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Bis(triazole) derivatives of organodigermanes: synthesis, structure, and properties

Kirill V. Zaitsev, Andrei D. Trubachev, Victor A. Tafeenko and Yurii F. Oprunenko

Table of Contents

NMR Spectra of [(1,4-C_2HN_3Bn)$GePh_2$]$_2$ (1)

General Methods and Remarks. All operations with germanium derivatives were conducted in a dry argon atmosphere using standard Schlenk techniques. ^{1}H NMR (400.130 MHz) and ^{13}C NMR (100.613 MHz) spectra were recorded on Bruker 400 or Agilent 400 spectrometers (at 295 K). Chemical shifts in the spectra are given in ppm relative to internal Me_4Si.

Solvents were dried by usual procedures. THF was stored over solid KOH and then distilled from sodium/benzophenone. NEt_3 was refluxed and distilled over sodium. Dichloromethane was distilled over CaH_2; $CDCl_3$ over CaH_2 under argon.

Initial compounds, 1,2-diethynyl-1,1,2,2-tetraphenyldigermane, $[HC{\equiv}C\text{-}GePh_2\text{-}]_2$, benzyl azide $PhCH_2N_3$[S1] were obtained using published procedures. Other reagents (Aldrich) were commercially available and were used as received.

Optical Spectroscopy. Absorption spectra were recorded on a Hitachi U-1900 spectrophotometer with respect to the solvent (MeCN). Fluorescence spectra were measured on a Hitachi F-7000 luminescence spectrometer in the 90° geometry. Solutions were measured in a standard quartz cell with 1.00-cm optical path length at room temperature (20°C). The measured fluorescence spectra were corrected for the inner filter effect according to the formula:

$$I = I_0 \cdot 10^{0.5(D_{\mathrm{ex}}+D_{\mathrm{em}})},$$

where I_0 is measured fluorescence intensity; D_{ex} and D_{em}, absorbance of solutions at excitation and registration wavelengths, respectively.

The fluorescence quantum yield was calculated by the reference dye method (a solution of rhodamine B in ethanol was used as reference):

$$Q = \frac{I}{I_{Rh}}\frac{D_{Rh}}{D}\left(\frac{n}{n_{Rh}}\right)^2 Q_{\mathrm{Rh}},$$

where I and I_{Rh} are integral fluorescence intensities of the measured solution and the rhodamine solution, respectively; D and D_{Rh}, absorbance at excitation wavelength of the measured solution and the rhodamine solution, respectively; n and n_{Rh} are refractive indices of MeCN and ethanol, respectively; Q_{Rh} is the rhodamine fluorescence quantum yield.

X-ray Crystallography. Single crystals were subjected to X-ray single crystal measurements at Pilatus100K diffractometer using graphite monochromatized MoK_α radiation. Details of the X-ray studies are given in Table S1 (see below). The structure was solved and refined using the SHELXTL program package. The structure was defined by direct statistical methods and refined by full-matrix anisotropic approximation for F^2 for all non-hydrogen atoms with ShelXL program. The hydrogen atoms were localized by direct method and refined in the isotropic approximation. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre with no. CCDC 2363351. This information can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Details of synthesis

Synthesis of *1,2-bis(1-benzyl-1H-1,2,3-triazol-4-yl)-1,1,2,2-tetraphenyldigermane, $[1,4\text{-}C_2HN_3(CH_2Ph)GePh_2\text{-}]_2$ (1)*

Method 1.

At 0°C benzyl azide (0.0277 g, 0.21 mmol, 2.1 eq.) was added slowly to a solution of $[HC{\equiv}C\text{-}GePh_2\text{-}]_2$ (0.0500 g, 0.10 mmol, 1.0 eq.), $[Cu(OAc)]_n$ in THF (5 mL) under argon atmosphere. The reaction mixture was stirred overnight, then all volatile materials were removed under reduced pressure and the residue was purified by flash column chromatography (silica gel 60, EtOAc/PE) to give $[1,4\text{-}C_2HN_3(CH_2Ph)GePh_2\text{-}]_2$ (**1**) as a white crystals (0.0316 g, 41%), mp 89°C; m.p.[S1] 89 °C.
^{1}H NMR ($CDCl_3$, 400.130 MHz): δ 7.46 (s, 2H, CHN=), 7.45-7.41 (m, 8H, Ph_H), 7.34-7.26 (m, 10H, Ph_H), 7.22-7.17 (m, 8H, Ph_H), 7.15-7.11 (m, 4H, Ph_H), 5.49 (s, 4H, $2CH_2$) ppm.
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.613 MHz): δ 142.77 (=CN), 135.79 (*ipso*-GeC_6H_5), 135.21, 128.28 (*o*/*m*-GeC_6H_5), 135.10 (*ipso*-$C_6H_5CH_2$), 134.97 (*p*-$C_6H_5CH_2$), 130.75 (=CHN), 128.95 (*p*-GeC_6H_5), 128.40, 127.72 (*o*/*m*-$C_6H_5CH_2$), 53.53 (CH_2).
NMR spectra correspond to the literature data.[S1]
EI/MS (70 eV) *m/z* (%): 693 (8) [M^+-Ph], 678 (9) [M^+-Bn], 652 (3) [M^+-Bn-CHN], 624 (1) [M^+-Bn-CHN-N_2], 385 (1) [$Ph_2Ge(C_2HN_3Bn)^+$], 227 (15) [Ph_2Ge^+], 150 (16) [$PhGe^+$], 91 (100) [Bn^+].

Method 2.

At 0°C benzyl azide (0.0279 g, 0.21 mmol, 2.1 eq.) was added slowly to a mixture of $[HC{\equiv}C\text{-}GePh_2\text{-}]_2$ (0.0500 g, 0.10 mmol, 1.0 eq.), $CuSO_4{\cdot}5H_2O$ (0.0026 g, 0.010 mmol, 10 mol. %), sodium ascorbate (0.0040 g, 0.02 mmol, 20 mol. %) in THF (5 mL) and water (5 mL) under argon atmosphere. The reaction mixture was stirred overnight, then all volatile materials were removed under reduced pressure and the residue was purified by flash column chromatography (silica gel 60, EtOAc/PE) to give $[1,4\text{-}C_2HN_3(CH_2Ph)GePh_2\text{-}]_2$ (**1**) as a white crystals (0.0216 g, 28%), mp 89 °C; m.p.[S1] 89°C.

Table S1. Crystallographic Data for Compound [(1,4-C_2HN_3Bn)$GePh_2$]$_2$ (**1**)

	[(1,4-C_2HN_3Bn)$GePh_2$]$_2$
empirical formula	$C_{21}H_{18}GeN_3$
M_w	384.97
temperature (K)	295(2)
size (mm)	0.28 x 0.20 x 0.15
cryst. system	monoclinic
space group	$P2_1/n$
a (Å)	12.5847(8)
b (Å)	9.0929(5)
c (Å)	16.1645(9)
α (deg)	90.00
β (deg)	97.697(3)
γ (deg)	90.00
V (Å^3)	1833.06(19)
Z	4
ρ_{cald}(g·cm^{-3})	1.395
abs coeff. (mm^{-1})	1.678
F(000)	788
θ range (deg)	2.200 – 26.999
no. of collected/unique rflns.	24403 / 3995
R_{int}	0.1544
data/restraints/params.	3995 / 0 / 226
goodness of fit on F^2	0.889
final *R* indices ($I > 2\sigma(I)$)	$R_1 = 0.0511$, $wR_2 = 0.0808$
R indices (all data)	$R_1 = 0.1584$, $wR_2 = 0.1095$
largest diff. peak/hole (e/Å^3)	0.461 / -0.766

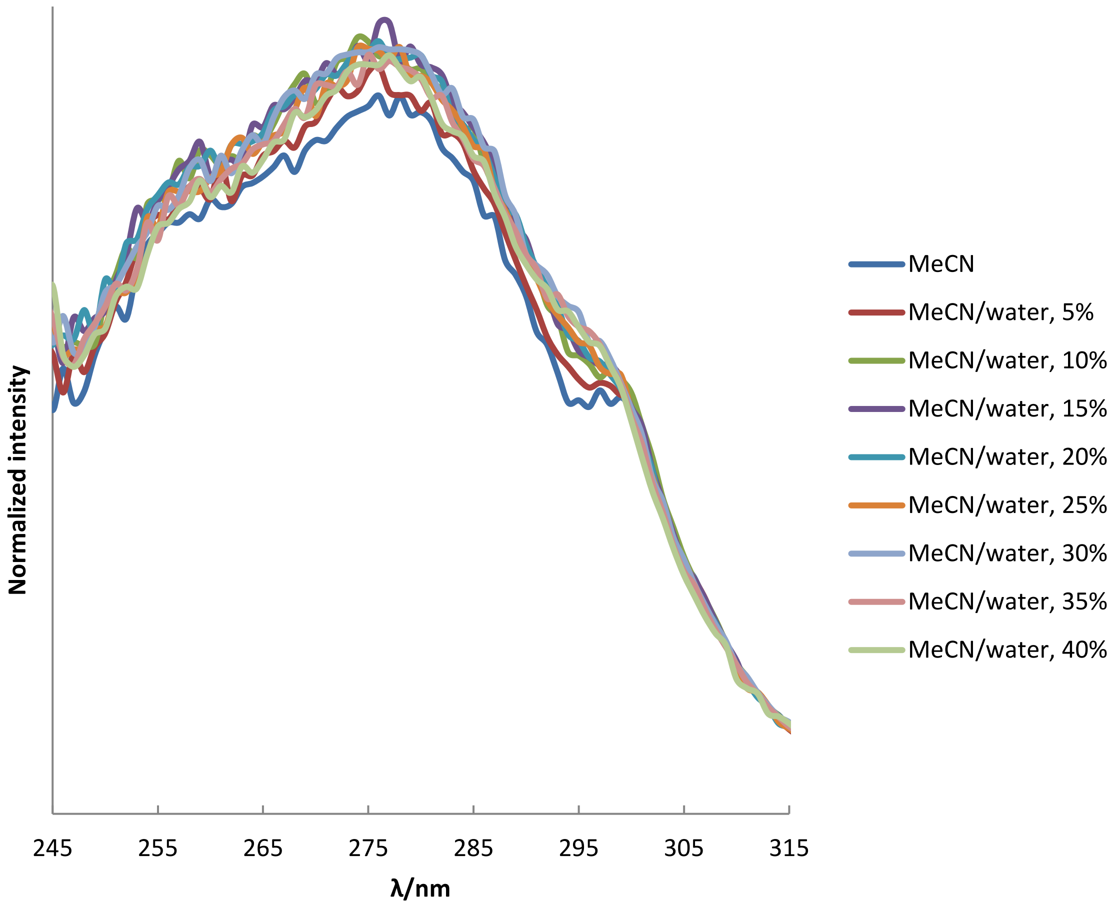

Fig. S1. Normalized excitation spectra of compound **1** in MeCN and in MeCN/water mixture.

NMR Spectra of $[(1,4\text{-}C_2HN_3Bn)GePh_2]_2$ (1)

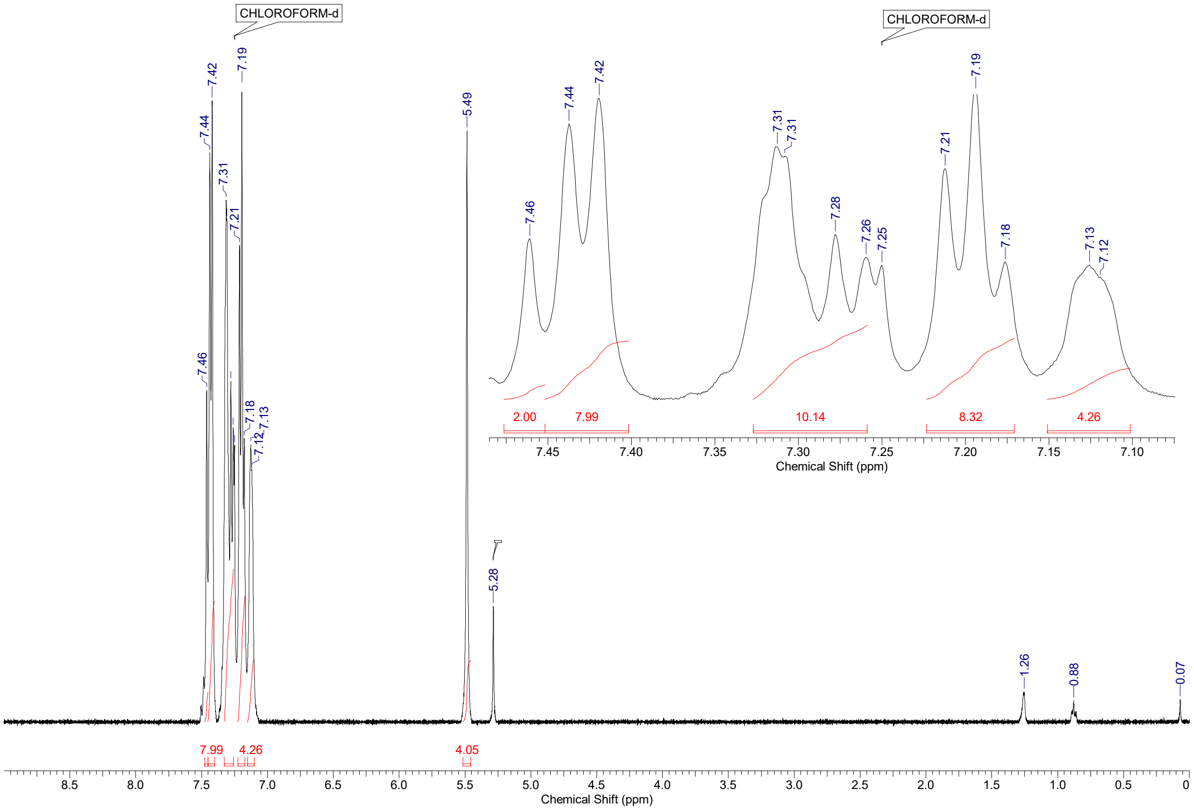

Fig. S2. NMR ^{1}H spectrum of $[1,4\text{-}C_2HN_3(CH_2Ph)GePh_2]_2$ (**1**) ($CDCl_3$, RT).

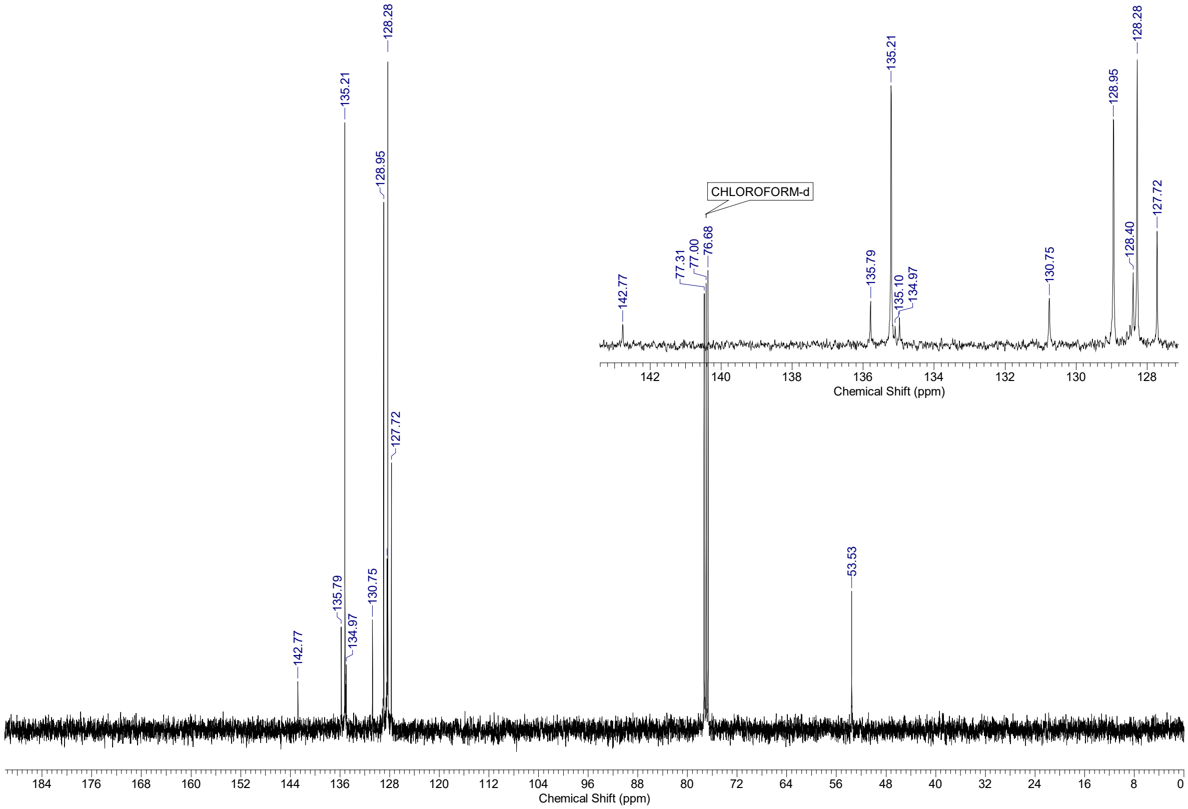

Fig. S3. NMR ^{13}C spectrum of $[1,4\text{-}C_2HN_3(CH_2Ph)GePh_2]_2$ (**1**) ($CDCl_3$, RT).

References

S1. K. V. Zaitsev, G. A. Veshchitsky, Y. F. Oprunenko, A. V. Kharcheva, A. A. Moiseeva, I. P. Gloriozov and E. K. Lermontova, *Chem.–Asian J.*, 2023, **18**, e202300753.