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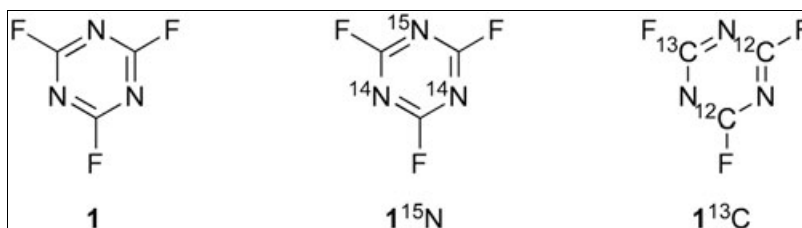
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Although 2,4,6-trifluoro-1,3,5-triazine, $C_3F_3N_3$, is a highly symmetrical molecule, its NMR parameters can be obtained by reducing its symmetry through the introduction of $^{14}N/^{15}N$ and $^{12}C/^{13}C$ isotopomers. Experimental and computed chemical shifts of cyanuric fluoride have been obtained for ^{13}C , ^{15}N , and ^{19}F . Spin-spin coupling constants have been measured and compared with previous experimental data and with the complete set of computed EOM-CCSD coupling constants.

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INTRODUCTION

In addition to being one of the most useful fluorinating agents in organic chemistry [1–3], cyanuric fluoride (**1**) is in itself a very interesting, highly symmetrical molecule [4–6]. This molecule has been well-characterized in terms of its NMR chemical shifts, including $\delta^{13}C = 173$ ppm [1], $\delta^{13}C \approx 172$ ppm [7], $\delta^{15}N = -168.8$ ppm [8,9], $\delta^{19}F \approx -33$ ppm [7], and $\delta^{19}F \approx -31.3$ ppm [10]. In contrast, only $^1J[^{13}C, ^{19}F] = 241$ Hz, $^3J[^{13}C, ^{19}F] = 18.7$ Hz [1] and $^2J[^{13}C, ^{15}N] = -52$ Hz [8,11] have been measured experimentally. Previously we reported high-level EOM-CCSD coupling constants for this molecule, including $^1J[^{13}C, ^{19}F] = -244.9$ Hz, $^4J[^{19}F, ^{19}F] = +7.8$ Hz [12], $^1J[^{13}C, ^{15}N] = -10.8$ Hz [13], $^2J[^{15}N, ^{19}F] = -51.3$ Hz [14], and $^4J[^{15}N, ^{19}F] = -3.6$ Hz [14]. In this note, we (i) compare computed and experimental values of chemical shifts, (ii) compare our experimental values of coupling constants with previous values, (iii) report previously undetermined experimental coupling constants, and (iv) compare our experimental data with the entire set of computed EOM-CCSD coupling constants.

RESULTS AND DISCUSSION

In a previous study, we developed empirical eqs. (1) and (2) to transform calculated absolute shieldings (σ , ppm) into chemical shifts (δ , ppm) for ^{13}C NMR and ^{15}N NMR, respectively [16].

$$\delta^{13}C = 175.7 - 0.963 \sigma^{13}C \quad (1)$$

$$\delta^{15}N = -152.0 - 0.946 \sigma^{15}C \quad (2)$$

To obtain a similar equation for ^{19}F NMR chemical shifts, we investigated a series of fluorine derivatives with chemical shifts that extend over a large range. The computed GIAO/B3LYP/6-311++G(d,p) shieldings for these molecules are reported in Table 1. The relationship between the experimental chemical shifts and the computed shieldings is given by eq. (3).

$$\delta^{19}F = 162.1 - 0.959 \sigma^{19}F \quad n = 23, R^2 = 0.997 \quad (3)$$

The fitted chemical shifts $\delta^{19}F$ reported in Table 1 are derived from this equation. Equations (1)–(3) have then been employed to convert calculated shieldings for ^{13}C , ^{15}N , and ^{19}F in cyanuric fluoride into chemical shifts for **1**. These values and the corresponding experimental chemical shifts are reported in Table 2. It is evident that the agreement between calculated and experimental values is excellent.

Spin-spin coupling constants of cyanuric fluoride are the second NMR property of interest. To obtain optimal values of chemical shifts and coupling constants, full line-shape iterations were employed to fit calculated and experimental spectra. To determine the coupling constants from the ^{13}C NMR spectrum (**1** ^{13}C), it was necessary to assume isotope shifts for the ^{19}F atoms: ^{19}F linked to $^{13}C = -29.790$ ppm; ^{19}F linked to $^{12}C = -29.690$ ppm ($\Delta\delta = 0.010$ ppm). These

Table 1Experimental chemical shifts [10], calculated shieldings, and fitted ^{19}F chemical shifts (ppm).

Molecule	Exp. $\delta^{19}\text{F}$	Calcd. $\sigma^{19}\text{F}$	Fitted $\delta^{19}\text{F}$
F ₂	422.9	-247.27	399.3
OF ₂	250	-81.48	240.3
NF ₃	146.9	4.83	157.5
Fluoropyridine	48.8	110.61	56.0
CFCl ₃	0.0	153.70	14.7
COF ₂	-23	187.93	-18.1
FCN	-29.7	195.80	-25.7
PF ₃	-34	199.11	-28.8
CF ₄	-63.3	231.31	-59.7
Pentafluoropyridine	-87.6	253.97	-81.4
C ₆ H ₅ F	-113.1	286.26	-112.4
BF ₃	-126.8	301.47	-127.0
Pentafluoropyridine	-134.1	304.86	-130.2
C ₂ F ₄	-135.2	303.37	-128.8
Tetrafluorofuran	-137	310.26	-135.4
BF ₃ OEt ₂	-152.8	334.39	-158.6
Pentafluoropyridine	-162	335.12	-159.3
SiF ₄	-164	347.11	-170.8
C ₆ F ₆	-164.9	336.87	-160.9
Tetrafluorofuran	-199	366.73	-189.6
C ₂ F ₂	-261.3	456.30	-275.5
CH ₃ F	-267.9	459.95	-279.0
ClF	-419.4	620.69	-433.1

Table 2

Calculated and experimental chemical shifts (ppm) of cyanuric fluoride.

Nucleus	Calcd. σ	Calcd. δ	Exp. δ (neat)	Exp. δ (CDCl ₃)
^{13}C	1.66	174.10	173.18	173 [1], 172 [7]
^{15}N	17.79	-168.83	-169.53	-168.8 [8,9]
^{19}F	195.82	-25.70	-29.72	-33 [7], -31.3 [10]

Due to the presence of ^{14}N atoms with spin = 1, the most complex NMR spectrum is that of $\mathbf{1}^{15}\text{N}$. This spectrum is shown in Fig. 1. By visual comparison, the best data were obtained using the following chemical shifts and coupling constants: two ^{19}F at two bonds from $^{15}\text{N} = -29.690$ ppm; one ^{19}F at four bonds from $^{15}\text{N} = -29.704$ ppm ($\Delta\delta = 0.014$ ppm); one ^{15}N and two ^{14}N all at -169.53 ppm; $^3J[^{13}\text{C}, ^{15}\text{N}] = -52.40$ Hz; $^4J[^{15}\text{N}, ^{19}\text{F}] = +1.11$; $^2J[^{14}\text{N}, ^{15}\text{N}] = -0.19$ Hz, and $^2J[^{14}\text{N}, ^{14}\text{N}] = +0.135$ Hz. Figure 1 illustrates the good agreement between the simulated and experimental spectra of $\mathbf{1}$.

The experimental coupling constants determined in this work and in previous studies [12–14] are reported in Table 3, along with the entire set of computed EOM-CCSD coupling constants. The excellent agreement between the experimentally measured coupling constants and the corresponding computed values can be seen in

chemical shifts were used in the calculation of coupling constants from the ^{19}F spectrum of the $\mathbf{1}^{13}\text{C}$ spectrum.

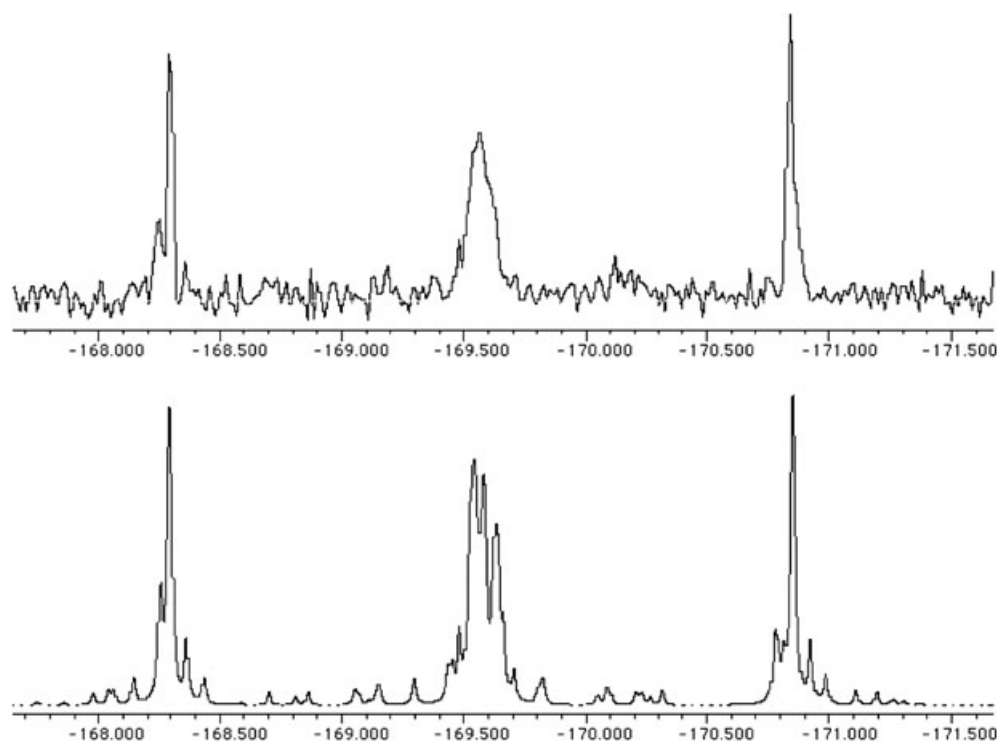
**Figure 1.** Experimental (top) and simulated (bottom) ^{15}N NMR spectrum of $\mathbf{1}$ at natural abundance.

Table 3

Experimental and calculated spin-spin coupling constants (Hz) of cyanuric fluoride.

	Exp.	Exp. this work	EOM-CCSD
$^2J[^{13}\text{C}, ^{13}\text{C}]$	–	–	+6.4
$^1J[^{13}\text{C}, ^{15}\text{N}]$	–	–	–10.8 [13]
$^3J[^{13}\text{C}, ^{15}\text{N}]$	–52 [8,11]	–52.40	–51.3
$^1J[^{13}\text{C}, ^{19}\text{F}]$	241 [1]	–239.20	–244.9 [12]
$^3J[^{13}\text{C}, ^{19}\text{F}]$	18.7 [1]	+19.10	+17.3
$^2J[^{15}\text{N}, ^{15}\text{N}]$	–	+0.27 ^a	–1.7 ^b
$^2J[^{15}\text{N}, ^{19}\text{F}]$	–	–52.40	–51.3 [14]
$^4J[^{15}\text{N}, ^{19}\text{F}]$	–	+1.11	–3.6 [14]
$^4J[^{19}\text{F}, ^{19}\text{F}]$	–	+11.20	+7.8 [12]

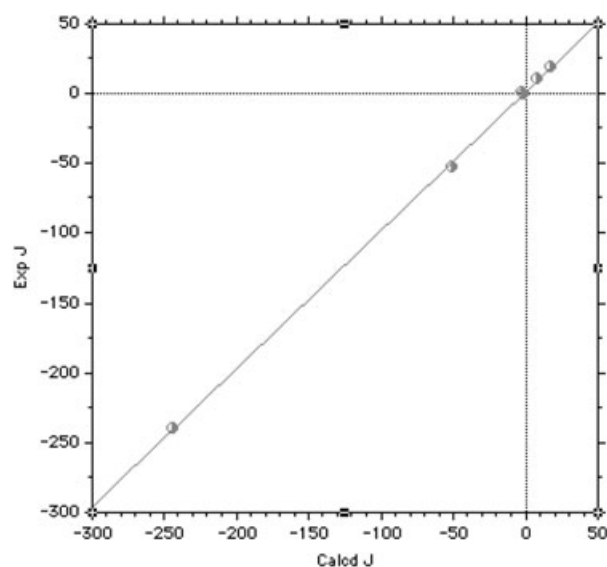
^aCorresponds to $^2J[^{14}\text{N}, ^{15}\text{N}] = -0.19$ Hz.^bCorresponds to $^2J[^{14}\text{N}, ^{15}\text{N}] = +1.2$ Hz.**Figure 2.** Experimental (neat) versus computed EOM-CCSD values of coupling constants, (J, Hz). The equation of the trendline is $J_{\text{exp.}} = (1.76 \pm 1.12) + (0.990 \pm 0.012) J_{\text{calcd.}}$, $n = 7$, $R^2 = 0.9993$.

Figure 2. The equation of the trendline can be used to predict experimental values for the two experimentally undetermined coupling constants, $^2J[^{13}\text{C}, ^{13}\text{C}] = +8.10$ Hz and $^1J[^{13}\text{C}, ^{15}\text{N}] = -8.92$ Hz.

EXPERIMENTAL AND COMPUTATIONAL METHODS

Cyanuric fluoride is a commercial product obtained from Sigma Aldrich. ^{13}C NMR, ^{19}F NMR, and ^{15}N NMR spectra were recorded at room temperature on a Varian Inova 400 NMR

spectrometer, equipped with a 5-mm PFG indirect detection ($^1\text{H}/^{19}\text{F}$ ^{15}N - ^{31}P) probe, operating at 376.27 MHz (^{19}F), 100.57 MHz (^{13}C), and 40.53 MHz (^{15}N). A first attempt to record the spectra in acetone- d_6 was abandoned because **1** reacts with this solvent. Subsequently, spectra were obtained from the neat liquid plus a DMSO- d_6 capillary for locking and a $^{15}\text{NO}_2\text{CH}_3$ capillary as a reference for the ^{15}N NMR spectrum. All NMR experiments were performed using standard Varian pulse sequences, with digital resolutions of 0.3–0.7 Hz. Lorentz–Gauss window functions were applied prior to Fourier transformations for the resolution-enhanced ^{19}F and ^{15}N spectra. Since most spectra exhibited second-order and isotopic effects, spectral simulations using the program gNMR5.0 [15] were required to obtain coupling constants.

Theoretical calculations of chemical shifts were carried out at the GIAO/B3LYP/6-311++G(d,p) level as described in a previous study [16]. Spin-spin coupling constants were calculated using the EOM-CCSD methodology with the Ahlrichs qzvp basis set, as in previous publications [12–14].

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