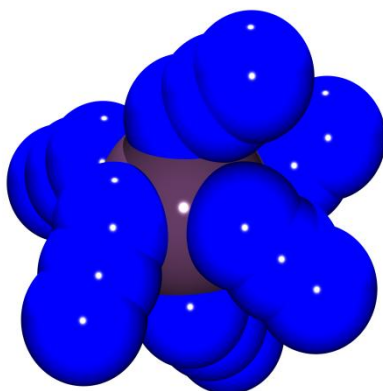


SUPPORTING INFORMATION

Binary Bismuth(III) Azides: $\text{Bi}(\text{N}_3)_3$, $[\text{Bi}(\text{N}_3)_4]^-$, and $[\text{Bi}(\text{N}_3)_6]^{3-}$

Axel Schulz and Alexander Villinger**



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1. Experimental

General Information. All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques.

Dichloromethane was purified according to a literature procedure,^[1] dried over P₄O₁₀ and freshly distilled prior to use. Tetrahydrofuran (THF) was dried over Na/benzophenone and freshly distilled prior to use, *n*-hexane was dried over Na/benzophenone/tetraglyme and freshly distilled prior to use. Ethanol and diethyl ether were freshly distilled prior to use. Bismuth triiodide BiI₃ (99%, Merck) was dried at 120°C prior to use. Bismuth trifluoride BiF₃ (99%, ABCR), Silver nitrate AgNO₃ (99%, VEB Feinchemie Sebnitz), sodium azide (99%, Acros) and tetraphenylphosphonium iodide [Ph₄P]I (99%, Aldrich) were used as received. Silver azide AgN₃ was dried at 70°C for several days prior to use. Tetraphenylphosphonium azide [Ph₄P][N₃]^[2] and tetraphenylphosphonium tetraiodobismuthate THF solvate [Ph₄P][BiI₄] · THF ^[3] have been reported previously, and were prepared according to modified procedures.

NMR: ¹⁴N{¹H} spectra were obtained on a Bruker AVANCE 500 spectrometer and were referenced externally. CD₂Cl₂ and CD₃CN were dried over P₄O₁₀, d₆-DMSO was dried over CaH₂.

IR: Nicolet 380 FT-IR with a Smart Orbit ATR device was used.

Raman: Bruker VERTEX 70 FT-IR with RAM II FT-Raman module, equipped with a Nd:YAG laser (1064nm), or Kaiser Optical Systems RXN1-785 nm was used.

CHN analyses: Analysator Flash EA 1112 from Thermo Quest, or C/H/N/S-Mikronalysator TruSpec-932 from Leco were used.

Melting points are uncorrected (EZ-Melt, Stanford Research Systems). Heating-rate 20 °C/min (clearing-points are reported).

DSC: DSC 823e from Mettler-Toledo (Heating-rate 5 °C/min) was used.

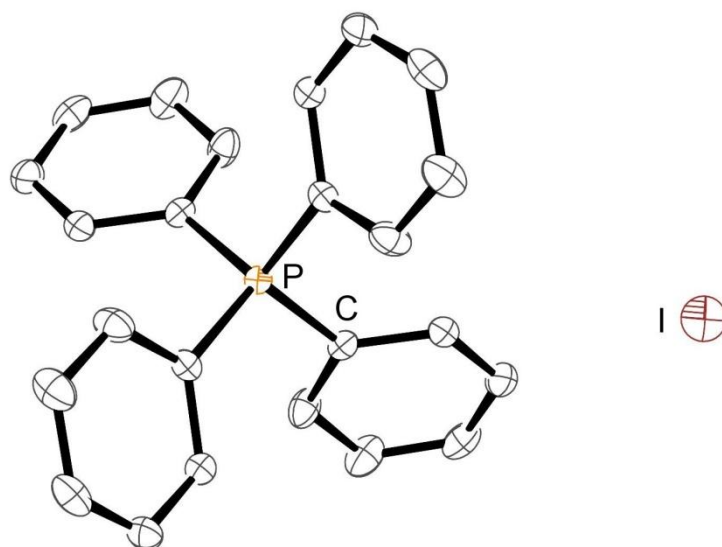
2. Structure elucidation

X-ray Structure Determination: X-ray quality crystals of **1** THF, **2**, 2 CH₂Cl₂, **3**, [Ph₄P]I, [Ph₄P][BiI₄] · THF and [Ph₄P]₂[B₂iI₉] · 3 CH₂Cl₂ were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperatures. The samples were cooled to 173(2) K during measurement. The data were collected on a Bruker Apex Kappa-II CCD diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$). The structures were solved by direct methods (*SHELXS-97*)^[4] and refined by full-matrix least squares procedures (*SHELXL-97*).^[5] Semi-empirical absorption corrections were applied (*SADABS*).^[6] All non hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

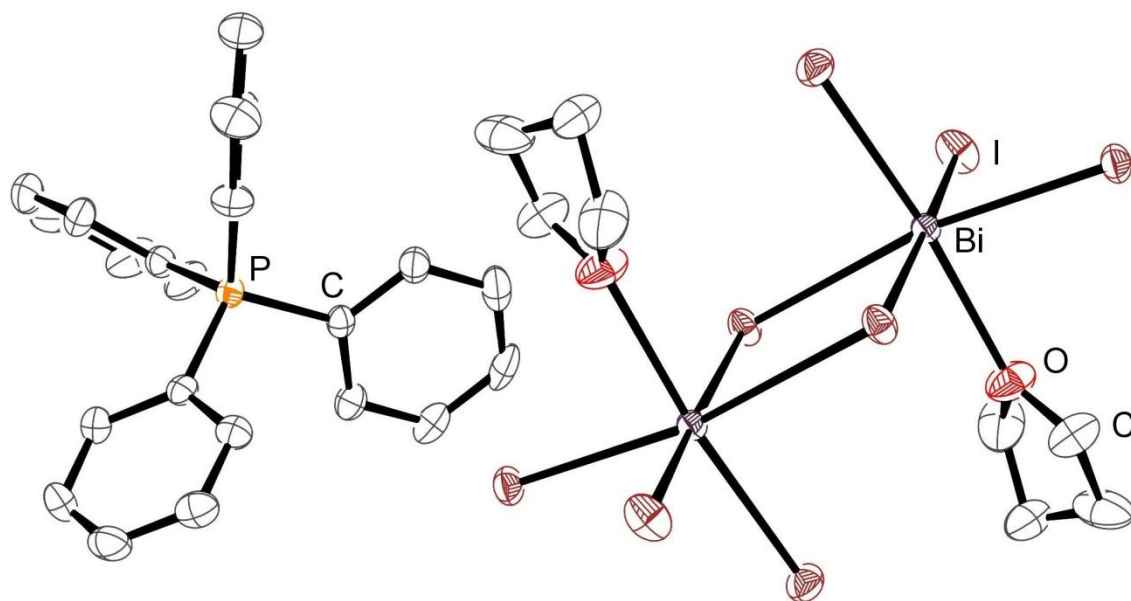
The position of two azide groups in **3** were found to be disordered and were split in two parts. The occupancy of each part was refined freely (N4/N5/N6: 0.58(4)/0.42(4), N16/N17/N18: 0.615(10)/0.385(10)). The THF molecule in [Ph₄P][BiI₄] · THF was found to be disordered and was split in two parts. The occupancy of each part was refined freely (C27/C28: 0.706(19)/ 0.294(19)).

Figure S1. Ortep representation of all species not shown in the manuscript. Thermal ellipsoids with 50% probability at 173 K, H atoms are omitted for clarity:

a) [Ph₄P]I



b) $[\text{Ph}_4\text{P}][\text{BiI}_4] \cdot \text{THF}$



c) $[\text{Ph}_4\text{P}]_3[\text{Bi}_2\text{I}_9] \cdot 3 \text{CH}_2\text{Cl}_2$

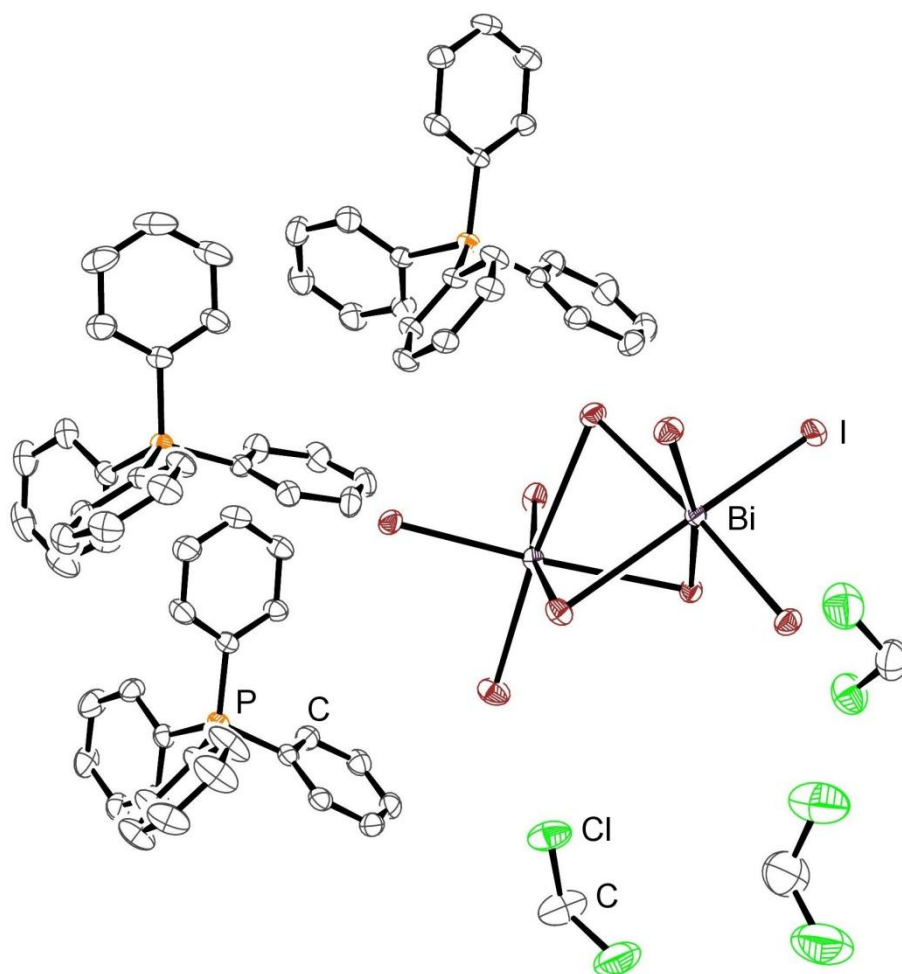


Table S1. Crystallographic details of **2**, **2** CH₂Cl₂, and **3**.

	2	2 CH ₂ Cl ₂	3
Chem. Formula	C ₂₄ H ₂₀ BiN ₁₂ P	C ₂₅ H ₂₂ BiCl ₂ N ₁₂ P	C ₇₂ H ₆₀ BiN ₁₈ P ₃
Form. Wght. [g mol ⁻¹]	716.47	801.40	1479.27
Colour	Yellow	Yellow	Yellow
Cryst. system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	8.1998(5)	7.9474(2)	13.3271(3)
<i>b</i> [Å]	24.0228(15)	13.0355(4)	22.6255(6)
<i>c</i> [Å]	13.5737(8)	15.5718(4)	21.9806(6)
<i>α</i> [°]	90.00	111.2960(10)	90.00
<i>β</i> [°]	90.985(2)	100.5440(10)	96.9230(10)
<i>γ</i> [°]	90.00	90.707(2)	90.00
<i>V</i> [Å ³]	2673.4(3)	1472.20(7)	6579.5(3)
<i>Z</i>	4	2	4
<i>ρ</i> _{calc.} [g cm ⁻³]	1.780	1.808	1.493
<i>μ</i> [mm ⁻¹]	6.693	6.263	2.812
<i>λ</i> _{MoKα} [Å]	0.71073	0.71073	0.71073
<i>T</i> [K]	173(2)	173(2)	173(2)
Measured reflections	47421	47251	92087
Independent reflections	11327	10535	19210
Reflections with <i>I</i> > 2σ(<i>I</i>)	7652	9213	13457
<i>R</i> _{int.}	0.0484	0.0406	0.0366
<i>F</i> (000)	1384	776	2984
<i>R</i> ₁ (<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)])	0.0343	0.0239	0.0304
w <i>R</i> ₂ (<i>F</i> ²)	0.0595	0.0502	0.0574
GooF	1.005	1.032	1.003
Parameters	343	370	903
CCDC #	784358	784359	784360

Table S2. Crystallographic details of [Ph₄P]I, [Ph₄P][BiI₄] · THF and [Ph₄P]₃[Bi₂I₉] · 3 CH₂Cl₂.

	[Ph ₄ P]I	[Ph ₄ P][BiI ₄] · THF	[Ph ₄ P] ₃ [Bi ₂ I ₉] · 3 CH ₂ Cl ₂
Chem. Formula	C ₂₄ H ₂₀ IP	C ₂₈ H ₂₈ BiI ₄ OP	C ₇₅ H ₆₆ Bi ₂ Cl ₆ I ₉ P ₃
Form. Wght. [g mol ⁻¹]	466.27	1128.05	2832.95
Colour	Colourless	Orange	Red
Cryst. system	Tetragonal	Triclinic	Triclinic
Space group	<i>I</i> -4	<i>P</i> -1	<i>P</i> -1
<i>a</i> [Å]	11.9375(4)	11.4458(3)	15.0961(5)
<i>b</i> [Å]	11.9375(4)	11.7578(3)	15.6828(5)
<i>c</i> [Å]	6.8917(2)	12.4671(3)	19.0023(5)
α [°]	90.00	92.2940(10)	93.3160(10)
β [°]	90.00	105.6450(10)	95.7870(10)
γ [°]	90.00	95.6720(10)	98.707(2)
<i>V</i> [Å ³]	982.09(5)	1603.82(7)	4412.0(2)
<i>Z</i>	2	2	
ρ_{calc} [g cm ⁻³]	1.577	2.336	2.132
μ [mm ⁻¹]	1.716	9.415	7.406
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073	0.71073
<i>T</i> [K]	173(2)	173(2)	173(2)
Measured reflections	3429	52382	116802
Independent reflections	1591	11498	31798
Reflections with <i>I</i> > 2σ(<i>I</i>)	1537	7998	25894
<i>R</i> _{int.}	0.0135	0.0492	0.0317
<i>F</i> (000)	464	1028	2612
<i>R</i> ₁ (<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)])	0.0167	0.0346	0.0271
<i>wR</i> ₂ (<i>F</i> ²)	0.0390	0.0505	0.0580
Goof	1.020	0.930	1.045
Parameters	59	323	856
CCDC #	-	-	-

Scheme S1. Numbering scheme of tetraphenylphosphonium tetraazidobismuthate

$[\text{Ph}_4\text{P}][\text{Bi}(\text{N}_3)_4]$ (**2**)

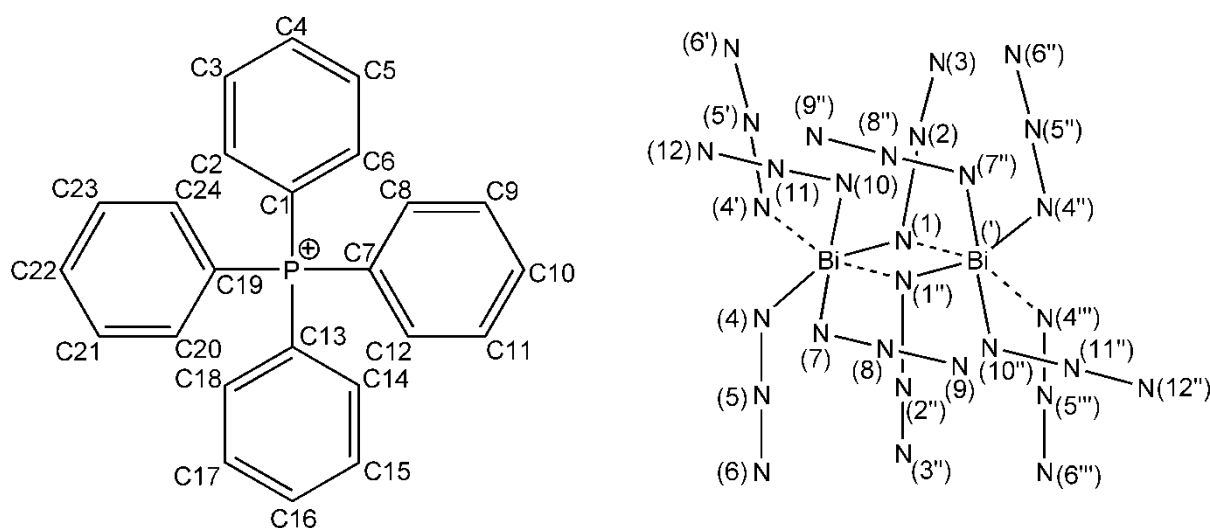


Table S3. Selected bond lengths (Å) angles (°) and torsion angles (°) of **2**.

N1—N2	1.216 (3)	N10—Bi—N4ⁱⁱ	77.48 (8)
N1—Bi	2.377 (2)	N7—Bi—N4ⁱⁱ	149.34 (8)
N1—Biⁱ	2.684 (2)	N1—Bi—N4ⁱⁱ	115.98 (7)
N2—N3	1.144 (3)	N4—Bi—N4ⁱⁱ	71.79 (9)
N4—N5	1.198 (3)	N1ⁱ—Bi—N4ⁱⁱ	126.44 (7)
N4—Bi	2.449 (2)	Bi—N1—N2—N3	-141 (7)
N4—Biⁱⁱ	2.717 (2)	Biⁱ—N1—N2—N3	52 (7)
N5—N6	1.144 (4)	Bi—N4—N5—N6	-178 (100)
N7—N8	1.207 (3)	Biⁱⁱ—N4—N5—N6	-25 (14)
N7—Bi	2.291 (2)	Bi—N7—N8—N9	-169 (9)
N8—N9	1.148 (4)	Bi—N10—N11—N12	-179 (100)
N10—N11	1.209 (3)	N11—N10—Bi—N7	-111.9 (2)
N10—Bi	2.273 (2)	N11—N10—Bi—N1	161.0 (2)
N11—N12	1.149 (3)	N11—N10—Bi—N4	-31.3 (2)
Bi—N1ⁱ	2.684 (2)	N11—N10—Bi—N1ⁱ	-176.95 (18)
Bi—N4ⁱⁱ	2.717 (2)	N11—N10—Bi—N4ⁱⁱ	41.5 (2)

P—C7	1.783 (3)	N8—N7—Bi—N10	-105.3 (2)
P—C19	1.796 (3)	N8—N7—Bi—N1	-24.7 (2)
P—C1	1.800 (3)	N8—N7—Bi—N4	171.3 (2)
P—C13	1.800 (3)	N8—N7—Bi—N1ⁱ	45.0 (2)
N2—N1—Bi	122.62 (16)	N8—N7—Bi—N4ⁱⁱ	-164.25 (18)
N2—N1—Biⁱ	125.68 (16)	N2—N1—Bi—N10	-1.0 (2)
Bi—N1—Biⁱ	110.60 (9)	Biⁱ—N1—Bi—N10	167.53 (11)
N3—N2—N1	177.5 (3)	N2—N1—Bi—N7	-88.5 (2)
N5—N4—Bi	122.90 (17)	Biⁱ—N1—Bi—N7	80.06 (10)
N5—N4—Biⁱⁱ	124.03 (18)	N2—N1—Bi—N4	-38.1 (4)
Bi—N4—Biⁱⁱ	108.21 (9)	Biⁱ—N1—Bi—N4	130.45 (18)
N6—N5—N4	178.5 (3)	N2—N1—Bi—N1ⁱ	-168.6 (3)
N8—N7—Bi	114.69 (19)	Biⁱ—N1—Bi—N1ⁱ	0.0
N9—N8—N7	177.6 (3)	N2—N1—Bi—N4ⁱⁱ	69.9 (2)
N11—N10—Bi	115.37 (19)	Biⁱ—N1—Bi—N4ⁱⁱ	-121.52 (8)
N12—N11—N10	176.7 (3)	N5—N4—Bi—N10	-124.8 (3)
N10—Bi—N7	86.95 (9)	Biⁱⁱⁱ—N4—Bi—N10	79.06 (10)
N10—Bi—N1	80.46 (8)	N5—N4—Bi—N7	-36.7 (2)
N7—Bi—N1	86.64 (9)	Biⁱⁱⁱ—N4—Bi—N7	167.14 (11)
N10—Bi—N4	83.06 (8)	N5—N4—Bi—N1	-88.0 (3)
N7—Bi—N4	80.30 (8)	Biⁱⁱⁱ—N4—Bi—N1	115.9 (2)
N1—Bi—N4	159.45 (8)	N5—N4—Bi—N1ⁱ	34.0 (3)
N10—Bi—N1ⁱ	147.46 (8)	Biⁱⁱⁱ—N4—Bi—N1ⁱ	-122.14 (8)
N7—Bi—N1ⁱ	79.52 (8)	N5—N4—Bi—N4ⁱⁱ	156.2 (3)
N1—Bi—N1ⁱ	69.40 (9)	Biⁱⁱⁱ—N4—Bi—N4ⁱⁱ	0.0
N4—Bi—N1ⁱ	122.86 (7)		

Symmetry codes: (i) $-x+2, -y, -z+2$; (ii) $-x+1, -y, -z+2$.

Scheme S2. Numbering scheme of tetraphenylphosphonium tetraazidobismuthate dichloromethane solvate $[\text{Ph}_4\text{P}][\text{Bi}(\text{N}_3)_4] \cdot \text{CH}_2\text{Cl}_2$ ($2 \text{ CH}_2\text{Cl}_2$)

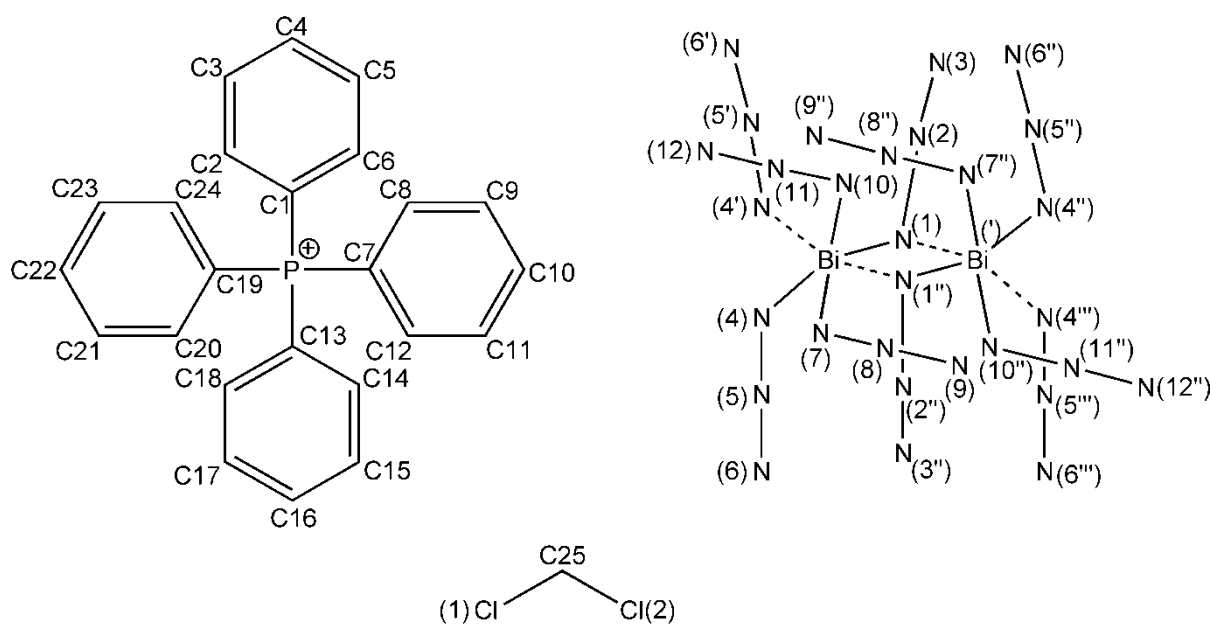


Table S4. Selected bond lengths (Å) angles (°) and torsion angles (°) of $2 \text{ CH}_2\text{Cl}_2$.

Bi1—N10	2.2971 (18)	Bi1—N4—Bi1ⁱ	106.90 (7)
Bi1—N7	2.3019 (19)	N6—N5—N4	178.1 (2)
Bi1—N1	2.3819 (18)	N8—N7—Bi1	115.19 (14)
Bi1—N4	2.4139 (18)	N9—N8—N7	178.1 (2)
Bi1—N4ⁱ	2.6344 (18)	N11—N10—Bi1	115.53 (14)
Bi1—N1ⁱⁱ	2.6471 (18)	N12—N11—N10	177.7 (2)
N1—N2	1.210 (3)	Cl2—C25—Cl1	111.42 (14)
N1—Bi1ⁱⁱ	2.6471 (17)	N10—Bi1—N1—N2	-18.39 (19)
N2—N3	1.142 (3)	N7—Bi1—N1—N2	-102.53 (19)
N4—N5	1.203 (3)	N4—Bi1—N1—N2	-46.2 (3)
N4—Bi1ⁱ	2.6344 (18)	N4ⁱ—Bi1—N1—N2	56.0 (2)
N5—N6	1.144 (3)	N1ⁱⁱ—Bi1—N1—N2	177.4 (2)
N7—N8	1.206 (2)	N10—Bi1—N1—Bi1ⁱⁱ	164.21 (9)
N8—N9	1.147 (3)	N7—Bi1—N1—Bi1ⁱⁱ	80.07 (8)
N10—N11	1.205 (2)	N4—Bi1—N1—Bi1ⁱⁱ	136.4 (2)

N11—N12	1.141 (3)	N4ⁱ—Bi1—N1—Bi1ⁱⁱ	-121.38 (7)
P1—C19	1.790 (2)	N1ⁱⁱ—Bi1—N1—Bi1ⁱⁱ	0.0
P1—C13	1.792 (2)	Bi1—N1—N2—N3	147 (6)
P1—C1	1.796 (2)	Bi1ⁱⁱ—N1—N2—N3	-36 (7)
P1—C7	1.797 (2)	N10—Bi1—N4—N5	-117.7 (2)
C25—C12	1.759 (3)	N7—Bi1—N4—N5	-33.0 (2)
C25—C11	1.772 (3)	N1—Bi1—N4—N5	-90.1 (3)
N10—Bi1—N7	84.05 (7)	N4ⁱ—Bi1—N4—N5	162.5 (2)
N10—Bi1—N1	81.64 (6)	N1ⁱⁱ—Bi1—N4—N5	41.2 (2)
N7—Bi1—N1	88.95 (7)	N10—Bi1—N4—Bi1ⁱ	79.76 (8)
N10—Bi1—N4	84.64 (7)	N7—Bi1—N4—Bi1ⁱ	164.44 (8)
N7—Bi1—N4	82.52 (6)	N1—Bi1—N4—Bi1ⁱ	107.4 (2)
N1—Bi1—N4	164.53 (7)	N4ⁱ—Bi1—N4—Bi1ⁱ	0.0
N10—Bi1—N4ⁱ	78.67 (7)	N1ⁱⁱ—Bi1—N4—Bi1ⁱ	-121.30 (7)
N7—Bi1—N4ⁱ	151.17 (6)	Bi1—N4—N5—N6	150 (7)
N1—Bi1—N4ⁱ	110.88 (6)	Bi1ⁱ—N4—N5—N6	-50 (8)
N4—Bi1—N4ⁱ	73.10 (7)	N10—Bi1—N7—N8	-106.80 (17)
N10—Bi1—N1ⁱⁱ	148.56 (6)	N1—Bi1—N7—N8	-25.10 (17)
N7—Bi1—N1ⁱⁱ	80.27 (6)	N4—Bi1—N7—N8	167.84 (18)
N1—Bi1—N1ⁱⁱ	71.05 (7)	N4ⁱ—Bi1—N7—N8	-159.99 (14)
N4—Bi1—N1ⁱⁱ	119.72 (6)	N1ⁱⁱ—Bi1—N7—N8	45.85 (16)
N4ⁱ—Bi1—N1ⁱⁱ	125.16 (6)	Bi1—N7—N8—N9	175 (100)
N2—N1—Bi1	126.42 (14)	N7—Bi1—N10—N11	-110.44 (18)
N2—N1—Bi1ⁱⁱ	124.58 (14)	N1—Bi1—N10—N11	159.75 (19)
Bi1—N1—Bi1ⁱⁱ	108.95 (7)	N4—Bi1—N10—N11	-27.43 (18)
N3—N2—N1	177.9 (2)	N4ⁱ—Bi1—N10—N11	46.37 (17)
N5—N4—Bi1	126.25 (15)	N1ⁱⁱ—Bi1—N10—N11	-170.68 (14)
N5—N4—Bi1ⁱ	124.34 (14)	Bi1—N10—N11—N12	-161 (7)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, -y+1, -z+1$.

Scheme S3. Numbering scheme of tris-tetraphenylphosphonium hexaazidobismuthate $[\text{Ph}_4\text{P}]_3[\text{Bi}(\text{N}_3)_6]$ (**3**)

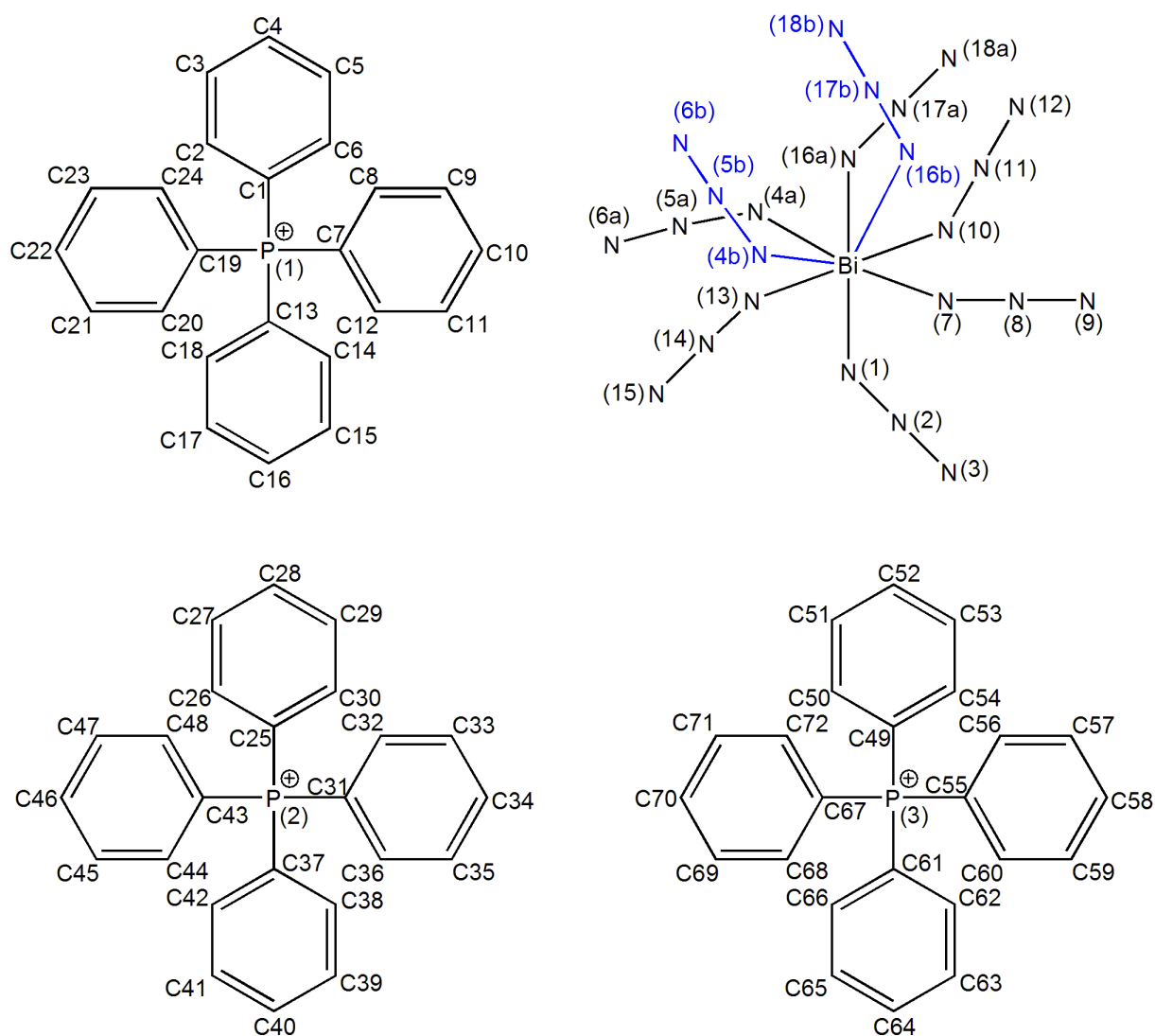


Table S5. Selected bond lengths (Å) angles (°) and torsion angles (°) of **3**.

Bi1—N4A	2.320 (16)	N16A—N17A—N18A	172.4 (17)
Bi1—N16B	2.326 (7)	N17B—N16B—Bi1	133.9 (17)
Bi1—N13	2.331 (2)	N18B—N17B—N16B	170 (3)
Bi1—N7	2.364 (2)	N4A—Bi1—N1—N2	36.4 (4)
Bi1—N4B	2.44 (2)	N16B—Bi1—N1—N2	132.1 (3)
Bi1—N10	2.478 (2)	N13—Bi1—N1—N2	−47.5 (2)
Bi1—N1	2.487 (2)	N7—Bi1—N1—N2	−64.7 (8)

Bi1—N16A	2.719 (5)	N4B—Bi1—N1—N2	30.7 (7)
N1—N2	1.188 (3)	N10—Bi1—N1—N2	-131.7 (2)
N2—N3	1.149 (3)	N16A—Bi1—N1—N2	115.5 (2)
N4A—N5A	1.27 (3)	Bi1—N1—N2—N3	-140 (6)
N5A—N6A	1.10 (2)	N13—Bi1—N4A—N5A	16.4 (19)
N4B—N5B	1.10 (4)	N7—Bi1—N4A—N5A	105.2 (19)
N5B—N6B	1.19 (3)	N10—Bi1—N4A—N5A	37 (4)
N7—N8	1.194 (3)	N1—Bi1—N4A—N5A	-68.7 (19)
N8—N9	1.140 (3)	N16A—Bi1—N4A—N5A	-177 (2)
N10—N11	1.188 (3)	Bi1—N4A—N5A—N6A	143 (46)
N11—N12	1.158 (3)	N16B—Bi1—N4B—N5B	-112 (3)
N13—N14	1.203 (3)	N13—Bi1—N4B—N5B	62 (3)
N14—N15	1.150 (3)	N7—Bi1—N4B—N5B	153 (3)
N17A—N18A	1.186 (18)	N10—Bi1—N4B—N5B	104 (3)
N16B—N17B	1.15 (3)	N1—Bi1—N4B—N5B	-20 (3)
N17B—N18B	1.15 (3)	Bi1—N4B—N5B—N6B	-138 (12)
N4A—Bi1—N13	84.3 (4)	N4A—Bi1—N7—N8	-163.2 (4)
N16B—Bi1—N13	174.0 (2)	N16B—Bi1—N7—N8	101.4 (3)
N4A—Bi1—N7	86.8 (5)	N13—Bi1—N7—N8	-78.8 (2)
N16B—Bi1—N7	97.5 (2)	N4B—Bi1—N7—N8	-158.5 (7)
N13—Bi1—N7	88.47 (7)	N10—Bi1—N7—N8	5.3 (2)
N16B—Bi1—N4B	101.5 (7)	N1—Bi1—N7—N8	-61.6 (8)
N13—Bi1—N4B	79.6 (6)	N16A—Bi1—N7—N8	118.2 (3)
N7—Bi1—N4B	77.2 (5)	Bi1—N7—N8—N9	171 (4)
N4A—Bi1—N10	167.6 (4)	N4A—Bi1—N10—N11	-132 (2)
N16B—Bi1—N10	96.2 (3)	N16B—Bi1—N10—N11	63.0 (3)
N13—Bi1—N10	84.10 (7)	N13—Bi1—N10—N11	-111.04 (19)
N7—Bi1—N10	88.53 (7)	N7—Bi1—N10—N11	160.35 (19)
N4B—Bi1—N10	158.6 (7)	N4B—Bi1—N10—N11	-151.7 (14)
N4A—Bi1—N1	94.4 (5)	N1—Bi1—N10—N11	-25.38 (19)
N16B—Bi1—N1	88.5 (2)	N16A—Bi1—N10—N11	84.6 (2)

N13—Bi1—N1	85.59 (7)	Bi1—N10—N11—N12	-168 (6)
N7—Bi1—N1	173.78 (8)	N4A—Bi1—N13—N14	-141.8 (5)
N4B—Bi1—N1	103.4 (5)	N16B—Bi1—N13—N14	-50 (2)
N10—Bi1—N1	89.03 (7)	N7—Bi1—N13—N14	131.30 (18)
N4A—Bi1—N16A	78.2 (4)	N4B—Bi1—N13—N14	-151.4 (6)
N13—Bi1—N16A	157.97 (17)	N10—Bi1—N13—N14	42.62 (18)
N7—Bi1—N16A	77.37 (16)	N1—Bi1—N13—N14	-46.86 (18)
N10—Bi1—N16A	111.92 (14)	N16A—Bi1—N13—N14	-179.2 (3)
N1—Bi1—N16A	108.84 (16)	Bi1—N13—N14—N15	-159 (5)
N2—N1—Bi1	119.54 (16)	N4A—Bi1—N16A—N17A	164.8 (14)
N3—N2—N1	177.0 (3)	N13—Bi1—N16A—N17A	-157.1 (12)
N5A—N4A—Bi1	124.5 (12)	N7—Bi1—N16A—N17A	-105.9 (13)
N6A—N5A—N4A	177.5 (16)	N10—Bi1—N16A—N17A	-22.7 (14)
N5B—N4B—Bi1	109.1 (19)	N1—Bi1—N16A—N17A	74.1 (13)
N4B—N5B—N6B	167 (3)	Bi1—N16A—N17A—N18A	-109 (14)
N8—N7—Bi1	123.20 (16)	N13—Bi1—N16B—N17B	-164 (3)
N9—N8—N7	175.8 (2)	N7—Bi1—N16B—N17B	15 (2)
N11—N10—Bi1	120.68 (17)	N4B—Bi1—N16B—N17B	-64 (2)
N12—N11—N10	177.6 (3)	N10—Bi1—N16B—N17B	104 (2)
N14—N13—Bi1	119.12 (15)	N1—Bi1—N16B—N17B	-167 (2)
N15—N14—N13	177.2 (2)	Bi1—N16B—N17B—N18B	-65 (19)
N17A—N16A—Bi1	133.4 (9)		

Scheme S4. Numbering scheme of tetraphenylphosphonium tetraiodobismuthate THF solvate $[\text{Ph}_4\text{P}][\text{BiI}_4] \cdot \text{THF}$.

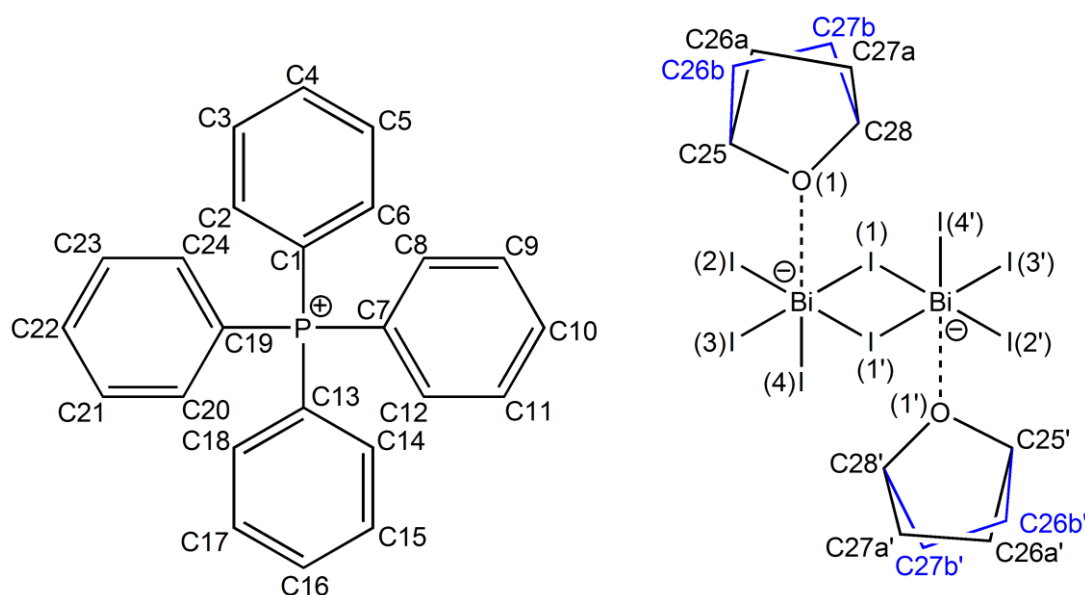


Table S6. Selected bond lengths (Å) angles (°) and torsion angles (°) of $[\text{Ph}_4\text{P}][\text{BiI}_4] \cdot \text{THF}$.

Bi—O1	2.625 (3)	C27A—C26A—C25	109.7 (16)
Bi—I4	2.9222 (3)	C25—C26B—C27B	101.1 (6)
Bi—I2	2.9325 (3)	C26B—C27B—C28	106.6 (5)
Bi—I3	2.9625 (3)	O1—C28—C27A	112.0 (10)
Bi—I1	3.2278 (3)	O1—C28—C27B	105.2 (5)
Bi—I1ⁱ	3.2415 (3)	C1—P—C13	110.36 (15)
I1—Biⁱ	3.2415 (3)	C1—P—C7	110.61 (15)
O1—C28	1.428 (5)	C13—P—C7	106.89 (15)
O1—C25	1.430 (5)	C1—P—C19	108.11 (15)
C25—C26B	1.485 (7)	C13—P—C19	109.99 (15)
C25—C26A	1.556 (14)	C7—P—C19	110.89 (15)
C26A—C27A	1.500 (17)	O1—Bi—I1—Biⁱ	-89.59 (6)
C27A—C28	1.464 (14)	I4—Bi—I1—Biⁱ	85.055 (7)
C26B—C27B	1.502 (10)	I2—Bi—I1—Biⁱ	-179.992 (8)
C27B—C28	1.519 (8)	I3—Bi—I1—Biⁱ	-91.97 (4)

P—C1	1.787 (3)	I1ⁱ—Bi—I1—Biⁱ	0.0
P—C13	1.790 (3)	I4—Bi—O1—C28	-103.8 (6)
P—C7	1.793 (3)	I2—Bi—O1—C28	40.3 (3)
P—C19	1.796 (3)	I3—Bi—O1—C28	131.6 (3)
O1—Bi—I4	173.53 (6)	I1—Bi—O1—C28	-48.0 (3)
O1—Bi—I2	90.23 (6)	I1ⁱ—Bi—O1—C28	-137.2 (3)
I4—Bi—I2	95.006 (8)	I4—Bi—O1—C25	75.6 (7)
O1—Bi—I3	85.81 (6)	I2—Bi—O1—C25	-140.3 (3)
I4—Bi—I3	97.837 (7)	I3—Bi—O1—C25	-48.9 (3)
I2—Bi—I3	91.344 (8)	I1—Bi—O1—C25	131.5 (3)
O1—Bi—I1	84.42 (6)	I1ⁱ—Bi—O1—C25	42.2 (3)
I4—Bi—I1	91.934 (7)	C28—O1—C25—C26B	17.7 (7)
I2—Bi—I1	88.296 (7)	Bi—O1—C25—C26B	-161.8 (6)
I3—Bi—I1	170.216 (7)	C28—O1—C25—C26A	-4.0 (9)
O1—Bi—I1ⁱ	89.52 (6)	Bi—O1—C25—C26A	176.4 (9)
I4—Bi—I1ⁱ	85.084 (7)	O1—C25—C26A—C27A	27 (2)
I2—Bi—I1ⁱ	177.524 (8)	C25—C26A—C27A—C28	-37 (2)
I3—Bi—I1ⁱ	91.095 (7)	O1—C25—C26B—C27B	-28.3 (12)
I1—Bi—I1ⁱ	89.228 (7)	C25—C26B—C27B—C28	28.4 (13)
Bi—I1—Biⁱ	90.772 (7)	C25—O1—C28—C27A	-20.7 (12)
C28—O1—C25	109.5 (3)	Bi—O1—C28—C27A	158.9 (11)
C28—O1—Bi	126.6 (2)	C25—O1—C28—C27B	1.1 (6)
C25—O1—Bi	124.0 (2)	Bi—O1—C28—C27B	-179.4 (5)
O1—C25—C26B	108.8 (4)	C26A—C27A—C28—O1	34 (2)
O1—C25—C26A	99.8 (10)	C26B—C27B—C28—O1	-19.1 (12)

Symmetry code: (i) $-x, -y+1, -z+1$.

Scheme S5. Numbering scheme of bis tetraphenylphosphonium nonaiododibismuthate dichloromethane tri solvate $[\text{Ph}_4\text{P}]_3[\text{Bi}_2\text{I}_9] \cdot 3 \text{CH}_2\text{Cl}_2$.

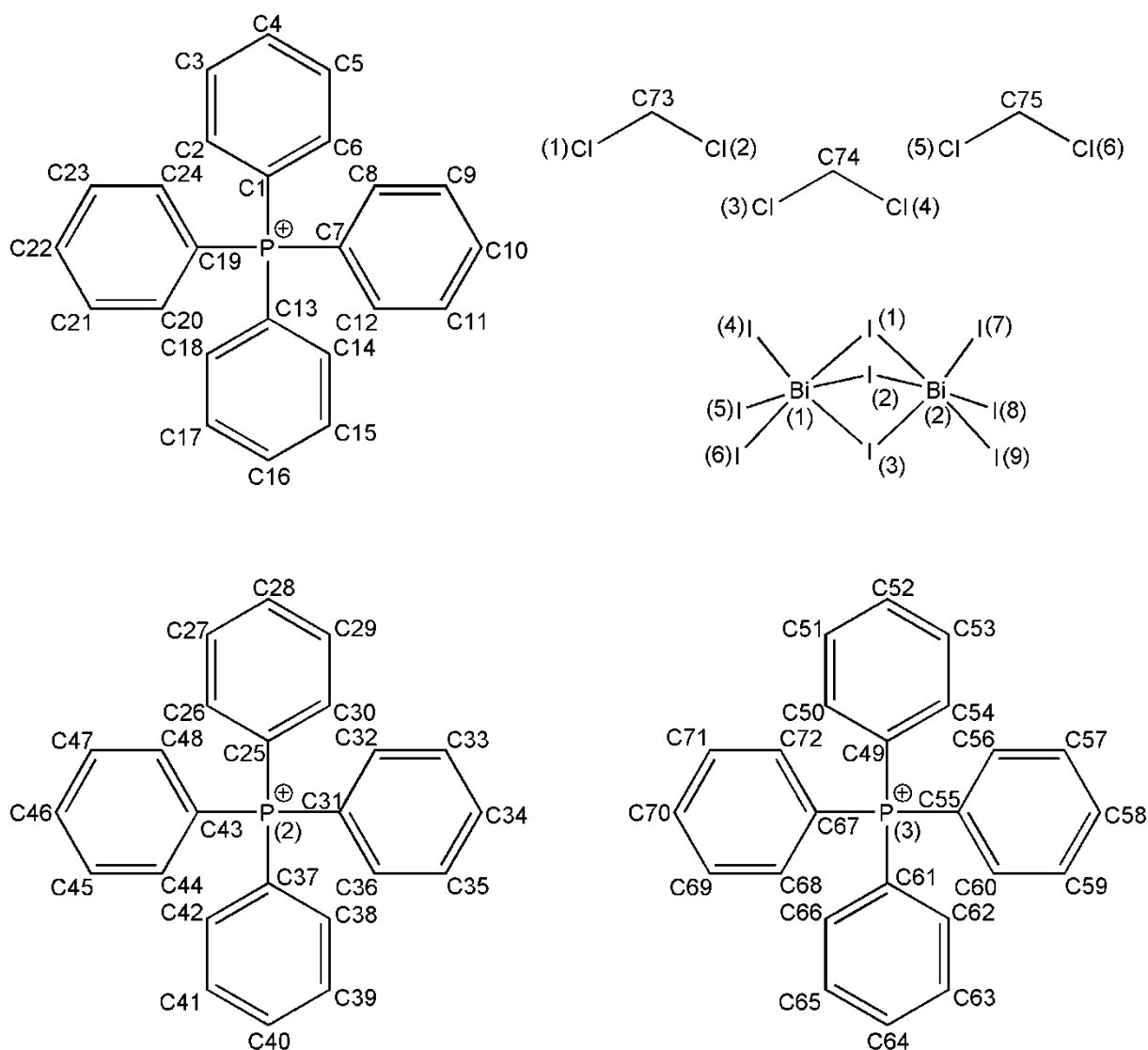


Table S7. Selected bond lengths (Å) angles (°) and torsion angles (°) of $[\text{Ph}_4\text{P}]_3[\text{Bi}_2\text{I}_9] \cdot 3 \text{CH}_2\text{Cl}_2$.

Bi1—I4	2.9427 (2)	I9—Bi2—I2	92.941 (6)
Bi1—I5	2.9858 (2)	I7—Bi2—I2	91.145 (6)
Bi1—I6	2.9921 (2)	I3—Bi2—I2	84.463 (6)
Bi1—I2	3.2187 (2)	I1—Bi2—I2	80.535 (5)
Bi1—I1	3.2276 (2)	Bi1—I1—Bi2	80.981 (5)
Bi1—I3	3.3084 (2)	Bi1—I2—Bi2	81.046 (5)

Bi2—I8	2.9697 (2)	Bi2—I3—Bi1	81.354 (5)
Bi2—I9	2.9929 (2)	I4—Bi1—I1—Bi2	-135.119 (6)
Bi2—I7	3.0123 (2)	I5—Bi1—I1—Bi2	128.779 (6)
Bi2—I3	3.1505 (2)	I6—Bi1—I1—Bi2	-4.26 (4)
Bi2—I1	3.2584 (2)	I2—Bi1—I1—Bi2	-43.304 (5)
Bi2—I2	3.2629 (2)	I3—Bi1—I1—Bi2	40.512 (5)
I4—Bi1—I5	96.072 (7)	I8—Bi2—I1—Bi1	-133.786 (6)
I4—Bi1—I6	91.584 (7)	I9—Bi2—I1—Bi1	-16.40 (3)
I5—Bi1—I6	95.189 (6)	I7—Bi2—I1—Bi1	132.928 (6)
I4—Bi1—I2	92.325 (6)	I3—Bi2—I1—Bi1	-42.763 (5)
I5—Bi1—I2	168.726 (6)	I2—Bi2—I1—Bi1	42.739 (5)
I6—Bi1—I2	92.077 (6)	I4—Bi1—I2—Bi2	136.593 (6)
I4—Bi1—I1	93.673 (6)	I5—Bi1—I2—Bi2	-1.58 (3)
I5—Bi1—I1	90.277 (6)	I6—Bi1—I2—Bi2	-131.736 (6)
I6—Bi1—I1	171.980 (6)	I1—Bi1—I2—Bi2	43.219 (5)
I2—Bi1—I1	81.669 (5)	I3—Bi1—I2—Bi2	-38.870 (5)
I4—Bi1—I3	173.256 (6)	I8—Bi2—I2—Bi1	-23.36 (4)
I5—Bi1—I3	88.330 (6)	I9—Bi2—I2—Bi1	126.426 (6)
I6—Bi1—I3	93.106 (6)	I7—Bi2—I2—Bi1	-138.611 (6)
I2—Bi1—I3	82.670 (6)	I3—Bi2—I2—Bi1	41.048 (5)
I1—Bi1—I3	81.167 (5)	I1—Bi2—I2—Bi1	-42.877 (5)
I8—Bi2—I9	96.091 (7)	I8—Bi2—I3—Bi1	130.913 (6)
I8—Bi2—I7	93.310 (7)	I9—Bi2—I3—Bi1	-133.051 (6)
I9—Bi2—I7	94.896 (6)	I7—Bi2—I3—Bi1	-35.22 (8)
I8—Bi2—I3	90.968 (7)	I1—Bi2—I3—Bi1	41.431 (5)
I9—Bi2—I3	85.690 (6)	I2—Bi2—I3—Bi1	-39.669 (5)
I7—Bi2—I3	175.594 (6)	I4—Bi1—I3—Bi2	-1.81 (6)
I8—Bi2—I1	89.602 (6)	I5—Bi1—I3—Bi2	-132.697 (6)
I9—Bi2—I1	167.529 (6)	I6—Bi1—I3—Bi2	132.194 (6)
I7—Bi2—I1	95.844 (6)	I2—Bi1—I3—Bi2	40.497 (5)
I3—Bi2—I1	83.121 (5)	I1—Bi1—I3—Bi2	-42.158 (5)

I8—Bi2—I2	169.548 (7)		
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Scheme S6. Numbering scheme of tetraphenylphosphonium iodide [Ph₄P]I.

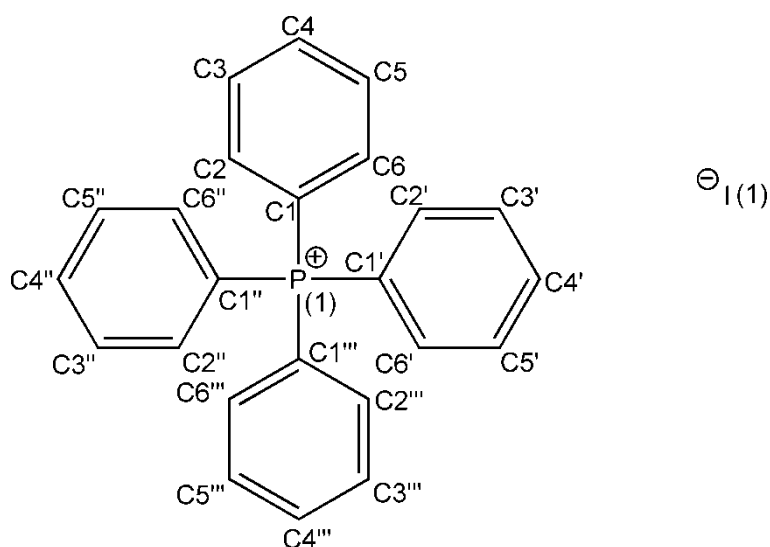


Table S8. Selected bond lengths (Å) angles (°) and torsion angles (°) of [Ph₄P]I.

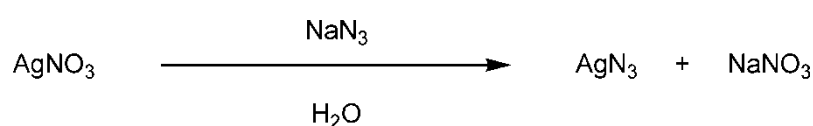
P1—C1	1.7956 (10)	C3—C2—C1	120.02 (11)
C1—C6	1.3982 (15)	C2—C3—C4	119.94 (12)
C1—C2	1.4017 (15)	C1ⁱ—P1—C1—C6	0.13 (10)
C5—C4	1.3838 (19)	C1ⁱⁱ—P1—C1—C6	-120.33 (11)
C5—C6	1.3953 (17)	C1ⁱⁱⁱ—P1—C1—C6	119.21 (12)
C1ⁱ—P1—C1	110.23 (3)	C1ⁱ—P1—C1—C2	178.50 (9)
C1ⁱ—P1—C1ⁱⁱ	110.23 (3)	C1ⁱⁱ—P1—C1—C2	58.04 (8)
C1—P1—C1ⁱⁱ	107.96 (6)	C1ⁱⁱⁱ—P1—C1—C2	-62.42 (7)
C1ⁱ—P1—C1ⁱⁱⁱ	107.96 (6)	C4—C5—C6—C1	2.04 (18)
C1—P1—C1ⁱⁱⁱ	110.23 (3)	C2—C1—C6—C5	-2.19 (17)
C1ⁱⁱ—P1—C1ⁱⁱⁱ	110.23 (3)	P1—C1—C6—C5	176.14 (9)
C6—C1—C2	119.97 (10)	C6—C5—C4—C3	0.4 (2)
C6—C1—P1	122.50 (8)	C6—C1—C2—C3	-0.09 (17)
C2—C1—P1	117.50 (8)	P1—C1—C2—C3	-178.50 (10)
C4—C5—C6	120.71 (11)	C1—C2—C3—C4	2.56 (19)
C5—C6—C1	119.14 (11)	C5—C4—C3—C2	-2.7 (2)
C5—C4—C3	120.13 (11)		

Symmetry codes: (i) $y-1/2, -x+1/2, -z+3/2$; (ii) $-x, -y+1, z$; (iii) $-y+1/2, x+1/2, -z+3/2$.

3. Synthesis of starting materials

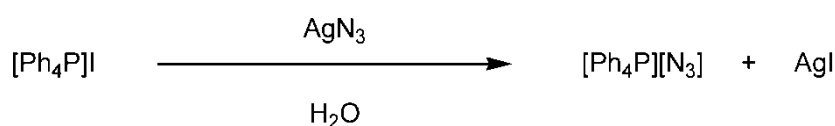
Caution! Covalent azides are potentially hazardous and can decompose explosively under various conditions! Especially $\text{Bi}(\text{N}_3)_3$ of this work is extremely shock-sensitive and can explode violently upon the slightest provocation. Appropriate safety precautions (safety shields, face shields, leather gloves, protective clothing) should be taken when dealing with large quantities.

3.1 Synthesis of silver azide AgN_3



To a stirred solution of sodium azide NaN_3 (0.715g, 11mmol) in water (dest., 50mL) a solution of silver nitrate AgNO_3 (1.689g, 10mmol) in water (dest., 30mL, acidified with one drop of concentrated HNO_3) is added at ambient temperatures under exclusion of light. The solvent is removed by decantation and the resulting colourless precipitate is washed several times with water, ethanol and diethyl ether, and is then divided into small portions. Drying at 70°C in an oven yields silver azide AgN_3 as a colourless solid.

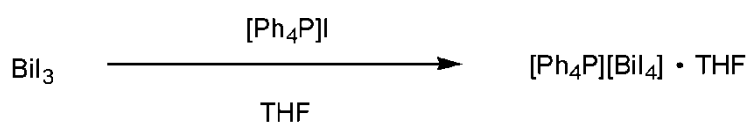
3.2 Synthesis of tetraphenylphosphonium azide $[\text{Ph}_4\text{P}][\text{N}_3]$



To a stirred suspension of tetraphenylphosphonium iodide $[\text{Ph}_4\text{P}]\text{I}$ (2.331g, 5.0mmol) in water (dest., 30mL), silver azide AgN_3 (neat, 0.675g, 4.5mmol) is added at ambient temperatures in one portion under exclusion of light. The resulting yellowish suspension is stirred for two hours and filtered (F4). The solvent is removed by rotary evaporation resulting in a colourless crystalline residue. Drying at 70°C for three hours yields 1.836g (4.815mol, 96%) tetraphenylphosphonium azide $[\text{Ph}_4\text{P}][\text{N}_3]$ as a colourless solid. Anal. calc. % (found): C, 75.58 (75.18); H, 5.29 (5.21); N, 11.02 (11.03). ^{14}N NMR (300 K, CH_2Cl_2 , 36.14 MHz): δ

= -139 (N_{β} , $\Delta\nu_{1/2} = 17$ Hz), -277 ($N_{\alpha/\gamma}$, $\Delta\nu_{1/2} = 44$ Hz). IR (ATR, 32 scans): 3283 (w), 3079 (w), 3047 (w), 3014 (w), 2990 (w), 1993 (s), 1585 (m), 1481 (m), 1433 (s), 1340 (w), 1313 (m), 1185 (m), 1159 (m), 1130 (w), 1104 (s), 1025 (w), 996 (m), 940 (w), 858 (w), 763 (s), 750 (m), 719 (s), 688 (s), 633 (w), 615 (w).

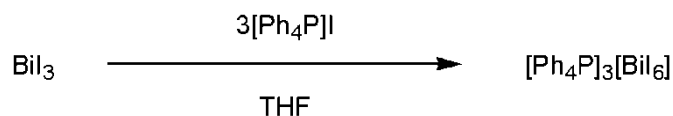
3.8 Synthesis of tetraphenylphosphonium tetraiodobismuthate THF solvate $[\text{Ph}_4\text{P}][\text{BiI}_4] \cdot \text{THF}$



Tetraphenylphosphonium iodide $[\text{Ph}_4\text{P}]\text{I}$ (0.933g, 2.0mmol) and bismuth triiodide BiI_3 (1.297g, 2.2mmol), are combined and dissolved in THF (35mL) at ambient temperatures. The resulting orange suspension is stirred for one hour and is then filtered (F4). The orange residue is washed with hot THF (10mL). Removal of solvent by decantation and drying *in vacuo* yields 2.196g (1.95mmol, 97%) of tetraphenylphosphonium tetraiodobismuthate tetrahydrofuran solvate $[\text{Ph}_4\text{P}][\text{BiI}_4] \cdot \text{THF}$ as an orange microcrystalline solid. Mp 209 °C (109°C loss of THF). Anal. calc. % (found): C, 29.81 (31.85); H, 2.50 (2.50). IR (ATR, 32 scans): 3065 (w), 3051 (w), 3016 (w), 2957 (w), 2941 (w), 2866 (w), 1582 (m), 1480 (m), 1455 (w), 1433 (s), 1393 (w), 1365 (w), 1338 (w), 1310 (m), 1182 (m), 1158 (m), 1130 (w), 1106 (s), 1069 (w), 1037 (m), 1026 (m), 994 (m), 976 (w), 928 (w), 915 (w), 871 (s), 846 (m), 756 (m), 752 (m), 744 (m), 720 (s), 686 (s), 666 (s), 615 (s). Raman (200 mW, 25 °C, 3000 scans, cm^{-1}): = 3291 (1), 3270 (1), 3241 (1), 3202 (1), 3151 (1), 3054 (2), 3019 (1), 2990 (1), 2955 (1), 2926 (1), 2880 (1), 1585 (2), 1573 (1), 1482 (1), 1439 (1), 1367 (1), 1339 (1), 1315 (1), 1275 (1), 1230 (1), 1184 (1), 1163 (1), 1109 (1), 1099 (1), 1026 (2), 1000 (3), 932 (1), 916 (1), 874 (1), 742 (4), 725 (3), 680 (4), 616 (1), 396 (1), 291 (1), 255 (4), 244 (3), 197 (4), 136 (10), 117 (7).

Crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of a saturated THF solution of $[\text{Ph}_4\text{P}][\text{BiI}_4]$ *in vacuo* at ambient temperatures.

3.9 Synthesis of tris-tetraphenylphosphonium hexaiodobismuthate [Ph₄P]₃[BiI₆]



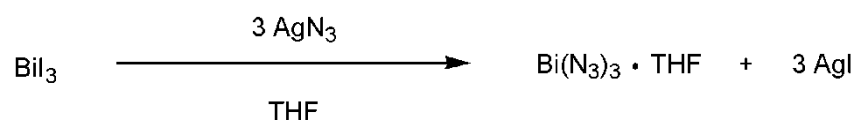
Tetraphenylphosphonium iodide [Ph₄P]I (1.399g, 3.0mmol) and bismuth triiodide BiI₃ (0.590g, 1.0mmol), are combined and dissolved in THF (15mL) at ambient temperatures. The resulting orange suspension is stirred for one hour and is then filtered (F4). The orange residue is washed with hot THF (10mL). Removal of solvent by decantation and drying *in vacuo* yields 1.961g (0.99mmol, 99%) of tris-tetraphenylphosphonium hexaiodobismuthate [Ph₄P]₃[BiI₆] as an orange microcrystalline solid. Mp 236 °C. Anal. calc. % (found): C, 43.49 (43.58); H, 3.04 (2.93). IR (ATR, 32 scans): 3077 (w), 3055 (w), 2854 (w), 1583 (m), 1480 (m), 1433 (s), 1336 (w), 1310 (m), 1186 (m), 1161 (m), 1105 (s), 1067 (w), 1026 (w), 995 (m), 927 (w), 846 (m), 747 (m), 720 (s), 686 (s), 615 (m). Raman (400 mW, 25 °C, 500 scans, cm⁻¹): = 3168 (1), 3142 (1), 3058 (5), 307 (1), 2991 (1), 2910 (1), 1585 (5), 1483 (1), 1439 (1), 1367 (1), 1338 (1), 1312 (1), 1188 (2), 1164 (2), 1099 (2), 1072 (1), 1028 (3), 1002 (6), 934 (1), 846 (1), 747 (1), 724 (1), 680 (2), 616 (1), 527 (1), 391 (1), 293 (1), 254 (2), 197 (2), 129 (10), 110 (10), 90 (7), 68 (5).

Recrystallisation from a saturated dichloromethane solution of [BiI₆][Ph₄P]₃ resulted in the deposition of a mixture of red and colourless crystals. The red crystals were identified as tris-tetraphenylphosphonium nonaiodobismuthate tris dichloromethane solvate [Ph₄P]₃[Bi₂I₉] · CH₂Cl₂, the colourless crystals were identified as tetraphenylphosphonium iodide [Ph₄P]I by X-ray structure determinations.

4. Synthesis of compounds

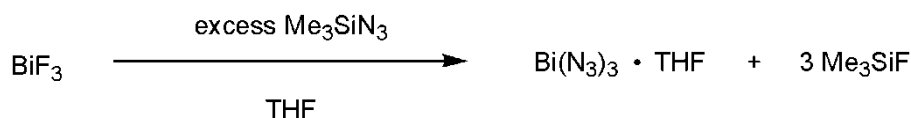
4.1 Synthesis of bismuth triazide tetrahydrofuran solvate $\text{Bi}(\text{N}_3)_3 \cdot \text{THF}$ (1 THF)

Procedure 1



To a stirred solution of bismuth triiodide BiI_3 (0.295g, 0.5mmol) in THF (10mL), silver azide AgN_3 (neat, 0.232g, 1.55mmol) is added in one portion at ambient temperatures. The resulting yellow suspension is stirred for two hours, resulting in an off-white suspension. Removal of solvent and drying *in vacuo* gives a pale brownish residue. The residue is resuspended in THF (15mL) and the resulting suspension is warmed to 50°C. The brownish residue is extracted several times by repeated backdistillation of solvent *in vacuo*. Removal of solvent from the filtrate *in vacuo* gives bismuth triazide THF solvate $\text{Bi}(\text{N}_3)_3 \cdot \text{THF}$ (**1 THF**) as a colourless solid in low yields.

Procedure 2

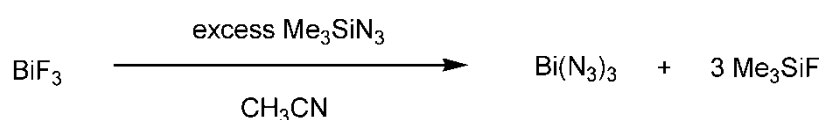


To a stirred suspension of bismuth trifluoride BiF_3 (0.133g, 0.5mmol) in THF (10mL), trimethylsilylazide Me_3SiN_3 (neat, 0.403g, 3.5mmol) is added dropwise at ambient temperatures. The resulting suspension is stirred for fifteen hours, resulting in a pearlescent suspension. Removal of solvent by filtration and drying of the residue *in vacuo* gives bismuth triazide tetrahydrofuran solvate $\text{Bi}(\text{N}_3)_3 \cdot \text{THF}$ (**1 THF**) as a colourless microcrystalline solid in almost quantitative yields.

Mp 248 °C (detonation). Anal. calc. % (found): C, 11.80 (11.06); H, 1.98 (1.65); N, 30.96 (30.41). IR (ATR, 32 scans): 3345 (w), 3282 (w), 2980 (m), 2953 (w), 2931 (w), 2888 (w), 2873 (w), 2108 (s), 2075 (s), 2046 (s), 1455 (w), 1469 (w), 1407 (w), 1318 (s), 1257 (s), 1197

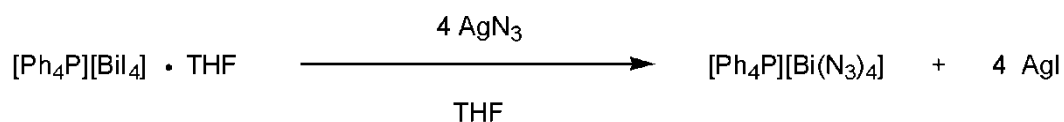
(w), 1180 (m), 1166 (w), 1139 (w), 1027 (s), 958 (w), 913 (m), 879 (m), 866 (s), 831 (m), 665 (w), 644 (s), 592 (m), 578 (m). Raman (100 mW, 25 °C, 3500 scans, cm^{-1}): = 3145 (1), 2983 (2), 2936 (2), 2908 (2), 2756 (2), 2107 (5), 2078 (1), 2043 (10), 1484 (1), 1447 (1), 1370 (1), 1325 (3), 1274 (1), 1183 (1), 1038 (1), 978 (1), 923 (1), 880 (1), 788 (1), 712 (1), 650 (2), 602 (1), 541 (1), 520 (1), 506 (1), 473 (1), 365 (1), 327 (3), 257 (1), 227 (1), 205 (4), 150 (2), 133 (3).

4.2 Synthesis of bismuth triazide $\text{Bi}(\text{N}_3)_3$ (**1**)



To a stirred suspension of bismuth trifluoride BiF_3 (0.133g, 0.5mmol) in acetonitrile (10mL), trimethylsilylazide Me_3SiN_3 (neat, 0.403g, 3.5mmol) is added dropwise at ambient temperatures. The resulting suspension is stirred for five days, resulting in an off-white suspension. Removal of solvent by filtration and drying of the residue *in vacuo* gives bismuth triazide $\text{Bi}(\text{N}_3)_3$ (**1**) as an off-white solid in almost quantitative yields. An attempted elemental analysis resulted in a violent detonation in the apparatus. Mp 154 °C (detonation). IR (ATR, 32 scans): 3354 (w), 3298 (w), 2118 (m), 2094 (m), 2051 (s), 1964 (w), 1325 (m), 1275 (w), 1260 (m), 655 (w) 646 (m), 602 (w), 589 (w), 578 (w). Raman (70 mW, 25 °C, 3 accumulations, cm^{-1}): = 2115 (4), 2084 (1), 2046 (6), 1334 (6), 1280 (3), 655 (4), 608 (3), 395 (4), 341 (10), 294 (5), 275 (6), 231 (6).

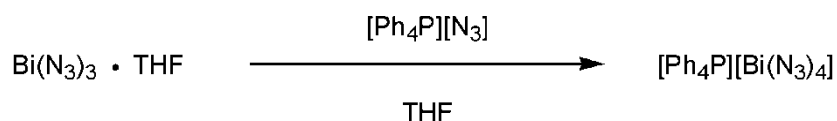
4.3 Synthesis of tetraphenylphosphonium tetraazidobismuthate $[\text{Ph}_4\text{P}][\text{Bi}(\text{N}_3)_4]$ (**2**)



To a stirred suspension of tetraphenylphosphonium tetraiodobismuthate tetrahydrofuran solvate $[\text{Ph}_4\text{P}][\text{BiI}_4] \cdot \text{THF}$ (0.564g, 0.5mmol) in THF (20mL), silver azide AgN_3 (neat, 0.303g, 2.02mmol) is added in one portion at ambient temperatures. The resulting

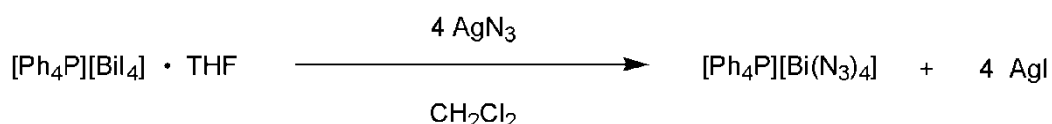
orange suspension is stirred for one hour, resulting in a yellowish suspension. Removal of solvent and drying *in vacuo* gives a yellowish residue. The yellowish residue is resuspended in THF (20mL) and the resulting suspension is warmed to 50°C and filtered. The yellowish residue is extracted several times by repeated backdistillation of solvent *in vacuo*. Removal of solvent from the filtrate *in vacuo* gives tetraphenylphosphonium tetraazidobismuthate $[\text{Ph}_4\text{P}][\text{Bi}(\text{N}_3)_4]$ (**2**) as a yellow microcrystalline solid in almost quantitative yields.

Procedure 2



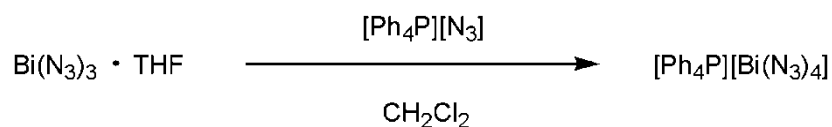
To a stirred suspension of bismuth triazide tetrahydrofuran solvate $\text{Bi}(\text{N}_3)_3 \cdot \text{THF}$ (**1** THF) (0.204g, 0.5mmol) in THF (20mL), tetraphenylphosphonium azide $[\text{Ph}_4\text{P}][\text{N}_3]$ (neat, 0.195g, 0.51mmol) is added in one portion at ambient temperatures. The resulting yellow suspension is stirred for eight hours. Removal of the colourless supernatant by decantation and drying *in vacuo* gives tetraphenylphosphonium tetraazidobismuthate $[\text{Ph}_4\text{P}][\text{Bi}(\text{N}_3)_4]$ (**2**) as a yellow microcrystalline solid in almost quantitative yields.

Procedure 3



To a stirred red solution of tetraphenylphosphonium tetraiodobismuthate tetrahydrofuran solvate $[\text{Ph}_4\text{P}][\text{BiI}_4] \cdot \text{THF}$ (0.564g, 0.5mmol) in dichloromethane (20mL), silver azide AgN_3 (neat, 0.303g, 2.02mmol) is added in one portion at ambient temperatures. The resulting yellow suspension is stirred for one hour and filtered. The yellowish residue is further extracted several times by repeated backdistillation of solvent *in vacuo*. Removal of solvent from the filtrate and short drying *in vacuo* gives tetraphenylphosphonium tetraazidobismuthate dichloromethane solvate $[\text{Ph}_4\text{P}][\text{Bi}(\text{N}_3)_4] \cdot \text{CH}_2\text{Cl}_2$ (**2** CH_2Cl_2) as a yellow microcrystalline solid in almost quantitative yields. The dichloromethane can be completely removed by prolonged drying *in vacuo* at 60°C.

Procedure 4



To a stirred suspension of bismuth triazide tetrahydrofuran solvate $\text{Bi(N}_3)_3 \cdot \text{THF}$ (**1** THF) (0.204g, 0.5mmol) in dichloromethane (20mL), tetraphenylphosphonium azide $[\text{Ph}_4\text{P}][\text{N}_3]$ (neat, 0.195g, 0.51mmol) is added in one portion at ambient temperatures. The resulting yellow suspension is stirred for eight hours, resulting in a yellow suspension. Removal of solvent and short drying *in vacuo* gives tetraphenylphosphonium tetraazidobismuthate dichloromethane solvate $[\text{Ph}_4\text{P}][\text{Bi(N}_3)_4] \cdot \text{CH}_2\text{Cl}_2$ (**2** CH_2Cl_2) as a yellow microcrystalline solid in almost quantitative yields. The dichloromethane can be completely removed by prolonged drying *in vacuo* at 60°C.

The reaction may also be carried out in an analogous manner in acetonitrile as solvent, but due to the good solubility of **2** and remarkable solubility of AgI, purification and crystallisation is more difficult and should be carried out in dichloromethane/*n*-hexane.

$[\text{Ph}_4\text{P}][\text{Bi(N}_3)_4]$ (**2**):

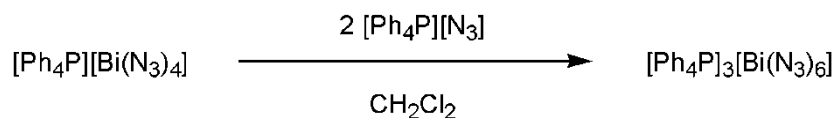
Mp 147 °C (254°C dec.). Anal. calc. % (found): C, 40.23 (39.43); H, 2.81 (2.24); N, 23.46 (22.99). ^{14}N NMR (300 K, CD_3CN , 36.14 MHz): $\delta = -135$ (N_β , $\Delta\nu_{1/2} = 84$ Hz), -252 (N_γ , $\Delta\nu_{1/2} = 380$ Hz). ^{14}N NMR (300 K, $\text{d}_6\text{-DMSO}$, 36.14 MHz): $\delta = -136$ (N_β , $\Delta\nu_{1/2} = 43$ Hz), -253 (N_γ , $\Delta\nu_{1/2} = 480$ Hz). IR (ATR, 32 scans): 3334 (w), 3288 (w), 3271 (w), 3090 (w), 3079 (w), 3055 (w), 3024 (w), 2992 (w), 2056 (m), 2016 (s), 1585 (w), 1574 (w), 1482 (m), 1440 (s), 1434 (s), 1395 (w), 1312 (s), 1275 (m), 1263 (s), 1188 (m), 1160 (m), 1104 (s), 1028 (w), 996 (m), 931 (w), 924 (w), 848 (w), 841 (w), 749 (m), 720 (s), 686 (s), 650 (m), 641 (m), 640 (m), 614 (w), 599 (m). Raman (200 mW, 25 °C, 400 scans, cm^{-1}): = 3172 (1), 3145 (1), 3062 (10), 3009 (1), 2960 (1), 2936 (2), 2909 (2), 2850 (1), 2755 (2), 2087 (6), 2061(1), 2036 (8), 2020 (2), 1587 (6), 1485 (1), 1439 (1), 1326 (3), 1267 (1), 1189 (1), 1164 (1), 1109 (1), 1099 (2), 1028 (4), 1001 (10), 964 (1), 922 (1), 726 (1), 679 (1), 651(1), 642 (1), 616 (1), 455 (2), 339 (4), 320 (2), 289 (2), 263 (1), 252 (1), 222 (1), 206 (1), 191 (1), 166 (1), 149 (1), 126 (4), 105 (9).

Crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of a saturated THF solution of **2** *in vacuo* at ambient temperatures.

[Ph₄P][Bi(N₃)₄] · CH₂Cl₂ (2 CH₂Cl₂): Mp 147 °C (ca. 100°C loss of solvent, 254°C dec.). Anal. calc. % (found): C, 37.47 (37.60); H, 2.77 (2.47); N, 20.97 (21.45). Crystals suitable for X-ray crystallographic analysis were obtained by layering a saturated dichloromethane solution of **2** CH₂Cl₂ with *n*-hexane and storage at ambient temperatures.

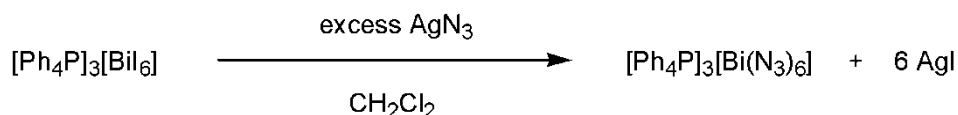
4.4 Synthesis of tris-tetraphenylphosphonium hexaazidobismuthate [Ph₄P]₃[Bi(N₃)₆] (**3**)

Procedure 1



To a stirred solution of tetraphenylphosphonium tetraazidobismuthate [Ph₄P][Bi(N₃)₄] (**2**) (0.358g, 0.5mmol) in dichloromethane (20mL), tetraphenylphosphonium azide [Ph₄P][N₃] (neat, 0.385g, 1.01mmol) is added in one portion at ambient temperatures. The resulting yellow solution is stirred for two hours. The solution is concentrated *in vacuo* to a volume of approximately 5mL and layered with *n*-hexane (2-3mL). Storage at ambient temperatures for two hours results in the deposition of yellow crystals. Removal of the colourless supernatant by decantation and drying *in vacuo* gives tris-tetraphenylphosphonium hexaazidobismuthate [Ph₄P]₃[Bi(N₃)₆] (**3**) as a yellow crystalline solid in almost quantitative yields.

Procedure 2



To a stirred red solution of tris-tetraphenylphosphonium hexaazidobismuthate [Ph₄P]₃[BiI₆] (0.994g, 0.5mmol) in dichloromethane (20mL), silver azide AgN₃ (neat, 0.525g, 3.5mmol) is added in one portion at ambient temperatures. The resulting yellow suspension is stirred for one hour. The solution is filtered (F4) and concentrated *in vacuo* to a volume of approximately 5mL and layered with *n*-hexane (2-3mL). Storage at ambient temperatures for

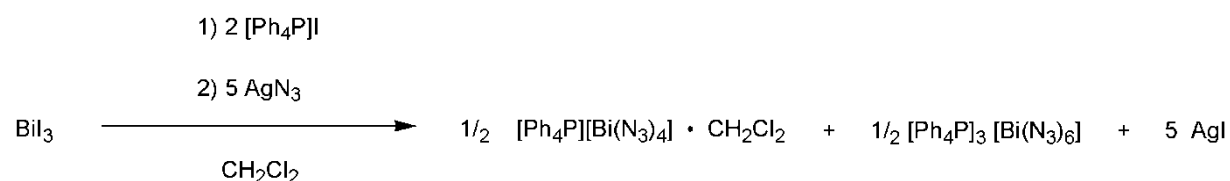
two hours results in the deposition of yellow crystals. Removal of the colourless supernatant by decantation and drying *in vacuo* gives tris-tetraphenylphosphonium hexaazidobismuthate $[\text{Ph}_4\text{P}]_3[\text{Bi}(\text{N}_3)_6]$ (**3**) as a yellow crystalline solid in almost quantitative yields.

The reaction may also be carried out in an analogous manner in acetonitrile as solvent, but due to the good solubility of **3** and remarkable solubility of AgI, purification and crystallisation is more difficult and should be carried out in dichloromethane/*n*-hexane.

Mp 179 °C (285°C dec.). Anal. calc. % (found): C, 58.46 (58.15); H, 4.09 (4.36); N, 17.04 (16.59). ^{14}N NMR (300 K, CD_3CN , 36.14 MHz): $\delta = -134$ (N_β , $\Delta\nu_{1/2} = 100$ Hz), -259 (N_γ , $\Delta\nu_{1/2} = 140$ Hz). ^{14}N NMR (300 K, d_6 -DMSO, 36.14 MHz): $\delta = -134$ (N_β , $\Delta\nu_{1/2} = 42$ Hz), -260 (N_γ , $\Delta\nu_{1/2} = 390$ Hz). ^{14}N NMR (300 K, CD_2Cl_2 , 36.14 MHz): $\delta = -132$ (N_β , $\Delta\nu_{1/2} = 28$ Hz), -257 (N_γ , $\Delta\nu_{1/2} = 250$ Hz). IR (ATR, 32 scans): 3300 (w), 3077 (w), 3056 (w), 2055 (m), 1994 (s), 1583 (m), 1481 (m), 1434 (s), 1312 (s), 1261 (m), 1186 (m), 1162 (m), 1104 (s), 1027 (w), 995 (s), 940 (w), 856 (w), 755 (m), 719 (s), 687 (s), 636 (m), 615 (m). Raman (200 mW, 25 °C, 1904 scans, cm^{-1}): = 3312 (1), 3170 (1), 3144 (1), 3063 (5), 2996 (1), 2909 (2), 2063 (2), 2025 (1), 2007 (1), 1587 (4), 1485 (1), 1441 (1), 1325 (3), 1264(3), 1189 (1), 1166 (1), 1109 (1), 1100 (2), 1030 (3), 1002 (7), 944 (1), 759 (1), 726 (1), 681 (2), 637 (1), 618 (2), 396 (1), 322 (3), 293 (2), 258 (2), 198 (2), 89 (10).

Crystals suitable for X-ray crystallographic analysis were obtained by layering a saturated dichloromethane solution of **3** with *n*-hexane and storage at ambient temperatures.

4.5 Attempted synthesis of bis-tetraphenylphosphonium pentazidobismuthate $[\text{Ph}_4\text{P}]_2[\text{Bi}(\text{N}_3)_5]$

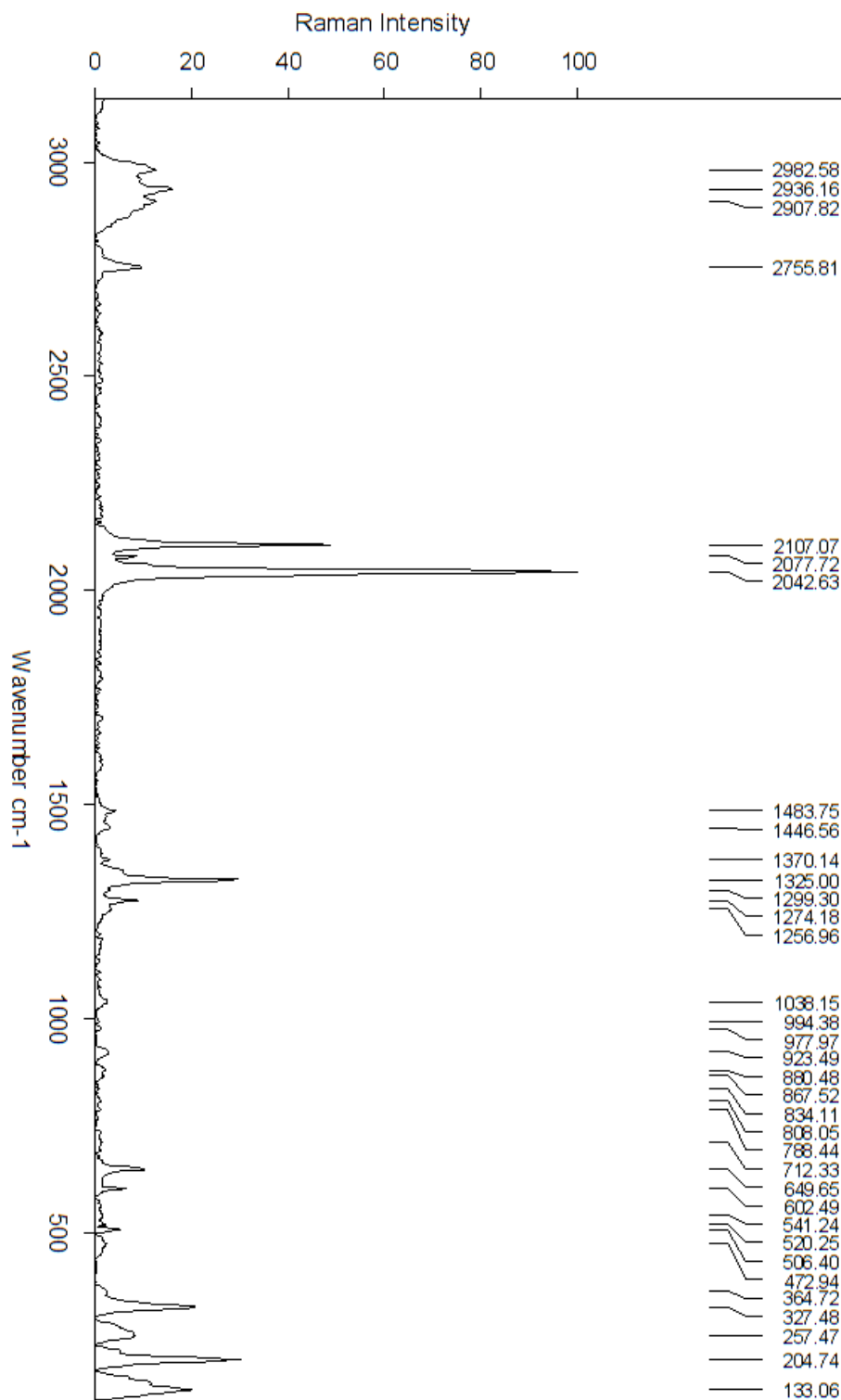


To a stirred solution of tetraphenylphosphonium iodide $[\text{Ph}_4\text{P}]\text{I}$ (0.466g, 1.0mmol) in dichloromethane (20mL), bismuth triiodide BiI_3 (neat, 0.295g, 0.5mmol) is added in one portion at ambient temperatures and the resulting red suspension is refluxed for ten minutes

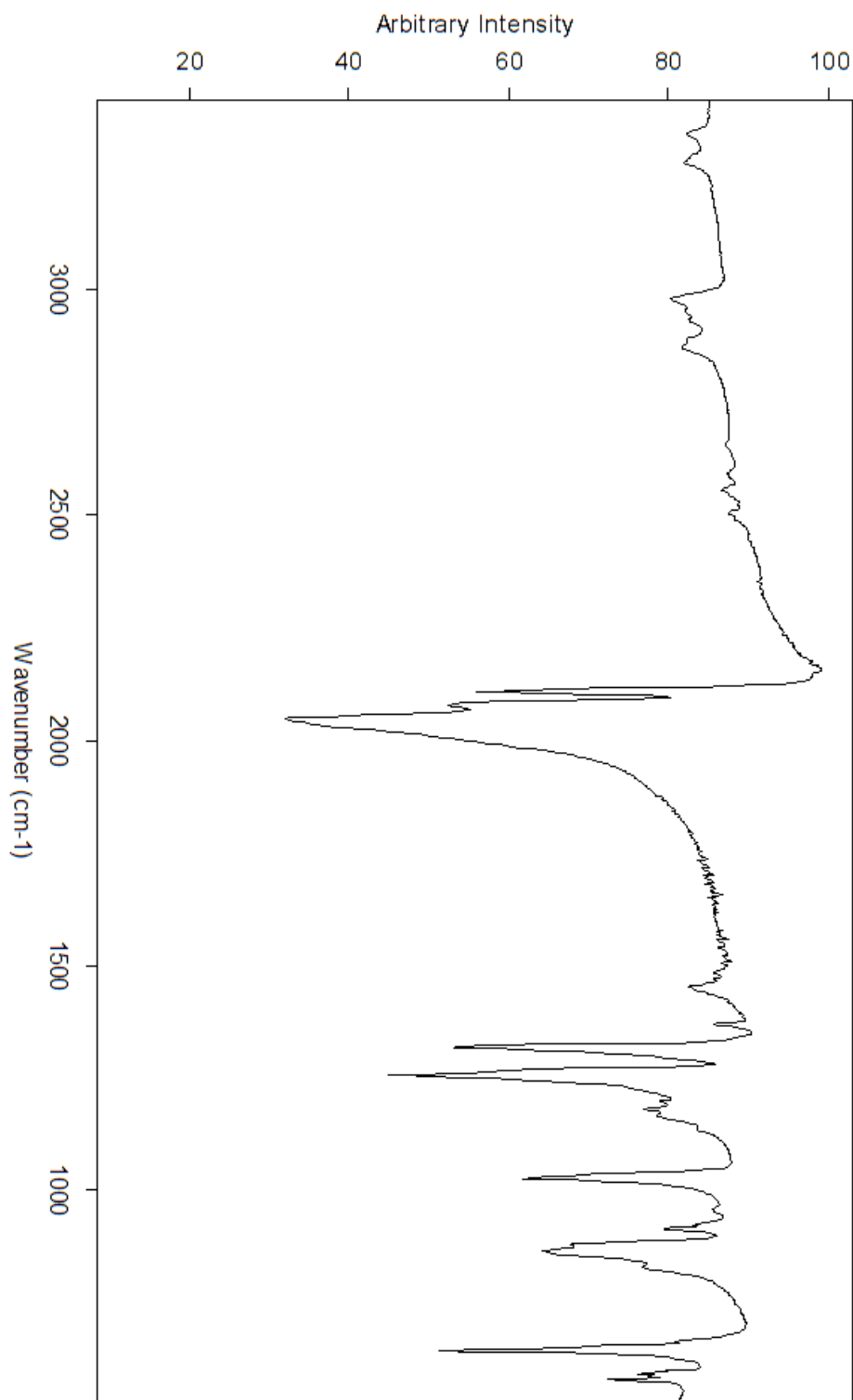
resulting in a clear red solution. The solution is allowed to cool to ambient temperatures, and silver azide AgN_3 (neat, 0.375g, 2.5mmol) is added in one portion at this temperature. The resulting yellow suspension is stirred for 30 minutes and filtered. The yellowish residue is further extracted and washed several times by repeated backdistillation of solvent *in vacuo*. The resulting yellow filtrate is concentrated *in vacuo* to a volume of approximately 5mL and layered with *n*-hexane (2-3mL). Storage at 5°C for one hour results in the deposition of yellow needle-like crystals and a yellow oily supernatant. The crystals could be identified as tetraphenylphosphonium tetraazidobismuthate dichloromethane solvate $[\text{Ph}_4\text{P}][\text{Bi}(\text{N}_3)_4] \cdot \text{CH}_2\text{Cl}_2$ (**2** CH_2Cl_2). Further concentration of the yellow supernatant by slow evaporation of solvent led to the deposition of yellow block-like crystals, which could be identified as tris-tetraphenylphosphonium hexaazidobismuthate $[\text{Ph}_4\text{P}]_3[\text{Bi}(\text{N}_3)_6]$ (**3**).

5. Raman and IR Spectra

5.1.1 Raman spectrum of bismuth triazide tetrahydrofuran solvate $\text{Bi}(\text{N}_3)_3 \cdot \text{THF}$ (1 THF).

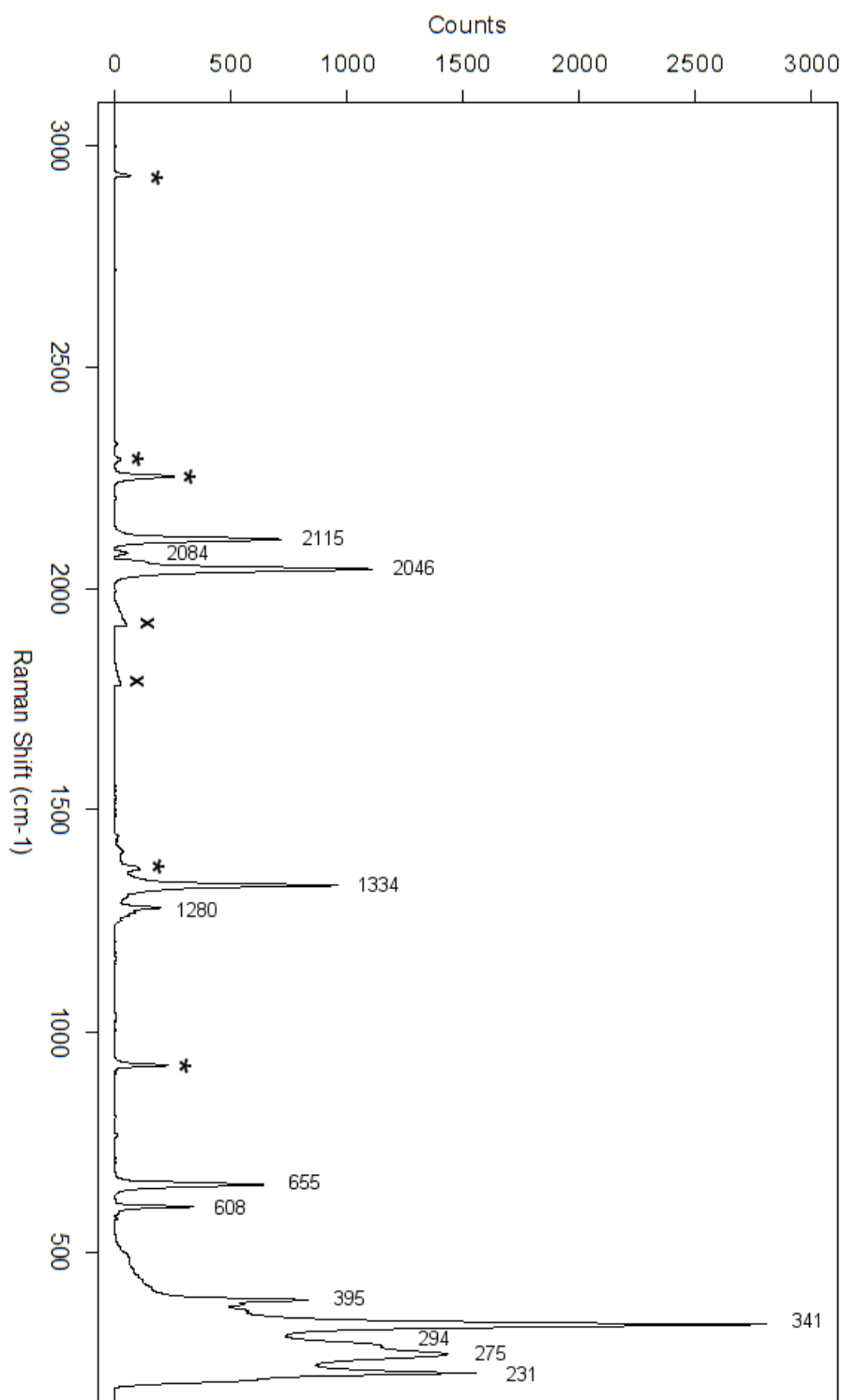


5.1.2 IR spectrum of bismuth triazide tetrahydrofuran solvate $\text{Bi}(\text{N}_3)_3 \cdot \text{THF}$ (1 THF).



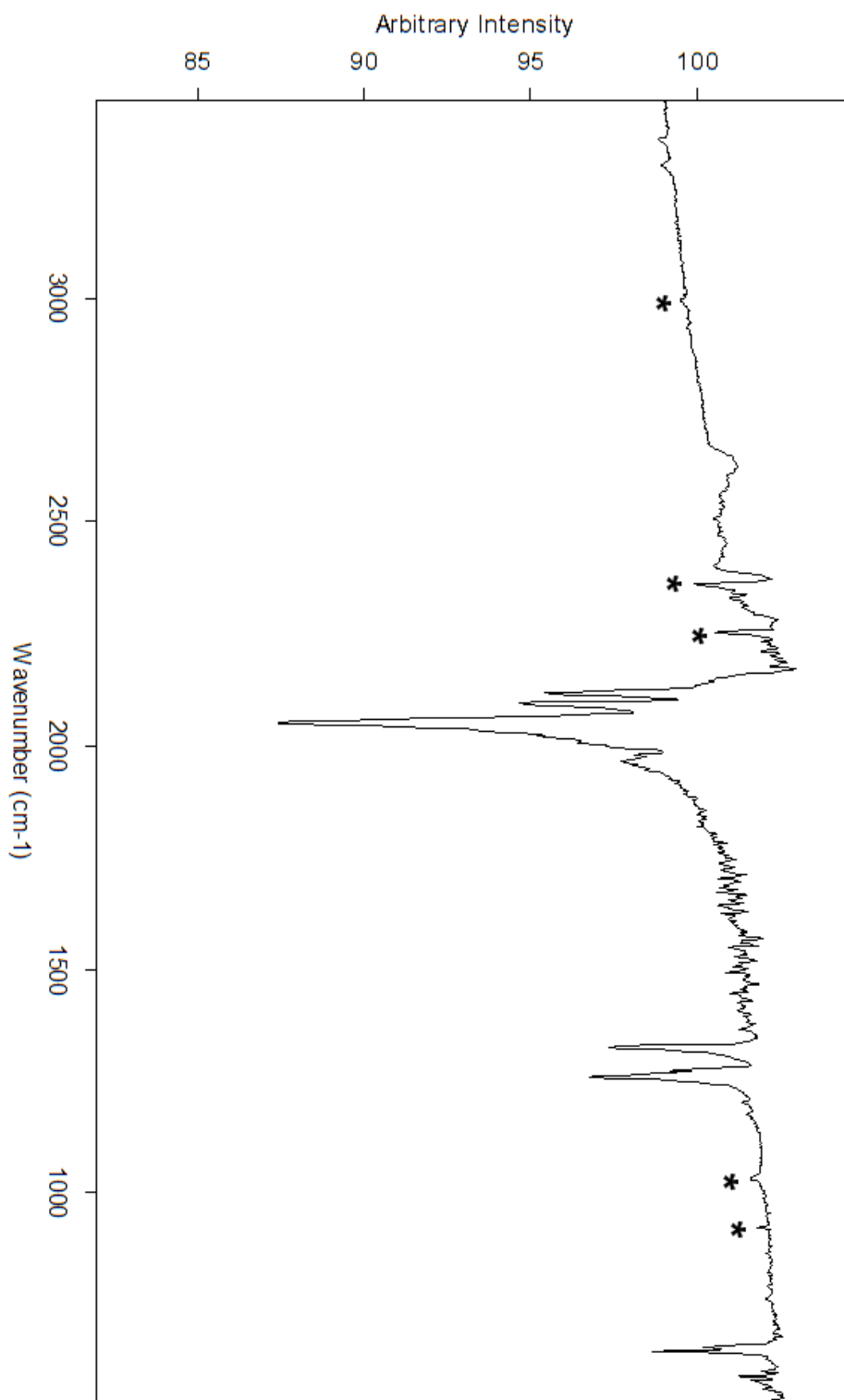
5.2.1 Raman spectrum of bismuth triazide $\text{Bi}(\text{N}_3)_3$ (1).

The compound was moistened with MeCN to prevent thermal decomposition by the raman laser during measurement. Bands belonging to MeCN are marked by an asterisk (*). The bands marked by a cross (x) at 1916 and 1781 cm^{-1} are absorption edges caused by the optical system.



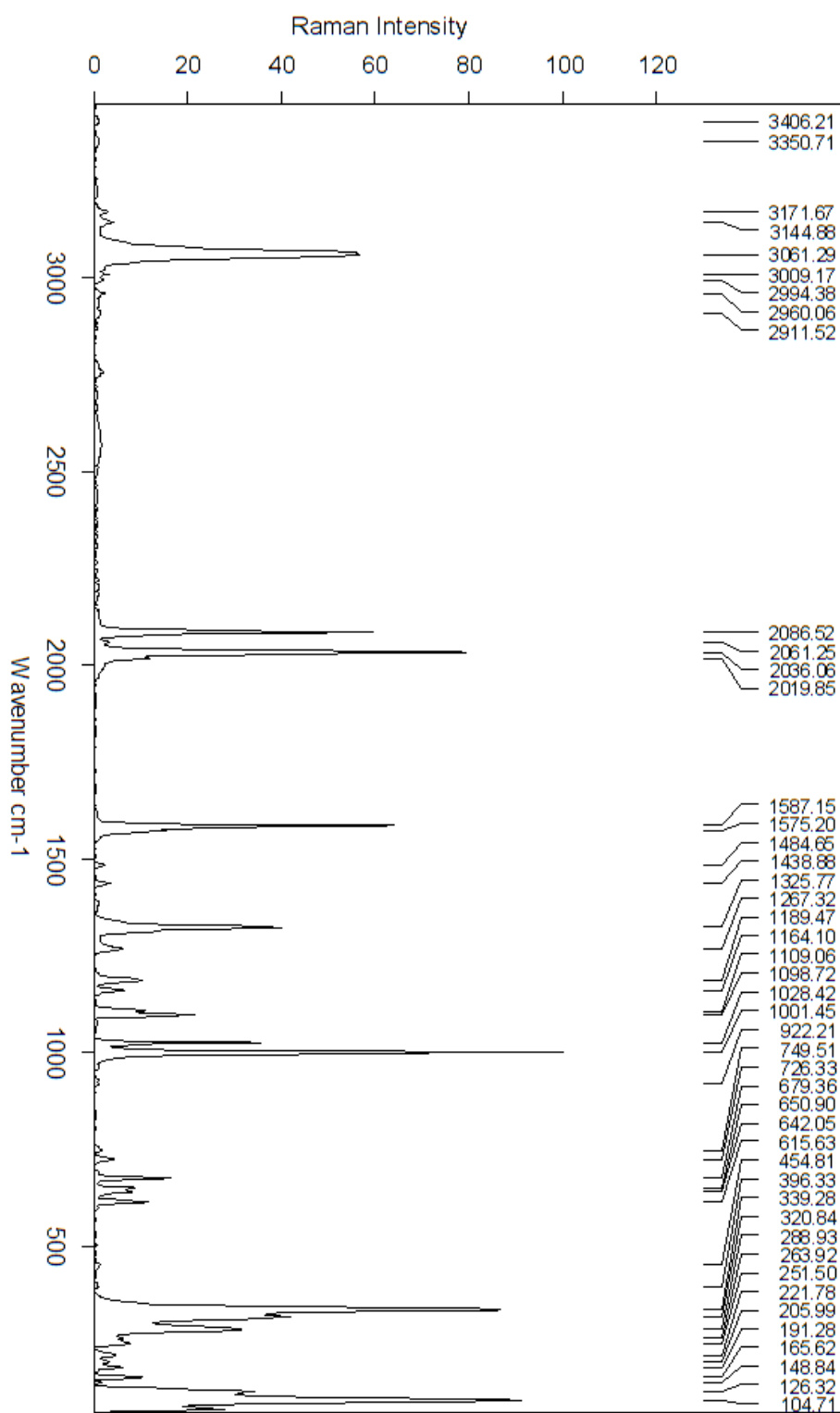
5.2.2 IR spectrum of bismuth triazide $\text{Bi}(\text{N}_3)_3$ (1).

The compound was moistened with MeCN. Bands belonging to MeCN are marked by an asterisk (*).

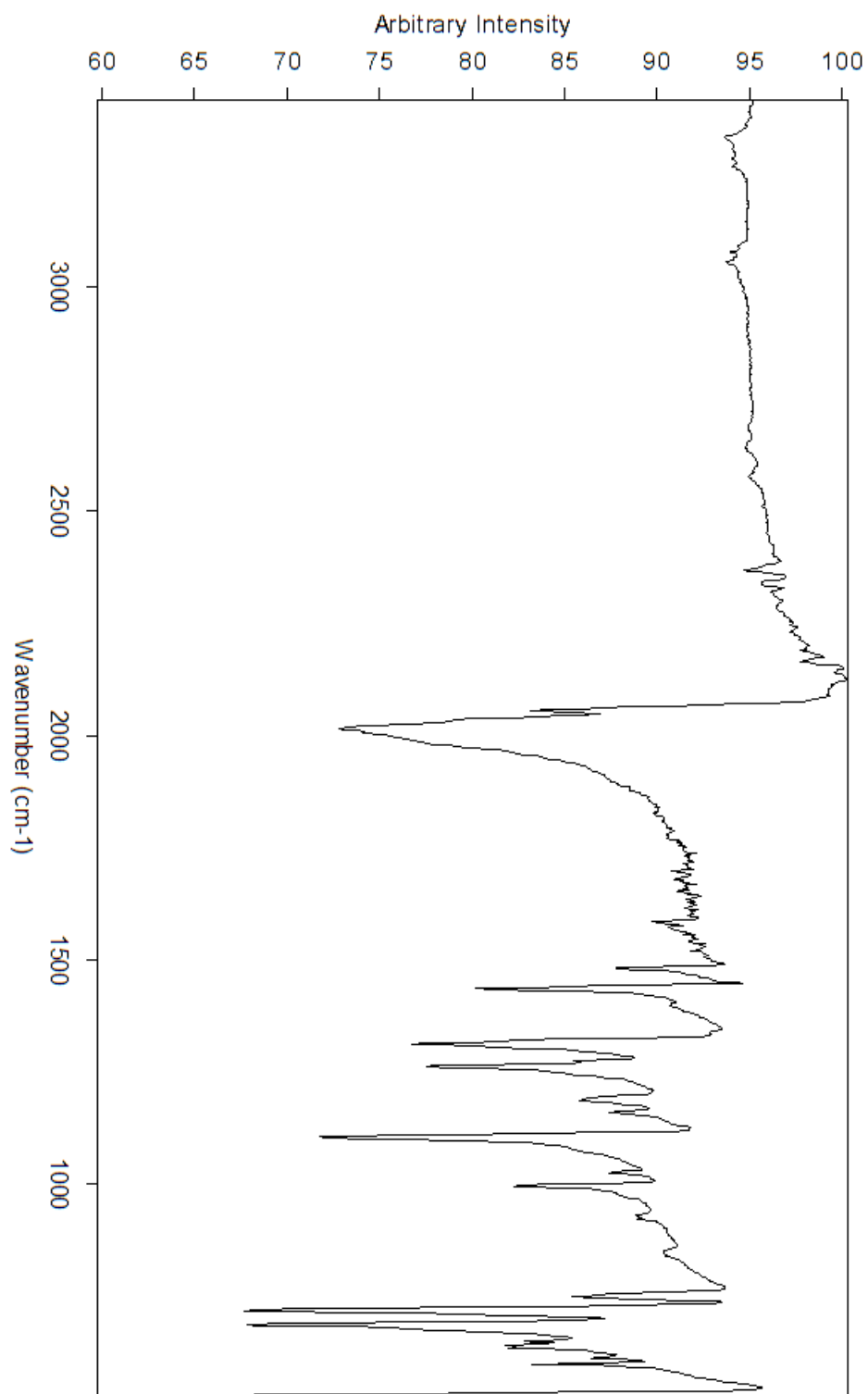


5.3.1 Raman spectrum of tetraphenylphosphonium tetraazidobismuthate [Ph₄P][Bi(N₃)₄]

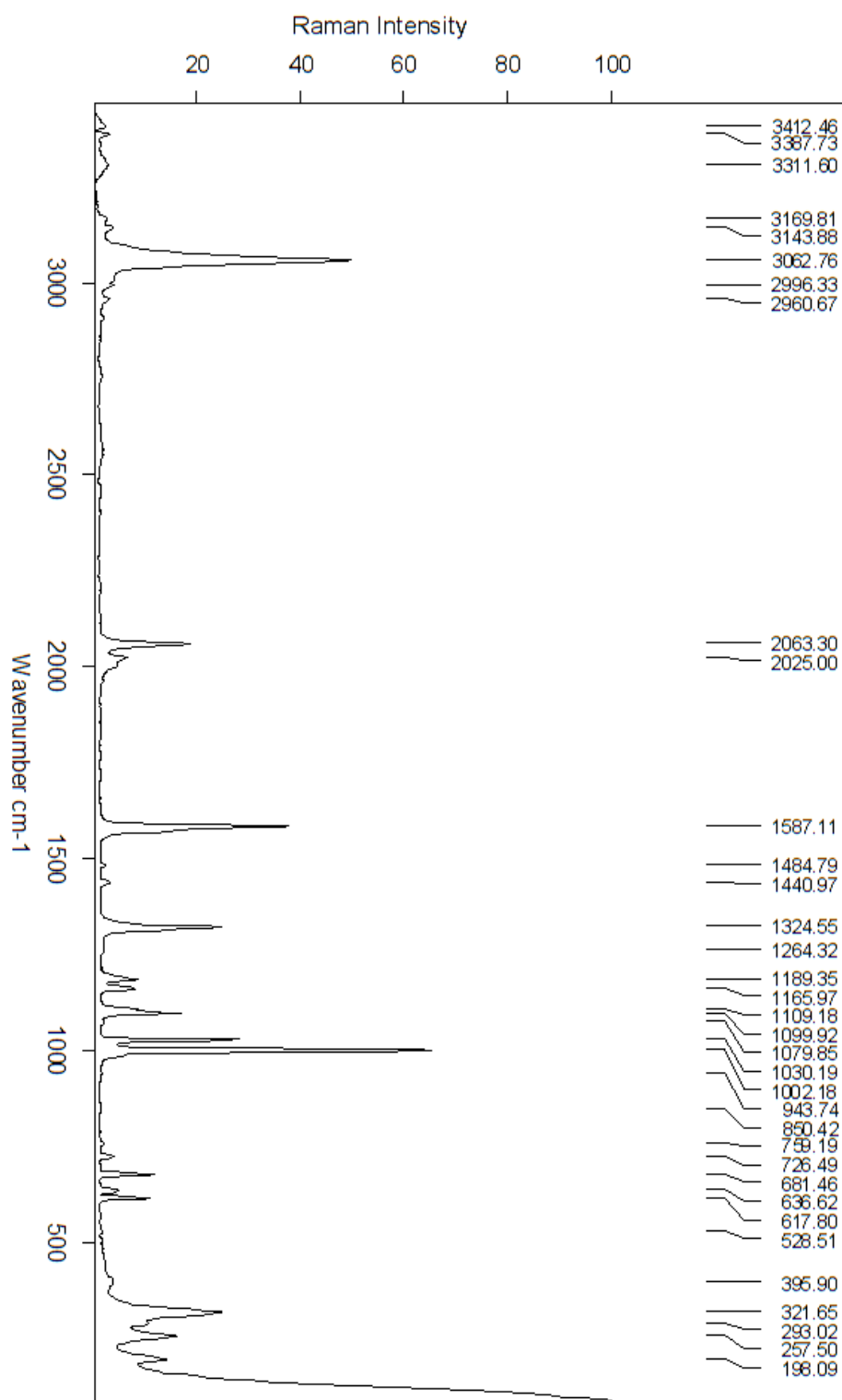
(2)



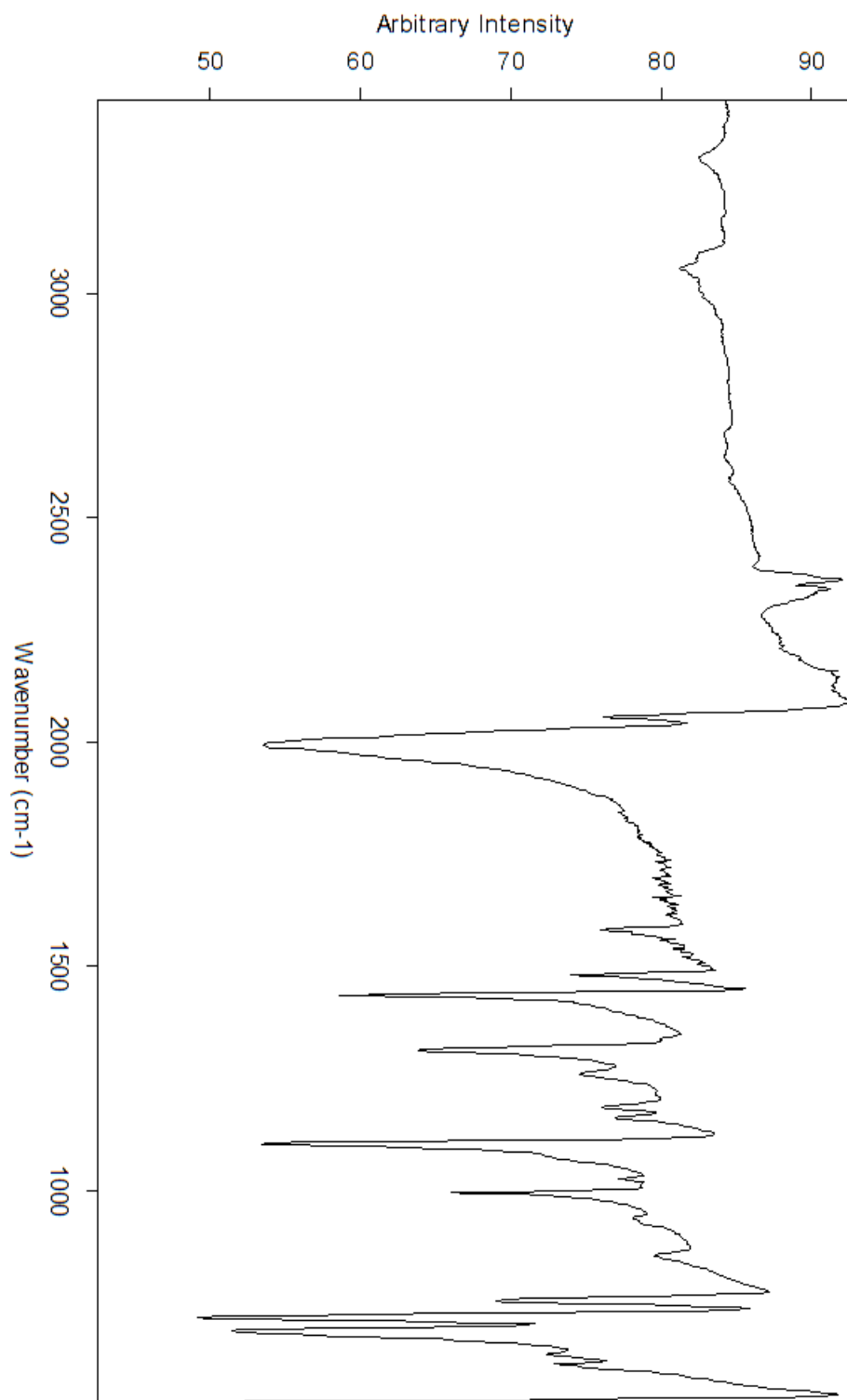
5.3.2 IR spectrum of tetraphenylphosphonium tetraazidobismuthate $[\text{Ph}_4\text{P}][\text{Bi}(\text{N}_3)_4]$ (2)



5.4.1 Raman spectrum of tetraphenylphosphonium hexaazidobismuthate $[\text{Ph}_4\text{P}]_3[\text{Bi}(\text{N}_3)_6]$ (3)



5.4.2 IR spectrum of tetraphenylphosphonium hexaazidobismuthate [Ph₄P]₃[Bi(N₃)₆] (3)



6. Computational details

All computations have been carried out with the G03 program package and the implemented version of the NBO program.^[7,8] For nitrogen a standard 6-31G(d) basis set was used and a quasi-relativistic pseudopotential (ECP78MWB) and a (4s4p1d)/[2s2p1d] basis sets for the Bi. The computations were carried out at the DFT level using the hybrid method B3LYP which includes a mixture of Hartree-Fock exchange with DFT exchange-correlation. Becke's three parameter functional where the non-local correlation is provided by the LYP expression (Lee, Yang, Parr correlation functional) was used which is implemented in Gaussian03. For a concise definition of the B3LYP functional see ref.^[9] The structure of all considered azides was fully optimized and characterized as minima by a frequency analysis.

Atomic charges, natural bond orbitals and the intramolecular donor-acceptor energies were determined using the NBO analysis. Population of Rydberg orbitals is rather small and has not been considered. The NBO analyses were carried out for the Hartree-Fock electron densities.

It should be emphasized that the computation was carried out for a single, isolated (gas-phase) species. There may well be significant differences among gas-phase, solution, and solid-state data.

Table S9. Theoretically obtained and experimentally observed vibrational frequencies along with an approximate assignment for C_3 symmetric **1** in the gas phase.

assignment	Computed frequencies (IR intensity in km/mol)
$\nu_{\text{NN,as,ip}}$	2256(743)
$\nu_{\text{NN,as,op}}$	2227(495)
$\nu_{\text{NN,s,ip}}$	1333(168)
$\nu_{\text{NN,s,op}}$	1320.6(137)
δ_{NNN}	640(9)
δ_{NNN}	589(8)
$\nu_{\text{Bi-N,ip}}$	413(6)
$\nu_{\text{Bi-N,op}}$	384(58)
δ_{BiNNN}	211(22)
δ_{BiNNN}	175(6)
δ_{NBiN}	72(1)
δ_{NBiN}	70(1)
δ_{BiNNN}	38(0)
δ_{BiNNN}	32(0)

ip = in phase

op = out of phase

Table S10. Theoretically obtained and experimentally observed vibrational frequencies along with an approximate assignment for C_2 symmetric **2** in the gas phase.

assignment	Computed frequencies (IR intensity in km/mol)
$\nu_{NN,as,ip}$	2232(515)
$\nu_{NN,as,op}$	2212(1830)
$\nu_{NN,as,op}$	2205(1)
$\nu_{NN,as,op}$	2198(1207)
$\nu_{NN,s,ip,axial}$	1380(25)
$\nu_{NN,s,op,axial}$	1372(223)
$\nu_{NN,s,ip,equatorial}$	1350(34)
$\nu_{NN,s,op,equatorial}$	1347(197)
δ_{NNN}	659(3),558(13),655(30),653(10), 625(12), 613(11),612(8),
$\nu_{Bi-N,ip,equatorial}$	373(9)
$\nu_{Bi-N,op,equatorial}$	352(81)
$\nu_{Bi-N,ip,axial}$	309(2)
$\nu_{Bi-N,op,axial}$	297(203)
δ_{BiNNN}	196(45)
δ_{BiNNN}	185(14)
δ_{NBiN}	166(9)
δ_{NBiN}	132(20)
δ_{BiNNN}	104(0),98(2),95(0),58(0),49(2),42(1), 35(2),32(1),23(1)

ip = in phase

op = out of phase

Table S11. Theoretically obtained and experimentally observed vibrational frequencies along with an approximate assignment for C_1 symmetric **3** in the gas phase.

assignment	Computed frequencies (IR intensity in km/mol)
$\nu_{\text{NN,as,ip}}$	2214(0)
$\nu_{\text{NN,as,op}}$	2178(0),2178(0),2174(2791),2174(2744),2173(3001),
$\nu_{\text{NN,s,ip}}$	1394(0)
$\nu_{\text{NN,s,op}}$	1393(0),1393(0),1390(89),1390(79),1390(78)
δ_{NNN}	658(35),658(35),657(2),657(0),656(0),656(0),655(0),641(0),641(57), 640(14),640(15),640(0),639(0)
$\nu_{\text{Bi-N,ip}}$	271(0)
$\nu_{\text{Bi-N,op}}$	223(0),222(0),222(233),221(232),216(261),
δ_{BiNNN}	120(0),119(48),
δ_{NBiN}	105(0),100(57),100(57),
δ_{BiNNN}	82(0),69(30),59(17),58(17),51(0),50(0),22(6),22(6),19(0),18(0), 16(0),14(0)12(1),10(1),

ip = in phase

op = out of phase

Summary of NBO-Analysis

Compound 1

Summary of Natural Population Analysis:

Natural Population						
Natural -----						
Atom No	Charge	Core	Valence	Rydberg	Total	

Bi 1	1.69581	78.00000	3.29301	0.01118	81.30419	
N 2	-0.70777	1.99951	5.68361	0.02464	7.70777	
N 3	-0.70777	1.99951	5.68361	0.02464	7.70777	
N 4	0.22064	1.99937	4.74965	0.03034	6.77936	
N 5	0.22064	1.99937	4.74965	0.03034	6.77936	
N 6	-0.07814	1.99961	5.05293	0.02560	7.07814	
N 7	-0.07814	1.99961	5.05293	0.02560	7.07814	
N 8	0.22064	1.99937	4.74965	0.03034	6.77936	
N 9	-0.07814	1.99961	5.05293	0.02560	7.07814	
N 10	-0.70777	1.99951	5.68361	0.02464	7.70777	
=====						
* Total *	0.00000	95.99550	49.75157	0.25293	146.00000	

(Occupancy) Bond orbital/ Coefficients/ Hybrids

1. (1.74293) BD (1)Bi 1 - N 2

(19.73%) 0.4442*Bi 1 s(4.16%)p23.01(95.74%)d 0.02(0.10%)

-0.2030 -0.0205 0.1254 0.0080 -0.8043

0.0549 0.5398 0.0145 0.0073 -0.0100

-0.0129 -0.0244 -0.0087

(80.27%) 0.8959* N 2 s(4.19%)p22.86(95.70%)d 0.03(0.12%)

0.0010 -0.2041 0.0147 0.2061 -0.0198

0.9230 -0.0216 -0.2479 -0.0168 -0.0246

-0.0068 -0.0157 0.0087 0.0142

25. (1.97396) LP (1)Bi 1 s(87.64%)p 0.14(12.36%)d 0.00(0.00%)

0.9361 -0.0043 0.0000 0.0000 0.0000

0.0000 0.3515 0.0084 0.0000 0.0000

0.0000 0.0000 -0.0009

Compound 2

Summary of Natural Population Analysis:

Natural Population						
Natural -----						
Atom No	Charge	Core	Valence	Rydberg	Total	
N 1	-0.70364	1.99953	5.67704	0.02707	7.70364	
N 2	-0.17881	1.99961	5.15341	0.02579	7.17881	
N 3	-0.70364	1.99953	5.67704	0.02707	7.70364	
N 4	0.22288	1.99938	4.74689	0.03085	6.77712	
N 5	0.22397	1.99938	4.74564	0.03101	6.77603	
N 6	-0.25150	1.99961	5.22675	0.02514	7.25150	
N 7	-0.66870	1.99952	5.64375	0.02543	7.66870	
N 8	0.22291	1.99938	4.74686	0.03085	6.77709	
N 9	-0.25151	1.99961	5.22676	0.02514	7.25151	
N 10	-0.66870	1.99952	5.64375	0.02543	7.66870	
N 11	0.22399	1.99938	4.74563	0.03101	6.77601	
N 12	-0.17877	1.99961	5.15337	0.02579	7.17877	
Bi 13	1.71151	78.00000	3.27740	0.01109	81.28849	
=====						
* Total *	-1.00000	101.99406	65.66430	0.34165	168.00000	

(Occupancy) Bond orbital/ Coefficients/ Hybrids

2. (1.57059) BD (1) N 1 -Bi 13

(92.15%) 0.9599* N 1 s(1.13%)p87.12(98.75%)d 0.11(0.12%)

0.0009 -0.1053 0.0157 0.8832 -0.0177

-0.2521 0.0112 -0.3785 0.0152 0.0150

0.0159 -0.0201 0.0127 -0.0127

(7.85%) 0.2802*Bi 13 s(2.85%)p29.91(85.18%)d 4.20(11.97%)

-0.1682 -0.0134 -0.6979 -0.0411 -0.1053

0.0056 -0.3837 0.4524 -0.1532 -0.0136

0.0010 0.2839 -0.1244

12. (1.65443) BD (1) N 7 -Bi 13

(84.92%) 0.9215* N 7 s(3.35%)p28.78(96.53%)d 0.04(0.12%)

0.0011 -0.1828 0.0102 0.3323 -0.0263

0.7922 -0.0165 0.4756 -0.0074 -0.0262

-0.0104 -0.0002 -0.0145 0.0136

(15.08%) 0.3883*Bi 13 s(2.97%)p30.34(90.00%)d 2.37(7.04%)

-0.1710 -0.0209 0.1051 -0.0041 -0.6974

-0.0453 -0.5440 -0.3233 0.1147 0.0105

0.0188 -0.2186 0.0947

45. (1.95756) LP (1)Bi 13 s(88.49%)p 0.13(11.43%)d 0.00(0.09%)

0.9407 -0.0041 0.0000 0.0000 0.0001

0.0000 -0.3353 0.0427 -0.0129 0.0000

0.0000 0.0245 -0.0105

Compound 3

Summary of Natural Population Analysis:

Natural Population						
Natural -----						
Atom No	Charge	Core	Valence	Rydberg	Total	
Bi	1	1.89853	78.00000	3.08761	0.01387	81.10147
N	2	-0.60663	1.99952	5.57904	0.02806	7.60663
N	3	-0.60217	1.99952	5.57470	0.02795	7.60217
N	4	-0.60796	1.99952	5.58037	0.02807	7.60796
N	5	-0.60195	1.99952	5.57447	0.02796	7.60195
N	6	-0.60445	1.99952	5.57690	0.02803	7.60445
N	7	-0.59639	1.99952	5.56866	0.02820	7.59639
N	8	0.21502	1.99940	4.75522	0.03035	6.78498
N	9	0.21305	1.99940	4.75725	0.03030	6.78695
N	10	0.21570	1.99940	4.75458	0.03033	6.78430
N	11	0.21258	1.99940	4.75774	0.03028	6.78742
N	12	0.21395	1.99940	4.75637	0.03028	6.78605
N	13	0.21038	1.99941	4.75998	0.03024	6.78962
N	14	-0.42319	1.99962	5.39835	0.02522	7.42319
N	15	-0.42693	1.99962	5.40205	0.02526	7.42693
N	16	-0.42202	1.99962	5.39720	0.02520	7.42202
N	17	-0.42833	1.99962	5.40346	0.02524	7.42833
N	18	-0.42142	1.99962	5.39654	0.02526	7.42142
N	19	-0.43777	1.99962	5.41292	0.02523	7.43777
=====						
* Total *	-3.00000	113.99126	97.49340	0.51534	212.00000	

(Occupancy) Bond orbital/ Coefficients/ Hybrids

1. (1.97928) BD (1)Bi 1 - N 3

(6.71%) 0.2591*Bi 1 s(0.05%)p99.99(99.94%)d 0.17(0.01%)

0.0101 -0.0211 -0.0270 0.0004 -0.6786

0.0358 -0.7319 0.0360 0.0035 0.0048

0.0027 0.0022 0.0066

(93.29%) 0.9659* N 3 s(66.64%)p 0.50(33.35%)d 0.00(0.01%)

-0.0005 0.8159 -0.0254 -0.1700 -0.0012

0.5461 -0.0107 0.0776 -0.0150 0.0057

-0.0001 0.0065 0.0039 0.0072

46. (1.94691) LP (1)Bi 1 s(99.95%)p 0.00(0.05%)d 0.00(0.00%)

0.9997 0.0005 0.0006 0.0007 0.0219

-0.0002 -0.0065 -0.0005 -0.0016 0.0003

-0.0009 0.0000 0.0016

7. References

- [1] C. B. Fischer, S. Xu, H. Zipse, *Chem. Eur. J.* **2006**, *12*, 5779.
- [2] a) R. Haiges, J. A. Boatz, T. Schroer, M. Yousufuddin, K. O. Christe, *Angew. Chem.* **2006**, *118*, 4948–4953; b) R. Haiges, T. Schroer, M. Yousufuddin, K. O. Christe, *Z. Anorg. Allg. Chem.* **2005**, *631*, 2691–2695. c) B. Neumüller, F. Schmock, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1243–1245.
- [3] H. Krautscheid, *Z. anorg. allg. Chem.* **1999**, *625*, 192–194.
- [4] G. M. Sheldrick: SHELXS-97: Program for the Solution of Crystal Structures, University of Göttingen, Germany 1997.
- [5] G. M. Sheldrick: SHELXL-97: Program for the Refinement of Crystal Structures, University of Göttingen, Germany 1997.
- [6] G. M. Sheldrick: SADABS. Version 2. University of Göttingen, Germany 2004.
- [7] Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

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- [8] a) E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, F. *NBO Version 3.1*; b) J. E. Carpenter, F. Weinhold, *J. Mol. Struct. (Theochem)* **1988**, 169, 41–62; c) F. Weinhold, J. E. Carpenter, *The Structure of Small Molecules and Ions*, Plenum Press, **1988**, 227; d) F. Weinhold, C. Landis, *Valency and Bonding. A Natural Bond Orbital Donor-Acceptor Perspective*, Cambridge University Press, **2005** and references therein.
- [9] a) C. W. Bauschlicher, H. Partridge, *Chem. Phys. Lett.*, **1994**, 231, 277; b) A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648; c) A. D. Becke, *Phys. Rev. A*, **1988**, 38, 3098; d) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, **1988**, 37, 785; e) S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, 58, 1200.