Synthesis and Characterization of Germa[*n*]pericyclynes

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The synthesis and characterization of novel pericyclynes comprising germanium atoms and acetylenes, germa[*n*]pericyclynes, are described. The prepared germa[4]-, [6]-, and [8]pericyclynes were compared by ^{13}C NMR spectroscopy, X-ray crystallography, cyclic voltammetry, UV-visible spectroscopy, fluorescence emission spectroscopy, Raman spectroscopy, and density functional theory calculation analyses.

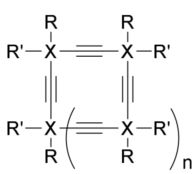

Fig. 1 Pericyclynes

Introduction

'[*N*]pericyclynes,' as named by Scott et al., are cyclic compounds composed of *n* acetylenic units on each side of the ring (Fig. 1).[1,2] Acyclic oligoalkynes or skipped-polyynes ([-R_2X-C≡C-]$_n$) have been investigated in detail. Pericyclynes, have also been investigated because of their unique electronic properties.[3] In particular, their strained structures due to reduced bond angles of vertexes may reinforce the through-space interaction between adjacent but non-conjugated alkynes.[4,5] In contrast, acyclic skipped polyynes exhibit no-conductivity or very small through-space interactions.[6] Moreover, cross-hyperconjugation between skipped alkynes has been recently focused as unexplored orbital interactions, and its strength can be tuned by choice of element X in Fig 1.[7] Hence, pericyclynes may display unique electrical and photochemical properties, and are expected to novel functional materials.

To date, various analogues have been reported in both synthetic[8–10] and theoretical studies.[11] Owing to the difficulty in their syntheses arising from strains, silapericyclynes (Si),[9] with larger heteroatom vertexes than carbopericyclynes (C)[2,8] have been reported with extended pericyclynes (conjugated polyynes in their sides).[12] Changing the vertex atoms to reduce the ring strains and bond angles may lead to the efficient synthesis of pericyclynes and facilitate the through-space interactions of alkynes. Phosphapericyclynes (P) have also been reported.[9] Group 14 elements seem to be efficient because of their stability and ease of handling. However, only carbon and silicon have been studied among Group 14 elements. In addition, the physical properties of pericyclynes have been rarely reported. Therefore, further studies on the other vertex atoms in terms of the ring strain and bond angles are strongly desired. Additionally, it is also possible that changing the vertex atoms in pericyclynes can tuned the conjugation between skipped polyynes, and their properties should be investigated.[7] Herein, we report the synthesis and characterization of novel germa[*n*]pericyclynes, containing germanium, a Group 14 element, on their vertexes.

Results and Discussion

The syntheses of germa[*n*]pericyclynes started with commercially available diphenylgermanium dichloride **1a** and diisopropylgermanium dichloride **1b** prepared from germanium(IV) chloride (Scheme 1). The diethynylation of **1a–b** afforded dialkynes **2a–b**. The coupling of the dianion species of **2a–b**, generated by lithiation using *n*-butyllithium, with **1a–b** followed by the cyclization afforded phenylated germa[4]-, [6]-, and [8]pericyclynes **3a–5a**, and isopropylated germa[6]- and [8]pericyclynes **4b** and **5b**. Isopropylated germa[4]-pericyclyne **3b** was not observed. This is probably due to the reactivity of **2a** which has reactive benzylic positions.

The germapericyclynes were obtained as crystals and analyzed by X-ray diffraction (XRD). The ring of **3a** was clearly planar; however, the analytical data of **4a** showed a chair conformation containing a solvent molecule inside the

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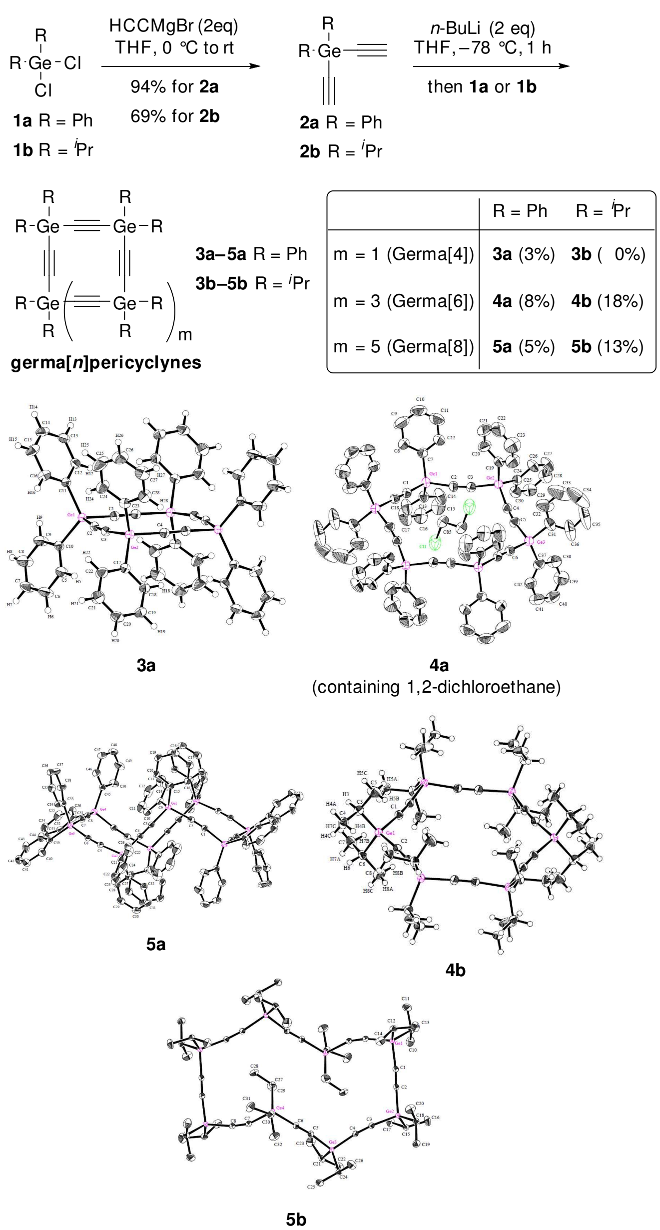
ring, indicating that germa[6]pericyclynes are promising clathrate molecules.[13] In contrast, isopropylated germa[6]pericyclyne **4b** was found to be planar. Germa[8]pericyclynes **5a** and **5b** were obtained in a zig-zag form. The crystal structure of **5a** indicated intramolecular π–π interaction between the phenyl rings to fold the molecule.



Scheme 1 Synthesis and ORTEP drawings of germapericyclynes

The XRD analyses showed that the bond angle of **3a** was 104° for the C–Ge–C, whereas the angle was 109° for the larger rings **4a** and **4b** (see the Supporting Information and cif data files). The bond angles of C–X–C were almost the same as the reported values of silapericyclynes.[8g–i] In contrast, the C–Ge–C bond angles of **5a** and **5b** varied from 104° to 108° probably because of the low symmetry of the molecule. The angles of Ge–C≡C, **3a**, **4a**, and **4b** were 171°, 174°, and 174°, respectively. These values are also the same as those of the reported sila[4]-, [6]pericyclynes (173°, and 175°, respectively).[9g,9h] The Ge–C≡C bond angles of **5a** and **5b** were 171–177°, and 162–178° while those of the sila[8]pericyclynes were reported 173°.[9g,9h]

In terms of the bond length, all germapericyclynes showed almost the same value (1.20–1.21 Å) for the C≡C bonds; no significant differences compared with those of silapericyclynes (1.19 Å for [4]; 1.21 Å for [6] and [8])[9g–h] and acetylene (1.21 Å)[9f] were found. The bond length of the Ge–C were 1.91 Å in all compounds. The distance between the neighbouring acetylenes in **3a** was 3.2 Å.[4,5a]

The Raman spectra of the powdered germapericyclynes were located at 2107 (**3a**), 2114 (**4a**), 2112 (**4b**), 2099 (**5a**), and 2098 cm^{-1} (**5b**), whereas the reported value for silapericyclynes was 2135 cm^{-1}.[9e,9f]

A large difference was observed in the ^{13}C NMR chemical shifts of **3a**. The acetylenic carbons of **3a** appeared at δ 110.4 ppm; however, those for the other four germa[6]- and [8]pericyclynes appeared at δ 107 ppm. This trend was similar to that of the silapericyclynes.[9g-i]

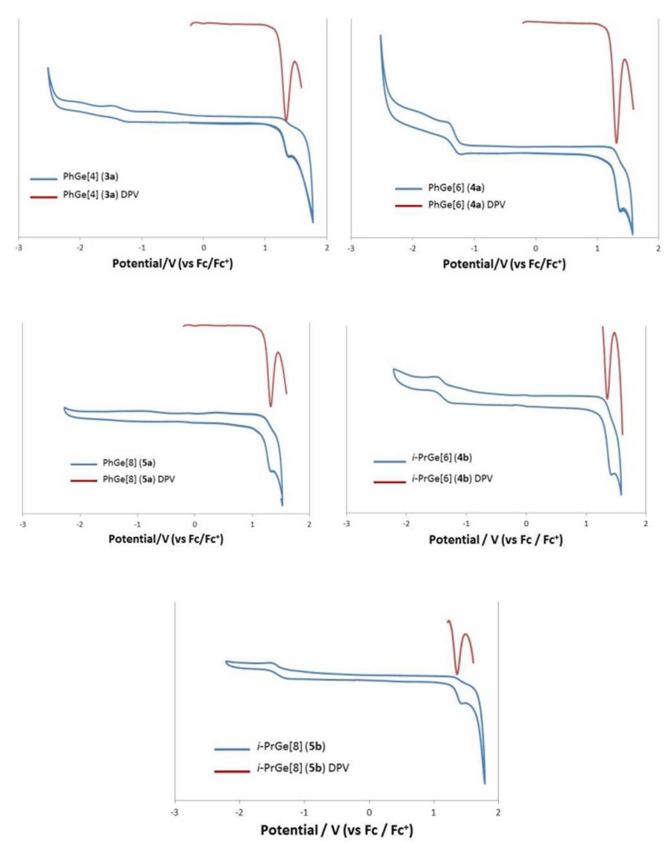


Fig. 2 Cyclic and differential pulse voltammograms of germa[*n*]pericyclynes (1.0 mM (**3a**, **4a**, **4b**, and **5b**); 0.5 mM (**5a**) in 0.1 M *n*-Bu_4NPF_6/CH_2Cl_2 solution; Scan rate = 0.1 V/s)

The cyclic voltammetry (CV) showed only oxidation potentials obtained by differential pulse voltammetry (DPV)

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(E_{ox}^{DPV} = 1.336 (**3a**), 1.312 (**4a**), 1.320 (**5a**), 1.352 (**4b**), and 1.356 V (**5b**); Fig. 2). The oxidation potentials of **4b** and **5b** were slightly higher than those of the corresponding phenyl compounds. To the best of our knowledge, this is the first example of the CV analysis of pericyclynes.

The UV-visible spectra were recorded initially in dichloromethane (Fig. 3 (a) and the Supporting Information). Two absorption maxima were observed at 227 and 261 nm (for **3a**: 227 nm (ε = 15900), 261 nm (2375); **4a**: 227 nm (17500), 261 nm (3010); **5a**: 228 nm (19440), 261 nm (4240), and **2a**: 225 nm (3840), 261 nm (531)). In contrast, the isopropyl derivatives, **4b** or **5b**, did not show specific absorption at 261 nm. Thus, the absorption at 261 nm was derived from the benzene rings. Although **3a** was highly strained and expected to show through-space conjugations between alkynes, only a small bathochromic shift was observed at 227 nm according to the increase in the number of alkyne moieties. Tykwinski et al. reported[14] that the ring strains did not affect the physical data of various analyses; our results were in accordance with this. However, compounds **3a**–**5a** were not soluble in hydrocarbons; therefore, the absorptions at shorter wavelength areas could not be investigated. However, the UV-visible spectra of isopropyl pericyclynes **4b** and **5b** could be obtained in *n*-hexane (Fig. 3 (b) and Supporting Information). Two shoulders were observed at 205 (**4b**: ε = 18683, **5b**: 22377) and 213 nm (**4b**: ε = 13919, **5b**: 17798), which were not observed in acyclic analogue **2b**. Because similar shoulders have been reported in the case of silapericyclylnes (204, 213, and 221 nm),[9f,9h] these values were assigned to the specific absorption of pericyclynes.

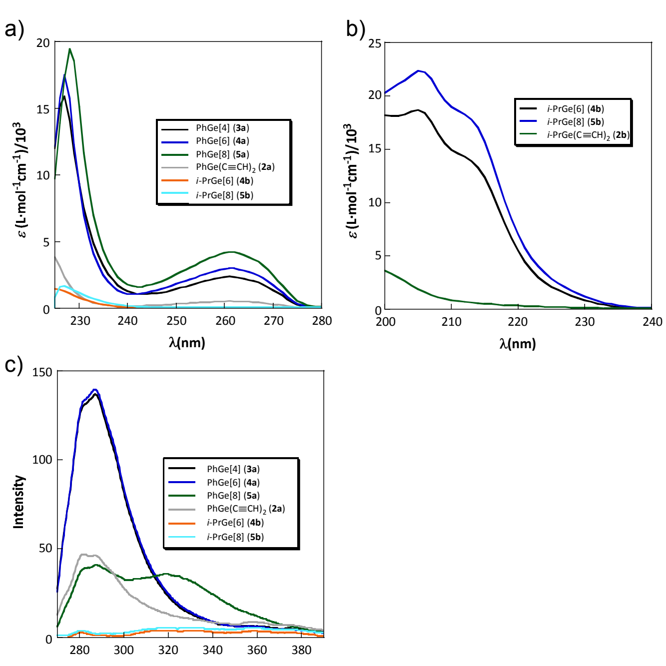

Fig. 3 UV-visible spectra (a: 0.1 mM in CH_2Cl_2, b: 0.1 mM in *n*-hexane) and fluorescence emission spectra (c: 0.1 mM in CH_2Cl_2, λ_{EXT} = 260 nm)

Similar fluorescence emission maxima were observed from **3a** and **4a** (λ_{EM} = 281 and 288 nm) and acyclic **2a** (282 and 288 nm) (Fig 3. (c) and Supporting Information). In particular, **3a** and **4a** showed almost the same intensity. In contrast, **5a** exhibited a different pattern. In addition to the 288 nm emission, an emission at 318 nm was observed, while the isopropyl derivative, **5b**, did not exhibit such emission. The results of UV-visible spectral and XRD analyses showed that this emission maximum can be attributed to the intramolecular π–π interaction of the phenyl moiety.

To estimate the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gaps of pericyclynes, the density functional theory (DFT) calculations of methyl-substituted pericyclynes were performed with the B3LYP/6-31G* basis set of Gaussian 09 to compare the ring size of the germapericyclynes and the pericyclynes containing other Group 14 elements (Fig. 3).[15] The HOMO–LUMO gap of the germapericyclynes was larger than that of the silapericyclynes. The difference of HOMO–LUMO gaps would be supported by the result that UV absorption of pericyclyne rings was observed at 221 nm in silapericyclynes[9f,9h] and at 213 nm in germapericyclynes. Among germa[4]-, [6]-, and [8]pericyclynes, the smallest HOMO–LUMO gap was observed in germa[4]pericyclyne, and interestingly, that of germa[6]pericyclyne was the largest. The smallest gap in germa[4]pericyclyne would be results of it planar ring and small C–Ge–C angles supporting through-space interaction between alkynes. However, as Tykwinski et al. reported,[14] these differences of gaps did not affect UV spectra. For HOMO energy levels, the germa[4]pericyclynes was the highest, and germa[6]pericyclynes was the lowest. This tendency matched the results of oxidation potentials of **3a**, **4a**, **5a**, **4b**, and **5b**. The through-space interactions between the C≡C bonds were estimated in the LUMO, even though they did not seem to enhance the physical data.[5] The low symmetry of germa[8]pericyclyne was also indicated by the HOMO orbitals.

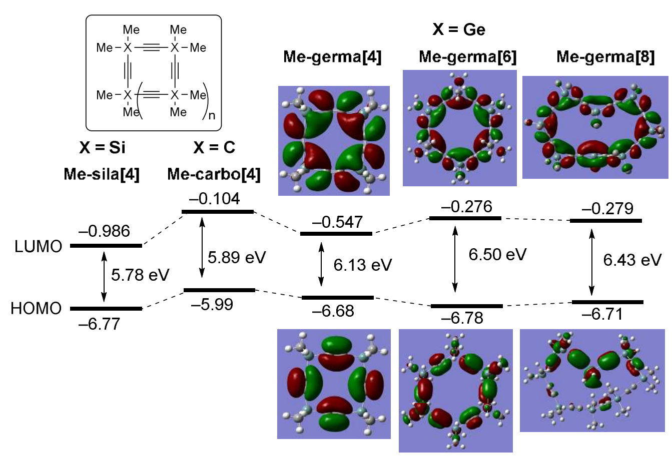

Fig. 3 HOMO-LUMO gaps of pericyclynes by B3LYP/6-31G* (Gaussian 09)

Conclusions

We synthesized and characterized germa[4]-, [6]-, and [8]pericyclynes comprising alternating germanium atoms and alkyne units. Their physical properties were evaluated by various spectral and XRD analyses. A small bathochromic shift of germa[*n*]pericyclynes was found in the UV-visible spectra. The through-space interactions were estimated by the DFT calculation. Germa[4]pericyclynes were found to have the smallest energy gap among the germapericyclynes. The cyclic voltammetry analysis showed the oxidation potentials.

Experimental

General information

^{1}H and ^{13}C NMR spectra were recorded using a Jeol JNM-ECP500 spectrometer (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR). Chemical shifts are reported as δ values in ppm and calibrated with respect to the residual solvent peak ($CDCl_3$, δ 7.26 for ^{1}H NMR and δ 77.00 for ^{13}C NMR) or tetramethylsilane (δ 0 for ^{1}H NMR). The abbreviations used are as follows: s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), br (broad peak), and m (complex multiplet). Melting points were measured using a Yanaco Micro melting point apparatus. Infrared spectra were measured using a Jasco FT-IR-4200 spectrometer. Mass spectra were recorded using a Jeol JMS-700 MStaion [EI (70 eV), CI, FAB, and ESI]. X-ray diffraction (XRD) analyses were performed using a Rigaku R-AXIS RAPID/S imaging plate diffractometer. Raman spectra were obtained using a Jasco laser Raman spectrophotometer, NRS-2100. The cyclic voltammetry measurements of the compounds were performed using a BAS electrochemical analyser ALS612D in dichloromethane containing n-Bu4NPF6 as the supporting electrolyte at 298 K (100 mV s^{-1}). The glassy carbon working electrode was polished using BAS polishing alumina suspension and rinsed with water before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to $Ag/AgNO_3$ and normalized with respect to Fc/Fc^{+}. Flash column chromatography was performed using Merck Silica gel 60. The progress of the reactions was monitored by silica gel thin layer chromatography (TLC) (Merck TLC Silica gel 60 F254). The purification of the mixture of germapericyclynes was performed using a LC-908 recycling preparative high-performance liquid chromatography (HPLC) equipped with a JAIGEL 2H-40 column made by Japan Analytical Industry Co., Ltd. Ethanol solutions of phosphomolybdic acid and anisaldehyde-acetic acid-sulfuric acid were used as the TLC stains. All the reagents were purchased from Sigma-Aldrich, Wako Pure Chemical Industries, Ltd, TCI (Tokyo Chemical Industry, Co. Ltd), Kanto Chemical Co. Inc., and Nakalai Tesque. Anhydrous tetrahydrofuran (THF) was purchased from Kanto Chemical. Density Functional Theory (DFT) calculations were performed using the Gaussian09, and the geometries of the molecules were optimized by employing the B3LYP density functionals and the 6-311G* basis set in this series of calculations.

Dichlorodiisopropylgermane (1b)

Isopropylmagnesium chloride (2.0 M THF solution, 117 mL, 223 mmol) was added dropwise to a stirred solution of germanium (IV) chloride (13.6 mL, 117 mmol) in THF (233 mL) for 4 h at −78 °C under nitrogen atmosphere, and the mixture was stirred for 13 h at the same temperature. After gradually warming up to −20 °C, the reaction was quenched with a saturated aqueous solution of ammonium chloride. The mixture was extracted with ether and washed with brine. The organic layer was dried over sodium sulfate, and the solvent was removed in vacuo (65 °C, 9 mmHg) to afford a 5:1 mixture of **1b** and triisopropylgermanium chloride as a colourless oil. The transformation to **2b** was performed without further purification to avoid decomposition. For an analytical sample, the mixture was purified by recycling preparative HPLC to afford **1b** (5.02 g, 19%). IR (NaCl, neat) ν_{max} 2954, 2869, 1465, 1388, 1226, 1008, 875, 583, 550 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.94 (sept, 2H, *J* = 7.5 Hz), 1.29 (d, 12H, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.2, 17.4; LRMS (EI) m/z = 229.97 (M^{+}).

Diethynyldiphenylgermane (2a)

Dichlorodiphenylgermane **1a** (1.0 g, 3.36 mmol) was added to a stirred ethynylmagnesium bromide (0.5 M in THF, 14.8 mL, 7.39 mmol) at 0 °C under nitrogen atmosphere. After 1 h, the reaction mixture was warmed up to ambient temperature and stirred for 43 h. The reaction was quenched with a saturated aqueous solution of ammonium chloride at 0 °C. The resulting mixture was extracted with ether, and the organic layer was washed with water and brine. The organic layer was dried over magnesium sulfate, and the solvent was removed in vacuo. The resulting residue was purified by silica gel column chromatography (hexane) to afford **2a** (874 mg, 94%) as a light pinkish crystal. R_f value 0.13 (hexane); m.p. 44.7–45.7 °C; IR (NaCl, neat) ν_{max} 3270, 2037, 1432, 1095, 735, 694, 512 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68–7.70 (m, 4H), 7.41–7.45 (m, 6H), 2.61 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.6, 132.7, 130.2, 128.6, 95.3, 82.3; LRMS (EI) *m*/*z* = 277 (M^{+}).

Diethynyldiisopropylgermane (2b)

A 5:1 mixture of dichlorodiisopropylgermane **1b** and chlorotriisopropylgermane (6.36 g of mixture, 87.3 mmol of **1b**) in THF (55mL) was added dropwise to a stirred solution of ethynylmagnesium bromide (0.5 M in THF, 175 mL, 87.3 mmol) in THF (55 mL) for 10 min at 0 °C. After 2 h, the mixture was warmed to ambient temperature and stirred for 20 h. The reaction was quenched with a saturated aqueous solution of ammonium chloride at 0 °C. The resulting mixture was extracted with ether, and the organic layer was washed with water and brine. The organic layer was dried over magnesium sulfate, and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (hexane) to afford **2b** (3.43 g, 69%) as a colourless oil. R_f value 0.35 (hexane); IR (NaCl, neat) ν_{max} 3290, 2945, 2864, 2032, 1464, 669 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.36 (s, 2H), 1.46 (sep, 2H, *J* = 7.0 Hz), 1.20 (d, 12H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 94.4, 82.8, 18.6, 16.4; LRMS (ESI) *m*/*z* = 232 $[M + Na]^{+}$.

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Synthesis of phenylated germa[*n*]pericyclynes (3a), (4a) and (5a)

n-Butyllithium (2.65 M in hexane, 2.53 mL, 2.72 mmol) was added dropwise to a stirred solution of diethynyldiphenylgermane **2a** (930 mg, 3.36 mmol) in THF (17 mL) at −78 °C under nitrogen atmosphere. After 2 h, dichlorodiphenylgermane **1a** (1.0 g, 3.36 mmol) was added at the same temperature, and the reaction mixture was stirred for 41 h. The reaction was quenched with a saturated aqueous solution of ammonium chloride at −78 °C and warmed up to room temperature. The resulting mixture was extracted with dichloromethane and washed with brine. The organic layer was dried over magnesium sulfate, and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (dichloromethane/hexane = 1/5 to 2/1) to afford the mixture of pericyclynes. The mixture was further purified by recycling preparative HPLC and recrystallization (dichloromethane/methanol) to afford octaphenylgerma[4]pericyclynes **3a** (55 mg, 3.3%), dodecaphenylgerma[6]pericyclynes **4a** (128mg, 7.6%), and hexadecaphenylgerma[8]pericyclynes **5a** (91 mg, 5.4%). All of them were obtained as a white powder.

Octaphenylgerma[4]pericyclyne (**3a**, CCDC 983323)
white powder; R_f value: 0.26 (dichloromethane/hexane = 3/10); m.p. 343.0–348.0 °C; IR (KBr, disc) ν_{max} 3070, 3023, 1484, 1432, 1186, 1095, 998, 735, 695, 681, 666, 462 cm^{-1}; Raman ν_{max} = 2107 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68–7.71 (m, 16H), 7.37–7.44 (m, 24H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.0, 132.8, 130.0, 128.4, 110.3; LRMS (ESI) *m/z* = 1026 [M + Na]$^+$. Recrystallization for XRD analysis was carried out using 1,2-dichloroethane.

Dodecaphenylgerma[6]pericyclyne (**4a**, CCDC 983324)
white powder; R_f value: 0.16 (dichloromethane/hexane = 3/10); m.p. 306.7–307.5 °C; IR (KBr, disc) ν_{max} 3071, 3051, 1644, 1485, 1433, 1095, 735, 695 cm^{-1}; Raman ν_{max} = 2114 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, 24H, *J* = 7.0 Hz), 7.31–7.43(m, 36H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.8, 133.5, 129.9, 128.4, 107.4; LRMS (ESI) *m/z* = 1526 [M + Na]$^+$. Recrystallization for XRD analysis was carried out using 1,2-dichloroethane.

Hexadecaphenylgerma[8]pericyclyne (**5a**, CCDC 983325)
Colourless crystal; R_f value: 0.12 (CH_2Cl_2/hexane = 3 / 10); m.p. 252.0–253.3 °C; IR (KBr) ν_{max} 3434, 3052, 1486, 1434, 1095, 736, 695 cm^{-1}; Raman ν_{max} = 2112 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67–7.70(m, 32H), 7.30–7.39 (m, 48H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.7, 133.4, 129.9, 128.5, 107.8; LRMS (ESI) m/z = 2030 [M + Na]$^+$. Recrystallization for the XRD analysis was carried out using dichloromethane.

Synthesis of isopropylated germa[*n*]pericyclynes (4b) and (5b)

n-Butyllithium (1.60 M in hexane, 7.75 mL, 12.4 mmol) was added dropwise to a stirred solution of diethynyldiisopropylgermane 2b (1.23 g, 5.90 mmol) in THF (60 mL) for 10 min at −78 °C under nitrogen atmosphere. After 2 h, a 5:1 mixture of dichlorodiisopropylgermane **2b** and chlorotriisopropylgermane (1.80 g of mixture, 6.49 mmol of **2b**) was added to the mixture at the same temperature and stirred for 18 h. The reaction mixture was warmed to 0 °C and treated with a saturated aqueous solution of ammonium chloride. The mixture was extracted with dichloromethane and washed with brine. The organic layer was dried over magnesium sulfate, and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (dichloromethane/hexane = 1/10 to 1/4) to afford the mixture of pericyclynes. Further purification was performed by recycling preparative HPLC and additional silica gel column chromatography to afford dodecaisopropylgerma[6]pericyclynes **4b** (193 mg, 18%) and hexadecaisopropylgerma[8]pericyclynes **5b** (140 mg, 13%). Both of them were obtained as a white powder.

Dodecaisopropylgerma[6]pericyclyne (**4b**, CCDC 983326)
White solid; R_f value: 0.11(hexane/CH_2Cl_2 = 10/1); m.p. 106.8–107.1 °C; IR (KBr, disc) ν_{max} 2943, 2885, 2863, 1461, 1003, 674 cm^{-1}; Raman ν_{max} = 2099 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.38 (sept, 12H, *J* = 7.5 Hz), 1.17 (d, 72H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 106.9, 18.9, 16.7; LRMS (ESI) *m/z* = 1120 [M + Na]$^+$. Recrystallization for the XRD analysis was carried out using THF.

Hexadecaisopropylgerma[8]pericyclynes (**5b**, CCDC 983327)
Colourless solid; R_f value: 0.11(hexane/CH_2Cl_2 = 10/1); m.p. 80.2–81.9 °C; IR (KBr, disc) ν_{max} 2943, 2885, 2863, 1461, 1005, 667 cm^{-1}; Raman ν_{max} = 2098 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.38 (sept, 16H, *J* = 7.5 Hz), 1.17 (d, 96H, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 107.1, 18.8, 16.6; LRMS (ESI) *m/z* = 1485 [M + Na]$^+$.

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Notes and references

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† Electronic Supplementary Information (ESI) available: The synthesis and characterization of germapericyclynes with UV-visible, fluorescence

emission spectra, CV (DPV), and crystallographic data (CCDC 983323–983327). See DOI: 10.1039/b000000x/

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