Heteroorganic betaines

2.* X-ray diffraction study of betaines containing the $^{+}P—C—Si—S^{-}$ fragment

V. N. Khrustalev,[a] N. N. Zemlyanskii,[b]* I. V. Borisova,[b] Yu. A. Ustynyuk,[c] and E. A. Chernyshev[b]*

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: +7 (095) 135 5085*

[b]*State Research Center of the Russian Federation "State Research Institute of the Chemistry and Technology of Organoelement Compounds," 38 sh. Entuziastov, 111123 Moscow, Russian Federation. Fax: +7 (095) 273 1323. E-mail: zemlyan@mail.cnt.ru*

[c]*Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory, 119899 Moscow, Russian Federation. Fax: +7 (095) 932 8846*

The structures of three silicon-containing organophosphorus betaines containing the $^{+}P—C—Si—S^{-}$ fragment were established by X-ray diffraction study. Due to the attractive electrostatic interaction between the anionic and cationic centers, the main chain adopts a *gauche* conformation, whereas this chain in the *S*-ethyl derivative of the phosphonic salt $[Ph_3P^{+}—CMe_2—SiMe_2SEt]Br^{-}$ adopts a *trans* conformation. The changes in the geometric parameters of betaines depending on the substituents at the phosphorus, carbon, and silicon atoms were analyzed. The P—S bond can in principle be formed, resulting in the closure of the four-membered ring provided that additional steric hindrances at the silicon atom occur.

Key words: silicon-containing organophosphorus betaines containing the thiolate center, X-ray diffraction study.

Previously,[1—3] we have reported the synthesis of betaines of the general formula $R^1{}_3P^{+}CR^2R^3SiR^4R^5S^{-}$ and demonstrated that their carbon analogs $R_3P^{+}CHMeC(C_6H_4X\text{-}p)_2S^{-}$ (R = Et or Ph; X = Me_2N)[1,4] were formed as intermediates in the thio Wittig reaction. In the present work, we performed X-ray diffraction study of betaines $Ph_3P^{+}CMe_2SiMe_2S^{-}$ (**1**), $Et_3P^{+}CHMeSiPh_2S^{-}$ (**2**), and $(Me_2N)_3P^{+}CMe_2SiMe_2S^{-}$ (**3**) as well as of the product of ethylation of compound **1**, *viz.*, the $[Ph_3P^{+}CMe_2SiMe_2SEt^{+}]Br^{-}$ salt (**4**) (the preliminary results have been published previously, see Ref. 5). We also carried out a comparative analysis of the structures of zwitterions **1**—**3** and betaine $R_3P^{+}CHMeC(C_6H_4X\text{-}p)_2S^{-}$ (R = Et; X = MeO) (**5**), crystallographic study of which has been performed recently.[6]

Results and Discussion

The principal geometric parameters of the molecules of betaines **1**—**3** and phosphonium salt **4** are given in Table 1.

Table 1. Selected geometric parameters of betaines **1**—**3** and salt **4**

Compound	Interatomic distances /Å				Bonds angles /deg		Dihedral angle P—C—Si—S /deg
	P—C	C—Si	Si—S^{-}	P...S	P—C—Si	C—Si—S	
$Ph_3P^{+}—CMe_2—SiMe_2—S^{-}$ (**1**)	1.825(4)	1.986(4)	2.048(2)	3.988(4)	115.6(2)	114.6(1)	56.1(2)
$Et_3P^{+}—CHMe—SiPh_2—S^{-}$ (**2**)	1.811(3)	1.934(4)	2.044(2)	3.681(4)	112.8(1)	114.7(2)	38.2(2)
$(Me_2N)_3P^{+}—CMe_2—SiMe_2—S^{-}$ (**3**)	1.830(4)	1.979(3)	2.037(2)	3.980(4)	115.7(2)	116.9(1)	50.4(2)
$[Ph_3P^{+}—CMe_2—SiMe_2—SEt]Br^{-} \cdot 0.5C_5H_5N$ (**4**)	1.839(5)	1.933(6)	2.140(3)	5.010(5)	116.6(3)	107.3(2)	177.0(2)

* For Part 1, see Ref. 1.

Translated from *Izvestiya Akademii Nauk, Seriya Khimicheskaya*, No. 5, pp. 931—934, May, 2000.

1066-5285/00/4905-0929 $25.00

In the crystals, the $^{+}P-C-Si-S^{-}$ main chains of betaines **1**—**3** (Figs. 1—3, respectively) adopt a sterically strained *gauche* conformation, which is apparently determined by the intramolecular Coulomb attractive $P^{+}...S^{-}$ interaction between the cationic and anionic centers. This suggestion is confirmed by the fact that the thermodynamically most favorable *trans* conformation is realized in the case of salt **4** (Fig. 4), in which such interaction is impossible. Steric strains in zwitterions **1**—**3** are manifested in the noticeable elongation of the P—C and C—Si bonds in the main chain (see Table 1) compared to the average values (1.800 and 1.863 Å, respectively[7]) as well as in the substantial increase in the C—Si—S^{-} bond angles at the silicon atom and in the P—C—Si bond angles compared to the ideal tetrahedral value (109.5°).

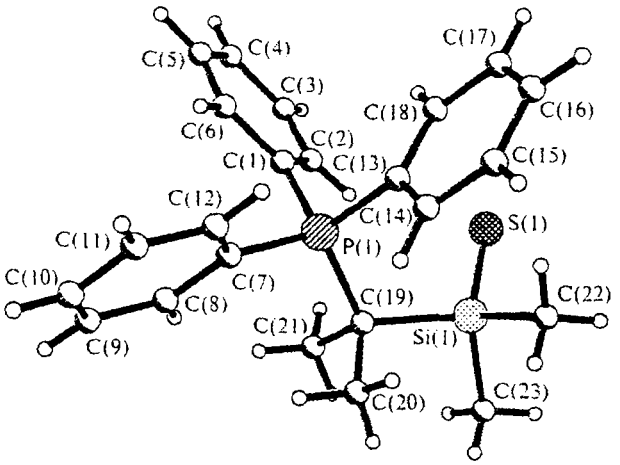

Fig. 1. Structure of betaine **1**.

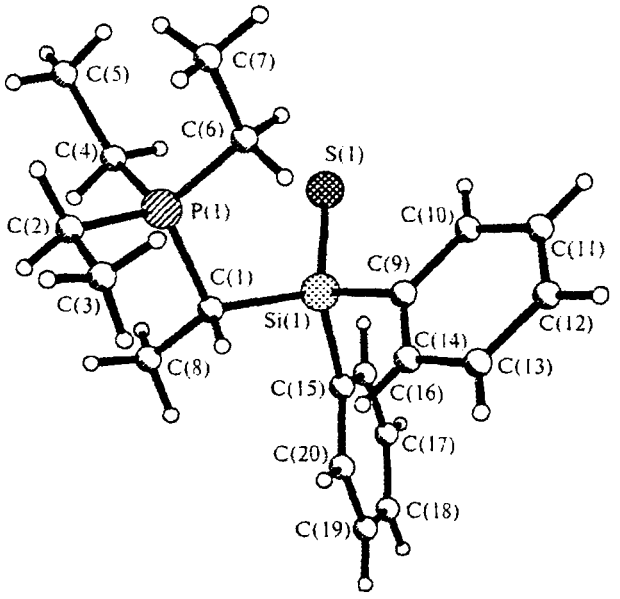

Fig. 2. Structure of betaine **2**.

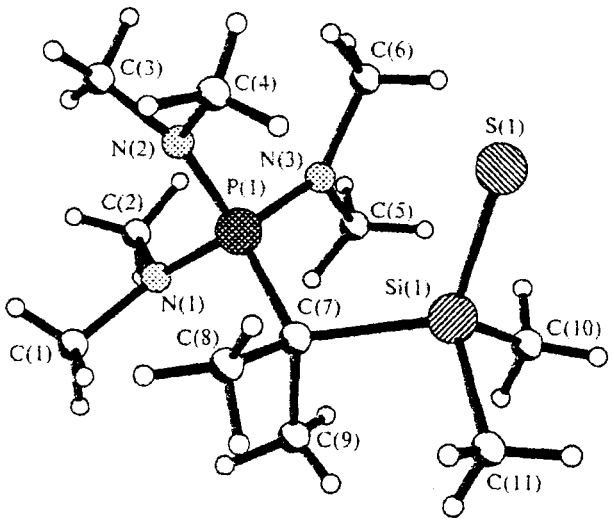

Fig. 3. Structure of betaine **3**.

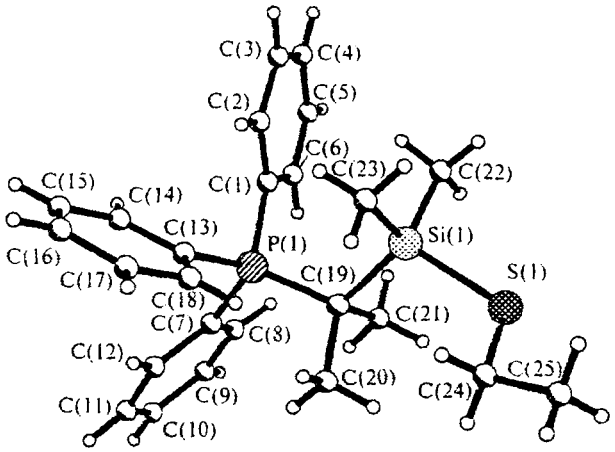

Fig. 4. Structure of the cation of salt **4**.

A decrease in the $^{+}P-C-Si-S^{-}$ dihedral angle in zwitterion **2** compared to those in structures **1** and **3** is accompanied by a decrease in the P...S distance and in the C—Si bond as well as by a reduction in distortion of the P—C—Si angle, which is indicative of the tendency for the closure of the four-membered ring. Apparently, the P and S atoms are brought into proximity due to the higher steric strain at the silicon atom and lower steric hindrances at the carbon atom of the main chain. It is not inconceivable that the introduction of even bulkier substituents at the silicon atom and the attachment of electronegative groups at the phosphorus atom provide favorable conditions for the formation of the thiasilaphosphetane structure. This suggestion is confirmed by the available evidence for the noticeable effect of the substituents on the stability of oxaphosphetanes.[8,9]

Table 2. Principal crystallographic data for betaines **1**—**3** and salt **4**

Parameter	**1**	**2**	**3**	**4** [a]
Molecular formula	$C_{23}H_{27}PSSi$	$C_{20}H_{29}PSSi$	$C_{11}H_{30}N_3PSSi$	$[C_{25}H_{32}PSSi]^+Br^- \cdot 0.5C_5H_5N$
M	394.6	360.55	295.5	542.6
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a/Å	9.881(5)	6.860(2)	9.423(4)	11.595(5)
b/Å	13.525(8)	8.887(2)	15.048(5)	14.758(6)
c/Å	15.691(9)	9.631(2)	11.901(4)	15.780(6)
α/deg	90	117.24(1)	90	90
β/deg	90	102.60(1)	92.88(2)	90.42(2)
γ/deg	90	97.53(1)	90	90
V/Å^3	2097(2)	491.1(2)	1685(1)	2700(2)
Z	4	1	4	4
T/°C	−120(2)	−120(2)	20(2)	−120(2)
d_{calc}/g cm^{-3}	1.250	1.219	1.165	1.335
θ_{max}/deg	27	27	28	26
N_{refl}, N'_{refl} [b]	3195, 1916 (c $I > 3\sigma(I)$)	2033, 2018	5210, 2130 (c $I > 3.5\sigma(I)$)	5884, 2530 (c $I > 3\sigma(I)$)
R factors	$R = 0.032$, $R_w = 0.034$	$R_1 = 0.044$, $wR_2 = 0.111$	$R = 0.066$, $R_w = 0.056$	$R = 0.043$, $R_w = 0.038$

[a] Solvate with pyridine

[b] N_{refl} is the number of measured reflections and N'_{refl} is the number of reflections used in the structure refinement.

The structures of organosilicon betaines **1**—**3** are similar to the structure of their carbon analog $Et_3P^+CHMeC(C_6H_4OMe\text{-}p)_2S^-$ (**5**).[6] This similarity consists in the *gauche* conformation of betaine **5**, the elongation of the P—C bond (1.845(7) Å), and the distortion of the angles at the atoms of the $^+P—C—C—S^-$ main chain (98.7(6)—117.6(3)°) as well as in the fact that the $^+P—C—E—S^-$ dihedral angles in zwitterions **5** (47.7(5)°, E = C) and **1**—**3** (E = Si) have close values.

The C—S$^-$ bond length (1.833 (6) Å) in zwitterion **5** is close to the standard value (the average C—S bond length is 1.820 Å[7]), whereas the Si—S$^-$ bond lengths in betaines **1**—**3** are smaller than the average length of the Si—S single bonds (2.145 Å).[7] The P...S distance (3.109 (5) Å) in betaine **5** is within the sum of the van der Waals radii (P—S is 3.6 Å)[10] and is substantially smaller than those in betaines **1**—**3**. Apparently, this difference results from the shorter C—C and C—S$^-$ bonds in the main chain of zwitterion **5** compared to the C—Si and Si—S$^-$ bonds in betaines **1**—**3** as well as from the higher steric overcrowding at the C atom in zwitterion **5** compared to the Si atom in compounds **1**—**3**. Therefore, the closure of the four-membered ring in betaines **1**—**3** and **5** is hindered primarily by the geometric factors.

Experimental

The syntheses of the compounds under study have been described previously.[1]

X-ray diffraction study. The unit cell parameters of all compounds and the intensities of independent reflections were measured on an automated four-circle Siemens P3/PC diffractometer (λ(Mo-Kα) radiation, graphite monochromator, θ/2θ scanning technique). All structures were solved by the direct method and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. In the crystal of salt **4**, the pyridine molecule of solvation was revealed from the difference Fourier synthesis. This molecule occupies a special position (an inversion center), which indicates that the molecule is disordered over two sites with equal occupancies. However, we failed to unambiguously determine the position of the nitrogen atom, and hence, all three independent atoms of the ring were refined as carbon atoms. The hydrogen atoms were placed in geometrically calculated positions and refined isotropically with fixed positional (the riding model) and thermal parameters. All calculations were carried out on an IBM PC/AT-486 computer with the use of the SHELXTL PLUS program package (PC Version 4.0[11] (compounds **1**, **3**, and **4**) or PC Version 5.0[12] (compound **2**)). The principal details of X-ray diffraction studies are given in Table 2. The complete tables of the bond lengths and the bond angles, the atomic coordinates, and the equivalent isotropic thermal parameters of the nonhydrogen atoms in the structures of **1**—**4** have been deposited with the Cambridge Structural Database.

We thank Professor E. Vedejs for placing at our disposal the preprint of his paper.[8]

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 96-03-33188a and 97-03-33783a).

References

1. I. V. Borisova, N. N. Zemlyanskii, A. K. Shestakova, Yu. A. Ustynyuk, and E. A. Chernyshev, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 922 [*Russ. Chem. Bull.*, 2000, **49**, 920 (Engl. Transl.)].
2. N. N. Zemlyanskii, I. V. Borisova, A. K. Shestakova, and Yu. A. Ustynyuk, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 2140 [*Russ. Chem. Bull.*, 1993, **42**, 2056 (Engl. Transl.)].

3. N. N. Zemlyanskii, I. V. Borisova, A. K. Shestakova, and Yu. A. Ustynyuk, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 2143 [*Russ. Chem. Bull.*, 1993, **42**, 2053 (Engl. Transl.)].
4. I. V. Borisova, N. N. Zemlyansky, A. K. Shestakova, and Yu. A. Ustynyuk, *Mendeleev Commun.*, 1996, 90.
5. N. N. Zemlyanskii, I. V. Borisova, Yu. A. Ustynyuk, S. V. Lindeman, Yu. T. Struchkov, and V. N. Khrustalev, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 339 [*Russ. Chem. Bull.*, 1994, **43**, 318 (Engl. Transl.)].
6. C. Puke, G. Erker, N. C. Aust, E.-U. Würtheim, and R. Fröhlich, *J. Am. Chem. Soc.*, 1998, **120**, 4863.
7. F. H. Allen, O. Kennard, D. G. Watson, A. G. Orpen, L. Brammer, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.
8. E. Vedejs and M. J. Peterson, in *Advances in Carbanion Chemistry*, Ed. V. Sniekus, JAI Press, Greenwich (CT), 1996, **2**, 1.
9. E. Vedejs and M. J. Peterson, *Top. Stereochem.*, 1994, **21**, 1.
10. A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
11. G. M. Sheldrick, *SHELXTL. PC Version 4.0*, Siemens Analytical X-Ray Instruments, Inc., Madison (WI), 1989.
12. G. M. Sheldrick, *SHELXTL, PC Version 5.0. An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*, Siemens Analytical X-Ray Instruments, Inc., Madison (WI), 1994.

Received December 15, 1998;
in revised form March 4, 1999