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O-N-Cl GEMINAL SYSTEMS. STRUCTURE OF *N*-CHLORO-*N*-METHOXY-4-TOLUENESULFONAMIDE AND *N*-METHOXY-4-TOLUENESULFONAMIDE

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Abstract

Aim.Structural analysis of chemical compounds plays a crucial role in understanding their properties and chemical behavior. In this study, the aim is to investigate the structure of *N*-chloro-*N*-methoxy-4-toluenesulfonamide and to compare it with N-methoxy-4-toluenesulfonamide structure. Methods. ^{1}H, and ^{13}C NMR spectroscopy, mass spectrometry, a single crystal X-ray diffraction study. Results. It was found that in the molecule of *N*-chloro-*N*-methoxy-4-toluenesulfonamide the amide nitrogen atom has a strongly pyramidal configuration. The sum of the bond angles centered on thisnitrogen atom is 324.1°. In *N*-methoxy-4-toluenesulfonamide the degree of pyramidality of the nitrogen atom is significantly lower, the sum of the bond angles centered on thisnitrogen atom is 331.0°. Structural analysis shows two notable features in *N*-chloro-*N*-methoxy-4-toluenesulfonamide. First, the N–Cl bond is elongated to 1.767(3) Å, exceeding the corresponding bond lengths in *N*-chloro-*N*-methoxyurea and *N*-chloro-*N*-methoxy-4-nitrobenzamide. Second, the N(1)–O(3)Me bond is shortened to 1.405(3) Å, relative to the values observed in *N*-methoxy-4-toluenesulfonamide and in dimethyl *N*-methoxy-*N*-(4-toluenesulfonyl)phosphoramidate. The most plausible explanation is that this bonds deformation may be caused by the action of the $n_{O(Me)}\rightarrow 6\bullet_{N\text{-}Cl}$anomeric effect. Conclusions. *N*-Chloro-*N*-methoxy-4-toluenesulfonamide, together with related *N*-alkoxy-*N*-chloro-R-sulfonamides, represents a distinct class of anomeric amides characterized by weakening of the N–Cl bond through an $n_{O(Alk)}\rightarrow 6\bullet_{N\text{-}Cl}$anomeric interaction. Thus, this work is important because it establishes a new concept in the chemistry of *N*-alkoxy-*N*-chloro-R-sulfonamides.

Keywords: *N*-chloro-*N*-methoxy-4-toluenesulfonamide; a single crystal X-ray diffraction structurestudy; anomeric amides.

O-N-Cl ГЕМІНАЛЬНІ СИСТЕМИ. СТРУКТУРА *N*-ХЛОР-*N*-МЕТОКСИ-4-ТОЛУЕНСУЛЬФОНАМІДА ТА *N*-МЕТОКСИ-4-ТОЛУЕНСУЛЬФОНАМІДА

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Анотація

Мета. Структурний аналіз хімічних сполук відіграє вирішальну роль у розумінні їх властивостей та хімічної поведінки. Метою цього дослідження є вивчення структури *N*-хлоро-*N*-метокси-4-толуенсульфонаміду та порівняння її зі структурою *N*-метокси-4-толуенсульфонаміду. Методи. Мас-спектрометрія, ^{1}H та ^{13}C ЯМР спектроскопія, рентгеноструктурний аналіз. Результати. Було виявлено, що в молекулі *N*-хлоро-*N*-метокси-4-толуенсульфонаміду амідний атом азоту має вельми пірамідальну конфігурацію. Сума його валентних кутів дорівнює 324.1°. У *N*-метокси-4-толуенсульфонаміді ступінь пірамідальності атома азоту значно менший, сума його валентних кутів становить 331.0°. Структурний аналіз показує дві значні особливості *N*-хлоро-*N*-метокси-4-толуенсульфонаміду. По-перше, зв'язок N–Cl є подовженим до 1.767(3) Å, що перевищує довжини відповідних зв'язків N–Cl у *N*-хлоро-*N*-метоксисечовині та *N*-хлоро-*N*-метокси-4-нітробензаміді. По-друге, зв'язок N–O(Me) скорочений до 1.405(3) Å порівняно зі значеннями, що спостерігаються у *N*-метокси-4-

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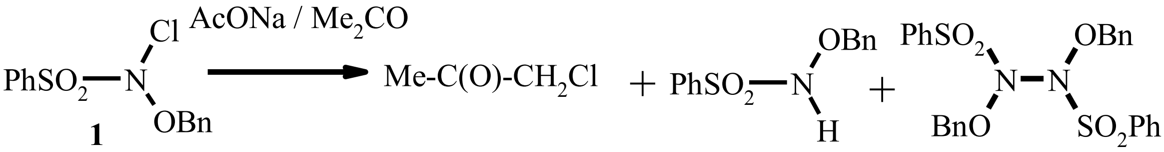
толуенсульфонаміді та диметил-*N*-метокси-*N*-(4-толуенсульфоніл)фосфорамідаті. Найбільш вдалим поясненням є те, що, ця деформація зв'язків може бути спричинена дією аномерного ефекту $n_{O(Me)}\rightarrow 6\bullet_{N\text{-}Cl}$. Висновки. *N*-Хлоро-*N*-метокси-4-толуенсульфонамід разом зі спорідненими *N*-алкокси-*N*-хлоро-R-сульфонамідами являє собою окремий клас аномерних амідів, що характеризуються дестабілізацією зв'язку N–Cl через аномерний ефект $n_{O(Alk)}\rightarrow 6\bullet_{N\text{-}Cl}$.

Ключові слова: *N*-хлоро-*N*-метокси-4-толуенсульфонамід; дослідження будови рентгенівською дифракцією монокристалу;аномерні аміди.

Introduction

N-Alkoxy-*N*-chlorosulfonamides areused in organic synthesis as a chlorinating agents [1–3]. *N*-Chloro-*N*-methoxybenzenesulfonamide is electrophilic chlorinating reagent for 1,3-diketones, β-ketoseters, phenols, heteroarenes and aromatic amins [1]. *N*-Benzyloxy-*N*-chlorobenzenesulfonamide **1** interaction with AcONa in acetone afforded chloroacetone, *N,N'*-bis(benzyloxy)-*N,N'*-bis(phenyl)hydrazine and *N*-benzyloxybenzenesulfonamide [2] (Scheme 1).



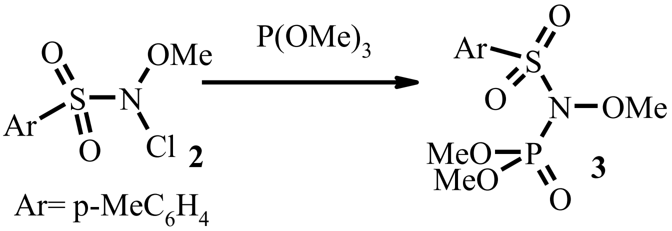
Scheme 1. **The interaction of *N*-benzyloxy-*N*-chlorobenzenesulfonamide (1) with AcONa in acetone [2]**

N-Alkoxy-*N*-chlorosulfonamides are a electrophilic chlorinating agents due to the strongly electron-withdawing effect of the sulfonyl group [2].

As you can see from the data above the nucleophilic substitution of the chlorine atom is impossible for *N*-alkoxy-*N*-chlorosulfonamides in contrast to the anomeric amides such as *N*-alkoxy-*N*-chloroureas [4–6], *N*-alkoxy-*N*-chloro-*N'*-arylureasureas [7] and *N*-alkoxy-*N*-chlorobenzamides [2; 8]. In these anomeric amides, a high degree of pyramidality of the amide nitrogen atom and the dominance of $n_{O(R)}\rightarrow 6\bullet_{N\text{-}Cl}$anomeric effect [4–8] areboth observed. On the other hand, the N–Cl bond polarization in *N*-alkoxy-*N*-chlorosulfonamides is unfavorable for nucleophilic substitution at the amide nitrogen atom [2; 9; 10].

N-Acyloxy-*N*-chlorobenzamides are electrofilic chlorinating agents as well [11–15]. For example, *N*-benzoyloxy-*N*-chlorobenzamide does not react with AcONa in MeCN [16]. These compounds represent a new class of anomeric amides, in which the amide nitrogen adopts a pyramidal configuration [11].

Recently we had converted *N*-chloro-*N*-methoxy-4-toluenesulfonylamide **2** indimethyl *N*-methoxy-*N*-(4-toluenesulfonyl)phosphoramidate **3** through its reaction with trimethyl phosphite [17] (Scheme 2).



Scheme 2. **Thesynthesis of compound 3 [17]**

Compound **3** can be considered as a formal product of nucleophilic substitution at the nitrogen atom [17].

Glover S.A. had proved that for anomeric amides a pyramidality of the nitrogen atom favors the $n_{O(R)}\rightarrow 6\bullet_{N\text{-}Cl}$anomeric effect realization [2; 9; 10]. This leads to a weakening of the N–Cl bond. The N–Cl bond weakening makes the nucleophilic substitution at the amide nitrogen atom possible. However, as shown with *N*-acyloxy-*N*-chlorobenzamides [11; 16], amides in which nucleophilic substitution of the chlorine atom does not occur can still be classified as anomeric amides. Thus, the aim of our study was to establish the structural features of *N*-chloro-*N*-methoxy-4-toluenesulfonamide **2** in comparison with the structural features of *N*-methoxy-4-toluenesulfonamide **4**. We have previously used this approach to study the structural features of *N*-acetoxy-*N*-benzyloxyurea [18] and *N*-benzyloxy-*N*-methoxyurea [19]. Increased interest in O–N–Cl geminal system [20] driven by its remarkable reactivity and unexplored potential, makes this research exceptionally timely and essential for advancing our understanding of these unique chemical entities.

Experimental part

^{1}H NMR spectra were recorded on a VARIAN VNMRS 400 spectrometer (400 MHz). ^{13}C NMR spectra were recorded on a VARIAN VNMRS 400 spectrometer (100 MHz). The solvent $CDCl_3$ was used. ^{1}H NMR chemical shifts relative to the residual solvent protons as an internal standard [$CDCl_3$: 7.260 ppm,] were reported. Solvent carbon atoms served as an internal standard for ^{13}C NMR spectra [$CDCl_3$: 77.16 ppm]. Mass spectra were recorded on a VG 70-70EQ mass spectrometer in fast atom bombardment mode (FAB). The solvents were purified and dried according to the standard procedures.

N-Methoxy-4-toluenesulfonamide (4). The solution of *N*-methoxyamine (0.571 g, 12.134 mmol) in MeCN (5 mL) was added to the solution of TsCl (1.157 g, 6.069 mmol) in MeCN (5 mL), then the solution of trietylamine (0.676 g, 6.675 mmol) in MeCN (5 mL) was added. The reaction mixture was maintained at 19 °C during 68 h, followed by boiling for 1 h. After that MeCN was evaporated under vacuum, the residue was extracted by benzene (30 mL). The PhH-extract was evaporated under vacuum, the residue was maintained at 60°C under vacuum (2 mmHg), then obtained residue was washed with water (15 mL), dried under vacuum (2 mmHg), giving 1.004 g (82 %) of *N*-methoxy-4-toluenesulfonamide **4** as a colorless crystals, mp 108–109 °C (benzene–hexane). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.448 (3H, s, Me); 3.789 (3H, s, NOMe); 7.035 (1H, br. s, NHO); 7.350 (2H, d, ^3J = 8.4 Hz, C(3)H,C(5)H $C_6H_4SO_2$); 7.814 (2H, d, ^3J = 8.4 Hz, C(3)H,C(5)H $C_6H_4SO_2$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 21.78 Me; 65.14 NOMe; 128.65 C(3)H, C(5)H $C_6H_4SO_2$; 129.85 C(2)H, C(6)H $C_6H_4SO_2$; 133.72 C(4)–Me, $C_6H_4SO_2$; 145.03 C(1)–SO_2 $C_6H_4SO_2$. Mass spectrum (FAB), *m/z* (I_{rel},%): 202 $[M+H]^+$ (34); 201 M^+ (54); 155 Ts^+ (100); 91 (54). Found, %: C 47.69; H 5.66; N 6.92. $C_8H_{11}NO_3S$. Calculated, %: C 47.75; H 5.51; N 6.96.

N-Chloro-N-methoxy-4-toluenesulfonamide (2). The solution of *tert*-butyl hypochlorite (165 mg, 1.520 mmol) in CH_2Cl_2 (3 mL) was added to the solution of *N*-methoxy-4-toluenesulfonamide **4** (102 mg, 0.507 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was maintained at 5 °C for 2 h, then it was evaporated under vacuum, the residue was kept at 2 mmHg for 20 min, washed with cold hexane, dried under vacuum, yielding 112 mg (94 %) of unstable *N*-chloro-*N*-methoxy-4-toluenesulfonamide **2** as a colorless crystals, mp 73–75 °C (CCl_4–hexane).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.494 (3H, s, Me); 3.797 (3H, s, NOMe); 7.418 (2H, d, ^3J = 8.4 Hz, C(3)H,C(5)H $C_6H_4SO_2$); 7.920 (2H, d, ^3J = 8.4 Hz, C(2)H,C(6)H $C_6H_4SO_2$). ^{13}C NMR (100.6093 MHz, $CDCl_3$, ppm): δ =22.01 Me; 63.38 NOMe; 127.54 C(4)–Me, $C_6H_4SO_2$; 129.79 C(3)H, C(5)H $C_6H_4SO_2$; 131.43 C(2)H, C(6)H $C_6H_4SO_2$; 146.93 C(1)–SO_2 $C_6H_4SO_2$.

*The study of the N-chloro-N-methoxy-4-toluenesulfonamide (**2**) structure.*

The colorless crystals of compound **2** are monoclinic,·$C_8H_{10}O_3ClS$, at −100.5 °C, ***a*** = 6.8922(6), ***b*** = 15.5147(10), ***c*** = 10.0740(7) Å, β =104.150(5)°, V = 1044.53(14) Å^3, M_r = 235.68, Z = 4, space group $P2_1/n$, d_{calc}= 1.499 g/cm^3, μ (MoK_α) = 0.546 mm^{-1}, F(000) = 488. Unit cell parameters and intensities of 14170 reflections (1834 independed, R_{int}=0.0572) were measured on the «Bruker APEX-II CCD» diffractometer (graphite monochromatedMo$K_\alpha$radiation, CCD detector, ω-scaning, $2\theta_{max}$= 50°).

The structure was solved by direct method of the program [21] with program modules [22] and [23]. Positions of the hydrogen atoms were located from electron density difference maps and refined by “riding” model with U_{iso} = nU_{eq} (n = 1.5 for methyl groups and n = 1.2 for other hydrogen atoms) of the carrier atom. Full-matrix least-squares refinement against F^2 in anisotropic approximation for non-hydrogen atoms using 1834 reflections was converged to wR_2 = 0.1090 (R_1 = 0.0431 for 1474 reflections with F>4σ(F), S = 1.031).

The atomic coordinates, molecular geometry parameters, and crystallographic data of compound **2** The atomic coordinates, molecular geometry parameters, and crystallographic data of compound **2** are preserved at the Cambridge Crystallographic Data Center, 12 Union Road, CB2, 1EZ UK [fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk and are available upon request with the CCDC 2506162 (**2**).

*The study of the N-methoxy-4-toluenesulfonamide (**4**) structure.*

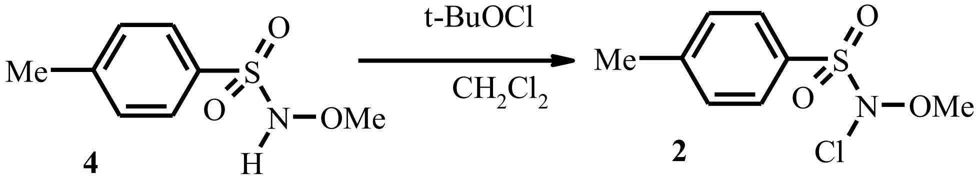
The colorless crystals of compound **4** are monoclinic,·$C_8H_{11}O_3S$, at -100.5°C, ***a*** = 7.9491(8), ***b*** = 5.2860(6), ***c*** = 22.5002(19) Å, β =90.173(6)°, V = 945.43(16) Å^3, M_r = 201.24, Z = 4, space group $P2_1/n$, d_{calc}= 1.414 g/cm^3, μ(MoK_α) = 0.316 mm^{-1}, F(000) = 424. Unit cell parameters and intensities of 12469 reflections (1663 independed, R_{int} = 0.0799) were measured on the «Bruker APEX-II CCD» diffractometer (graphite monochromatedMo$K_\alpha$radiation, CCD detector, ω-scaning, $2\theta_{max}$ = 50°).

The structure was solved by direct method of the program [21] with program modules [22] and [23]. Positions of the hydrogen atoms were located from electron density difference maps and refined by "riding" model with $U_{iso} = nU_{eq}$ (n = 1.5 for methyl groups and n = 1.2 for other hydrogen atoms) of the carrier atom. The hydrogen atom of the amide group has been refined in the isotropic approximation. Full-matrix least-squares refinement against F^2 in anisotropic approximation for non-hydrogen atoms using 1663 reflections was converged to $wR_2 = 0.1122$ ($R_1 = 0.0477$ for 1288 reflections with $F>4\sigma(F)$, S = 1.022).

The atomic coordinates, molecular geometry parameters, and crystallographic data of compound **4** are preserved at the Cambridge Crystallographic Data Center, 12 Union Road, CB2, 1EZ UK [fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk and are available upon request with the CCDC2506161 (**4**).

Discussion

Chlorination of *N*-methoxy-4-toluenesulfonamide **4** with *tert*-butyl hypochlorite afforded unstable *N*-chloro-*N*-methoxy-4-toluenesulfonamide **2** with almost quantitative yield (Scheme 2).



Scheme 3. **The synthesis of *N*-chloro-*N*-methoxy-4-toluenesulfonamide**

N-Chloro-*N*-methoxy-4-toluenesulfonamide **2** and *N*-methoxy-4-toluenesulfonamide **4** structure has been established by the ^1H and ^{13}C NMR spectra. Also, the structure of compounds **4** and **2** has been confirmed by the X-ray diffraction (XRD) study (Figures 1–3).

The ^1H NMR spectra of compounds **4** and **2** show such a common characteristics as singlet of Me group (at 2.448 ppm for **4** and 2.494 ppm for **2**) and singlet of NOMe group (at 3.789 ppm for **4** and 3.797 ppm for **2**).

The ^{13}C NMR spectra of compounds **4** and **2** demonstrate three common characteristics. They are: 1) the chemical shift of the carbon atom of the Me group (at 21.78 ppm for **4** and 22.01 ppm for **2**); 2) the chemical shift of the carbon atom of the NOMe group (at 65.14 ppm for **4** and 63.3 ppm for **2**); 3) the chemical shift of the C(1)–SO_2 carbon atom (at 145.03 ppm for **4** and 146.93 ppm for **2**).

The structure of *N*-methoxy-4-toluenesulfonamide **4** is represented in Figure 1.

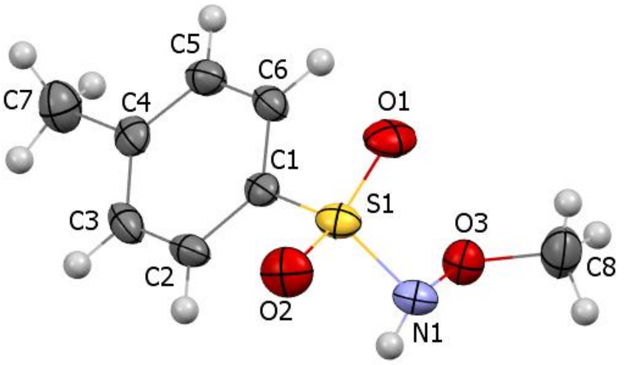


Fig. 1. Molecular structure of *N*-methoxy-4-toluenesulfonamide 4 according to X-ray diffraction data. The thermal ellipsoids are shown with a probability of 50 %

In the molecule of *N*-methoxy-4-toluenesulfonamide **4** the N(1) atom has pyramidal configuration. The sum of the bond angles centered on N(1) atom (Σβ) is 331.0°. This phenomenon is untypical for amides and ureas.

The N(1)–O(3) bond length is 1.421(3) Å, the N(1)–S(1) bond length is 1.646(3) Å.

The *N*-methoxy group is in +*sc*-conformation toward to the tolyl moiety (the C(1)–S(1)–N(1)–O(3) torsion angleis 55.2(2)°). The C(8)H_3-group is rotated to S(1)–N(1) bond (the S(1)–N(1)–O(3)–C(8) torsion angle is – 115.5(2)°).

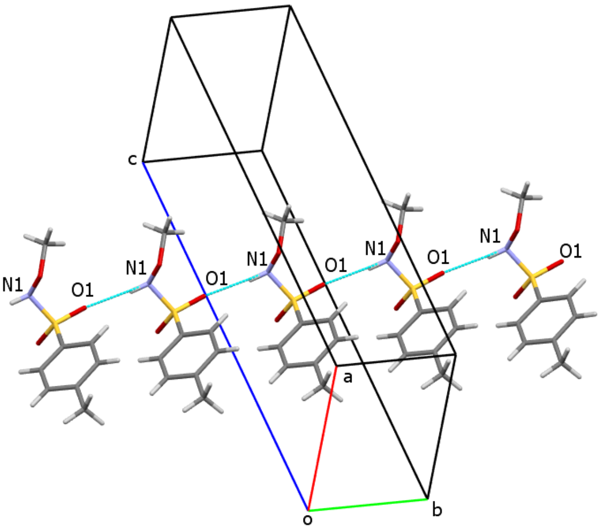


Fig. 2. Chains of *N*-methoxy-4-toluenesulfonamide 4 molecules in a crystal. The hydrogen bonds are shown as blue lines

In the crystal the molecules of *N*-methoxy-4-toluenesulfonamide **4** formed chains along [010] crystallographic direction (Figure 2) as a result of the intermolecular hydrogen bonds N(1)–H…O(1)' (the x,y-1,z symmetry operation; the H…O distance is 2.23(3) Å, the N–H…O angle is 170(3)°).

Figure 3 presents the structure of *N*-chloro-*N*-methoxy-4-toluenesulfonamide **2**.

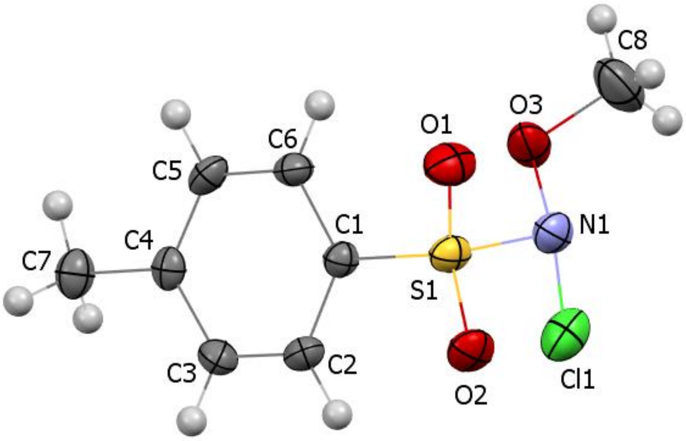


Fig. 3. Molecular structure of *N*-chloro-*N*-methoxy-4-toluenesulfonamide 2 according to X-ray diffraction data. The thermal ellipsoids are shown with a probability of 50 %

In the molecule of *N*-chloro-*N*-methoxy-4-toluenesulfonamide **2** the N(1) atom has a strongly pyramidal configuration. The sum of the bond angles centered on N(1) atom (Σβ) is 324.1°. A similar increase in degree of pyramidality when replacing a hydrogen atom with a chlorine atom is observed in *N*-alkoxy-*N*-chloroureas [4,6] and *N*-alkoxy-*N*-chlorobenzamides [8]. In anomeric *N*-chloro-*N*-methoxyureaΣβ is 329.0° [4], in anomeric *N*-chloro-*N*-methoxy-4-nitrobenzamide Σβ is 337.5°[8]. The N(1)–O(3) bond (length is 1.405(3) Å) is shortened compared to the same bond in the molecule of *N*-methoxy-4-toluenesulfonamide **4**. In the molecule ofdimethyl *N*-methoxy-*N*-(4-toluenesulfonyl)phosphoramidate **3** the corresponding N–O bond is longer (1.439(2) Å [17]).

In the molecule of *N*-chloro-*N*-methoxy-4-toluenesulfonamide **2** the N(1)–Cl(1) bond (length is 1.767(3) Å) is elongated compared to the N–Cl bond in such anomeric amides as *N*-chloro-*N*-methoxyurea (1.7563(11) Å [4]) and *N*-chloro-*N*-methoxy-4-nitrobenzamide (1.7288(14) Å [8]). If we take into account that the average length of the N–Cl bond for *N*-chloroimides is in the range of 1.676–1.691 Å, and for *N*-chlorodialkylamines 1.757–1.791 Å [24], then this N(1)–Cl(1) bond in compound **2** appears to be very elongated.

Such an elongation of the N(1)–Cl(1) bond and the corresponding N(1)–O(3) bond shortening in *N*-chloro-*N*-methoxy-4-toluenesulfonamide **2** are an evidence of the action of the $n_{O(Me)}\rightarrow6\bullet_{N\text{-}Cl}$ anomeric effect. Thus, *N*-chloro-*N*-methoxy-4-toluenesulfonamide **2** and other *N*-alkoxy-*N*-

chloro-R-sulfonamides can be considered as anomeric amides, similar to *N*-acyloxy-*N*-chlorobenzamides [11].

The observed N(1)–Cl(1) bond elongation in *N*-chloro-*N*-methoxy-4-toluenesulfonamide **2** indicates that this bond is highly destabilized and can be considered as a potential reaction center. This is also confirmed by the interaction of *N*-chloro-*N*-methoxy-4-tolyenesulfonamide **2** with trialkyl phosphites [17].

The *N*-methoxy group is in +*sc*-conformation toward to the tolyl moiety (the C(1)–S(1)–N(1)–O(3) torsion angleis 54.9(2)°). The C(8) H_3-group is rotated to S(1)–N(1) bond (the S(1)–N(1)–O(3)–C(8) torsion angle is 140.7(2)°).

In *N*-chloro-*N*-methoxy-4-toluenesulfonamide **2** the S(1)–N(1) bond (the length is 1.739(3) Å) is longer then than similar S–N bond in *N*-methoxy-4-toluenesulfonamide **4** (the length is 1.646(3) Å) and compound **3** (the length is 1.6744(16) Å [17]).

Conclusions

We have found that in *N*-chloro-*N*-methoxy-4-toluenesulfonamide **2**, the nitrogen atom adopts a pronounced pyramidal configuration. This is accompanied by elongation of the N(1)–Cl(1) bond and shortening of the N(1)–O(3)Me bond due to the $n_{O(Me)} \rightarrow \sigma^*_{N-Cl}$ anomeric effect. Thus, this work establishes a new concept in the chemistry of *N*-alkoxy-*N*-chloro-R-sulfonamides.

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