Supplementary Material (ESI) for Chemical Communications

Supporting Informations

Triazides of Heavy Group 15 Elements

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Caution!

Antimony and bismuth azide compounds are potentially toxic and can decompose explosively under various conditions! They should be handled only on a scale of less than 2 mmol with appropriate safety precautions (safety shields, safety glasses, face shields, leather gloves, protective clothing, such as leather suits, and ear plugs). Teflon containers should be used, whenever possible, to avoid hazardous fragmentation. Ignoring safety precautions can lead to serious injuries.

Experimental Section

Reactions were carried out in traps constructed from FEP tubes. Volatile materials were handled in a stainless steel-Teflon-FEP or Duran glass vacuum line. Nonvolatile materials were handled in the dry argon atmosphere of a glove box. The CH_2Cl_2 was dried over CaH_2 and degassed prior to use. The $(CH_3)_3SiN_3$ and pyridine were purified by fractional condensation prior to use. The SbF_3 was purified by sublimation. The BiF_3 was commercially available and used as received. A Bruker Avance 500 spectrometer was used for NMR spectroscopy. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to internal $CDCl_3$ (^{1}H: δ = 7.26; ^{13}C: δ = 77.0), $^{14}N\{^{1}H\}$ spectra to external CH_3NO ($\delta(^{14}N)$ = 0). The Raman spectra were recorded with a Bruker FT-Ramanspectrometer RFS 100/S using the 1064 nm line of a Nd:YAG laser. The backscattered (180°) radiation was sampled and analysed (Stoke range: 50 to 4000 cm^{-1}). The powdered samples were measured in melting point capillaries (typical operation parameters: 8000 scans and a resolution of 2 cm^{-1}) using a laserpower of 100 mW. IR spectra were recorded on a Alpha-T FT-IR spectrometer with a single reflection ATR sampling module.

General synthesis of $E(N_3)_3$ (E = Sb 1, Bi 2)

A sample of EF_3 (SbF_3: 0.10 g (0.56 mmol; BiF_3: 0.10 g (0.38 mmol)) was loaded in the glovebox into a FEP reaction trap. 3 mL of Me_3SiN_3 was condensed into the trap and the resulting suspension was slowly warmed to ambient temperature over a period of 6 h. After

stirring the suspension for 7 days, all volatile components were pumped off, yielding the triazides as colorless (**1**) and light yellow (**2**) solids in quantitative yields.

$Sb(N_3)_3$ (1): M.p: Detonation at 248 °C (sealed capillary). Yield 0.14 g (100%). IR (ATR, 32 scans): ν = 2080 (s), 1326 (m), 1242 (s), 1162 (w), 659 (s), 584 (m), 440 (m) cm^{-1}. Raman (100 mW, 25 °C, 8000 Scans): ν = 2122, 2094, 2078, 1329, 1261, 1247, 659, 386, 263, 244, 208, 140, 113, 81 cm^{-1}. ^{14}N NMR (500 MHz, CH_2Cl_2, 25 °C): δ = -134 (N_β, $\Delta\mu_{1/2}$ = 26 Hz), -169 (N_γ, $\Delta\mu_{1/2}$ = 34 Hz), -321 (N_α, $\Delta\mu_{1/2}$ = 170 Hz).

$Bi(N_3)_3$ (2): M.p: Detonation at 254 °C (sealed capillary). Yield 0.13 g (100 %). IR (ATR, 32 scans): ν = 2056 (s), 1317 (m), 1252 (s), 1175 (w), 649 (m), 590 (m) cm^{-1}. Raman (100 mW, 25 °C, 8000 Scans): ν = 2103, 2069, 2054, 1333, 1319, 1271, 1254, 652, 590, 342, 309, 250, 230, 202, 178, 167, 131, 117, 85 cm^{-1}. ^{14}N NMR (500 MHz, CH_2Cl_2, 25 °C): δ = -135 (N_β, $\Delta\mu_{1/2}$ = 20 Hz), -170 (N_γ, $\Delta\mu_{1/2}$ = 32 Hz), -324 (N_α, $\Delta\mu_{1/2}$ = 140 Hz).

Synthesis of $(Py)_2$-$Bi(N_3)_3$ (3)

3 mL of CH_2Cl_2 and 2 mL of pyridine were condensed in a FEP reaction trap filled with 0.10 g (0,30 mmol) $Bi(N_3)_3$ and the resulting mixture was warmed to ambient temperature over a period of 6 h. Single crystals of **3** were obtained from this solution after storage at 0 °C for 48 h.

M.p: Detonation at 250 °C (sealed capillary). IR (ATR, 32 scans): ν = 3311 (w), 2954 (w), 2922 (w), 2853 (w), 2040 (s), 2022 (s), 1721 (w), 1625 (w), 1595 (m), 1485 (w), 1439 (m), 1316 (s), 1254 (s), 1214 (m), 1145 (w), 1063 (m), 1033 (w), 1002 (m), 746 (m), 698 (s), 642 (m), 618 (m), 593 (w), 521 (w), 417 (w) cm^{-1}. Raman (100 mW, 25 °C, 8000 Scans): ν = 3188, 3144, 3066, 2996, 2963, 2918, 2095, 2044, 1596, 1572, 1486, 1444, 1327, 1274, 1215, 1150, 1064, 1035, 1003, 650, 620, 602, 417, 336, 309, 253, 223, 197, 165, 103, 84 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.29 (m, H-2), 7.68 (m, H-3), 8.62 (d, H-1) ppm. $^{13}C\{^{1}H\}$ NMR (500 MHz, $CDCl_3$, 25 °C): δ = 123.7 (C-2), 135.9 (C-3), 149.9 (C-1) ppm. ^{14}N NMR (500 MHz, CH_2Cl_2, 25 °C): δ = -66 (N_{py}, $\Delta\mu_{1/2}$ = 120 Hz), -135 (N_β, $\Delta\mu_{1/2}$ = 25 Hz), -172 (N_γ, $\Delta\mu_{1/2}$ = 480 Hz), -325 (N_α, $\Delta\mu_{1/2}$ = 580 Hz) ppm.

*Single Crystal Structure Determination of **1** and **3***

The crystals were mounted on nylon loops in inert oil. Data were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (mono-chromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) at 100 K. The structures were solved by Direct Methods (SHELXS-97)[1] and refined anisotropically by full-matrix least-squares on F^2 (SHELXL-97)[2]. Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Buker AXS APEX2). Hydrogen atoms were refined using a riding model.

Details of the crystal structure determination of **1** may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de,) on quoting the deposition number CSD-422405. CCDC-803386 contains the supplementary crystallographic data of complex **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

References

[1] G. M. Sheldrick, *Acta Crystallogr.* 1990, **A46**, 467.

[2] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures University of Göttingen, Göttingen (Germany) **1997**. (see also Sheldrick, G. M. Acta Crystallogr. 2008, **A64**, 112)

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	N_9Sb	
Formula weight	247.84 Da	
Density (calculated)	2.811 g cm^{-3}	
F(000)	228	
Temperature	103(1) K	
Crystal size	0.07 x 0.05 x 0.01 mm	
Crystal colour	colourless	
Crystal description	plate	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	$P\ \bar{1}$	
Unit cell dimensions	a = 6.6694(6) Å	α = 83.651(5)°
	b = 6.9045(6) Å	β = 65.850(5)°
	c = 7.0314(6) Å	γ = 83.595(5)°
Volume	292.85(4) $Å^3$	
Z	2	
Cell measurement reflections used	2561	
Cell measurement theta min/max	2.97° to 25.12°	
Diffractometer control software	Bruker AXS APEX 2 Vers.3.0/2009	
Diffractometer measurement device	Bruker D8 KAPPA series II with APEX II area detector system	
Diffractometer measurement method	Data collection strategy APEX 2/COSMO	
Theta range for data collection	2.98° to 25.20°	
Completeness to theta = 25.20°	96.3 %	
Index ranges	-7<=*h*<=7, -8<=*k*<=8, -7<=*l*<=8	
Computing data reduction	Bruker AXS APEX 2 Vers.3/2009	
Absorption coefficient	4.642 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Empirical absorption correction	Bruker AXS APEX 2 Vers.3/2009	

Max. / min. transmission	0.75 / 0.64
R(merg) before/after correction	0.0511 / 0.0359
Computing structure solution	Bruker AXS SHELXTL Vers. 2008/4/(c) 2008
Computing structure refinement	Bruker AXS SHELXTL Vers. 2008/4/(c) 2008
Refinement method	Full-matrix least-squares on F^2
Reflections collected	3719
Independent reflections	1012 [*R*(int) = 0.0275]
Data / restraints / parameters	933 / 0 / 91
Goodness-of-fit on F^2	1.120
Weighting details	$w = 1/[\sigma^2 (Fo^2)+ (0.0212*P)^2+2.1026*P]$ where $P = (Fo^2+2Fc^2)/3$
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0254, *wR*2 = 0.0622
R indices (all data)	*R*1 = 0.0303, *wR*2 = 0.0639
Largest diff. peak and hole	1.269 and -0.802 eÅ^{-3}
Comment	The crystallization was performed on the diffractometer at a temperature of 296 K with a sublimation procedure using focussed infrared-laser-radiation according to: R. Boese, M. Nussbaumer, "In Situ Crystallisation Techniques", in: "Organic Crystal Chemistry", Ed. D.W. Jones, Oxford University Press, Oxford, England, (1994) 20-37. For proper centring the crystal was removed from the capillary and mounted on a nylon loop.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^{2} x 10^3) for for **1**. *U*(eq) is defined as one third of the trace of the orthogonalized *Uij* tensor.

	x	*y*	*z*	*U*(eq)
Sb(1)	1700(1)	4538(1)	6846(1)	15(1)
N(1)	1364(9)	6458(7)	9185(8)	19(1)
N(2)	1992(9)	8114(8)	8589(8)	19(1)
N(3)	2559(10)	9634(8)	8088(9)	28(1)
N(4)	3750(8)	6537(7)	4561(8)	19(1)
N(5)	2798(8)	7867(7)	3815(8)	20(1)
N(6)	2000(9)	9062(8)	3070(9)	27(1)
N(7)	-1127(8)	6091(7)	6556(8)	18(1)
N(8)	-2619(8)	6668(7)	8172(8)	18(1)
N(9)	-4045(9)	7186(8)	9623(9)	25(1)

Table 3. Bond lengths [Å] and angles [°] for for **1**.

Sb(1)-N(4)	2.119(5)	N(4)-Sb(1)-N(7)	89.92(19)
Sb(1)-N(7)	2.136(5)	N(4)-Sb(1)-N(1)	88.4(2)
Sb(1)-N(1)	2.151(5)	N(7)-Sb(1)-N(1)	88.52(19)
N(1)-N(2)	1.231(7)	N(2)-N(1)-Sb(1)	117.8(4)
N(2)-N(3)	1.125(7)	N(3)-N(2)-N(1)	178.5(6)
N(4)-N(5)	1.248(7)	N(5)-N(4)-Sb(1)	116.1(4)
N(5)-N(6)	1.128(7)	N(6)-N(5)-N(4)	177.4(6)
N(7)-N(8)	1.235(7)	N(8)-N(7)-Sb(1)	117.1(4)
N(8)-N(9)	1.133(8)	N(9)-N(8)-N(7)	177.4(6)

Table 4. Intermolecular contacts [Å] and angles [°] for for **1**.

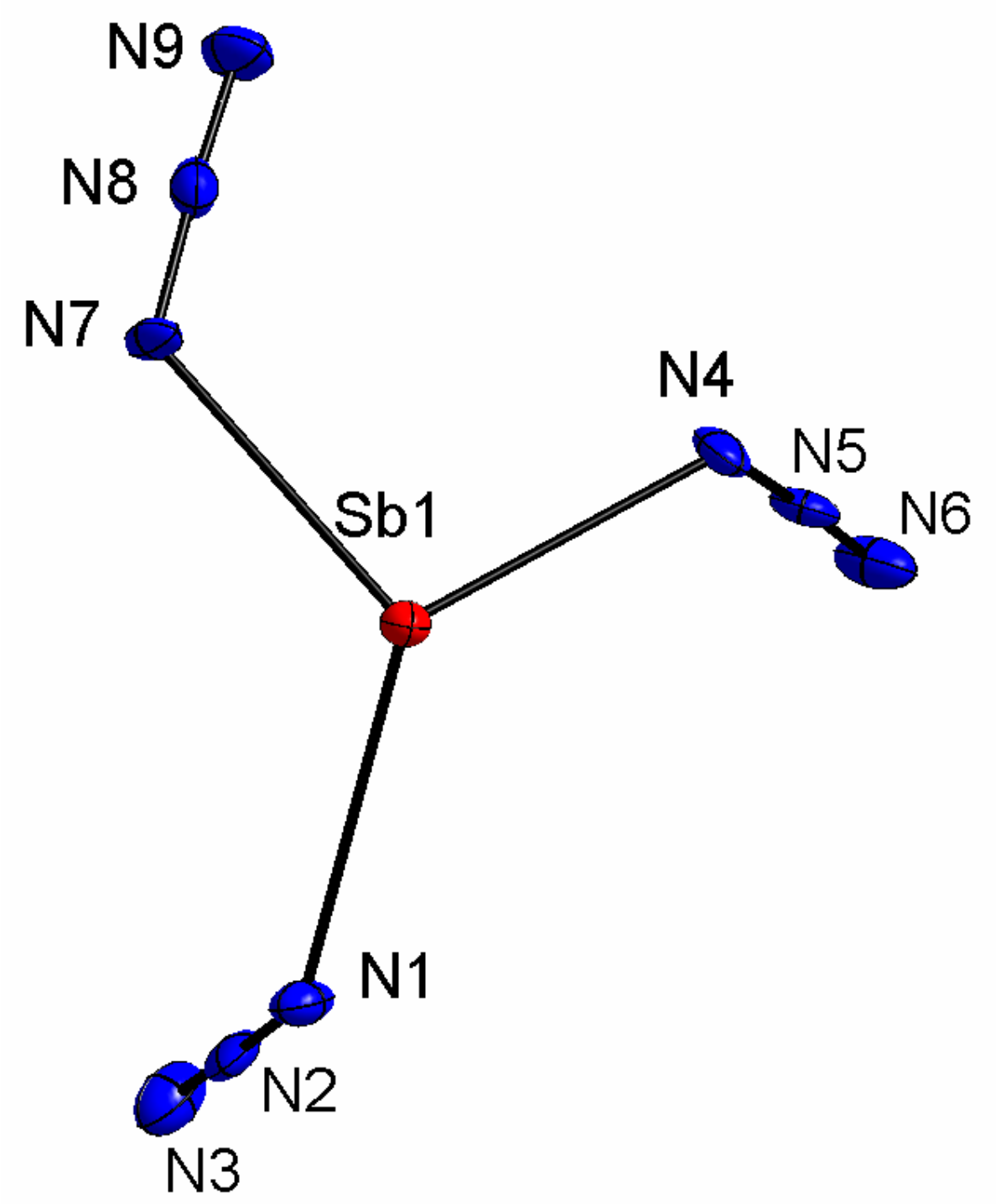
Sb(1) – N(1)_$1	2.768 (5)
Sb(1) – N(4)_$2	2.819 (5)
Sb(1) – N(7)_$3	2.659 (5)
N(1) – Sb(1) – N(1)_$1	65.1 (2)
N(1) – Sb(1) – N(4)_$2	99.2 (2)
N(1) – Sb(1) – N(7)_$3	149.7 (2)
N(4) – Sb(1) – N(1)_$1	152.3 (2)
N(4) – Sb(1) – N(4)_$2	65.2 (2)
N(4) – Sb(1) – N(7)_$3	77.5 (2)
N(7) – Sb(1) – N(1)_$1	82.1 (2)
N(7) – Sb(1) – N(4)_$2	153.5 (2)
N(7) – Sb(1) – N(7)_$3	65.1 (2)
N(1)_$1 – Sb(1) – N(4)_$2	124.1 (1)
N(1)_$1 – Sb(1) – N(7)_$3	121.6 (2)

Symmetry transformations used to generate equivalent atoms:
$1 -x, -y+1, -z+2
$2 -x+1, -y+1, -z+1
$3 -x, -y+1, -z+1

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	*U*11	*U*22	*U*33	*U*23	*U*13	*U*12
Sb(1)	12(1)	20(1)	11(1)	0(1)	-4(1)	-2(1)
N(1)	23(3)	22(3)	10(3)	0(2)	-5(2)	-6(2)
N(2)	24(3)	25(3)	12(3)	0(2)	-12(2)	-3(2)
N(3)	40(4)	25(3)	26(3)	3(3)	-19(3)	-9(3)
N(4)	11(3)	26(3)	16(3)	6(2)	-1(2)	-5(2)
N(5)	16(3)	24(3)	10(3)	1(2)	3(2)	-3(2)
N(6)	22(3)	29(3)	18(3)	4(2)	0(3)	5(2)
N(7)	11(3)	29(3)	9(3)	-4(2)	-3(2)	8(2)
N(8)	15(3)	22(3)	20(3)	2(2)	-10(3)	-4(2)
N(9)	17(3)	38(3)	16(3)	-3(3)	-2(3)	6(3)

Figure 1



Asymmestric unit of **1**. Thermal ellipsiods shown at 50% probability levels.

Table 1. Crystal data and structure refinement for **3**.

Empirical formula	$C_{10}H_{10}BiN_{11}$
Formula weight	493.27 Da
Density (calculated)	2.208 g cm^{-3}
F(000)	920
Temperature	100(2) K
Crystal size	0.15 x 0.10 x 0.10 mm
Crystal colour	colourless
Crystal description	prism
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	$Cmc2_1$
Unit cell dimensions	a = 21.7967(16) Å α = 90°
	b = 10.8375(8) Å β = 90°
	c = 6.2825(5) Å γ = 90°
Volume	1484.06(19) $Å^3$
Z	4
Cell measurement reflections used	9892
Cell measurement theta min/max	3.4° to 30.7°
Diffractometer control software	Bruker AXS APEX 2 Vers.3.0/2009
Diffractometer measurement device	Bruker D8 KAPPA series II with
	APEX II area detector system
Diffractometer measurement method	Data collection strategy APEX 2/COSMO
Theta range for data collection	1.87° to 30.55°
Completeness to theta = 30.55°	99.9 %
Index ranges	-31<=*h*<=31, -15<=*k*<=15, -8<=*l*<=8
Computing data reduction	Bruker AXS APEX 2 Vers.3/2009
Absorption coefficient	11.896 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Empirical absorption correction	Bruker AXS APEX 2 Vers.3/2009
Max. / min. transmission	0.7461 / 0.5245
R(merg) before/after correction	0.1000/ 0.0586
Computing structure solution	Bruker AXS SHELXTL Vers. 2008/4/(c) 2008
Computing structure refinement	Bruker AXS SHELXTL Vers. 2008/4/(c) 2008

Refinement method	Full-matrix least-squares on F^2
Reflections collected	31065
Independent reflections	2319 [R(int) = 0.0327]
Data / restraints / parameters	2234 / 1 / 106
Goodness-of-fit on F^2	1.114
Weighting details	$w = 1/[\sigma^2 (Fo^2)+ (0.0121*P)^2+0.5372*P]$ where $P = (Fo^2+2Fc^2)/3$
Final R indices [I>2sigma(I)]	$R1$ = 0.0126, $wR2$ = 0.0284
R indices (all data)	$R1$ = 0.0138, $wR2$ = 0.0287
Absolute structure parameter	-0.001(6)
Absolute structure details	Flack H.D., Acta Cryst. A39 (1983) 876-881
Largest diff. peak and hole	1.038 and -0.762 eÅ^{-3}
Treatment of hydrogen atoms	Riding model on idealized geometries with the 1.2 fold isotropic displacement parameters of the equivalent Uij of the corresponding carbon atom.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **3**. *U*(eq) is defined as one third of the trace of the orthogonalized *Uij* tensor.

	x	*y*	*z*	*U*(eq)
Bi(1)	5000	8704(1)	8770(1)	11(1)
N(1)	5000	7507(3)	11747(5)	19(1)
N(2)	5000	6405(3)	11396(6)	27(1)
N(3)	5000	5365(4)	11149(8)	79(2)
N(4)	4350(1)	9933(2)	10736(3)	15(1)
N(5)	3853(1)	10211(2)	10004(3)	13(1)
N(6)	3376(1)	10494(2)	9404(3)	23(1)
N(7)	3997(1)	7443(2)	8050(3)	16(1)
C(1)	3516(1)	7347(2)	9372(4)	19(1)
C(2)	2982(1)	6727(2)	8832(9)	22(1)
C(3)	2945(1)	6177(2)	6843(5)	24(1)
C(4)	3439(2)	6274(2)	5477(5)	26(1)
C(5)	3953(1)	6916(2)	6149(4)	22(1)

Table 3. Bond lengths [Å] and angles [°]for **3**.

Bi(1)-N(1)	2.277(3)	N(4)#2-Bi(1)-N(4)#3	60.92(8)
Bi(1)-N(4)	2.304(2)	N(4)-Bi(1)-N(7)	83.13(7)
Bi(1)-N(7)	2.618(2)	N(4)#1-Bi(1)-N(7)	155.27(7)
Bi(1)-N(4)#2	2.797(2)	N(7)-Bi(1)-N(4)#2	74.61(6)
N(1)-N(2)	1.214(4)	N(7)#1-Bi(1)-N(4)#2	125.54(7)
N(2)-N(3)	1.138(5)	N(7)-Bi(1)-N(7)#1	113.27(9)
N(4)-N(5)	1.213(3)	N(2)-N(1)-Bi(1)	114.3(3)
N(5)-N(6)	1.148(3)	N(3)-N(2)-N(1)	177.4(5)
N(7)-C(5)	1.327(3)	N(5)-N(4)-Bi(1)	119.25(15)
N(7)-C(1)	1.341(3)	N(5)-N(4)-Bi(1)#4	125.40(16)
C(1)-C(2)	1.386(3)	Bi(1)-N(4)-Bi(1)#4	111.00(8)
C(2)-C(3)	1.387(6)	N(6)-N(5)-N(4)	176.8(2)
C(3)-C(4)	1.380(5)	C(5)-N(7)-C(1)	117.9(2)
C(4)-C(5)	1.385(4)	C(5)-N(7)-Bi(1)	116.13(18)
		C(1)-N(7)-Bi(1)	125.88(16)
N(1)-Bi(1)-N(4)	83.62(9)	N(7)-C(1)-C(2)	122.9(3)
N(1)-Bi(1)-N(4)#2	149.40(4)	C(1)-C(2)-C(3)	118.5(3)
N(1)-Bi(1)-N(7)	81.04(6)	C(4)-C(3)-C(2)	118.9(3)
N(4)-Bi(1)-N(4)#2	75.42(4)	C(3)-C(4)-C(5)	118.6(3)
N(4)-Bi(1)-N(4)#1	75.96(10)	N(7)-C(5)-C(4)	123.3(3)
N(4)#1-Bi(1)-N(4)#2	111.86(4)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,z #2 x,-y+2,z-1/2 #3 -x+1,-y+2,z-1/2

#4 -x+1,-y+2,z+1/2

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	*U*11	*U*22	*U*33	*U*23	*U*13	*U*12
Bi(1)	9(1)	13(1)	10(1)	0(1)	0	0
N(1)	21(2)	21(1)	13(1)	4(1)	0	0
N(2)	40(2)	24(2)	16(2)	5(1)	0	0
N(3)	177(7)	22(2)	38(3)	11(2)	0	0
N(4)	10(1)	22(1)	13(1)	-2(1)	1(1)	1(1)
N(5)	11(1)	17(1)	12(1)	-3(1)	2(1)	1(1)
N(6)	14(1)	32(1)	22(1)	-4(1)	-2(1)	6(1)
N(7)	15(1)	18(1)	16(1)	0(1)	0(1)	-4(1)
C(1)	20(1)	18(1)	20(1)	0(1)	0(1)	-2(1)
C(2)	15(1)	18(1)	32(1)	2(2)	4(2)	-2(1)
C(3)	20(1)	18(1)	33(2)	3(1)	-9(1)	-5(1)
C(4)	35(2)	25(1)	19(1)	-1(1)	-6(1)	-10(1)
C(5)	24(1)	24(1)	18(1)	0(1)	2(1)	-8(1)

Table 5. Hydrogen coordinates ($x\ 10^4$) and displacement parameters ($Å^2\ x\ 10^3$) for **3**.

	x	*y*	*z*	*U*(eq)
H(1)	3543	7720	10737	23
H(2)	2648	6681	9803	26
H(3)	2587	5741	6427	28
H(4)	3426	5908	4104	32
H(5)	4291	6983	5202	26

Table 6. Torsion angles [°]for **3**.

N(4)#1-Bi(1)-N(1)-N(2)	-141.74(5)	N(4)#1-Bi(1)-N(7)-C(5)	178.30(19)
N(4)-Bi(1)-N(1)-N(2)	141.74(5)	N(4)-Bi(1)-N(7)-C(5)	146.0(2)
N(7)-Bi(1)-N(1)-N(2)	57.72(5)	N(7)#1-Bi(1)-N(7)-C(5)	-53.2(2)
N(7)#1-Bi(1)-N(1)-N(2)	-57.72(5)	N(4)#2-Bi(1)-N(7)-C(5)	69.32(19)
N(4)#2-Bi(1)-N(1)-N(2)	95.10(17)	N(4)#3-Bi(1)-N(7)-C(5)	34.0(2)
N(4)#3-Bi(1)-N(1)-N(2)	-95.10(17)	N(1)-Bi(1)-N(7)-C(1)	54.8(2)
N(1)-Bi(1)-N(4)-N(5)	-125.8(2)	N(4)#1-Bi(1)-N(7)-C(1)	2.4(3)
N(4)#1-Bi(1)-N(4)-N(5)	149.20(16)	N(4)-Bi(1)-N(7)-C(1)	-29.8(2)
N(7)-Bi(1)-N(4)-N(5)	-44.11(19)	N(7)#1-Bi(1)-N(7)-C(1)	130.92(18)
N(7)#1-Bi(1)-N(4)-N(5)	-177.69(16)	N(4)#2-Bi(1)-N(7)-C(1)	-106.5(2)
N(4)#2-Bi(1)-N(4)-N(5)	31.72(17)	N(4)#3-Bi(1)-N(7)-C(1)	-141.83(19)
N(4)#3-Bi(1)-N(4)-N(5)	81.52(17)	C(5)-N(7)-C(1)-C(2)	-0.1(4)
N(1)-Bi(1)-N(4)-Bi(1)#4	76.35(8)	Bi(1)-N(7)-C(1)-C(2)	175.72(19)
N(4)#1-Bi(1)-N(4)-Bi(1)#4	-8.64(11)	N(7)-C(1)-C(2)-C(3)	0.4(4)
N(7)-Bi(1)-N(4)-Bi(1)#4	158.05(9)	C(1)-C(2)-C(3)-C(4)	-0.4(4)
N(7)#1-Bi(1)-N(4)-Bi(1)#4	24.5(2)	C(2)-C(3)-C(4)-C(5)	0.1(4)
N(4)#2-Bi(1)-N(4)-Bi(1)#4	-126.13(11)	C(1)-N(7)-C(5)-C(4)	-0.2(4)
N(4)#3-Bi(1)-N(4)-Bi(1)#4	-76.32(11)	Bi(1)-N(7)-C(5)-C(4)	-176.4(2)
N(1)-Bi(1)-N(7)-C(5)	-129.4(2)	C(3)-C(4)-C(5)-N(7)	0.2(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,z #2 x,-y+2,z-1/2 #3 -x+1,-y+2,z-1/2

#4 -x+1,-y+2,z+1/2

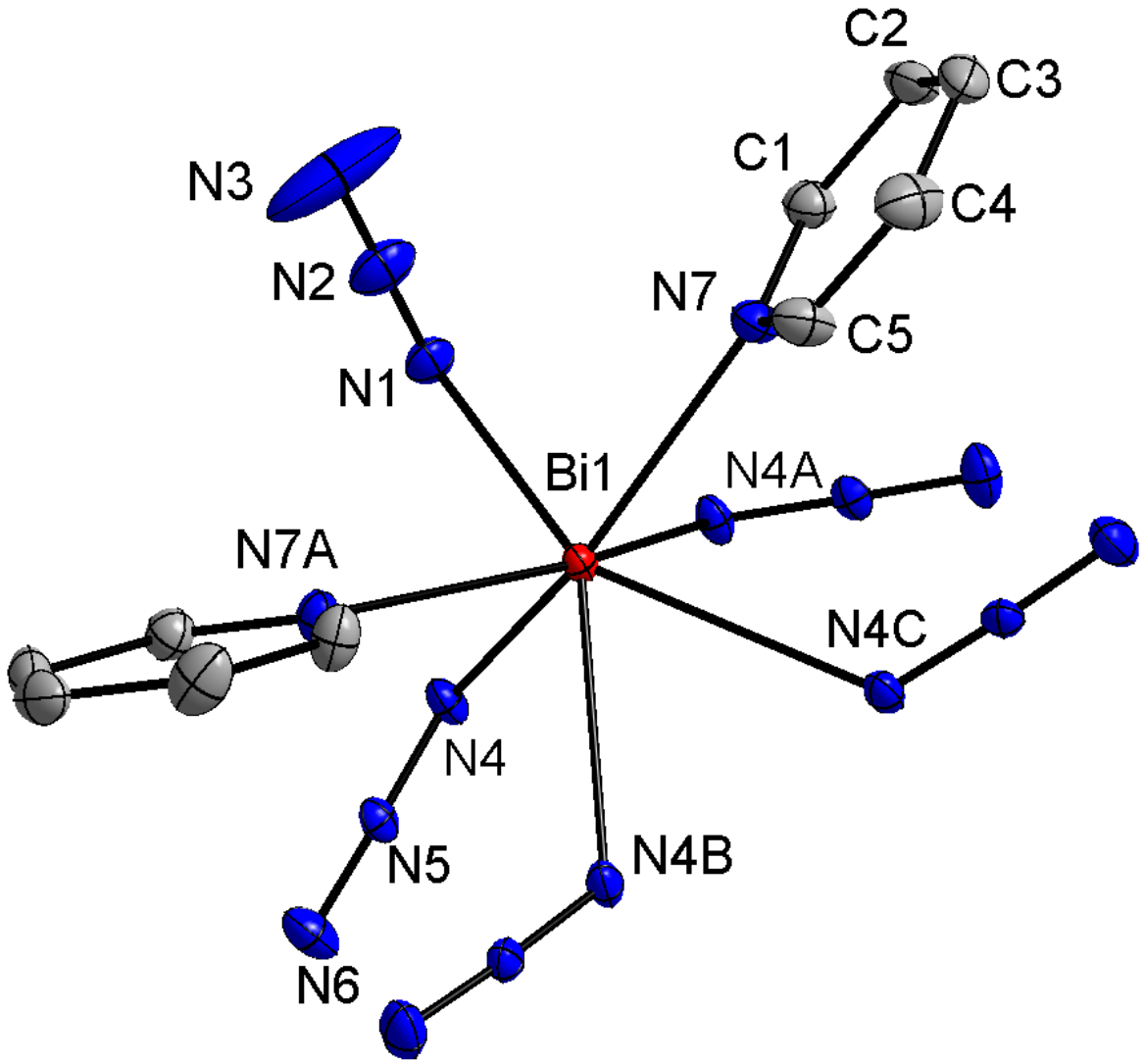
Table 7. Hydrogen bonds for **3** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2)...N(6)#5	0.95	2.59	3.268(3)	128.6

Symmetry transformations used to generate equivalent atoms:

#5 -x+1/2,y-1/2,z

Figure 2



Asymmetric unit of **3**. Thermal ellipsiods shown at 50% probability levels.

Computational Studies

All geometries were fully optimized within the designated symmetry constraints (using tightened convergence criteria and improved integration grids) at the density functional theory level, employing the B3LYP and BP86 exchange-correlation functionals [1] as implemented in the Turbomole V6.0 quantum chemistry program package [2,3]. A triple-zeta valence quality Gaussian type function basis set termed def2-TZVP [4] has been used throughout. The core electrons of the Bi atom were replaced with a scalar relativistiv effective core potential [5]. In the BP86 computations the resolution-of-the-identity approximation was employed, making use of an appropriate auxiliary basis set [6]. This level of theory has also been employed to verify that the optimized structures were minima by frequency analyses making use of analytical second derivatives [7].

Atom coordinates, energies and frequencies of all optimized geometries are given below.

[1] (a) P. A. M. Dirac; Proc. Roy. Soc. (London) A 123 (1929) 714. (b) J. C. Slater; Phys. Rev. 81 (1951) 385. (c) S. Vosko, L.Wilk, M. Nussair; Can. J. Phys. 58 (1980) 1200. (d) A. D. Becke; Phys. Rev. A 38 (1988) 3098. (e) C. Lee, W. Yang, and R. G. Parr; Phys. Rev. B 37 (1988) 785. (f) A. D. Becke,; J. Chem. Phys. 98 (1993) 5648. (g) J. P. Perdew; Phys. Rev. B 33 (1986) 8822.

[2] TURBOMOLE V6.0 2009, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com

[3] (a) R. Ahlrichs, M. Bär, M. Häser, H. Horn, and C. Kölmel; Chem. Phys. Lett. 162 (1989) 165. (b) O. Treutler and R. Ahlrichs, J. Chem. Phys. 102 (1995) 346. (c) M. von Arnim and R. Ahlrichs; J. Chem. Phys. 111 (1999) 183.

[4] F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys. 7 (2005) 3297.

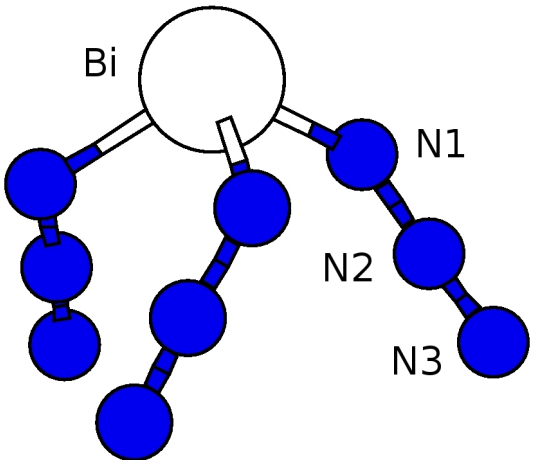
[5] B. Metz, H. Stoll, and M. Dolg, J. Chem. Phys. 113 (2000) 2563.

[6] . Weigend, Phys. Chem. Chem. Phys. 8 (2006) 1057.

[7] P. Deglmann, K. May, F. Furche, and R. Ahlrichs, Chem. Phys. Lett. 384 (2004) 103.

Calculated Structures and Frequencies

Figure 3



BP86/def2-TZVP-calculated C_3-symmetrical structure of $Bi(N_3)_3$.

Energy (in Hartree) and atomic corrdinates (in Å) of the BP86/def2-TZVP-calculated C_3-symmetrical structure of $Bi(N_3)_3$:

```
Energy = -707.7129931738
Bi     0.0000000     0.0000000    -1.8106910
N     -1.3906848    -1.3323815    -0.7573443
N     -1.0188723    -1.9759376     0.2239646
N     -0.7567260    -2.6182869     1.1369434
N     -0.4585338     1.8705591    -0.7573443
N     -1.2017760     1.8703381     0.2239646
N     -1.8891400     1.9644873     1.1369434
N      1.8492186    -0.5381776    -0.7573443
N      2.2206483     0.1055995     0.2239646
N      2.6458659     0.6537995     1.1369434
```

Vibrational frequencies of the BP86/def2-TZVP-calculated C_3-symmetrical structure of $Bi(N_3)_3$:

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	e	27.09	0.15865	YES	YES
8	e	27.09	0.15865	YES	YES
9	a	36.72	0.29878	YES	YES
10	e	65.12	0.41864	YES	YES
11	e	65.12	0.41864	YES	YES
12	a	76.05	0.37977	YES	YES
13	e	163.82	4.00378	YES	YES
14	e	163.82	4.00378	YES	YES
15	a	194.37	16.62553	YES	YES
16	e	357.63	61.29850	YES	YES
17	e	357.63	61.29850	YES	YES
18	a	388.31	5.22633	YES	YES

19	e	574.97	2.45292	YES	YES
20	e	574.97	2.45292	YES	YES
21	a	575.25	3.09213	YES	YES
22	a	622.69	2.35510	YES	YES
23	e	623.15	2.95433	YES	YES
24	e	623.15	2.95433	YES	YES
25	e	1277.83	113.09546	YES	YES
26	e	1277.83	113.09546	YES	YES
27	a	1287.01	125.11628	YES	YES
28	e	2125.56	474.81241	YES	YES
29	e	2125.56	474.81241	YES	YES
30	a	2150.31	628.44679	YES	YES

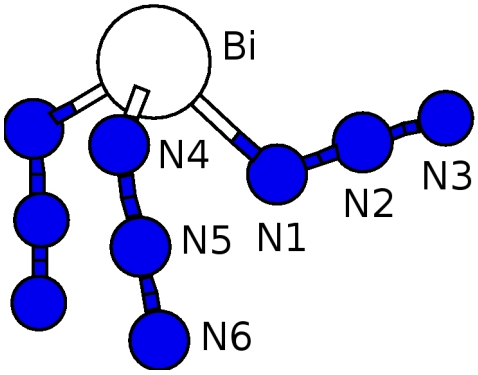
Energy (in Hartree) and atomic corrdinates (in Å) of the B3LYP/def2-TZVP-calculated C_3-symmetrical structure of $Bi(N_3)_3$:

```
Energy = -707.2041532475
Bi     0.0000000    0.0000000   -1.8259954
N     -1.3709089   -1.3215156   -0.7593389
N     -1.0070319   -1.9454235    0.2280931
N     -0.7411108   -2.5592284    1.1399109
N     -0.4590116    1.8479997   -0.7593389
N     -1.1812702    1.8448269    0.2280931
N     -1.8458014    1.9214350    1.1399109
N      1.8299205   -0.5264842   -0.7593389
N      2.1883021    0.1005965    0.2280931
N      2.5869122    0.6377935    1.1399109
```

Vibrational frequencies of the B3LYP/def2-TZVP-calculated C_3-symmetrical structure of $Bi(N_3)_3$:

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	e	29.50	0.22307	YES	YES
8	e	29.50	0.22307	YES	YES
9	a	38.50	0.25118	YES	YES
10	e	73.32	0.51071	YES	YES
11	e	73.32	0.51071	YES	YES
12	a	82.43	0.41766	YES	YES
13	e	172.96	5.21844	YES	YES
14	e	172.96	5.21844	YES	YES
15	a	205.81	20.57237	YES	YES
16	e	370.94	68.10485	YES	YES
17	e	370.94	68.10485	YES	YES
18	a	404.37	7.92860	YES	YES
19	e	607.13	4.17318	YES	YES
20	e	607.13	4.17318	YES	YES
21	a	607.84	4.30364	YES	YES
22	a	653.81	2.92152	YES	YES
23	e	654.20	5.65188	YES	YES
24	e	654.20	5.65188	YES	YES
25	e	1313.98	163.07240	YES	YES
26	e	1313.98	163.07240	YES	YES
27	a	1327.34	197.18776	YES	YES
28	e	2200.44	563.91025	YES	YES
29	e	2200.44	563.91025	YES	YES
30	a	2230.41	846.86187	YES	YES

Figure 4



BP86/def2-TZVP-calculated C_s-symmetrical structure of $Bi(N_3)_3$.

Energy (in Hartree) and atomic corrdinates (in Å) of the BP86/def2-TZVP-calculated C_s-symmetrical structure of $Bi(N_3)_3$:

```
Energy = -707.7115539326
Bi    -0.4539545    -1.5447165     0.0000000
N     -1.2425930     0.5070263     0.0000000
N     -2.4583375     0.6922216     0.0000000
N     -3.5732580     0.9690870     0.0000000
N      0.8907462    -1.1969506    -1.6895274
N      1.2799661    -0.0635649    -1.9726683
N      1.6887153     0.9496200    -2.3198416
N      0.8907462    -1.1969506     1.6895274
N      1.2799661    -0.0635649     1.9726683
N      1.6887153     0.9496200     2.3198416
```

Vibrational frequencies of the BP86/def2-TZVP-calculated C_s-symmetrical structure of $Bi(N_3)_3$:

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1	a"	-41.14	0.00000	YES	YES
2	a"	-11.77	0.00000	YES	YES
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7		0.00	0.00000	-	-
8		0.00	0.00000	-	-
9	a'	29.23	0.10259	YES	YES
10	a'	52.52	1.36792	YES	YES
11	a"	89.58	0.69525	YES	YES
12	a'	115.47	5.93234	YES	YES
13	a'	137.22	2.98721	YES	YES
14	a"	164.59	8.33074	YES	YES
15	a'	198.55	13.32084	YES	YES
16	a"	358.59	68.88265	YES	YES
17	a'	362.55	56.48315	YES	YES
18	a'	390.53	5.81672	YES	YES
19	a"	573.73	0.10760	YES	YES
20	a"	574.34	4.21146	YES	YES
21	a'	577.05	7.96503	YES	YES
22	a'	623.30	0.80359	YES	YES
23	a"	623.98	1.99767	YES	YES
24	a'	630.67	3.79726	YES	YES
25	a"	1275.66	105.85533	YES	YES

26	a'	1281.38	193.70425	YES	YES
27	a'	1287.56	88.47277	YES	YES
28	a"	2121.62	354.86834	YES	YES
29	a'	2127.81	931.63865	YES	YES
30	a'	2147.07	521.27916	YES	YES

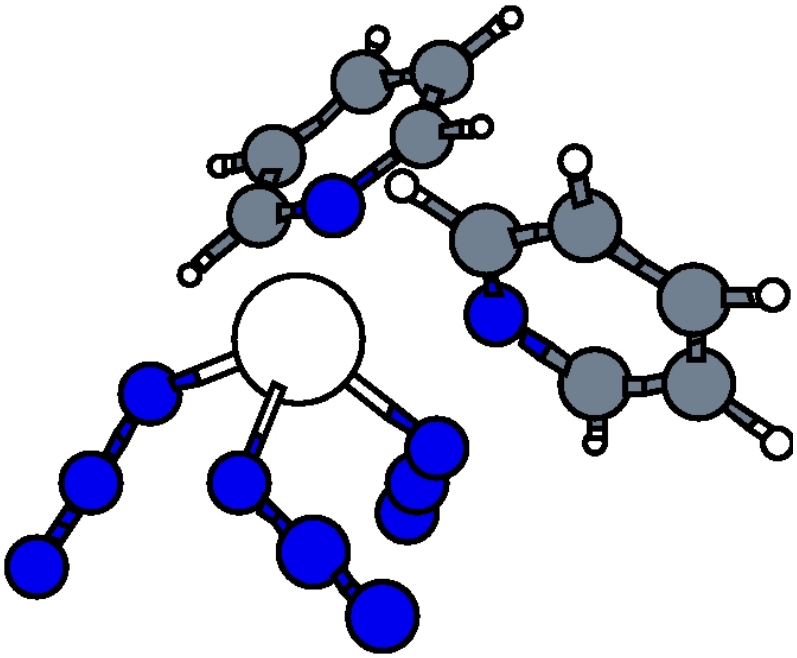
Energy (in Hartree) and atomic corrdinates (in Å) of the B3LYP/def2-TZVP-calculated C_s-symmetrical structure of $Bi(N_3)_3$:

```
Energy = -707.2025187082
Bi    -0.4509910   -1.5529855    0.0000000
N     -1.2403783    0.4876188    0.0000000
N     -2.4439073    0.6941569    0.0000000
N     -3.5420587    0.9737195    0.0000000
N      0.8874344   -1.1870511   -1.6727956
N      1.2761356   -0.0598503   -1.9495995
N      1.6750976    0.9456465   -2.2777008
N      0.8874344   -1.1870511    1.6727956
N      1.2761356   -0.0598503    1.9495995
N      1.6750976    0.9456465    2.2777008
```

Vibrational frequencies of the B3LYP/def2-TZVP-calculated C_s-symmetrical structure of $Bi(N_3)_3$:

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1	a"	-41.86	0.00000	YES	YES
2	a"	-11.24	0.00000	YES	YES
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7		0.00	0.00000	-	-
8		0.00	0.00000	-	-
9	a'	31.02	0.11399	YES	YES
10	a'	55.99	1.41000	YES	YES
11	a"	94.29	0.80748	YES	YES
12	a'	122.23	6.47333	YES	YES
13	a'	146.49	3.64126	YES	YES
14	a"	173.74	10.18706	YES	YES
15	a'	208.60	16.46730	YES	YES
16	a"	373.13	76.77620	YES	YES
17	a'	375.11	65.13545	YES	YES
18	a'	405.45	8.88875	YES	YES
19	a"	605.90	0.00609	YES	YES
20	a"	607.06	7.40864	YES	YES
21	a'	609.40	11.62419	YES	YES
22	a'	653.05	1.25294	YES	YES
23	a"	654.81	3.91494	YES	YES
24	a'	660.78	6.77663	YES	YES
25	a"	1309.92	151.52653	YES	YES
26	a'	1319.79	281.74674	YES	YES
27	a'	1330.69	150.10179	YES	YES
28	a"	2196.93	416.62325	YES	YES
29	a'	2202.30	1157.59603	YES	YES
30	a'	2227.96	704.63455	YES	YES

Figure 5



BP86/def2-TZVP-calculated C_1-symmetrical structure of Py_2-$Bi(N_3)_3$.

Energy (in Hartree) and atomic corrdinates (in Å) of the BP86/def2-TZVP-calculated C_1-symmetrical structure of Py_2-$Bi(N_3)_3$:

```
Energy = -1204.519670886
Bi    -1.3389254     0.4145418    -0.0819615
N     -0.5900977    -1.6924772    -0.0059502
N     -0.7438349    -2.3912260    -1.0000999
N     -0.8466166    -3.1063077    -1.8961012
N     -2.7646334     0.1563409    -1.8048259
N     -3.9038489    -0.2619609    -1.6364856
N     -4.9858477    -0.6434611    -1.5579164
N      0.3452518     0.5045262    -2.3286529
C     -0.1530795     0.3981163    -3.5734668
H     -1.2376395     0.2837441    -3.6362489
C      0.6575261     0.4240109    -4.7093121
H      0.2078554     0.3305423    -5.6976819
C      2.0360005     0.5637306    -4.5506990
H      2.6963993     0.5849475    -5.4186340
C      2.5568689     0.6710073    -3.2597583
H      3.6278784     0.7767460    -3.0872248
C      1.6750140     0.6354198    -2.1811267
H      2.0449561     0.7083754    -1.1550249
N     -3.0584144     0.0715037     1.3363788
N     -2.9290643    -0.6272850     2.3279732
N     -2.8772061    -1.2716841     3.2840419
N      0.1398506     0.3263562     2.2723273
C      0.6067782    -0.8219863     2.7943766
H      0.4424818    -1.7157349     2.1895139
C      1.2559558    -0.8735956     4.0284500
H      1.6115013    -1.8289877     4.4135959
C      1.4252208     0.3069712     4.7508324
H      1.9242364     0.2985514     5.7207166
C      0.9370078     1.5001111     4.2145486
H      1.0402560     2.4458702     4.7462254
C      0.3007998     1.4606544     2.9756632
H     -0.1026305     2.3726392     2.5265272
```

Vibrational frequencies of the BP86/def2-TZVP-calculated C_1-symmetrical structure of Py_2-$Bi(N_3)_3$:

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	16.97	0.48779	YES	YES
8	a	18.01	0.48702	YES	YES
9	a	19.13	0.90151	YES	YES
10	a	23.24	0.11443	YES	YES
11	a	25.05	0.50007	YES	YES
12	a	30.71	0.05170	YES	YES
13	a	39.23	0.25341	YES	YES
14	a	50.53	2.90125	YES	YES
15	a	56.36	4.87508	YES	YES
16	a	61.30	0.81415	YES	YES
17	a	73.83	3.50268	YES	YES
18	a	80.52	1.14779	YES	YES
19	a	81.04	2.93811	YES	YES
20	a	87.69	0.65148	YES	YES
21	a	97.02	1.60736	YES	YES
22	a	109.56	4.10167	YES	YES
23	a	117.67	4.07874	YES	YES
24	a	129.84	3.70637	YES	YES
25	a	164.28	17.90601	YES	YES
26	a	172.78	11.21233	YES	YES
27	a	185.07	25.96880	YES	YES
28	a	329.49	102.29032	YES	YES
29	a	332.45	69.55127	YES	YES
30	a	358.97	16.45636	YES	YES
31	a	371.20	0.02481	YES	YES
32	a	371.69	0.06204	YES	YES
33	a	407.02	2.83663	YES	YES
34	a	407.40	2.26686	YES	YES
35	a	588.20	3.54137	YES	YES
36	a	590.45	4.44627	YES	YES
37	a	591.90	2.98826	YES	YES
38	a	610.37	17.91025	YES	YES
39	a	611.43	10.01877	YES	YES
40	a	629.81	3.59304	YES	YES
41	a	633.02	5.18544	YES	YES
42	a	638.81	2.74139	YES	YES
43	a	644.84	0.36891	YES	YES
44	a	645.04	0.21571	YES	YES
45	a	694.89	48.34001	YES	YES
46	a	696.30	48.61210	YES	YES
47	a	742.41	11.93498	YES	YES
48	a	743.50	12.51009	YES	YES
49	a	865.75	0.11847	YES	YES
50	a	867.71	0.09530	YES	YES
51	a	927.85	0.06859	YES	YES
52	a	930.08	0.03157	YES	YES
53	a	969.99	0.08149	YES	YES
54	a	973.10	0.08436	YES	YES
55	a	984.03	0.04955	YES	YES
56	a	987.87	0.35307	YES	YES
57	a	994.88	29.33455	YES	YES
58	a	995.69	15.39471	YES	YES
59	a	1021.79	4.00516	YES	YES

60	a	1022.56	3.01729	YES	YES
61	a	1058.81	0.20031	YES	YES
62	a	1059.94	0.47045	YES	YES
63	a	1064.32	22.99305	YES	YES
64	a	1064.71	15.45793	YES	YES
65	a	1145.94	2.05605	YES	YES
66	a	1146.33	1.84763	YES	YES
67	a	1206.36	33.46360	YES	YES
68	a	1208.11	30.67727	YES	YES
69	a	1290.21	82.00842	YES	YES
70	a	1290.88	3.26007	YES	YES
71	a	1292.64	9.15380	YES	YES
72	a	1295.38	139.80070	YES	YES
73	a	1304.82	97.52133	YES	YES
74	a	1344.27	3.00332	YES	YES
75	a	1344.74	3.29895	YES	YES
76	a	1435.67	26.96888	YES	YES
77	a	1435.89	24.09797	YES	YES
78	a	1469.65	1.79570	YES	YES
79	a	1470.45	1.59217	YES	YES
80	a	1569.67	2.35936	YES	YES
81	a	1569.89	2.59757	YES	YES
82	a	1587.92	24.53536	YES	YES
83	a	1588.90	25.87690	YES	YES
84	a	2114.97	970.10954	YES	YES
85	a	2120.47	435.10018	YES	YES
86	a	2134.90	800.36137	YES	YES
87	a	3076.52	8.33739	YES	YES
88	a	3082.70	6.81277	YES	YES
89	a	3098.04	19.05748	YES	YES
90	a	3106.18	9.04726	YES	YES
91	a	3109.92	0.58326	YES	YES
92	a	3112.26	0.94305	YES	YES
93	a	3126.29	8.11630	YES	YES
94	a	3127.86	7.82804	YES	YES
95	a	3132.36	14.16584	YES	YES
96	a	3133.98	11.47834	YES	YES

Energy (in Hartree) and atomic corrdinates (in Å) of the B3LYP/def2-TZVP-calculated C_1-symmetrical structure of Py_2-$Bi(N_3)_3$:

```
Energy = -1203.685427197
Bi    -1.3690307    0.4361552   -0.0826810
N     -0.6331331   -1.6571395   -0.0039801
N     -0.7727138   -2.3589454   -0.9883458
N     -0.8665502   -3.0641864   -1.8726315
N     -2.7806316    0.1592761   -1.7909791
N     -3.9031769   -0.2840479   -1.6297446
N     -4.9599933   -0.6873080   -1.5490880
N      0.3533228    0.5006483   -2.3663782
C     -0.1414909    0.4194594   -3.6056526
H     -1.2189647    0.3315513   -3.6774366
C      0.6674240    0.4374023   -4.7351302
H      0.2212234    0.3657596   -5.7181106
C      2.0418247    0.5413927   -4.5728019
H      2.6998113    0.5553108   -5.4328268
C      2.5594302    0.6224657   -3.2857665
H      3.6242738    0.6999191   -3.1104006
C      1.6774031    0.5974504   -2.2153315
H      2.0458777    0.6513849   -1.1961352
N     -3.0637468    0.0943491    1.3341537
N     -2.9615048   -0.6381335    2.2942473
N     -2.9257455   -1.3083064    3.2129748
N      0.1413237    0.3454114    2.3191586
C      0.6485752   -0.7914096    2.8065815
```

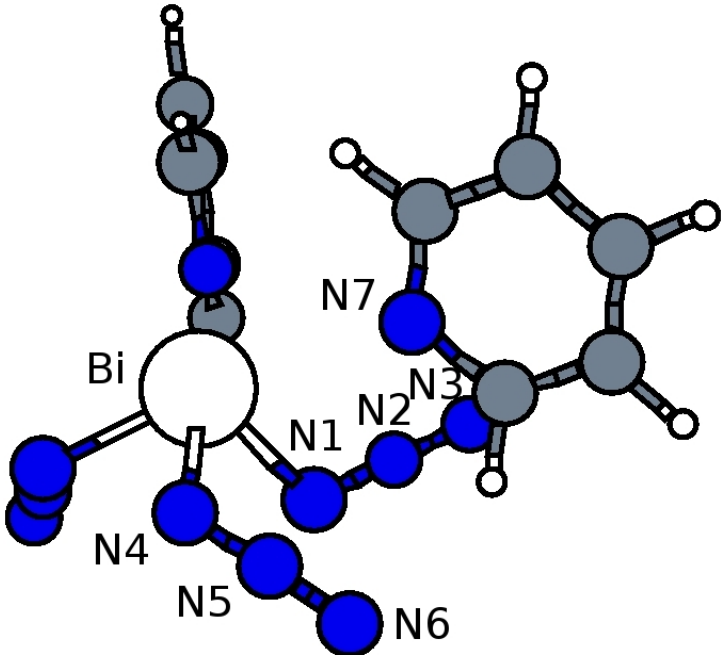
H	0.5102428	-1.6720006	2.1915022
C	1.3077957	-0.8512908	4.0277855
H	1.6965780	-1.7959571	4.3838125
C	1.4431572	0.3113578	4.7732216
H	1.9474882	0.2970825	5.7314117
C	0.9131745	1.4939250	4.2716032
H	0.9889515	2.4232781	4.8202722
C	0.2708078	1.4611160	3.0428819
H	-0.1620032	2.3640295	2.6238141

Vibrational frequencies of the B3LYP/def2-TZVP-calculated C_1-symmetrical structure of Py_2-$Bi(N_3)_3$:

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	16.37	0.52739	YES	YES
8	a	17.83	0.56761	YES	YES
9	a	20.41	0.42517	YES	YES
10	a	22.99	0.26090	YES	YES
11	a	26.12	0.58683	YES	YES
12	a	31.53	0.05268	YES	YES
13	a	39.65	0.19843	YES	YES
14	a	50.09	3.63660	YES	YES
15	a	57.00	5.50199	YES	YES
16	a	64.17	0.99957	YES	YES
17	a	71.87	3.55087	YES	YES
18	a	77.70	3.31753	YES	YES
19	a	80.77	1.12136	YES	YES
20	a	92.06	1.24565	YES	YES
21	a	101.22	0.68227	YES	YES
22	a	107.87	4.13634	YES	YES
23	a	116.74	4.11999	YES	YES
24	a	134.74	3.60578	YES	YES
25	a	174.99	18.02765	YES	YES
26	a	181.04	13.43266	YES	YES
27	a	195.38	29.53326	YES	YES
28	a	342.60	108.23752	YES	YES
29	a	347.03	77.26784	YES	YES
30	a	377.13	19.46835	YES	YES
31	a	392.02	0.02501	YES	YES
32	a	392.55	0.03993	YES	YES
33	a	425.76	3.44076	YES	YES
34	a	426.10	2.45092	YES	YES
35	a	620.18	5.05941	YES	YES
36	a	622.51	4.98283	YES	YES
37	a	623.95	5.74490	YES	YES
38	a	630.60	20.41205	YES	YES
39	a	631.49	12.44218	YES	YES
40	a	661.76	5.09054	YES	YES
41	a	665.14	7.46813	YES	YES
42	a	667.59	0.04007	YES	YES
43	a	667.65	0.39886	YES	YES
44	a	670.23	4.31064	YES	YES
45	a	718.72	49.38465	YES	YES
46	a	720.01	48.61874	YES	YES
47	a	769.81	14.31000	YES	YES
48	a	770.55	14.76762	YES	YES
49	a	897.35	0.12205	YES	YES
50	a	898.87	0.09896	YES	YES

51	a	967.16	0.04957	YES	YES
52	a	969.09	0.03576	YES	YES
53	a	1011.42	0.03918	YES	YES
54	a	1013.32	0.06960	YES	YES
55	a	1022.57	32.11186	YES	YES
56	a	1023.24	12.64011	YES	YES
57	a	1024.82	2.85203	YES	YES
58	a	1028.08	0.02963	YES	YES
59	a	1051.67	9.95540	YES	YES
60	a	1052.18	9.17396	YES	YES
61	a	1087.84	0.06772	YES	YES
62	a	1088.82	0.18302	YES	YES
63	a	1094.56	21.50957	YES	YES
64	a	1094.84	13.14093	YES	YES
65	a	1177.18	3.17771	YES	YES
66	a	1177.58	2.93651	YES	YES
67	a	1244.15	33.59875	YES	YES
68	a	1245.64	30.34080	YES	YES
69	a	1287.72	0.23067	YES	YES
70	a	1288.81	0.05634	YES	YES
71	a	1330.34	147.63668	YES	YES
72	a	1335.99	218.45009	YES	YES
73	a	1350.76	158.11029	YES	YES
74	a	1394.70	2.84753	YES	YES
75	a	1395.29	2.65875	YES	YES
76	a	1480.93	29.18423	YES	YES
77	a	1481.11	27.50527	YES	YES
78	a	1521.11	1.98132	YES	YES
79	a	1521.62	2.07450	YES	YES
80	a	1617.81	3.56280	YES	YES
81	a	1618.03	3.28206	YES	YES
82	a	1636.92	34.09320	YES	YES
83	a	1637.66	33.86724	YES	YES
84	a	2187.18	1178.45158	YES	YES
85	a	2192.75	569.59794	YES	YES
86	a	2210.63	984.51109	YES	YES
87	a	3149.90	7.97126	YES	YES
88	a	3154.28	6.70163	YES	YES
89	a	3176.61	7.78048	YES	YES
90	a	3178.19	4.61828	YES	YES
91	a	3183.29	3.56115	YES	YES
92	a	3187.33	2.40803	YES	YES
93	a	3196.77	8.04089	YES	YES
94	a	3198.12	7.57298	YES	YES
95	a	3202.91	13.39491	YES	YES
96	a	3204.31	10.94169	YES	YES

Figure 6



BP86/def2-TZVP-calculated C_s-symmetrical structure of Py_2-Bi$(N_3)_3$.

Energy (in Hartree) and atomic corrdinates (in Å) of the BP86/def2-TZVP-calculated C_s-symmetrical structure of Py_2-Bi$(N_3)_3$:

```
Energy = -1204.513950393
Bi    -1.6559817     0.7124258     0.0000000
N     -1.6054751    -1.5218878     0.0000000
N     -0.5149414    -2.0768708     0.0000000
N      0.4675969    -2.6811807     0.0000000
N     -3.2814844     0.8133824    -1.5473661
N     -3.2701218     0.0687418    -2.5125434
N     -3.3259386    -0.6030520    -3.4505207
N      0.0970864     0.3253727    -2.1777587
C      0.0224279    -0.7272819    -3.0115744
H     -0.7210308    -1.4876683    -2.7682009
C      0.8334604    -0.8522526    -4.1399430
H      0.7300304    -1.7234612    -4.7859813
C      1.7602439     0.1516095    -4.4164746
H      2.4090837     0.0836360    -5.2905732
C      1.8411676     1.2481264    -3.5556527
H      2.5480457     2.0584648    -3.7332997
C      0.9905452     1.2913433    -2.4533762
H      1.0208850     2.1367959    -1.7600879
N     -3.2814844     0.8133824     1.5473661
N     -3.2701218     0.0687418     2.5125434
N     -3.3259386    -0.6030520     3.4505207
N      0.0970864     0.3253727     2.1777587
C      0.0224279    -0.7272819     3.0115744
H     -0.7210308    -1.4876683     2.7682009
C      0.8334604    -0.8522526     4.1399430
H      0.7300304    -1.7234612     4.7859813
C      1.7602439     0.1516095     4.4164746
H      2.4090837     0.0836360     5.2905732
C      1.8411676     1.2481264     3.5556527
H      2.5480457     2.0584648     3.7332997
C      0.9905452     1.2913433     2.4533762
H      1.0208850     2.1367959     1.7600879
```

Vibrational frequencies of the BP86/def2-TZVP-calculated C_s-symmetrical structure of Py_2-$Bi(N_3)_3$:

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a'	13.04	1.18918	YES	YES
8	a"	13.92	0.07572	YES	YES
9	a'	15.03	0.45551	YES	YES
10	a"	18.18	0.25717	YES	YES
11	a'	36.00	1.09447	YES	YES
12	a'	40.13	0.31617	YES	YES
13	a"	42.70	0.27557	YES	YES
14	a"	44.40	0.15640	YES	YES
15	a"	58.30	1.17368	YES	YES
16	a'	61.41	2.48923	YES	YES
17	a"	67.61	6.65933	YES	YES
18	a'	73.33	3.42473	YES	YES
19	a'	84.83	1.12228	YES	YES
20	a"	88.15	0.53720	YES	YES
21	a'	91.16	5.66354	YES	YES
22	a"	100.78	6.58497	YES	YES
23	a"	117.39	1.16041	YES	YES
24	a'	128.20	4.76105	YES	YES
25	a'	151.80	1.20751	YES	YES
26	a"	162.95	26.51840	YES	YES
27	a'	171.22	13.31736	YES	YES
28	a"	330.37	130.73754	YES	YES
29	a'	338.45	61.80758	YES	YES
30	a'	363.09	22.90950	YES	YES
31	a"	373.34	0.02347	YES	YES
32	a'	374.33	0.41100	YES	YES
33	a"	406.39	1.69618	YES	YES
34	a'	407.38	4.67063	YES	YES
35	a"	586.27	3.15988	YES	YES
36	a'	588.40	4.42484	YES	YES
37	a"	590.13	4.58259	YES	YES
38	a"	610.52	17.15172	YES	YES
39	a'	610.99	6.93976	YES	YES
40	a"	631.14	0.58180	YES	YES
41	a'	633.83	8.57664	YES	YES
42	a'	640.34	1.80295	YES	YES
43	a"	644.59	0.22732	YES	YES
44	a'	645.15	0.05310	YES	YES
45	a"	693.94	23.98816	YES	YES
46	a'	695.42	69.81141	YES	YES
47	a"	741.83	6.28017	YES	YES
48	a'	741.98	14.07426	YES	YES
49	a"	863.91	0.55031	YES	YES
50	a'	864.88	0.06335	YES	YES
51	a"	922.94	0.40872	YES	YES
52	a'	924.40	0.14748	YES	YES
53	a"	962.57	0.96384	YES	YES
54	a'	963.25	0.08384	YES	YES
55	a"	984.32	0.47000	YES	YES
56	a'	984.39	0.01684	YES	YES
57	a"	994.35	31.22952	YES	YES
58	a'	994.74	10.80583	YES	YES
59	a"	1024.30	1.87224	YES	YES

60	a'	1024.83	1.07000	YES	YES
61	a"	1061.04	0.77035	YES	YES
62	a'	1061.57	4.15202	YES	YES
63	a"	1063.18	20.75292	YES	YES
64	a'	1063.62	7.67854	YES	YES
65	a"	1146.49	0.30837	YES	YES
66	a'	1146.53	3.33540	YES	YES
67	a"	1205.71	19.31431	YES	YES
68	a'	1206.95	10.54887	YES	YES
69	a'	1288.94	77.37834	YES	YES
70	a"	1292.48	1.96779	YES	YES
71	a'	1292.58	0.51738	YES	YES
72	a"	1304.08	170.16583	YES	YES
73	a'	1307.57	37.21265	YES	YES
74	a"	1345.76	1.04757	YES	YES
75	a'	1346.32	2.72896	YES	YES
76	a"	1434.61	2.83685	YES	YES
77	a'	1434.88	52.39077	YES	YES
78	a"	1472.76	0.25339	YES	YES
79	a'	1473.37	0.07867	YES	YES
80	a"	1570.67	0.09158	YES	YES
81	a'	1571.27	1.98237	YES	YES
82	a"	1589.04	37.40233	YES	YES
83	a'	1589.26	21.27914	YES	YES
84	a'	2106.59	487.22087	YES	YES
85	a"	2108.47	1380.46483	YES	YES
86	a'	2124.39	306.56102	YES	YES
87	a"	3073.35	0.89944	YES	YES
88	a'	3074.04	18.55121	YES	YES
89	a"	3109.68	4.12832	YES	YES
90	a'	3109.71	1.65637	YES	YES
91	a"	3115.71	0.00650	YES	YES
92	a'	3115.79	0.29362	YES	YES
93	a"	3128.35	0.66011	YES	YES
94	a'	3128.41	17.25622	YES	YES
95	a"	3136.52	9.16578	YES	YES
96	a'	3136.57	2.90789	YES	YES

Energy (in Hartree) and atomic corrdinates (in Å) of the B3LYP/def2-TZVP-calculated C_s-symmetrical structure of Py_2-$Bi(N_3)_3$:

```
Energy = -1203.679830666
Bi    -1.6855772    0.7973992    0.0000000
N     -1.5267489   -1.4026483    0.0000000
N     -0.4347207   -1.9340879    0.0000000
N      0.5488274   -2.5032546    0.0000000
N     -3.2160401    0.7549583   -1.6190389
N     -3.5226782   -0.2633300   -2.2006714
N     -3.8430451   -1.1812008   -2.7916765
N      0.1946822    0.4111744   -2.1654451
C     -0.0367933   -0.5388251   -3.0770936
H     -0.8651223   -1.2092597   -2.8798988
C      0.7290173   -0.6787954   -4.2268477
H      0.4992673   -1.4642909   -4.9341417
C      1.7800906    0.2023100   -4.4403028
H      2.3974078    0.1206717   -5.3261846
C      2.0253820    1.1915804   -3.4963788
H      2.8327812    1.9010504   -3.6204154
C      1.2065154    1.2562158   -2.3782215
H      1.3676450    2.0190366   -1.6231821
N     -3.2160401    0.7549583    1.6190389
N     -3.5226782   -0.2633300    2.2006714
N     -3.8430451   -1.1812008    2.7916765
N      0.1946822    0.4111744    2.1654451
C     -0.0367933   -0.5388251    3.0770936
```

H	-0.8651223	-1.2092597	2.8798988
C	0.7290173	-0.6787954	4.2268477
H	0.4992673	-1.4642909	4.9341417
C	1.7800906	0.2023100	4.4403028
H	2.3974078	0.1206717	5.3261846
C	2.0253820	1.1915804	3.4963788
H	2.8327812	1.9010504	3.6204154
C	1.2065154	1.2562158	2.3782215
H	1.3676450	2.0190366	1.6231821

Vibrational frequencies of the B3LYP/def2-TZVP-calculated C_s-symmetrical structure of Py_2-$Bi(N_3)_3$:

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1	a"	-22.84	0.00000	YES	YES
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7		0.00	0.00000	-	-
8	a'	9.08	0.17328	YES	YES
9	a'	14.99	0.89150	YES	YES
10	a"	18.83	0.37423	YES	YES
11	a"	29.57	0.91039	YES	YES
12	a'	32.16	0.24963	YES	YES
13	a'	37.93	1.80840	YES	YES
14	a"	38.81	0.36285	YES	YES
15	a"	52.68	0.13760	YES	YES
16	a'	57.41	2.29610	YES	YES
17	a"	63.63	8.40004	YES	YES
18	a'	68.37	1.39756	YES	YES
19	a'	80.97	3.84631	YES	YES
20	a"	83.14	0.15661	YES	YES
21	a'	92.23	3.96863	YES	YES
22	a"	98.98	4.94664	YES	YES
23	a"	123.18	0.13740	YES	YES
24	a'	146.99	2.77371	YES	YES
25	a'	154.04	7.58044	YES	YES
26	a"	177.09	28.39040	YES	YES
27	a'	193.73	23.40248	YES	YES
28	a"	338.97	128.50072	YES	YES
29	a'	352.62	77.95839	YES	YES
30	a'	383.25	17.31807	YES	YES
31	a"	390.89	0.04150	YES	YES
32	a'	392.10	0.23203	YES	YES
33	a"	425.12	1.27699	YES	YES
34	a'	426.53	4.82966	YES	YES
35	a"	619.22	1.68356	YES	YES
36	a"	620.37	12.71937	YES	YES
37	a'	621.80	9.40439	YES	YES
38	a"	629.72	15.58732	YES	YES
39	a'	630.20	7.94968	YES	YES
40	a"	659.65	2.88861	YES	YES
41	a'	661.15	9.42587	YES	YES
42	a"	667.53	0.12946	YES	YES
43	a'	668.10	0.77529	YES	YES
44	a'	669.53	3.22586	YES	YES
45	a"	718.94	23.78225	YES	YES
46	a'	720.78	77.46851	YES	YES
47	a"	769.37	7.22314	YES	YES
48	a'	769.61	20.13475	YES	YES
49	a"	897.90	0.10946	YES	YES
50	a'	899.07	0.01830	YES	YES

51	a"	963.37	0.00618	YES	YES
52	a'	965.66	0.02209	YES	YES
53	a"	1009.11	0.11938	YES	YES
54	a'	1010.08	0.08155	YES	YES
55	a"	1022.32	29.69310	YES	YES
56	a'	1022.72	14.28460	YES	YES
57	a"	1025.87	0.17817	YES	YES
58	a'	1025.96	0.01213	YES	YES
59	a"	1053.14	9.26271	YES	YES
60	a'	1053.81	2.86620	YES	YES
61	a"	1089.42	0.00015	YES	YES
62	a'	1090.20	2.24101	YES	YES
63	a"	1093.50	16.90803	YES	YES
64	a'	1093.94	9.91291	YES	YES
65	a"	1177.40	0.73168	YES	YES
66	a'	1177.44	4.61320	YES	YES
67	a"	1243.14	16.73077	YES	YES
68	a'	1244.64	14.86175	YES	YES
69	a"	1288.51	0.00479	YES	YES
70	a'	1288.52	0.03489	YES	YES
71	a'	1341.86	137.69358	YES	YES
72	a"	1345.69	191.41216	YES	YES
73	a'	1352.82	136.19955	YES	YES
74	a"	1394.98	1.29121	YES	YES
75	a'	1395.86	2.35090	YES	YES
76	a"	1479.60	4.85249	YES	YES
77	a'	1479.95	49.61008	YES	YES
78	a"	1523.38	1.31476	YES	YES
79	a'	1524.15	0.37621	YES	YES
80	a"	1619.22	0.25407	YES	YES
81	a'	1620.00	2.74877	YES	YES
82	a"	1636.89	47.59379	YES	YES
83	a'	1637.20	27.00332	YES	YES
84	a"	2179.79	877.62115	YES	YES
85	a'	2190.87	772.62321	YES	YES
86	a'	2205.42	766.16932	YES	YES
87	a"	3148.87	4.63083	YES	YES
88	a'	3149.71	17.75604	YES	YES
89	a"	3175.96	4.78672	YES	YES
90	a'	3176.01	1.37247	YES	YES
91	a"	3181.82	1.38292	YES	YES
92	a'	3181.87	0.50083	YES	YES
93	a"	3197.68	0.00019	YES	YES
94	a'	3197.73	17.83296	YES	YES
95	a"	3205.04	8.89622	YES	YES
96	a'	3205.09	2.63497	YES	YES