

Azidotris(trifluoromethyl)germane, (CF₃)₃GeN₃: Spectroscopic Characterization and Density Functional Computations[†]

Thomas M. Klapötke* and Axel Schulz[‡]

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, U.K.

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Azidotris(trifluoromethyl)germane, (CF₃)₃GeN₃, was prepared from activated silver azide and iodotris(trifluoromethyl)germane in a neat reaction or in dichloromethane or toluene solution, respectively. (CF₃)₃GeN₃ is a colorless, highly volatile liquid (mp ca. –85 °C) which was identified from MS data. The new compound was characterized by multinuclear solution NMR (¹³C, ¹⁴N, ¹⁹F) and gas-phase IR spectroscopy. The structure and the vibrational spectrum of (CF₃)₃GeN₃ were computed employing density functional theory calculations (DFT) at the self-consistent level with the nonlocal exchange functional of Becke (B) and the nonlocal correlation functional of Lee, Yang, and Parr (B-LYP). The results of the DFT calculation and *experimentally obtained* vibrational spectra are in good agreement. The DFT computation at the correlated level (B-LYP) predicts the vibrational modes reasonably well, and no scaling was required.

Introduction

We have been studying the reactions of various nitrogen, phosphorus, arsenic, and antimony halides with silver azide and activated sodium azide.^{1–3} In 1992/1994 Ang et al. published structural studies on the trifluoromethyl-substituted arsenic azides (CF₃)As(N₃)₂ and (CF₃)₂AsN₃,⁴ and there is also a report on the preparation of ionic trimethylazidoarsonium compounds.⁵ In 1995 we reported the synthesis of the first binary arsenic azide species As(N₃)₃ and [As(N₃)₄]⁺.³

In contrast to the chemistry of halogen azides and group 15 azides, which has been explored in the last years,^{1,6,7} studies on heavier group 14 azide compounds (e.g. those of Ge, Sn, Pb) are still very limited. The gas-phase structure of a carbon-bound azide, CF₃N₃, was reported in 1984,⁸ and the chemistry of trimethylsilyl and trimethylstannyl azides has been studied extensively.^{1,9ab} There is also one report on a binary triazido-carbonium cation (SbCl₆[–] salt).^{9c} To our knowledge, there is only one report on a well-established example of covalently

bound germanium azide, H₃GeN₃.¹⁰ In order to predict which other R₃Ge moiety would be predestined to give a stable compound of the type R₃GeN₃, we applied the *element displacement principle*, which provides a periodic system of functional groups (“paraelements”).¹¹ [N.B. The *paraelement principle* was first introduced by Haas¹² (cf. the *hydrogen displacement principle*¹³). A link between this concept and transition metals was provided by Hoffmann in the *isobal concept*.¹⁴] Chlorine azide, ClN₃, is known to have a high tendency for formation¹⁵ and to be one of the most stable halogen azides.¹ Using the fluorine-like CF₃ radical (group electronegativity 3.3),¹⁶ the first-order derivative paraelement (CF₃)₃Ge can be obtained which resembles chlorine (cf. (group) electronegativities: Cl, 2.8; (CF₃)₃Ge, 2.75).^{16b} Consequently, we here report on the reaction of (CF₃)₃GeI with freshly prepared and activated silver azide. Reaction of (CF₃)₃GeI and AgN₃ results in the formation of the germanium azide species (CF₃)₃GeN₃ (**1**) (eq 1). Pure (CF₃)₃GeN₃ was obtained from the neat starting materials. Subsequently, (CF₃)₃GeN₃ was identified from MS data and characterized by its ¹³C, ¹⁴N, and ¹⁹F NMR and gas-phase IR spectra.



In recent studies the quality of density functional calculations for relatively large and heavy halogen- and pseudohalogen-

[†] Dedicated to Professor Dr. mult. Dr. h.c. Alois Haas on the occasion of his 65th birthday.

[‡] Some computations were performed at the TU Berlin.

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- (16) (a) Klapötke, T. M.; Tornieporth-Oetting, I. C. *Nichtmetallchemie*; VCH: Weinheim, New York, 1994. (b) The group electronegativity of the R₃Ge group (R = CF₃) was estimated from the semiempirically calculated values IP(R₃Ge) = 11.5 eV and E_A(R₃Ge) = 6.1 eV giving EN(R₃Ge, Mulliken) = 8.8 eV, and with EN(Pauling) = 0.336[EN(Mulliken) – 0.615], the group electronegativity can be estimated to EN(R₃Ge, Pauling) = 2.75 eV.^{16a}

Table 1. Multinuclear NMR Data: Chemical Shifts δ (ppm) [Line Widths (Hz)], Coupling Constants J (Hz)

	solvent	$^{13}\text{C}^a$	^{14}N	^{19}F	$^{73}\text{Ge}^b$
resonance freq (MHz)		50.323	14.462	188.313	6.981
Me_4Ge	CD_2Cl_2	-0.4 q $^1J = 124.5$			0.0 [2.0]
$(\text{CF}_3)_3\text{GeI}$	CD_2Cl_2	123.5 q, sep $^1J = 336, ^3J = 5$		-53.7 s	-219 [100]
$(\text{CF}_3)_3\text{GeI}$	$\text{C}_6\text{D}_5\text{CD}_3$	127.7 q, sep $^1J = 333, ^3J = 5$		-52.3 s	n.o.
$(\text{CF}_3)_3\text{GeN}_3$	CD_2Cl_2	126.7 q, sep $^1J = 314, ^3J = 5$	-148.9 [23] -191.8 [35] -330.4 [300]	-57.1 s	n.o.
$(\text{CF}_3)_3\text{GeN}_3$	$\text{C}_6\text{D}_5\text{CD}_3$	128.5 q, sep $^1J = 314, ^3J = 5$	-145.1 [28] -186.8 [54] -332.8 [350]	-54.7 s	n.o.

^a q = quartet; sep = septet. ^b n.o. = not observed.

containing molecules was tested. It has been established that usually the calculated vibrational frequencies are in excellent agreement with the experimental values.^{7,17} Therefore, we decided to theoretically compute the structural features and the vibrational spectrum of $(\text{CF}_3)_3\text{GeN}_3$ employing density functional theory.

Experimental Section

Caution! Covalent and ionic azides are very toxic, and appropriate safety precautions should be taken. Although no explosion was observed in our studies, pure silver azide and all covalently bound germanium azides should be handled with respect.

1. Materials. The synthesis of silver azide has been previously described.¹⁸ For activation prior to reaction, freshly prepared AgN_3 was dried (under vacuum, over P_4O_{10}), loaded into the reaction vessel, and suspended in 10 mL of R-11 (CFCl_3 , Merck). The suspension was then treated in an ultrasonic bath to obtain very fine silver azide (large surface). The R-11 was pumped off, and the *activated* AgN_3 (large surface area) was either used in a neat reaction (IR experiments) or suspended in CD_2Cl_2 or $\text{C}_6\text{D}_5\text{CD}_3$, respectively (see below).

2. Preparation of $(\text{CF}_3)_3\text{GeN}_3$. For the preparation of samples for NMR spectroscopy, a reaction vessel was used consisting of one bulb and one 10 mm NMR tube which were separated by a frit.¹⁹ The bulb was loaded with 0.36 g (2.46 mmol, 2-fold excess) of activated AgN_3 (see above). The dry AgN_3 was then suspended in 8 mL of CD_2Cl_2 (or $\text{C}_6\text{D}_5\text{CD}_3$), and 0.5 g (1.23 mmol) of $(\text{CF}_3)_3\text{GeI}$ was added to the suspension at 0 °C. The reaction mixture was stirred for 2 h at 0 °C, and the solution was then directly filtered into the NMR tube which was flame-sealed. The remaining precipitate was identified as a mixture of unreacted AgN_3 and formed AgI .

For the preparation of samples for IR spectroscopy, a 10 cm gas cell with a directly attached reaction vessel (15 cm³) was used. In the reaction vessel, dry, activated AgN_3 was prepared (0.72 g, 4.92 mmol, 4-fold excess) and reacted with 0.5 g (1.23 mmol) of $(\text{CF}_3)_3\text{GeI}$. The neat reaction mixture was allowed to react at room temperature for 1 h and was carefully shaken several times. By variation of the temperature of the reaction vessel, the pressure of the product in the gas phase was controlled (see below, Figure 2); mp = -85 °C.

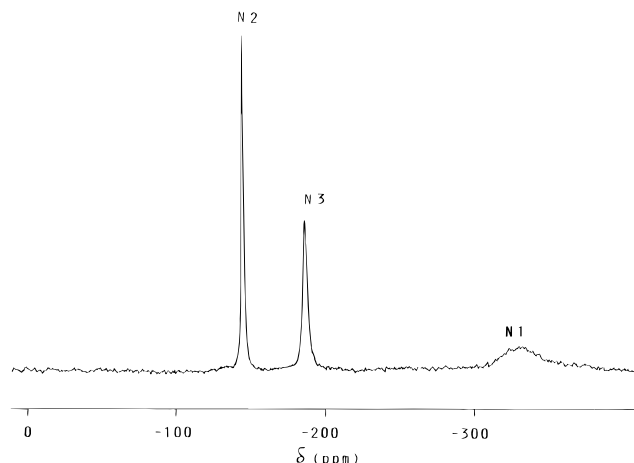


Figure 1. ^{14}N NMR spectrum of $(\text{CF}_3)_3\text{GeN}_3$ (connectivity $\text{R}_3\text{Ge}-\text{N}1-\text{N}2-\text{N}3$) (14.462 MHz, toluene- d_8 solution, 22 °C).

3. Vibrational Spectroscopy. Infrared spectra were recorded at 20 °C by using a 10 cm gas cell equipped with NaCl windows on a Philips PU9800 FTIR spectrophotometer.

4. NMR Spectroscopy. All NMR spectra (^{13}C , ^{14}N , ^{19}F , ^{73}Ge) were recorded in 10 mm NMR tubes in CD_2Cl_2 or $\text{C}_6\text{D}_5\text{CD}_3$ solution (see Table 1) at 20 °C using a Bruker SY 200 spectrometer operating at the frequencies as indicated in Table 1. All spectra are reported in ppm on the δ scale and are referred to external TMS (^{13}C), MeNO_2 (^{14}N), CFCl_3 (^{19}F), or $(\text{CH}_3)_4\text{Ge}$ (^{73}Ge), respectively. Peak positions appearing downfield (high-frequency) of the reference are reported as *plus* and those upfield (low-frequency) of the reference are reported as *minus*.

5. Computational Methods. The structure and vibrational data were calculated by using the density functional theory²⁰ with the program package Gaussian 94.²¹ For all atoms a standard 6-31G(d,p) basis set was used and the computations were done at the DFT level with the local exchange functional^{22,23} extended by the nonlocal

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Table 2. ^{14}N NMR Data for $(\text{CF}_3)_3\text{GeN}_3$, $\text{As}(\text{N}_3)_3$, and IN_3 : Chemical Shifts δ (ppm) Relative to MeNO_2 [Line Widths $\Delta\nu$ (Hz)] (Connectivity: X–N1–N2–N3)

	N1	N2	N3	ref
$(\text{CF}_3)_3\text{GeN}_3$	–332.8 [350]	–145.1 [28]	–186.8 [54]	this work
$\text{As}(\text{N}_3)_3$	–318.0 [150]	–131.1 [15]	–165.2 [30]	3b
IN_3	–351.2 [350]	–121.9 [20]	–156.6 [65]	3a

Table 3. Observed and Calculated Vibrational Wavenumbers (cm^{-1}) for $(\text{CF}_3)_3\text{GeN}_3$

IR (gas)	calcd ^a	int ^b	assign ^c
2245 w			$2 \times \nu_{\text{sym}}(\text{N}_3)$
2145 s	2164	496	$\nu_{\text{asym}}(\text{N}_3)$
1625 w, br			impurity
1351 m			$2 \times \delta(\text{Ge}-\text{N}_3)$
1270 s	1286	136	$\nu_{\text{sym}}(\text{N}_3)$
1197 sh	1142	152	$\nu(\text{CF}, \text{CF}_3)$
1175 vs	1126	456	$\nu(\text{CF}, \text{CF}_3)$
	1120	539	
1163 sh	1110	183	$\nu(\text{CF}, \text{CF}_3)$
	1105	293	
1132 sh	1090	6	$\nu(\text{CF}, \text{CF}_3)$
1070 w	1080	9	$\nu(\text{CF}, \text{CF}_3)$
1032 w	1080	16	$\nu(\text{CF}, \text{CF}_3)$
948 m	1060	11	$\nu(\text{CF}, \text{CF}_3)$
735 m			impurity
672 m	658	16	$\nu(\text{Ge}-\text{N}_3)$
562 sh	564	6	$\gamma(\text{N}_3)$
512 m	492	21	$\delta(\mathbf{1})$

^a Ab initio B-LYP/6-31G(d,p); $\geq 500 \text{ cm}^{-1}$. ^b Intensities in km mol^{-1} . ^c $\nu(\text{CF}, \text{CF}_3)$ indicates a predominantly C–F stretching mode which involves one or more C–F groups in one or more CF_3 units.

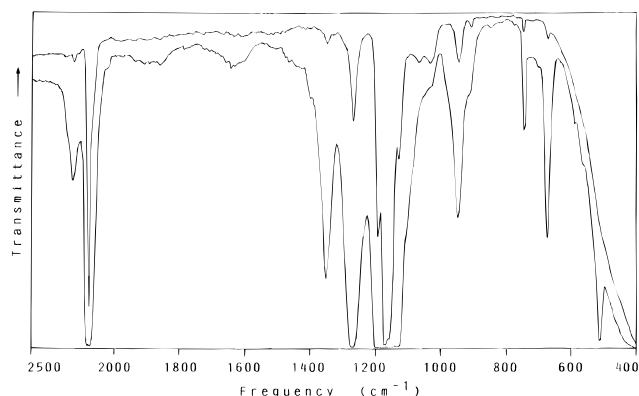


Figure 2. Gas-phase IR spectra of $(\text{CF}_3)_3\text{GeN}_3$ (10 cm gas cell, NaCl windows): top, low pressure (ca. 1 Torr); bottom, high pressure (ca. 3 Torr).

exchange functional of Becke (B).²⁴ Correlation was taken into consideration by using the nonlocal correlation functional of Lee, Yang, and Parr (B-LYP).²⁵

Results and Discussion

The new compound azidotris(trifluoromethyl)germane, $(\text{CF}_3)_3\text{GeN}_3$ (**1**), was prepared according to eq 1 and undoubtedly identified from mass spectrometry by a peak corresponding to the molecular ion.²⁶

Azidotris(trifluoromethyl)germane was fully characterized by multinuclear NMR spectroscopy (Table 1). For the covalently bound species, three well-resolved resonances were found in the ^{14}N NMR spectrum (Figure 1) and assignment of the

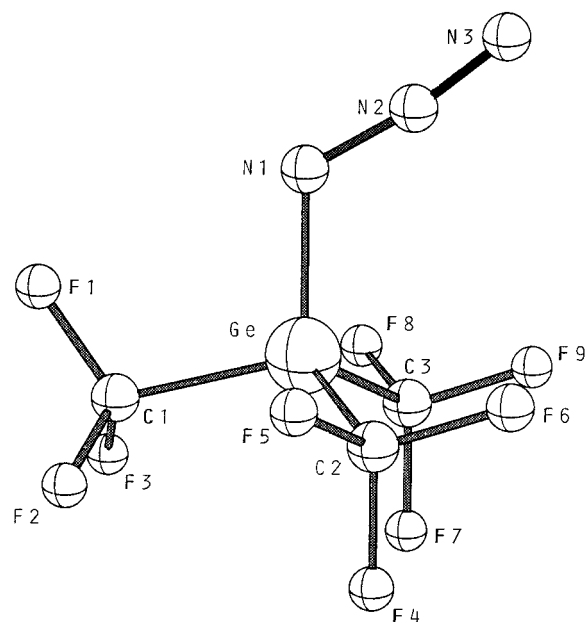


Figure 3. B-LYP/6-31G(d,p)-optimized structure of $(\text{CF}_3)_3\text{GeN}_3$, C_s symmetry.

Table 4. Structural Parameters for $(\text{CF}_3)_3\text{GeN}_3$ (Fully Optimized at B-LYP Level of Theory, 6-31G(d,p) Basis Set)

bond	value (\AA)	angle	value (deg)
N3–N2	1.157	N1N2N3	172.1
N1–N2	1.248	N2N1Ge	120.3
Ge–N1	1.874	N1GeC1	104.2
Ge–C1	1.994	N1GeC2	109.8
Ge–C2	1.990	GeC1F1	112.3
Ge–C3	1.990	GeC1F2	110.0
C1–F1	1.358	GeC2F3	111.2
C1–F2	1.368	GeC2F5	110.6
C1–F3	1.368	GeC2F6	109.9
C2–F4	1.366	C1GeC2	111.1
C2–F5	1.364	C2GeC3	110.7
C2–F6	1.368	GeN1N2N3	180.0
C3–F7	1.366	N2N1GeC2	60.9
C3–F8	1.364	N1GeC1F1	0.0
C3–F9	1.368	C1GeC2C3	123.3

individual resonances to N1, N2, and N3 (connectivity: Ge–N1–N2–N3) was made on the basis of the arguments given in earlier work by Witanowski²⁷ and three reports on ^{14}N data of covalent azides by us.^{3,28} The individual chemical shifts as well as line widths found for **1** nicely compare to those of the structurally closely related $\text{As}(\text{N}_3)_3$ and also IN_3 (cf. electronegativities, Allred/Rochow: Ge, 2.0; As, 2.2; I, 2.2) (Table 2). Presumably, as a result of the large quadrupole moment of ^{14}N , spin–spin splitting which has been estimated to be less than 30 Hz was not observed (cf. line widths, Table 2).²⁹ The relatively small difference in the ^{19}F chemical shifts between $(\text{CF}_3)_3\text{GeI}$ and $(\text{CF}_3)_3\text{GeN}_3$ (cf. Table 1) is in agreement with the azide unit being considered as a pseudohalogen with a group electronegativity close to that of bromine.⁷ I.e. EN(Mulliken) (eV): Cl, 8.3; N₃, 7.7; Br, 7.5 eV^{7a} [cf. $\delta(^{19}\text{F})$: $(\text{CF}_3)_2\text{PI}$, 55.4 ppm; $(\text{CF}_3)_2\text{PBr}$, 59.5 ppm].³⁰ Despite several attempts, we were not able to obtain a ^{73}Ge NMR spectrum of **1**. However, this is not very surprising since the very low frequency nucleus ^{73}Ge generally presents a problem owing to the quadrupole moment which has severely limited the range of molecules

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studied.^{31,32} (N.B. Under the same conditions, we obtained a very good ⁷³Ge NMR spectrum of the highly symmetric (CH₃)₄-Ge, Table 1.)

Table 3 summarizes the computed and experimentally observed (Figure 2) frequencies of (CF₃)₃GeN₃. The frequencies (and intensities) obtained from the DFT computation are generally in good agreement with the experimental values. This finding is nicely in agreement with earlier studies comparing the quality of ab initio and density functional computations predicting the vibrational data for main group compounds.^{7,17} It may be of interest to mention that the $\nu(\text{Ge-N}_3)$ stretching mode which can lead to dissoziation appears at 672 cm⁻¹. There are two other modes which to some extent also involve a Ge-N₃ vibration; these were computed to appear at 349 and 280 cm⁻¹, respectively.

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Table 4 summarizes the computed structural parameters of (CF₃)₃GeN₃. The molecular structure of **1** was fully optimized at the B-LYP/6-31G(d,p) level and is shown in Figure 3. As expected for a covalently bound azide, **1** displays a bent *trans* configuration with a N-N-N bond angle of 172° and two significantly different N-N bond lengths. In an earlier study,⁷ we could establish that uncorrelated ab initio (HF) and DFT (B) calculations are of similar qualities. The density functional computation usually gives better bond angles, but the HF method results in better distances and vice versa. At correlated levels, both methods, ab initio (MP2) and density functional theory (B-LYP), compare nicely with the experimental data. This gives credence to the computed structure of (CF₃)₃GeN₃ which was calculated at the electron correlated density functional B-LYP level of theory.

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