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O-Trimethylsilyl-*N*-phenylsulfonylacetimidate: Synthesis and Structure

A. Yu. Nikonov[a], I. V. Sterkhova[a],*, N. A. Kolyvanov[a], V. Yu. Serykh[a], and N. F. Lazareva[a]

[a] *Favorsky Irkutsk Institute of Chemistry, Siberian Branch of Russian Academy of Sciences, Irkutsk, 664033 Russia*
**e-mail: irina_sterkhova@irioch.irk.ru*

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Abstract—A method for silylation of *N*-acetylbenzenesulfonamide has been proposed. The structural features of the obtained *O*-trimethylsilyl-*N*-phenylsulfonylacetimidate have been studied by means of NMR and IR spectroscopy as well as single-crystal X-ray diffraction analysis.

Keywords: *N*-acylaryl sulfonamides, *O*-trimethylsilyl-*N*-phenylsulfonylacetimidate, silylation, silicon-containing sulfonamides

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Silylation of organic compounds is widely applied in organic and analytical chemistry as well as in materials science [1–4]. Trisorganylsilyl fragments are efficient protective groups blocking the O-, N-, and S-reactive sites [3, 5]. The introduction of a silyl group in organic compounds alters their reactivity, improves the solubility in nonpolar solvents, and increases the volatility. Enhanced volatility allows the use of GLC and mass spectrometry for isolation and analysis of organic species [3, 6].

A series of organosilicon compounds [$R^1R^2R^3SiCl$, R_3SiNR_2, and $(Me_3Si)_2NH$] have been used to introduce a silyl group in the compounds structure. O- or N-TMS- and O,N-bis(TMS) derivatives of carboxylic and sulfonic acid amides and the related compounds are among the most efficient and convenient laboratory-scale donors of trimethylsilyl (TMS) groups [1–3, 7–9]. Silicon-containing derivatives of N-acylarylsulfonamides $RC(O)N(SiMe_3)SO_2Ar$ are of special interest, yet the data on these compounds have been scarce. To the best of our knowledge, they have been mentioned only in a few reports [10–12]. This study aimed to elaborate a method of *N*-acetylbenzenesulfonamide **1** silylation and investigate the structure of the reaction products.

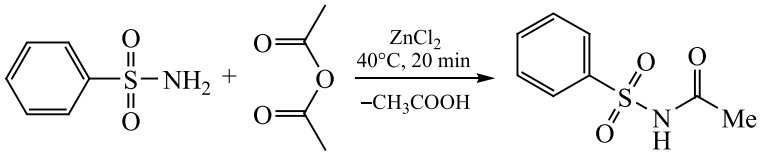
N-Acetylbenzenesulfonamide **1** was prepared as described elsewhere [13]. Acylation of benzenesulfonamide with acetic anhydride in the presence of a catalytic amount of $ZnCl_2$ occurred in bulk and afforded compound **1** in 90% yield (Scheme 1).

N-Acetylbenzenesulfonamide reacted with trimethylchlorosilane in benzene medium, the yield of the silylation product **2** being 68%. The reaction occurred at room temperature in the presence of triethylamine as hydrogen chloride acceptor (Scheme 2).

Structure of compound **2** was studied by means of IR and NMR spectroscopy as well as X-ray diffraction analysis. The crystal suitable for the latter were obtained via recrystallization.

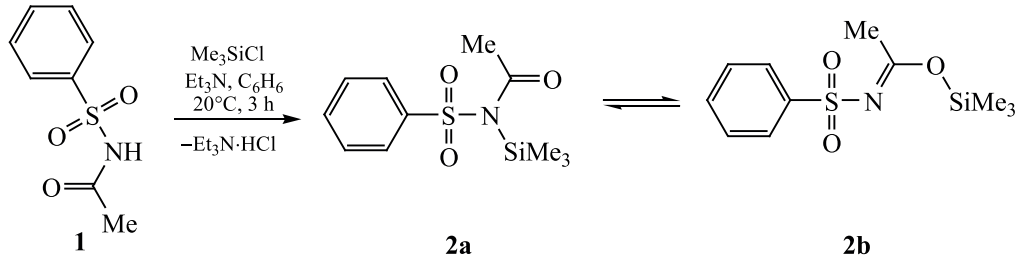
According to the X-ray diffraction analysis data, compound **2** in the crystal exists in the form of the O-silylated derivative **2b**—*O*-trimethylsilyl-*N*-phenylsulfonylacetimidate. Molecular structure of

Scheme 1.



1 (90%)

Scheme 2.



imidate **2b** is shown in Fig. 1, and selected structural parameters of it are listed in Table 1. A single molecule of compound **2b** was found in the independent part of the unit cell. Structural analogs of imidate **2b** without a $SiMe_3$ group were found in the Cambridge Crystallographic Data Centre [14–22]. Comparative analysis of those compounds revealed very close values of the $C_{Ph}SN$ bond angle 98.8–100.2° (98.76° for imidate **2b**) and SNC one 120.4–128.6° (122.75° for imidate **2b**), yet the values of the $C_{Ph}SNC$ torsion angle were significantly different. The range of the latter covered about 50° (123°–176°), being equal to 161.87° for imidate **2b**. Evidently, the difference was due to the presence of bulky substituents in the structural analogs. For example, the closest value of the $C_{Ph}SNC$ angle was observed for isopropyl-3-(*tert*-butylcarbonylamino)-3-cyclohexyl-2-methyl-*N*-(4-nitrophenylsulfonyl)propaneimidate (163.5°) [24]. The S–N and N=C distances in imidate **2b** were 1.637 and 1.286 Å, respectively, very close to the corresponding values for the structural analogs (1.633 and 1.285 Å, respectively, on the average) [14–22]. The adjacent molecules of imidate **2b** in the crystal were linked via CH···O short contacts of the hydrogen atoms of the MeC(O) and Me_3Si methyl groups and the phenyl ring with the oxygen atoms of the S=O and Me_3SiO groups (Fig. 2). The intermolecular bonds length was of 2.492–2.717 Å.

The amido-imidate tautomeric equilibrium in the silylated carboxamides is dependent on the nature of the substituents in the amide moiety as well as external factors (temperature and solvent) [7, 23–27]. However, such structures have been earlier studied only using spectral methods. Herein we investigated the structure of compound **2** by means of the density functional theory DFT [B3LYP functional and 6-311G(d) basis set]. The obtained data revealed the most stable conformers of the tautomers **2a** and **2b** as minimums in the potential energy surface as well as the transition state with the energy maximum corresponding to the energy barrier of the **2a**→**2b** transition. Relative energy of tautomer **2a** was 7.9 kcal/mol higher in comparison with tautomer **2b**. The simulated energy barrier height was 12 kcal/mol relative to tautomer **2a** and 19.9 kcal/mol with respect to tautomer **2b**.

In summary, silylation of *N*-acetylbenzenesulfonamide afforded *O*-trimethylsilyl-*N*-phenylsulfonylacetimidate as the only product. Its structure was confirmed by means of X-ray diffraction analysis, IR and NMR spectroscopy, and quantum-chemical simulation. As in the case of carboxamides, the amido-imidate tautomerism was possible for *N*-acylbenzenesulfonamides [28]. The X-ray diffraction analysis data suggested the imidate form of the prepared compound in the solid state. Likely,

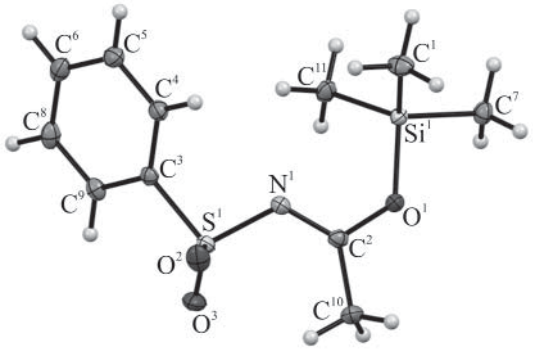


Fig. 1. General view of molecule of compound **2b** in the crystal.

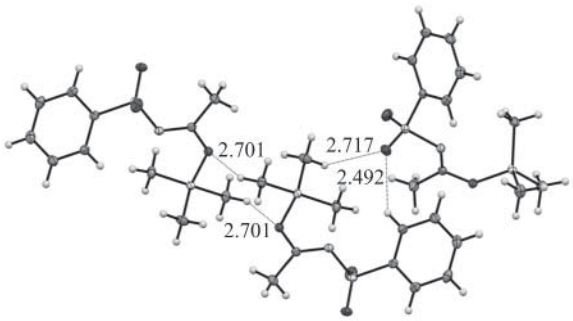


Fig. 2. Intermolecular short contacts in the crystal of imide **2b**.

Table 1. Selected bond lengths, bond angles, and torsion angles in the molecule of compound **2b**

Bond	*d*, Å	Bond angle	φ, deg	Torsion angle	θ, deg
$Si^1–O^1$	1.713(1)	$O^1Si^1C^1$	111.8(1)	$C^7Si^1O^1C^2$	–159.0(1)
$S^1–N^1$	1.637(1)	$O^1Si^1C^7$	101.3(1)	$C^1Si^1O^{11}C^2$	–40.5(1)
$Si^1–C^1$	1.851(1)	$N^1S^1C^3$	98.7(1)	$O^2S^1N^1C^2$	84.4(1)
$Si^1–C^7$	1.850(1)	$O^7Si^1C^1$	111.3(1)	$O^3S^1N^{11}C^2$	–47.9(1)
$S^1–O^2$	1.439(1)	$C^2O^1Si^1$	126.7(1)	$C^3S^1N^1C^{22}$	–161.9(1)
$S^1–O^3$	1.441(1)	$C^2N^1S^1$	122.8 (1)	$S^1N^1C^2O^1$	175.2(1)
$S^1–C^3$	1.765(1)	$O^3S^1O^2$	117.3(1)	$S^1N^1C^2C^{10}$	–5.5(2)
$O^1–C^2$	1.323(1)	$O^2S^1N^1$	109.5(1)	$Si^1O^1C^2N^1$	–8.2(2)
$N^1–C^2$	1.286(2)	$O^3S^1N^1$	112.4(1)	$Si^1O^1C^2C^{10}$	172.4(1)
$C^3–C^4$	1.388(2)	$N^1C^2O^1$	118.3(1)	$C^3C^4C^5C^6$	1.4(2)
$C^2–C^{10}$	1.496(2)	$N^1C^2C^{10}$	128.9(1)	$N^1S^1C^3C^4$	129.6(1)

O-trimethylsilyl-*N*-phenylsulfonylacetimidate was formed via the substitution of the imidate proton with the trimethylsilyl group and was a kinetically as well as thermodynamically favorable reaction product.

EXPERIMENTAL

NMR spectra of a solution in $CDCl_3$ were recorded using a Bruker DPX-400 spectrometer [400.1 (^{1}H), 100.6 (^{13}C), and 79.5 MHz (^{29}Si)] with HMDS and cyclohexane as internal references. IR spectra were recorded using a Bruker Vertex 70 spectrometer. X-ray diffraction analysis was performed using a Bruker D8 Venture diffractometer (MoK_α radiation, λ = 0.71073 Å) in the φ- and ω-scanning mode. The structure was solved and refined via a direct method using SHELX software suite [29]. The absorption was accounted for using SADABS software. The non-hydrogen atoms were refined under anisotropic approximation using SHELX software [29]. The crystallographic data for compound **1** were deposited at the Cambridge Crystallographic Data Centre (CCDC 1947408). Quantum-chemical simulation was performed using GAUSSIAN-09 software suite [30].

The crystals of compound **2b** were colorless, prismatic, 0.40×0.50×0.50 mm, $C_{11}H_{17}NO_3SSi$, *M* 271.40, monoclinic crystal system, space group $P2_1/c$, $\theta_{min}/\theta_{max}$ = 2.33/30.12, *T* = 100 K, *a* = 9.8204(4), *b* = 8.1281(3), *c* = 17.0421(8) Å, β = 94.249(2)°, *V* = 1356.6(1) Å^3, *Z* = 4, d_{calc} = 1.329 g/cm^3, *F*(000) = 576, μ = 0.323 mm^{-1}. 36439 reflections were collected including 3977 independent, 158 parameters were refined, *R* = 2.95, R_w = 0.0376 (over all reflections), goodness of fit over F^2 1.045, $\Delta\rho_{max}/\Delta\rho_{min}$ = 0.341/–0.399 *e*/Å^3.

***N*-Acetylbenzenesulfonamide (1)**. A mixture of 1.20 g (7.63 mmol) of benzenesulfonamide, 1 g (9.8 mmol, excess) of acetic anhydride, and 0.05 g of $ZnCl_2$ was heated on a water bath at 40–45°C with vigorous stirring until complete dissolution of the benzenesulfonamide precipitate and the formation of colorless low-viscous solution (10 min). After that, the mixture was heated at the same temperature at stirring during 10 min and then the pressure was reduced to ~10–15 mmHg, the temperature being gradually raised to 60–65°C. The mixture was kept at those temperature and pressure during 15 min, and the residue was cooled to room temperature. ~1.36 g of compound **1** was obtained (yield ~90%). Spectral parameters of the obtained compound were identical to the reference ones [31].

***O*-Trimethylsilyl-*N*-phenylsulfonylacetimidate (2b).** A mixture of 0.5 g (4.62 mmol) of trimethylchlorosilane and 5 mL of benzene was slowly added to a solution of 0.91 g (4.56 mmol) of *N*-acetylbenzenesulfonamide **1** and 0.5 g (5 mmol) of triethylamine in 15 mL of benzene at vigorous stirring. The obtained mixture was stirred during 3 h at room temperature; the precipitate was filtered and washed with 20 mL of benzene; the solvent was evaporated off. The obtained yellowish transparent residue was distilled in vacuum. Yield 68% (0.84 g), bp 185°C (3–4 mmHg). IR spectrum (KBr), ν, cm^{-1}: 757, 784, 851, 1039, 1095, 1162, 1255, 1333, 1597, 1727, 2961, 3068. ^{1}H NMR spectrum, δ, ppm: 0.22 s [9H, $(CH_3)_3Si$], 2.49 s [3H, $CH_3C(O)$], 7.5–7.9 m (5H, $PhSO_2$). ^{13}C NMR spectrum, δ_C, ppm: –0.42 (CH_3Si), 22.16 [$\underline{C}H_3C(O)$], 126.45 (C^o), 128.67 (C^m), 132.36 (C^p), 141.73 (C^i), 174.12 [$CH_3\underline{C}(O)$]. ^{29}Si NMR spectrum: δ_{Si} 27.0 ppm. Found, %: C 49.12; H 6.27; N 5.05; S 11.67; Si 10.49. $C_{11}H_{17}NO_3SSi$. Calculated, %: C 48.68; H 6.31; N 5.16; S 11.81; Si 10.35.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

REFERENCES

1. Kashutina, M.V., Ioffe, S.L., and Tartakovskii, V.A., Russ. *Chem. Rev*., 1975, vol. 44, no. 9, p. 1620. https://doi.org/10.1070/RC1975v044n09ABEH002373
2. Mizhiritskii, M.D. and Yuzhelevskii, Yu.A., Russ. *Chem. Rev*., 1987, vol. 56, no. 4, p. 355. https://doi.org/10.1070/RC1987v056n04ABEH003276
3. Look, G., *Silylating Agents*, Buchs: Fluka Chemie AG, 1995.
4. Auner, N. and Weis, J., *Organosilicon Chemistry From Molecules to Materials*, Weinheim: VCH, 1994.
5. Greene, T.W. and Wuts, P.G.M., *Protective Groups in Organic Synthesis*, New York: John Wiley and Sons, 1999.
6. Splitter, J.S. and Turecek, F., *Applications of Mass Spectrometry to Organic Stereochemistry*, Weinheim: VCH, 1994.
7. Klebe, J.F., *Acc. Chem. Res*., 1970, vol. 3, no. 9, p. 299. https://doi.org/10.1021/ar50033a003
8. Verboom, W., Visser, G.W., and Reinhoudt, D.N., *Synthesis*, 1981, no. 10, p. 807. https://doi.org/10.1055/s-1981-29605
9. Gihani, M.T. and Heaney, H., *Synthesis*, 1998, no. 4, p. 357. https://doi.org/10.1055/s-1998-2043
10. Shinichi, I. and Iwao, O., *J. Organometal. Chem*., 1979, vol. 169, no. 2, p. 171. https://doi.org/10.1016/S0022-328X(00)81156-0
11. Iwao, O., Shinichi, I., and Yoichiro, N., *J. Chem. Soc. Chem. Commun*., 1974, no. 20, p. 826. https://doi.org/10.1039/c39740000826
12. Gordetsov, F.S., Vostokov, I.A., Dergunov, Yu.I., and Mushkin, Yu.I., *Zh. Obshch. Khim*., 1974, vol. 44, no. 11, p. 2456.
13. Reddy, C.R., Mahipal, B., and Yaragorla, S.R., *Tetrahedron Lett*., 2007, vol. 48, no. 42, p. 7528. https://doi.org/10.1016/j.tetlet.2007.08.048
14. Deng, H., Han, T., Zhao, E., Kwok, R.T.K., Lam, J.W.Y., and Tang, B.Z., *Polym. Chem*., 2016, vol. 7, no. 36, p. 5646. https://doi.org/10.1039/C6PY01337F
15. Yao, Z.-J., Li, K., Zhang, J.-Y., Wang, Y., and Deng, W., *Inorg. Chim. Acta*, 2016, vol. 450, p. 118. https://doi.org/10.1016/j.ica.2016.05.032
16. Anugu, R.R. and Chegondi, R., *J. Org. Chem*., 2017, vol. 82, no. 13, p. 6786. https://doi.org/10.1021/acs.joc.7b00936
17. Peng, J., Cui, H., and Chen, J.C., *Sci. China. Chem*., 2011, vol. 54, p. 81. https://doi.org/10.1007/s11426-010-4137-2
18. Nikolaev, V., Hennig, L., Sieler, J., Rodina, L., Schulze, B., and Nikolaev, B., *Org. Biomol. Chem*., 2005, vol. 3, no. 22, p. 4108. https://doi.org/10.1039/b508317f
19. Shen, R. and Huang, X., *J. Org. Chem*., 2007, vol. 72, no. 10, p. 3961. https://doi.org/10.1021/jo070239z.
20. Dabbagh, H.A., Modarresi-Alam, A.R., Tadjarodi, A., and Taeb, A., *Tetrahedron*, 2002, vol. 58, no. 13, p. 2621. https://doi.org/10.1016/S0040-4020(02)00130-8
21. Nguyen, H.V., Matsubara, R., and Kobayashi, S., *Angew. Chem. Int. Ed*., 2009, vol. 48, no. 32, p. 5927. https://doi.org/10.1002/anie.200900309
22. Matsubara, R., Berthiol, F., and Kobayashi, S., *J. Am. Chem. Soc*., 2008, vol. 130, no. 6, p. 1804. https://doi.org/10.1021/ja077054u
23. Bassindale, A.R. and Posner, T.B., *J. Organomet. Chem*., 1979, vol. 175, no. 2, p. 273. https://doi.org/10.1016/S0022-328X(00)84548-9
24. Jancke, H., Engelhardt, G., Wagner, S., Dirnens, W., Herzog, G., Thieme, E., and Rühlmann, K., *J. Organomet. Chem*., 1977, vol. 134, no. 1, p. 21. https://doi.org/10.1016/S0022-328X(00)93609-X
25. Fukui, M., Itoh, K., Ishii, Y., *J. Chem. Soc. Perkin Trans. 2*, 1972, no. 9, p. 1043. https://doi.org/10.1039/P29720001043
26. Albanov, A.I., Larin, M.F., Pestunovich, V.A., Voronkov, M.G., Kramarova, E.P., and Baukov, Yu.I., *Zh. Obshch. Khim.*, 1981, vol. 51, no. 2, p. 488.
27. Otter, J.C., Adamson, C.L., Yoder, C.H., and Rheingold, A.L., *Organometallics*, 1990, vol. 9, no. 5, p. 1557. https://doi.org/10.1021/om00119a030.
28. Padrela, L., Zeglinski, J., and Ryan, K., *Cryst. Growth Des*., 2019, vol. 19, no. 2, p. 613. https://doi.org/10.1021/acs.cgd.8b01015
29. Sheldrick, G.M., *Acta Crystallogr. (A)*, 2008, vol. 64, p. 112. https://doi.org/10.1107/S0108767307043930

30. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G.A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H.P., Izmaylov, A.F., Bloino, J., Zheng, G., Sonnenberg, J.L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J.A., Jr., Peralta, J.E., Ogliaro, F., Bearpark, M., Heyd, J.J., Brothers, E., Kudin, K.N., Staroverov, V.N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J.C., Iyengar, S.S., Tomasi, J., Cossi, M., Rega, N., Millam, J.M., Klene, M., Knox, J.E., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Martin, R.L., Morokuma, K., Zakrzewski, V.G., Voth, G.A., Salvador, P., Dannenberg, J.J., Dapprich, S., Daniels, A.D., Farkas, O., Foresman, J.B., Ortiz, J.V., Cioslowski, J., and Fox, D.J., *Gaussian 09*, Revision A.01, Gaussian, Inc., Wallingford CT, 2009.

31. Taylor, J.E., Jones, M.D., Williams, J.M.J., and Bull, S.D., *J. Org. Chem*., 2012, vol. 77, no, p. 2808. https://doi.org/10.1021/jo202647f