Syntheses and crystal structures of azafulleroid and aziridinofullerene bearing silyl or germyl benzene

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ABSTRACT

Addition of silyl and germylmethyl azides (**1**) to fullerene C_{60} at 50 °C through [2+3] cycloaddition led to the formation of the triazoline adducts (**2**). Subsequently, heating **2** at 100 °C in the solid state, caused N_2 extrusion producing two different isomers, [5,6]-azafulleroid (**3**) and [6,6]-aziridinofullerene (**4**). The ^{13}C NMR spectrum of **3** had an absence of resonances in the aliphatic region for the fullerene C_{60} cage, showing a fulleroid with C_S symmetry. In contrast, **4** exhibited one sp^3 resonance in the aliphatic region for the fullerene C_{60} cage, indicative of an aziridinofullerene with C_{2V} symmetry. However, MALDI-TOF mass characterization was hampered because ion peaks corresponding to the bis-adduct are detected in positive ion mode measurements, whereas the ion peaks [M−N$_2$]$^-$ for **2a** as well as [M]$^-$ for **3a** and **4a** are observed in negative ion measurements. In an effort to obtain X-ray data, silyl and germylphenyl groups were introduced to form intermolecular complexes with fullerene C_{60}. The X-ray structures of **3c** and **3d** revealed a strong enhancement of homoconjugation in the bridged annulene moiety based on POAV analysis. The X-ray structures of **3c,d** and **4c** were confirmed with the detection of silyl and germylphenyl-C_{60} interactions, similar to dimethoxyphenyl-C_{60} interactions.

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1. Introduction

Among the various fullerenes and fullerene derivatives, only a limited number of X-ray structures have been reported. Crystals of fullerenes and many chemically modified fullerenes suitable for X-ray diffraction studies have been difficult to obtain due to poor crystal quality and high symmetry. In order to synthesize acceptable crystalline compounds, cocrystallization with porphyrin, benzene and other such compounds has been important [1]. Another method involves, appending a bulky metal complex to the fullerene or inclusion into bowl-shaped molecules such as cyclodextrin, calixarene and cyclotriveratrylene which lowers the symmetry and can also produce ordered structures [2]. Of note is the fact that some of the methoxybenzenes and benzylether fullerene derivatives showed interesting intermolecular donor–acceptor interactions, that is, close contact between the methoxybenzene or benzylether and a neighboring C_{60}, thus forming a chain of interacting fullerene cages in the crystal. To further evaluate this, the structures of cycloadducts, methanofullerenes and endohedral methallofullerenes were successfully characterized [3]. It was found that the silyl and germyl derivatives of fullerenes formed intermolecular complexes, enabling the structures of silyl- and germylphenyl-substituted azafulleroid and aziridinofullerene to be characterized by X-ray analysis [4].

2. Results and discussion

A mixture of fullerene C_{60} and trimethylsilylmethylazide (**1a**) in *o*-dichlorobenzene (ODCB) was heated at 50 °C for 6 h to give a dark brown solid triazoline adduct (**2a**) in 28% yield, as shown in Scheme 1. The ^{13}C NMR spectrum of **2a** exhibited the presence of 2 sp^3 resonances for the fullerene C_{60} cage, indicative of a methanofullerene, i.e., the triazoline derivative with C_S symmetry. Subsequently heating **2a** at 100 °C for 33 h in the solid state produced a mixture of the corresponding [5,6]-azafulleroid (**3a**) and [6,6]-aziridinofullerene (**4a**). The isomers were separated by column chromatography (silica gel: CS$_2$) to give dark brown solid **3a** in 19% yield, and **4a** in 1% yield, with 33% of the C_{60} recovered. The ^{13}C NMR spectrum of **3a** had an absence of resonances in the aliphatic region for the C_{60} cage, typical of a fulleroid with C_S symmetry. In contrast, **4a** exhibited one sp^3 resonance in the aliphatic region for the C_{60} cage, indicative of a methanofullerene with C_{2V} symmetry (see Fig. 1). Moreover, heating of either **2a** or **3a** at 170 °C in ODCB affords **4a**.

These chemical correlations and the symmetries of the products based on the ^{13}C NMR data are consistent with the reported reaction: [2+3] addition of azide followed by loss of N$_2$ producing two different isomers, the azafulleroid and aziridinofullerene [5]. However, MALDI-TOF mass characterization is hampered because the ion peaks corresponding to the bis-adduct are detected in positive ion mode measurements, whereas the ion peaks [M−N$_2$]$^-$ for **2a** as well as [M]$^-$ for **3a** and **4a** are observed in negative ion

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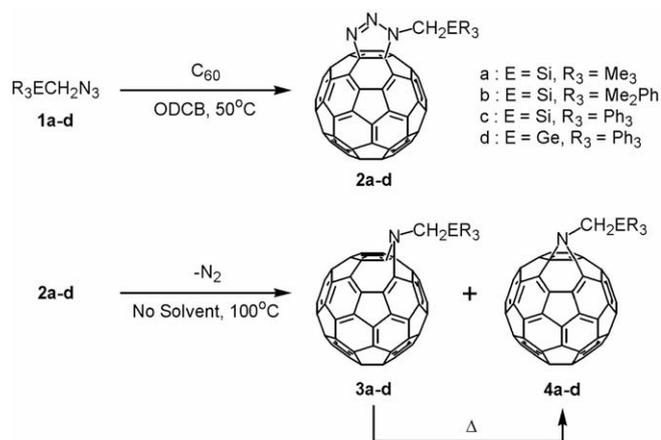
Scheme 1. Syntheses of azafulleroid **3** and aziridinofullerene **4**.

measurement, as shown in Fig. 2. In an effort to obtain X-ray data, silyl and germylphenyl groups were introduced, forming intermolecular complexes with C_{60}, similar to methoxybenzene derivatives. Instead of trimethylsilylmethylazide (**1a**), dimethylphenylsilylmethylazide (**1b**), triphenylsilylmethylazide (**1c**) and triphenylgermylmethylazide (**1d**) were employed, affording three adducts, **2b–d** (36%, 31% and 26% yield), **3b–d** (22%, 41% and 41% yield) and **4b–d** (4%, 3% and 9% yield), respectively, with some C_{60} recovered (42%, 27% and 33% yield). Yields of **4b–d** increased upon heating a solution of **2b–d** or **3b–d** in ODCB at 170 °C for 24 h. This thermal dependence of yield shows that the aziridinofullerenes **4a–d** are more stable than the corresponding azafulleroids **3a–d**. To further clarify the thermal isomerization, the relative stabilities of **3a–d** and **4a–d** were calculated at the B3LYP/6-31G** level (see Scheme 2 and Table 1). The theoretical calculations were in good agreement with the experimental results.

Finally, proving the hypothesis valid, **3c,d** and **4c** were isolated as black prismatic single crystals by diffusion crystallization from toluene/CS_2 or benzene/CS_2. The crystal structures of **3c**, **3d** and **4c** with partial atomic numbering are shown in Fig. 3. These compounds crystallize in space group $P\bar{1}$ with one $Ph_3SiCH_2NC_{60}$ or $Ph_3GeCH_2NC_{60}$ molecule and one solvent molecule (toluene or benzene) in the unit cell. The C1–C5 addition regiochemistry for **3c** and **3d** is [5,6] as seen in the crystal structures shown in Figs. 3 and 4. The C1–C5 distances (2.134 and 2.141 Å) for **3c** and **3d** are clearly non-bonded. This distance is of the same order of magnitude as in $C_{70}CCl_2$ fulleroid (2.135 (1) Å) and $C_{60}C_3NPyPh_2$ bisfulleroid (2.279 (4) Å) [6]. For **3c** and **3d**, the C5–C6 (1.380 (3) and 1.384 (3) Å), C7–C8 (1.401 (3) and 1.406 (3) Å) and C9–C1 (1.386 (3) and 1.391 (3) Å) bonds possess double bond character, whereas the others are single bonds (1.451 (3)–1.486 (3) and 1.444 (3)–1.483 (3) Å, respectively). Thus, **3c** and **3d** have an open-bridged annulene structure as shown in Scheme 1. The fulleroid preserves 60π electrons, similar to C_{60}, which depends on the presence of a homoconjugate interaction in the bridged annulene moiety. The pyramidalization angles based on X-ray geometry for **3c** and **3d** are 7.1° and 7.3° (C1, C5), 9.5° and 9.6° (C2, C4), 10.5° and 10.6° (C3), 10.0° and 9.9° (C6, C9), and 11.0° and 11.0° (C7, C8), which are similar to the reported values for C_{60}NH (8.1°, 10.0°, 10.4°, 10.2° and 10.9°, respectively) (see Fig. 3 and Table 2) [7c]. The pyramidalization angle for normal fullerene C_{60} is 11.6°, and therefore, the values for **3c** and **3d** indicate that the azafulleroid preserves the structure of fullerene C_{60}. The 3D-HMO resonance integral $\beta_{1.5}$ equals 0.39 β and 0.38 β for **3c** and **3d**, respectively (C1 and C5 averaged for X-ray crystal data), which ex-

ceeds the reported value of 0.32 β for C_{60}NH, evidence of a strong enhancement of homoconjugation in the bridged annulene moiety. The C1–C6 addition geometry and distance (1.590 (4) Å) for **4c** suggests the presence of a [6,6] transannular bond between C1 and C6, and the aza-cyclopropane (aziridine) structure shown in Fig. 3. The distance is of the same order of magnitude as in C_{60}CPh(Ph-(OMe)$_2$) methanofullerene (1.614 (7) Å) and C_{60}C(Ph-OMe)$_2$ methanofullerene (1.625 Å). B3LYP/6-31G** calculations were also in good agreement with the transannular bond length: 2.157 Å for **3c**, 2.160 Å for **3d**, and 1.592 Å for **4c**.

Inspection of the crystal packing of **3c** · toluene shown in Fig. 5 (top), shows that one of silylphenyl rings is positioned close to a neighboring fullerene molecule by face-to-face (π–π) interaction. The shortest distance between one silylphenyl ring and the C_{60} moiety is in the 3.384 Å range. These interactions continue on to the next molecule, resulting in an infinite chain. A second type of interaction places a silylphenyl hydrogen atom close to the edge-
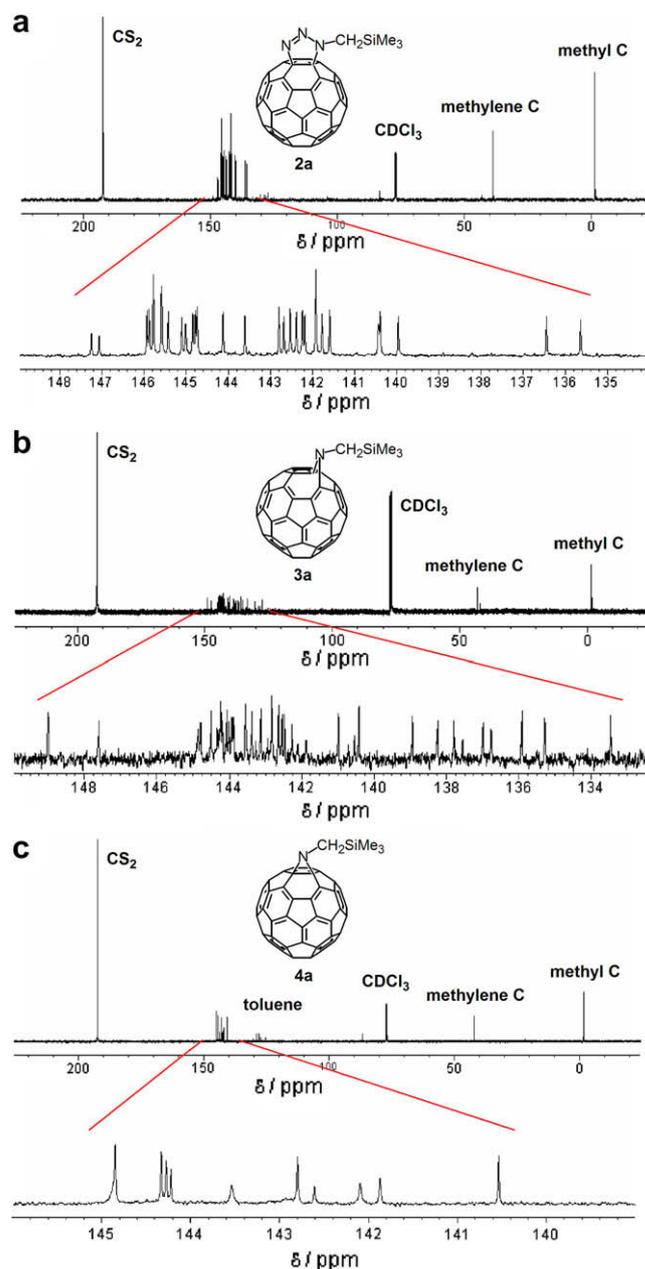
Fig. 1. ^{13}C NMR spectra in a CS_2: $CDCl_3$ = 3:2 solution; (a) **2a**, (b) **3a** and (c) **4a**.
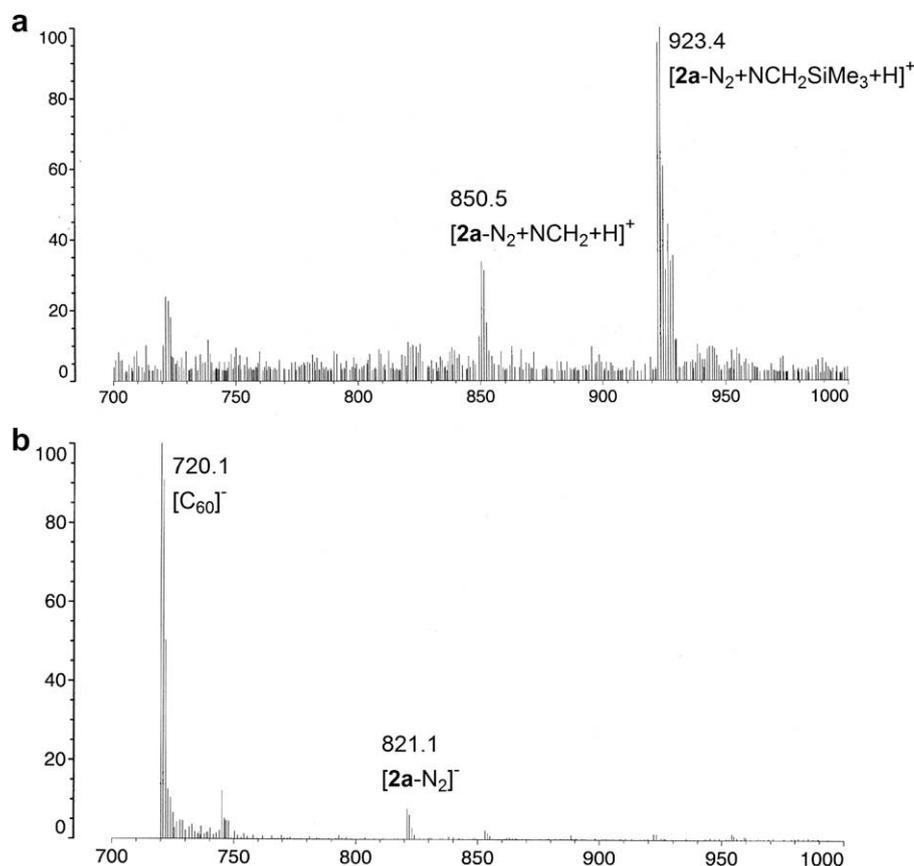
Fig. 2. MALDI-TOF mass spectra of **2a** in a 1,1,4,4-tetraphenyl-1,3-butadiene matrix; (a) positive ion reflectron mode and (b) negative ion reflectron mode.
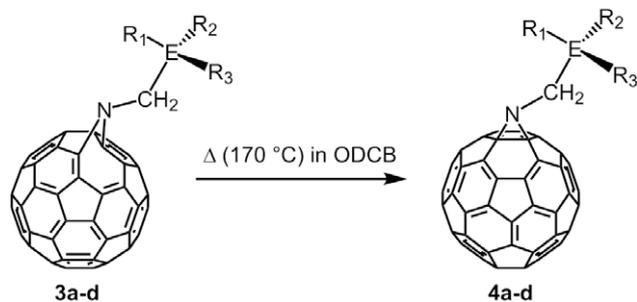
Scheme 2. Isomerization of azafulleroid **3** to aziridinofullerene **4**.

Table 1
Relative energies (kcal mol^{-1}) of **3a–d** and **4a–d** calculated at the B3LYP/ 6-31G** basis set.

	Azafulleroid (**3**)	Aziridinofullerene (**4**)
a: E = Si, $R_1 = R_2 = R_3 = Me$	+0.69	0.00
b-1: E = Si, $R_1 = Ph, R_2 = R_3 = Me$	+0.78	0.00
b-2: E = Si, $R_1 = Me, R_2 = Ph, R_3 = Me$	+0.95	0.00
b-3: E = Si, $R_1 = R_2 = Me, R_3 = Ph$	+0.87	0.00
c: E = Si, $R_1 = R_2 = R_3 = Ph$	+1.23	0.00
d: E = Ge, $R_1 = R_2 = R_3 = Ph$	+0.43	0.00

to-face on another C_{60} in the next infinite chain. These edge-to-face (CH/π) silylpheny-C_{60} interactions are in the 2.733–2.892 Å range. Although toluene solvent molecules are omitted for clarity, toluene also contacts with C_{60} in the next infinite chain, face-to-face, in the 3.290–3.394 Å range.

In order to insure that the silylphenyl group alone is capable of interacting with neighboring fullerenes, single crystal growth of **3c** from CH_2Cl_2/CS_2 solvent resulting in crystallization without solvent inclusion was attempted, as shown in Fig. 5 (bottom). The crystal packing of **3c** shows no face-to-face contacts between the silylphenyl groups and C_{60}, but has three edge-to-face silylphenyl-C_{60} interactions in the 2.632–2.855 Å range. The crystal packing of **4c** · benzene and **3d** · toluene showed additional interactions, specifically four (**4c**) and two (**3d**) edge-to-face interactions between silylphenyl groups, and two (**4c**) and four (**3d**) edge-to-face silylphenyl group-C_{60} interactions in the 2.845–2.854 Å and 2.780–2.862 Å range, respectively. Thus, interactions occur with and without participation of solvent, a likely explanation for the ordered structures of these crystals.

In conclusion, the X-ray structures of azafulleroid **3c**, **3d** and aziridinofullerene **4c** have been obtained with the help of effective silyl and germylphenyl-C_{60} interactions. These results suggest that the introduction of silyl and germylphenyl groups can be useful in obtaining crystals of chemically modified fullerenes [12].

3. Experimental

3.1. General data

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECP500 operating at 500 or 125 MHz, respectively. IR spectra were recorded on a JASCO FT/IR-4100. MALDI-TOF mass spectra were recorded on a Shimadzu AXIMA-CFR. EI mass spectra were recorded on a JEOL JMS-AX505H. UV spectra were recorded on a JASCO V-550. GPLC (gel permeation liquid chromatography) was performed on an LC-908 (Japanese Analytical Industry, Co., Ltd.)
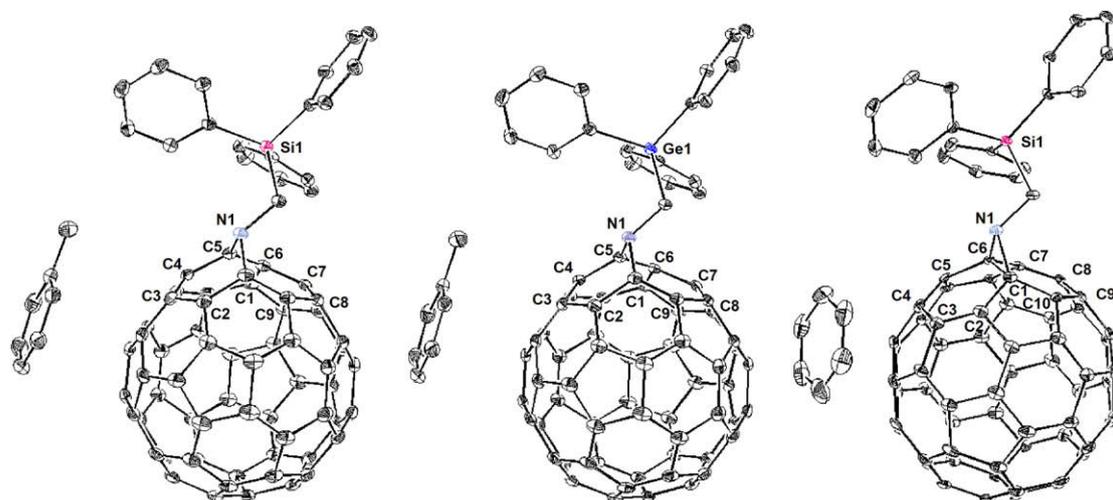
Fig. 3. X-ray crystal structures of **3c** · toluene (left), **3d** · toluene (middle) and **4c** · toluene (right).

C$_{60}$NR : [5,6]open
3c : R = NCH$_2$SiPh$_3$
3d : R = NCH$_2$GePh$_3$
C$_{60}$NH : R = NH

C$_{60}$NR : [6,6]close
4c : R = NCH$_2$SiPh$_3$
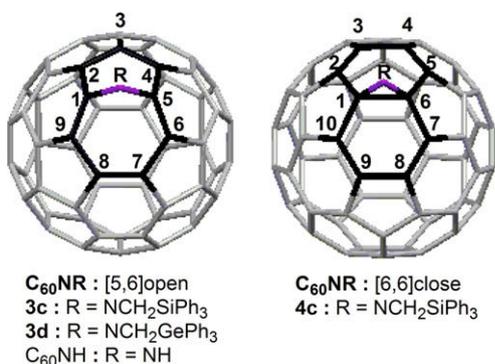
Fig. 4. The partial atomic numbering of azafulleroid **3** ([5,6]open, left) and aziridinofullerene **4** ([6,6]close, right).

Table 2
Pyramidalization angles (°) of **3c** and **3d** based on X-ray and calculated geometries.

	C1, C5	C2, C4	C3	C6, C9	C7, C8
3c[a]	7.1	9.5	10.5	10.0	11.0
3c[b]	7.6	9.6	10.5	10.0	10.9
3d[a]	7.3	9.6	10.6	9.9	11.0
3d[b]	7.6	9.6	10.5	9.9	10.9
C$_{60}$NH[c]	8.1	10.0	10.4	10.2	10.9

[a] Geometry of X-ray crystal data.
[b] Geometry optimized using B3LYP/6-31G** basis set.
[c] See Ref. [7c].

equipped with JAIGEL 1H and 2H columns (eluent: toluene). Melting points were determined on a Yanaco MP-S3.

3.2. Azide compounds **1b**–**d**

3.2.1. Typical procedure: dimethylphenylsilylmethylazide (**1b**)

A mixture of Me$_2$PhSiCH$_2$Cl (5.18 mmol) and NaN$_3$ (6.23 mmol, 1.2 equiv.) in DMPU (15 ml) was stirred heating at 80 °C for 14 h under argon atmosphere. The reaction mixture was washed with water, extracted with toluene and hexane, and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure, and the crude product was purified by GPLC (eluent: toluene) to afford Me$_2$PhSiCH$_2$N$_3$.
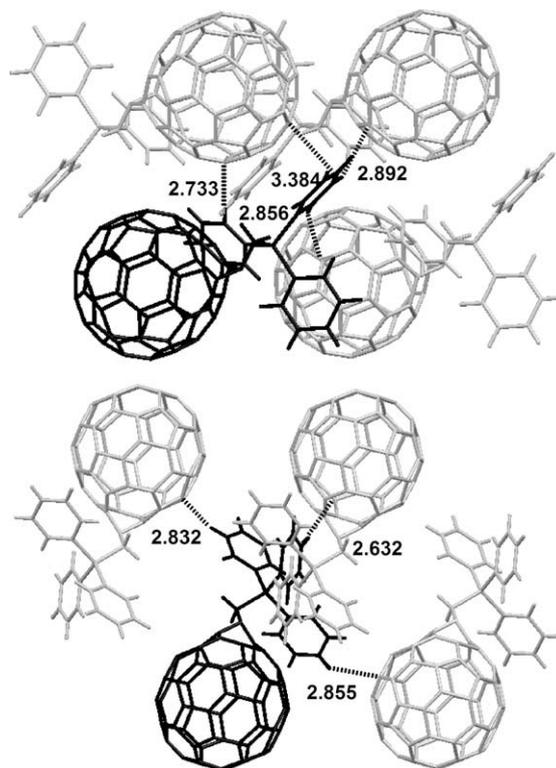
Fig. 5. Crystal packing of **3c** · toluene (top) and **3c** (bottom), with close contacts among silylphenyl groups and neighboring fullerenes shown in dashed lines.

Yield: 76% (yellow oil). ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.40 (6H, s), 2.98 (2H, s,), 7.38–7.54 (5H, m); ^{13}C NMR (125 MHz, CDCl$_3$) δ −4.14, 41.43, 128.04, 129.73, 133.64, 136.07; IR (neat) υ = 2083 cm^{-1}; MS (EI) calcd. for C$_8$H$_{11}$Si ([M−CH$_2$N$_3$]$^+$), 135, found, 135.

3.2.2. Triphenylsilylmethylazide (**1c**)

Yield: 76% (colorless crystals). m.p. 99 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.61 (2H, s), 7.39–7.57 (15H, m); ^{13}C NMR (125 MHz, CDCl$_3$) δ 39.59, 128.15, 130.21, 132.35, 135.70; IR (KBr) υ = 2098 cm^{-1}; MS (MALDI-TOF mass) calcd. for C$_{19}$H$_{18}$N$_3$Si ([M+H]$^+$), 316, found, 316.

3.2.3. Triphenylgermylmethylazide (1d)

Yield: 63% (colorless crystals). m.p. 92 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.68 (2H, s), 7.40–7.52 (15H, m); ^{13}C NMR (125 MHz, CDCl$_3$) δ 39.78, 128.49, 129.58, 134.90, 135.37; IR (KBr) υ = 2089 cm^{-1}; MS (EI) calcd. for C$_{18}$H$_{15}$Ge ([M−CH$_2$N$_3$]$^+$), 305, found, 305.

3.3. Triazoline adducts 2a–d

3.3.1. Ttypical procedure: [6,6]-(1-N-trimethylsilylmethyl-triazoline)-C$_{60}$ (2a)

A mixture of fullerene C$_{60}$ (0.500 mmol) and (1a) (0.501 mmol, 1.0 equiv.) in ODCB (36 ml) was stirred heating at 50 °C for 6 h under argon atmosphere. The solvent was removed under reduced pressure, and the crude product was purified by GPLC (eluted toluene) to afford Me$_3$SiCH$_2$N$_3$C$_{60}$ (2a) as a black solid.

Yield: 28% (black solid). m.p. >300 °C; ^{1}H NMR (500 MHz, CS$_2$:CDCl$_3$ = 3:2) δ 0.50 (9H, s), 3.62 (2H, s); ^{13}C NMR (125 MHz, CS$_2$:CDCl$_3$ = 3:2) δ −1.43, 38.59, 83.17, 103.99, 135.64, 136.44, 139.96, 140.40, 140.43, 141.59, 141.78, 141.92, 142.19, 142.25, 142.39, 142.53, 142.68, 142.80, 143.61, 144.13, 144.75, 144.78, 144.85, 145.00, 145.10, 145.42, 145.58, 145.78, 145.87, 145.93, 147.06, 147.25; MS (MALDI-TOF mass) calcd. for C$_{64}$H$_{10}$N$_3$Si ([M−N$_2$−H]$^-$), 821, found, 821; UV–Vis (toluene) λ_{max}/nm (ε) 427 (2900).

3.3.2. [6,6]-(1-N-dimethylphenylsilylmethyl-triazoline)-C$_{60}$ (2b)

Yield: 36% (black solid). m.p. >300 °C; ^{1}H NMR (500 MHz, CS$_2$:CDCl$_3$ = 3:2) δ 0.82 (6H, s), 3.82 (2H, s), 7.41–7.44 (5H, m); ^{13}C NMR (125 MHz, CS$_2$:CDCl$_3$ = 3:2) δ −2.87, 38.14, 83.09, 104.03, 127.96, 129.56, 130.28, 132.60, 133.75, 135.71, 136.24, 136.47, 139.98, 140.25, 140.41, 141.62, 141.80, 141.92, 141.94, 142.20, 142.25, 142.40, 142.56, 142.70, 143.63, 144.13, 144.71, 144.81, 144.88, 145.11, 145.45, 145.60, 145.61, 145.77, 145.81, 145.90, 145.94, 147.11, 147.28; MS (MALDI-TOF mass) calcd. for C$_{69}$H$_{12}$N$_3$Si ([M−N$_2$−H]$^-$), 883, found, 883; UV–Vis (toluene) λ_{max}/nm (ε) 427 (3200).

3.3.3. [6,6]-(1-N-triphenylsilylmethyl-triazoline)-C$_{60}$ (2c)

Yield: 31% (black solid). m.p. >300 °C; ^{1}H NMR (500 MHz, CS$_2$:CDCl$_3$ = 3:2) δ 4.44 (2H, s), 7.45–7.78 (15H, m); ^{13}C NMR (125 MHz, CS$_2$:CDCl$_3$ = 3:2) δ 35.89, 82.85, 104.33, 128.00, 132.60, 135.58, 135.73, 136.50, 139.98, 140.02, 140.35, 141.60, 141.75, 141.88, 142.16, 142.23, 142.35, 142.50, 142.65, 143.57, 144.10, 144.63, 144.75, 144.83, 145.04, 145.37, 145.55, 145.57, 145.68, 145.79, 145.84, 145.90, 147.04, 147.23; MS (MALDI-TOF mass) calcd. for C$_{79}$H$_{16}$N$_3$Si ([M−N$_2$−H]$^-$), 1007, found, 1007; UV–Vis (toluene) λ_{max}/nm (ε) 427 (3300).

3.3.4. [6,6]-(1-N-triphenylgermylmethyl-triazoline)-C$_{60}$ (2d)

Yield: 26% (black solid). m.p. >300 °C; ^{1}H NMR (500 MHz, CS$_2$:CDCl$_3$ = 3:2) δ 4.47 (2H, s), 7.39–7.66 (15H, m); ^{13}C NMR (125 MHz, CS$_2$:CDCl$_3$ = 3:2) δ 36.28, 82.83, 104.78, 128.41, 129.38, 134.95, 134.97, 135.72, 136.59, 140.03, 140.43, 141.68, 141.83, 141.91, 141.95, 142.23, 142.28, 142.43, 142.58, 142.72, 143.65, 144.17, 144.66, 144.74, 144.84, 144.91, 145.12, 145.45, 145.63, 145.65, 145.72, 145.85, 145.94, 145.98, 147.14, 147.32; MS (MALDI-TOF mass) calcd. for C$_{79}$H$_{17}$N$_3$Ge ([M−N$_2$+S]$^-$), 1085, found, 1085.

3.4. Azafulleroid 3a–d and aziridinofullerene 4a–d

3.4.1. Typical procedure: [5,6]-(1-N-trimethylsilylmethyl-azafulleroid)-C$_{60}$ (3a) and [6,6]-(1-N-trimethylsilylmethyl-fulleroaziridine)-C$_{60}$ (4a)

Solid Me$_3$SiCH$_2$N$_3$C$_{60}$ (2a) (0.019 mmol) was heated at 100 °C for 33 h under argon atmosphere. The crude product was purified by column chromatography (eluent: CS$_2$) to afford the azafulleroid Me$_3$SiCH$_2$NC$_{60}$ (3a) as the major product, and the aziridinofullerene Me$_3$SiCH$_2$NC$_{60}$ (4a) as the minor. Aziridinofullerene Me$_3$SiCH$_2$NC$_{60}$ (4a) (0.019 mmol) was also obtained by heating a solution of Me$_3$SiCH$_2$N$_3$C$_{60}$ (2a) in ODCB (2 ml) at 170 °C for 24 h under argon atmosphere. The crude product was purified by column chromatography (eluent: CS$_2$) or GPLC (eluent: toluene) to afford 4a as the major product.

3a: yield: 19% (black solid). m.p. >300 °C; ^{1}H NMR (500 MHz, CS$_2$:CDCl$_3$ = 3:2) δ 0.38 (9H, s), 3.44 (2H, s); ^{13}C NMR (125 MHz, CS$_2$:CDCl$_3$ = 3:2) δ −1.63, 43.00, 133.47, 135.28, 135.91, 136.76, 136.98, 137.55, 137.79, 138.24, 138.94, 140.42, 140.98, 142.27, 142.47, 142.54, 142.64, 142.83, 143.12, 143.37, 143.55, 143.88, 143.93, 144.01, 144.07, 144.19, 144.23, 144.50, 144.79, 147.59, 149.00; MS (MALDI-TOF mass) calcd. for C$_{64}$H$_{10}$NSi ([M−H]$^-$), 821, found, 821.

4a: yield: 17%: when obtained as the major product (black solid). m.p. >300 °C; ^{1}H NMR (500 MHz, CS$_2$:CDCl$_3$ = 3:2) δ 0.49 (9H, s), 3.25 (2H, s); ^{13}C NMR (125 MHz, CS$_2$:CDCl$_3$ = 3:2) δ −1.91, 41.91, 86.69, 140.53, 141.87, 142.09, 142.61, 142.80, 143.54, 144.22, 144.27, 144.33, 144.84; MS (MALDI-TOF mass) calcd. for C$_{64}$H$_{10}$NSi ([M−H]$^-$), 821, found, 821.

3.4.2. [5,6]-(1-N-dimethylphenylsilylmethyl-azafulleroid)-C$_{60}$ (3b) and [6,6]-(1-N-dimethylphenylsilylmethyl-fulleroaziridine)-C$_{60}$ (4b)

3b: yield: 22% (black solid). m.p. >300 °C; ^{1}H NMR (500 MHz, CS$_2$:CDCl$_3$ = 3:2) δ 0.66 (6H, s), 3.62 (2H, s), 7.36–7.76 (5H, m); ^{13}C NMR (125 MHz, CS$_2$:CDCl$_3$ = 3:2) δ −3.26, 42.62, 127.97, 129.48, 133.50, 133.84, 134.15, 135.31, 135.96, 136.91, 136.97, 137.56, 137.80, 138.26, 138.95, 140.46, 141.02, 142.29, 142.50, 142.57, 142.67, 142.82, 142.88, 142.96, 143.15, 143.31, 143.39, 143.56, 143.91, 144.01, 144.09, 144.22, 144.52, 144.81, 147.60, 148.72; MS (MALDI-TOF mass) calcd. for C$_{69}$H$_{12}$NSi ([M−H]$^-$), 883, found, 883.

4b: yield: 19%: when obtained as the major product (black solid). m.p. >300 °C; ^{1}H NMR (500 MHz, CS$_2$:CDCl$_3$ = 3:2) δ 0.76 (6H, s), 3.42 (2H, s), 7.36–7.77 (5H, m); ^{13}C NMR (125 MHz, CS$_2$:CDCl$_3$ = 3:2) δ −3.62, 41.49, 86.41, 127.36, 127.70, 129.55, 129.83, 134.11, 134.76, 136.18, 140.33, 141.87, 142.05, 142.58, 142.78, 143.54, 144.24, 144.27, 144.29, 144.86; MS (MALDI-TOF mass) calcd. for C$_{69}$H$_{12}$NSi ([M−H]$^-$), 883, found, 883.

3.4.3. [5,6]-(1-N-triphenylsilylmethyl-azafulleroid)-C$_{60}$ (3c) and [6,6]-(1-N-triphenylsilylmethyl-fulleroaziridine)-C$_{60}$ (4c)

3c: yield: 41% (black solid). m.p. >300 °C; ^{1}H NMR (500 MHz, CS$_2$:CDCl$_3$ = 3:2) δ 4.23 (2H, s), 7.41–7.78 (15H, m); ^{13}C NMR (125 MHz, CS$_2$:CDCl$_3$ = 3:2) δ 41.31, 125.17, 128.06, 129.97, 132.80, 133.60, 135.41, 136.06, 136.80, 137.28, 137.50, 137.86, 138.23, 138.98, 140.49, 141.03, 142.32, 142.50, 142.54, 142.64, 142.89, 142.95, 143.14, 143.33, 143.37, 143.52, 143.80, 143.85, 143.99, 144.04, 144.14, 144.17, 144.49, 144.75, 147.55, 148.32; MS (MALDI-TOF mass) calcd. for C$_{79}$H$_{16}$NSi ([M−H]$^-$), 1007, found, 1007.

4c: yield: 33%: when obtained as the major product (black solid). m.p. >300 °C; ^{1}H NMR (500 MHz, CS$_2$:CDCl$_3$ = 3:2) δ 4.03 (2H, s), 7.40–7.85 (15H, m); ^{13}C NMR (125 MHz, CS$_2$:CDCl$_3$ = 3:2) δ 39.72, 86.15, 128.12, 130.00, 132.62, 136.17, 140.12, 141.87, 142.04, 142.53, 142.78, 143.53, 144.26, 144.87; MS (MALDI-TOF mass) calcd. for C$_{79}$H$_{16}$NSi ([M−H]$^-$), 1007, found, 1007; UV–Vis (toluene) λ_{max}/nm (ε) 428 (2600), 498 (1800).

3.4.4. [5,6]-(1-N-triphenylgermylmethyl-azafulleroid)-C$_{60}$ (3d) and [6,6]-(1-N-triphenylgermylmethyl-fulleroaziridine)-C$_{60}$ (4d)

3d: yield: 41% (black solid). m.p. >300 °C; ^{1}H NMR (500 MHz, CS$_2$:CDCl$_3$ = 3:2) δ 4.35 (2H, s), 7.42–7.78 (15H, m); ^{13}C NMR (125 MHz, CS$_2$:CDCl$_3$ = 3:2) δ 41.91, 128.35, 129.29, 134.81,

135.11, 135.92, 136.75, 137.05, 137.34, 138.17, 138.94, 140.11, 140.43, 140.96, 142.32, 142.43, 142.49, 142.61, 142.76, 142.84, 142.90, 143.09, 143.33, 143.47, 143.77, 143.80, 143.94, 144.01, 144.13, 144.26, 144.42, 144.71, 144.85, 147.50, 148.21; MS (MAL-DI-TOF mass) calcd. for $C_{79}H_{17}NGe$ ([M+S]$^-$), 1085, found, 1085.

4d: yield: 9%: when obtained as the major product (black solid). m.p. >300 °C; ^1H NMR (500 MHz, CS_2:$CDCl_3$ = 3:2) δ 4.17 (2H, s), 7.40–7.78 (15H, m); ^{13}C NMR (125 MHz, CS_2:$CDCl_3$ = 3:2) δ 40.78, 86.36, 128.47, 129.41, 134.88, 135.36, 140.15, 141.89, 142.03, 142.57, 142.80, 142.90, 143.57, 144.30, 144.32, 144.90; MS (MAL-DI-TOF mass) calcd. for $C_{79}H_{17}NGe$ ([M+S]$^-$), 1085, found, 1085.

3.5. X-ray crystallography

Single crystals of **3c**, **3d** and **4c** suitable for X-ray diffraction study were mounted on a Rigaku RAXIS RAPID S Imaging Plate diffractometer with Mo Kα (graphite monochromated, $\lambda = 0.71073$) radiation. Crystal data and statistics are summarized in Tables 3 and 4. The structures were solved by direct methods (SHELXS-97 [8] and SIR 2004 [9]) using the WinGX v1.70.01 interface [10]. The non-hydrogen atoms were refined anisotropically by full-matrix least-square methods (SHELXL-97) [8]. The hydrogen atoms were placed at calculated positions and kept fixed. In subsequent refinement, the function $\sum \omega(F_o^2 - F_c^2)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $wR_2 = [\sum \omega(F_o^2 - F_c^2)^2 / \sum(\omega F_o^4)]^{1/2}$.

3.5.1. Crystallographic data for 3c · toluene and 3c
See Table 3.

Table 3
Crystal data and data collection parameters.

	3c · toluene	3c
Empirical formula	$C_{86}H_{25}NSi$	$C_{79}H_{17}NSi$
Formula weight	1100.16	1008.03
Temperature (K)	150 (2)	150 (2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.9609 (15)	10.140 (6)
b (Å)	13.423 (3)	13.348 (7)
c (Å)	18.859 (4)	16.682(11)
α (°)	101.006 (7)	76.47 (2)
β (°)	96.025 (7)	86.077 (17)
γ (°)	106.643 (9)	74.259 (19)
Volume (Å^3)	2337.1 (8)	2113 (2)
Z	2	2
Density (calculated) (g/cm^3)	1.563	1.584
Absorption coefficient (mm^{-1})	0.114	0.118
$F(000)$	1124	1024
Crystal size (mm)	$0.50 \times 0.50 \times 0.20$	$0.75 \times 0.38 \times 0.30$
Theta range for data collection (°)	3.02–27.48	3.08–27.47
Index ranges	$-12 \leqslant h \leqslant 11$	$-12 \leqslant h \leqslant 13$
	$-17 \leqslant k \leqslant 17$	$-16 \leqslant k \leqslant 17$
	$-23 \leqslant l \leqslant 24$	$-21 \leqslant l \leqslant 21$
Reflections collected	22685	22379
Independent reflections [$R_{(int)}$]	10568 (0.0356)	8823 (0.0911)
Completeness to theta (%)	98.5	91.2
Absorption correction	None	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	10568/0/893	8823/0/730
Goodness-of-fit (GOF) indicator	1.035	1.048
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0535$, $wR_2 = 0.1224$	$R_1 = 0.1258$, $wR_2 = 0.3092$
R indices (all data)	$R_1 = 0.0711$, $wR_2 = 0.1310$	$R_1 = 0.2338$, $wR_2 = 0.3740$
Largest difference peak and hole (e Å^{-3})	0.402 and −0.451	0.672 and −0.325

Table 4
Crystal data and data collection parameters.

	3d · toluene	4c · benzene
Empirical formula	$C_{86}H_{25}NGe$	$C_{85}H_{23}NSi$
Formula weight	1144.66	1086.13
Temperature (K)	150 (2)	150 (2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.993 (2)	10.040 (5)
b (Å)	13.433(2)	13.292 (9)
c (Å)	18.848(4)	18.748 (9)
α (°)	101.149 (11)	100.53 (19)
β (°)	96.146 (8)	97.75 (24)
γ (°)	106.582 (8)	106.11 (18)
Volume (Å^3)	2343.6 (8)	2317.1 (23)
Z	2	2
Density (calculated) (g/cm^3)	1.622	1.557
Absorption coefficient (mm^{-1})	0.717	0.114
$F(000)$	1160	1108
Crystal size (mm)	$0.75 \times 0.38 \times 0.30$	$0.75 \times 0.18 \times 0.10$
Theta range for data collection (°)	3.01–27.48	3.00–27.48
Index ranges	$-12 \leqslant h \leqslant 10$	$-13 \leqslant h \leqslant 12$
	$-17 \leqslant k \leqslant 17$	$-17 \leqslant k \leqslant 17$
	$-24 \leqslant l \leqslant 24$	$-24 \leqslant l \leqslant 24$
Reflections collected	22862	22379
Independent reflections [$R_{(int)}$]	10646 (0.0338)	10400 (0.0886)
Completeness to theta (%)	99.0	97.9
Absorption correction	None	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	10646/0/793	10400/0/784
Goodness-of-fit (GOF) indicator	1.013	1.033
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0461$, $wR_2 = 0.1109$	$R_1 = 0.0857$, $wR_2 = 0.1345$
R indices (all data)	$R_1 = 0.0600$, $wR_2 = 0.1174$	$R_1 = 0.1715$, $wR_2 = 0.1585$
Largest difference peak and hole (e Å^{-3})	0.606 and −0.624	0.349 and −0.490

3.5.2. Crystallographic data for 3d · toluene and 4c · benzene
See Table 4.

3.6. Computational studies

Calculations were carried out on HPC-P4/GLW and HPC3000-XC104T workstations provided by HPC Inc. in Japan. All geometric optimizations were optimized by DFT calculations at the B3LYP/6-31G** level using Gaussian 03 programs with no symmetry restrictions [11]. The POAV/3D-HMO analyses were performed using the POAV3 program [7c].

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[12] One of reviewers recommended a carbon analog (E = C in Scheme 1) as comparison with silyl and germylphenyl groups. However, the corresponding Ph$_3$CCH$_2$N$_3$ is unknown compound. The reaction of triphenylmethyl derivatives such as Ph$_3$CCH$_2$X (X = halogen, MgX, etc.) as starting compound seems to undergo an appreciable amount of a phenyl migration to afford Ph$_2$C=C(Cl)Ph or Ph$_2$CXCHPh [J.C. Charlton, I. Dostrovsky, E.D. Hughes, Nature 167 (1951) 986; E.Grovenstein, A.B. Cottingham, L.T. Gelbaum, J. Org. Chem. 43 (1978) 3332]. So in the synthetic point of view, triphenylsilyl or germyl groups are more easily accessible.