

# Vibrational, Electronic, and Structural Properties of 6-Nitro- and 6-Amino-2-Trifluoromethylchromone: An Experimental and Theoretical Study

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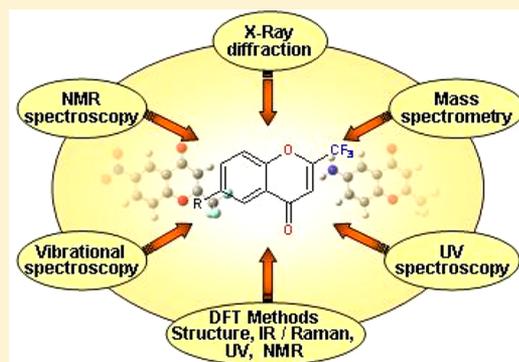
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## Supporting Information

**ABSTRACT:** Two 2-trifluoromethylchromones, 6-nitro-2-trifluoromethylchromone (**1**) and 6-amino-2-trifluoromethylchromone (**2**) were synthesized and characterized by NMR (<sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F), UV–vis, vibrational (IR and Raman) spectroscopy, MS spectrometry, and compound **1** also by single structural X-ray diffraction methods. This substance crystallizes in the monoclinic *P2<sub>1</sub>/c* space group with *Z* = 4 molecules per unit cell. In the solid, the fused rings and the amino group of **1** are coplanar and the trifluoromethyl group adopts a nearly staggered conformation. The NMR, vibrational, and electronic spectra were discussed and assigned with the assistance of DFT calculations.



## 1. INTRODUCTION

Chromones, an important class of oxygen-containing heterocyclic compounds, are widespread in nature.<sup>1</sup> The existence of chromones as parent compounds in a plant's life-cycle is well-known, mostly as dyes in plant leaves, fruits, and flowers.<sup>2–4</sup> In addition, 2-methylchromone derivatives are important in the synthesis of other heterocycles, since they are usually readily cleaved at the pyrone ring via nucleophilic attack at the C2 position.<sup>4</sup> This property has been used to prepare a variety of rearranged products and heterocyclic molecules.<sup>3</sup>

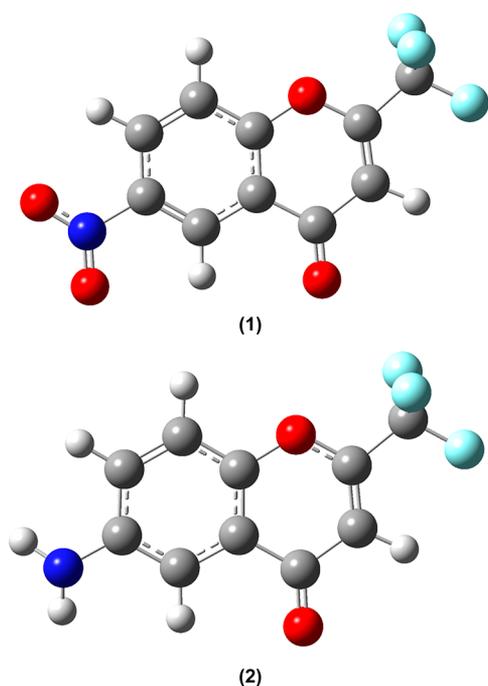
On the contrary, 2-perfluoroalkyl derivatives of chromones have never been found in nature. The first 2-trifluoromethyl-substituted chromones<sup>5</sup> were prepared long time ago, but such fluorinated molecules have been scarcely studied. The trifluoromethyl substituent is an important group, because its presence in organic molecules increases their applicability as pharmaceuticals or agrochemicals. Pharmacological properties such as fat solubility or metabolic stability are improved when aromatic substrates are functionalized with this substituent.<sup>6</sup> Despite its importance, there are no good general methods for the introduction of the trifluoromethyl group into organic molecules. Recently, a catalytic reaction for the addition of this useful group has been described.<sup>7</sup> In the past decade, Sosnovskikh and his group have devoted considerable attention to the study of

the synthesis and reactivity of 2-polyfluoroalkylchromones.<sup>8–15</sup> Significant differences in the reactivity between 2-alkyl- and 2-trifluoromethylchromones with respect to nucleophilic reagents were observed.<sup>8</sup> The introduction of the trifluoromethyl group into the C2 position of chromone causes activation of the pyrone ring due to the strong electron withdrawing capacity of the –CF<sub>3</sub> group. Besides, this property has been found to enhance the electrophilic character at cationic sites in superelectrophiles leading to a higher positive charge delocalization.<sup>16</sup> Recently, we reported a simple one-pot synthesis procedure for 2-perfluoromethylchromones, establishing a new synthetic route for molecules containing the strong electron-withdrawing trifluoromethyl group.<sup>17</sup> Until now, to the best of our knowledge, the title compounds were not thoroughly investigated. For 6-nitro-2-trifluoromethylchromone (**1**), the <sup>1</sup>H NMR assignment and some bands of the FT-IR spectrum were reported,<sup>18</sup> while the 6-amino-2-trifluoromethylchromone (**2**), is described for the first time in this paper. The vibrational spectra of 7-amino-4-trifluoromethylcoumarin, an isomer of **2**, were assigned on the basis of normal coordinates calculation.<sup>19</sup> Vibrational spectra of related chromones were

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analyzed both by computational and experimental methods.<sup>20,21</sup> Moreover, UV absorption spectra of chromones were recently subject of study, especially by the good agreement between experimental spectra and those obtained by theoretical calculations.<sup>22–24</sup> This work presents the results of a complete study of 6-nitro-2-trifluoromethylchromone (**1**) and 6-amino-2-trifluoromethylchromone (**2**), depicted in Figure 1. The optimization



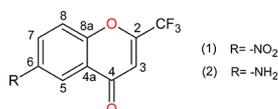
**Figure 1.** Optimized structures (B3LYP/6-311++g(d,p)) of 6-nitro-2-trifluoromethylchromone (**1**) and 6-amino-2-trifluoromethylchromone (**2**).

of both geometries were performed using the DFT/B3LYP method and different basis sets to assist the interpretation and the assignment of experimental IR and Raman, UV–vis and <sup>1</sup>H and <sup>13</sup>C NMR spectra. Moreover, the crystal structure of **1** was determined by X-ray diffraction methods, and their experimental parameters were used to validate the theoretical results.

## 2. EXPERIMENTAL SECTION

**2.1. 6-Nitro-2-trifluoromethylchromone (1). Synthesis.** **1** was obtained, according to literature procedure, by the reaction of 2-trifluoromethylchromone<sup>17</sup> and HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> and then recrystallized from ethanol (mp 155–156 °C). Single crystals, adequate for structural X-ray diffraction work, were obtained from slow evaporation of initially unsaturated alcoholic solutions at controlled temperatures. <sup>1</sup>H NMR: δ = 9.06 (1H, d, J = 2.7 Hz, H-5); 8.60 (1H, dd, J = 9.1 and 2.7 Hz, H-7); 7.75 (1H, d, J = 9.1 Hz, H-8); 6.82 ppm (1H, s, H-3). <sup>13</sup>C NMR: δ = 175.1 (C-4); 158.2 (C-8a); 152.8 (q, J = 40 Hz, C-2); 145.4 (C-6); 129.2 (C-7); 124.1 (C-5); 122.4 (C-4a); 120.3 (C-8); 118.2 (q, J = 275 Hz, CF<sub>3</sub>); 111.0 ppm (C-3). <sup>19</sup>F NMR: δ = -72.10 ppm. For atom numbering see Chart 1.

**Chart 1. Structure and Atom Numbering for NMR Analysis of 1 and 2**

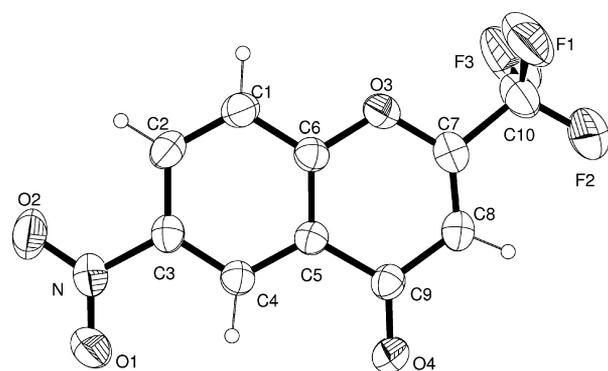


**Table 1. Crystal Data and Structure Refinement Results for 6-Nitro-2-trifluoromethylchromone (1)**

empirical formula	C <sub>10</sub> H <sub>4</sub> F <sub>3</sub> NO <sub>4</sub>
formula weight	259.14
temperature	295(2) K
wavelength	1.54184 Å
crystal system	monoclinic
space group	P2 <sub>1</sub> /c
unit cell dimensions	a = 6.1217(6) Å b = 10.888(1) Å c = 15.598(2) Å β = 99.16(1)°
volume	1026.4(2) Å <sup>3</sup>
Z	4
density (calculated)	1.677 Mg/m <sup>3</sup>
absorption coefficient	1.475 mm <sup>-1</sup>
F(000)	520
crystal size	0.22 × 0.13 × 0.10 mm <sup>3</sup>
θ range for data collection	4.97–70.98°
index ranges	−7 ≤ h ≤ 5, −13 ≤ k ≤ 10, −18 ≤ l ≤ 19
reflections collected	3752
independent reflections	1983 [R(int) = 0.0221]
observed reflections [I > 2σ(I)]	1370
completeness to θ = 70.98°	99.7%
absorption correction	semiempirical from equivalents
max. and min transmission	1.00000 and 0.833 75
refinement method	full-matrix least-squares on F <sup>2</sup>
data/restraints/parameters	1983/0/179
goodness-of-fit on F <sup>2</sup>	1.052
final R indices [I > 2σ(I)]	R1 = 0.0553, wR2 = 0.1483
R indices (all data)	R1 = 0.0746, wR2 = 0.1726
largest diff. peak and hole	0.247 and −0.237 e-Å <sup>-3</sup>

MS: m/z (%) = 259 ([M]<sup>+</sup>, 100), 75 ([C<sub>6</sub>H<sub>3</sub>]<sup>+</sup>, 83), 213 ([M − NO<sub>2</sub>]<sup>+</sup>, 43), 157 ([C<sub>8</sub>H<sub>4</sub>F<sub>3</sub>]<sup>+</sup>, 43), 137 ([C<sub>6</sub>H<sub>3</sub>NO<sub>3</sub>]<sup>+</sup>, 30), 107 ([C<sub>6</sub>H<sub>3</sub>O<sub>2</sub>]<sup>+</sup>, 25), 74 (25), 229 ([M − NO]<sup>+</sup>, 21), 62 (21), 63 (20), 30 (15), 173 ([C<sub>8</sub>H<sub>4</sub>F<sub>3</sub>O]<sup>+</sup>, 12), 201 ([C<sub>9</sub>H<sub>4</sub>F<sub>3</sub>O<sub>2</sub>]<sup>+</sup>, 6), 240 (5); 214 (5); 212 (5); 185 ([C<sub>9</sub>H<sub>4</sub>F<sub>3</sub>O]<sup>+</sup>, 5). UV–vis (methanol): λ<sub>max</sub> 240 and 287 nm.

**2.2. 6-Amino-2-trifluoromethylchromone (2). Synthesis.** **2** was obtained from 6-nitro-2-trifluoromethylchromone (**1**) following the procedure reported by Merlic<sup>25</sup> with slight modifications. Iron powder (3.36 g, 60.16 mmol), water (5 mL), and concentrated HCl (100 μL), were added sequentially to a solution of 6-nitro-2-trifluoromethylchromone (1.1 g, 4.25 mmol) in ethanol (22 mL). The reaction mixture was stirred at 90 °C for 1 h and then filtered out. The residue was washed twice with 10 mL of hot ethanol and the filtrates were collected with the first portion. The resulting yellow solution was allowed to cool to room temperature and then stored in a freezer overnight. After filtration, the solid was recrystallized in ethanol. The yellow crystalline solid (mp 186–188 °C) was suitable for spectroscopic studies. <sup>1</sup>H NMR: δ = 7.39 (1H, s, overlapped with H-5, H-8); 7.35 (1H, d, J = 2.9 Hz, H-5); 7.08 (1H, dd, J = 2.9 and 8.8 Hz, H-7); 6.64 (1H, s, H-3); 3.97 ppm (2H, br-s, NH<sub>2</sub>). <sup>13</sup>C NMR: δ = 177.0 (C-4); 152.3 (q, J = 43 Hz, C-2); 149.2 (C-8a); 145.0 (C-6); 124.1 (C-4a); 123.1 (C-7); 119.3 (C-8); 118.7 (q, J = 274 Hz, CF<sub>3</sub>); 109.3 (C-3); 107.6 ppm (C-5). <sup>19</sup>F NMR: δ = -71.90 ppm. For atom numbering see Chart 1. MS: m/z (%) = 229 ([M]<sup>+</sup>, 100), 201 ([M − CO]<sup>+</sup>, 12), 135 ([C<sub>7</sub>H<sub>5</sub>NO<sub>2</sub>]<sup>+</sup>, 12), 107 ([C<sub>6</sub>H<sub>5</sub>NO]<sup>+</sup>, 14), 79 ([C<sub>5</sub>H<sub>5</sub>N]<sup>+</sup>, 30), 52 (29). UV–vis (methanol): λ<sub>max</sub> 205, 241, and 376 nm.



**Figure 2.** Plot of 6-nitro-2-trifluoromethylchromone (**1**) showing the labeling of the non-H atoms and their displacement ellipsoids to the 30% probability level.

### 2.3. Instrumentation. Infrared and Raman Spectroscopy.

Infrared absorption spectra in KBr pellets were recorded on a LUMEX Infra LUM FT-02 spectrometer with a resolution of

$2\text{ cm}^{-1}$  in the range from  $4000$  to  $400\text{ cm}^{-1}$ . Raman spectra of the solid were measured in Pyrex standard capillaries (2.5-mm i.d.) on a Bruker IFS 66 spectrometer (spectral resolution  $4\text{ cm}^{-1}$ ), equipped with a 1064 nm Nd:YAG laser, in the range from  $3500$  to  $100\text{ cm}^{-1}$ .

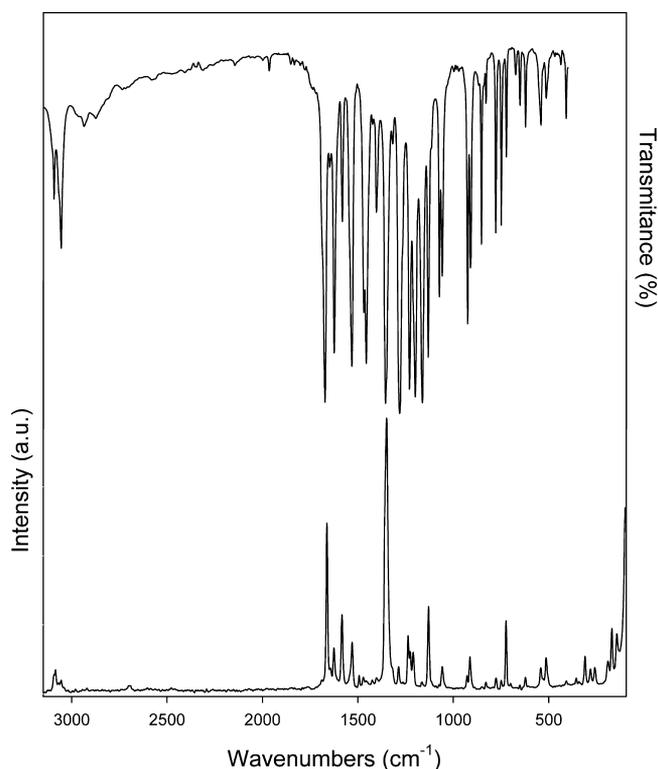
**NMR Spectra.** The  $^1\text{H}$  (200.0 MHz),  $^{19}\text{F}$  (188.7 MHz), and  $^{13}\text{C}$  (50.3 MHz) NMR spectra of the title compounds were recorded on a Varian Mercury Plus 200 spectrometer. The sample was dissolved in  $\text{CDCl}_3$  in a 5 mm NMR tube. Chemical shifts,  $\delta$ , for  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra are given in ppm relative to TMS ( $\delta = 0\text{ ppm}$ ) and are referenced by using the residual non deuterated solvent signal. For  $^{19}\text{F}$  NMR spectrum, a 0.05% trifluoroacetic acid (TFA) in  $\text{CDCl}_3$  solution was used as external reference ( $\delta = -71.00\text{ ppm}$ ). Coupling constants,  $J$ , are reported in Hz, being the singlet, doublet, double doublet, and quartet marked as s, d, dd, and q, respectively.

**UV-Visible Spectroscopy.** The spectra of **1** and **2** in methanol were recorded using a quartz cell (10 mm optical path length) on a ChromTech CT-5700 UV/vis spectrophotometer, with 2.0 nm spectral bandwidth. Measurements were carried out in the spectral region from 190 to 700 nm.

**Table 2.** Selected Structural Parameters<sup>a,b</sup> of **1** (Calculated and Experimental) and **2** (Calculated)

param	expt (1)	calcd (1)	calcd (2)	param	expt (1)	calcd (1)	calcd (2)
$r(\text{C1}-\text{C2})$	1.367(4)	1.382	1.382	$\angle(\text{O1}-\text{N}-\text{O2})$	123.9(3)	125.1	–
$r(\text{C1}-\text{C6})$	1.386(4)	1.398	1.395	$\angle(\text{O1}-\text{N}-\text{C3})$	118.3(2)	117.6	–
$r(\text{C2}-\text{C3})$	1.386(4)	1.401	1.414	$\angle(\text{O2}-\text{N}-\text{C3})$	117.8(3)	117.3	–
$r(\text{C3}-\text{C4})$	1.366(3)	1.381	1.393	$\angle(\text{H1}-\text{N}-\text{H2})$	–	–	112.9
$r(\text{C3}-\text{N})$	1.466(3)	1.481	1.391	$\angle(\text{H1}-\text{N}-\text{C3})$	–	–	116.7
$r(\text{C4}-\text{C5})$	1.395(4)	1.400	1.399	$\angle(\text{H2}-\text{N}-\text{C3})$	–	–	116.4
$r(\text{C5}-\text{C6})$	1.390(3)	1.401	1.398	$\angle(\text{O3}-\text{C7}-\text{C10})$	110.0(3)	110.3	110.6
$r(\text{C5}-\text{C9})$	1.468(3)	1.484	1.481	$\angle(\text{O3}-\text{C6}-\text{C1})$	116.2(2)	116.4	116.9
$r(\text{C6}-\text{O3})$	1.372(3)	1.368	1.379	$\angle(\text{O3}-\text{C6}-\text{C5})$	121.5(2)	121.6	122.0
$r(\text{C7}-\text{C8})$	1.320(4)	1.341	1.345	$\angle(\text{O4}-\text{C9}-\text{C8})$	123.6(2)	123.1	122.9
$r(\text{C7}-\text{O3})$	1.353(3)	1.352	1.343	$\angle(\text{O4}-\text{C9}-\text{C5})$	122.4(2)	123.2	123.2
$r(\text{C7}-\text{C10})$	1.499(4)	1.515	1.513	$\angle(\text{F1}-\text{C10}-\text{F2})$	106.4(4)	108.1	107.8
$r(\text{C8}-\text{C9})$	1.447(4)	1.468	1.465	$\angle(\text{F1}-\text{C10}-\text{F3})$	106.4(4)	107.6	107.8
$r(\text{C9}-\text{O4})$	1.227(3)	1.219	1.224	$\angle(\text{F2}-\text{C10}-\text{F3})$	108.4(4)	108.1	107.3
$r(\text{C10}-\text{F1})$	1.299(4)	1.346	1.348	$\angle(\text{F1}-\text{C10}-\text{C7})$	112.3(3)	110.9	111.2
$r(\text{C10}-\text{F2})$	1.306(4)	1.341	1.348	$\angle(\text{F2}-\text{C10}-\text{C7})$	110.7(3)	110.9	111.2
$r(\text{C10}-\text{F3})$	1.275(5)	1.346	1.343	$\angle(\text{F3}-\text{C10}-\text{C7})$	112.4(3)	110.9	111.3
$r(\text{N}-\text{O1})$	1.217(3)	1.222	–	$\Phi(\text{C3}-\text{C4}-\text{C5}-\text{C9})$	–178.3	179.9	–179.8
$r(\text{N}-\text{O2})$	1.219(3)	1.224	–	$\Phi(\text{C6}-\text{O3}-\text{C7}-\text{C10})$	0.4	–179.9	–179.9
$r(\text{N}-\text{H1})$	–	–	1.009	$\Phi(\text{C6}-\text{O3}-\text{C7}-\text{C8})$	179.2	0.0	0.1
$r(\text{N}-\text{H2})$	–	–	1.009	$\Phi(\text{O1}-\text{N}-\text{C3}-\text{C4})$	1.7	0.0	–
$\angle(\text{C1}-\text{C2}-\text{C3})$	119.0(3)	119.3	121.3	$\Phi(\text{O1}-\text{N}-\text{C3}-\text{C2})$	–179.9	179.9	–
$\angle(\text{C1}-\text{C6}-\text{C5})$	122.3(2)	122.0	120.9	$\Phi(\text{O2}-\text{N}-\text{C3}-\text{C2})$	2.5	0.0	–
$\angle(\text{C2}-\text{C1}-\text{C6})$	118.9(3)	118.9	119.2	$\Phi(\text{O2}-\text{N}-\text{C3}-\text{C4})$	–175.9	179.9	–
$\angle(\text{C2}-\text{C3}-\text{N})$	118.4(2)	118.7	120.1	$\Phi(\text{H1}-\text{N}-\text{C3}-\text{C4})$	–	–	–157.6
$\angle(\text{C2}-\text{C3}-\text{C4})$	122.8(3)	119.1	118.5	$\Phi(\text{H1}-\text{N}-\text{C3}-\text{C2})$	–	–	25.2
$\angle(\text{C3}-\text{C4}-\text{C5})$	118.8(2)	122.2	120.9	$\Phi(\text{H2}-\text{N}-\text{C3}-\text{C2})$	–	–	162.7
$\angle(\text{C4}-\text{C3}-\text{N})$	118.8(2)	119.2	121.4	$\Phi(\text{H2}-\text{N}-\text{C3}-\text{C4})$	–	–	–20.1
$\angle(\text{C4}-\text{C5}-\text{C6})$	118.2(2)	118.6	119.1	$\Phi(\text{O4}-\text{C9}-\text{C5}-\text{C4})$	–1.1	179.9	0.1
$\angle(\text{C4}-\text{C5}-\text{C9})$	121.5(2)	121.1	121.0	$\Phi(\text{O4}-\text{C9}-\text{C8}-\text{C7})$	178.3	–179.9	179.8
$\angle(\text{C5}-\text{C9}-\text{C8})$	114.0(2)	113.7	113.9	$\Phi(\text{F2}-\text{C10}-\text{C7}-\text{C8})$	–7.3	0.0	0.0
$\angle(\text{C6}-\text{C5}-\text{C9})$	120.3(2)	120.2	119.9	$\Phi(\text{F2}-\text{C10}-\text{C7}-\text{O3})$	173.8	179.9	–179.9
$\angle(\text{C7}-\text{C8}-\text{C9})$	120.8(3)	120.6	120.7	$\Phi(\text{F1}-\text{C10}-\text{C7}-\text{O3})$	55.1	59.7	59.8
$\angle(\text{C7}-\text{O3}-\text{C6})$	117.8(2)	118.8	118.4	$\Phi(\text{F1}-\text{C10}-\text{C7}-\text{C8})$	–126.1	–120.2	120.2
$\angle(\text{C8}-\text{C7}-\text{O3})$	125.5(3)	125.0	125.1	$\Phi(\text{N}-\text{C3}-\text{C4}-\text{C5})$	176.1	–179.9	–177.2
$\angle(\text{C8}-\text{C7}-\text{C10})$	124.5(3)	124.7	124.3	$\Phi(\text{F3}-\text{C10}-\text{C7}-\text{O3})$	–64.8	–59.8	–59.7
				$\Phi(\text{F3}-\text{C10}-\text{C7}-\text{C8})$	114.0	120.2	–120.2

<sup>a</sup>Atom numbering taken from Figure 2. <sup>b</sup>Experimental data from X-ray diffraction and computed parameters at B3LYP/6-311++g(d,p).

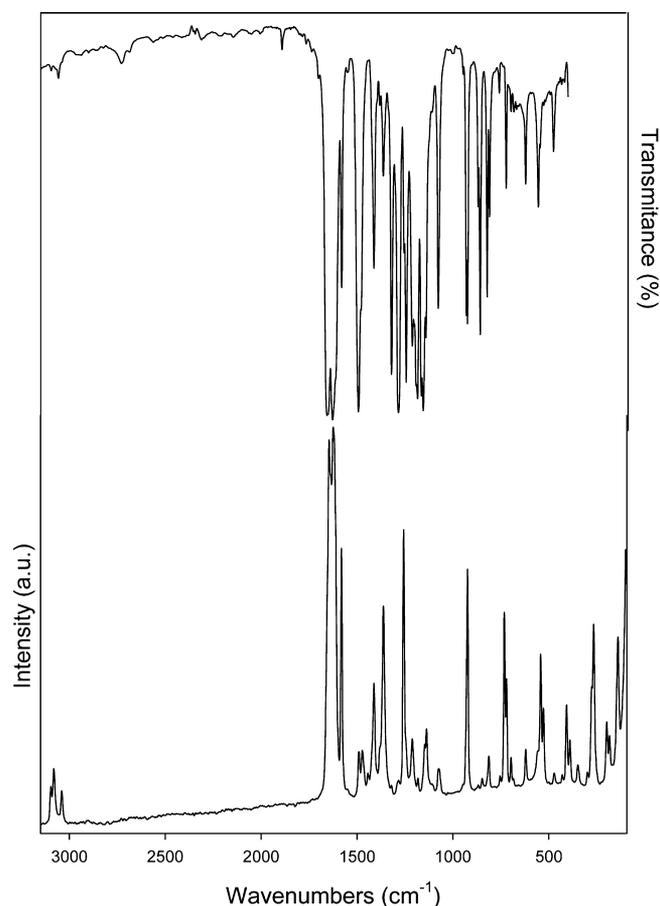


**Figure 3.** Infrared spectrum of the solid (upper trace, KBr pellets) and Raman spectrum (lower trace) of 6-nitro-2-trifluoromethylchromone (**1**) at room temperature.

**Mass spectrometry.** The MS determinations were performed by injection of methanol solutions ( $\sim 1 \mu\text{L}$ ) in an HP 5890 Chromatograph coupled to an HP 5972 A mass selective detector. An HP5-MS capillary column (30 m x 0.25 mm x 5  $\mu\text{m}$ ) has been used, with  $\text{H}_2$  as the carrier gas (0.6 mL/min). The temperature set points were: 200 °C in the split injector, 300 °C in the interface, 185 °C in the ion source and the oven ramp started at 80 °C and ended at 200 °C with a heat rate of 10 °C/min. The electron energy was 70 eV with a mass range of 50–350 amu and a pressure in the mass spectrometer lower than  $10^{-5}$  Torr. The mass spectra of **1** and **2** are shown in Figures S1 and S2 (Supporting Information).

**X-ray diffraction data.** A complete data set for 6-nitro-2-trifluoromethylchromone (**1**) was collected on an Oxford Xcalibur, Eos, Gemini CCD diffractometer with graphite-monochromated  $\text{CuK}\alpha$  ( $\lambda = 1.54184 \text{ \AA}$ ) radiation. X-ray diffraction intensities were collected ( $\omega$  scans with  $\vartheta$  and  $\kappa$ -offsets), integrated and scaled with CrysAlisPro<sup>26</sup> suite of programs. The unit cell parameters were obtained by least-squares refinement (based on the angular settings for all collected reflections with intensities larger than seven times the standard deviation of measurement errors) using CrysAlisPro. Data were corrected empirically for absorption employing the multiscan method implemented in CrysAlisPro. The structure was solved by direct methods with SHELXS-97<sup>27</sup> and the molecular model refined by full-matrix least-squares procedure on  $F^2$  with SHELXL-97.<sup>28</sup> All hydrogen atoms were located in a difference Fourier map phased on the heavier atoms and refined at their found positions with isotropic displacement parameters. Crystal data and structure refinement results are summarized in Table 1.

**2.4. Computational Methods.** Theoretical calculations were performed using the program package Gaussian 03.<sup>29</sup> Preliminary geometry optimization for **1** and **2**, was carried out



**Figure 4.** Infrared spectrum of the solid (upper trace, KBr pellets) and Raman spectrum (lower trace) of 6-amino-2-trifluoromethylchromone (**2**).

with the density functional theory (B3LYP) method by using the 6-31+g(d) basis set and scans of the potential energy surface (in steps of 30°) by means of the 6-311+g(d) level of theory. Final optimizations and vibration frequency calculations were implemented employing the 6-311++g(d,p) basis set. The computed vibrational properties correspond, in all cases, to potential energy minima with no imaginary values for the frequencies. Electronic transitions were calculated within the framework of the time-dependent density functional theory (6-311+g(d)).<sup>30</sup>

The  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts were calculated with the B3LYP/6-31+g(d) and 6-311+g(2d,p) optimized geometries by GIAO method (gauge including atomic orbital),<sup>31</sup> using the corresponding TMS shielding, calculated at the same level of theory, as the reference. This value was taken as a constant, which is subtracted from the calculated isotropic chemical shielding of a given nucleus to convert them in chemical shifts.

### 3. RESULTS AND DISCUSSION

**3.1. Structure of 6-Nitro-2-trifluoromethylchromone 1 Determined by Single X-ray Diffraction.** The solid state molecular structure of **1** is shown in the ORTEP<sup>32</sup> plot of Figure 2. The corresponding interatomic bond distances and angles are given in Table 2, where they are compared with the corresponding computed geometrical parameters (B3LYP/6-311++g(d,p)).

Because of an extended  $\pi$ -bonding electronic structure, the organic skeleton is planar (*rms* deviation of atoms from the best

Table 3. Experimental and Calculated Frequencies ( $\text{cm}^{-1}$ ) and Tentative Assignment of Fundamental Vibration Modes in 6-Nitro-2-trifluoromethylchromone (1)

mode	experimental		calculated <sup>b</sup>		assignment <sup>d</sup>
	IR <sup>a</sup>	Raman	frequency	intensity <sup>c</sup>	
$\nu_1$			3236	3 (112)	$\nu(\text{C8-H})$
$\nu_2$	3098(w)	3094(6)	3232	4 (93)	$\nu(\text{C2-H}); \nu(\text{C1-H})$
$\nu_3$		3085(9)	3231	11 (34)	$\nu(\text{C4-H})$
$\nu_4$	3056(w)	3055(4)	3209	<1 (77)	$\nu(\text{C1-H}); \nu(\text{C2-H})$
$\nu_5$	1678(vs)	1662(62)	1737	372 (119)	$\nu(\text{C9-O4})$
$\nu_6$			1690	30 (68)	$\nu(\text{C8-C7})$
$\nu_7$	1624(s)	1625(16)	1660	136 (27)	$\nu(\text{C3-C4}); \nu(\text{C1-C6}); \nu(\text{C7-C8})$
$\nu_8$	1579(w)	1583(29)	1622	32 (55)	$\nu(\text{C4-C5}); \nu(\text{C1-C2}); \nu(\text{C5-C6})$
$\nu_9$	1535(s)	1530(19)	1588	149 (48)	$\nu_{\text{as}}(\text{NO}_2); \nu(\text{C2-C3}); \nu(\text{C5-C6})$
$\nu_{10}$			1499	77 (4)	$\delta(\text{C4-H}); \delta(\text{C1-H}); \delta(\text{C2-H})$
$\nu_{11}$	1460(vs)		1469	100 (1)	$\nu(\text{C5-C9}); \nu(\text{C1-C2}); \nu(\text{C4-C5})$
$\nu_{12}$	1404(m)	1402(5)	1406	43 (6)	$\nu(\text{C7-O3}); \nu(\text{C3-C4}); \nu(\text{C1-C6}); \delta(\text{C8-H})$
$\nu_{13}$			1372	71 (9)	$\nu(\text{C1-C2}); \nu(\text{C3-C4}); \nu(\text{C5-C6})$
$\nu_{14}$	1355(vs)	1351(100)	1369	285 (305)	$\nu_{\text{s}}(\text{NO}_2); \nu(\text{N-C3}); \nu(\text{C5-C6})$
$\nu_{15}$	1283(vs)	1286(9)	1292	225 (2)	$\delta(\text{C1-H}); \delta(\text{C2-H}); \delta(\text{C4-H}); \nu(\text{C7-C10})$
$\nu_{16}$	1230(s)	1237(21)	1281	152 (7)	$\delta(\text{C8-H}); \nu(\text{C7-C10})$
$\nu_{17}$	1198(s)	1226(15)	1251	168 (5)	$\delta(\text{C1-H}); \delta(\text{C4-H})$
$\nu_{18}$		1210(15)	1232	44 (94)	$\nu(\text{C6-O3}); \nu(\text{C7-C10}); \nu(\text{C5-C9})$
$\nu_{19}$	1164(s)	1167(5)	1184	259 (2)	$\nu_{\text{as}}(\text{CF}_3)$
$\nu_{20}$			1151	81 (9)	$\delta(\text{C1-H}); \delta(\text{C2-H})$
$\nu_{21}$	1131(vs)	1130(32)	1140	293 (3)	$\nu_{\text{as}}(\text{CF}_3)$
$\nu_{22}$	1073(s)		1132	94 (29)	$\nu(\text{C3-N}); \delta(\text{C8-H}); \delta(\text{C4-H})$
$\nu_{23}$			1078	20 (14)	$\delta(\text{C4-H}); \delta(\text{C4-C5-C9})$
$\nu_{24}$	1056(m)	1057(9)	1071	78 (3)	$\nu_{\text{s}}(\text{CF}_3); \nu(\text{C7-O3}); \delta(\text{C8-H}); \delta_{\text{s}}(\text{CF}_3)$
$\nu_{25}$			991	<1 (<1)	$\gamma(\text{C1-H}); \gamma(\text{C2-H}); \gamma(\text{C4-H})$
$\nu_{26}$			969	13 (<1)	$\gamma(\text{C4-H})$
$\nu_{27}$	926(s)	928(6)	934	65 (2)	$\delta(\text{C8-C7-O3})$
$\nu_{28}$	909(s)	913(17)	921	25 (12)	$\delta(\text{C2-C3-C4}); \delta(\text{C9-C8-C7})$
$\nu_{29}$	854(m)		900	40 (<1)	$\gamma(\text{C8-H})$
$\nu_{30}$	827(w)		847	31 (<1)	$\gamma(\text{C1-H}); \gamma(\text{C2-H})$
$\nu_{31}$	819(vw)		840	10 (2)	$\delta(\text{NO}_2); \delta(\text{C2-C3-C4})$
$\nu_{32}$	777(m)	776(6)	784	23 (3)	$\delta(\text{C5-C9-C8}); \delta(\text{C5-C9-C4})$
$\nu_{33}$			765	<1 (<1)	$\gamma(\text{C8-H}); \gamma(\text{C4-H}); \gamma(\text{C1-H}); \gamma(\text{C2-H}); \gamma(\text{C9-O4})$
$\nu_{34}$	748(m)	749(4)	733	17 (2)	$\gamma(\text{NO}_2); \gamma(\text{C2-H}); \gamma(\text{C4-H}); \gamma(\text{C1-C6-O3})$
$\nu_{35}$	720(m)	723(26)	721	15 (17)	$\delta_{\text{s}}(\text{CF}_3); \delta(\text{C6-C1-C2}); \delta(\text{C4-C5-C3})$
$\nu_{36}$			699	<1 (<1)	$\gamma(\text{O3-C7-C8})$
$\nu_{37}$	674(w)		678	2 (<1)	$\gamma(\text{C1-H}); \gamma(\text{C5-C9-C8}); \gamma(\text{C8-H})$
$\nu_{38}$	650(w)		657	4 (<1)	$\delta(\text{C2-C3-C4}); \delta(\text{C1-C6-C5})$
$\nu_{39}$	621(w)	622(6)	624	12 (2)	$\delta(\text{C5-C9-O4}); \delta(\text{C1-C6-O3})$
$\nu_{40}$		543(9)	548	4 (2)	$\delta_{\text{as}}(\text{CF}_3); \delta(\text{C5-C9-C8}); \delta(\text{N-C3-C4})$
$\nu_{41}$	541(w)	515(14)	544	9 (4)	$\delta_{\text{as}}(\text{CF}_3); \delta(\text{O4-C9-C8})$
$\nu_{42}$			525	1 (1)	$\gamma(\text{C2-C3-C4}); \gamma(\text{C5-C6-C1}); \gamma(\text{C6-O3-C7})$
$\nu_{43}$			516	2 (7)	$\delta(\text{O-N-C3}); \delta(\text{C5-C9-C8}); \delta(\text{C3-C4-C5})$
$\nu_{44}$	511(w)		510	3 (1)	$\delta_{\text{as}}(\text{CF}_3); \gamma(\text{C2-C3-C4}); \gamma(\text{C1-C6-C5})$
$\nu_{45}$			506	1 (2)	$\delta(\text{C6-O3-C7})$
$\nu_{46}$			441	2 (<1)	$\gamma(\text{C4-C5-C6}); \gamma(\text{C6-C1-C2})$
$\nu_{47}$			406	6 (<1)	$\tau(\text{C8-C7-CF}_3)$
$\nu_{48}$			352	<1 (1)	$\gamma(\text{C2-C1-C6}); \gamma(\text{C7-O3-C6})$
$\nu_{49}$			335	<1 (1)	$\delta(\text{C7-CF}_3)$
$\nu_{50}$			305	3 (4)	$\delta(\text{C9-C5-C4}); \delta(\text{C2-C3-N})$
$\nu_{51}$			274	<1 (<1)	$\gamma(\text{C9-C8-C7})$
$\nu_{52}$			253	1 (4)	$\delta(\text{C10-C7-C8}); \delta(\text{N-C3-C2})$
$\nu_{53}$			181	2 (1)	$\delta(\text{N-C3-C4}); \delta(\text{O3-C7-C10})$
$\nu_{54}$			167	4 (<1)	$\tau(\text{C1-C6-O3-C7}); \tau(\text{O4-C9-C8-C7})$
$\nu_{55}$			147	5 (<1)	$\tau(\text{O4-C9-C5-C4})$
$\nu_{56}$			116	<1 (1)	$\tau(\text{C8-C7-CF}_3); \tau(\text{O4-C9-C5-C4})$
$\nu_{57}$			114	2 (<1)	$\pi_{\text{ip}}(\text{CF}_3)$
$\nu_{58}$			45	2 (1)	$(\text{C2-C3-NO}_2); (\text{CF}_3\text{-C7-O3})$

Table 3. continued

mode	experimental		calculated <sup>b</sup>		assignment <sup>d</sup>
	IR <sup>a</sup>	Raman	frequency	intensity <sup>c</sup>	
$\nu_{59}$			40	<1 (1)	$\tau(\text{C2-C3-NO}_2)$
$\nu_{60}$			32	<1 (2)	$\tau(\text{C8-C7-CF}_3)$

<sup>a</sup>vs, very strong; s, strong; w, weak; vw, very weak; sh, shoulder. <sup>b</sup>6-311++g(d,p). <sup>c</sup>Calculated intensities: IR in km mol<sup>-1</sup> and Raman (in parentheses) in Å<sup>4</sup> amu<sup>-1</sup>. <sup>d</sup> $\nu$ ,  $\delta$ ,  $\gamma$  and  $\tau$  represent stretching, in-plane deformation, out-of-plane deformation and torsion modes.

least-squares plane of 0.065 Å). The observed covalent bond structure confirms and quantifies what it is expected for this molecule from organic chemistry's rules. Particularly, the observed aromatic ring C–C bond distances are in the 1.366(3)–1.395(4) Å range as expected for a resonant structure. Within the fused heterocycle C–O distances are 1.353(3) and 1.372(3) Å. C5–C9 and C8–C9 distances of 1.468(3) and 1.447(4) Å indicate the single character of these bonds while the value  $d(\text{C7-C8}) = 1.320(4)$  Å agrees with the formally double bond nature expected for this link. The trifluoromethyl group adopts a nearly staggered conformation. The nitro group shows N–O bond distances which are equal to within experimental accuracy [1.217(3) and 1.219(3) Å] and a O–N–O angle of 123.9(3)°.

**3.2. Structural Properties.** Potential energy curves (B3LYP/6-311+g(d)) for internal rotations around the –CF<sub>3</sub> and –NO<sub>2</sub> or –NH<sub>2</sub> groups for **1** and **2**, respectively, were performed to evaluate the minima energy structures adopted by the title compounds. The molecules are mainly characterized by a flat orientation throughout their structures (see Figure 2). The –CF<sub>3</sub> group has the same orientation in both compounds with one fluorine atom in the plane of the molecule (*syn* respect to the C=C bond). This configuration is adopted probably to minimize the interaction with the bridged oxygen atom.

The –NO<sub>2</sub> group in compound **1** is in the same plane as the molecular skeleton. Moreover, the –NH<sub>2</sub> group in compound **2** has both hydrogen atoms slightly deviated above the molecular plane, see Table 2.

**3.3. Vibrational Spectroscopy.** The IR and Raman spectra of solid 6-nitro-2-trifluoromethylchromone (**1**) and 6-amino-2-trifluoromethylchromone (**2**) are shown in Figure 3 and Figure 4, while the tentative assignment of the observed and computed fundamental vibrational modes are presented in Table 3 and Table 4, respectively. Only the most relevant characteristic functional groups of the molecules will be discussed.

**6-Nitro-2-trifluoromethylchromone (1).** Aromatic nitro compounds have strong absorptions due to asymmetric and symmetric stretching vibrations of the –NO<sub>2</sub> group. Hydrogen bonding has a little effect on the NO<sub>2</sub> asymmetric stretching vibrations.<sup>33,34</sup> The asymmetric and symmetric NO<sub>2</sub> stretching bands of **1** have been assigned to the IR observed bands at 1535 (Raman: 1530 cm<sup>-1</sup>) and 1355 cm<sup>-1</sup> (Raman: 1351 cm<sup>-1</sup>), respectively, taking into account the predicted values (6-311+g(d,p)) and the assignment in 1-fluoro-3-nitrobenzene.<sup>34</sup>

The in- and out-of-plane deformations of the –NO<sub>2</sub> group, predicted as very weak absorbing modes, are attributed to the weak and medium IR bands at 819 and 748 cm<sup>-1</sup> bands, respectively, and no counterparts were observed in the Raman spectra. The C–N stretching mode can be assigned to the strong IR band at 1073 cm<sup>-1</sup> (calculated at 1132 cm<sup>-1</sup>), which was not detected in Raman. The  $\nu(\text{C=O})$  vibration is associated with the very strong absorption band at 1678 cm<sup>-1</sup> (IR) and to the medium intense dispersion observed at 1662 cm<sup>-1</sup> in Raman and it is strongly coupled with the alkene  $\nu(\text{C=C})$  predicted at 1690 cm<sup>-1</sup>.

Moreover, this mode is observed at 1652 (IR) and 1670 cm<sup>-1</sup> (Raman) in chromone<sup>35</sup> and at 1728 (IR) and 1739 cm<sup>-1</sup> (Raman) in chromone-2-carboxylic acid.<sup>35</sup>

The assignment of the C–H and C–C stretching modes was based on the results reported for chromone<sup>35</sup> and phenol<sup>36</sup> (see Table 3).

**6-Amino-2-trifluoromethylchromone.** The prominent IR bands at 3429 and 3345 cm<sup>-1</sup> (see Figure 4) are assigned to the  $\nu_{\text{as}}\text{NH}_2$  and  $\nu_{\text{s}}\text{NH}_2$  stretching modes (calculated: 3678 and 3578 cm<sup>-1</sup>), while only a very weak band is observed in the Raman spectra at 3351 cm<sup>-1</sup> corresponding to the  $\nu_{\text{s}}\text{NH}_2$  stretching. The location of these bands is in good agreement with those in some related aminochromones.<sup>37</sup> The out-of-plane bending of the NH<sub>2</sub> group is predicted, by quantum chemical calculations, as a strong band at 509 cm<sup>-1</sup> but this vibration was not detected in IR and Raman. This inconsistency could be attributed to the fact that the –NH<sub>2</sub> group is involved in intermolecular interactions.

The IR strong band at 1320 cm<sup>-1</sup> can be attributed to the C–N stretching mode (calculated at 1330 cm<sup>-1</sup>) which was not detected in Raman.

The very intense band at 1641 (IR) and the one at 1635 cm<sup>-1</sup> (Raman) are assigned to the  $\nu(\text{C=O})$  stretching (calculated: 1713 cm<sup>-1</sup>). These values are in good agreement with those reported for amino substituted chromones.<sup>37</sup> The amino group located on the aromatic ring shifts the frequency of the carbonyl group down, when comparing with the nitro compound (see Table 4) and other related 2-trifluoromethyl substituted chromones.<sup>17</sup>

Most of the observed spectral positions and intensities of the bands for both compounds are in good agreement with the corresponding values derived from quantum chemical calculations and with related compounds.

**3.4. Electronic Spectroscopy.** The electronic spectra in methanol of 6-nitro-2-trifluoromethylchromone (**1**) ( $2.9 \times 10^{-5}$  M) and 6-amino-2-trifluoromethylchromone (**2**) ( $2.4 \times 10^{-5}$  M) are shown in Figures 5 and 7, together with simulated spectra obtained from calculated electronic transitions. Absorption maxima of both compounds are compared with calculated values in Tables 5 and 6, which also include tentative assignments. For simplicity, only the dominant transitions (chosen according to their oscillator strength) are used to assign the observed bands. From these results, it can be concluded that the calculated transitions closely reproduce the experimental electronic spectra.

**6-Nitro-2-trifluoromethylchromone (1).** Figure 6 shows the MO's (HOMO, highest occupied MO; LUMO, lowest unoccupied MO) mainly involved in the electronic transitions used to assign the experimental bands.

The observed bands (see Table 5) at 203 and 212 nm are dominated by one-electron transitions, from the HOMO-4 to the LUMO+1 and HOMO-1 to the LUMO+2, respectively, despite minor contributions from other one-electron excitations. They are assigned to transitions calculated at 219 and 224 nm,

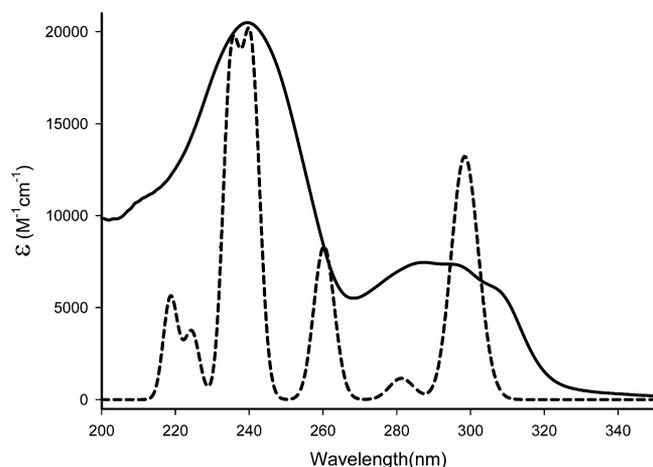
Table 4. Experimental and Calculated Frequencies ( $\text{cm}^{-1}$ ) and Tentative Assignment of Fundamental Vibration Modes in 6-Amino-2-trifluoromethylchromone (2)

mode	experimental		calculated <sup>b</sup>		assignment <sup>d</sup>
	IR <sup>a</sup>	Raman	frequency	intensity <sup>c</sup>	
$\nu_1$	3429(s)		3678	23 (60)	$\nu_{\text{as}}(\text{NH}_2)$
$\nu_2$	3345(s)	3351(5)	3578	42 (279)	$\nu_{\text{s}}(\text{NH}_2)$
$\nu_3$	3234(m)	3240(6)	3231	3 (108)	$\nu(\text{C8-H})$
$\nu_4$		3096(10)	3201	1 (135)	$\nu(\text{C1-H}); \nu(\text{C2-H})$
$\nu_5$		3081(15)	3184	6 (50)	$\nu(\text{C4-H})$
$\nu_6$	3056(vw)	3039(9)	3167	10 (109)	$\nu(\text{C2-H}); \nu(\text{C1-H})$
$\nu_7$	1641(vs)	1635(100)	1713	415 (188)	$\nu(\text{C9-O4})$
$\nu_8$	1611(m)		1677	39 (61)	$\nu(\text{C7-C8})$
$\nu_9$	1579(m)	1581(73)	1666	170 (105)	$\delta(\text{NH}_2)$
$\nu_{10}$			1650	7 (40)	$\nu(\text{C4-C5}); \nu(\text{C1-C2}); \nu(\text{C5-C6})$
$\nu_{11}$	1546(vw)		1614	18 (38)	$\nu(\text{C2-C3}); \nu(\text{C5-C6}); \nu(\text{C7-C8})$
$\nu_{12}$	1492(vs)	1489(19)	1516	204 (6)	$\delta(\text{C4-H}); \delta(\text{C1-H}); \delta(\text{C2-H})$
$\nu_{13}$		1472(19)	1488	54 (23)	$\nu(\text{C5-C9}); \nu(\text{C1-C2}); \nu(\text{C4-C5})$
$\nu_{14}$	1411(m)	1411(36)	1416	77 (70)	$\nu(\text{C7-O3}); \nu(\text{C3-C4}); \nu(\text{C1-C6}); \delta(\text{C8-H})$
$\nu_{15}$	1363(w)	1362(58)	1375	21 (44)	$\nu(\text{C5-C6}); \nu(\text{C2-C3})$
$\nu_{16}$	1320(s)		1330	87 (8)	$\nu(\text{N-C3}); \nu(\text{C4-C5})$
$\nu_{17}$	1283(vs)		1294	145 (12)	$\delta(\text{C1-H}); \delta(\text{C2-H}); \delta(\text{C4-H}); \nu(\text{C7-C10})$
$\nu_{18}$	1255(w)	1257(75)	1266	106 (76)	$\delta(\text{C8-H}); \nu(\text{C7-C10})$
$\nu_{19}$	1243(s)		1251	255 (1)	$\delta(\text{C1-H}); \delta(\text{C4-H}); \delta(\text{C7-C10})$
$\nu_{20}$	1210(m)	1211(23)	1218	24 (17)	$\nu(\text{C5-C9}); \nu(\text{C7-C10}); \nu(\text{C6-O3})$
$\nu_{21}$	1184(vs)		1176	220 (2)	$\nu_{\text{as}}(\text{CF}_3); \delta(\text{C1-H}); \delta(\text{C2-H}); \delta(\text{C4-H})$
$\nu_{22}$	1163(s)		1157	75 (15)	$\delta(\text{C1-H}); \delta(\text{C2-H})$
$\nu_{23}$	1154(vs)		1131	294 (3)	$\nu_{\text{as}}(\text{CF}_3)$
$\nu_{24}$			1099	32 (8)	$\delta(\text{N-C3-C4})$
$\nu_{25}$			1087	29 (1)	$\delta(\text{C4-H}); \delta(\text{C4-C5-C9})$
$\nu_{26}$	1074(m)	1074(15)	1076	34 (3)	$\nu_{\text{s}}(\text{CF}_3); \delta(\text{C8-C7-O3})$
$\nu_{27}$			957	1 (<1)	$\gamma(\text{C1-H}); \gamma(\text{C2-H}); \gamma(\text{C4-H})$
$\nu_{28}$	931(m)		936	45 (10)	$\delta(\text{C8-C7-O3}); \delta(\text{C1-C2-C3})$
$\nu_{29}$	923(m)	924(65)	933	28 (20)	$\delta(\text{C1-C2-C3}); \delta(\text{C9-C8-C7}); \nu_{\text{s}}(\text{CF}_3)$
$\nu_{30}$			902	6 (1)	$\gamma(\text{C4-H}); \gamma(\text{C8-H})$
$\nu_{31}$	857(s)		887	48 (<1)	$\gamma(\text{C8-H}); \gamma(\text{C4-H})$
$\nu_{32}$	820(m)		828	35 (<19)	$\gamma(\text{C2-H}); \gamma(\text{C1-H})$
$\nu_{33}$	807(w)		816	18 (3)	$\delta(\text{C6-C1-C2}); \delta(\text{C4-C5-C3}); \delta(\text{C-F}_3)$
$\nu_{34}$			763	<1 (<1)	$\gamma(\text{C1-H}); \gamma(\text{C5-C9-C8}); \gamma(\text{C8-H}); \gamma(\text{C4-H})$
$\nu_{35}$		732(56)	736	2 (14)	$\delta(\text{C6-C1-C2}); \delta(\text{C5-C4-C3})$
$\nu_{36}$	721(w)		716	7 (9)	$\delta_{\text{s}}(\text{CF}_3); \delta(\text{C6-C1-C2}); \delta(\text{C3-C4-C5})$
$\nu_{37}$		697(19)	698	<1 (<1)	$\gamma(\text{O3-C7-C8})$
$\nu_{38}$			697	1 (<1)	$\gamma(\text{C1-H}); \gamma(\text{C5-C9-C8}); \gamma(\text{C8-H}); \gamma(\text{C4-H}); \gamma(\text{C2-H})$
$\nu_{39}$	620(w)	620(21)	622	14 (2)	$\delta(\text{C5-C9-O4}); \delta(\text{C1-C6-O3})$
$\nu_{40}$	553(vw)		563	18 (3)	$\gamma(\text{C1-H}); \gamma(\text{C5-C9-C8}); \gamma(\text{C8-H}); \gamma(\text{C2-H})$
$\nu_{41}$	547(vw)	542(45)	557	9 (3)	$\delta_{\text{as}}(\text{CF}_3); \delta(\text{O4-C9-C8})$
$\nu_{42}$			539	1 (10)	$\delta(\text{C5-C9-C8}); \delta(\text{N-C3-C4})$
$\nu_{43}$		527(31)	532	5 (3)	$\delta(\text{C5-C9-C8}); \delta(\text{C6-O3-C7})$
$\nu_{44}$			518	14 (2)	$\delta_{\text{as}}(\text{CF}_3); \gamma(\text{C1-C6-C5})$
$\nu_{45}$			509	315 (13)	$\gamma(\text{NH}_2)$
$\nu_{46}$	473(vw)		474	20 (<1)	$\delta(\text{C6-O3-C7})$
$\nu_{47}$			441	2 (<1)	$\gamma(\text{C4-C5-C6}); \gamma(\text{C6-C1-C2})$
$\nu_{48}$			393	1 (3)	$\delta(\text{N-C3-C2})$
$\nu_{49}$		389(23)	386	8 (2)	$\gamma(\text{C2-C1-C6}); \gamma(\text{C7-O3-C6})$
$\nu_{50}$			343	<1 (1)	$\delta(\text{C7-CF}_3)$
$\nu_{51}$			302	18 (<1)	$\rho(\text{NH}_2)$
$\nu_{52}$			289	2 (<1)	$\gamma(\text{C9-C8-C7}); \rho(\text{NH}_2)$
$\nu_{53}$		265	271	2 (5)	$\delta(\text{C10-C7-C8}); (\text{N-C3-C2})$
$\nu_{54}$			239	7 (2)	$\delta(\text{N-C3-C4}); \delta(\text{O3-C7-C10})$
$\nu_{55}$			177	1 (<1)	$\tau(\text{O4-C9-C5-C4})$
$\nu_{56}$			158	3 (<1)	$\tau(\text{C7-C8-CF}_3); (\text{O4-C9-C5-C4})$
$\nu_{57}$			131	1 (1)	$\pi_{\text{ip}}(\text{CF}_3)$
$\nu_{58}$			123	4 (1)	$\tau(\text{C2-C3-NH}_2); (\text{CF}_3-\text{C7-O3})$

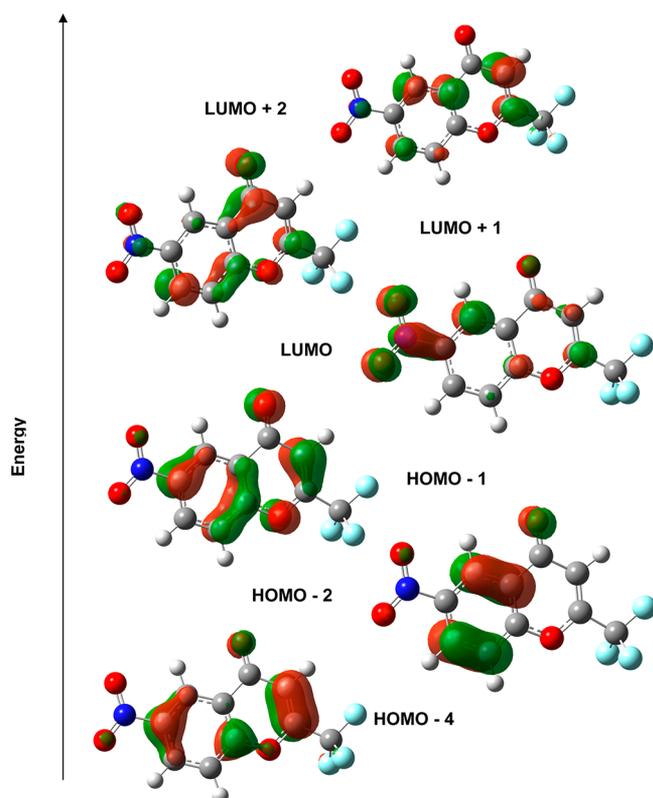
Table 4. continued

mode	experimental		calculated <sup>b</sup>		assignment <sup>d</sup>
	IR <sup>a</sup>	Raman	frequency	intensity <sup>c</sup>	
$\nu_{59}$			53	<1 (3)	$\tau(\text{C2-C3-NH}_2)$
$\nu_{60}$			31	1 (2)	$\tau(\text{C8-C7-CF}_3)$

<sup>a</sup>Key: vs, very strong; s, strong; w, weak; vw, very weak; sh, shoulder. <sup>b</sup>6-311++g(d,p). <sup>c</sup>Calculated intensities: IR in  $\text{km mol}^{-1}$  and Raman (in parentheses) in  $\text{\AA}^4 \text{amu}^{-1}$ . <sup>d</sup> $\nu$ ,  $\delta$ ,  $\gamma$ , and  $\tau$  represent stretching, in-plane deformation, out-of-plane deformation and torsion modes.

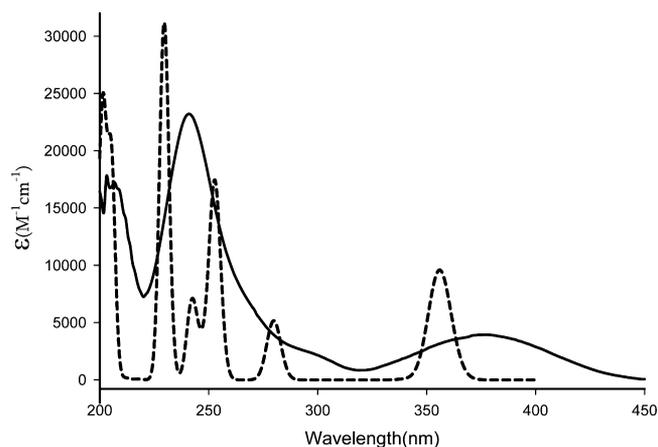


**Figure 5.** Experimental (full trace,  $2.9 \times 10^{-5}$  M in methanol) and calculated electronic spectra (B3LYP/6-311+g(d), dashed trace) of 6-nitro-2-trifluoromethylchromone (1).



**Figure 6.** Molecular orbitals involved in the electronic transitions of 6-nitro-2-trifluoromethylchromone (1). The energy scale is only qualitative and does not represent the actual energy of the molecular orbitals.

respectively. The absorption at 240 nm arises from the contribution of transitions from HOMO-4 to the LUMO and HOMO-2 to



**Figure 7.** Experimental (full trace,  $2.4 \times 10^{-5}$  M in methanol) and calculated electronic spectra (B3LYP/6-311+g(d), dashed trace) of 6-amino-2-trifluoromethylchromone (2).

**Table 5. Electronic Spectra of  $2.9 \times 10^{-5}$  M Methanolic Solution of 6-Nitro-2-trifluoromethylchromone (1)<sup>a</sup>**

experimental <sup>b</sup>	calculated <sup>c</sup>	assignment
203	219 (0.057)	HOMO-4 → LUMO+1 (89%)
212	224 (0.037)	HOMO-1 → LUMO+2 (75%)
240	235 (0.184)	HOMO-4 → LUMO (92%)
	240 (0.189)	HOMO-2 → LUMO+1 (87%)
287	260 (0.085)	HOMO-1 → LUMO+1 (47%)
		HOMO-2 → LUMO (36%)
293 <sup>d</sup>	281 (0.012)	HOMO-2 → LUMO (58%)
		HOMO-1 → LUMO+1 (33%)
306 <sup>d</sup>	298 (0.135)	HOMO-1 → LUMO (95%)

<sup>a</sup>Calculated electronic transitions (B3LYP/6-311+g(d)) are also shown and only those relevant for the assignments are listed. <sup>b</sup>Absorption maxima are given in nm. <sup>c</sup>Oscillator strengths of calculated transitions, shown in parentheses, are in atomic units. <sup>d</sup>Shoulder.

the LUMO+1 orbital, both ruled by one-electron excitation. The calculated wavelengths are 235 and 240 nm, respectively.

The observed absorption at 287 nm is assigned to a sole one-electron excitation from the HOMO-1 to the LUMO+1 with an important contribution from a HOMO-2 → LUMO excitation. This band is attributed to a calculated transition at 260 nm.

The shoulders at 293 and 306 nm are due to singlet electron excitations. The absorption at 293 nm corresponds to nearly equal contribution from HOMO-2 → LUMO and HOMO-1 → LUMO+1 transitions, whereas the one at 306 nm to a dominant excitation from the HOMO-1 to the LUMO. The calculated transitions are 281 and 298 nm, respectively.

The observed bands at 203, 212, and 287 nm correspond to transitions involving both fused rings. Moreover, the bands at 240, 293, and 306 nm are mainly dominated by transitions from both rings to the N-C bond with substantial contribution of transitions that occur also in both rings (see Figure 6).

**Table 6.** Electronic Spectra of  $2.4 \times 10^{-5}$  M Methanolic Solution of 6-Amino-2-trifluoromethylchromone (**2**)<sup>a</sup>

experimental <sup>b</sup>	calculated <sup>c</sup>	assignment
	196 (0.251)	HOMO-4 → LUMO (73%)
203	201 (0.185)	HOMO-2 → LUMO+1 (51%) HOMO-3 → LUMO+1 (20%) HOMO-4 → LUMO (17%)
207 <sup>d</sup>	205 (0.154)	HOMO-3 → LUMO+1 (71%) HOMO-2 → LUMO+1 (16%)
241	229 (0.250)	HOMO-3 → LUMO (38%) HOMO → LUMO+2 (32%) HOMO-3 → LUMO+1 (11%)
	242 (0.055)	HOMO-3 → LUMO (45%) HOMO → LUMO+3 (24%) HOMO → LUMO+2 (20%)
	253 (0.138)	HOMO-2 → LUMO (83%)
294	280 (0.041)	HOMO → LUMO+1 (86%)
377	356 (0.077)	HOMO → LUMO (97%)

<sup>a</sup>Calculated electronic transitions (B3LYP/6-311+g(d)) are also shown and only those relevant for the assignments are listed. <sup>b</sup>Absorption maxima are given in nm. <sup>c</sup>Oscillator strengths of calculated transitions, shown in parentheses, are in atomic units. <sup>d</sup>Shoulder.

6-Amino-2-trifluoromethylchromone (**2**). Figure 8 shows the MO's that participate in electronic transitions used to

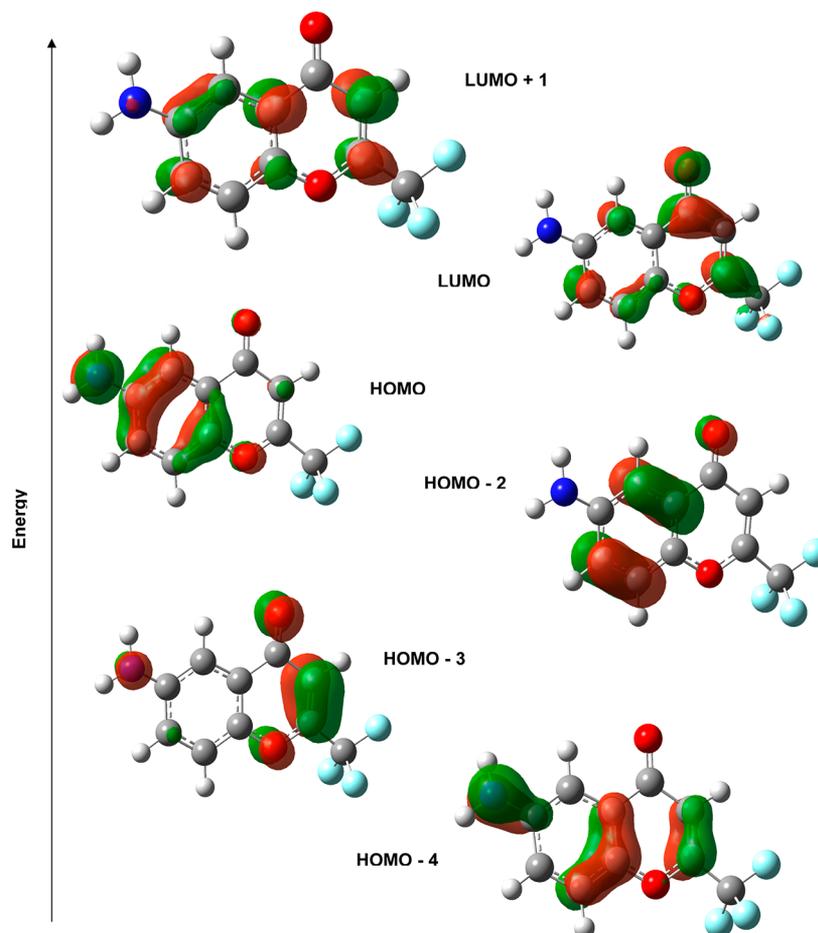
**Table 7.** Comparison between Experimental and Calculated NMR Chemical Shifts in ppm for **1** and **2**<sup>a,b</sup>

	<b>1</b>		<b>2</b>	
	expt	6-311+g(2d,p)	exp.	6-311+g(2d,p)
3-H	6.80	6.87 (−0.07)	6.64	6.71 (−0.07)
5-H	9.00	9.63 (−0.63)	7.39	7.67 (−0.28)
7-H	8.58	8.96 (−0.38)	7.08	7.13 (−0.05)
8-H	7.75	7.68 (+0.07)	7.37	7.47 (−0.10)
2-C	152.8	160.1 (−7.3)	152.7	158.6 (−5.9)
3-C	124.1	129.6 (−5.5)	109.3	115.1 (−5.8)
4-C	175.1	179.3 (−4.2)	177.0	180.0 (−3.0)
5-C	111.0	117.1 (−6.1)	107.6	112.1 (−4.5)
6-C	145.4	151.4 (−6.0)	145.0	151.4 (−6.4)
7-C	129.2	134.0 (−4.8)	123.1	123.6 (−0.5)
8-C	120.3	122.9 (−2.6)	119.3	123.5 (−4.2)
4a-C	122.4	130.4 (−8.0)	124.1	132.0 (−7.9)
8a-C	158.2	165.5 (−7.3)	149.2	155.4 (−6.2)
CF <sub>3</sub>	118.2	130.1 (−11.9)	118.7	130.8 (−12.1)

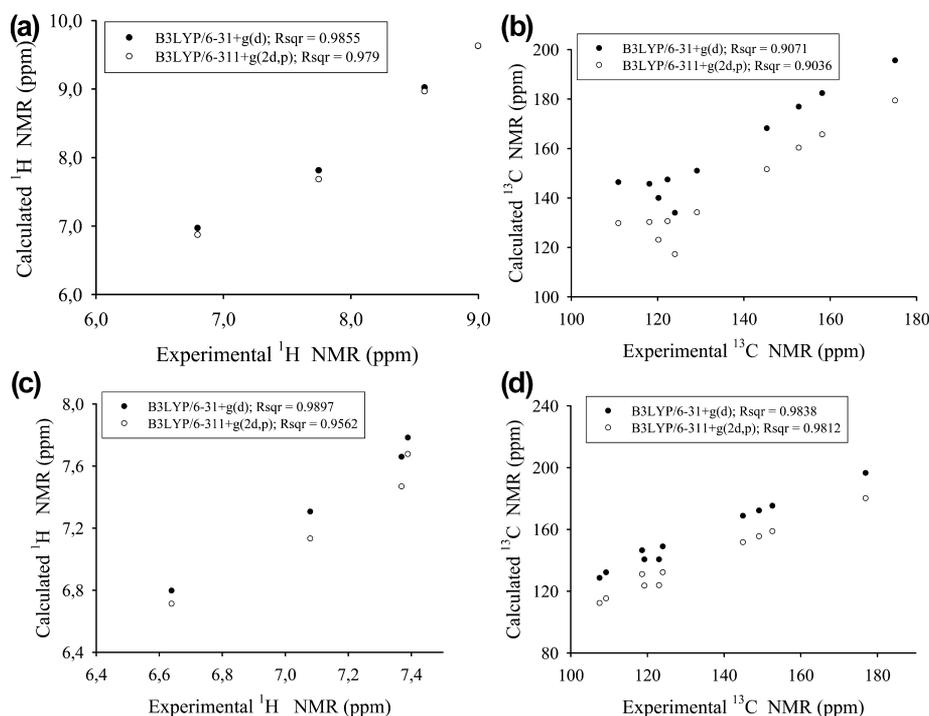
<sup>a</sup> $\Delta = \delta_{\text{exp}} - \delta_{\text{calc}}$  in parentheses. For atom numbering, see Chart 1. <sup>b</sup>For comparison between experimental, B3LYP/6-31+g(d), and B3LYP/6-311+g(2d,p) see Table S4 (Supporting Information).

attribute the observed bands of the UV–vis spectrum. All cases correspond to one-electron excitations, see Table 6.

At low wavelengths, the experimental spectrum shows a band at 203 nm and a shoulder at 207 nm. The band is dominated by



**Figure 8.** Molecular orbitals involved in the electronic transitions of 6-amino-2-trifluoromethylchromone (**2**). The energy scale is only qualitative and does not represent the actual energy of the molecular orbitals.



**Figure 9.** Comparison of experimental and theoretical chemical shifts of **1**, (a)  $^1\text{H}$ , (b)  $^{13}\text{C}$ , and **2**, (c)  $^1\text{H}$ , (d)  $^{13}\text{C}$ , calculated at the B3LYP/6-31+g(d) and B3LYP/6-311+g(2d,p) levels of the theory.

a transition from HOMO-2 orbital to the LUMO+1 one, with contributions from HOMO-3  $\rightarrow$  LUMO+1 and HOMO-4  $\rightarrow$  LUMO excitations. The shoulder is mainly due to a transition from HOMO-3 to the LUMO+1, besides other minor contributions. They are assigned to transitions calculated at 201 and 205 nm, respectively.

The observed band at 241 nm is mainly generated by excitations from HOMO-3  $\rightarrow$  LUMO and HOMO  $\rightarrow$  LUMO+2 (calculated wavelength 230 nm); HOMO-3  $\rightarrow$  LUMO and HOMO  $\rightarrow$  LUMO+3 (calculated wavelength 242 nm) and HOMO-2  $\rightarrow$  LUMO (calculated wavelength 253 nm).

The absorption at 294 and 377 nm are attributed to dominant excitations from the HOMO to the LUMO+1 and from the HOMO to the LUMO, respectively, whereas that the computed transitions are 280 and 356 nm.

The observed bands at 203 and 207 nm correspond to transitions within the aromatic ring. The band at 241 nm results from transitions that involve both fused rings. The bands at 294 and 377 nm are basically dominated by excitations from the aromatic fragment to orbitals that extend throughout the molecule (see Figure 8).

A complete description of the electronic spectra and involved orbitals of both compounds can be found in Supporting Information.

**3.5. NMR Spectroscopy.** After full geometry optimization with the GAUSSIAN G03 program package (see computational methods in Experimental Section) the  $^1\text{H}$ , and  $^{13}\text{C}$  chemical shifts were calculated with the GIAO method.<sup>31</sup> Table 7 shows the experimental and calculated chemical shifts (B3LYP/6-311+g(2d, p)) for both compounds, while data obtained with the low level of calculation (B3LYP/6-31+g(d)) were also included in Table S4 (Supporting Information). The experimental and calculated chemical shifts showed a linear relationship with R-square values for each compound above 0.9036.

The following correlations  $\delta_{\text{calc}} = a \delta_{\text{exp}} + b$  given in Figure 9a–d were obtained. Part a: B3LYP/6-31+g(d) ( $R^2 = 0.9855$ ;  $a = 1.2197$ ;  $b = 1.4434$ ), B3LYP/6-311+g(2d,p) ( $R^2 = 0.979$ ;  $a = 1.2652$ ;  $b = 1.8781$ ), Part b: B3LYP/6-31+g(d) ( $R^2 = 0.9071$ ;  $a = 0.9357$ ;  $b = 31.658$ ), B3LYP/6-311+g(2d,p) ( $R^2 = 0.9036$ ;  $a = 0.9364$ ;  $b = 15.018$ ), Part c: B3LYP/6-31+g(d) ( $R^2 = 0.9897$ ;  $a = 1.2565$ ;  $b = 1.5616$ ), B3LYP/6-311+g(2d,p) ( $R^2 = 0.9562$ ;  $a = 1.1782$ ;  $b = 1.1432$ ), Part d: B3LYP/6-31+g(d) ( $R^2 = 0.9838$ ;  $a = 0.9762$ ;  $b = 25.364$ ), B3LYP/6-311+g(2d,p) ( $R^2 = 0.9812$ ;  $a = 0.9755$ ;  $b = 8.8912$ ).

A good agreement between experimental and calculated  $^1\text{H}$  NMR spectra is observed for **1** and **2** compounds employing both basis sets, with values of  $\Delta$  between +0.07 and  $-0.63$  ppm. However, the B3LYP/6-31+g(d) basis set proved to be not suitable for predicting  $^{13}\text{C}$  NMR spectra and a better accuracy was obtained using the triple- $\zeta$  basis set 6-311+g(2d,p). In this case, the  $\Delta$ -values found for the carbon atoms of the chromone ring differ up to  $-8.0$  ppm. The greatest discrepancy was found in the prediction of the  $-\text{CF}_3$  chemical shift, with values of  $\Delta = -11.9$  and  $-12.1$  ppm for compounds **1** and **2**, respectively (see Table 7). This fact suggests that the isotropic shielding of the fluorine atoms is underestimated by theoretical calculations. A more severe disagreement was observed in the calculated chemical shifts of this group in some trifluoromethyl tetraisoquinolines.<sup>38</sup>

## 4. CONCLUSION

Because of an extensive  $\pi$ -bonding electronic structure, both compounds adopt an almost planar conformation. The quantum chemical calculations reflects this behavior with the  $-\text{CF}_3$  group staggered and one fluorine atom *syn* respect to the  $\text{C}=\text{C}$  bond. Besides, X-ray crystal structure of **1** shows also an atomic arrangement similar to that predicted by calculations, but with the trifluoromethyl group slightly off from the staggered conformation (*ca.*  $7^\circ$ ), probably due to packing effects. The experimental

and theoretical structural parameters of compound **1** are similar to those obtained by theoretical calculations of compound **2**, suggesting that the change of a deactivating group in the aromatic ring by an activating one, causes no appreciable effect on the interatomic distances and bond angles. The NO<sub>2</sub> moiety is in the same plane as the rings, with the experimental torsion angle O1–N–C3–C4 of 1.7°, while the predicted value results 0°. For **2**, the orientation of the NH<sub>2</sub> group is slightly deviated from the planarity (dihedral angle H1–N–C3–C2 = 25.2°), as expected for the sp<sup>3</sup> hybridization for the N atom. The GIAO method was found suitable for estimating the <sup>1</sup>H and <sup>13</sup>C chemical shifts in both compounds, but it underestimates the isotropic shielding of the strong electron withdrawing fluorine atoms. For this reason, the <sup>13</sup>C calculated chemical shift of the –CF<sub>3</sub> group showed significant disagreement with the experimental data.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Complete description of the electronic spectra, complete ref 29, mass spectrum of 6-nitro-2-trifluoromethylchromone (**1**) (Figure S1), mass spectrum of 6-amino-2-trifluoromethylchromone (**2**) (Figure S2), crystallographic information for 6-nitro-2-trifluoromethyl chromone, including atomic coordinates and equivalent isotropic displacement parameters (Table S1), anisotropic displacement parameters (Table S2), and hydrogen atoms positions (Table S3) and comparison between experimental and B3LYP calculated NMR chemical shifts in ppm for **1** and **2** (Table S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of this manuscript.

### Notes

The authors declare no competing financial interest.

**Crystal Data.** A CIF file with details of the crystal structure reported in the paper has been deposited with the Cambridge Crystallographic Data Centre (12 Union Road, Cambridge CB2 1EZ, U.K. Fax: +44–1223/336–033. E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)) and can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html)), reference number CCDC 913967.

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## ■ REFERENCES

- (1) Ellis, G. P. *Naturally Occurring Chromones*. In *The Chemistry of Heterocyclic Compounds. Chromenes, Chromanones and Chromones*; John Wiley and Sons Inc.: New York, 1997; Vol. 31; pp 455–480.
- (2) Harborne, J. B.; Williams, C. A. *Advances in Flavonoid Research since 1992*. *Phytochemistry* **2000**, *55*, 481–504.
- (3) Khadem, S.; Marles, R. J. Chromone and Flavonoid Alkaloids: Occurrence and Bioactivity. *Molecules* **2012**, *17*, 191–206.
- (4) Ibrahim, M. A.; Ali, T. E.; Alnamer, Y. A.; Gabr, Y. A. Synthesis and Chemical Reactivity of 2-Methylchromones. *ARKIVOC* **2010**, (i), 98–135.
- (5) Whalley, W. B. Organic Fluoro-compounds. Part VI. Some Trifluoromethyl-chromones and -coumarins. *J. Chem. Soc.* **1951**, 3235–3238.
- (6) Cho, E. J.; Senecal, T. D.; Kinzel, T.; Zhang, Y.; Watson, D. A.; Buchwald, S. L. The Palladium-catalyzed Trifluoromethylation of Aryl Chlorides. *Science* **2010**, *328*, 1679–1681.
- (7) Ritter, T. Catalysis: Fluorination Made Easier. *Nature* **2010**, *466*, 447–448.
- (8) Sosnovskikh, V. Y.; Kutsenko, V. A. Interaction of 2-Trichloromethylchromones with Ethylenediamine. A Simple Synthesis of 2-(2-Hydroxyaroylmethylene)imidazolidines. *Mendeleev Commun.* **1999**, *9*, 206–208.
- (9) Sosnovskikh, V. Y.; Kutsenko, V. A.; Morozov, M. Y. Reactions of 3-Amino-1-aryl- and 3-Amino-1-(2-thienyl)-4,4,4-trifluoro-2-buten-1-ones with 2-Aminoethanol. *Mendeleev Commun.* **1998**, *8*, 126–127.
- (10) Sosnovskikh, V. Y.; Kutsenko, V. A.; Yachevskii, D. S. Steric Factor in Reactions of Substituted 2-Trifluoromethylchromones with Ammonia and Primary Amines. *Mendeleev Commun.* **1999**, *9*, 204–205.
- (11) Sosnovskikh, V. Y.; Mel'nikov, M. Y. A Novel Synthesis of 2-Acylmethyleneimidazolidines. *Mendeleev Commun.* **1998**, *8*, 243–244.
- (12) Sosnovskikh, V. Y.; Moshkin, V. S.; Kodess, M. I. A Reinvestigation of the Reactions of 3-Substituted Chromones with Hydroxylamine. Unexpected Synthesis of 3-Amino-4H-chromeno[3,4-d]isoxazol-4-one and 3-(Diaminomethylene)chroman-2,4-dione. *Tetrahedron Lett.* **2008**, *49*, 6856–6859.
- (13) Sosnovskikh, V. Y.; Usachev, B. I. Unexpected Influence of Tetra- and Pentafluoroethyl Groups on the Direction of Reactions of 2-Polyfluoroalkylchromones with 2-Aminoethanol. *Mendeleev Commun.* **2000**, *10*, 240–241.
- (14) Sosnovskikh, V. Y.; Usachev, B. I. A Convenient Synthesis of 4(5)-(2-Hydroxyaroyl)-5(4)-trifluoromethyl-1,2,3-triazoles from 2-Trifluoromethylchromones and Chromen-4-imines. *Mendeleev Commun.* **2002**, *12*, 75–76.
- (15) Sosnovsky, G. The Chemistry Of Trichloromethanesulfonyl Chloride. *Chem. Rev.* **1958**, *58*, 509–540.
- (16) O'Connor, M. J.; Boblak, K. N.; Topinka, M. J.; Kindelin, P. J.; Briski, J. M.; Zheng, C.; Klumpp, D. A. *J. Am. Chem. Soc.* **2010**, *132*, 3266–3267.
- (17) Henao Castañeda, I. C.; Ulic, S. E.; Della Védova, C. O.; Metzler-Nolte, N.; Jios, J. L. One-pot synthesis of 2-trifluoromethylchromones. *Tetrahedron Lett.* **2011**, *52*, 1436–1440.
- (18) Sosnovskikh, V. Y.; Usachev, B. I. 2-polyfluoroalkylchromones: Nitration and chlorination of 2-trifluoromethylchromones. *Russ. Chem. Bull.* **2000**, *49*, 2074–2076.
- (19) Arjunan, V.; Puvirasan, N.; Mohan, S.; Murugesan, P. Fourier Transform Infrared and Raman Spectral Assignments and Analysis of 7-Amino-4-trifluoromethylcoumarin. *Spectrochim. Acta, Part A* **2007**, *67*, 1290–1296.
- (20) Sundaraganesan, N.; Mariappan, G.; Manoharan, S. Molecular Structure and Vibrational Spectroscopic Studies of Chrysin Using HF and Density Functional Theory. *Spectrochim. Acta, Part A* **2012**, *87*, 67–76.
- (21) Arjunan, V.; Subramanian, S.; Mohan, S. FTIR and FTR Spectral Studies of 2-Amino-6-bromo-3-formylchromone. *Spectrochim. Acta, Part A* **2004**, *60*, 995–1000.
- (22) Polly, R.; Taylor, P. R. Calculations of the Absorption Spectrum of Chromone. *J. Phys. Chem. A* **1999**, *103*, 10343–10347.

- (23) Preat, J.; Jacquemin, D.; Wathelet, V.; André, J.-M.; Perpète, E. A. TD-DFT Investigation of the UV Spectra of Pyranone Derivatives. *J. Phys. Chem. A* **2006**, *110*, 8144–8150.
- (24) Cornard, J. P.; Dangleterre, L.; Lapouge, C. DFT and TD-DFT Investigation and Spectroscopic Characterization of the Molecular and Electronic Structure of the Zn(II)-3-Hydroxyflavone Complex. *Chem. Phys. Lett.* **2006**, *419*, 304–308.
- (25) Merlic, C. A.; Motamed, S.; Quinn, B. Structure Determination and Synthesis of Fluoro Nissl Green: An RNA-Binding Fluorochrome. *J. Org. Chem.* **1995**, *60*, 3365–3369.
- (26) *CrysAlisPro*, 1.171.33.48 ed.; Oxford Diffraction Ltd.: release 15-09-2009 CrysAlis171.NET.
- (27) Sheldrick, G. M. *SHELXS-97. Program for Crystal Structure Resolution*; University of Göttingen: Göttingen, Germany, 1997.
- (28) Sheldrick, G. M. *SHELXL-97. Program for Crystal Structures Analysis*; Univ. of Göttingen: Göttingen, Germany, 1997.
- (29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; et al. *Gaussian 03*; Revision B.04 ed.; Gaussian, Inc.: Pittsburgh PA, 2003.
- (30) Dreuw, A.; Head-Gordon, M. Single-Reference ab Initio Methods for the Calculation of Excited States of Large Molecules. *Chem. Rev.* **2005**, *105*, 4009–4037.
- (31) Ditchfield, R. Self-consistent Perturbation Theory of Diamagnetism. *Mol. Phys.* **1974**, *27*, 789–807.
- (32) Johnson, C. K. ORTEP-II. Report ORNL-5318; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.
- (33) Sundaraganesan, N.; Ilakiamani, S.; Saleem, H.; Wojciechowski, P. M.; Michalska, D. FT-Raman and FT-IR Spectra, Vibrational Assignments and Density Functional Studies of 5-Bromo-2-nitropyridine. *Spectrochim. Acta, Part A* **2005**, *61*, 2995–3001.
- (34) Mahadevan, D.; Periandy, S.; Ramalingam, S. Comparative Vibrational Analysis of 1,2-Dinitro Benzene and 1-Fluoro-3-nitro Benzene: A Combined Experimental (FT-IR and FT-Raman) and Theoretical Study (DFT/B3LYP/B3PW91). *Spectrochim. Acta, Part A* **2011**, *84*, 86–98.
- (35) Machado, N. F. L.; Valero, R.; Domingos, H. S.; Tomkinson, J.; Batista de Carvalho, L. A. E.; Otero, J. C.; Marques, M. P. M. Conformational Behaviour of Antioxidant Chromones. A Vibrational Spectroscopy Study. *Vib. Spectrosc.* **2012**, *63*, 325–337.
- (36) Michalska, D.; Bieńko, D. C.; Abkowitz-Bieńko, A. J.; Latajka, Z. Density Functional, Hartree–Fock, and MP2 Studies on the Vibrational Spectrum of Phenol. *J. Phys. Chem.* **1996**, *100*, 17786–17790.
- (37) Kupcewicz, B.; Grazul, M.; Lorenz, I.-P.; Mayer, P.; Budzisz, E. The Synthesis, Spectroscopic Properties and X-ray Structure of Zn(II) Complexes with Amino Derivatives of Chromone. *Polyhedron* **2011**, *30*, 1177–1184.
- (38) Cakmak, I. GIAO Calculations of Chemical Shifts in Enantiometrically Pure 1-Trifluoromethyl Tetrahydroisoquinoline Alkaloids. *J. Mol. Struct. (THEOCHEM)* **2005**, *716*, 143–148.