

Thermochemistry of Furancarboxylic Acids

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The relative stabilities of 2- and 3-furancarboxylic acids have been studied, using an experimental thermochemical investigation and high-level ab initio calculations. The enthalpies of combustion and sublimation of 2- and 3-furancarboxylic acids were measured and the gas-phase enthalpies of formation at 298.15 K were determined. Standard ab initio molecular orbital calculations at the G2(MP2) and G2 levels were performed, and a theoretical study on the molecular and electronic structures of the studied compounds has been conducted. Calculated enthalpies of formation, using atomization and isodesmic bond separation reactions, are compared with the experimental data. Experimental and theoretical results show that 3-furancarboxylic acid is thermodynamically more stable than the 2-isomer. A comparison of the substituent effect of the carboxylic group in benzene, thiophene, and furan rings has been made.

1. Introduction

Although thermochemistry is concerned with the evaluation of energetic changes in chemical reactions, thermochemical interest is not restricted to determination of the heat of reactions. One of the purposes of thermochemistry is to derive the enthalpies of formation of compounds from their elements, and to relate them to structure and chemical binding.^{1–3}

If benzenes are the paradigm of aromatic molecules,⁴ furans and thiophenes are the simplest representatives of stable aromatic structures that contain oxygen and sulfur.^{5a} Their structures can be assumed to be derived from benzene by the replacement of two annular CH groups by O or S, respectively. Furan and thiophene obey the $4n + 2\pi$ electron rule, and they are considered to be aromatic compounds. Mulliken population analysis of the π -electron distribution in furan and thiophene suggests a greater aromaticity of thiophene, relative to furan.⁵ This has been attributed to the size of the heteroatom, which determines the degree of delocalization of electron density in the ring. The commonly accepted order of aromaticity is as follows: benzene > thiophene > furan.

The study of the structural features of furan and its derivatives has received great attention, because of the presence of these units in a variety of natural and synthetic products. 2- and 3-Furancarboxylic acids have different applications. They have been used in cosmetic or pharmaceutical formulations for topical application, because their anti-inflammatory, anti-irritant, and antimicrobial effects.^{6a} They have also been used as compounds for enhancing plant resistance to stress.^{6b} Furancarboxylic acids have been proved as hypolipidemic agents.^{6c} 2-furancarboxylic acid also exhibits antitumor properties.^{6d}

However, the studies of energetics⁷ of furan derivatives are still scarce; the 2-furan derivatives are the main compounds that are studied. Thermochemical data, such as the enthalpy of formation, is often helpful in the understanding of the contrasting structural and reactivity trends exhibited by oxygen- and sulfur-containing compounds. In earlier work,⁸ we have studied the

energetics of 2- and 3-thiophenecarboxylic acids and their relationship with thiophene, in comparison to benzoic acid and benzene, concluding that the 2-isomer is destabilized, in comparison with the analogous substituted benzene, by 4.1 kJ mol⁻¹. In the case of the 3-isomer, we found that significant differences do not exist between the substituent effect produced by a carboxylic group in benzene and in thiophene in this position. The purpose of this work is to study the energetics of 2- and 3-furancarboxylic acids (2- and 3-furoic acids) and their relationship with furan, in comparison to benzoic and thiophenecarboxylic acids, and their relationship with benzene and thiophene, respectively.

The approach selected is a combination of the experimental determination of their enthalpies of formation and high-level ab initio calculations.

2. Experimental Section

2.1. Material and Purity Control. 2- and 3-Furancarboxylic acids (with mass fractions of 0.98 and 0.99, respectively) were commercially available from Lancaster. 2-Furancarboxylic acid was purified by crystallization twice: the first crystallization was from water and the second was from chloroform. 3-Furancarboxylic acid was purified by crystallization twice from water. The samples were carefully dried under vacuum at 50 °C. Determination of purities, as assessed by differential scanning calorimetry (DSC), using the fractional fusion technique,⁹ and gas chromatography (GC), indicated that the mole fraction of impurities in the compounds was <0.001. The samples were studied by DSC over the temperature range between $T = 258$ K and their fusion melting points ($T = 402.5$ K for 2-furancarboxylic acid and $T = 394.8$ K for 3-furancarboxylic acid); no transitions in the solid state were observed over the temperature range that was studied for each compound.

2.2. Procedure for Thermochemical Measurements. **2.2.1. Calorimetry.** An isoperibol calorimeter equipped with a static combustion bomb was used to measure the energy of combustion. The apparatus and procedure have been described in the work by Roux and co-workers.¹⁰ The initial temperature of the combustion experiments was chosen so that the final calorimeter

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TABLE 1: Physical Properties at $T = 298.15$ K

compound	M (g mol ⁻¹)	ρ (g cm ⁻³)	$(\partial V/\partial T)_p$ ($\times 10^{-7}$ dm ³ g ⁻¹ K ⁻¹)	c_p (J K ⁻¹ g ⁻¹)
cotton	27.700	1.5	9.69 ^a	1.48
2-furancarboxylic acid	112.0835	1.503 ^b	(3.354) ^c	1.17 ^d
3-furancarboxylic acid	112.0835	1.503 ^e	(3.354) ^c	1.14 ^d

^a Value taken from ref 13. ^b Value taken from ref 14. ^c Value in parentheses was estimated. ^d See ref 12. ^e Value taken from ref 15.

temperature would be near 298.15 K, and the energy of reaction was always referenced to the final temperature of 298.15 K. The energy equivalent of the calorimeter, ϵ (calor), was determined from the combustion of benzoic acid, using NIST Standard Reference Sample 39j, which has a massic energy of combustion, $\Delta_c u$, under the conditions specified on the NIST certification, of $-(26434 \pm 3)$ J g⁻¹. From nine calibration experiments, the ϵ (calor) value was determined to be (14271.8 ± 3.6) J K⁻¹, where the uncertainty quoted is the standard deviation of the mean. Frequent calibration experiments were made throughout the series of combustion experiments.

The energy of combustion of 2- and 3-furancarboxylic acids was determined, in the same way as the calibration experiments, by burning the solid samples, in pellet form, in oxygen inside the bomb, with 1 cm³ of water added. The combustion bomb was flushed and filled with oxygen to a pressure of $p = 3.04$ MPa. Under these conditions, no carbon or CO was found. The empirical formula and massic energy of combustion of our cotton-thread fuse—C_{1.000}H_{1.740}O_{0.870} and $-(17410 \pm 37)$ J g⁻¹, respectively—were determined in our laboratory. The nitric acid content in the bomb liquid was determined by titration with 0.1 mol dm⁻³ NaOH(aq). The corrections for nitric acid formation¹¹ were based on a value of -59.7 kJ mol⁻¹ for the standard molar energy of formation of 0.1 mol dm⁻³ HNO₃(aq) from N₂(g), O₂(g), and H₂O(l). All samples were weighed with a Mettler AT-21 microbalance, and apparent mass to mass corrections were made. After disassembly of the calorimeter, the bomb gases were slowly released and the absence of CO was checked with Dragër tubes (sensitivity level were $\sim 1 \times 10^{-6}$ mass fraction). For the apparent mass to mass corrections, conversion of the energy of the actual bomb process to that of the isothermal process, and correction to standard states, we have used the values of density (ρ), massic heat capacity (c_p), and $(dV/dT)_p$, respectively, that are given in Table 1. Heat capacities were determined by DSC in our laboratory.¹² Corrections to standard states were made according to Hubbard et al.¹⁶ The atomic weights of the elements were those recommended by IUPAC in 2000.¹⁷

A differential scanning calorimeter (model Pyris 1, Perkin–Elmer) equipped with an intracooler unit was used in this research, to measure the heat capacities of the compounds, to control the purity, and to study the phase transitions of the samples. Its temperature scale was calibrated by measuring the melting temperature of the recommended high-purity reference materials: hexafluorobenzene, benzoic acid, tin, and indium.^{18,19} The power scale was calibrated using high-purity indium (mass fraction of >0.99999) as reference material.^{18,19} Heat capacities were determined following the method that was described recently in the work of Roux et al.²⁰ After calibration, several runs with high-purity benzoic acid and indium as reference materials¹⁹ were performed under the same conditions as the experimental determinations, for checking throughout the entire process.

2.2.2. Knudsen-Effusion Method. The vapor pressures, as a function of temperature of the 2- and 3-furancarboxylic acids, were measured by a mass-loss Knudsen-effusion method, using

the procedure previously described in the work of Jiménez and co-workers.²¹ The Knudsen cell was placed into a stainless-steel sublimation chamber, which was connected to a high-vacuum system (1×10^{-4} Pa), and immersed in a bath that was thermostatically controlled to ± 0.005 K. The temperature for each experiment, T , is measured with a calibrated platinum resistance thermometer. The mass loss of the sample (Δm) during each effusion experiment was measured by weighing the cell before and after each effusion time period (t).

The vapor pressure (p) for each temperature T was calculated by means of the equation

$$p = \left(\frac{\Delta m}{W_a a t} \right) \left(\frac{2\pi RT}{M} \right)^{1/2} \quad (1)$$

where a is the area of the effusion orifice and W_a is the corresponding Clausing coefficient.²² The membrane for the measurements of vapor pressure was a tantalum foil with a length of $l = (0.021 \pm 0.004)$ mm. The area of the effusion orifice was $a = (0.799 \pm 0.003) 10^{-3}$ cm², and the Clausing coefficient²² was $W_a = (0.958 \pm 0.009)$.

2.2.3. Computational Details. Standard ab initio molecular orbital calculations²³ were performed with the Gaussian98 series of programs.²⁴ The energies of the studied compounds were calculated using Gaussian-2 theory, at the G2(MP2)²⁵ and G2²⁶ levels.

G2(MP2) and G2 correspond effectively to calculations at the QCISD(T)/6-311+G(3df,2p) level on MP2(full)/6-31G(d) optimized geometries, incorporating scaled HF/6-31G(d) zero-point vibrational energies and a so-called higher-level correction to accommodate the remaining deficiencies.

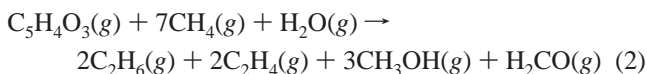
We have also reoptimized the geometries at the MP2(full)/6-31G(3df,2p) level, to obtain more-reliable molecular structures for the compounds studied.

The bonding characteristics of the compounds studied have been investigated using a population partition technique: the natural bond orbital (NBO) analysis of Reed and Weinhold.^{27,28} The NBO formalism provides values for the atomic natural total charges and describes the bonding in terms of the natural hybrids centered on each atom. The NBO analyses have been performed using the NBO program,²⁹ implemented in the Gaussian98 package. Calculations were performed on the MP2 charge densities, to explicitly include electron correlation effects.

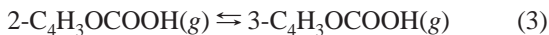
2.2.4. Theoretical Determination of Heats of Formation. In standard Gaussian- n theories, theoretical enthalpies of formation are calculated through atomization reactions. We have detailed this method in previous studies.^{30,31}

Raghavachari et al.³² proposed to use a standard set of isodesmic reactions—the “bond separation reactions”²³—to derive the theoretical enthalpies of formation. This method has been detailed in previous studies.^{30,31}

In the case of furancarboxylic acids, the bond separation reaction, using their classical valence bond structures, is as follows:



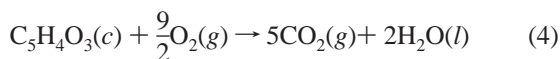
As it is evident, the 2- and 3-isomers have the same products, regardless of whether they are formed from atomization or bond separation reactions, so many errors are expected to cancel if one also examines the isomerization reaction:



3. Results and Discussion

The results of the combustion experiments for the 2- and 3-furancarboxylic acids are given in Table 2. The symbols in this table have the same meaning as those in the work by Westrum.³³ The experimental values have been derived in the same manner as those in ref 16. The energy of solution of carbon dioxide in water at 298.15 K, $\Delta_{\text{sol}}U(\text{CO}_2)$, was assumed to be $-17.09 \text{ kJ mol}^{-1}$, and the solubility constant, $K(\text{CO}_2)$, was assumed to be $0.03440 \text{ mol dm}^{-3} \text{ atm}^{-1}$ at 298.15 K.¹¹

Table 3 gives the derived molar energies and enthalpies of combustion that have been derived from the combustion reaction of 2- and 3-furancarboxylic acids, in the crystalline state at $T = 298.15 \text{ K}$, and correspond to the reaction



In accordance with the normal thermochemical practice, the uncertainties assigned are, in each case, twice the overall standard deviation of the mean and include the uncertainties in calibration.³⁴ To derive $\Delta_f H_m^\circ(\text{cr})$ from $\Delta_c H_m^\circ(\text{cr})$, the standard molar enthalpies of formation of $\text{H}_2\text{O}(\text{l})$ and $\text{CO}_2(\text{g})$ at $T = 298.15 \text{ K}$, which are $-(285.839 \pm 0.042)$ and $-(393.51 \pm 0.13) \text{ kJ mol}^{-1}$, respectively, were used.³⁵

The results of our Knudsen-effusion experiments for the 2- and 3-furancarboxylic acids are summarized in Table 4. An equation of the type

$$\ln p = -BT^{-1} + A \quad (5)$$

where p is given in pascals and T is given in Kelvin, was fitted to the results of Table 4 by the least-squares method. The quantities $\delta p/p$ are the fractional deviations of the experimental vapor pressures from those computed using eq 5. The greatest error for the vapor pressure p in Table 4 is $5 \times 10^{-3}p$, computed as the sum of the estimated errors of all quantities in eq 1. The parameters A and B for 2- and 3-furancarboxylic acids are given in Table 5. The enthalpies of sublimation at the mean temperature θ of their experimental ranges have been calculated from the corresponding B values and are also listed in Table 5. The uncertainties assigned to the values of $\Delta_{\text{sub}}H_m^\circ(\theta)$ are based on the standard deviations of the B values.

The sublimation enthalpy at $T = 298.15 \text{ K}$ was derived using the same equation as that in ref 36. The value of $C_{p,m}^\circ(\text{g})$ has been calculated using the group contribution scheme of Rihani,³⁷ and the value of $C_{p,m}^\circ(\text{cr})$ has been taken from the experimental results that were determined in our laboratory.¹²

The standard molar enthalpies of sublimation and formation in crystalline and gaseous states for 2- and 3-furancarboxylic acids at $T = 298.15 \text{ K}$ are given in Table 6. 2-Furancarboxylic acid has been previously studied by combustion calorimetry by Landrieu et al.³⁸ and Parks et al.³⁹ The value of the enthalpy of formation in the solid state, as determined by Landrieu et al.³⁸ and derived by Cox and Pilcher,¹ $-(503.3 \pm 2.1) \text{ kJ mol}^{-1}$, does not agree with our value within the bounds of the combined

uncertainties. The value reported by Parks et al.,³⁹ $-(498.4 \pm 1.1) \text{ kJ mol}^{-1}$, agrees well with that obtained in this work.

Vapor pressures of 2-furancarboxylic acid were determined by Bradley et al.⁴⁰ The value obtained for the enthalpy of sublimation, $(108.4 \pm 2.4) \text{ kJ mol}^{-1}$, is in disagreement with the value obtained in this work. No experimental data for the enthalpies of combustion and sublimation of 3-furancarboxylic acid have been found in the literature.

3.1. Molecular and Electronic Structures. Structural data, as measured by X-ray diffraction (XRD), for 2-furancarboxylic acid^{14,41,42} and 3-furancarboxylic acid¹⁵ have been described in the literature. In the crystal, both furancarboxylic acids are composed of centrosymmetric hydrogen-bonded dimers, which form approximately planar layers of molecules. In the case of 3-furancarboxylic acid, the dimers are held together by a system of two different types of long $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds that link ring H atoms with the carboxy and furan O atoms of the adjacent dimers, respectively, whereas in 2-furancarboxylic acid, the ring hetero O atom does not participate in the interdimer bonding system.¹⁵

The calculated molecular structures, optimized at the MP2-(full)/6-31G(3df,2p) level of theory, are planar for the two compounds that have been studied. They are shown in Figure 1. Bond distances and bond angles are collected in Tables S1 and S2 in the Supporting Information and are compared with the available experimental data. There is a very good agreement between the experimental and calculated geometric parameters for both compounds studied.

In both optimized structures, the O atom of the OH group is facing the O atom of the ring (see Figure 1). The corresponding rotational isomers with the O atom of the carbonyl group facing the O atom of the ring are very similar, in regard to energy. At the G2(MP2) level, the differences between both type of structures are only 0.5 and 1.3 kJ mol^{-1} for 2- and 3-furancarboxylic acids, respectively. A similar result was obtained by John and Radom⁴³ in an ab initio molecular orbital study on substituted furans. They concluded that the energy difference between the $\text{OCC}=\text{O}$ cis and trans isomers of 2-furancarboxylic acid is not very great, with a slight preference for the trans structure. These results are consistent with the experimental structures for thiophene and selenophene carboxylic acids,⁴⁴ in both of which the hydroxyl group faces the ring heteroatom. However, in 2-furancarboxylic acid, the experimental structure determined by Goodwin and Thomson,⁴¹ and refined by Hudson,⁴² using XRD, indicates that the configuration of the carboxyl group is reversed, with the carbonyl group facing the ring O atom ($\text{OCC}=\text{O}$ cis). In the last experimental determination of the crystal structure of 2-furancarboxylic acid, Gilmore et al.¹⁴ suggested that the dimensions of the carboxyl group imply that the H atom is disordered, as in benzoic acid. As John and Radom have noted,⁴³ these results are undoubtedly influenced by intermolecular hydrogen bonding and other solid-phase effects.

It is interesting to note that the valency angle on the furan O atom, $\text{C}_2\text{O}_3\text{C}_5$, is intermediate between the tetrahedral angle and a right angle. This fact is consistent with the three 2-compounds (furan, thiophene, and selenophenecarboxylic acids), where the experimental angles at the O, S, and Se atoms are 105.7° ,¹⁴ 92° ,⁴⁴ and 87° ,⁴⁴ respectively. These angles follow the same pattern that the $\text{H}-\text{X}-\text{H}$ angles in the simple hydrides: 103.4° , 92.3° , and 91.3° for $\text{X} = \text{O}, \text{S},$ and Se , respectively.⁴⁵ Note that had the $\text{C}-\text{O}-\text{C}$ angle been more tetrahedral, or even more similar to 120° , as a reflect trigonal (i.e., classical $\text{sp}^2 \pi$ atoms), the strain of the molecule would have been higher.

TABLE 2: Results of Combustion Experiments of the Two Furancarboxylic Acid Isomers at $T = 298.15\text{ K}^a$

Parameter	Value					
	2-Furancarboxylic Acid					
m' (compound) (g) ^b	0.959606	0.954213	0.948521	0.950775	0.956463	0.947108
m'' (fuse) (g) ^b	0.002484	0.002399	0.002401	0.002304	0.002404	0.002642
$\Delta T_c = T_f - T_i + \Delta T_{\text{corr}}$ (K)	-1.2275	-1.2208	-1.2136	-1.2167	-1.2237	-1.2123
ϵ (calor) ($-\Delta T_c$) (kJ) ^c	-17.5188	-17.4236	-17.3198	-17.3641	-17.4647	-17.3020
ϵ (cont.) ($-\Delta T_c$) (kJ) ^d	-0.0203	-0.0202	-0.0201	-0.0201	-0.0202	-0.0200
ΔU_{ign} (kJ) ^e	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008
ΔU_{dec} (HNO ₃) (kJ) ^f	0.0016	0.0015	0.0011	0.0012	0.0012	0.0008
ΔU (corrected to standard states) (kJ) ^g	0.0174	0.0173	0.0172	0.0172	0.0173	0.0171
$-m'' \Delta_c u^\circ$ (fuse) (kJ)	0.0433	0.0418	0.0419	0.0402	0.0419	0.0461
$\Delta_c u^\circ$ (compound) (kJ g ⁻¹)	-18.2117	-18.2165	-18.2166	-18.2218	-18.2168	-18.2210
$\langle \Delta_c u^\circ (298.15\text{ K}) \rangle$ (kJ g ⁻¹)			-18.2174 ± 0.0015			
	3-Furancarboxylic Acid					
m' (compound) (g) ^b	0.928742	0.928282	0.934601	0.969560	0.927772	0.942960
m'' (fuse) (g) ^b	0.002261	0.002260	0.002203	0.002267	0.002513	0.002695
$\Delta T_c = T_f - T_i + \Delta T_{\text{corr}}$ (K)	-1.1854	-1.1861	-1.1928	-1.2382	-1.1847	-1.2052
ϵ (calor) ($-\Delta T_c$) (kJ) ^c	-16.9173	-16.9276	-17.0235	-17.6720	-16.9078	-17.2003
ϵ (cont.) ($-\Delta T_c$) (kJ) ^d	-0.0195	-0.0196	-0.0197	-0.0205	-0.0195	-0.0199
ΔU_{ign} (kJ) ^e	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008
ΔU_{dec} (HNO ₃) (kJ) ^f	0.0009	0.0008	0.0012	0.0007	0.0011	0.0009
ΔU (corrected to standard states) (kJ) ^g	0.0168	0.0168	0.0169	0.0176	0.0168	0.0171
$-m'' \Delta_c u^\circ$ (fuse) (kJ)	0.0394	0.0394	0.0384	0.0395	0.0438	0.0470
$\Delta_c u^\circ$ (compound) (kJ g ⁻¹)	-18.1739	-18.1941	-18.1745	-18.1875	-18.1778	-18.1922
$\langle \Delta_c u^\circ (298.15\text{ K}) \rangle$ (kJ g ⁻¹)			-18.1833 ± 0.0037			

^a For a definition of the symbols, see refs 16 and 33. $T_{\text{th}} = 298.15\text{ K}$, $V_{\text{bomb}} = 0.380\text{ dm}^3$, $p_{\text{gas}} = 3.04\text{ MPa}$, and $m_{\text{water}}^i = 10.00\text{ g}$. ^b Masses obtained from apparent mass. ^c ϵ (calor) represents the energy equivalent of the entire system, less the content of the bomb. ^d ϵ (cont.) represents the energy equivalent of the content of the bomb: ϵ (cont.) ($-\Delta T_c$) = ϵ^i (cont.) ($T^i - 298.15\text{ K}$) + ϵ^i (cont.) ($298.15\text{ K} - T_f + \Delta T_{\text{corr}}$). ^e Experimental energy of ignition. ^f Experimental energy of formation of nitric acid. ^g ΔU (corrected to standard states) is the sum of items 81–85, 87–90, 93, and 94 in ref 16.

TABLE 3: Standard Molar Energy of Combustion and Enthalpies of Combustion and Formation at $T = 298.15\text{ K}$

compound	$\Delta_c U_m^\circ$ (kJ mol ⁻¹)	$\Delta_c H_m^\circ$ (kJ mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ mol ⁻¹)
2-furancarboxylic acid	-2041.9 ± 1.3	-2040.7 ± 1.3	-498.5 ± 1.4
3-furancarboxylic acid	-2038.1 ± 1.5	-2036.9 ± 1.5	-502.4 ± 1.6

The entire carboxyl group seems to be attracted by the ring O atom in 2-furancarboxylic acid, with the angles C₁–C₂–C₃ and C₂–C₁–O₁ being larger than C₁–C₂–O₃ and C₂–C₁–O₂, respectively (see Tables S1 and S2 in the Supporting Information). A consequence of these differences is an abnormal nonbonded contact between the O atom of the OH group and the ring O atom.¹⁴ This O₂–O₃ distance, 2.62 Å, is shorter than the sum of the van der Waals radii (3.04 Å).⁴⁶ This same behavior has been observed in a previous study on 2-thiophenecarboxylic acid.⁸

Both the furan ring and the carboxyl group have electrons with orbitals of π -symmetry and it would thus be expected that conjugation would occur, provided the groups were coplanar. Therefore, planar molecules are favored, and this has been observed in furancarboxylic acids.^{14,15,41,42} Only Gilmore et al.¹⁴ have reported a slight deviation of the COOH group, with respect to the plane of the furan ring. In both compounds, there is resonance between the furan O atom and the COOH group through the ring,⁴⁷ as it is represented in Figure 2. If this hypothesis is correct, the bond between C₃ and C₄ in 2-furancarboxylic acid would have more double-bond character than the same bond in 3-furancarboxylic acid. This fact is observed in the experimental structures, in that the C₃–C₄ bond length is slightly shorter in 2-furancarboxylic acid (1.411 Å vs 1.429 Å). Similarly, the C₅–O₃ bond length should be shorter in the 2-isomer and C₂–O₃ should be shorter in the 3-isomer. The calculated and experimental values follow this pattern (see Tables S1 and S2 in the Supporting Information).

We have also calculated the Wiberg bond indices,⁴⁸ B_i . The bond index between two atoms is a measure of the bond order

and, hence, of the bond strength between these two atoms. They are shown in Figure 3. As can be seen, the bond orders are consistent with the previous hypothesis, and the C₃–C₄ bond has more double-bond character in 2-furancarboxylic acid.

The length of the bond C₁–C₂ (or C₁–C₃) linking the carboxyl group to the furan ring indicates that conjugation occurs between the two parts of the molecule. One result of this would be to shorten still further one or both of the C–O₃ bonds, and the C₃–C₄ bond, in the furan ring of furancarboxylic acids from the lengths observed in furan itself (C–O bond length is 1.362 Å, as measured by microwave spectroscopy,^{49,50} and 1.368 Å, as measured by electron XRD;⁵¹ C₃–C₄ bond length is 1.431 and 1.430 Å, as measured by microwave spectroscopy,^{49,50} and 1.428 Å, as measured by XRD⁵¹). This shortening is observed in the calculated values; however, some of the experimental results are inconclusive. Goodwin and Thomson have noted⁴¹ that a high electron concentration of furancarboxylic acids in these bonds is suggested by the relatively large dissociation constants ($\text{p}K_{\text{a}}$ values in aqueous solution of 2- and 3-furancarboxylic acids, at 20 °C: 3.15 and 3.97, respectively, as determined by potentiometry),⁵² as compared with that of benzoic acid ($\text{p}K_{\text{a}} = 4.19$, at 25 °C).⁴⁶ However, that conjugation should have the opposite effect. Electron donation to the carboxyl group should destabilize the anion more than the neutral acid, according to the resonance forms given in Figure 2. Therefore, the enhanced acidity of both the furoic and thiophenecarboxylic acids is probably due to the fact that the inductive effect of the heteroatom is more influential than the resonance effect and it decreases with the distance (2-furoic acid is more acidic than the 3-isomer).

To our knowledge, there are three experimental determinations of the infrared spectra of 2-furancarboxylic acid^{53–55} and two in the case of 3-furancarboxylic acid.^{55,56} We have collected the experimental vibrational frequencies and the calculated frequencies at the HF/6-31G(d) level, scaled by the factor 0.8953 that has been recommended by Scott and Radom,⁵⁷ for both

TABLE 4: Vapor Pressures of Furancarboxylic Acids

temperature, T (K)	time for experiment, t (s)	mass of sublimed substance, Δm (mg)	vapor pressure, p (Pa)	$10^2(\delta p/p)^a$
2-Furancarboxylic Acid				
284.65	39600	0.884	0.106	-0.616
289.04	33600	1.22	0.175	0.868
292.37	29700	1.603	0.260	0.677
295.01	30120	2.36	0.380	
297.89	29700	3.26	0.535	-1.23
300.72	28800	4.57	0.776	0.0653
303.9	29340	6.48	1.08	0.116
3-Furancarboxylic Acid				
282.84	36000	2.11	0.279	0.635
285.83	32700	2.79	0.408	-1.60
288.78	31200	3.87	0.596	0.242
292.27	26700	5.01	0.905	-1.38
294.81	24300	6.30	1.26	0.477
297.81	21600	7.96	1.80	0.391

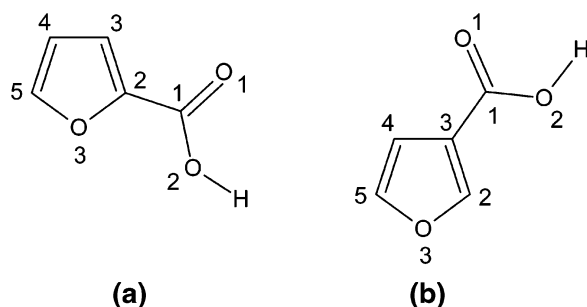
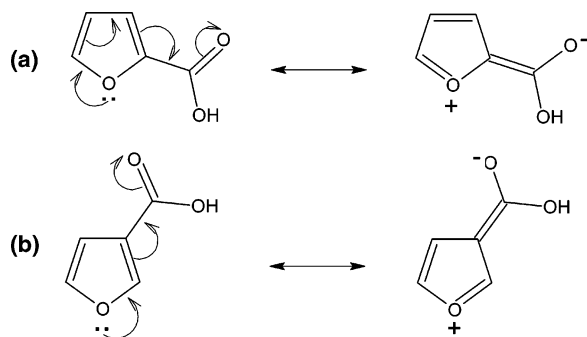
^a δp denotes deviation of the experimental vapor pressures from the values computed using eq 5.

TABLE 5: Molar Enthalpies of Sublimation

compound	θ (K)	A	B	$\Delta_{\text{sub}}H_m^\circ(\theta)$ (kJ mol ⁻¹)
2-furancarboxylic acid	294.28	35.1 ± 0.6	10635.0 ± 181.5	88.4 ± 1.5
3-furancarboxylic acid	290.33	35.8 ± 0.2	10479.7 ± 55.1	87.1 ± 0.5

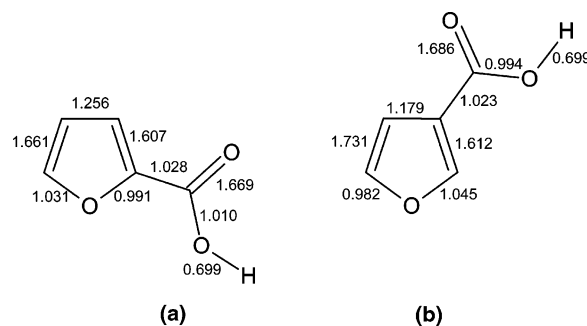
TABLE 6: Standard Molar Enthalpies at $T = 298.15$ K

compound	$\Delta_f H_m^\circ(\text{cr})$ (kJ mol ⁻¹)	$\Delta_{\text{sub}} H_m^\circ$ (kJ mol ⁻¹)	$\Delta_f H_m^\circ(\text{g})$ (kJ mol ⁻¹)
2-furancarboxylic acid	-498.5 ± 1.4	88.2 ± 1.5	-410.3 ± 2.1
3-furancarboxylic acid	-502.4 ± 1.6	86.6 ± 0.5	-415.8 ± 1.7

**Figure 1.** Molecular conformations of the two studied compounds: (a) 2-furancarboxylic acid and (b) 3-furancarboxylic acid.**Figure 2.** Resonance structures of (a) 2-furancarboxylic acid and (b) 3-furancarboxylic acid.

studied compounds, in Tables S3 and S4 of the Supporting Information. An assignment of the frequencies to the different normal vibrational modes of the molecules is beyond the scope of this work.

In the investigation of the electronic structure of the five-membered ring heterocycles, understanding of the π -system is of basic importance. The rings are aromatic, according to Hückel's rule. The π -system can be built from four electrons

**Figure 3.** Wiberg bond indices calculated for (a) 2-furancarboxylic acid and (b) 3-furancarboxylic acid, calculated at the MP2(full)/6-31G-(3df,2p) level.

provided by the π -molecular orbitals of the *cis*-butadiene fragment and two electrons that originate from the p_z lone pair orbital of the heteroatom.⁵⁸ The other heteroatom lone pair is incorporated into the σ -system.

We have performed a population analysis, using the natural bond orbital (NBO) analysis,^{27,28} to obtain the natural atomic charges (the nuclear charges minus the summed natural populations of the natural atomic orbitals on the atoms) that characterize the ground electronic state of the furancarboxylic acids. The calculated charges located at the heavy atoms for both compounds are reported in Figure 4. As can be seen, the negative charge is located at the three O atoms and at the C₃ and C₄ atoms of the furan ring, being more negative in the case of the carboxylic O atoms. The positive charge is located, overall, at the C atom of the COOH group, and also at the C atoms of the ring that are bonded to the O atom. The charge distribution does not appreciable change with the position of the carboxylic group; only a small charge redistribution occurs on the atoms of the furan ring.

The NBO analysis also describes the bonding in terms of the natural hybrid orbitals. In the compounds that have been studied, the hybridization of the furan O atom is sp^2 , with ca. 67% of the structure having p character, whereas the hybridization of carbonyl O atoms is $sp^{1.4}$, with only 58% of the structure having p character, and that of the hydroxylic O atoms is similar to sp^2 to form the C–O bonds and $sp^{3.4}$ to form the O–H bonds.

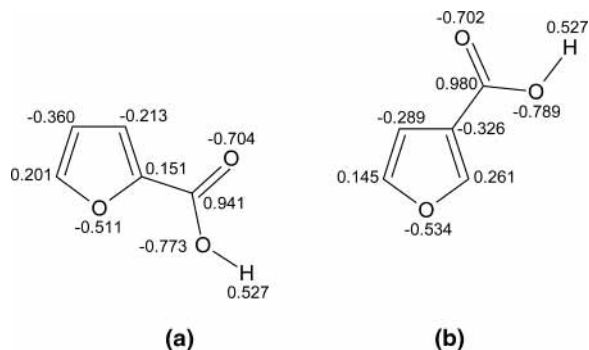


Figure 4. NBO atomic charges calculated for (a) 2-furancarboxylic acid and (b) 3-furancarboxylic acid, calculated at the MP2(full)/6-31G(3df,2p) level.

A comparison of furancarboxylic acids with thiophenecarboxylic acids shows that the hybridization of the O atoms of the COOH group is exactly the same, but there is a great difference with respect to the heteroatom of the ring. In thiophenecarboxylic acids, the hybridization of the S atom is sp^4 , with more than 78% of the structure having p character.

O atoms have sp ($sp^{0.7}$, $sp^{1.3}$, and $sp^{1.9}$ in the case of O₁, O₂, and O₃ atoms, respectively) and p lone pairs that may delocalize into the vicinal antibonding orbitals. Through orbital occupancies and second-order perturbation energy lowering, ΔE^2 , which is due to the interaction of the donor and acceptor orbitals, one can fix the exact orbitals that are involved in the charge-transfer process. Occupancies and energy lowerings of the orbitals involved in the delocalization of the lone pairs of O atoms in 2- and 3-furancarboxylic acids are shown in Table S5 of the Supporting Information.

Several studies on compounds that involve atoms with different types of lone pairs (O, S, Se) have shown that the effect of the charge delocalization should not be analyzed only on the basis of $p_x \rightarrow \sigma_{CX}^*$ hyperconjugations, because orbital interactions that involve sp lone pairs, that is, $sp_x \rightarrow \sigma_{CX}^*$, are not negligible.⁵⁹ This behavior is observed in the compounds studied.

Figure 5 presents the electrostatic potential contours for the studied compounds. Most relevant, the regions of highest electron density (V_{\min}) are easily located and assigned to the lone electron pairs on O atoms. These are the regions in the molecules studied that are subject to electrophilic attack.

An important characteristic of the ground electronic state of a molecule is the ionization potential (IP). The first IP for 2-furancarboxylic acid has been experimentally determined⁶⁰ by means of photoelectron spectroscopy. There are two experimental vertical values: 9.16 eV^{60a} and 9.32 eV.^{60b}

We have calculated the IP values for the studied compounds, according to Koopmans' theorem.^{61,62} The IPs and the electron affinities (EAs) correspond approximately to the negatives of the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively.

$$IP = -E_{\text{HOMO}} \quad (6a)$$

$$EA = -E_{\text{LUMO}} \quad (6b)$$

The calculated IP value for 2-furancarboxylic acid is 9.08 eV, obtained at the MP2(full)/6-31G(3df,2p) level, and it is in good agreement with one of the experimental values. For 3-furancarboxylic acid, we have obtained an IP value of 9.09 eV. Comparing these values with those calculated for 2- and

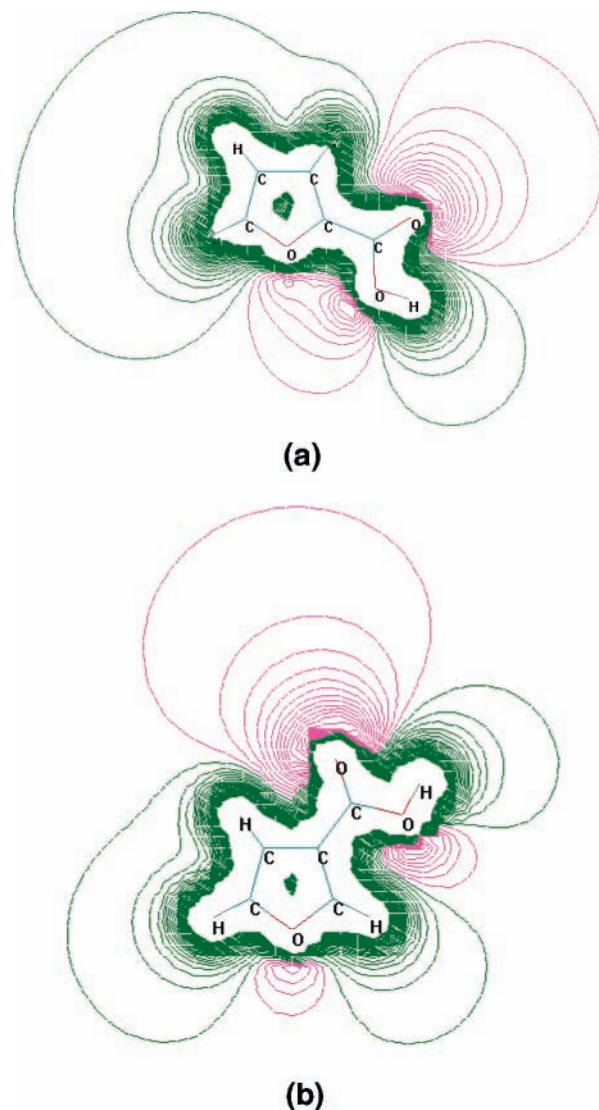


Figure 5. Electrostatic potential contours obtained for (a) 2-furancarboxylic acid and (b) 3-furancarboxylic acid.

3-thiophenecarboxylic acids (9.24 and 9.22 eV, respectively),⁸ there is a HOMO stabilization when S is the heteroatom in the ring.

Electron affinities of -2.57 and -3.11 eV have been obtained for 2- and 3-furancarboxylic acids, respectively.

3.2. Theoretical Enthalpies of Formation. G2(MP2)²⁵ and G2²⁶ calculated energies, at 0 K, for 2- and 3-furancarboxylic acids are given in Table 7. To calculate enthalpy values at 298 K, the difference between the enthalpy at temperature T and 0 K can be evaluated according to standard thermodynamics.⁶³ G2(MP2) and G2 enthalpies at 298 K, for the compounds studied, are also collected in Table 7.

It has been reported^{32,64-66} that the G2 family of computational methods (notably G2(MP2)²⁵ and G2²⁶ itself), allows the reliable estimation of the standard enthalpies of formation in the gas phase of a variety of compounds. In many cases, the computed magnitudes agree with the experimental data, within ~ 7.5 kJ mol⁻¹.⁶⁶

We have obtained, in this study, theoretical values of the enthalpy of formation of both compounds studied at G2(MP2) and G2 levels of theory, using both of the aforementioned methods. The values calculated using atomization reactions have been modified introducing spin-orbit corrections and bond additivity corrections (BAC).⁶⁷ This procedure has been detailed

TABLE 7: G2(MP2)- and G2-Calculated Energies at 0 K (E_0) and Enthalpies at 298 K (H_{298}) for the Compounds Studied

compound	G2(MP2)		G2	
	E_0	H_{298}	E_0	H_{298}
2-furancarboxylic acid	-417.974397	-417.966954	-417.984425	-417.976982
3-furancarboxylic acid	-417.976298	-417.968834	-417.986290	-417.978827

TABLE 8: G2(MP2)- and G2-Calculated Enthalpies of Formation of the Compounds Studied, Both from Atomization and from Bond Separation Isodesmic Reactions^a

compound	G2(MP2)		G2		experiment
	atomization	bond separation	atomization	bond separation	
2-furancarboxylic acid	-409.6	-404.2	-411.9	-408.1	-410.3 ± 2.1
3-furancarboxylic acid	-414.5	-409.2	-416.8	-413.0	-415.8 ± 1.7

^a All values given in units of kJ mol^{-1} .

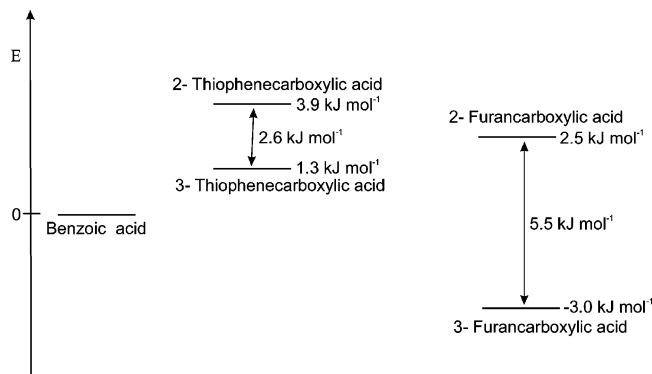
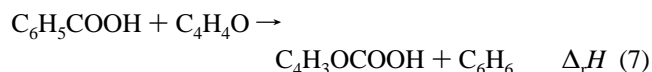


Figure 6. Comparison in the energetic effects observed in 2-furancarboxylic acid, 3-furancarboxylic acid, and thiophenecarboxylic acid in reference with benzoic acid.

in a previous study.⁶⁸ Calculated and experimental values obtained are shown in Table 8. This table shows that the $\Delta_f H_m^\circ$ values for 2- and 3-furancarboxylic acids, calculated from G2(MP2) and G2 energies using both theoretical schemes, are in very good agreement with the experimental values, although the best values were obtained using atomization reactions. In thiophenecarboxylic acids,⁸ the best agreement between experimental and theoretical values were also obtained at the G2 level, using atomization reactions. Comparison of our experimental and theoretical results for the enthalpies of formation of the two isomers of furancarboxylic acids shows that the 3-furancarboxylic acid is more stable, thermodynamically, than the 2-isomer. This same behavior has been observed in the isomers of thiophenecarboxylic acid. The isomerization enthalpy obtained from reaction 3 gives a value of -5.5 kJ mol^{-1} from experimental results. From theoretical calculations at both the G2(MP2) and G2 levels, a value of -4.9 kJ mol^{-1} is obtained. The agreement between both values is excellent.

Our experimental results allow us to make a comparative analysis with the analogous substituted benzene. This can be done by the evaluation of the energetic of reaction 7:



Using the enthalpies of formation taken from the literature for benzene ($82.7 \pm 1.1 \text{ kJ mol}^{-1}$),⁷ benzoic acid ($-295.4 \pm 0.2 \text{ kJ mol}^{-1}$),⁶⁹ and furan ($-34.7 \pm 0.6 \text{ kJ mol}^{-1}$),^{1,7} we obtain the values given in Figure 6. This figure shows the comparison in the energetic effects observed in 2- and 3-furancarboxylic acids and thiophenecarboxylic acid⁸ in reference with benzoic acid. In the five-membered heterocyclic compounds, the 3-carboxylic isomers are more stable than the 2-isomers. The

substitution of an H atom for a COOH group in the furan ring in the 3-position produces a slightly larger stability than that from substitution of a carboxyl group in a benzene ring. 2-Furancarboxylic acid is destabilized by 2.5 kJ mol^{-1} , probably because of the through-space interaction between the O atom of hydroxyl group with the O atom of the ring, whereas 3-furancarboxylic acid is stabilized by 3.0 kJ mol^{-1} .

The differences between the relative stability energies for furancarboxylic and thiophenecarboxylic acids can also be evaluated from reaction 8:



Using the enthalpies of formation of thiophene ($115.0 \pm 1.0 \text{ kJ mol}^{-1}$),⁷ furan ($-34.7 \pm 0.6 \text{ kJ mol}^{-1}$),^{1,7} 2- and 3-thiophenecarboxylic acids (-259.2 ± 1.9 and $-261.8 \pm 1.7 \text{ kJ mol}^{-1}$, respectively),⁸ the enthalpies of reaction ($\Delta_r H$) for reaction 8 for the 2- and 3-isomers are -1.4 and -4.3 kJ mol^{-1} , respectively. In both cases, 2- and 3-furancarboxylic acids are more stable than the corresponding thiophenecarboxylic acids.

4. Conclusions

The experimental enthalpies of formation of 2- and 3-furancarboxylic acids have been determined. Theoretical calculations of the enthalpies of formation at the G2(MP2) and G2 levels agree well with the experimental values. The best agreement was obtained using atomization reactions. From experimental and theoretical results, 3-furancarboxylic acid is more stable than the 2-isomer.

Molecular and electronic structures for the compounds studied have been obtained from theoretical calculations. The entire carboxyl group seems to be attracted by the furan O atom in 2-furancarboxylic acid. The O atom of the OH group is facing the heteroatom of the ring. The O—O bond distance is shorter than the sum of the van der Waals radii. This attraction does not occur in the 3-isomer.

Comparison of experimental and theoretical enthalpies of formation shows that furancarboxylic acid isomers are more stable than the corresponding thiophenecarboxylic acids.

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Supporting Information Available: Tables S1 and S2 show the calculated and experimental bond distances and bond angles, Tables S3 and S4 show the calculated and experimental vibrational frequencies, and Table S5 show the results of the

NBO analysis (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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