7] performed in the range of temperatures between 306 and 470 K,[8] where the enthalpy of vaporization reported for 2-formylphenol is identical (at T = 298.15 K, difference is only 0.1 kJ/mol, value recalculated in ref 3) to that accounted more recently by Ribeiro da Silva and Araújo.[2] Other thermodynamic values available in the literature for the formylphenols are the gas-phase acidity (enthalpy and Gibbs free energy for the reaction of deprotonation) and the ionization energy (IE) for 4-formylphenol. The

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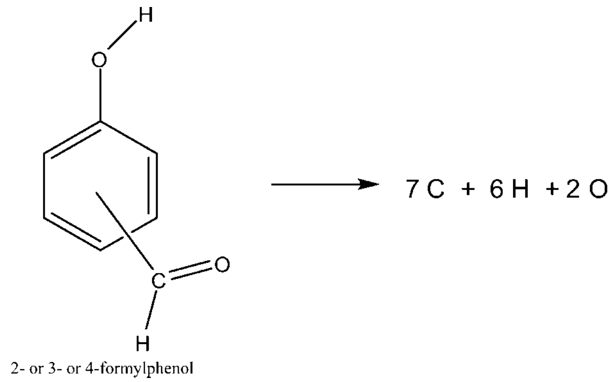

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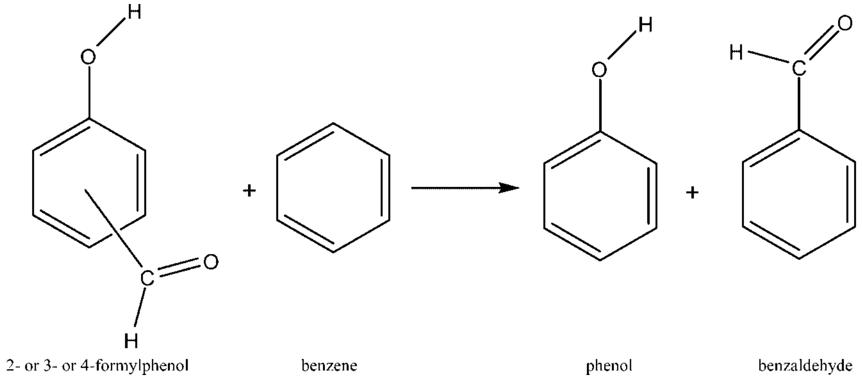


(2)

corresponding values are $\Delta H_{\mathrm{acid}}(\mathrm{g}) = 1393 \pm 9$ kJ/mol,[9,10] $\Delta G_{\mathrm{acid}}(\mathrm{g}) = 1364 \pm 8$ kJ/mol,[9,10] and IE = 899 ± 2 kJ/mol.[11,12]

With respect to the formylaniline (aminobenzaldehyde) isomers, at least to our knowledge, thermochemical results for these compounds are even scarcer. The exceptions are the vertical IE and the enthalpy of sublimation ($\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$, measured in the range of temperatures between 298 K − 318 K) available for *N*-formylaniline; the corresponding values are IE = 830 kJ/mol,[13,14] and $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$=78 kJ/mol.[15,16]

In the present work, computational thermochemistry is employed in the calculation of gas-phase standard enthalpies of formation and enthalpies of dissociation (O−H, N−H, and C−H), of deprotonation (acidity) and of ionization for the formylphenols and formylanilines. The data computed in the present work is used to support one of the two experimental gaseous enthalpies of formation for 2-formylphenol and is also used to fulfill lacks in the compilations of thermochemical data. Finally, comparison with results previously obtained for similar compounds,[17–22] and where intramolecular hydrogen bonding has important stabilization effects, is also performed.

2. Computational Details

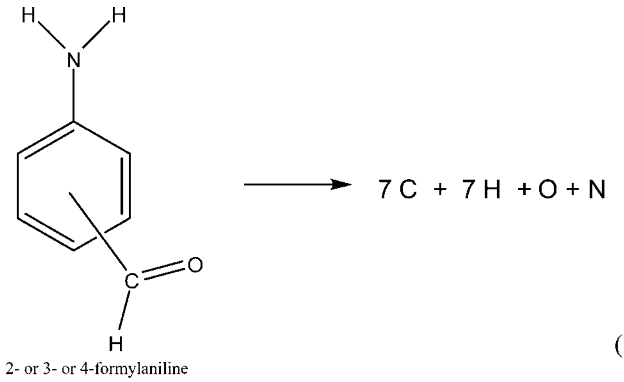
The G3(MP2)//B3LYP composite approach was used throughout this work.[23] The enthalpies of formation of the seven different molecules considered in this work were estimated after the consideration of several gas-phase reactions shown below: These reactions have been chosen on the basis of the available experimental thermochemical data for the compounds there used.

The computations carried out with the G3(MP2)//B3LYP 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 QCISD(T) energy is done in a manner that follows the Gaussian-3 philosophy, albeit using a second-order Moller−Plesset perturbation[24] instead of MP4 as in the original G3 method.[25] The composite calculations were carried out by means of the Gaussian 03 computer code.[26] The energies computed at $T = 0$ K were thermally corrected for $T = 298.15$ K by introducing the vibrational, translational, rotational, and pV terms. The vibrational term is based on the vibrational wave numbers calculated at the B3LYP/6-31G(d) level. The same computational approach was used to calculate also the ionization enthalpies, enthalpies of deprotonation (EoD, gas-phase acidities) and O−H, N−H and C−H BDEs. For that purpose, the G3(MP2)//B3LYP computations were also extended to cationic, anionic and radicalar species obtained from the parent formylphenols or formylanilines.

Finally, in order to clarify some data, additional calculations were performed with the B3LYP[27,28] approach, based on the density functional theory, together with the 6-311+G(2d,2p) basis set.[29]

3. Results and Discussion

The structures of the title compounds optimized with the G3(MP2)//B3LYP approach (B3LYP/6-31G(d) level of theory) are compared with the geometries optimized for phenol, aniline and benzaldehyde in Figure 1. The full set of Cartesian coordinates is given as Supporting Information. The molecules shown in this Figure may be divided in two different classes depending whether the structures are (i) planar or (ii) not planar. All the structures belong to the first class with the exceptions of aniline, 3-formylaniline and 4-formylaniline with dihedral angles $\angle(H_{13}-N_{10}-C_5-H_{14}) = 130.1°$, $\angle(H_{13}-N_{10}-C_5-H_{14}) = 132.6°$ and $\angle(H_{13}-N_{10}-C_5-H_{14}) = 138.3°$, respectively. In the cases of *N*-formylaniline and 2-formylaniline, the compounds are planar due to the presence of short $C_1-H_{12}\cdots O_{15}$ ($d = 2.249$ Å) and $N_2-H_{13}\cdots O_{15}$ ($d = 1.940$ Å) contacts, respectively, allowing additional delocalization throughout the six-member cycles ($\cdots H_{12}-C_1-C_2-N_7-C_{13}-O_{15}\cdots$ in *N*-formylaniline and $\cdots H_{13}-N_2-C_1-C_7-C_{12}-O_{15}\cdots$ in 2-formylaniline, Figure 1) fulfilled by those internal hydrogen bonds. These cycles



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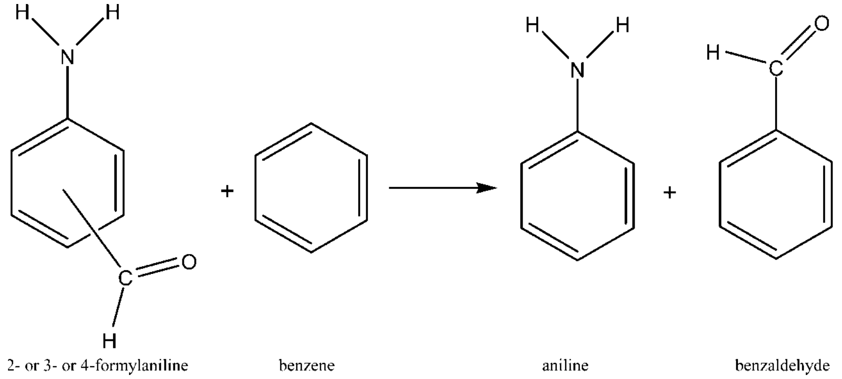


(4)

resemble that found in 2-formylphenol where a very short $O_2-H_{13}\cdots O_{14}$ contact (d = 1.751 Å) is calculated and those previously found in several different β-diketones.[30] In the latter compound, the vicinity between the adjacent OH and COH groups causes a shortening of the C−OH and C−COH bonds and an elongation of the C(H)=O bond when compared with the bond lengths in phenol and benzaldehyde, and may be regarded as evidence of electronic delocalization throughout the $\cdots H_{13}-O_2-C_1-C_3-C_8-O_{15}\cdots$ cycle.

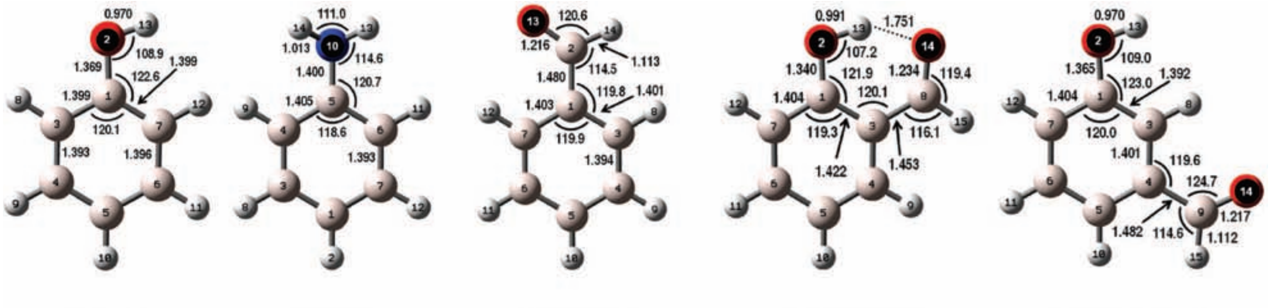
A global analysis of the structures depicted in Figure 1 shows that the differences between the geometric parameters calculated for 3- and 4-formyl derivatives of aniline and phenol are similar to those calculated for phenol, aniline and benzaldehyde. Nevertheless, it is important to point out here that the meta/para effects in the calculated structures are negligible but clearly seen, as noticed by the shortening of the C-OH bond lengths in the phenolic compounds (C-NH_2 in the case of the anilines) on going from phenol (aniline) to 3- and 4-formyl derivatives. In the cases of aniline and 3- and 4-formylanilines, the decrease of the C-NH_2 distance from aniline >3-formylaniline >4-formylaniline is accompanied by an increase of the HNCH dihedral angle (increase of the planarity of the amino group) showing evidence of some electron donation from the amino group to the COH substituent. This is accompanied by a small but noticeable decrease of the C-COH bond length in the 4-formyl derivatives of phenol and aniline.

The enthalpies of formation, calculated with the G3(MP2)//B3LYP approach and reactions of atomization or isodesmic (group substitution), for the three formylphenols and for the four formylanilines are compiled in Table 1. For all compounds, the results calculated with each of the reactions, i.e., atomization or group substitution, are almost identical with a maximum difference of only 4.3 kJ/mol.[31] Importantly, the calculated enthalpies of formation for 2- and 4-formylphenols are in excellent agreement with the available experimental data. In the case of the former compound, the calculated results lie between the two available experimental values.[2,3]

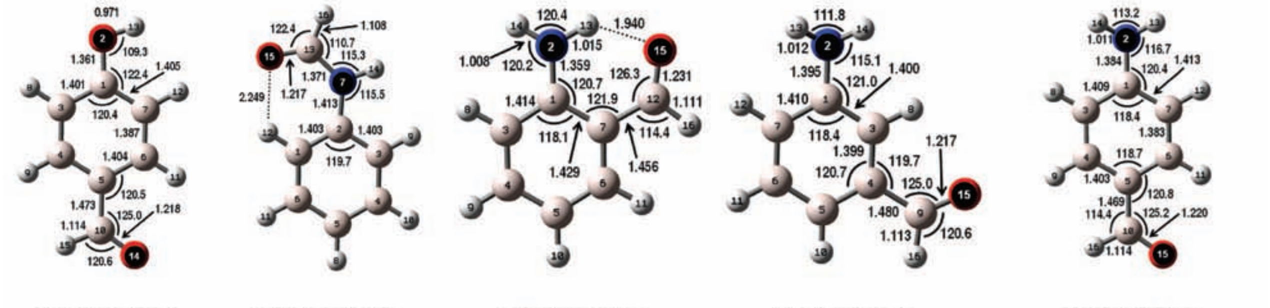
The gas-phase enthalpy of formation for 2-formylphenol calculated with the reaction of group substitution is −241.7 kJ/mol (this value is in principle more accurate than that calculated with the atomization reaction since the similarity between the reactants and products in the case of the reaction of group substitution may cancel systematic computational errors). Interestingly, this value differs by 3.4 kJ/mol from the experimental result determined by Bernardes and Minas da Piedade[3] and 4.9 kJ/mol from the result of Ribeiro da Silva and Araújo.[2] Since both groups have a solid background in thermochemical measurements, one is tempted to suggest that the best value for the enthalpy of formation of 2-formylphenol would be the mean of the two experimental results, i.e., $\Delta_f H_m^o(g)-242.0 \pm 3.3$ kJ/mol. More scientifically sound, this is the same as the sum of the enthalpies of formation in the condensed state due to Bernardes and Minas da Piedade[3] and of vaporization due to Ribeiro da Silva and Araújo[2] (or that of Stull[7]), which results in $\Delta_f H_m^o(g) = -241.2 \pm 2.8$ kJ/mol, not far from the mean value above.

In the case of the 4-formylphenol compound, the calculated enthalpy of formation with the group substitution differs by only 0.6 kJ/mol from the value due to Bernardes and Minas da Piedade.[3] This excellent agreement supports the results calculated for 2- and 3-formylphenols but also those calculated for the four formylanilines.

The comparison of the standard molar enthalpies of formation calculated for the three formylphenol isomers shows that the stability of the compounds varies in the order 2-formylphenol $\gg$ 4-formylphenol > 3-formylphenol, showing the importance of the intramolecular hydrogen bond in the stabilization of these compounds. Similarly, the 2-formylaniline is more stable than the para and meta isomers. The enthalpic difference between the enthalpies calculated for 2- and 3-formylanilines is $\Delta = \sim 16$ kJ/mol (either with the atomization or group substitution reactions) which may be compared with the difference ($\Delta = \sim 24$ kJ/mol) found in the case of the 2- and 3-formylphenols. These differences are related with the lengths of the intramo-



(a) phenol (b) aniline (c) benzaldehyde (d) 2-formylphenol (e) 3-formylphenol



(f) 4-formylphenol (g) *N*-formylaniline (h) 2-formylaniline (i) 3-formylaniline (j) 4-formylaniline

Figure 1. Selected geometrical parameters from G3(MP2)//B3LYP calculations (B3LYP/6-31G(d)) for phenol, aniline, benzaldehyde, formylphenols and formylanilines.

TABLE 1: Comparison between Calculated and Experimental Gas-Phase Enthalpies of Formation (kJ/mol) for Formylphenols and Formylanilines[a]

compound	atomization reaction[b]	group substitution[c]	experimental
2-formylphenol	−244.0 (5.7[d]; −1.6[e])	−241.7 (3.4[d]; −4.9[e])	−238.3 ± 2.5[d] −245.6 ± 2.2[e]
3-formylphenol	−220.0	−217.6	
4-formylphenol	−222.1 (0.8[d])	−219.7 (−0.6[e])	−220.3 ± 2.0[d]
N-formylaniline	−64.9	−60.7	
2-formylaniline	−55.2	−50.9	
3-formylaniline	−38.9	−34.7	
4-formylaniline	−43.3	−39.1	

[a] Difference between experimental and computational values is given inside parentheses. [b] Reactions described by eqs 1 and 3 for formylphenols and formylanilines, respectively. [c] Reactions described by eqs 2 and 4 for formylphenols and formylanilines, respectively. [d] Reference 3. [e] Reference 2.

lecular hydrogen bonds in the ortho compounds, which seem to be more effective in the case of 2-formylphenol than in the case of 2-formylaniline, and hence the stabilization in the former species is higher. The calculations show also that the most stable formylaniline is *N*-formylaniline, i.e., that with the COH group replacing one H atom from the amino group of aniline, with a gas-phase enthalpy of formation of −64.9 kJ/mol (atomization) or −60.7 kJ/mol (group substitution). The *N*-formylaniline species is ~10 kJ/mol more stable than the ortho isomer.

Gas-phase experimental standard molar enthalpies of formation, $T = 298.15$ K, exist in the literature for some isomers of formylphenol. i.e., values for benzoic acid, $\Delta_f H_m^o(g) = -294.0 \pm 2.2$ kJ/mol, 1,3-benzodioxole (methylenedioxybenzene), $\Delta_f H_m^o(g) = -142.7 \pm 2.9$ kJ/mol, phenyl formate (formic acid phenyl ester), $\Delta_f H_m^o(g) = -215.8 \pm 3.0$ kJ/mol, 2-furacrolein (3-(2-furyl)-2-propenal), $\Delta_f H_m^o(g) = -105.9 \pm 2.3$ kJ/mol, and tropolone (2-hydroxy-2,4,6-cycloheptatriene-1-one), $\Delta_f H_m^o(g) = -155.4 \pm 1.5$ kJ/mol. All these experimental values were taken from the compilation of thermochemical data due to Pedley.[32] We have combined these experimental $\Delta_f H_m^o$ with the G3(MP2)//B3LYP enthalpies of the reactions of isomerization (Supporting Information) in the estimation of the enthalpies of formation of the three different formylphenols. The full set of new standard molar enthalpies of formation for the formylphenols and the calculated enthalpies of isomerization are compared with available experimental data in Table S1 (Supporting Information). The calculated enthalpies of formation (values inside square brackets in Table S1) based on reactions S1, S3, S4 and S5 (Supporting Information) are practically the same; i.e., they are included in the intervals [−237.5; −240.2] kJ/mol in the case of 2-formylphenol, [−213.4; −216.1] kJ/mol in the case of 3-formylphenol, and [−215.5; −218.3] kJ/mol in the case of 4-formylphenol. These values are in excellent agreement with the calculated and experimental standard molar enthalpies of formation reported in Table 1, but shifted to more positive values by ~1−7 kJ/mol. When reaction S2 is considered (isomerization to 1,3-benzodioxole, Supporting Information), the calculated values are 15−20 kJ/mol more positive than the values calculated with the other four isomerization reactions, which is a consequence of the double ring in the products of the reaction described by equation S2, while in the reactants only a ring is present; the double ring is not present in the products of the reactions described by equations S1, S3, S4 and S5. The calculated enthalpies of formation reported in Table S1 (Supporting Information) for compounds 2- and 4-formylphenol give strong support to the $\Delta_f H_m^o(g)$ calculated for 3-formylphenol, and that was not determined by experimental thermochemistry

TABLE 2: Calculated Gas-Phase Bond Dissociation Enthalpies (BDE), Enthalpies of Deprotonation (EoD) and Ionization Enthalpies (IE)[a]

	BDE			EoD			
compound	C−H	N−H	O−H	C−H	N−H	O−H	IE
phenol			377.2 (365.1; 359.4)[b]			1462.2	832.0
aniline		391.1 (384.7; 379.0)[c]			1536.5		758.1
benzaldehyde	380.8 (380.1; 374.4)[d]			1625.5			936.4
2-formylphenol	390.5 (390.3; 384.7)		409.8 (401.6; 395.9)	1586.0		1431.1	850.6
3-formylphenol	382.4 (381.7; 376.1)		385.0 (373.7; 368.0)	1618.3		1424.1	863.4
4-formylphenol	380.8 (379.6; 374.0)		383.3 (375.1; 369.4)	1630.3		1395.3[e]	864.7[f]
N-formylaniline	393.3 (392.5; 386.8)	420.4 (408.5; 402.8)		1560.3	1453.8		816.8[g]
2-formylaniline	387.4 (384.6; 379.0)	412.0 (410.8; 405.1)		1626.4	1485.7		779.2
3-formylaniline	381.5 (380.9; 375.2)	397.2 (391.4; 385.8)		1631.1	1497.4		789.8
4-formylaniline	380.9 (378.6; 373.0)	397.5 (395.6; 389.9)		1641.3	1461.5		791.2

[a] All values were calculated with the G3(MP2)//B3LYP approach except those inside parenthesis that were calculated at the (RO)B3LYP/6-311+G(2d,2p)//(U)B3LYP/6-311+G(2d,2p) level of theory. The leftmost result inside the parentheses was calculated considering the exact energy of the hydrogen atom while the rightmost result was calculated using the B3LYP value.[37] [b] Available experimental results vary in the range [362.8; 378.2] kJ/mol.[5] There is not a definite value yet since two different groups support two different results, i.e., 371.3 ± 2.3 kJ/mol,[38] and 362.8 ± 2.9 kJ/mol.[39] [c] Available experimental results vary in the range [368.2; 386.2] kJ/mol.[5] Selected value in ref 5 is 375.3 kJ/mol.[40] [d] Available experimental results vary in the range [348.0; 383.1] kJ/mol.[5] Selected value in ref 5 is 371.1 ± 10.9 kJ/mol.[41] [e] Experimental result is 1393 ± 9 kJ/mol.[9,10] [f] Experimental result is 899 ± 2 kJ/mol.[11,12] [g] Experimental result is 830 kJ/mol.[13,14]

up to now. We suggest that the value −218.8 ± 3.8 kJ/mol,[33] should be considered in future compilations of thermochemical data.

The G3(MP2)//B3LYP approach was also considered for the calculation of bond dissociation enthalpies (BDE), enthalpies of deprotonation (EoD) and ionization enthalpies (IE) for the title compounds. The gas-phase values for these quantities are reported in Table 2 and structural data for the radicals and anions appear in the Supporting Information. Starting with the calculated BDEs for phenol (O−H BDE), aniline (N−H BDE) and benzaldehyde (C−H BDE), and by comparing them with the available experimental results, it is found that the G3(MP2)//B3LYP approach yields values that are systematically more positive than the recommended BDEs in the compilation of chemical bond energies due to Luo.[5] Nevertheless, in the cases of phenol and benzaldehyde, the calculated values are within the range of available experimental values. In the past, it was proposed that the use of the B3LYP approach together with a restricted-open formalism for the radicals was a good choice for the calculation of O−H BDEs of phenol and its derivatives.[34,35] The effect of the basis sets on the calculation of O−H BDEs with the B3LYP was also analyzed formerly and it was found that the consideration of large basis sets augmented with diffuse functions was a necessary condition for nice agreement with available experimental results.[36,37] Thus, for comparison purposes, we have also calculated the BDEs with the B3LYP approach and considering the 6-311+G(2d,2p) basis set (results inside parenthesis in Table 2). If the exact energy of the hydrogen atom is used, it is found that the B3LYP result for phenol lies between the two recommended values, that the B3LYP value for aniline is included in the range of available experimental data, and that the difference between the B3LYP and G3(MP2)//B3LYP values for benzaldehyde is almost negligible. If the B3LYP energy of hydrogen atom is considered, it is found that the calculated values are in much better agreement with the recommend values for benzaldehyde and aniline and also with the lowest result for phenol. Therefore, we suggest the readers to consider the results calculated with the B3LYP approach, together with the DFT energy of the hydrogen atom, as the best values included in Table 2. Thus, the data included in Table 2 show that the weakest bond in 2-formylphenol and in the four different formylanilines is the C−H bond of the COH substituent. Furthermore, depending on the computational approach, the C−H bond may be considered the weakest bond in 3- and 4-formylphenols. In the latest case, the uncertainty associated with the calculations lead us to suggest that the energy required to cleave the C−H (COH substituent) or N−H bonds is degenerate. At the G3(MP2)//B3LYP level of theory, the weakest bond is the C−H bond in 4-formylphenol while the B3LYP results predict the O−H bond in 3-formylphenol to be the easiest to break. Finally, considering only the BDEs of Table 2, the phenol compound is suggested to be the most effective antioxidant.

The gas-phase enthalpies of deprotonation (gas-phase acidities) reported in Table 2 show that the most acidic protons in the phenolic compounds are those of the O−H group while, in the anilines, the most acidic protons are those of the amino group. The enthalpic difference between the acidity of the ring−CO(−H) proton and ring−O(−H) protons is larger than 154 kJ/mol in the case of the formylphenols and the acidity of the ring−CO(−H) proton and ring−NH(−H) protons is larger than 106 kJ/mol in the case of formylanilines. Interestingly, the ring−O(−H) and ring−N(−H) protons are much more acidic in the formyl compounds than those in phenol and aniline, respectively. In the case of the ring−CO(−H) protons, these are more acidic than the same type of proton in benzaldehyde only in the cases of 2-formylphenol and *N*-formylaniline. Finally, it is encouraging that the lowest EoD calculated for 4-formylphenol is in excellent agreement with the available experimental result due to Fujio et al.[9,10] Furthermore, excellent agreement between theoretical and experimental deprotonation enthalpies was also found in previous works dealing with anilines and phenols.[17,18,21] These findings give additional support to the quality of the enthalpies of deprotonation reported in Table 2.

The calculated ionization enthalpies are also reported in Table 2, and it is found that the G3(MP2)//B3LYP values for the formyl derivatives of phenol and aniline are between the calculated numbers for phenol or aniline and benzaldehyde. Thus, the energy required to extract an electron in the phenol and aniline derivatives obtained by the introduction of a COH substituent increases, which is in agreement with the fact that the formyl group is known to be an electron acceptor. It is found that the calculated IEs for 4-formylphenol and *N*-formylaniline are lower than the experimental results by 34 and 13 kJ/mol, respectively. In a recent work dealing with the thermochemistry of the three fluoroanilines,[21] we found that the IE calculated with the G3(MP2)//B3LYP approach for 4-fluoroaniline was in excellent agreement with one of the experimental results (difference smaller than 3 kJ/mol) and that it differed by almost 30 kJ/mol from another experimental value.[21] Therefore, the present ionization enthalpies may be used with relative confidence.

4. Conclusions

The composite G3(MP2)//B3LYP approach was considered for the calculation of some thermochemical parameters of the formyl derivatives of phenol and aniline, which were compared with calculated data for phenol, aniline and benzaldehyde. The experimental gas-phase standard molar enthalpies of formation, at $T = 298.15$ K, of 2- and 4-formylphenols were used to check the computational approach used. The calculated gas-phase enthalpies using a group substitution reaction were −241.7 and −219.7 kJ/mol for 2- and 4-formylphenol conformers, respectively. These two values are in excellent agreement with the experimental results, i.e., −238.3 ± 2.3 kJ/mol or −245.6 ± 2.2 kJ/mol and −220.3 ± 2.0 kJ/mol, respectively. In the case of the 2-formylphenol compound, the calculated value is in excellent agreement with our suggested experimental value, $\Delta_f H^o_m(g) = -241.2 \pm 2.8$ kJ/mol, obtained from the experimental enthalpies of formation in the condensed state due to Bernardes et al.[3] and of vaporization due to Ribeiro da Silva and co-workers.[2] Therefore, the calculated enthalpies of formation for the 3-formylphenol and the four different formylanilines should be of very good quality. In the case of the formylphenols, five different reactions of isomerization were also used in the estimation of gas-phase enthalpies of formation and to support the values calculated either with atomization and group substitutions reactions.

Finally, the G3(MP2)//B3LYP approach was also used in the calculation of C−H, N−H, and O−H bond dissociation enthalpies, enthalpies of deprotonation of the C−H, N−H, and O−H bonds and ionization enthalpies. It was found that, at the G3(MP2)//B3LYP level of theory, the C−H bond is the easiest to cleave in all compounds. In the cases of 3- and 4-formylphenols, this picture is changed if the (RO)B3LYP/6-311+G(2d,2p)//(U)B3LYP/6-311+G(2d,2p) computational approach is used to calculate the BDEs and the O−H bond is weaker by ∼10 and 5 kJ/mol, respectively. Importantly, the O−H bond in phenol is much weaker than the C−H or N−H or O−H bonds in the title compounds. The introduction of the formyl substituent in phenol and aniline is found to decrease the calculated enthalpies of deprotonation in the parent compounds, and the ionization enthalpies have values between those calculated for phenol or aniline and benzaldehyde.

Supporting Information Available: A scheme showing the reactions of isomerization, Table S1, with calculated gas-phase enthalpies of isomerization and enthalpies of formation for the three formylphenols, tables with Cartesian coordinates (Table S2) and enthalpic data (Tables S3 and S4) for most stable configurations of all compounds, and Table S5 with the experimental $\Delta_f H^o_m(g)$. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Following the rules of organic nomenclature, the correct names for *N*-, 2-, 3- and 4-formylanilines are *N*-phenylformamide, 2-aminobenzaldehyde, 3-aminobenzaldehyde, and 4-aminobenzaldehyde, respectively, while the use of 2-, 3-, and 4-formylphenols is correct. In order to demonstrate that the same group is inserted in the structure of phenol or into aniline, *N*-, 2-, 3- and 4-formylaniline will be used throughout this work.

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