Experimental and Computational Thermodynamic Study of Three Monofluoronitrobenzene Isomers

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The present work reports the thermodynamic study performed on three monofluorinated nitrobenzene derivatives by a combination of experimental techniques and computational approaches. The standard ($p° = 0.1$ MPa) molar enthalpies of formation in the liquid phase of the three isomers of fluoronitrobenzene were derived from the standard molar energies of combustion, in oxygen, at $T = 298.15$ K, measured by rotating bomb combustion calorimetry. The vapor pressure study of the referred compounds was done by a static method and, from the obtained results, the phase diagrams were elaborated, and the respective triple point coordinates, as well as the standard molar enthalpies of vaporization, sublimation and fusion, at $T = 298.15$ K, were determined. The combination of some of the referred thermodynamic parameters yielded the standard ($p° = 0.1$ MPa) molar enthalpies of formation in the gaseous phase, at $T = 298.15$ K, of the studied compounds: $\Delta_f H_m^o$(2-fluoronitrobenzene, g) $= -(102.4 \pm 1.5)$ kJ·mol^{-1}, $\Delta_f H_m^o$(3-fluoronitrobenzene, g) $= -(128.0 \pm 1.7)$ kJ·mol^{-1}, and $\Delta_f H_m^o$(4-fluoronitrobenzene, g) $= -(133.9 \pm 1.4)$ kJ·mol^{-1}. Using the empirical scheme developed by Cox, values of standard molar enthalpies of formation in the gaseous phase were estimated and afterwards compared with the ones obtained experimentally, and both were interpreted in terms of the molecular structure of the compounds. The theoretically estimated gas-phase enthalpies of formation were calculated from high-level ab initio molecular orbital calculations at the G3(MP2)//B3LYP level of theory. The computed values compare very well with the experimental results obtained in this work and show that 4-fluoronitrobenzene is the most stable isomer from the thermodynamic point of view. Furthermore, this composite approach was also used to obtain information about the gas-phase basicities, proton and electron affinities and, finally, adiabatic ionization enthalpies.

1. Introduction

Most halogenated aromatic compounds, besides having a large number of applications, are known to be severe pollutants and have a high environmental impact.

The use of halogenated nitrobenzenes as basic chemical intermediates in the synthesis of various halogenated and nonhalogenated aromatic compounds is extensively described in the literature.[1-7] The structure of these compounds contributes to their interest because they contain a halogen atom, classified as both a π donor and a σ acceptor, and a nitro group, known as a typical electron-withdrawing group, as substituents on a common benzene ring. These compounds have important pharmaceutical, industrial, and agricultural applications, being used in the manufacture of dyes,[8,9] synthetic pesticides,[10-12] synthetic rubbers,[13] and so forth. Despite their important implications, the energetics of these compounds is not sufficiently documented.

The chemical properties of fluorine make fluorinated compounds very appealing as synthetic precursors of multiple biologically relevant compounds, and there has been an expanding development of safer and more practical methods for the synthesis of fluorine-containing molecules. Actually, fluorine is a common feature in synthetic active molecules, for both agrochemicals and pharmaceuticals, since its incorporation

increases the molecule activity, binding selectivity, lipophilicity, and bioavailability.[14,15]

Fluoronitrobenzene derivatives, in particular, are used as precursors in the synthesis of aromatic polyamides and polyimides. Because of their high glass transition temperature, this class of polymers exhibits high thermal stability, good mechanical properties, and chemical resistance.[16,17] They are also one of the most important high-performance and electronic polymers, with electrical properties such as electrochromism, photoconductivity, and electroluminescence and show increasing potential as active components for a wide range of electronic and optoelectronic devices, such as organic light emitting diodes and photoreceptor devices.[18-20] The use of fluorinated nitrobenzenes as intermediates in the synthesis of benzimidazole[21-23] and pyrazole[24] derivatives has also been reported.

These reasons greatly contribute to the importance of understanding the reactivity and the relation between the energetics and structural properties of these compounds, which are essential for technological applications.

The present work is part of a broad research project, being carried out in the University of Porto Chemical Research Center, on the systematic study of the energetics of halogenated derivatives of various aromatic compounds such as anilines,[25-27] nitroanilines,[28-30] nitrobenzenes,[31,32] phenols,[33,34] and so forth. As a part of this project, we have studied the thermochemistry of three monofluoronitrobenzene isomers (see Figure 1).

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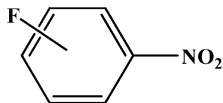
Figure 1. Structural formula of the fluoronitrobenzene isomers.

With this purpose, the standard ($p° = 0.10$ MPa) molar enthalpies of formation, at $T = 298.15$ K, of the referred compounds, in the liquid phase, were derived from the respective massic energies of combustion, determined by rotating-bomb combustion calorimetry.

The vapor pressure study of the condensed phases of the referred compounds was done by an indirect method, using a static apparatus based on a capacitance diaphragm gage.[35] From the obtained results, it was possible to perform a phase transition study and to construct the respective phase diagrams of the studied compounds and determine their triple point coordinates. The enthalpies of vaporization, sublimation, and fusion were also derived from these results.

The standard molar enthalpies of vaporization of the compounds, at $T = 298.15$ K, were used to derive the standard molar enthalpies of formation in the gaseous phase. The obtained experimental values of the standard molar enthalpies of formation in the gaseous phase, at $T = 298.15$ K, were then compared with the ones estimated by the Cox[36] empiric method and interpreted in terms of the molecular structure of the compounds.

Additionally, 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.

2. Experimental Section

Materials and Purity Control. The compounds 2-fluoronitrobenzene [CAS 1493-27-2], 3-fluoronitrobenzene [CAS 402-67-5], and 4-fluoronitrobenzene [CAS 350-46-9] were acquired from Sigma-Aldrich Chemical Co., with an estimated minimum purity of 0.98 (mass fraction). The referred compounds are liquid at room temperature and were purified by successive fractional distillations under reduced pressure. The final purity of each fluoronitrobenzene isomer was checked by gas chromatography, performed on an Agilent 4890D gas chromatograph equipped with an HP-5 column, cross-linked, 5% diphenyl and 95% dimethylpolysiloxane (15 m × 0.530 mm i.d. × 1.5 μm film thickness), and using nitrogen as carrier gas. The temperature of the injector was set at 473 K, and the oven temperature was programmed as follows: 323 K (1 min), ramp at 10 K·min⁻¹, 473 K (20 min). No impurities greater than 10^{-3} in mass fraction could be detected in the samples of the fluoronitrobenzene isomers used for calorimetric and vapor pressure studies.

Rotating Bomb Combustion Calorimetry Measurements. A calorimetric method was applied to determine the massic energies of combustion of the studied compounds, from which the respective standard molar enthalpies of combustion were derived. An isoperibol rotating-bomb combustion calorimeter, originally constructed at the University of Lund following the design formerly developed by Stig Sunner,[37] was used. The apparatus, as well as the operating technique, have already been described in detail,[38–40] so only a brief summary of the apparatus is presented here.

The combustion bomb used was a stainless steel twin valve platinum lined bomb with all the internal fittings constructed in platinum. It has an internal volume of 0.258 dm³ and a wall thickness of 1 cm. The bomb is suspended from the lid of the calorimeter can, to which is added a mass of

approximately 5222.5 g of distilled water, weighed with a Mettler PM 11-N balance, sensitivity $\pm(1 \times 10^{-1})$ g, with a previously weighed Perspex vessel. For each experiment, a correction was applied to the energy equivalent regarding the difference between the mass of water used and the reference mass of 5222.5 g. The mechanism that supports the bomb from the lid of the calorimeter also permits the simultaneous axial and end-over-end rotation of the combustion bomb, allowing the solution placed in the bomb to wash all its internal surfaces, yielding a homogeneous final solution. The calorimeter can is inserted in an isothermal jacket, which consists of a thermostatic bath containing a cavity of exactly the same shape as the calorimeter can, but 1 cm larger in overall dimensions, enclosed by a hollow lid. The jacket and lid are filled with water maintained at a temperature of ca. 303.5 K to $\pm(1 \times 10^{-3})$ K using a temperature controller (Tronac PTC 41).

Calorimeter temperatures were automatically collected at regular intervals of 10 s using a Hewlett-Packard (HP-2804A) quartz crystal thermometer, sensitivity $\pm(1 \times 10^{-4})$ K, interfaced to a PC programmed to collected data and to compute the adiabatic temperature change. Data acquisition and control of the calorimeter were performed using a version of the LAB-TERMO program.[41] At least 100 temperature readings were taken for the main period and for both initial and final periods. For all combustion experiments, the ignition temperature was estimated so that the final temperature would be as close as possible to $T = 298.15$ K.

The electrical energy for ignition was determined from the change in potential across a capacitor (1400 μF) when discharged through a platinum wire ($\phi = 0.05$ mm, Goodfellow, mass fraction 0.9999). For each combustion experiment of the fluoronitrobenzene isomers, the rotation of the bomb was started when the temperature rise in the main-period reached about 0.63 of its total value and was continued throughout to the end of the experiment. With this procedure, the frictional work of the bomb rotation and stirring is automatically included in the temperature corrections for the work of water stirring and for the heat exchanged with the thermostatted jacket, as shown by Good et al.[42]

The calorimetric system was conventionally calibrated, and the energy equivalent of the calorimeter was determined from the combustion of benzoic acid (NIST Standard Reference Material 39j) having a massic energy of combustion under bomb conditions of $-(26434 \pm 3)$ J·g⁻¹.[43] Calibration experiments were carried out without bomb rotation, in oxygen at the pressure of 3.04 MPa, and with 1.00 cm³ of deionized water added to the bomb, all this according to the procedure suggested by Coops et al.[44] The mean of a set of seven calibration experiments led to the value of the energy equivalent of the calorimeter: ε(calor) = (25157.4 $\pm$ 1.1) J·K⁻¹,[33] where the uncertainty quoted is the standard deviation of the mean.

The combustion experiments of the three fluoronitrobenzenes were carried out in oxygen, at $p = 3.04$ MPa, in the presence of 10.00 cm³ of water and with bomb-rotation, as already cited. The liquid compounds were burnt enclosed in polyethylene bags, $\Delta_c u° = -(46282.4 \pm 4.8)$ J·g⁻¹,[45] a value measured in our laboratory by combustion of polyethylene samples. All the necessary weighing was made on a Mettler Toledo AE 240 balance, with a sensitivity of $\pm(1 \times 10^{-5})$ g, and necessary corrections from apparent mass to true mass were performed. The specific densities,[46] used to calculate the true mass from the apparent mass in air for 2-, 3-, and 4-fluoronitrobenzene were 1.338 g·cm⁻³, 1.325 g·cm⁻³, and 1.33 g·cm⁻³, respec-

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tively. The relative atomic masses used in the calculation of all molar quantities throughout this paper were those recommended by the IUPAC Commission in 2005,[47] yielding 141.0999 g·mol^{-1}, for the molar mass of the fluoronitrobenzene isomers.

The nitric acid formed was analyzed by the Devarda's alloy method.[48] Corrections for nitric acid formation were based on -59.7 kJ·mol^{-1} for the standard molar energy of formation in which 0.1 mol·dm^{-3} HNO$_3$(aq) is formed from O$_2$(g), N$_2$(g), and H$_2$O(l).[49] For the cotton thread fuse of empirical formula CH$_{1.686}$O$_{0.843}$, $\Delta_c u^o = -16240$ J·g^{-1},[44] a value that has been confirmed in our laboratory. Corrections to the standard state, ΔU_Σ, were made as described by Good and Scott[50] for fluorine-containing compounds, based on the method developed by Hubbard et al.,[51] including the values for the solubility of carbon dioxide in hydrofluoric acid solutions, provided by Cox et al.[52] The value of the pressure coefficient of massic energy $(\partial u/\partial p)_T$ for the studied compounds was assumed to be -0.2 J·g^{-1}·MPa^{-1} at $T = 298.15$ K, a typical value for most organic compounds.[53]

Vapor Pressure Measurements. The vapor pressures of the condensed phases of the three fluoronitrobenzene isomers were measured using a static apparatus, previously tested and described in detail.[35,54] This apparatus is equipped with one of two available MKS capacitance diaphragm absolute gauges, operating at self-controlled constant temperatures: Baratron 631A01TBEH ($T_{gauge} = 423$ K) for measuring pressures in the range 0.3−130 Pa and in the sample temperature range 253−413 K (gauge 1), and Baratron 631A11TBFP ($T_{gauge} = 473$ K) for measuring pressures in the range 3−1300 Pa and in the sample temperature range 253−463 K (gauge 2). The temperature of the condensed sample is measured using a platinum resistance thermometer Pt100 class 1/10 (in a four wire connection), which is in good thermal contact with the sample, calibrated by comparison with a SPRT (25 Ω; Tinsley, 5187A). The uncertainty of the temperature measurements is estimated to be less than $\pm(1 \times 10^{-2})$ K. 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. The uncertainty in the vapor pressure measurements increase linearly with the pressure, being adequately described by the expression $\sigma(p/\text{Pa}) = 0.01 + 0.0025(p/\text{Pa})$ for gauge 1 and $\sigma(p/\text{Pa}) = 0.1 + 0.0025(p/\text{Pa})$ for gauge 2.[35]

3. Computational Details

Standard ab initio molecular orbital calculations were performed with the Gaussian 03 series of programs.[55] The G3MP2B3 composite method was used throughout this work.[56] This is a variation of the G3MP2 theory,[57] which uses the B3LYP density functional method[58,59] for geometries and zero-point energies. The B3LYP functional uses a combination of the hybrid three-parameter Becke's functional, first proposed by Becke,[58] together with the Lee−Yang−Parr nonlocal correlation functional.[60]

The computations carried out with the G3MP2B3 composite approach use the B3LYP method and the 6-31G(d) basis set for both the optimization of geometry and calculation of frequencies. Introduction of high-order corrections to the B3LYP/6-31G(d) enthalpy is done in a manner that follows the Gaussian-3 philosophy, albeit using a second-order Moller−Plesset perturbation instead of MP4 as in the original G3 method.[61]

The enthalpy of formation of the three different isomers was estimated after consideration of the following gas-phase atomization and isodesmic reactions:
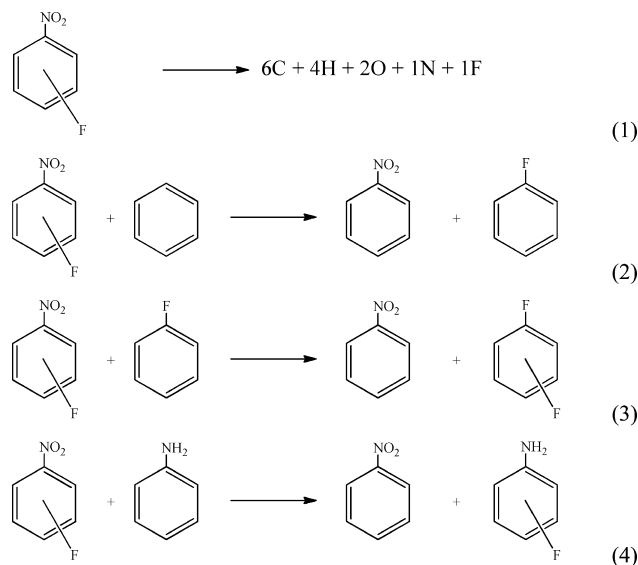
These reactions have been chosen on the basis of the available experimental thermochemical data for the compounds there used.

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 also calculate 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 the three isomers.

4. Results and Discussion

Experimental Enthalpies of Formation, in the Liquid Phase. Detailed results for a typical combustion experiment of each compound are given in Table 1. The values of the energy associated with the isothermal bomb process, $\Delta U(\text{IBP})$, were calculated from eq 5:

$$\Delta U(\text{IBP}) = -\{\varepsilon(\text{calor}) + \Delta m(\text{H}_2\text{O})c_p(\text{H}_2\text{O},l)\}\Delta T_{ad} + (T_i - 298.15\,\text{K})\varepsilon_i + (298.15\,\text{K} - T_i - \Delta T_{ad})\varepsilon_f + \Delta U_{ign} \tag{5}$$

where $\Delta m(\text{H}_2\text{O})$ is the deviation of the mass of water added to the calorimeter from 5222.5 g, the mass assigned to $\varepsilon(\text{calor})$, $c_p(\text{H}_2\text{O, l})$ is the heat capacity of liquid water, ε_i and ε_f are, respectively, the energy equivalent of the bomb contents in the initial and final state, ΔT_{ad} is the calorimeter temperature change corrected for the heat exchange, work of stirring, and the frictional work of bomb rotation, and ΔU_{ign} is the electrical energy of ignition. ΔU_Σ is the energy correction to the standard state (Washburn correction) derived as recommended in the literature for compounds containing fluorine.[50] The remaining quantities are as previously defined.[51,53] The detailed results for all the combustion experiments of each compound, together with the mean value of the standard massic energies of combustion, $\Delta_c u^o$, are presented in the Supporting Information (Tables S1−S3).

The individual values of the standard massic energy of combustion, $\Delta_c u^o$, for all the combustion experiments of each compound, together with the mean values, $\langle \Delta_c u^o \rangle$, and their standard deviations of the mean, are listed, for each compound,

TABLE 1: Typical Combustion Results at $T = 298.15$ K ($p° = 0.1$ MPa), for the Fluoronitrobenzene Isomers

experiment[a]	2-fluoronitrobenzene	3-fluoronitrobenzene	4-fluoronitrobenzene
m(cpd)/g	0.69461	0.64411	0.66848
m'(fuse)/g	0.00241	0.00246	0.00270
m''(polyethylene)/g	0.17675	0.15405	0.16551
T_i/K	297.1972	297.3149	297.2733
T_f / K	298.1207	298.1501	298.1481
ΔT_{ad}/K	0.90523	0.81777	0.85739
ε_i/J$\cdot$K^{-1}	51.76	51.59	51.65
ε_f/J$\cdot$K^{-1}	53.48	53.14	53.27
ε(calor)$_{corr}$/J$\cdot$K^{-1}	25152.0	25150.7	25157.8
Δm(H$_2$O)/g	−1.3	−1.6	0.1
$-\Delta U$(IBP)[b]/J	22813.94	20608.47	21613.11
ΔU(fuse)/J	39.14	39.95	43.85
ΔU(polyethylene)/J	8180.45	7130.03	7660.11
ΔU(HNO$_3$)/J	39.82	34.21	34.57
ΔU(ign)/J	1.18	1.18	1.19
ΔU_Σ/J	30.11	29.60	29.90
$-\Delta_c u°$/J$\cdot$g^{-1}	20910.18	20764.59	20710.69

[a] m(cpd), m'(fuse), and m''(polyethylene) are, respectively, the mass of compound burnt, the mass of fuse (cotton), and the mass of polyethylene used in each experiment; T_i is the initial temperature rise; T_f is the final temperature rise; ΔT_{ad} is the corrected temperature rise; ε_i and ε_f are the energy equivalent of contents in the initial and final states, respectively; ε(calor)$_{corr}$ is the energy equivalent of the calorimeter; Δm(H$_2$O) is the deviation of mass of water added to the calorimeter from 5222.5 g; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU(fuse) is the energy combustion of the fuse (cotton); ΔU(polyethylene) is the energy of combustion of polyethylene; ΔU(HNO$_3$) is the energy correction for the nitric acid formation; ΔU(ign) is the electrical energy for ignition; ΔU_Σ is the standard state correction; $\Delta_c u°$ is the standard massic energy of combustion. [b] ΔU(IBP) includes ΔU(ign).

TABLE 2: Individual Values of the Standard ($p° = 0.1$ MPa) Massic Energies of Combustion, $\Delta_c u°$, for the Fluoronitrobenzenes, at $T = 298.15$ K

2-fluoronitrobenzene	3-fluoronitrobenzene	4-fluoronitrobenzene
$-\Delta_c u°$/J$\cdot$g^{-1}		
20910.18	20764.59	20710.69
20920.81	20780.12	20717.90
20927.25	20787.52	20727.05
20922.09	20775.60	20724.47
20912.77	20763.04	20727.48
20926.79	20760.68	20719.46
$-\langle\Delta_c u°\rangle$/J$\cdot$g^{-1a}		
20920.0 ± 2.9	20771.9 ± 4.4	20721.2 ± 2.6

[a] Mean value and standard deviation of the mean.

TABLE 3: Derived Standard ($p° = 0.1$ MPa) Molar Values in the Liquid Phase, at $T = 298.15$ K[a]

compound	$(-\Delta_c U_m°(l))/$ (kJ$\cdot$mol^{-1})	$(-\Delta_c H_m°(l))/$ (kJ$\cdot$mol^{-1})	$(-\Delta_f H_m°(l))/$ (kJ$\cdot$mol^{-1})
2-fluoronitrobenzene	2951.8 ± 1.1	2949.9 ± 1.1	161.9 ± 1.5
3-fluoronitrobenzene	2930.9 ± 1.4	2929.0 ± 1.4	182.8 ± 1.7
4-fluoronitrobenzene	2923.8 ± 1.0	2921.9 ± 1.0	189.9 ± 1.4

[a] The associated uncertainties are twice the overall standard deviation of the mean, and include the contributions from the calibration with benzoic acid and from the energy of combustion of auxiliary materials.

in Table 2. The values of $\Delta_c u°$ refer to the idealized combustion reaction of fluoronitrobenzenes, yielding HF$\cdot$10H$_2$O(l) as the only fluorine-containing product in the final state, according to eq 6:

$$C_6H_4O_2NF(l) + 5.75 \, O_2(g) + 8.5 \, H_2O(l) \rightarrow 6 \, CO_2(g) + 0.5 \, N_2(g) + HF \cdot 10H_2O(l) \quad (6)$$

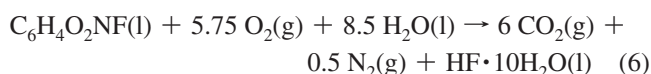Table 3 lists the derived values of the standard molar energies and enthalpies of combustion, $\Delta_c U_m°(l)$ and $\Delta_c H_m°(l)$, as well as the standard molar enthalpies of formation, $\Delta_f H_m°(l)$,

TABLE 4: Experimental Data on Vapor Pressure of 2-Fluoronitrobenzene[a]

T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa
			Crystalline Phase					
257.90	0.323	−0.001	259.41	0.405	0.003	260.96	0.499	−0.001
258.41	0.347	−0.002	259.93	0.432	−0.001	261.44	0.534	−0.001
258.89	0.375	0.002	260.45	0.465	0.000			
			Liquid Phase					
267.24	1.19	0.01	300.02	23.77	−0.09	332.83	232.8	0.20
270.24	1.60	−0.02	302.97	30.37	0.31	335.81	275.9	−2.20
273.20	2.15	−0.04	306.00	37.72	−0.16	338.78	331.1	0.20
276.18	2.92	−0.01	308.97	47.63	0.38	341.74	390.4	−1.50
279.14	3.99	0.09	311.99	58.29	−0.54	344.73	462.3	−0.90
282.11	5.22	0.07	314.96	72.78	0.18	347.70	542.1	−2.60
285.06	6.72	−0.02	317.95	88.40	−0.86	350.69	639.8	0.80
288.06	8.82	0.02	320.93	109.3	0.20	353.71	749.7	1.60
291.07	11.48	0.06	323.91	132.8	0.00	356.69	874.7	3.90
294.05	14.69	0.00	326.87	162.2	1.50	359.67	1017	7.00
297.04	18.75	−0.04	329.87	192.1	−1.90			

[a] $\Delta p = p - p_{calc}$, where p_{calc} is calculated from the Clarke and Glew eq 7, with parameters given in Table 7.

for the three isomers in the liquid phase, at $T = 298.15$ K, which were derived from the values of $\Delta_c H_m°(l)$ and from the following standard molar enthalpies formation, at $T = 298.15$ K: $\Delta_f H_m°(CO_2, g) = -(393.51 \pm 0.13)$ kJ$\cdot$mol^{-1};[62] $\Delta_f H_m°(H_2O, l) = -(285.830 \pm 0.040)$ kJ$\cdot$mol^{-1};[62] and $\Delta_f H_m°(HF\cdot10H_2O, l) = -(322.034 \pm 0.650)$ kJ$\cdot$mol^{-1}.[63] The uncertainties assigned to the standard molar energies of combustion correspond, in each case, to twice the overall standard deviation of the mean and include the contributions from the calibration with benzoic acid and from the energy of combustion of polyethylene used as the combustion auxiliar.[64,65]

Vapor Pressures and Enthalpies of Phase Transitions. The results of the measured vapor pressures for the liquid (both stable and supercooled) and crystalline phases of the studied fluoronitrobenzene isomers are presented in Tables 4, 5, and 6.

The measured vapor pressures for the crystalline phase of the 2-fluoronitrobenzene were performed through a very small temperature interval. These measurements were repeated at each temperature until perfect agreement of results was achieved. This

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TABLE 5: Experimental Data on Vapor Pressure of 3-Fluoronitrobenzene[a]

T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa
				Crystalline Phase				
255.38	0.75	0.01	262.40	1.85	−0.02	268.21	3.89	0.02
256.38	0.85	0.00	263.36	2.10	−0.02	269.20	4.40	0.04
257.39	0.97	0.00	264.33	2.38	−0.01	270.20	4.91	−0.01
258.38	1.11	0.00	265.28	2.72	0.03	271.19	5.48	−0.06
259.37	1.26	−0.01	266.24	3.10	0.07	272.17	6.17	−0.05
260.43	1.45	0.00	267.23	3.50	0.07	273.18	6.95	−0.06
261.42	1.64	−0.01						
				Liquid Phase				
259.39[b]	1.93	0.00	289.07	28.89	0.05	318.95	238.1	−1.70
262.37[b]	2.62	0.00	292.05	36.14	−0.34	321.91	287.7	−0.50
265.26[b]	3.50	0.00	295.05	45.91	−0.06	324.95	345.5	−1.00
268.22[b]	4.64	−0.02	298.01	57.63	0.22	327.85	408.9	−2.60
271.20[b]	6.17	0.00	301.02	71.86	0.28	330.90	491.8	0.80
274.17[b]	8.15	0.04	303.96	88.47	0.14	333.80	580.4	1.70
277.15	10.52	−0.07	306.99	110.2	1.10	336.86	685.3	−0.20
280.13	13.80	0.07	309.94	132.5	−1.00	339.84	807.5	2.10
283.11	17.81	0.11	312.95	164.4	1.30	342.82	946.8	3.70
286.07	22.71	0.08	315.91	195.3	−2.40	345.80	1102	2.00

[a] Δp = p − p_calc, where p_calc is calculated from the Clarke and Glew eq 7, with parameters given in Table 7. [b] Supercooled liquid.

TABLE 6: Experimental Data on Vapor Pressure of 4-Fluoronitrobenzene[a]

T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa
				Crystalline Phase				
258.90	0.59	−0.02	267.74	1.86	0.01	283.10	10.33	−0.20
260.46	0.74	−0.01	269.25	2.26	0.05	285.09	12.92	−0.08
261.92	0.89	−0.01	275.18	4.52	0.12	287.08	15.92	−0.09
263.37	1.08	0.00	277.13	5.60	0.12	289.07	19.49	−0.16
264.82	1.32	0.03	279.12	6.87	0.04	291.06	23.53	−0.53
266.30	1.57	0.02	281.09	8.58	0.10			
				Liquid Phase				
272.22[b]	4.83	−0.01	300.98	53.15	−0.33	327.42	314.3	0.00
275.18[b]	6.42	0.05	302.47	60.05	0.36	329.85	362.6	−0.90
278.15[b]	8.37	0.04	304.95	71.22	−0.23	332.38	423.3	1.50
281.12[b]	10.84	0.01	309.93	101.2	−0.30	334.87	487.3	0.20
284.10[b]	13.99	−0.01	312.48	121.7	0.90	337.35	559.9	−0.60
287.08[b]	17.90	−0.08	314.93	142.4	0.00	339.83	642.9	−0.70
290.06[b]	22.78	−0.17	317.45	167.5	−0.60	342.32	735.2	−2.20
293.09	29.24	0.00	319.91	197.9	0.90	344.80	842.7	0.30
296.02	36.38	−0.38	322.44	233.2	1.90	347.17	952.7	−2.00
298.52	44.56	0.07	324.93	271.8	1.80	349.76	1089	−3.00

[a] Δp = p − p_calc, where p_calc is calculated from the Clarke and Glew eq 7, with parameters given in Table 7. [b] Supercooled liquid.

procedure enabled the presentation of the results for the crystalline phase of this compound with three decimal figures.

The experimental results of the solid and liquid vapor pressures were fitted (independently) by the Clarke and Glew equation (eq 7):[66]

$$R \ln\left(\frac{p}{p^{\circ}}\right) = -\frac{\Delta_{cd}^{g}G_{m}^{\circ}(\theta)}{\theta} + \Delta_{cd}^{g}H_{m}^{\circ}(\theta)\left(\frac{1}{\theta} - \frac{1}{T}\right) +$$
$$\Delta_{cd}^{g}C_{p,m}^{\circ}(\theta)\left[\left(\frac{\theta}{T}\right) - 1 + \ln\left(\frac{T}{\theta}\right)\right] \quad (7)$$

where p is the vapor pressure at the temperature T, p° is a selected reference pressure (in this study, $p^{\circ} = 10^{5}$ Pa), θ is a selected reference temperature (in this study, $\theta = 298.15$ K), R is the molar gas constant ($R = 8.31447$ J $\cdot$K$^{-1}\cdot$mol^{-1}), $\Delta_{cd}^{g}G_{m}^{\circ}$ is the difference in molar Gibbs energy between the gaseous and the crystalline or liquid phases (condensed phases) at the selected reference pressure, and $\Delta_{cd}^{g}H_{m}^{\circ}$ is the difference in molar enthalpy between the gaseous and condensed phases. The third

adjustable parameter is $\Delta_{cd}^{g}C_{p,m}^{\circ}$ which represents the difference between the heat capacities of the perfect gas and of the condensed phase. The experimental results of these terms are presented in Table 7.

The least-squares nonlinear fitting of the experimental (p,T) data of the crystalline phases to eq 7 was performed using the estimated value $\Delta_{cr}^{g}C_{p,m}^{\circ} = -24.5$ J$\cdot$K$^{-1}\cdot$mol^{-1}, derived using eq 8.[67] This equation is a rearrangement of eq 9 proposed by Chickos et al.[68] for estimation of $\{C_{p,m}^{\circ}(g) - C_{p,m}^{\circ}(cr)\}$, at the temperature 298.15 K, from a known value of $C_{p,m}^{\circ}(cr)$.

$$\Delta_{cr}^{g}C_{p,m}^{\circ}(\theta)/(J\cdot K^{-1}\cdot mol^{-1}) = -\{0.9 + 0.176C_{p,m}^{\circ}(g)\} \quad (8)$$

$$\Delta_{cr}^{g}C_{p,m}^{\circ}(\theta)/(J\cdot K^{-1}\cdot mol^{-1}) = -\{0.75 + 0.15C_{p,m}^{\circ}(cr)\} \quad (9)$$

In the case of the studied isomers, the value of $C_{p,m}^{\circ}(g) = 134.23$ J$\cdot$K$^{-1}\cdot$mol^{-1}, applied in eq 8, was derived from the data of Domalski and Hearing[69] and Ribeiro da Silva et al.,[29] using a second-order group additivity approach developed by Benson et al.:[70]

$$\{(4 \times \mathbf{C_B} - (H)(C_B)_2) + \mathbf{C_B}-(F)(C_B)_2 + \mathbf{C_B} - (NO_2)(C_B)_2\} \quad (10)$$

where $C_{p,m}^{\circ}[\mathbf{C_B} - (H)(C_B)_2, g] = 13.61$ J$\cdot$K$^{-1}\cdot$mol^{-1},[69] $C_{p,m}^{\circ}[\mathbf{C_B} - (F)(C_B)_2, g] = 26.10$ J$\cdot$K$^{-1}\cdot$mol^{-1},[69] and $C_{p,m}^{\circ}[\mathbf{C_B} - (NO_2)(C_B)_2, g] = 53.69$ J$\cdot$K$^{-1}\cdot$mol^{-1}.[29]

The results of $\Delta_{cd}^{g}C_{p,m}^{\circ}$, also presented in Table 7, were derived directly from the regression of the fitting of eq 7 to the liquid vapor pressure−temperature data. This table also contains the experimental temperature intervals, the difference in molar entropy between the gaseous and condensed phases, $\Delta_{cr,l}^{g}S_{m}^{\circ}(\theta)$, at three different temperatures: 298.15 K, the mean experimental temperature, and the triple point; the (p,T) coordinates of the triple point are also presented. As the mathematical uncertainties derived from the fitting of eq 7 to the experimental results for the enthalpy of vaporization look rather small (about 5 times smaller than the uncertainties derived for the enthalpy of vaporization at the mean temperature when using the Clausius−Clapeyron equation), the uncertainties for the enthalpies of vaporization were estimated to be 5 times greater than the values derived from the fitting of eq 7 (see Table 9).

Figures 2, 3, and 4 represent the phase diagrams (ln p vs 1000/T) at low pressures of the three isomers.

Table 8 presents the enthalpies of fusion derived as the difference between the molar enthalpies of sublimation and of vaporization, at $T = 298.15$ K and at the temperature of the triple point. At $T = 298.15$ K, all the studied compounds are liquids. The volatilities of the *meta*- and *para*-isomers are similar with the *ortho*-isomer being the less volatile liquid according to the values of $\Delta_{l}^{g}G_{m}^{\circ}(298.15 \text{ K})$ presented in Table 7. The relatively lower value of this volatility of this isomer is clearly due to the stronger intermolecular forces present in its liquid phase, which yield the highest enthalpy of vaporization of the three studied compounds.

Experimental Enthalpies of Formation, in the Gaseous Phase. Table 9 summarizes the derived standard molar enthalpies of formation in the gaseous phase, $\Delta_{f}H_{m}^{\circ}(g)$, at $T = 298.15$ K, for the three fluoronitrobenzene isomers. The obtained experimental results clearly reveal that the 2-fluoronitrobenzene

TABLE 7: Parameters of the Clarke and Glew Equations (Eq 7), Derived from Static Vapor Pressure Results for Crystalline and Liquid Fluoronitrobenzene Isomers

phase	ΔT (K)	θ (K)	$\Delta_{cr,l}^{g}G_{m}^{o}(\theta)$ (kJ·mol⁻¹)	$\Delta_{cr,l}^{g}H_{m}^{o}(\theta)$ (kJ·mol⁻¹)	$\Delta_{cr,l}^{g}S_{m}^{o}(\theta)$ (J·K⁻¹·mol⁻¹)	$p(\theta)$ (Pa)	R^2	$\Delta_{g}^{cr,l}C_{p,m}^{o}$ (J·K⁻¹·mol⁻¹)	s^g
				2-Fluoronitrobenzene					
crystalline		298.15[a]	19.02 ± 0.11	78.37 ± 0.76	199.1 ± 2.6	46.54			
	257.90−261.44	259.67[b]	26.75 ± 0.01	79.31 ± 0.76	202.4 ± 2.9	0.42	0.9995	24.5[e]	0.005
		267.43[c]	25.18 ± 0.02	79.12 ± 0.76	201.7 ± 2.8	1.21			
liquid[d]		298.15	21.05 ± 0.01	59.47 ± 0.06	128.9 ± 0.2	20.52			
	267.24−359.67	313.46[b]	19.11 ± 0.01	57.85 ± 0.04	123.6 ± 0.1	65.40	1.0000	105.0 ± 3.5[f]	0.008
		267.43[c]	25.18 ± 0.02	62.70 ± 0.04	140.3 ± 0.2	1.21			
				3-Fluoronitrobenzene					
crystalline		298.15[a]	17.08 ± 0.03	72.26 ± 0.25	185.1 ± 0.8	101.8			
	255.38−273.18	264.28[b]	23.40 ± 0.01	73.09 ± 0.25	188.0 ± 0.9	2.37	0.9998	24.5[e]	0.010
		275.32[c]	21.33 ± 0.01	72.82 ± 0.25	187.0 ± 0.9	8.99			
liquid[d]		298.15	18.47 ± 0.01	54.78 ± 0.03	121.8 ± 0.1	58.10			
	259.39−345.80	302.60[b]	17.95 ± 0.01	54.42 ± 0.03	120.5 ± 0.1	79.72	1.0000	80.9 ± 2.5[f]	0.005
		275.32[c]	21.33 ± 0.01	56.62 ± 0.03	128.2 ± 0.1	8.99			
				4-Fluoronitrobenzene					
crystalline		298.15[a]	18.93 ± 0.03	70.88 ± 0.28	174.2 ± 0.9	48.26			
	258.90−291.06	274.98[b]	22.99 ± 0.01	71.45 ± 0.28	176.2 ± 1.0	4.29	0.9998	24.5[e]	0.019
		292.70[c]	19.88 ± 0.02	71.01 ± 0.28	174.7 ± 1.0	28.36			
liquid[d]		298.15	19.20 ± 0.01	56.03 ± 0.04	123.5 ± 0.1	43.28			
	272.22−349.76	310.99[b]	17.64 ± 0.01	55.09 ± 0.03	120.4 ± 0.1	108.9	1.0000	73.4 ± 2.9[f]	0.005
		292.70[c]	19.88 ± 0.01	56.43 ± 0.03	124.9 ± 0.1	28.36			

[a] Given that, at $T = 298.15$ K, the studied compounds are in the liquid phase, the presented thermodynamic parameters for the crystalline phase are considered virtual. [b] Mean temperature. [c] Temperature of triple point. [d] Including supercooled liquid. [e] Estimated value. [f] Adjustable parameter. [g] s is the standard deviation of the fit defined as $s = [(\sum_{i=1}^{n}(\ln p - \ln p_{calc})_{i}^{2})/(n - m)]^{1/2}$, where n is the number of experimental points used in the fit and m is the number of adjustable parameters in the Clarke and Glew equation.
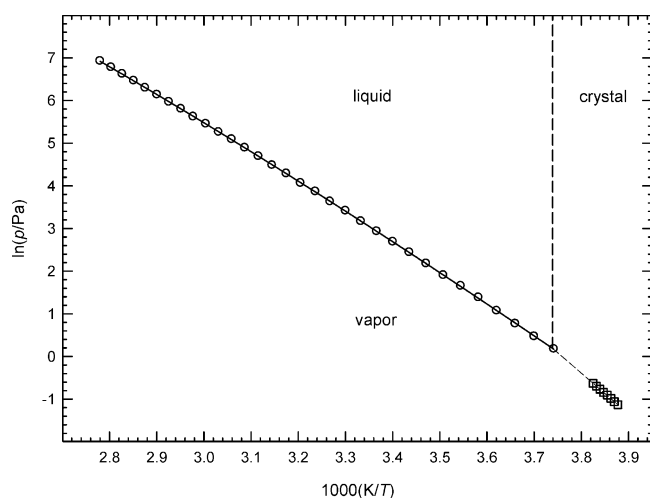
Figure 2. Phase diagram of 2-fluoronitrobenzene at low pressures. ○, stable liquid vapor pressures; □, sublimation vapor pressures.
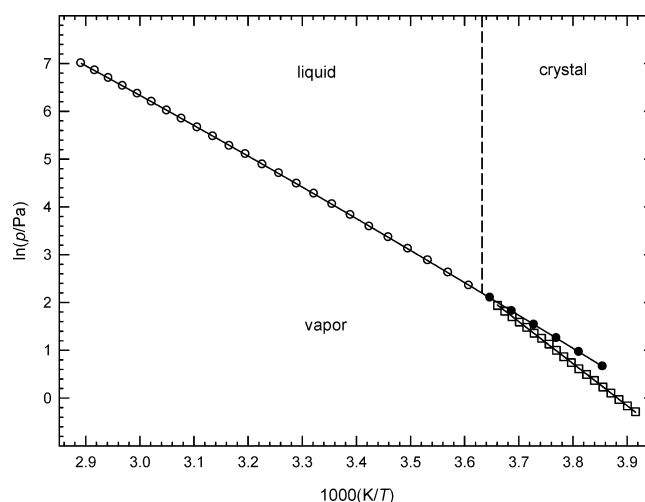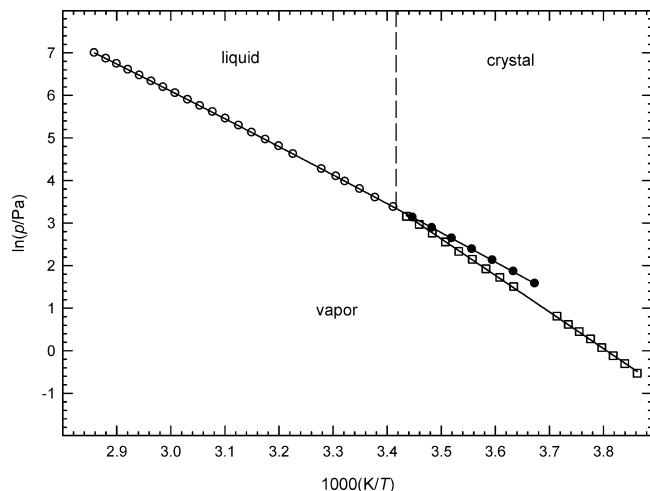

Figure 3. Phase diagram of 3-fluoronitrobenzene at low pressures. ○, stable liquid vapor pressures; ●, supercooled liquid vapor pressures; □, sublimation vapor pressures.

isomer is enthalpically less stable than the other two isomers. As it can be seen from the scheme in Figure 5, when the substitution of a fluorine atom occurs in the *ortho* position of the aromatic ring, the enthalpic effect of stabilization is less significant due to the steric effect caused by the proximity between the fluorine atom and the NO_2 group in the aromatic ring. This enthalpic effect was also noted in the other *ortho*-halonitrobenzene[31,32] and *ortho*-halonitroaniline derivatives[28−30] studied in this laboratory.[71]

The *ortho*- and *meta*-isomers of disubstituted benzenes generally possess similar physical-chemical properties, whereas they differ from the *para*-isomer[72] with the exception of nitrobenzenes, in which the *ortho*-isomer is quite different from the *meta*- and *para*-isomers. The *meta*- and *para*-halonitrobenzenes generally have a planar structure, but it was found that the equilibrium conformations for *ortho*-isomers are nonplanar,

due to the fact that the NO_2 group is twisted from the benzene ring plane because of steric hindrance. This twisting commonly takes place in *ortho*-disubstituted benzenes (i.e., NO_2, $N(CH_3)_2$, OCH_3, CHO, $COCH_3$, and CO_2CH_3).[73]

This particular substituent effect must be interpreted in terms of a complex balance of steric, inductive, and resonance effects. As for the inductive and resonance effects, the nitro group is a strong electron withdrawing group, whose potential is maximized when it is coplanar with the aromatic π ring. However, it was found that the extent of the conjugation of the nitro group with the aromatic ring is very small, and so the resonance stabilization has a relatively small contribution to the structure of the nitroaromatic compounds when compared to the steric repulsion present between the *ortho*-substituents and the oxygen atoms of the nitro group.[74] The presence of strong steric

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Figure 4. Phase diagram of 4-fluoronitrobenzene at low pressures. ○, stable liquid vapor pressures; ●, supercooled liquid vapor pressures; □, sublimation vapor pressures.

TABLE 8: Standard (p^o = 0.1 MPa) Molar Enthalpies of Fusion, at T = 298.15 K and at the Temperature of the Triple Point

compound	θ (K)	$\Delta_{cr}^l H_m^o(\theta)$ (kJ·mol^{-1})
2-fluoronitrobenzene	298.15	18.90 ± 0.82
	267.43[a]	16.42 ± 0.79
3-fluoronitrobenzene	298.15	17.48 ± 0.29
	275.32[a]	16.20 ± 0.29
4-fluoronitrobenzene	298.15	14.85 ± 0.34
	292.70[a]	14.58 ± 0.32

[a] Triple point.

TABLE 9: Standard (p^o = 0.1 MPa) Molar Enthalpies of Formation, in Condensed and Gaseous Phases, and Standard Molar Enthalpies of Vaporization, at T = 298.15 K[a]

compound	$(-\Delta_f H_m^o(l))/$ (kJ·mol^{-1})	$(\Delta_l^g H_m^o(298.15\ K))/$ (kJ·mol^{-1})	$(-\Delta_f H_m^o(g))/$ (kJ·mol^{-1})
2-fluoronitrobenzene	161.9 ± 1.5	59.47 ± 0.30	102.4 ± 1.5
3-fluoronitrobenzene	182.8 ± 1.7	54.78 ± 0.15	128.0 ± 1.7
4-fluoronitrobenzene	189.9 ± 1.4	56.03 ± 0.20	133.9 ± 1.4

[a] The uncertainties of the standard enthalpies of vaporization were estimated to be about 5 times greater than those calculated from the fitting of the liquid vapor pressure results to eq 7, presented in Table 7.

repulsions between the fluorine atom and the closest oxygen of the nitro group induces the twisting of the nitro group from the benzene ring plane, favoring a nonplanar arrangement, which decreases the conjugation between the benzene π orbital and the nitro group π orbital, justifying the *ortho*-isomer lower stability. Comparing to the *meta*- and *para*-isomers, the decreasing conjugation reduces the electron-withdrawing effect of the nitro group in *ortho*-halonitrobenzene and increases the electron density of the benzene ring π orbital, giving to the *ortho*-isomer particular electronic properties.[75]

As previously cited, all *ortho*-halonitrobenzene are nonplanar, and several structural studies have been performed in order to better define the structural characteristics of these compounds. Molecular structure studies performed on fluoronitrobenzenes by Correll et al.[76] and by Shishkov et al.,[77] using rotational spectroscopy and gas-phase electron diffraction, respectively, both detected rotation of the nitro group and determined the angle of rotation: 31.7° and 37.6°, respectively. Electronographic studies performed by Batyukhnova et al.[78] on 2-chloronitroben-
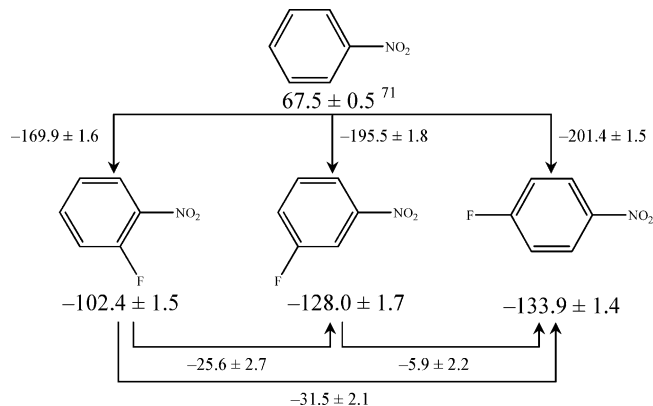
Figure 5. Enthalpic effect of substitution of a fluorine atom in the *ortho*, *meta*, and *para* positions of the aromatic ring of nitrobenzene and isomerization energies (all values are in kJ·mol^{-1}).

**TABLE 10: Dihedral Angles in *ortho*-Halonitrobenzenes**

ortho-XNO$_2$benz.	X = F	X = Cl	X = Br	X = I
φ(C−N)/°	31.7[63] 37.6[64]	33.9[65]	43.3[66]	60.0[67]

zene confirmed that the gaseous molecule is not planar, with a dihedral angle of 33.9°, between the planes of the benzene ring and of the nitro group. Batyukhnova et al.[79] also studied the 2-bromonitrobenzene by gas-phase electron diffraction, and obtained a dihedral angle of 43.3° for this molecule. The *ortho*-iodonitrobenzene was studied by Samdal et al.,[80] in the gaseous state, by an electron diffraction method, which yielded a dihedral angle of 60.0°.

A compilation of this information on the dihedral angles determined for the *ortho*-halonitrobenzene isomers is given in Table 10. Analyzing the presented information, a correlation between the dihedral angle and the size of the halogen atom is clear. The smallest dihedral angle is found for 2-fluoronitrobenzene (31.7°),[76] and the largest one is found for 2-iodonitrobenzene (60°).[80] The fluorine atom presents the highest electronegativity as well as the smallest atomic radius of all halogens, so the steric repulsions caused by the overlap of its electronic clouds are less significant than those caused by larger halogen atoms such as bromine and iodine. Consequently, the rotation angle for 2-fluoronitrobenzene is lower than those reported for the other *ortho*-halonitrobenzene derivatives. As the atomic radius increases along the halogen series (F < Cl < Br < I), the overlap of electron clouds of the halogen atom and the closest oxygen atom of the nitro group is more significant, and the C−N bond is forced to twist in a larger angle to reduce the repulsive forces.

Enthalpies of Formation Estimated with the Cox Scheme. The enthalpies of formation in the gaseous state may also be estimated by empirical methodologies such as the one suggested by Cox,[36] whose empirical scheme is based on the transferability of enthalpic group contributions in benzene derivatives, assuming that each group in the benzene ring produces a characteristic enthalpic increment in the enthalpy of formation in the gaseous phase. It is also necessary to include a correction term of +4 kJ·mol^{-1} whenever two substituents are in *ortho*-position and when three substituents are in consecutive carbon atoms of the aromatic ring. Using the methodology introduced by Cox and taking into account the scheme presented in Figure 6, the values of the gas-phase standard molar enthalpies of formation for the fluoronitrobenzene isomers can be estimated from the literature values
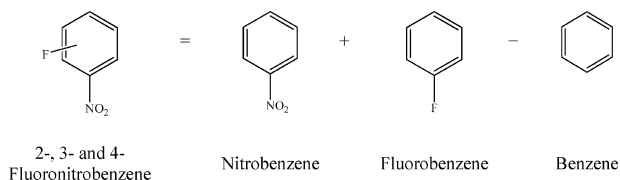
Figure 6. Empirical scheme for estimation of $\Delta_f H_m^o(g)$ by the Cox scheme.

TABLE 11: Experimental and Estimated (Cox Scheme and Computational Calculations) Gas-Phase Enthalpies of Formation of the Three Fluoronitrobenzene Isomers

	$-\Delta_f H_m^o(g)/kJ \cdot mol^{-1}$		
compound	experimental	Cox scheme	$\Delta^a/kJ \cdot mol^{-1}$
2-fluoronitrobenzene	102.4 ± 1.5	127.0 ± 1.6	24.6 ± 2.4
3-fluoronitrobenzene	128.0 ± 1.7	131.0 ± 1.6	3.0 ± 2.3
4-fluoronitrobenzene	133.9 ± 1.4	131.0 ± 1.6	-2.9 ± 2.1

^{a} Difference between the experimental and the estimated values.

of $\Delta_f H_m^o(\text{benzene,g}) = (82.6 \pm 0.7)$ kJ·mol^{-1},[71] $\Delta_f H_m^o$(fluorobenzene,g) $= -(115.9 \pm 1.4)$ kJ·mol^{-1},[71] and $\Delta_f H_m^o$(nitrobenzene,g) $= (67.5 \pm 0.5)$ kJ·mol^{-1}.[71]

The estimated value of $\Delta_f H_m^o(g)$ derived from the application of the Cox scheme[36] to the *ortho*-fluoronitrobenzene is $-(127.0 \pm 1.6)$ kJ·mol^{-1}, while the estimated value for both the *meta* and *para* isomers is $-(131.0 \pm 1.6)$ kJ·mol^{-1}, which are listed in Table 11 along with the experimental results and the deviation between them. In the cases of the *meta* and *para* isomers, the estimated values are in very good agreement with the experimental values, with calculated deviations of (3.0 ± 2.3) kJ·mol^{-1} and $-(2.9 \pm 2.1)$ kJ·mol^{-1}, respectively, which are very well within the limit of acceptance of ± 10 kJ·mol^{-1} for agreement between experimental and estimated values indicated by Cox for his scheme.[36]

However, in the case of the *ortho* isomer, the Cox approach leads to a deviation between experimental and estimated values of (24.6 ± 2.2)kJ·mol^{-1}, which is clearly out of the acceptance limit previously referred. It is concluded that the reason why the experimental value shows lower enthalpic stability than the estimated one is related with the additional steric destabilization previously discussed for this isomer, and the rotation of the nitro group to a nonplanar position with the benzene ring. The consequent decrease in conjugation with the benzene ring leads to a lower enthalpic stabilization. The enthalpic correction of $+4$ kJ·mol^{-1} suggested by Cox, is not sufficient to account for the destabilization effects that occur when the *ortho* pair of substituents are an halogen atom and the nitro group and a higher value of enthalpic correction is needed. Ribeiro da Silva et al.[28] suggested an additional correction term of $\sim$22 kJ·mol^{-1} in this case, in addition to the $+4$ kJ·mol^{-1} correction already recommended by Cox. The applicability of this correction factor has already been confirmed for the other compounds exhibiting the same behavior.[29−32] Taking into consideration that additional correction, the yielded deviation, (2.6 ± 2.2) kJ·mol^{-1}, is well within the limit of acceptance.

Gas-Phase: Molecular Structures. The optimized geometries of the three monofluoronitrobenzene isomers calculated at the G3(MP2)//B3LYP level of theory are reported in Figure 7. Within this approach, the geometry optimization is carried out at the B3LYP/6-31G(d) level of theory. Bond distances and angles are included.

As discussed above, all the studied compounds are planar except the 2-fluoronitrobenzene, where a rotation of the nitro
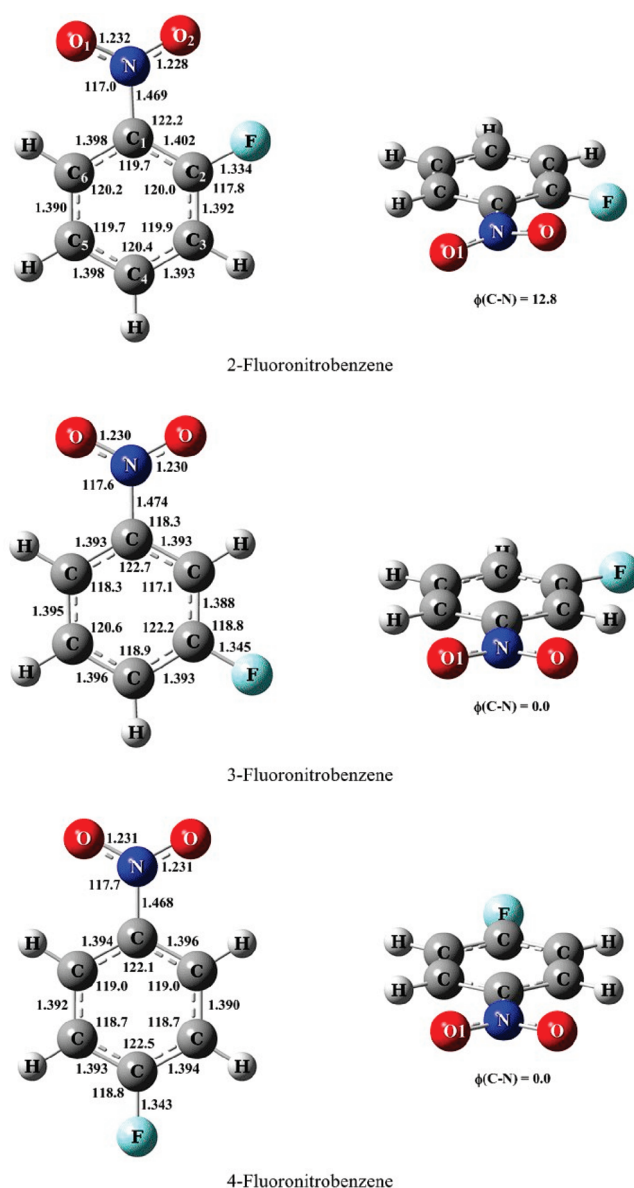
Figure 7. Front and side views of the B3LYP/6-31G(d) optimized structures of the three different isomers of fluoronitrobenzene. Distances are given in Å and angles in degrees. The atom numbering is the same for all the three isomers.

group respect to the plane containing the benzene ring is observed to avoid steric repulsion with the fluorine atom in position *ortho*. This is in agreement with the Shishkov et al.[77,81] experimental observations by gas electron diffraction. From Figure 7 it can be seen that the shortest C−F distance is that from the 2-fluoronitrobenzene. This can be explained as a polar effect due to the nitro group.

Selected structural parameters for 2-fluoronitrobenzene, 3-fluoronitrobenzene, and 4-fluoronitrobenzene obtained in this work using the B3LYP/6-31G(d) approach are collected in Tables S4, S5, and S6, in the Supporting Information, along with available experimental and computational data; a very good agreement was found.

At the G3(MP2)//B3LYP level, the most stable isomer is the 4-fluoronitrobenzene followed by the 3-fluoronitrobenzene, which is 3.2 kJ·mol^{-1} less stable and, finally, the 2-fluoronitrobenzene, which lies 27.9 kJ·mol^{-1} above the most stable one.

Gas-Phase Theoretical Enthalpies of Formation. The gas-phase enthalpies of formation of the three studied isomers were

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TABLE 12: Comparison between the Experimental and Computed G3(MP2)//B3LYP Gas-Phase Enthalpies of Formation of the Three Isomers of Fluoronitrobenzene, at $T = 298.15$ K^a

	$-\Delta_f H_m^o(g)/kJ \cdot mol^{-1}$				
	G3(MP2)//B3LYP				
compound	atomization reaction (eq 1)	eq 2	eq 3	eq 4	experimental value
2-fluoronitrobenzene	100.7(1.7)	99.9(2.5)	97.6(4.8)	96.9(5.5)	102.4 ± 1.5
3-fluoronitrobenzene	125.5(2.5)	124.7(3.3)	122.7(5.3)	127.8(0.2)	128.0 ± 1.7
4-fluoronitrobenzene	128.7(5.2)	127.9(6.0)	126.1(7.8)	131.4(2.5)	133.9 ± 1.4

^{a} Enthalpic differences between the experimental and computed values are given in parentheses.

TABLE 13: G3(MP2)//B3LYP Computed Gas-Phase Basicities, $\Delta G_{basicity}$, PA, EA, and IE, at $T = 298.15$ K, for the Three Isomers of Fluoronitrobenzene^a

compound	$\Delta G_{basicity}$	PA	EA	IE
2-fluoronitrobenzene	788.4(O₁)	788.8(O₁)	92.0 [104.2 ± 9.6]^b	958.0 [951.3]^c
	787.2(O₂)	787.8(O₂)		
3-fluoronitrobenzene	776.1(O₁)	775.0(O₁)	106.2 [119.6 ± 9.6]^b	961.4 [953.3]^c
	776.0(O₂)	774.9(O₂)		
4-fluoronitrobenzene	787.5(O₁)	786.5(O₁)	91.8 [108.1 ± 9.6]^b	962.8 [955.2]^c
	787.5(O₂)	786.5(O₂)		

^{a} All values are given in kJ·mol^{-1}. Whenever available, experimental values are given in brackets. ^{b} Chowdhury, S., Heinis T., Grimsrud E. P., Kebarle P. *J. Phys. Chem.* **1986**, *90*, 2747−2752. ^{c} Palmer, M. H., Moyes, W., Spiers, M., Ridyard, A., Neil, J. *J. Mol. Struct.* **1979**, *55*, 243−263.

estimated taking into account the computed enthalpies of reactions described by eqs 1−4 and the experimental enthalpies of formation in the gaseous phase of the other atoms and molecules there involved. The values of $\Delta_f H_m^o(g)$ were as follows: carbon, 716.7 kJ·mol^{-1},[82] hydrogen, 218.0 kJ·mol^{-1},[82] oxygen, 249.2 kJ·mol^{-1},[82] nitrogen, 472.7 kJ·mol^{-1},[82] fluorine, 79.4 kJ·mol^{-1},[82] benzene, 82.6 kJ·mol^{-1},[71] nitrobenzene, 67.5 kJ·mol^{-1},[71] fluorobenzene, −115.9 kJ·mol^{-1},[71] 1,2-difluorobenzene, −293.7 kJ·mol^{-1},[71] aniline, 87.1 kJ·mol^{-1},[71] 2-fluoroaniline, −107.2 kJ·mol^{-1},[71] 1,3-difluorobenzene, −309.2 kJ·mol^{-1},[71] 3-fluoroaniline, −115.6 kJ·mol^{-1},[71] 1,4-difluorobenzene, −306.7 kJ·mol^{-1},[71] and 4-fluoroaniline, −190.6 kJ·mol^{-1}.[71]

The calculated enthalpies of formation along with the experimental values are registered in Table 12. As it can be seen from the table, the agreement between the experimental and G3(MP2)//B3LYP calculated values is fairly good. The maximum deviations from the experimental results are 5.5 and 4.8 kJ·mol^{-1} for 2-fluoronitrobenzene, 5.3 and 3.3 kJ·mol^{-1} for 3-fluoronitrobenzene, and 7.8 and 6.0 kJ·mol^{-1} for 4-fluoronitrobenzene. These deviations are within the interval defined by the uncertainty associated with the experimental and calculated values.[56]

The computed G3(MP2)//B3LYP enthalpies for the studied compounds, auxiliary molecules, and atoms used in the atomization and working reactions are listed in Table S7 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 monofluoronitrobenzene. The calculated values of gas-phase basicity ($\Delta G_{basicity}$), proton (PA) and electron affinities (EA) and adiabatic ionization enthalpies (IE) are represented in Table 13.

The calculated gas-phase basicities show that the most basic species will be the 2- and 4-fluoronitrobenzene followed by the 3-fluoronitrobenzene. The proton affinity follows the same pattern. This can be explained due to the conjugation effect between the fluorine atom and the nitro group; 2- and 4-fluoronitrobenzene present conjugation while 3-fluoronitrobenzene does not. No experimental or computational data have been

found in the literature for comparison with our results on gas-phase basicity and proton affinity.

As it can be seen from Table 13, the addition of an electron to 3-fluoronitrobenzene is more favorable than the addition to 2- or 4-fluoronitrobenzene. This is due to the fact that the lone-pair from fluorine is now delocalized within the whole molecule, something that did not occur for the neutral species, where the lone-pair was only in resonance with the benzene ring. The calculated and experimental[83] electron affinities are in good agreement, taking into account the experimental uncertainty. Regarding the ionization enthalpies, it is possible to conclude that all of the three studied isomers have almost the same electron donor capacity. Our calculated values are in good agreement with the experimental ones,[84] reproducing exactly the same qualitative order, with the 2-fluoronitrobenzene being the species that releases the electron easier.

5. Final Remarks

The G3(MP2)//B3LYP approach was used to estimate the gas-phase enthalpies of formation of all three isomers of monofluoronitrobenzene, at $T = 298.15$ K, by considering several appropriate working reactions. All computed values are in agreement with the experimental data here reported, all being in the range of the experimental and computational uncertainties. Other thermodynamic properties were also calculated by means of this composite method.

Supporting Information Available: Details of all the combustion calorimetry experiments for the three fluoronitrobenzenes studied, as well as the fully optimized structures and the calculated energies of all compounds are given. This material is available free of charge via the Internet at http://pubs.acs.org.

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