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Heteroorganic betaines

7.* Synthesis and structure of a germanium-containing organophosphorus betaine $Et_3P^+—CHMe—GeMe_2—S^-$

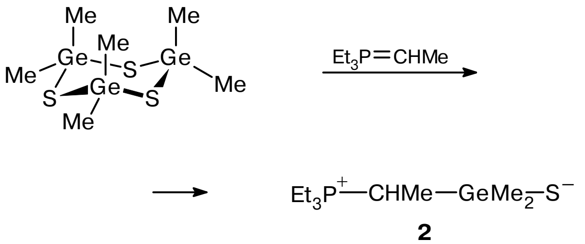
I. V. Borisova,[a] N. N. Zemlyanskii,[a] V. N. Khrustalev,[b] M. G. Kuznetsova,[a] Yu. A. Ustynyuk,[c] and M. S. Nechaev[c]

[a]State Research Center of the Russian Federation
"State Research Institute of Chemistry and Technology of Organoelement Compounds",
38 sh. Entuziastov, 111123 Moscow, Russian Federation.
Fax: +7 (095) 273 1323. E-mail: zemlyan@mail.cnt.ru
[b]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5085.
[c]Department of Chemistry, M. V. Lomonosov Moscow State University,
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 2677. E-mail: yust@nmr.chem.msu.su

Germanium-containing organophosphorus betaine $Et_3P^+—CHMe—GeMe_2—S^-$ was synthesized by the reaction of hexamethylcyclotrigermatrithiane with $Et_3P=CHMe$. The structure of the betaine was established by X-ray diffraction analysis and multinuclear NMR spectroscopy. In the crystal, the $P^+—C—Ge—S^-$ main chain of the molecule adopts a folded *cis-gauche* conformation due to strong Coulomb interactions between the anionic and cationic centers. The equilibrium geometry of the isolated molecule was calculated within the framework of the density functional theory (the PBE functional, the TZ2P basis set). The calculated geometric characteristics are in qualitative agreement with the X-ray data. The structure of the betaine is compared with the structure of its silicon-containing analog studied previously.

Key words: heteroorganic betaines, phosphorus ylides, organogermanium compounds, X-ray diffraction analysis, NMR spectroscopy, quantum chemistry, density functional theory.

The chemistry of heteroorganic betaines has been investigated extensively in recent years.[2,3] Previously, we have synthesized and studied in detail first representatives of organophosphorus betaines (**1**) containing the $R_3P^+—CR^1R^2—ER^3R^4—X^-$ structural fragment (**1a**: E = C, Si, or Ge; X = cyclopentadienylidene, C_5H_4, or fluorenylidene $C_{13}H_8$; **1b**: E = C or Si; X = S).[4—9] In the present study, we prepared germanium-containing organophosphorus betaine **2** by the reaction of hexamethylcyclotrigermatrithiane with $Et_3P=CHMe$.



2

Compound **2** was obtained as colorless crystals, which are virtually insoluble in hydrocarbons, poorly soluble in C_6H_6 and ether, moderately soluble in THF in the cold, and more readily soluble in pyridine. The reactions of hexamethylcyclotrigermatrithiane $(Me_2GeS)_3$ with phosphorus ylides $Ph_3P=CRR'$ containing the Ph groups at the phosphorus atom, unlike those of organocyclosilthianes, are more complicated processes giving rise to mixtures of products.

The parameters of the NMR spectra of betaine **2** are similar to those of its silicon analogs based on the same phosphorus ylide.[7] As in the case of the thermally stable Si-containing analog, the difference between the spin-spin coupling constant $^1J_{PC}$ for the $P^+—C—Ge—S^-$ fragment in betaine **2** and the same constant for the Et_4P^+ cation is rather small (9.7 Hz). Previously,[9] we have found that this difference, which characterizes the change in the degree of the *s* character of the central P—C bond, correlates with the thermal stability of betaines in solutions. Thus, the smaller the absolute value of this difference the more stable betaine.

According to the X-ray diffraction data, the $P^+—C—Ge—S^-$ main chain of betaine **2** (Fig. 1, Table 1), like those of Si,P-betaines **1b** studied previously,[8] adopts the *cis-gauche* conformation due to Coulomb interactions between the charged centers of the molecule. This conformation is characterized by

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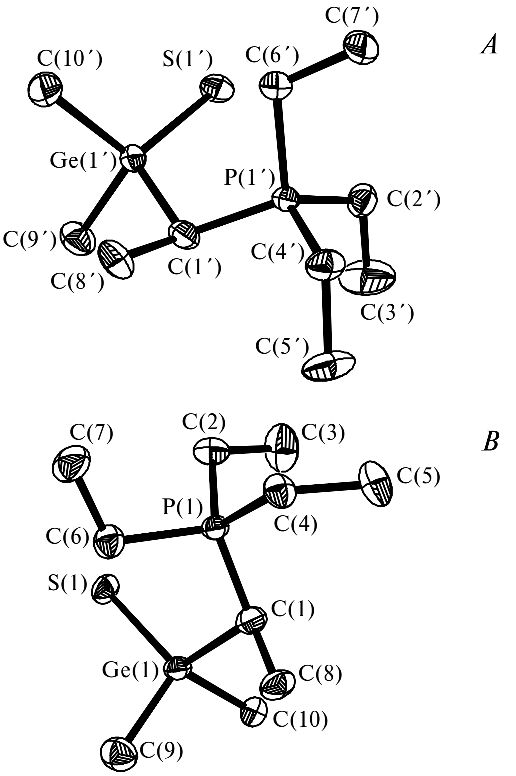

Fig. 1. Molecular structure of compound **2**; two independent molecules are shown (thermal ellipsoids with the 50% probability).

Table 1. Geometric parameters of molecule **2** determined by X-ray diffraction analysis and calculated within the framework of the density functional theory PBE/TZ2P (the bond lengths are given in Å; the bond angles and torsions angles are given in degrees)

Parameter	X-ray data		PBE/TZ2P
	A	*B*	
Bond	*d*/Å		
P(1)—C(1)	1.783(3)	1.785(2)	1.815
P(1)—C(2)	1.791(3)	1.794(3)	1.836
P(1)—C(4)	1.808(2)	1.808(3)	1.836
P(1)—C(6)	1.826(3)	1.817(3)	1.857
C(1)—C(8)	1.531(3)	1.540(4)	1.537
C(1)—Ge(1)	2.041(3)	2.031(3)	2.108
Ge(1)—S(1)	2.1400(3)	2.1400(3)	2.157
Ge(1)—C(9)	1.958(3)	1.967(3)	1.994
Ge(1)—C(10)	1.952(3)	1.955(3)	1.989
Bond angle		ω/deg	
C(1)—P(1)—C(2)	112.24(13)	112.24(12)	108.49
C(1)—P(1)—C(4)	111.51(12)	111.(86)	108.68
C(1)—P(1)—C(6)	109.67(13)	109.15(12)	108.44
P(1)—C(1)—Ge(1)	114.35(13)	114.88(12)	110.84
C(8)—C(1)—Ge(1)	110.48(17)	110.56(18)	112.24
C(1)—Ge(1)—C(9)	106.93(12)	99.54(12)	102.83
C(1)—Ge(1)—C(10)	98.99(11)	106.57(13)	103.51
C(1)—Ge(1)—S(1)	114.86(7)	115.47(7)	111.15
Torsion angle		τ/deg	
P(1)—C(1)—Ge(1)—S(1)	25.86(16)	27.32(16)	25.97

noticeable steric strains, which are manifested in elongation of the C—Ge bond in the P^+—C—Ge—S^- main chain (2.032(3) and 2.041(3) Å in two crystallographically independent molecules) compared to the Ge—Me bonds (1.952(3)—1.967(3) Å) and in substantial deviations of all bond angles at the Ge atom from the ideal tetrahedral angle (109.5°). The most pronounced deviations are observed for the P^+—C—Ge bond angles (114.35(13)° and 114.88(12)° in two independent molecules) and the C—Ge—S^- bond angles (114.86(7)° and 115.47(7)°, respectively).

The P^+—C—Ge—S^- torsion angle in the main chain of betaine **2** (25.9(2)° and 27.3(2)°) is substantially smaller that those in the organosilicon analogs (38.2—56.1°). Due to the longer C—Ge bond, the P^+...S^- nonbonding distances (3.774(2) and 3.810(2) Å) are larger than the shortest P^+...S^- distance in silicon-containing organophosphorus betaines (3.681(4) Å), which we have found in betaine Et_3P^+—C(H)Me—$SiPh_2$—S^-. At the same time, the P—C bond in the P^+—C—Ge—S^- main chain of betaine **2** (1.783(3) and 1.785(2) Å) is substantially shorter than the analogous bonds in Si,P-betaines (1.807(3)—1.830(4) Å). The Ge—S^- bond length (2.140(7) Å in both independent molecules) agrees well with the known Ge—S^- bond lengths in sulfur-germanium anions with the adamantane structure $Ge_4S_{10}^{4-}$.[10—12]

Betaine **2** is rather stable. After irradiation of a solution of **2** in C_5D_5N with UV light using a medium-pressure mercury lamp at ~20 °C for 45 h, the conversion was at most 60% (the NMR spectral data). Under these conditions, the main reaction proceeded as the retro-Wittig cleavage of the $GeMe_2$—CHMe bond (the yield was ~90%). The Corey—Chaykovsky reaction accompanied by the elimination of Et_3P accounted for approximately 10% of the reaction products. The reactivity of betaine **2** will be discussed in more detail elsewhere.

The geometry of the isolated betaine molecule Et_3P^+—CHMe—$GeMe_2$—S^- (see Fig. 1 and Table 1) was calculated within the framework of the density functional theory, which we have successfully used in the theoretical studies of the structures and reactivities of silicon-containing organophosphorus betaines **1**.[1,13] The calculated geometric parameters of **2** are in good agreement with the X-ray diffraction data. The P^+—C—Ge—S^- fragment of the main chain adopts the *cis-gauche* conformation (the dihedral angle is 25.9°) due to strong Coulomb interactions between the charged centers (Table 2). According to the results of calculations, the central Ge—C bond (2.108 Å) is elongated compared to the Ge—Me bonds (1.994 and 1.989 Å), and the P^+—C—Ge (110.8°) and C—Ge—S^- (111.2°) bond angles in the P^+—C—Ge—S^- main chain are larger than the tetrahedral value (109.4°). Both these facts are consistent with the experimental data and can be considered as consequences of noticeable steric strains in molecule **2**.

Table 2. Charge distribution (*q*) and the dipole moment of molecule **2** calculated by the PBE/TZ2P method

Atom	*q*/au	Atom	*q*/au
Ge(1)	+0.297	C(6)	−0.205
S(2)	−0.460	C(7)	−0.092
C(3)	−0.140	C(8)	−0.095
P(4)	+0.407	C(9)	−0.094
C(5)	−0.210	C(10)	−0.110

Note. The dipole moment is equal to 9.73 D.

The noticeable deviation of the calculated C—Ge bond length (2.108 Å) from those determined by X-ray diffraction analysis (2.032 and 2.041 Å; δ 0.07 Å) may be associated with the effects of the crystal packing, which were not taken into account in the calculations of the equilibrium geometry of the isolated molecule. Generally, these effects play a particularly important role in polar molecules and molecules containing bulky groups. The differences in the other bond lengths and bond angles are at most 0.04 Å and 4°, respectively, which is typical of the method used for calculations. The theoretical investigation of the structures and reactivities of the model betaine $Me_3P^+—CH_2—GeMe_2—S^-$ and its analogs will be reported in a subsequent publication.

Experimental

The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AM360 instrument in C_5D_5N. The chemical shifts in the ^1H and ^{13}C NMR spectra were measured relative to the signals of the solvent with an accuracy of ±0.01 and ±0.05 ppm, respectively, and were converted to the δ scale. The spin-spin coupling constants are given with an accuracy of ±0.1 Hz. The assignment of the signals in the ^{13}C NMR spectra was made using the APT procedure.

Crystals of **2** ($C_{10}H_{25}GePS$, $M = 280.92$) are monoclinic, space group *C*2/*c*, at 110 K: $a = 30.322(3)$, $b = 7.1160(7)$, $c = 28.715(3)$ Å, $\beta = 112.417(2)°$, $V = 5727.7(10)$ Å^3, $Z = 16$, $d_{calc} = 1.303$ mg cm^{-3}, $F(000) = 2368$, $\mu = 2.361$ mm^{-1}.

The unit cell parameters and the intensities of 21029 reflections were measured on an automated SMART CCD 1000 diffractometer ($T = 110$ K, λMo-Kα radiation, ω scanning technique, scan step was 0.3°, frames were exposed for 10 s, $\theta_{max} = 30°$). The absorption correction was applied using the SADABS program.[14] The structure was solved by the direct method and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The hydrogen atoms were placed in geometrically calculated positions and refined isotropically with fixed positional (the riding model) and thermal parameters ($U_{iso}(H) = 1.5U_{eq}(C)$ for the Me groups and $U_{iso}(H) = 1.2U_{eq}(C)$ for the remaining atoms). The final *R* factors were as follows: $R_1 = 0.0410$ for 6783 independent reflections with $I > 2\sigma(I)$ and $wR_2 = 0.1053$ for all 8119 independent reflections. All calculations were carried out with the use of the SHELXTL PLUS program package (Version 5.10).[15]

The calculations within the framework of the density functional theory were carried out with the use of the original program.[16] The exchange-correlation energy was calculated using the generalized gradient approximation and the PBE hybrid functional.[17] The one-electron wave functions were expanded with the use of the extended three-exponential atomic basis set TZ2P of the grouped Gaussian functions containing the polarization functions. The stationary point was identified from the analysis of the Hessian matrix. The second derivatives with respect to the atomic coordinates were calculated analytically. The atomic charges were calculated by the Hirshfeld method.

Betaine $Et_3P^+—CHMe—GeMe_2—S^-$ was synthesized *in vacuo* (10^{-3} Torr) in a glass vessel with the use of the technique of broken partition walls and tubes described previously.[7] Other operations were carried out in a glove box under an atmosphere of oxygen-free argon. Tetrahydrofuran was distilled over $LiAlH_4$, stored over sodium benzophenone ketyl, and distilled over the latter into reaction vessels immediately before use. The starting reagents, *viz.*, $(Me_2GeS)_3$ [18,19] and $Et_3P=CHMe$,[20] were prepared according to procedures reported previously.

$Et_3P=CHMe$ (1.3 g, 8.87 mmol) was placed in a glass tube with an easily breakable partition wall and added to a solution of $(Me_2GeS)_3$ (1.22 g, 3.02 mmol) in THF (15 mL). The blue color of the reaction mixture, which was observed immediately after mixing of the reagents, rapidly disappeared, and a white precipitate formed. The mixture was kept at ~20 °C for 16 h. Then the residue was filtered off, washed with THF, and dried *in vacuo*. A finely crystalline white powder was obtained in a yield of 2.1 g (84.3%). Crystals suitable for X-ray diffraction analysis were obtained by crystallization from pyridine. M.p. 135 °C (in a sealed evacuated capillary). Found (%): C, 42.69; H, 8.91; S, 11.31. $C_{10}H_{25}GePS$. Calculated (%): C, 42.75; H, 8.97; S, 11.41. ^1H NMR (C_5D_5N), δ: 0.61, 0.64 (both s, 3 H each, nonequivalent Me_2Ge); 1.32 (td, 9 H, $\underline{Me}CH_2$, $^3J_{H,H} = 7.7$ Hz; $^3J_{H,P} = 17.2$ Hz); 1.32 (dd, 3 H, $\underline{Me}CHP$, $^3J_{H,H} = 7.6$ Hz; $^3J_{H,P} = 18.6$ Hz); 1.56 (qd, 1 H, $MeC\underline{H}$, $^3J_{H,H} = 7.6$ Hz; $^2J_{H,P} = 15.6$ Hz); 2.68—2.87 (complex multiplet, AB portion of the $ABMX_3$ spectrum, 6 H, CH_2P). ^{13}C NMR (C_5D_5N), δ: 6.39 (d, $\underline{C}H_3CH_2P^+$, $^2J_{C,P} = 5.3$ Hz); 6.70 (br.s, MeGe); 8.93 (d, MeGe, $^3J_{C,P} = 5.2$ Hz); 10.60 (d, $\underline{C}H_3CHP^+$, $^2J_{C,P} = 5.0$ Hz); 13.12 (d, $CH_3\underline{C}H_3P^+$, $^1J_{C,P} = 48.8$ Hz); 14.09 (d, CHP^+, $^1J_{C,P} = 38.2$ Hz). ^{31}P NMR (C_5D_5N), δ: 43.53.

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