# Synthesis and Characterization of N-Methyl-Substituted Germocanes. Crystal Structure of MeN(CH$_2$CH$_2$O)$_2$GeBr$_2$

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The reaction of GeHal$_4$ with MeN(CH$_2$CH$_2$OSiMe$_3$)$_2$ affords dihalogermocanes MeN(CH$_2$CH$_2$O)$_2$GeHal$_2$ (**1**, Hal = Br; **2**, Hal = Cl). Treatment of Me$_2$Ge(NMe$_2$)$_2$ with MeN(CH$_2$CH$_2$OH)$_2$ leads to dimethylgermocane MeN(CH$_2$CH$_2$O)$_2$GeMe$_2$ (**3**). The composition and structure of **1-3** were established by elemental analyses, $^1$H, $^{13}$C NMR spectroscopy, and mass spectrometry. The crystal structure of **1** is reported; structural data obtained from geometry DFT optimization on **1** are in good agreement with experimental results. Values of the electron density in the N→Ge bond critical point and the Laplacian of charge density for **1-3** indicate a closed-shell interaction between the Ge and N atoms.

*Key words:* Germocanes, Transannular Interaction, Crystal Structure, DFT Calculations

## Introduction

Germatranes (type **A**) are an intensively studied class of compounds with a hypervalent germanium atom [1]. These compounds received special attention due to speculations about the nature of the N→Ge transannular interaction. In contrast, germocanes (type **B**) – closely related analogues of germatranes – have been little studied [2 – 16]. However, one might expect that these compounds even possess a greater chemical and structural flexibility in comparison to germatranes (**A**) owing to the variability of the substituents R, X, and Y and their influence on structures and chemical properties:
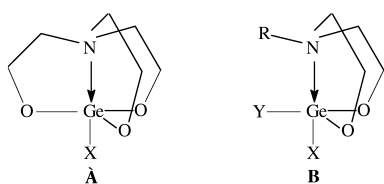


Chart 1.

According to the literature several synthetic methods have been applied to achieve the formation of the germocane skeleton. A common approach to ger-

mocanes is the reaction between GeO$_2$, (RGeO$_{1.5}$)$_n$, XYGeH$_2$, XYGeCl$_2$ or XYGe(OR)$_2$ with different dialkanolamines [2, 7 – 9, 11 – 16]; other methods have been less investigated. Treatment of GeCl$_4$ with RN(CH$_2$CH$_2$OSiMe$_3$)$_2$ (R = Me, $i$-C$_3$H$_7$) leads to the corresponding 2,2-dichlorogermocanes [4].

Up to now no chemical properties of germocanes were investigated except for a reaction of 2,2-dihydroxygermocanes with bidentate ligands [11 – 14] and the germocane–germatrane rearrangement [3].
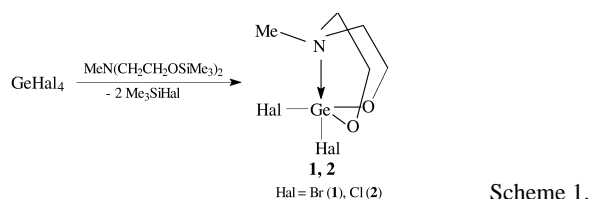
Structures of germocanes has been explored by X-ray diffraction studies in the solid state [5, 6, 9, 10, 12, 15], by $^1$H, $^{13}$C [11, 12], and $^{73}$Ge NMR spectroscopy in solutions [8], and by mass-spectrometry (electron impact) in the gas phase [2, 4]. But in contrast to germatranes [1b] the relationship between key structural parameters of germocanes and electronic and steric properties of substituents adjacent to the Ge and N atoms has still not been studied.

Continuing our investigations in metallatrane chemistry [17] we focussed our efforts on the synthesis and characterization of germocanes **1-3**. In spite of the fact that compound **2** has been prepared earlier, no spectroscopic data for this germocane were pub-

lished [4]. Our motivation was to prepare compounds **1–3**, to investigate the products by $^1$H and $^{13}$C NMR spectroscopy and to confirm and characterize the intramolecular N→Ge bond in these derivatives by X-ray studies and DFT calculations.

## Results and Discussion

2,2-Dihalogermocanes **1** and **2** were prepared by the reaction of the corresponding GeHal$_4$ with an equimolar quantity of MeN(CH$_2$CH$_2$OSiMe$_3$)$_2$ according to Scheme 1:

$$\text{GeHal}_4 \xrightarrow[\text{- 2 Me}_3\text{SiHal}]{\text{MeN(CH}_2\text{CH}_2\text{OSiMe}_3)_2}$$

**1, 2**

Hal = Br (**1**), Cl (**2**)                    Scheme 1.

Treatment of bis(dimethylamino)dimethylgermane with N-methyldialkanolamine led to germocane **3** in quantitative yield (Scheme 2). We suggest that this method might be very useful in the future for the synthesis of various other germocanes.

$$\text{Me}_2\text{Ge(NMe}_2)_2 \xrightarrow[\text{- 2 HNMe}_2]{\text{MeN(CH}_2\text{CH}_2\text{OH)}_2}$$

**3**                    Scheme 2.
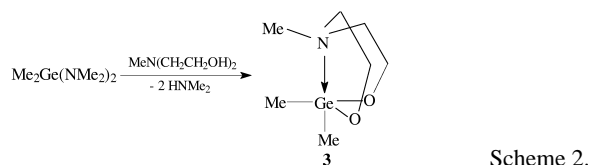
$^1$H and $^{13}$C NMR spectra of compounds **1-3** are in good agreement with suggested structures. In the $^1$H NMR spectrum of **3** (CDCl$_3$, 298 K) signals of the methylene protons of the germocane skeleton appear as a set of two pseudo-triplets, forming an AA'XX' spin system. Apparently, Berry pseudo-rotation [18a] occurring in solutions of germocane **3** is the reason of this pattern. Compound **3** possesses a short N→Ge contact in CDCl$_3$ solution which has been confirmed by the presence of strong NOEs from the H$^0$ protons of the Me–N group to the H$^1$ protons of the Me–Ge groups (Chart 2).

Signals of the methylene protons of the germocane skeleton in **1** and **2** (298 K) appear as a set of two multiplets, forming an ABXY spin system. This pattern is a general feature of the "ocane" framework for a variety of germocanes containing electronegative substituents bound to the germanium atom [11, 13]. In contrast to

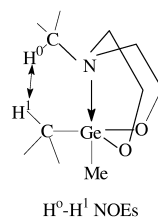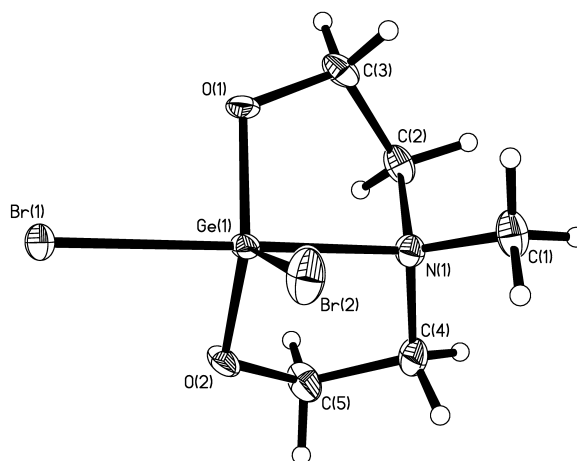H$^0$-H$^1$ NOEs                    Chart 2.

Fig. 1. Molecular structure of **1**.

germocane **3**, germocanes **1** and **2** exist in CDCl$_3$ solutions at room temperature only in one "frozen" conformation. The $^1$H NMR spectrum of compound **2** in DMSO-d$_6$ remains unchanged over a temperature range of 298–383 K.

Centers of the NCH$_2$ and OCH$_2$ proton signals in the $^1$H NMR spectra of **1** and **2** are displaced to lower fields compared to those in compound **3**. According to Tandura *et al.* [18b], this implies a strengthening of the N→Ge bond in **1** and **2** in comparison with **3** in CDCl$_3$ solution.

The molecular structure of **1** is shown in Fig. 1; representative bond lengths and angles are summarized in Table 1. The coordination polyhedron at the germanium atom in **1** is typical for germocane derivatives and represents a slightly distorted trigonal bipyramide with N(1) and Br(1) atoms in apical positions and oxygen atoms O(1), O(2) and bromine Br(2) occupying equatorial sites. The germanium atom is slightly displaced towards the Br(1) atom from the equatorial plane ($\Delta$Ge = 0.06 Å). The N(1)-Ge(1)-Br(1) fragment is close to linearity (170.3(1)°). This value is typical for germocane derivatives studied earlier (171.0(4)–178.7(3)°) [6, 10]. The N(1)-Ge(1) distance in **1** (2.166(5) Å) lies within the standard range

Table 1. Selected bond lengths [Å] and angles [°] for **1**.

| | | | |
|---|---|---|---|
| Ge(1)-O(1) | 1.784(4) | O(2)-C(5) | 1.438(7) |
| Ge(1)-O(2) | 1.789(4) | N(1)-C(1) | 1.482(8) |
| Ge(1)-N(1) | 2.166(5) | N(1)-C(2) | 1.487(9) |
| Ge(1)-Br(2) | 2.3215(9) | N(1)-C(4) | 1.495(8) |
| Ge(1)-Br(1) | 2.4148(8) | C(2)-C(3) | 1.53(1) |
| O(1)-C(3) | 1.428(7) | C(4)-C(5) | 1.522(9) |
| O(1)-Ge(1)-O(2) | 124.3(2) | C(5)-O(2)-Ge(1) | 117.5(4) |
| O(1)-Ge(1)-N(1) | 85.8(2) | C(1)-N(1)-C(2) | 110.3(5) |
| O(2)-Ge(1)-N(1) | 85.0(2) | C(1)-N(1)-C(4) | 110.2(5) |
| O(1)-Ge(1)-Br(2) | 116.2(2) | C(2)-N(1)-C(4) | 112.4(5) |
| O(2)-Ge(1)-Br(2) | 119.2(2) | C(1)-N(1)-Ge(1) | 119.1(4) |
| N(1)-Ge(1)-Br(2) | 94.2(1) | C(2)-N(1)-Ge(1) | 100.8(4) |
| O(1)-Ge(1)-Br(1) | 91.5(1) | C(4)-N(1)-Ge(1) | 103.7(3) |
| O(2)-Ge(1)-Br(1) | 88.9(2) | N(1)-C(2)-C(3) | 107.0(5) |
| N(1)-Ge(1)-Br(1) | 170.3(1) | O(1)-C(3)-C(2) | 109.6(5) |
| Br(2)-Ge(1)-Br(1) | 95.38(3) | N(1)-C(4)-C(5) | 108.5(5) |
| C(3)-O(1)-Ge(1) | 116.3(4) | O(2)-C(5)-C(4) | 109.6(5) |

Table 2. Main geometrical parameters calculated for MeN $(CH_2CH_2O)_2GeX_2$ (**1**, X = Br; **2**, X = Cl; **3**, X = Me) and $N(CH_2CH_2O)_3GeX$ (**4**, X = Br; **5**, X = Cl; **6**, X = Me) and calculated Ge–N bond properties.

| Compound | N→Ge, Å | Ge–O$_{aver}$, Å | Ge–X$_{ax}$, Å | Ge–X$_{eq}$, Å | $\rho(\mathbf{r}_b)$, au | $V^2\rho(\mathbf{r}_b)$, au |
|---|---|---|---|---|---|---|
| **1** | 2.219 | 1.844 | 2.352 | 2.399 | 0.0675 | 0.074 |
| **4**[a] | 2.289 | 1.828 | 2.354 | – | 0.0595 | 0.072 |
| **2** | 2.218 | 1.837 | 2.190 | 2.232 | 0.0675 | 0.074 |
| **5**[b] | 2.289 | 1.825 | 2.193 | – | 0.0595 | 0.072 |
| **3** | 2.293 | 1.898 | 1.966 | 1.981 | 0.0530 | 0.067 |
| **6** | 2.377 | 1.844 | 1.954 | – | 0.0495 | 0.060 |

[a] X-ray data for **4**: Ge-N = 2.09(2)Å, (Ge-O)$_{average}$ = 1.78(2) Å Ge–Br = 2.360(4) Å [20a]; [b] X-ray data for **5**: Ge-N = 2.096(3) Å, (Ge-O)$_{average}$ = 1.773(3) Å, Ge–Cl = 2.209(1) Å [20b].

for germocanes with electronegative substituents attached to the germanium atom (2.080(3) – 2.16(1) Å) [6, 12] and is shorter than that in 2,2-di(2-thienyl)-N-methylgermocane (2.446(8) Å) [15]. Thus, the latter clearly verifies the existence of a N→Ge transannular bond in **1**, this bond being shorter than that in $i$-$C_4H_9N(CH_2CH_2CH_2)_2GeCl_2$ (2.389(4) Å) [19]. This is in good accordance with a general trend observed in "atrane" structures: the higher the electronegativity of the equatorial groups the shorter the M−N transannular distances. The nitrogen atom has an approximately tetrahedral environment with bond angles ranging from 110.8(4) – 119.1(4)° and is shifted towards the Ge atom. Both five-membered metallacycles -Ge-O-C-C-N- are not planar with maximum deviation from least-squares planes of the C(2) (0.30 Å) and the C(4) (0.24 Å) atoms. The conformation of the eight-membered ring –Ge-O-C-C-N-C-C-O– may be regarded as a boat-chair, while previously studied germocanes exhibit boat-boat conformation [6, 10].

A closely related analogue of **1**, 1-bromogermatrane $N(CH_2CH_2O)_3GeBr$ (**4**), possesses a shorter transannular distance N→Ge (2.09(2) Å) [20a] than that in compound **1**, possibly indicating a N→Ge transannular interaction in germatrane **4** which is stronger than that in germocane **1**. However, it should be noted that steric requirements in tricyclic systems are more stringent than those in bicyclic systems. Thus, the forementioned shortening of the N→Ge distance in germatrane **4** may be due to the steric effects of the tricyclic cage. Data from a comparison of **1** and **4** are consistent with the idea that a transannular interaction in bicyclic structures is stronger than that in analogous tricyclic structures [21], documented by the greater value of $\Delta$Ge for 1-bromogermatrane (**4**) (0.11 Å) than for in compound **1** (0.06 Å) as well as the shorter Ge–Br distance in 1-bromogermatrane (**4**) (2.360(4) Å) [20a] in comparison with the same value of the axial germanium–bromine bond in germocane **1** (Ge–Br(1) = 2.4148(8) Å).

Considering the fact that crystal field forces affect weak interactions such as transannular bond N→Ge in germatranes [22] we have carried out DFT calculations on germocanes **1-3** and on closely related germatranes – $N(CH_2CH_2O)_3GeX$ – **4** (X = Br), **5** (X = Cl), **6** (X = $CH_3$) up to the PBE level of theory. The most important calculated geometrical parameters of these compounds, values of the electron density in the N→Ge bond critical point [$\rho(\mathbf{r}_b)$], and values of the Laplacian of charge density in these points are listed in Table 2.

There is good agreement between the geometrical parameters of **1**, **4** [20a], and **5** [20b] for the solid phase (X-ray data) and for the free molecules (calculated data). However, calculated values of the Ge–N distances for these compounds are somewhat longer ($\sim$ 0.2 Å) than those found in the solid state. An explanation for these discrepancies is the weakness of the transannular bond in compounds **1**, **4**, and **5**, which are exposed to crystal field effects and dipole-dipole interactions in the solid state [22]. At the same time, calculated Ge–O bond distances are slightly longer than those obtained from relevant X-ray data. Values of the electron density in the Ge–N critical point and the Laplacian of charge densities for **1-6** give evidence for an interaction between the Ge and N atoms which is a closed-shell interaction [23]. Analo-
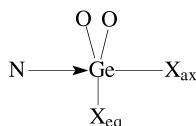
Chart 3.

gous results were recently found for 1-methylsilatrane, $N(CH_2CH_2O)_3SiCH_3$ [24].

The Ge–N bond distances in the pairs **1** // **4**, **2** // **5**, and **3** // **6** are shorter in germocanes **1-3** in comparison with germatranes **4-6**. Analogously, values of the electron density in the Ge–N bond critical point are greater for germocanes **1-3** than in those for germatranes **4-6**. Data presented in Table 2 confirm that the strength of the Ge–N transannular interaction in germocanes is greater than that in the corresponding germatranes.

Finally it should be noted that according to the concept of a three-center-four-electron (3c-4e) bond, which originated in principle from the paper of Musher [25], the Ge–$X_{ax}$ bond distance should be longer than the Ge–$X_{eq}$ bond distance in germocanes (Chart 3).

X-ray data for compound **1** (the Ge–Br(1)$_{ax}$ bond distance is longer than the Ge–Br(2)$_{eq}$ bond distance) are in accordance with the (3c-4e) bond theory. However, the calculated Ge–$X_{eq}$ bond distances are longer than the calculated Ge–$X_{ax}$ bond distances in germocanes **1-3**. This fact was also previously found for the calculated geometry of a closely related silocane $HN(CH_2CH_2O)_2Si(OH)_2$ [21]. Moreover, theoretical calculations show that no 3c-4e bond scheme exists for similar trigonal-bipyramidal structures such as the anion $[SiF_5]^-$ [26]. We conclude that more experimental and theoretical results are needed to clarify the bonding situation in the Ge–N transannular interaction of germocanes.

## Experimental Section

All solvents were dried by standard methods and distilled prior to use. All manipulations were carried out in an argon atmosphere using standard Schlenk techniques. $Me_2Ge(NMe_2)_2$ [27] and $MeN(CH_2CH_2OSiMe_3)_2$ [28] were prepared according to the literature. NMR spectra were recorded on a Varian VXR 400 spectrometer. The chemical shift values were referenced internally to residual solvent resonances and reported in ppm relative to TMS. Mass spectra (EI-MS) were recorded on a VARIAN CH-7a instrument using electron impact ionisation at 70 eV. All assignments are made with reference to the most abundant isotopes. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of Moscow State University.

*2,2-Dibromo-6-methyl-1,3-dioxa-6-aza-2-germacyclooctane (**1**)*

A mixture of $MeN(CH_2CH_2OSiMe_3)_2$ (5.27 g, 0.02 mol) and $GeBr_4$ (7.84 g, 0.02 mol) in $CHCl_3$ solution (15 ml) was refluxed for 3 h. A white precipitate was filtered off, washed with cold $CHCl_3$ (2 × 3 ml) and dried *in vacuo* to give 5.80 g of **1** (83%). – $^1$H NMR (400 MHz, $CDCl_3$): $\Delta$ = 2.64 (s, 3 H, $NCH_3$); 2.91, 3.0 (2 m, 4 H, $NCH_2$); 4.03 (m, 4 H, $OCH_2$). – $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ = 44.88 ($NCH_3$), 54.76 ($NCH_2$), 59.37 ($OCH_2$). – MS (EI, 70 eV): $m/z$ (%) = 349 (0.5) [M$^+$], 319 (33) [M$^+$- $CH_2O$], 270 (82) [M$^+$–Br], 240 (82) [M$^+$–Br–$CH_2O$]. – $C_5H_{11}Br_2GeNO_2$ (349.54): calcd. C 17.19, H 3.17, N 4.01; found C 17.42, H 3.26, N 3.88.

*2,2-Dichloro-6-methyl-1,3-dioxa-6-aza-2-germacyclooctane (**2**)*

A procedure similar to that for **1** was used except that the refluxing time was 9 h. $MeN(CH_2CH_2OSiMe_3)_2$ (5.27 g, 0.02 mol), $GeCl_4$ (4.29 g, 0.02 mol), $CHCl_3$ (15 ml). Yield – 4.22 g (81%) (white solid). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.67 (s, 3 H, $NCH_3$); 2.88, 2.98 (2 m, 4 H, $NCH_2$); 3.92 (m, 4 H, $OCH_2$). – $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ = 44.37 ($NCH_3$), 54.95 ($NCH_2$), 58.74 ($OCH_2$). – MS (EI, 70 eV): $m/z$ (%) = 261 (1.2) [M$^+$], 231 (32) [M$^+$–$CH_2O$], 226 (45) [M$^+$–Cl]. – $C_5H_{11}Cl_2GeNO_2$ (260.64): calcd. C 23.05, H 4.26, N 5.38; found C 22.85, H 4.40, N 5.23.

*2,2,6-Trimethyl-1,3-dioxa-6-aza-2-germacyclooctane (**3**)*

A solution of $MeN(CH_2CH_2OH)_2$ (0.69 g, 5.8 mmol) and $Me_2Ge(NMe_2)_2$ (1.1 g, 5.8 mmol) in toluene (25 ml) was stirred for 10 h at 70 °C. All volatiles were evaporated *in vacuo*. 1.27 g (100%) of **3** was obtained. – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.44 (s, 6 H, $GeCH_3$), 2.34 (s, 3 H, $NCH_3$), 2.55 (t, 4 H, $NCH_2$), 3.70 (t, 4 H, $OCH_2$). – $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ = 1.47 ($GeCH_3$), 43.71 ($NCH_3$), 59.02 ($NCH_2$), 61.69 ($OCH_2$). – $C_7H_{17}GeNO_2$ (219.80): calcd. C 38.27, H 7.80, Ge 33.02; found C 38.10, H 7.88, Ge 33.16.

*X-ray crystal structure determination*

Crystal data for **1**: $C_5H_{11}Br_2O_2Ge_1N_1$, M = 349.56, monoclinic, $a$ = 6.9729(4), $b$ = 12.1262(7), $c$ = 11.5639(7) Å, $\beta$ = 90.800(2)°, $V$ = 977.7(1) Å$^3$, space group $P2_1/n$, $Z$ = 4, $D_c$ = 2.375 g/cm$^3$, F(000) = 664, $\mu$(Mo-K$_\alpha$) = 11.263 mm$^{-1}$, a colourless plate with dimensions *ca.* 0.40 × 0.30 × 0.04 mm. A total of 6001 reflections (2225 unique, $R_{int}$ = 0.1108) were measured on a Bruker SMART diffractometer (graphite monochromatized Mo-K$_\alpha$ radiation, $\lambda$ = 0.71073 Å) at 120(2) K. Data were collected in the range 2.43 < $\theta$ < 27.50 (−8 ≤ $h$ ≤ 9, −13 ≤ $k$ ≤ 15, −13 ≤

$I \leq 15$) using $\omega$ scan mode. The structure was solved by direct methods [29] and refined by full matrix least-squares on $F^2$ [30] with anisotropic thermal parameters for all non-hydrogen atoms. All H atoms were placed in calculated positions and refined using a riding model. The final residuals were: $R_1 = 0.0690$, $wR_2 = 0.1858$ for 1944 reflections with $I > 2\sigma(I)$ and 0.0754, 0.1929 for all data and 102 parameters. Goof = 1.063, maximum $\Delta\rho = 3.606\,\mathrm{e}\times\mathrm{\AA}^{-3}$.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-202412. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int.code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

*Calculations*

The non-empirical generalized gradient approximation (GGA) for the exchange-correlation functional of Perdew *et al.* was employed [31]. Calculations were performed using the program "PRIRODA" developed by Laikov, which implements an economical computational procedure [32]. Large orbital basis sets of contracted Gaussian-type functions of the size (8s3p2d):[4s3p2d] for H, (14s8p3d2f):[8s4p3d2f] for C, (14s8p3d2f):[8s4p3d2f] for N, (14s8p3d2f):[8s4p3d2f] for O, (20s15p3d2f):[13s9p3d2f] for Cl, (25s19p14d3f):[18s14p9d3f] for Ge, and (25s19p14d 3f):[18s14p9d3f] for Br were used. Full geometry optimization was performed for a number of structures followed by vibrational frequency calculation using analytical first and second derivatives. Each structure has been characterized by the vibrational analysis. The present theoretical method has given very useful results in the organometallic chemistry of Si, Cr, Ti, Zr, Sb and Bi [33].

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