# Energetic Study Applied to the Knowledge of the Structural and Electronic Properties of Monofluorobenzonitriles

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S *Supporting Information*
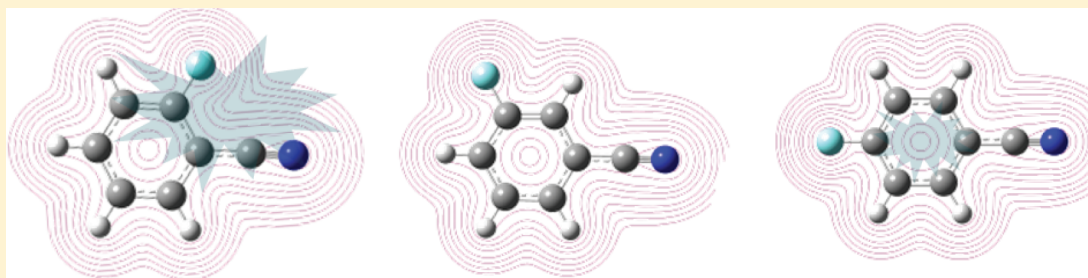
ABSTRACT: The present work reports an energetic and structural study of 2-fluoro-, 3-fluoro-, and 4-fluorobenzonitrile. The standard molar enthalpies of formation, in the condensed phase, of the three isomers were derived from the standard molar energies of combustion, in oxygen, at T = 298.15 K. The standard molar enthalpies of vaporization or sublimation (for 4-fluorobenzonitrile), at T = 298.15 K, were measured using high-temperature Calvet microcalorimetry. The combination of these two parameters yields the standard molar enthalpies of formation in the gaseous phase. The vapor-pressure study of the referred compounds was performed by a static method, and the enthalpies of phase transition derived from the application of the Clarke and Glew equation. Theoretically estimated gas-phase enthalpies of formation, basicities, proton and electron affinities, and adiabatic ionization enthalpies were calculated from the G3MP2B3 level of theory. In order to evaluate the electronic properties, the geometries were reoptimized at MP2/cc-pVTZ level, and the QTAIM and NICS were computed. On the basis of the donor−acceptor system, another approach for evaluating the electronic effect for these compounds, using the NBO is suggested. The UV−vis spectroscopy study for the three isomers was performed. The intensities and the band positions were correlated with the thermodynamic properties calculated computationally.

■ INTRODUCTION

The high electronegativity of the fluorine atom strengthens the C−F bonds, giving to the organic compounds greater thermal and oxidative stability.[1] The small size of the fluorine atom together with its physical−chemical properties makes the fluorine atom behave like a polar hydrogen. Across the years, the substitution of hydrogen by a fluorine atom has been a strategy applied to the improvement of biologic activity in pharmaceutical products. The fluorinated benzonitrile isomers are involved in synthesis of inhibitors of the parasitic enzyme of *Trypanosoma cruzi* responsible for Chagas' disease[2] as well as of other inhibitors used in cancer therapy and in treatment of tumors displaying mutated proteins[3,4] and, even, in a new potential type of antidiabetic agent without side effects such as hypoglycemia.[5] The fluorobenzonitrile derivatives also play an important role in the structure of the nonsteroidal ligands of the progesterone receptor, offering great potential for tissue and receptor selectivity and, therefore, reducing the side effects of the steroidal progestins.[6,7] These benzonitrile derivatives also embrace the synthetic precursors of antifungal against *Candida*, *Aspergillus*, and *Cryptococcus* species.[8,9]

Beyond the study of the effect of the benzonitrile derivatives in the synthesis of products with relevant biologic activity, over the past years, exhaustive electrochemical studies have been performed,[10−13] and the molecular structures of the fluorobenzonitriles[14−19] have been the subject of intense work not only at the experimental level but also at the computational level.

The aim of the present work is to contribute to the knowledge of the thermodynamic and thermochemical properties of the 2-, 3-, and 4-fluorobenzonitrile isomers in order to better understand the energetic nature of their bonds and the change of the electron density of benzonitrile when a hydrogen atom is replaced by a fluorine atom in different positions.

More and more, the development of computational chemistry has made remarkable progress, being able to reproduce even better the electronic effects present in the molecules. The quantum theory of atoms in molecules (QTAIM) and natural bond orbital (NBO) are examples of quantum chemical models based in electron density of molecules.

Table 1. Derived Mean Values of Standard ($p° = 0.1$ MPa) Massic, $\langle \Delta_c u° \rangle$, and Molar Energies of Combustion, $\Delta_c U_m°$, Standard Molar Enthalpies of Combustion, $\Delta_c H_m°$, and Standard Molar Enthalpies of Formation, in the Condensed Phase, $\Delta_f H_m°(cr,l)$, of the Three Fluorobenzonitriles, at $T = 298.15$ K

compd	$-\langle \Delta_c u° \rangle/(J \cdot g^{-1})$	$-\Delta_c U_m°(cr,l)/(kJ \cdot mol^{-1})$	$-\Delta_c H_m°(cr,l)/(kJ \cdot mol^{-1})$	$-\Delta_f H_m°(cr,l)/(kJ \cdot mol^{-1})$
2-fluorobenzonitrile	28672.4 ± 2.7	3472.6 ± 1.2	3473.2 ± 1.2	32.1 ± 1.6
3-fluorobenzonitrile	28680.0 ± 3.2	3473.5 ± 1.2	3474.1 ± 1.3	31.2 ± 1.7
4-fluorobenzonitrile	28493.8 ± 1.0	3450.9 ± 1.1	3451.5 ± 1.1	53.8 ± 1.6

The QTAIM theory of Bader[20] uses the electron density, ρ_{CP}, the Laplacian of the electron density, $\nabla^2 \rho_{CP}$, and the bond ellipticity, ε_{CP}, to evaluate the changes of electron density and the nature of a chemical bond. The ρ_{CP} is a measure of the bond strength whereas the $\nabla^2 \rho_{CP}$ evaluates the extent of the depletion or concentration of the bonding density. The ε_{CP} is related with the extent of density that is preferentially accumulated in a given plan, allowing to measure the extent of conjugation and the π-character of the bond.

The NBOs analysis provides an efficient method for the study of the electronic effects in molecular systems, taken into consideration all possible interactions between the "filled" orbital (the donor) and "empty" orbital (the acceptor). These noncovalent donor−acceptor interactions can be quantified energetically by means of the second-order perturbation interaction energy, $\Delta E^{(2)}$.[21]

The nucleus-independent chemical shifts (NICS) method evaluates the delocalization of the π electron in the ring through the chemical shifts by using ghost atoms (Bq) placed at the geometric center of the ring and 1 Å above the ring center (NICS +1). At the geometric center of the ring, the isotropic NICS, σ_{iso}, is strongly affected by the σ framework. Even 1 Å above the ring center, the σ contributions are smaller but still influence the NICS value.[22] The out-of-plane NICS values, σ_{zz}, are a very good alternative since they are based on total contribution to the out-of-plane component of the NICS tensor (zz) that contains the information most relevant for aromatic evaluations.[23]

The goal of the experimental thermochemical study, presented in this work, is to determine the standard ($p° = 0.1$ MPa) molar enthalpies of formation of the monofluorobenzonitrile isomers, in the gaseous phase, at $T = 298.15$ K. This parameter can be related to structural and electronic properties of a molecule, since the effects of intermolecular forces do not apply in the gaseous phase. For the studied isomers, this energetic parameter was calculated combining the respective standard molar enthalpies of formation, in the condensed phase, derived from the standard massic energies of combustion, at $T = 298.15$ K, measured by rotating-bomb combustion calorimetry, and the standard molar enthalpies of sublimation or vaporization, at the same temperature, measured by Calvet microcalorimetry. The vapor-pressure studies of the condensed phases of the benzonitrile derivatives were done by an indirect method, using a static apparatus based on a capacitance diaphragm gauge.[24] The enthalpies of phase transition derived from these results were compared with those obtained by Calvet microcalorimetry.

The experimental energetic study of the three fluorobenzonitrile isomers was complemented with theoretical calculations. The gas-phase standard molar enthalpies of formation of these compounds were estimated computationally as well as the gas-phase basicities, proton and electron affinities and adiabatic ionization enthalpies. The results are discussed in terms of the electronic and structural properties of the benzonitrile derivatives, which are correlated with enthalpic increments, in the gaseous phase.

The electronic properties were determined using the characteristics observed in the bands of the UV−vis spectra and using computational methodologies such as QTAIM, NBO, and NICS

RESULTS AND DISCUSSION

Combustion Calorimetry Results. Detailed results for each combustion experiment performed for each isomer of monofluorobenzonitriles studied are presented in Tables S1−S3 in Supporting Information. The energy of the isothermal bomb process, ΔU (IBP) is calculated through the eq 1, correcting the energy equivalent, ε(calor), for the deviation, Δm (H_2O), of the mass of water used in the calorimeter (5222.5 g)

$$\Delta U(\text{IBP}) = -\{\varepsilon(\text{calor}) + \Delta m(H_2O)c_p(H_2O, l)\}\Delta T_{ad}$$
$$+ (T_i - 298.15 \text{ K})\varepsilon_i$$
$$+ (298.15 \text{ K} - T_i - \Delta T_{ad})\varepsilon_f + \Delta U_{ign} \quad (1)$$

where ΔT_{ad} is the calorimeter temperature change corrected for the heat exchange, the work of stirring, and the frictional work of the bomb rotation. The remaining terms were previously defined in the literature.[25]

The mean values of the standard massic energies of combustion, $\langle \Delta_c u° \rangle$ listed in Table 1, are referred to the combustion reaction of the monofluorobenzonitrile isomers, yielding $HF \cdot 10H_2O(l)$ as the only fluorine-containing product in the final state, as described by eq 2.

$$C_7H_4NF(cr, l) + 7.75O_2(g) + 8.5H_2O(l)$$
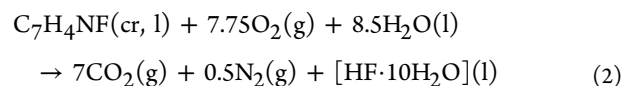$$\rightarrow 7CO_2(g) + 0.5N_2(g) + [HF \cdot 10H_2O](l) \quad (2)$$

Table 1 lists the derived standard molar energies and enthalpies of combustion and the standard molar enthalpies of formation, in condensed phase, for the three isomers studied, at $T = 298.15$ K. The uncertainty assigned to the standard molar energy of combustion corresponds to twice the overall standard deviation of the mean and includes the contributions from the calibration with benzoic acid and the auxiliary quantities used. To derive $\Delta_f H_m°(cr)$ from $\Delta_c H_m°(cr)$, the following standard molar enthalpies of formation, at $T = 298.15$ K were used: $\Delta_f H_m°(CO_2,g) = -(393.51 \pm 0.13)$ kJ·mol^{-1},[26] $\Delta_f H_m°(H_2O,l) = -(285.830 \pm 0.040)$ kJ·mol^{-1}[26] and $\Delta_f H_m°(HF \cdot 10H_2O,l) = -(322.034 \pm 0.650)$ kJ·mol^{-1}.[27]

Vapor Pressure Measurements. The vapor pressure measurements at different temperatures of the condensed phases of the studied compounds are presented in Tables S4−S6 in the Supporting Information. Figure 1 presents the variation of ln p with $1000/T$ for the liquid phase of the 2-fluorobenzonitrile, and the phase diagrams (ln p against $1000/T$) for the 3- and 4-fluorobenzonitrile isomers are presented in Figures 2 and 3. The standard molar enthalpies, entropies, and Gibbs energies of the phase transition of each compound at the mean temperature of the experimental temperature range (Table 2) and at
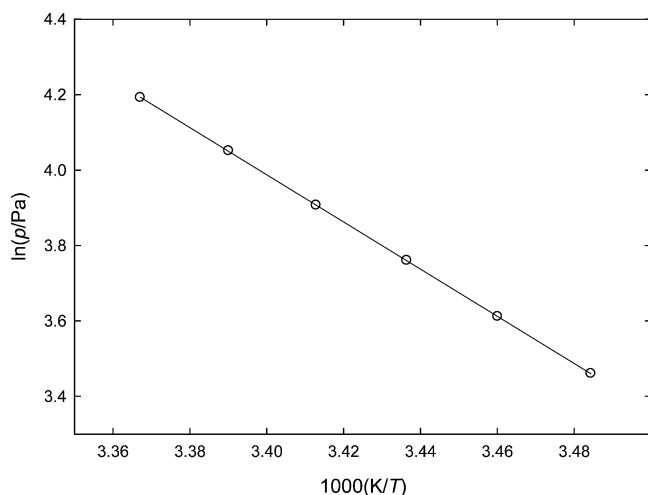
Figure 1. Variation of ln p with $1000/T$ for the liquid phase of 2-fluorobenzonitrile.
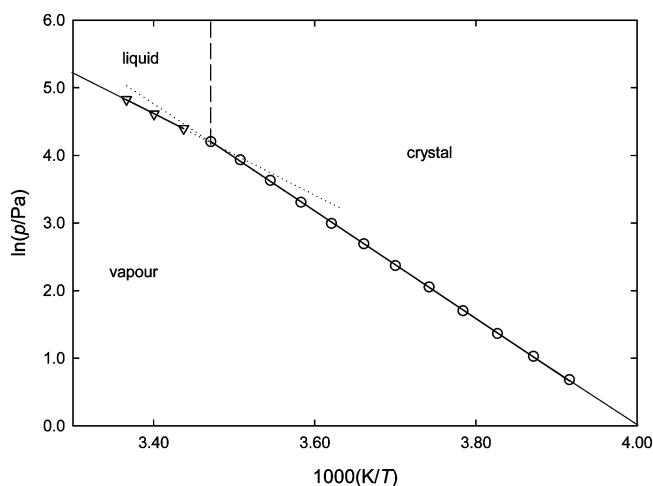
Figure 2. Phase diagram of 3-fluorobenzonitrile: $\triangledown$, liquid vapor pressures, $\bigcirc$, crystalline vapor pressures. Triple point coordinates: $T = 287.66$ K, $p = 64.13$ Pa.
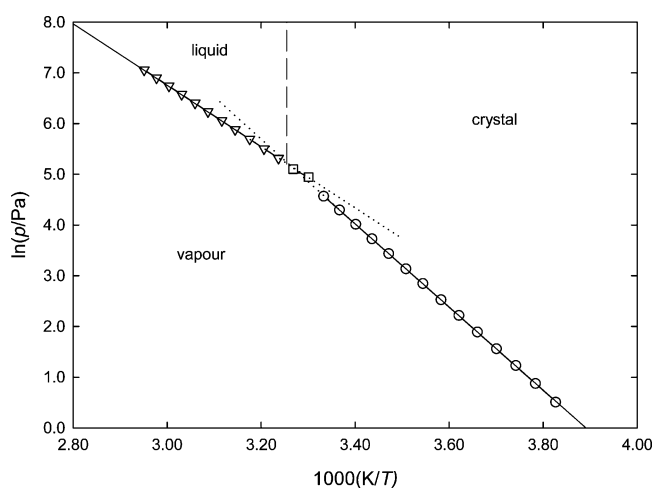
Figure 3. Phase diagram of 4-fluorobenzonitrile: $\triangledown$, liquid vapor pressures; $\square$, under cooled liquid vapor pressures; $\bigcirc$, crystalline vapor pressures. Triple point coordinates: $T = 307.31$ K, $p = 184.8$ Pa.

$T = 298.15$ K (Table 3) were derived from the Clarke and Glew equation:[28]

$$R \ln\left(\frac{p}{p^o}\right) = -\frac{\Delta_{cr,l}^g G_m^o}{\theta} + \Delta_{cr,l}^g H_m^o(\theta)\left(\frac{1}{\theta} - \frac{1}{T}\right) + \Delta_{cr,l}^g C_{p,m}^o(\theta)\left[\left(\frac{\theta}{T}\right) - 1 + \ln\left(\frac{T}{\theta}\right)\right] \quad (3)$$

The heat capacity of the studied isomers, in the gaseous phase, was estimated as being 146.22 J·K^{-1}·mol^{-1} by using the Domalski and Hearing method,[29] which is an extension of the second-order group-additivity method, first developed by Benson and co-workers,[30] by eq 4.

$$C_{p,m}^o(FC_6H_4CN)_g = 4 \times [C_B(H)(C_B)_2]_g + [C_B(F)(C_B)_2]_g + [C_B(CN)(C_B)_2]_g \quad (4)$$

where $[C_B(H)(C_B)_2]_g = 13.61$ J·K^{-1}·mol^{-1}, $[C_B(F)(C_B)_2]_g = 26.10$ J·K^{-1}·mol^{-1}, and $[C_B(CN)(C_B)_2]_g = 41.09$ J·K^{-1}·mol^{-1}.

Equation 5 was applied for the determination of $C_{p,m}^o$, in the liquid phase, using the following parameters:[29] $[C_B(H)(C_B)_2]_l = 22.68$ J·K^{-1}·mol^{-1}, $[C_B(F)(C_B)_2]_l = 37.09$ J·K^{-1}·mol^{-1}, and $[C_B(CN)(C_B)_2]_l = 51.80$ J·K^{-1}·mol^{-1}.

$$C_{p,m}^o(FC_6H_4CN)_l = 4 \times [C_B(H)(C_B)_2]_l + [C_B(F)(C_B)_2]_l + [C_B(CN)(C_B)_2]_l \quad (5)$$

The same equation system was applied for the calculation of the heat capacity of the crystalline phase of the benzonitrile isomers, using 20.13, 32.05, and 33.65 J·K^{-1}·mol^{-1} for $[C_B(H)(C_B)_2]_{cr}$, $[C_B(F)(C_B)_2]_{cr}$, and $[C_B(CN)(C_B)_2]_{cr}$, respectively.

The $[C_B(CN)(C_B)_2]_{cr}$ parameter was derived from the $C_{p,m}^o$ (4-nitrobenzonitrile,cr) = 165.13 J·K^{-1}·mol^{-1}[31] at $T = 298.15$ K, through eq 6

$$[C_B(CN)(C_B)_2]_{cr} = C_{p,m}^o(4\text{-}NO_2C_6H_4CN)_{cr} -4 \times [C_B(H)(C_B)_2]_{cr} - [C_B(NO_2)(C_B)_2]_{cr} \quad (6)$$

where $[C_B(NO_2)(C_B)_2]_{cr}$ is 50.96 J·K^{-1}·mol^{-1}.

Therefore, the derived values of heat of capacities of sublimation and of vaporization are $\Delta_{cr}^g C_{p,m}^o = -24.6$ J·K^{-1}·mol^{-1} and $\Delta_l^g C_{p,m}^o = -58.0$ J·K^{-1}·mol^{-1}, respectively.

Table 4 lists the triple-point coordinates for 3- and 4-fluorobenzonitrile, together with the enthalpies and entropies of fusion of these isomers at $T = 298.15$ K. Because of the low melting point of the 2-fluorobenzonitrile isomer ($T_m = 259.45$ K[19]), only the liquid phase of this compound could be studied. Although the melting point of the 3-fluorobenzonitrile reported in the literature is 257.15 K,[32] this value was reevaluated recently by Vasylyeva and Merz using differential scanning calorimetry measurements, at 285.65 K,[19] which is in good agreement with the temperature of the triple point of the 3-fluorobenzonitrile (287.66 K) derived through the intersection of the liquid and the solid vapor-pressure lines.

The temperature of the triple point of the 4-fluorobenzonitrile was found to be 307.31 K, which is in agreement with the temperature of fusion presented in the Aldrich catalogue (305.15 to 307.15) K.[32] The value derived from the vapor

Table 2. Derived Parameters of Clarke and Glew Equation from Vapor Pressures Results for Different Physic States of the Fluorobenzonitrile Isomers, at Mean Temperature $\langle T \rangle$

phase	ΔT/K	$\langle T \rangle$/K	$\Delta_{cr,1}^{g}H_{m}^{o}(\langle T \rangle)/(kJ \cdot mol^{-1})$	$\Delta_{cr,1}^{g}G_{m}^{o}(\langle T \rangle)/(kJ \cdot mol^{-1})$	$\Delta_{cr,1}^{g}S_{m}^{o}(\langle T \rangle)/(J \cdot K^{-1} \cdot mol^{-1})$	$p(\langle T \rangle)$/Pa
			2-fluorobenzonitrile			
liquid	287.00−296.99	292.00	52.0 ± 0.1	18.64 ± 0.01	114.2 ± 0.3	46.3
			3-fluorobenzonitrile			
crystalline	255.35−288.10	271.73	66.1 ± 0.3	19.78 ± 0.01	170.5 ± 1.1	15.8
liquid	290.92−297.05	293.99	50.0 ± 1.2	16.87 ± 0.01	112.7 ± 4.1	101
			4-fluorobenzonitrile			
crystalline	261.33−300.04	280.69	68.2 ± 0.1	20.59 ± 0.01	169.6 ± 0.4	14.7
liquid	302.95−338.85	320.90	50.5 ± 0.1	14.55 ± 0.01	112.0 ± 0.3	438

Table 3. Values of the Standard Molar Enthalpies, $\Delta_{cr,1}^{g}H_{m}^{o}$(298.15 K), Entropies, $\Delta_{cr,1}^{g}S_{m}^{o}$(298.15 K), and Gibbs Energies, $\Delta_{cr,1}^{g}G_{m}^{o}$(298.15 K), of the Transition Phase, at T = 298.15 K for the Studied Compound

phase	$\Delta_{cr,1}^{g}H_{m}^{o}$(298.15 K)/(kJ·mol^{-1})	$\Delta_{cr,1}^{g}G_{m}^{o}$(298.15 K)/(kJ·mol^{-1})	$\Delta_{cr,1}^{g}S_{m}^{o}$(298.15 K)/(J·K^{-1}·mol^{-1})	p (298.15K)/Pa
		2-Fluorobenzonitrile		
liquid	51.6 ± 0.1	17.95 ± 0.01	112.9 ± 0.3	71.6
		3-fluorobenzonitrile		
crystalline	65.4 ± 0.3	15.84 ± 0.03	166.2 ± 1.0	168
liquid	49.8 ± 1.2	16.40 ± 0.02	112.0 ± 4.0	134
		4-fluorobenzonitrile		
crystalline	67.7 ± 0.1	17.64 ± 0.01	167.9 ± 0.3	81.2
liquid	51.8 ± 0.1	17.14 ± 0.01	116.2 ± 0.3	99.4

Table 4. Triple-Point Coordinates and Standard (p^{o} = 0.1 MPa) Molar Enthalpies and Entropies of Fusion for 3- and 4-Fluorobenzonitrile Isomers at T = 298.15 K

| compd	T_{tp}/K	p_{tp}/Pa	$\Delta_{cr}^{1}H_{p,m}^{o}$(298.15 K)/(kJ·mol^{-1})	$\Delta_{cr}^{1}S_{p,m}^{o}$(298.15 K)/(J·K^{-1}·mol^{-1})
3-fluorobenzonitrile	287.66	64.13	15.6 ± 1.2	54.2 ± 4.8
4-fluorobenzonitrile	307.31	184.8	15.9 ± 0.1	51.75 ± 0.04

pressure measurements is 4.3 K lower than the one obtained by Vasylyeva and Merz (311.65 K).[19]

Figure 4, taken from ref 19, represents the packing views of the planes and layers of the three fluorinated isomers. The X-ray crystallography data shows the presence of the same type of intermolecular interactions and similar structural aggregation in 3- and 4-fluorobenzonitrile isomers. The 3-fluorobenzonitrile molecules are arranged antiparallel in planes and in layers, with each one formed by C−H···N, which involves the hydrogen in the *ortho* position to the cyano group, and C−H ··· F interactions,[19] while the 4-fluorobenzonitrile isomers are all antiparallel in planes but parallel in layers formed by the same type of intermolecular interactions.[18,33]

Britton[18] found that the dipole−dipole interactions of the cyano group and fluorine atom, with the same group and atom of the layer below or above them, are unfavorable. Even though the distance between the layers of the 4-isomer is smaller than in 3-fluorobenzonitrile, the repulsions caused by the dipole−dipole interaction may give more flexibility between different layers.

a

b

c
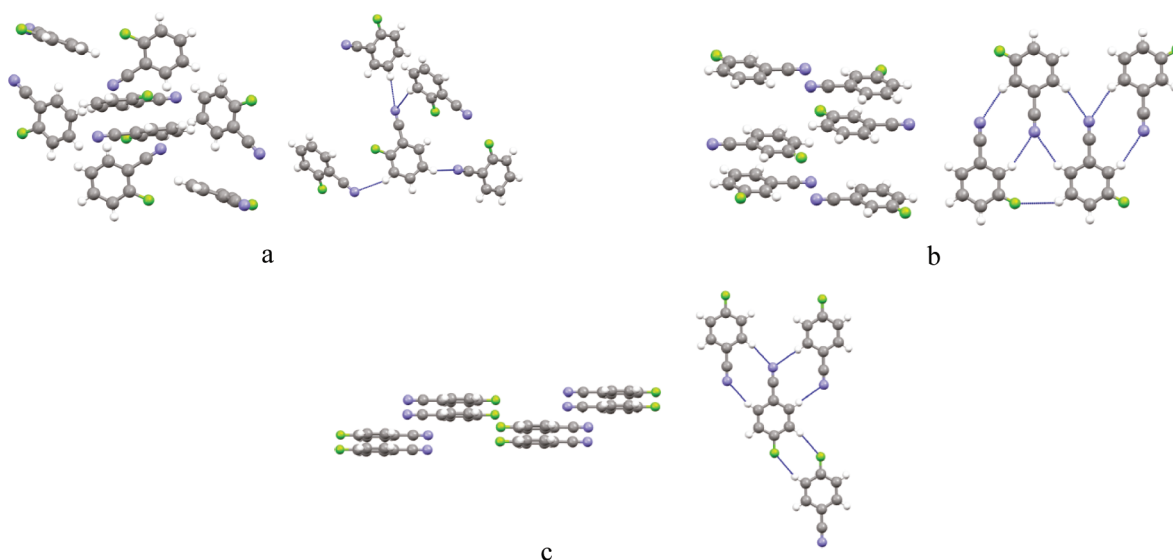
Figure 4. Packing view of planes (on left) and of layers (on right) of the 2-fluorobenzonitrile (a), 3-fluorobenzonitrile (b) and 4-fluorobenzonitrile (c).[19]

This possible behavior, together with the similar structural aggregation of the 3-fluorobenzonitrile, could be the explanation for the similarity of the values of the entropies of sublimation of the two isomers.

Table 5 lists the results of the standard molar enthalpies of sublimation and vaporization derived by Calvet microcalorimetry.

Table 5. Standard ($p° = 0.1$ MPa) Molar Enthalpies of Sublimation or Vaporization, $\Delta_{cr,l}^{g}H_m^o$, for the Three Fluorobenzonitrile Isomers, at $T = 298.15$ K, Determined by Calvet Microcalorimetry

compd	T/K	$\Delta_{cr,l}^{g}H_m^o(T)$/ (kJ·mol^{-1})	$\Delta_{298.15K}^{T}H_m^o(g)$/ (kJ·mol^{-1})	$\Delta_{cr,l}^{g}H_m^o$ (298.15 K)/ (kJ·mol^{-1})
2-fluorobenzonitrile	339.9	59.1 ± 0.1	4.0	55.1 ± 0.6
3-fluorobenzonitrile	339.9	57.6 ± 0.1	4.0	53.6 ± 0.6
4-fluorobenzonitrile	318.5	69.2 ± 0.2	1.6	67.6 ± 0.5

The standard molar enthalpies of transition phase at $T = 298.15$ K were calculated from the values measured at the predefined temperature, T, using the values of $\Delta_{298.15K}^{T}H_m^o(g)$ also presented in the table. The uncertainties of $\Delta_{cr,l}^{g}H_m^o(T)$ were calculated as the standard deviations of the mean of the five individual experimental results and the uncertainties of $\Delta_{cr,l}^{g}H_m^o(298.15$ K) are twice the value derived considering those uncertainties and the uncertainties in the calibration constant.

The calorimetric value of the standard molar enthalpy of sublimation of 4-fluorobenzonitrile is equal to the value derived from the vapor pressure measurements. The enthalpies of vaporization of the 2- and 3-isomers derived from the vapor pressure measurements are, respectively, 3.5 and 3.8 kJ·mol^{-1} lower than the results derived from the microcalorimetric experiments. Considering the short temperature range and the small number of (p, T) experimental points that could be measured for these two liquids, the calorimetric values of enthalpies of vaporization were selected for the calculation of the enthalpy of formation, in the gaseous phase.

Experimental Enthalpies of Formation in the Gaseous Phase. Table 6 summarizes the derived standard molar enthalpies

Table 6. Standard ($p° = 0.1$ MPa) Molar Enthalpies of Formation, in Condensed and Gaseous Phase, and Standard Molar Enthalpies of Sublimation for 4-Fluorobenzonitrile and Vaporization for the Other Isomers at $T = 298.15$ K

compd	$-\Delta_f H_m^o(cr,l)$/ (kJ·mol^{-1})	$\Delta_{cr,l}^{g}H_m^o(298.15K)$/ (kJ·mol^{-1})	$\Delta_f H_m^o(g)$/ (kJ·mol^{-1})
2-fluorobenzonitrile	32.1 ± 1.6	55.1 ± 0.6	23.0 ± 1.7
3-fluorobenzonitrile	31.1 ± 1.7	53.6 ± 0.6	22.4 ± 1.8
4-fluorobenzonitrile	53.8 ± 1.6	67.6 ± 0.5	13.8 ± 1.7

of formation in the gaseous phase, $\Delta_f H_m^o(g)$, at $T = 298.15$ K for the three fluorobenzonitrile isomers, where the enthalpies of vaporization and sublimation, in case of the 4-fluorobenzonitrile, were determined by Calvet microcalorimetry once the 2- and 3-fluorobenzonitrile isomers were burned in the liquid phase.

The enthalpic increments associated to the interaction (steric and/or electronic effects) of the fluorine atom with the cyano group, $\delta(F\cdots CN)$, at different positions, can be calculated through the application of the eq 7, where the following values were used: $\Delta_f H_m^o(benzonitrile,g) = 215.7 \pm 2.1$ kJ·mol^{-1},[34]

$\Delta_f H_m^o(fluorobenzene,g) = -115.9 \pm 1.4$ kJ·mol^{-1}[34] and $\Delta_f H_m^o(benzeno,g) = 82.6 \pm 0.5$ kJ·mol^{-1}.[34]

$$\delta(F\cdots CN) = \quad (7)$$
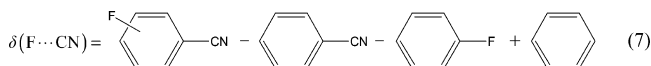
According to the results obtained [$\delta(o$-F$\cdots$CN)= (5.8 ± 3.1) kJ·mol^{-1}, $\delta(m$-F$\cdots$CN)=(5.3 ± 3.1) kJ·mol^{-1}, and $\delta(p$-F$\cdots$CN) = −(3.4 ± 3.1) kJ·mol^{-1}], the 2- and 3-fluorbenzonitrile isomers have a similar destabilizing enthalpic effect, while the 4-fluorobenzonitrile is the only isomer that, although very small, presents a stabilizing effect, from the enthalpic point of view.

Gas-Phase Molecular Structures. The optimized geometries of the three isomers of fluorobenzonitrile calculated at the G3(MP2)//B3LYP and MP2/cc-pVTZ levels of theory and the respective Cartesian coordinates are listed in Tables S7−S9 in the Supporting Information. Figure 5 reports the bond distances and the angles obtained with the MP2/cc-pVTZ approach. Our results are in a very good agreement with observations of Dutta et al.[35] and Varadwaj et al.[36]

Calculated Enthalpies of Formation. The gas-phase enthalpies of formation of the three studied isomers were estimated taking into account the computed enthalpies of the following gas-phase working reactions described by eqs 8−10, chosen on the basis of the available experimental thermochemical data in the gaseous phase of the other atoms and molecules involved.

$$\text{Fluorobenzonitrile} \longrightarrow 7C + 4H + N + F, \quad (8)$$

Fluorobenzonitrile   Benzene   →   Benzonitrile   Fluorobenzene (9)

Fluorobenzonitrile   Nitrobenzene   →   Benzonitrile   Fluoronitrobenzene (10)
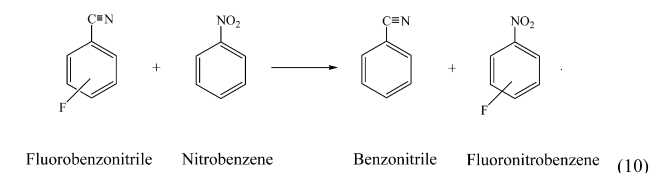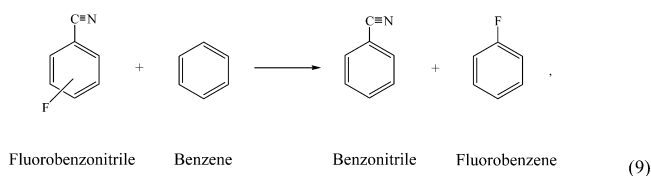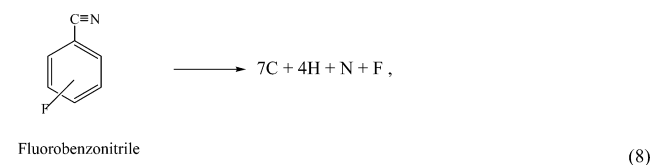
The values of $\Delta_f H_m^o(g)$ used were as follows: carbon, 716.7 kJ·mol^{-1},[37] nitrogen, 472.7 kJ·mol^{-1},[37] hydrogen, 218.0 kJ·mol^{-1},[37] fluorine, 79.4 kJ·mol^{-1},[37] nitrobenzene, 67.5 kJ·mol^{-1},[34] 2-fluoronitrobenzene, −102.4 kJ·mol^{-1},[38] 3-fluoronitrobenzene, − 128.0 ± 1.7 kJ·mol^{-1}[38] and 4-fluoronitrobenzene, −133.9 ± 1.4 kJ·mol^{-1}.[38]

The calculated enthalpies of formation along with the experimental values are registered in Table 7. As it can be seen from this table, the agreement between the experimental and G3MP2B3 calculated values is fairly good. The maximum deviations from the experimental results come from the atomization reaction and are 7.6 kJ·mol^{-1} for 2-fluorobenzonitrile, 3.7 kJ· mol^{-1} for 3-fluorobenzonitrile, and 9.7 kJ·mol^{-1} for 4-fluorobenzonitrile. These deviations are of the same order of magnitude defined by the uncertainty associated to the experimental and calculated values.[39]
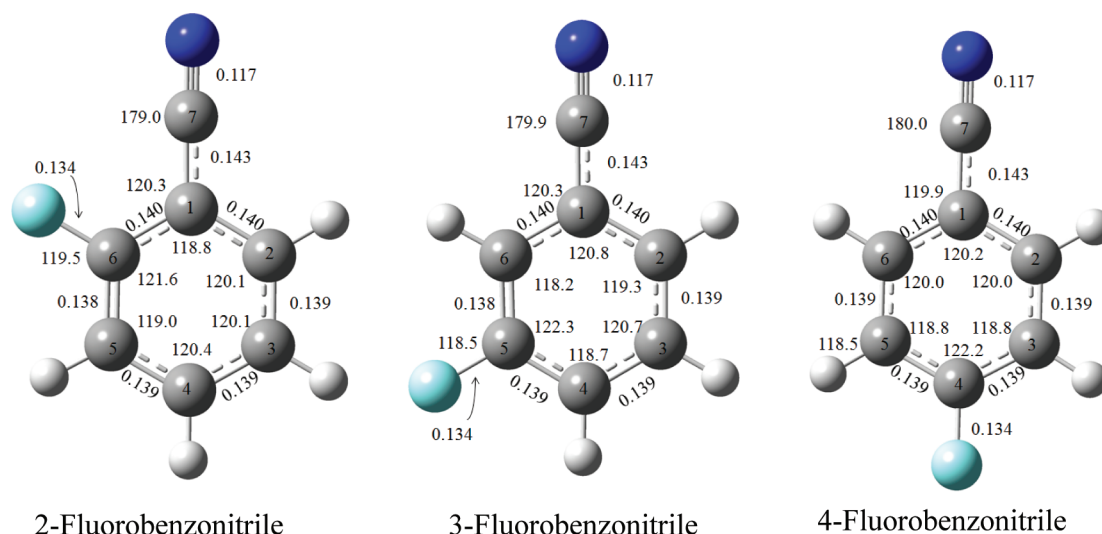
Figure 5. MP2/cc-pVTZ-optimized geometries of the three isomers of fluorobenzonitrile. Distances are given in nanometers and angles in degrees.

Table 7. Comparison between the Experimental and Computed G3MP2B3 Gas-Phase Enthalpies of Formation of the Three Isomers of Fluorobenzonitrile at T = 298.15 K[a]

| | $\Delta_f H_m^o(g)/(kJ\cdot mol^{-1})$ | | | |
| | G3MP2B3 | | | |
compd	eq 1	eq 2	eq 3	exptl value
2-fluorobenzonitrile	30.6 (−7.6)	27.1 (−4.1)	24.6 (−1.6)	23.0 ± 1.7
3-fluorobenzonitrile	26.1 (−3.7)	22.6 (−0.2)	19.3 (3.1)	22.4 ± 1.8
4-fluorobenzonitrile	23.5 (−9.7)	20.0 (−6.2)	13.9 (−0.1)	13.8 ± 1.7

[a]Enthalpic differences between the experimental and computed values are given in parentheses.

Table 8. G3MP2B3-Computed Gas-Phase Basicities ($\Delta G_{basicity}$), Proton (PA) and Adiabatic Electron (EA) Affinities, and Adiabatic Ionization Enthalpies (IE) at T = 298.15 K for the Three Isomers of Fluorobenzonitrile along with the Values for Benzonitrile and Fluorobenzene[a]

compd	$\Delta G_{basicity}/(kJ\cdot mol^{-1})$	$PA/(kJ\cdot mol^{-1})$	$EA/(kJ\cdot mol^{-1})$	$IE/(kJ\cdot mol^{-1})$
fluorobenzene			−77.24	896.69 (887.66) [40]
benzonitrile	809.7	805.7 (811.5)	12.47 (25.09 ± 9.6) [41]	950.97 (938.95) [42]
2-fluorobenzonitrile	801.5	797.5	28.1	955.2 (943.6) [43]
3-fluorobenzonitrile	793.7	790.2	35.3	957.3 (944.6) [43]
4-fluorobenzonitrile	803.5	798.2	−21.7	943.2 (939.8) [43]

[a]When possible, experimental values are given in brackets.

The computed G3MP2B3 enthalpies for the studied compounds, auxiliary molecules, and atoms used in the atomization and working reactions are listed in Table S10 in the Supporting Information.

Other Gas-Phase Thermodynamic Properties. The G3(MP2)//B3LYP approach was used to compute other thermodynamic properties for the three isomers of fluorobenzonitrile. The calculated values of gas-phase basicity ($\Delta G_{basicity}$), proton (PA) and adiabatic electron affinities (EA), and adiabatic ionization enthalpies (IE) are registered in Table 8.

The calculated gas-phase basicities allow us to propose the following basicity order: 4-fluorobenzonitrile ≈ 2-fluorobenzonitrile > 3-fluorobenzonitrile. This fact can be explained by analyzing the stability of the corresponding cation. For 4- and 2-fluorobenzonitriles, the positive charge is stabilized by the fluorine atom, but in the case of 3-fluorobenzonitrile this stabilization cannot occur. The proton affinity follows the same pattern.

As can be seen from Table 8, the addition of an electron to 2- and 3-fluorobenzonitrile is favorable as their positive values of the electron affinities show for both isomers. On the other hand, the incoming electron is not stabilizing the 4-fluorobenzonitrile because it occupies an antibonding orbital and destabilizes the whole molecule. Finally, regarding the ionization enthalpies, it is possible to conclude that 4-fluorobenzonitrile is the species which looses the electron easier.

No experimental or computational data have been found in the literature for comparison with our results on none of these properties excluding ionization enthalpies. In this case, the available experimental data[43] is in very good agreement with our calculations predicting the same qualitative order, as the 4-fluorobenzonitrile species releases an electron easier, followed by the 2-fluorobenzonitrile, and finally, the 3-fluorobenzonitrile.

NBO and QTAIM Analysis: Donor–acceptor Interactions. Tables S16−S18 (Supporting Information) present the

sum of all relevant interactions given in Tables S11–S15 in the Supporting Information.

As the cyano group is an electron acceptor by inductive effect, the redistribution of the electron density is done through σ bonds from the ring to the C–N bond. In this case, the inductive effect of cyano group was calculated as being the sum of the stabilization energies of sigma bonds from the ring to the C–N bond, discounting to this sum all the stabilization energies that comes in opposite direction: $\sigma_{ring} \rightarrow \sigma^*_{ring} + \sigma_{ring} \rightarrow \sigma^*_{C–C(N)} + \sigma_{ring} \rightarrow \sigma^*_{C–N} - \sigma_{C–C(N)} \rightarrow \sigma^*_{ring} - \sigma_{C–C(N)} \rightarrow \sigma^*_{C–N} - \sigma_{C–N} \rightarrow \sigma^*_{C–C(N)} - \sigma_{C–N} \rightarrow \sigma^*_{ring} - n_{sN} \rightarrow \sigma^*_{C–C(N)}$. The fluorine atom is also an electron acceptor by the same electronic effect as the cyano group, so the respective inductive effect was calculated using the same logic: $\sigma_{ring} \rightarrow \sigma^*_{ring} + \sigma_{ring} \rightarrow \sigma^*_{C–F} - \sigma_{C–F} \rightarrow \sigma^*_{ring} - n_{sF} \rightarrow \sigma^*_{ring}$. For the calculation of the mesomeric effect for the cyano group, which is also an electron acceptor, all the interactions resulting from the p-orbital overlap from the ring to the CN group are taken in consideration, removing the opposite interactions: $\pi_{ring} \rightarrow \pi^*_{ring} + \pi_{ring} \rightarrow \pi^*_{C–N} - \pi_{C–N} \rightarrow \pi^*_{ring} + n_{pF} \rightarrow \pi^*_{C–N}$. Being an electron donor, the same system was applied to the calculation of the mesomeric effect for the fluorine atom: $\pi_{ring} \rightarrow \pi^*_{ring} + n_{pF} \rightarrow \pi^*_{ring} - n_{pF} \rightarrow \pi^*_{C–N}$.

When comparing the electronic effects of the cyano group and of the fluorine atom in benzonitrile and fluorobenzene, presented in Table 9, one sees that the 4-fluorobenzonitrile

Table 9. Inductive and Mesomeric Effect Derived from Second-Order Perturbation Interaction Energies Present in Fluorobenzonitrile Isomers[a]

	inductive effect		mesomeric effect	
compd	CN	F	CN	F
benzonitrile	114.9		1117.3	
fluorobenzene		127.2		1166.1
2-fluorobenzonitrile	110.8	134.6	1128.4	1150.0
3-fluorobenzonitrile	101.0	126.5	1113.6	1151.1
4-fluorobenzonitrile	115.3	140.7	1141.8	1170.8

[a]All values are in kJ·mol^{-1}.

isomer is the one that has the highest values in all electronic effects; this strong electron delocalization explains the stabilization effect that was found by the enthalpic increments associated to the interaction of fluorine atom with cyano group, at different positions, presented in section Experimental Enthalpies of Formation, in the Gaseous Phase.

As shown in Table 10, the ellipticity of the C–N bond in 4-fluorobenzonitrile shows a largest triple character, even greater

Table 10. Bond Ellipticity, ε, for Benzonitrile, Fluorobenzene, and the Fluorobenzonitrile Isomers

compd	C–F	C–C7	C7–N
benzonitrile		0.055	0.012
fluorobenzene	0.058		
2-fluorobenzonitrile	0.037	0.061	0.013
3-fluorobenzonitrile	0.063	0.057	0.016
4-fluorobenzonitrile	0.055	0.061	0.009

than the one on benzonitrile, due to electron density accumulated in the perpendicular plane as result of the higher mesomeric effect, as confirmed by NBO analysis.

The ellipticity of the C–F bond in the 2-fluorobenzonitrile isomer shows the greatest simple bond character of all isomers

and of fluorobenzene. On the other hand, the C–CN has a strong intermediate character between the single and double bond, even higher than the same bond in benzonitrile, while this isomer presents a similar triple character as the C–N bond of benzonitrile. This behavior may indicate that the steric effect felt in 2-fluorobenzonitrile is the result of the interaction of the triple bond of the cyano group with the fluorine atom, which may explain the destabilizing enthalpy effect found in this isomer. The blocking of fluorine atom by the cyano group in 2-fluorobenzonitrile is confirmed by the lowest mesomeric effect of the fluorine atom, when compared with fluorobenzene and by the mesomeric effect of cyano group, which is larger than that in 3-fluorobenzonitrile and slightly bigger than the one in benzonitrile, as shown in Table 9. The increase in conjugation between the cyano group and the ring is supported by the experimental IR frequency of the cyano group in benzonitrile and 2-, 3-, and 4-fluorobenzonitrile, respectively, at 2230,[44] 2238,[41] 2235,[41] and 2238 cm^{-1}.[41]

Nucleus-Independent Chemical Shift (NICS) Analysis. Table 11 lists the isotropic (σ_{iso}) and out-of-plane (σ_{zz}) NICS

Table 11. Isotropic (σ_{iso}) and Out-of-Plane (σ_{zz}) NICS Values for the Monofluorobenzonitrile Isomers at the B3LYP/6-311++G(2df,2pd) Level of Theory[a]

	NICS(0)		NICS(+1)	
compd	σ_{iso}	σ_{zz}	σ_{iso}	σ_{zz}
2-fluorobenzonitrile	−9.75	−13.99	−9.87	−26.71
3-fluorobenzonitrile	−9.96	−14.56	−9.99	−27.07
4-fluorobenzonitrile	−9.92	−14.18	−9.91	−26.76

[a]All values in ppm.

values for the benzenic ring for each isomer. For the fluorobenzonitrile isomers studied in this work, it is possible to observe from the out-of-plane NICS (+1) values that the isomer 3-fluorobenzonitrile preserves the aromaticity of the ring, showing the weak conjugation between the substituents in the ring. This conclusion is supported by the smaller values of their mesomeric effect when compared with the others isomers calculated, previously, by NBO. When the fluorine atom is in *para* and in *ortho* positions to the cyano group, the aromaticity of the benzonitrile ring decreases. In fact, the 4-fluorobenzonitrile isomer shows a higher aromaticity than 2-fluorobenzonitrile. As mentioned in the NBO analysis, the blocking of the conjugation between the fluorine atom and the ring of the 2-fluorobenzonitrile isomer may favor the extension of the mesomeric effect of CN, reducing the electron density in the ring and, consequently, a decrease of the aromaticity. The value obtained for 4-fluorobenzonitrile reflects the conjugation between the substituents. As the fluorine atom gives electron density by mesomeric effect and the cyano group removes it, there is equilibrium of the electron density in the ring.

Correlation between Energetic and Spectroscopic Data. The UV–vis spectra of the three benzonitrile isomers, studied in dichloromethane, are presented in Figure 6. The wavelength of the absorptivity maximum in the primary band of the three isomers is located at 231 nm, with similar intensities. The shifts of this band for the corresponding band of benzene (204 nm)[45] are due to the electronic effects of the substituents.

The difference in intensity observed in secondary bands may be due to the increase of the symmetry of the 4-fluorobenzonitrile when compared with the other two isomers.
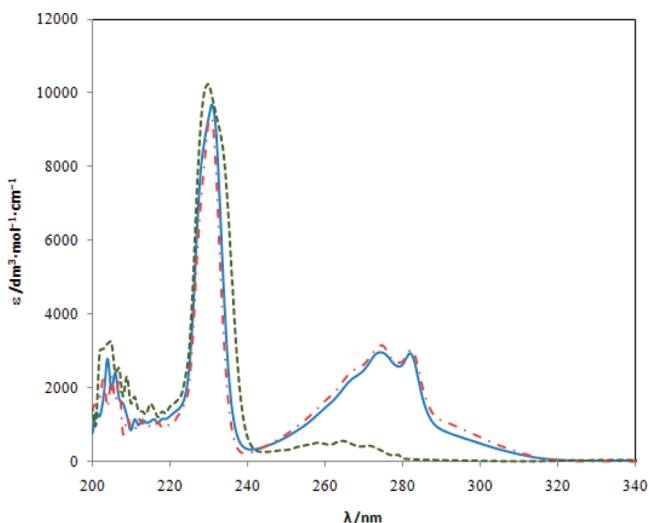
Figure 6. UV−vis spectra of the studied isomers in dichlorometane: (—) 2-fluorobenzonitrile; (− · —) 3-fluorobenzonitrile; (---) 4-fluorobenzonitrile.

The absorptivity maximum of the 4-fluorobenzonitrile in the secondary band (550 dm^3·mol^{-1}·cm^{-1}) is lower than the value of the fluorobenzene (1290 dm^3·mol^{-1}·cm^{-1})[42] and of the benzonitrile (1000 dm^3·mol^{-1}·cm^{-1}),[42] but it is higher than the value obtained to benzene (204 dm^3·mol^{-1}·cm^{-1}).[42] The electronic affinity can explain the shift of the secondary band of the 4-fluorobenzonitrile. The destabilizing effect of the addition of an electron will increase the gap between the energy levels of ligand and antiligand orbitals. As a consequence, the transition $\pi \rightarrow \pi^*$ requires a higher energy, causing the band to shift to shorter wavelengths.

CONCLUSIONS

A detailed picture of the relation between the energetic and structural properties of the monofluorobenzonitrile isomers has been obtained by the combination of a range of experimental techniques which were used to obtain important thermodynamic parameters of the isomers, together with computational data, UV−vis spectroscopic techniques, and X-ray crystallography literature data.

NBO and QTAIM methodologies were applied to study electronic and steric effects on the isomers, showing the stabilization of 4-fluorobenzonitrile by mesomeric and inductive effects from both substituents and destabilization in 2-fluorobenzonitrile as a result of the steric interaction between the fluorine atom and the triple bond of the cyano group.

The aromaticity of the ring of each isomer, evaluated by NICS, correlates well with the electronic effects, showing the higher electronic density in the ring of the 3-fluorobenzonitrile.

The G3MP2B3 approach was used to estimate the gas-phase enthalpies of formation of all the isomers of fluorobenzonitrile, at T = 298.15 K, considering several appropriate working reactions. All computed values are in agreement with the experimental data reported here, since all are in the range of the experimental and computational uncertainties. Other thermodynamic properties were also calculated by means of this composite method.

The calculation of the electron affinity value for 4-fluorobenzonitrile indicates that the addition of one electron destabilizes the molecule; the shift of the secondary band of the UV−vis spectra supports that thermodynamic computed value.

EXPERIMENTAL SECTION

Materials and Purity Control. The 2-fluorobenzonitrile (CAS 394-47-8), 3-fluorobenzonitrile (CAS 403-54-3), and 4-fluorobenzonitrile (CAS 1194-02-1) were obtained commercially, with assessed minimum purity of 0.99 (mass fraction). The liquids 2- and 3-fluorobenzonitrile were purified by repeated fractional distillations under reduced pressure with a few milligrams of phosphorus pentoxide and then stored under nitrogen atmosphere. The 4-fluorobenzonitrile was purified by recrystallization in hexane, followed by sublimation under reduced pressure at room temperature.

The final purity of each isomer was checked by gas chromatography, using a column, 5% diphenyl and 95% dimethylpolysiloxane, under nitrogen pressure as carrier gas. No impurities greater than 10^{-3} in mass fraction could be detected in the samples of the monofluorobenzonitrile isomers used for the calorimetry and vapor pressure studies.

The true mass of the studied compounds were calculated from the apparent mass in air using the specific densities: 1.12 g·cm^{-3},[32] 1.13 g·cm^{-3},[32] and 1.32 g·cm^{-3}[18] for 2-, 3-, and 4-fluorobenzonitrile isomers, respectively.

Benzoic acid NIST Standard Reference Material, sample 39j,[46] was used without any further purification to calibrate the rotating bomb calorimeter, while *n*-undecane (mass fraction purity >0.999) and naphthalene (mass fraction purity >0.99) were used to calibrate the high-temperature Calvet microcalorimeter.

The relative atomic masses used in the calculation of all molar quantities throughout this paper were those recommended by IUPAC Commission in 2009,[47] yielding 121.1118 g·mol^{-1} for the molar mass of the monofluorobenzonitrile isomers.

Procedure for Rotating Bomb Combustion Calorimetry Measurements. The enthalpies of combustion of the three fluorinated benzonitrile isomers were measured using an isoperibol rotating bomb calorimeter formerly developed at the University of Lund, Sweden, according to the design of Professor Stig Sunner,[48] and installed in the Department of Chemistry and Biochemistry of Porto.

Since the use of a platinum-lined bomb[49] is recommended for the combustion of fluorine-containing compounds, the combustion experiments were performed with a twin valve bomb of internal volume 0.329 dm^{-3}, lined with platinum with all internal fittings also platinum lined.

After being filled with oxygen, the bomb was suspended in the inverted position on the lid of the calorimeter, which supports a mass of distilled water previously weighed in a Perspex vessel, using a Mettler PM 11-N balance, with a sensitivity of the ±10^{-1} g. For each experiment, a correction for deviation from 5222.5 g of mass of water added was made.

Calorimetric temperatures were measured with an uncertainty within the bounds of ±(1 × 10^{-4}) K every 10 s, using a quartz thermometer interfaced to a microcomputer programmed to compute the adiabatic temperature change, by means of the LABTERMO program.[50] For all combustion experiments, the ignition temperature was chosen so that the final temperature of the main period would be as close as possible to T = 298.15 K. Thus, the ignition was made after at least of 100 temperature readings by the discharge of a 1400 μF capacitor through the platinum ignition wire (ϕ = 0.05 mm, Goodfellow, mass fraction 0.9999), using a cotton thread fuse, with $\Delta_c u^o$ = −16250 J·g^{-1},[51] a value previously confirmed in our laboratory. The rotation of the bomb was started when the temperature had risen to 63% of its final value and then continued throughout the rest of the experiment, a procedure described by Good et al.,[52] who have shown that the frictional work due to the rotation of the bomb is automatically accounted in the temperature corrections for the work of the water stirring and for the heat exchanged with the surrounding isothermal jacket. After ignition, 100 readings were taken for the main and for the after periods.

The energetic equivalent of the calorimeter was determined by the combustion of benzoic acid (NIST Standard Reference Material 39j), with $\Delta_c u^o$ = (26434 ± 3) J·g^{-1},[53] without rotation of the bomb, following the procedure described in the literature.[48] The obtained value

of the energy equivalent was found to be $\varepsilon(calor) = (25157.4 \pm 1.1)$ J·g^{-1}, as the mean of seven calibrations experiments, where the uncertainty quoted is the standard deviation of the mean. The accuracy of the combustion calorimetry for the organic fluorine compounds was previously checked by measuring the energy of combustion of the recommended test substance,[54] 4-fluorobenzoic acid. The standard massic energy of combustion obtained for the reaction with HF·10H$_2$O(l) as the single fluorine-containing product in the final state was $\Delta_c u^o = -(21865.1 \pm 2.0)$ J·g^{-1},[55] in excellent agreement with the recommend value $\Delta_c u^o = -(21860 \pm 4)$ J·g^{-1}.[51]

The three fluorobenzonitrile isomers were burned enclosed in polyethylene bags, under oxygen pressure of $p = 3.04$ MPa, in the presence of 10.00 cm^{-3} of deionized water. The value of the standard massic energy of combustion of polyethylene, $\Delta_c u^o = -(46282.4 \pm 4.8)$ J·g^{-1}, was measured in our laboratory. For each compound, the pressure coefficient of massic energy, $(\partial u/\partial p)_T$, at $T = 298.15$ K, was assumed to be -0.2 J·g^{-1}·MPa^{-1}, a typical value for most organic compounds.[56]

The nitric acid formed from the combustion of the fluorobenzonitrile samples and from the traces of atmospheric nitrogen remaining inside the bomb was analyzed by Devarda's alloy method,[57] and corrections for the nitric acid formed were based on $\Delta_f U_m^o = -59.7$ kJ·mol^{-1},[58] from $1/2N_2(g)$, $5/4O_2(g)$, and $1/2H_2O(l)$. Corrections to the standard state, ΔU_Σ, were made by the procedure given by Good and Scott[2] for fluorine-containing compounds, based on the method developed by Hubbard et al.,[59] including the values for the solubility of carbon dioxide in hydrofluoric acid solutions, as given by Cox et al.[60]

All the necessary weightings for the combustion experiments were made on a Mettler Toledo AE245 balance, with a sensitivity of $\pm(1 \times 10^{-5})$ g, and corrections from the apparent mass in air to the true mass were introduced.

Procedure for Calvet Microcalorimetry Measurements. The standard molar enthalpies of sublimation or vaporization were measured using the vacuum sublimation drop-microcalorimetric technique of Skinner et al.;[61] the detailed description of the apparatus used has been reported in the literature.[62]

The samples of approximately 5–8 mg contained in a thin glass capillary and a blank reference capillary were simultaneously dropped, at room temperature, in the respective twin calorimetric cells, held at a predefined temperature of 338 K for the liquid isomers and 318 K for the solid isomer. The thermal corrections for the differences in the mass of both glass capillary tubes and for the different sensibilities of the two calorimetric cells were determined in separated experiments and were minimized, as far as possible, by dropping tubes of nearly equal mass into each twin calorimeter cells.[62]

The observed standard molar enthalpies of sublimation or vaporization, $\Delta_{l,cr,298.15K}^{g,T} H_m^o$, have been corrected to $T = 298.15$ K using the values of $\Delta_{298.15K}^T H_m^o(g)$ estimated by a group additivity shown in Scheme 1, based on data of Stull et al.[63]

Scheme 1. Group Scheme for $\Delta_{298.15K}^T H_m^o(g)$ Estimation
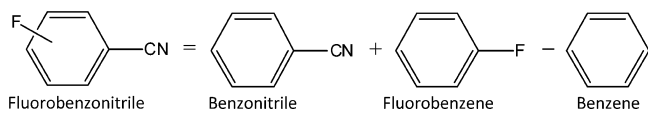
The microcalorimeter was calibrated in situ for these measurements using the reported standard molar enthalpy of vaporization of undecane (56.580 ± 0.566) kJ·mol^{-1} [64] for 2- and 3-fluorobenzonitrile and of sublimation of naphthalene (72.6 ± 0.6) kJ.mol^{-1} [61] for the solid 4-fluorobenzonitrile. The calibration constants, k, of the calorimeter were $k(T = 338$ K$) = 1.0114 \pm 0.0025$ and $k(T = 318$ K$) = 1.0109 \pm 0.0015$ for the vaporization and sublimation experiments, respectively. All of the necessary weights were performed on a Mettler CH-8608 analytical balance with a sensitivity of $\pm(1 \times 10^{-7})$ g.

Procedure for Vapor Pressure Measurements. The vapor pressures of the three compounds were measured at different temperatures using a static apparatus equipped with a capacitance diaphragm gauge, previously tested and described in detail.[24] Two different Baratron manometers operating at self-controlled constant temperatures were used for the vapor pressure measurements of 4-fluorobenzonitrile for the solid and liquid phases: gauge I, Baratron 631A01 TBEH ($T_{gauge} = 423$ K), for measuring pressures in the range 0.3–130 Pa and in the temperature range 253–473 K and gauge II, Baratron 631A11 TBFP ($T_{gauge} = 473$K), for measuring pressures in the range 3–1330 Pa and in the temperature range 253–463 K. The study of the vapor pressures of the 2- and 3-fluorobenzonitrile isomers was performed using only the gauge I. The temperature of the condensed samples was measured using a platinum resistance thermometer Pt100 class 1/10 (in four wire connection). This thermometer was calibrated by comparison with a SPRT (25 Ω, Tinsley, 5187 A).

The uncertainty of the temperature measurements is estimated to be better than $\pm(1 \times 10^{-2})$ K, and the uncertainty in the pressure measurements is satisfactorily described by the expression $\sigma(p/Pa) = 0.01 + 0.0025(p/Pa)$.[65]

To avoid condensation of the vapor, the tubing between the condensed sample and the pressure gauge is kept at a temperature higher than the temperature of the sample and lower than the temperature of the gauge.

Procedure for UV–vis Spectroscopy. The structures of the three benzonitrile isomers were experimentally characterized by UV–vis spectroscopy using a diode array spectrophotometer, with temperature control. The UV–vis spectra were carry out in quartz cells within a wavelength range between 190 to 500 nm, at $T = 298.15$ K. The solutions used for the UV–vis measurements were obtained by rigorous dilution of a known mass of each compound in dichloromethane. Before the measurement of each compound a blank measurement was performed. The wavelength accuracy of the spectrophotometer was evaluated through the measurement of a test sample of caffeine solution (10 mg/L in water).

Computational Details. Standard ab initio molecular orbital calculations were performed with the Gaussian 03 series of programs.[66] The G3(MP2)//B3LYP composite method was used throughout this work.[39] This is a variation of G3MP2 theory[67] which uses the B3LYP density functional method[68,69] for geometries and zero-point energies. The B3LYP functional uses a combination of the hybrid three-parameter Becke's functional, first proposed by Becke,[65] together with the Lee–Yang–Parr nonlocal correlation functional.[70]

The computations carried out with 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 Moller–Plesset perturbation instead of MP4 as in the original G3 method.[71] 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 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 and gas-phase basicities. For that purpose, the G3MP2B3 computations were also extended to cationic, anionic, and radicalar species of these compounds.

The geometries of the fluorinated benzonitrile derivatives were reoptimized at the MP2/cc-pVTZ level, and the NBO analysis[72] was performed using the NBO program.[73] The larger is the second-order perturbation interaction energy value, $\Delta E^{(2)}$, the more intensive is the interaction between the donor and acceptor orbitals, and usually, the greater is the extent of conjugation of the whole system.

The QTAIM calculations were performed with the AIMAll program package[74] using the formatted checkpoint file obtained from the geometry optimization at the same level of theory. When the bond is cylindrically symmetric as the simple and triple bond, the bond ellipticity, ε_{CP}, is, ideally, zero. In a double bond, there is a distortion in the symmetry of the electron density and the ε_{CP} reaches the maximum.[75]

The aromaticity of the benzenic ring of the monofluorobenzonitrile isomers was assessed by the nucleus independent chemical shift

(NICS) method.[76,77] The values of the total magnetic shielding were computed by the standard GIAO procedure at the B3LYP/6-311++G(2df,2pd) level of theory, using the reoptimized geometries. As for the calculations of the enthalpies, all of the analyses were also carried out with the Gaussian 03 package.[66]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed description of the rotative-bomb calorimetry and Calvet microcalorimetry, together with their respective experiments for 2-, 3-, and 4-fluorobenzonitrile. Detailed tables of the static vapour pressure results of the three fluorobenzonitrile isomers. Cartesian coordinates of the optimized structures for the three fluorinated benzonitrile isomers from G3(MP2)//B3LYP and MP2/cc-pVTZ calculations as well as, the enthalpies at $T = 298.15$ K, computed by G3(MP2)//B3LYP and quantum theory of atoms in molecules, natural bond orbital, and nucleus-independent chemical shifts from MP2/cc-pVTZ calculations. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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