*Russian Chemical Bulletin, Vol. 43, No. 10, October, 1994*

# Preparation of *N*-chloroacetyl-*N′*-arylsulfonylureas and the crystal structure of *N*-chloroacetyl-*N′*-(4-methylphenylsulfonyl)urea

*N. R. Fedotova,*[a*] *I. A. Litvinov,*[b] *and O. N. Kataeva*[b]

[a]*A. M. Butlerov Research Institute, Kazan' State University,*
*18 ul. Lenina, 420008 Kazan', Russian Federation.*
*Fax: +7 (843 2) 380 994*
[b]*A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Scientific Center*
*of the Russian Academy of Sciences, 8 ul. Akad. Arbuzova, 420083 Kazan', Russian Federation.*
*Fax: +7 (843 2) 752 253*

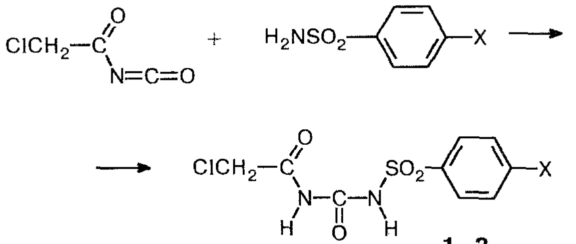
Novel arylsulfonylureas were prepared by the reaction of chloroacetyl isocyanate with arylsulfamides. The structures of the compounds synthesized were determined by IR and $^1$H NMR spectra. An X-ray structural analysis of *N*-chloroacetyl-*N′*-(4-methylphenylsulfonyl)urea was carried out. It was found that the molecule has the *anti-syn* conformation stabilized by an intramolecular H-bond. In the crystal, the molecules are combined into centrosymmetrical dimers by intermolecular hydrogen bonds. The compounds considered exhibit moderate fungicide activity.

**Key words:** *N*-chloroacetyl-*N′*-arylsulfonylureas, X-ray diffraction analysis, hydrogen bonds, chloroacetyl isocyanate, arylsulfamides, biological activity.

Substituted arylsulfonylureas are known[1] to exhibit a wide range of biological activity. Highly active pesticides and remedies have been found among these compounds. Despite the active search for novel derivatives in the series of arylsulfonylheterylureas, studies of their physicochemical and biological properties have only begun to be carried out quite recently.[2]

The purpose of the present work has been to prepare novel substituted arylsulfonylureas and to determine their structures and biological activity.

*N*-Chloroacetyl-*N′*-arylsulfonylureas (**1** and **2**) were prepared by the reaction of chloroacetyl isocyanate with arylsulfamides according to the method described by us previously:[3]


X = H (**1**), Me (**2**)

**1—2**

The structures of compounds **1** and **2** were determined by the IR and $^1$H NMR spectral data and by X-ray diffraction analysis. The IR spectra recorded in vaseline oil and in $CHCl_3$ solutions of various concentrations exhibit absorption bands corresponding to ν(C=O), ν(NH), and ν($SO_2$). Solid samples of **1** and **2**, similarly to benzoylphenylureas,[4] exhibit one intense band in the 1650—1680 cm$^{-1}$ region associated with carbonyl groups bound by a hydrogen bond. In dilute solutions, the bands of the carbonyl groups overlap and are manifested as a broadened intense band in the 1720—1680 cm$^{-1}$ region having inflections on the low-frequency side at 1680—1685 cm$^{-1}$. For solid samples, the absorption bands of the NH group are recorded in the 3110—3300 cm$^{-1}$ region. In the spectra of dilute solutions, bands at 3280 cm$^{-1}$ associated with intramolecular hydrogen bonds and those at 3380 cm$^{-1}$ corresponding to intermolecular hydrogen bonds were observed. The band at 3450 cm$^{-1}$ was assigned to free vibrations of the NH group. The $^1$H NMR spectra of **1** and **2** in $CHCl_3$ contain two one-proton singlets at 11—12 ppm and 9—10 ppm assigned to the hydrogen atoms of the sulfamide and amide groups, respectively, similarly to the previously reported data.[2]

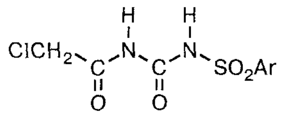
One may suggest that of the four conformations possible for compounds **1** and **2**, the *anti-anti*-conformation does not exist due to steric reasons, as has been reported for *N*-methyl-*N′*-phenylurea.[5]

In order to determine the preferred conformation in the solid state, we carried out an X-ray structural study of *N*-chloroacetyl-*N′*-(4-methylphenylsulfonyl)urea **2**.

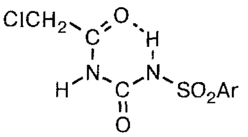
---

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1786—1788, October, 1994.

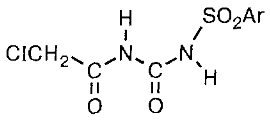
1066-5285/94/4310-1691 $12.50



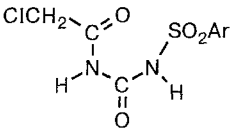
*syn-syn* **A**



*anti-syn* **B**



*syn-anti* **C**



*anti-anti* **D**

The structure of the molecule is shown in Fig. 1. The coordinates of the nonhydrogen atoms are presented in Table 1 and the main geometric parameters are listed in Table 2.

**Table 1.** Atomic coordinates (×10$^4$), equivalent isotropic temperature factors

$$B_{\mathrm{iso}}^{\mathrm{eq}} = -4/3 \sum_{i=1}^{3}\sum_{j=1}^{3}(a_i, a_j) \cdot B(i,j)$$

for nonhydrogen atoms, and isotropic temperature factors for hydrogen atoms of structure **2**

| Atom | *x* | *y* | *z* | $B$/Å$^2$ |
|---|---|---|---|---|
| Cl | 1096.0(6) | −1273(3) | 8503.9(4) | 7.40(3) |
| S | 1267.7(5) | −6488(2) | 10853.9(4) | 4.06(2) |
| O(1) | 1942.0(1) | −7837(5) | 10843.0(1) | 5.50(6) |
| O(2) | 597.0(1) | −7850(5) | 10836.0(1) | 5.62(6) |
| O(7) | 149.0(1) | −2830(4) | 10403.5(9) | 3.79(5) |
| O(8) | 1911.0(1) | −3061(6) | 9542.0(1) | 6.67(7) |
| N(1) | 1274.0(1) | −4629(6) | 10354.0(1) | 3.91(6) |
| N(2) | 847.0(1) | −1455(5) | 9793.0(1) | 3.50(6) |
| C(1) | 1297.0(2) | −4328(6) | 11357.0(1) | 3.39(7) |
| C(2) | 1962.0(2) | −3272(7) | 11523.0(1) | 4.21(8) |
| C(3) | 1981.0(2) | −1517(8) | 11909.0(1) | 4.77(9) |
| C(4) | 1359.0(2) | −808(8) | 12138.0(1) | 4.54(8) |
| C(5) | 710.0(2) | −1902(9) | 11965.0(2) | 5.2(2) |
| C(6) | 673.0(2) | −3668(8) | 11582.0(1) | 4.79(9) |
| C(7) | 715.0(2) | −2989(6) | 10199.0(1) | 3.35(7) |
| C(8) | 1407.0(2) | −1562(8) | 9484.0(1) | 4.41(8) |
| C(9) | 1348.0(2) | 367(9) | 9065.0(2) | 5.9(1) |
| C(10) | 1393.0(3) | 1220(1) | 12546.0(2) | 6.7(7) |
| H(1) | 157.0(1) | −4590(6) | 10230.0(1) | 3.0(7) |
| H(2) | 234.0(2) | −3600(7) | 11330.0(1) | 5.6(9) |
| H(2N) | 51.0(1) | −360(5) | 9730.0(1) | 3.0(6) |
| H(3) | 239.0(2) | −6600(9) | 12030.0(1) | 7(1) |
| H(5) | 29.0(2) | −1440(7) | 12110.0(1) | 6.1(9) |
| H(6) | 28.0(2) | −4320(8) | 11470.0(1) | 6.4(9) |
| H(9.1) | 95.0(2) | 1400(1) | 9080.0(2) | 10(1) |
| H(9.2) | 178.0(2) | 990(9) | 9030.0(2) | 8(1) |
| H(10.1) | 137.0(3) | 700(2) | 12780.0(3) | 19(2) |
| H(10.2) | 111.0(3) | 2000(2) | 12520.0(3) | 27(3) |
| H(10.3) | 168.0(3) | 1900(2) | 12570.0(3) | 20(3) |

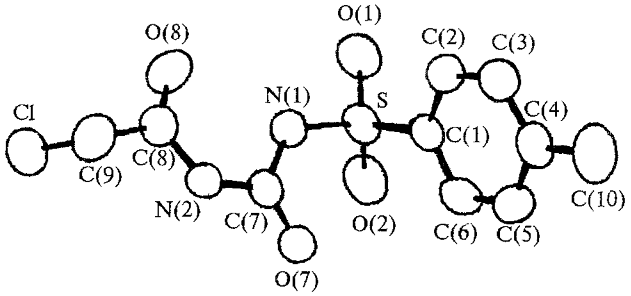


**Fig. 1.** The structure of molecule **2**.

In the previously studied structures of asymmetrically substituted derivatives, the *syn-syn*-conformation of the urea fragment,[6,7] which is the most favorable for steric reasons, has been observed. The *anti-syn*-conformation is characteristic of arylsulfonylheterylureas.[2,8,9] In the structure studied by us, molecules **2** also exist as the *anti-syn*-conformation. This conformation may be stabilized by an N(1)—H...O(8) intramolecular hydrogen bond (see Fig. 1) having the following parameters: the N(1)—H distance is 0.65(4) Å, N(1)...O(8) is 2.672(4) Å, H...O(8) is 2.15(3) Å, and the N(1)—H...O(8) angle is 139(2)°. This hydrogen bond closes a planar (within 0.05 Å) six-membered heterocycle, HN(1)C(7)N(2)C(8)O(8), (see Fig. 1). Both nitrogen atoms have plane-trigonal coordination (the sums of bond angles are 359.9 and 360°). The planar conformation of the urea moiety is favorable for the conjugation of the lone electron pairs (LEP) of the nitrogen atoms with the $\pi$-systems of the C=O double bonds. Redistribution of the bond lengths corresponding to the presence of this conjugation occurs in the structures of substituted ureas.[5—7] In the structure of **2**, this phenomenon is not observed: the C=O bond lengths are 1.211(4) and 1.212(4) Å, *i.e.*, these bonds are noticeably shorter than those reported previously[5—7] (1.234(3)—1.248(1) Å) and are nearly identical to those in

**Table 2.** Bond lengths (*d*) and angles (ω) in molecule **2**

| Bond | *d*/Å | Angle | ω/deg |
|---|---|---|---|
| S—O(1) | 1.426(3) | O(1)—S—O(2) | 120.9(2) |
| S—O(2) | 1.419(3) | O(1)—S—N(1) | 102.4(2) |
| S—N(1) | 1.654(4) | O(1)—S—C(1) | 110.2(2) |
| S—C(1) | 1.752(4) | O(2)—S—N(1) | 108.3(2) |
| Cl—C(9) | 1.765(6) | O(2)—S—C(1) | 109.0(2) |
| O(7)—C(7) | 1.211(4) | N(1)—S—C(1) | 104.9(3) |
| O(8)—C(8) | 1.212(4) | S—N(1)—C(7) | 123.9(3) |
| N(1)—C(7) | 1.376(3) | C(7)—N(2)—C(8) | 129.5(3) |
| N(1)—H(1) | 0.65(4) | O(7)—C(7)—N(1) | 123.6(4) |
| N(2)—C(7) | 1.385(5) | O(7)—C(7)—N(2) | 121.3(3) |
| N(2)—C(8) | 1.365(5) | N(1)—C(7)—N(2) | 115.0(4) |
| N(2)—N(2N) | 0.86(3) | O(8)—C(8)—N(2) | 123.4(4) |
| C(8)—C(9) | 1.505(6) | O(8)—C(8)—C(9) | 122.4(4) |
| | | N(2)—C(8)—C(9) | 114.1(4) |
| | | Cl—C(9)—C(8) | 108.9(4) |

arylsulfonylureas[2,8] (1.208(4)—1.211(4) Å); on the other hand, the C(7)—N(1,2) bonds (1.376(3) and 1.385(5) Å) are longer than those found previously[5—7] (1.335(4)—1.365(4) Å).

A similar difference in the lengths of N—C bonds was observed in the molecules of sulfonylheterylureas,[2] and we explained it by the fact that the LEP of the N(2) atom is involved in conjugation with the π-system of the triazine ring, rather than with the carbonyl group of the urea moiety. The LEP of the N(2) atom in molecule **2** may be involved in conjugation with the π-system of the C(8)=O(8) bond. Some shortening of the N(2)—C(8) bond, (1.365(5) Å), may also be due to this conjugation.

The geometry of the arylsulfamide group is normal. The conformation of the chloromethyl group is favorable for interaction between the π-system of the C(8)=O(8) bond and the antibonding orbital of the C—Cl bond (the O(8)—C(8)—C(9)—Cl torsion angle is 74.3°).

In the crystal, molecules **2** are combined into centrosymmetrical dimers by the N(2)—H...O(7′) ($-x$, $-y$, $2-z$) hydrogen bonds; the N(2)—H distance is 0.86(3) Å, N(2)...O(7) is 2.904(4) Å, H...O(7) is 2.06(3) Å, the N(2)—H...O(7) angle is 168(3)°.

Thus, we prepared novel *N*-chloroacetyl-*N*′-arylsulfonylureas and carried out an X-ray structural study of one of these compounds. According to the X-ray structural data, the molecule exists as the *anti-syn*-conformation stabilized by an intramolecular hydrogen bond. The molecules of known biologically active heterylsulfonylureas exist in the same conformation. Primary screening of compounds **1** and **2** showed that they possess moderate fungicide activity with respect to fungi and bacteria.

## Experimental

IR spectra were recorded on a Specord M-80 spectrophotometer in the 400—3600 cm$^{-1}$ range for suspensions in vaseline oil on KBr plates and for solutions in $CHCl_3$. The $^1H$ NMR spectra were run on a Tesla BS-467 instrument (60 MHz). Anhydrous solvents were used for washing and recrystallization.

Single crystals of **2** are monoclinic; they were grown from a toluene solution. At 20 °C, $a$ = 18.412(6), $b$ = 5.173(1), $c$ = 26.881(7) Å, β = 93.78(2)°, $Z$ = 8, $d_{calc}$ = 1.51 g cm$^{-3}$, space group *I*2/a (irregular position of the *C*2/c group). Unit cell parameters and the intensities of 1072 independent reflections with $F^2 > 3\sigma$ were measured on an Enraf Nonius CAD-4 four-circle automatic diffractometer (λ(Mo-Kα), graphite monochromator, ω/(5/3 θ)-scanning, $\omega < 25°$). The structure was solved by the direct method using the MULTAN program and refined in the isotropic and then in the anisotropic approximation. All of the hydrogen atoms were identified from the differential series and refined isotropically at the final step. The final residual factors were: $R$ = 0.036, $R_w$ = 0.048.

The calculations were carried out on a PDP 11/23 computer using the programs of the SDP complex.

***N*-Chloroacetyl-*N*′-phenylsulfonylurea (1).** Benzenesulfamide (1.405 g, 0.008 mol) was added to a stirred solution of chloroacetyl isocyanate (1.07 g, 0.008 mol) in 20 mL of abs. toluene over a period of 3 h. The resulting crystals were filtered off and recrystallized from a benzene—toluene mixture to give 1.92 g (78 %) of compound **1**. M.p. 165 °C. IR (vaseline oil), ν/cm$^{-1}$: 1680, 1720 (C=O); 3270, 3380 (NH); 1145, 1360 ($SO_2$). $^1H$ NMR ($CHCl_3$), δ: 3.23 (s, 2 H, $CH_2$—Cl); 7.85 (m, 5 H, $C_6H_5$); 10.32 (s, 1 H, NHCO); 11.87 (s, 1 H, $NHSO_2$). Found (%): C, 39.12; H, 3.22; N, 10.23. $C_9H_9ClN_2O_4S$. Calculated (%): C, 39.05; H, 3.25; N, 10.12.

***N*-Chloroacetyl-*N*′-(4-methylphenylsulfonyl)urea (2).** Toluenesulfamide (2.3 g, 0.008 mol) in abs. toluene was added to a solution of chloroacetyl isocyanate (0.96 g, 0.008 mol) in abs. toluene. After 24 h the solid part of the reaction mixture was filtered off. Fractional crystallization from toluene and ethanol gave 2.24 g (69 %) of compound **2** as white crystals. M.p. 185 °C. IR (vaseline oil), ν/cm$^{-1}$: 1650, 1740 (C=O); 3250, 3360 (NH); 1140, 1350 ($SO_2$). $^1H$ NMR ($CHCl_3$), δ: 2.67 (s, 3 H, $CH_3$—C(6)); 3.32 (s, 2 H, $CH_2$—); 7.89 (m, 4 H, $C_6H_4$); 9.54 (s, 1 H, NHCO); 11.97 (s, 1 H, $NHSO_2$). Found (%): C, 41.33; H, 3.65; N, 9.94. $C_{10}H_{11}ClN_2O_4S$. Calculated (%): C, 41.30; H, 3.70; N, 9.60.

## References

1. V. K. Promonenkov, V. I. Sorokin, L. M. Nesterova, O. N. Fedorova, and T. E. Granina, *Sul'fonilgeterilmocheviny* [*Sulfonylheterylureas*], NIITEKhIM, Moscow, 1985 (in Russian).
2. V. I. Sorokin, S. N. Golosov, A. N. Kornilov, D. S. Yufit, Yu. T. Struchkov, and V. N. Drozd, *Khim. Geterotsikl. Soedin.*, 1993, 960 [*Chem. Heterocycl. Compd.*, 1993 (Engl. Transl.)].
3. USSR patent 1559660, *Byul. izobret.*, 1990, 56.
4. T. Sotomatsu, Y. Nakagawa, and T. Fujita, *Pestic. Biochem. and Physiol.*, 1987, **27**, 156.
5. W. A. Brett, P. Rademacher, and R. Boese, *Acta Crystallogr.*, 1990, **46**, 880.
6. G. Husroon and G. W. M. Tiemessen, *Acta Crystallogr., B*, 1976, **32**, 1604.
7. S. Kashino and M. Haisa, *Acta Crystallogr., B*, 1977, **33**, 855.
8. A. S. Vyazgin, D. S. Yufit, Yu. T. Struchkov, A. N. Kornilov, E. N. Vetrova, V. I. Sorokin, and V. N. Drozd, *Izv. TSKhA* [*Bull. Timiryazev Agricult. Acad.*], 1988, 180 (in Russian).
9. D. S. Yufit, Yu. T. Struchkov, A. N. Kornilov, M. A. Amanova, V. I. Sorokin, V. N. Knyazev, and V. N. Drozd, *Izv. TSKhA* [*Bull. Timiryazev Agricult. Acad.*], 1990, 185 (in Russian).

*Received April 14, 1994;*
*in revised form June 28, 1994*