Structure of N^S-butyl-N^O-phenyl(thiooxamide)

M. M. Krayushkin, L. G. Vorontsova, M. G. Kurella, I. V. Zavarzin, and V. N. Yarovenko*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328

The molecular and crystal structure of N^S-butyl-N^O-phenyl(thiooxamide) (**1**) has been established by X-ray structural analysis. The thiooxamide fragment and the phenyl ring are coplanar. The conformation of **1** is stabilized by NH...O and NH...S hydrogen bonds. No conjugation between the thioamide and the oxamide fragments of the molecule occurs. In the crystal, the centrosymmetrically related molecules **1** are linked in dimers through NH...O′ intermolecular hydrogen bonds.

Key words: N^S-Butyl-N^O-phenyl(thiooxamide), X-ray structural analysis, conformation.

Monothiooxamides were obtained early in the 20th century; however, their potentialities in heterocyclic synthesis are still poorly understood.[1] Nevertheless, approaches to the synthesis based on conversions of amide and thioamide groups appear to be promising for obtaining compounds containing 1,2,4- and 1,2,5-oxadiazoles, triazoles, pyrimidines, and pyrazoles. With the aim of performing target syntheses of these compounds, we began to study reactivities and structures of monothiooxamides, in particular with aromatic substituents, which were not described previously.

In this work, the crystal and molecular structures of N^S-butyl-N^O-phenyl(thiooxamide) (**1**) synthesized by the procedure reported previously[2] have been established by X-ray structural analysis.

The structure of molecule **1** is shown in Fig. 1. The H(N(1)) atom forms an intramolecular H(N(1))...S hydrogen bond with the following parameters: N(1)...S 2.955(4), H(N(1))...S 2.36(5) Å, and the N(1)—H(N(1))...S angle 105°. The H(N(2)) atom is involved in a bifurcated hydrogen bond: the intramolecular H(N(2))...O hydrogen bond (N(2)...O 2.636(5), H(N(2))...O 1.99 Å, the N(2)—H(N(2))...O angle 103°) and the intermolecular H(N(2))...O′ hydrogen bond with molecule **1**′ ($-x$, $-y+1$, $-z$). The parameters of the intermolecular hydrogen bond are as follows: N(2)...O′ 2.901(5), H(N(2))...O′ 1.94(4) Å, the N(2)—H(N(2))...O′ angle 127(3)°. Therefore, in the crystal centrosymmetric dimers are formed *via* intermolecular hydrogen bonds. All the above-mentioned parameters of hydrogen bonds are in agreement with the data in the literature.[3,4]

A substantial shortening of the H...S and H...N distances compared to those of the normal van der Waals contacts (2.92 and 2.45 Å, respectively)[5] is indicative of strong intramolecular and intermolecular hydrogen bonds. This is also confirmed by the data of IR spectroscopy: the frequencies of N—H stretching vibrations in compound **1** (3280 and 3232 cm^{-1}) are substantially lower than that typical of the nonbonded amino group (3500 cm^{-1}).

Except for the Bu substituent, the molecule is planar (plane *A*): the maximum deviation of the atoms from this plane is no more than 0.04 Å. The butyl substituent is also nearly planar (plane *B*); the *A*/*B* angle is 82.2°. In the thiooxamide fragment, the S and O atoms are in *trans* positions, whereas the S and N atoms are in s-*cis* positions with respect to the C—C bond. The conformation of the molecule is stabilized by

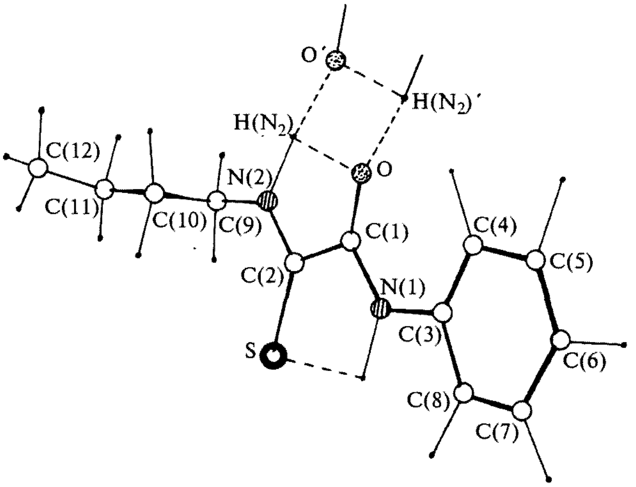


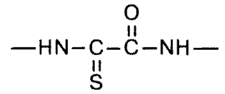
Fig. 1. Molecular structure of **1**.

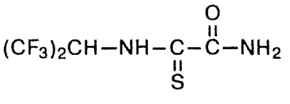
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 485—487, February, 1996.

Table 1. Atomic coordinates in molecule **1** (×10^4 for nonhydrogen atoms, ×10^3 for hydrogen atoms) and isotropic thermal parameters U_{iso})*

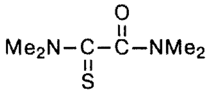
Atom	x	y	z	U_{iso}	Atom	x	y	z
N(1)	5305(1)	7254(3)	6549(9)	5.0	H(N(1))	501(3)	634(5)	587(15)
N(2)	4467(1)	8731(2)	2351(8)	4.2	H(N(2))	481(2)	958(3)	343(10)
O	5376(1)	9041(3)	6142(8)	5.7	H(4)	615(3)	888(6)	916(16)
S	4233(0)	6625(1)	2648(3)	5.8	H(5)	696(3)	871(6)	1176(16)
C(1)	5134(2)	8100(3)	5499(10)	4.3	H(6)	713(3)	688(5)	1364(15)
C(2)	4600(2)	7872(4)	3355(11)	4.8	H(7)	635(3)	526(6)	1211(16)
C(3)	5780(2)	7184(3)	8551(10)	4.5	H(8)	548(3)	540(6)	882(18)
C(4)	6178(2)	8062(4)	9649(12)	5.4	H(9)	380(3)	793(6)	−103(16)
C(5)	6641(2)	7865(5)	11659(13)	6.3	H(9′)	414(3)	945(5)	−156(12)
C(6)	6686(2)	6869(4)	12380(12)	5.3	H(10)	319(3)	807(6)	345(16)
C(7)	6269(3)	6004(7)	11246(18)	9.3	H(10′)	350(3)	968(6)	329(16)
C(8)	5821(2)	6182(4)	9280(11)	4.9	H(11)	310(3)	973(6)	−154(19)
C(9)	3961(2)	8761(4)	0326(11)	4.3	H(11′)	270(3)	830(6)	−129(17)
C(10)	3403(2)	8869(4)	2173(11)	4.7	H(12)	202(3)	947(5)	036(17)
C(11)	2886(2)	8976(4)	0044(12)	4.4	H(12′)	255(3)	1006(6)	296(14)
C(12)	2339(2)	9239(4)	1839(13)	5.4	H(12″)	209(4)	870(7)	347(21)

* Isotropic thermal parameters for H atoms are in the range 5.5—9.6 Å^2.

two strong intramolecular hydrogen bonds. The  $-\mathrm{HN}-\underset{\underset{\displaystyle S}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-\mathrm{NH}-$ fragment in the molecule of monosubstituted thiooxamide **2** have the same structure (see Ref. 6). To the contrary, in tetrasubstituted thiooxamide **3** (see Ref. 7), the NCS and NCO groups are twisted with respect to each other by 87.4.°


$(CF_3)_2CH-NH-\underset{\underset{\displaystyle S}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$

2


$Me_2N-\underset{\underset{\displaystyle S}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-NMe_2$

3

Noteworthy is the C(1)—C(2) bond length in molecule **1** (1.524 Å), which is substantially longer than the standard value for the single C(sp^2)—C(sp^2) bond in conjugated systems (1.46—1.48 Å[8]), which is indicative of the absence of conjugation between the thioamide and the amide fragments. In molecules **2** and **3**, the analogous bond is also elongated (1.513 and 1.533 Å, respectively), *i.e.*, this fact is independent of the nature of substituents and of the conformation of the molecule and is typical of the structures with the thiooxamide group. The results obtained are in agreement with the data of spectroscopic studies and quantum-chemical calculations reported in the literature.[9,10]

Table 2. Bond lengths (*d*) and bond angles (ω) in molecule **1**

Bond	d/Å	Angle	ω/deg
S—C(2)	1.668(5)	C(1)—N(1)—C(3)	130.1(10)
O—C(1)	1.250(5)	C(2)—N(2)—C(9)	124.0(9)
N(1)—C(1)	1.325(7)	N(1)—C(1)—C(2)	115.6(10)
N(2)—C(2)	1.295(6)	N(1)—C(1)—O	124.9(7)
C(1)—C(2)	1.523(6)	C(2)—C(1)—O	119.9(11)
N(1)—C(3)	1.423(7)	N(2)—C(2)—C(1)	112.5(10)
N(2)—C(9)	1.472(6)	N(2)—C(2)—S	126.9(6)
C(3)—C(4)	1.372(6)	C(1)—C(2)—S	120.6(10)
C(4)—C(5)	1.449(8)	N(1)—C(3)—C(4)	122.8(12)
C(5)—C(6)	1.353(8)	N(1)—C(3)—C(8)	115.4(9)
C(6)—C(7)	1.386(9)	C(4)—C(3)—C(8)	121.7(9)
C(7)—C(8)	1.404(10)	C(3)—C(4)—C(5)	116.5(13)
C(8)—C(3)	1.359(7)	C(4)—C(5)—C(6)	119.7(11)
C(9)—C(10)	1.541(7)	C(5)—C(6)—C(7)	119.1(18)
C(10)—C(11)	1.543(7)	C(6)—C(7)—C(8)	119.0(10)
C(11)—C(12)	1.588(8)	C(7)—C(8)—C(1)	121.0(12)
		N(2)—C(9)—C(10)	108.0(3)
		C(9)—C(10)—C(11)	107.9(3)
		C(10)—C(11)—C(12)	108.6(4)

The C(1)—O and N(1)—C(3) bonds (1.250 and 1.423 Å, respectively) are noticeably elongated compared to the standard values (C=O 1.22 and C_{ar}—N(sp^2) 1.36 Å),[8] which points to the fact that the electron density delocalization occurs predominantly in the amide fragment and a weak conjugation occurs between the amino group and the phenyl ring. Other bond lengths are close to standard values:[8] N(2)—C(2) and N(1)—C(1) bond lengths (1.295 and 1.325 Å, respectively) correspond to one-and-a-half order bonds in conjugated systems, whereas the C(2)—S bond length (1.668 Å) corresponds to the double bond. The bond angles also have normal values except for the anomalously large C(1)—N(1)—C(3) angle (130.1°), which is determined by the fact that the atoms of the amide group and of the benzene cycle tend to be located at distances of the allowed van der Waals contacts:[5] H(4)...O 2.27, H(4)...C(1) 2.83, H(4)...

N(1) 2.77, C(1)...C(4) 3.02, and O...C(3) 2.96 Å, and, thus, to decrease the steric hindrance in this region.

Experimental

N^S-Butyl-N^O-phenyl(thiooxamide) (1) was obtained by the reaction of chloroacetanilide with butylamine and sulfur according to the known procedure.[2] The yield was 28 %, m.p. 58—60 °C. Found (%): C, 61.18; H, 6.80; N, 12.02; S, 13.68. $C_{12}H_{16}N_2OS$. Calculated (%): C, 61.02; H, 6.78; N, 11.86; S, 13.56. ^1H NMR (acetone-d_6), δ: 0.96 (t, 3 H, Me); 1.40 (m, 2 H, CH_2); 1.75 (m, 2 H, CH_2); 3.80 (m, 2 H, CH_2); 7.19—7.82 (m, 5 H, Ph); 10.0—10.6 (br.s, 2 H, NH).

Crystals of **1** were grown from EtOH as light yellow needles; the crystals are monoclinic: a = 22.437(2) Å, b = 12.897(1) Å, c = 4.557(1) Å, γ = 102.86(1)°, V = 1285.64 Å^3, Z = 4, space group $P2_1/n$, $C_{12}H_{16}N_2OS$.

The unit-cell parameters and intensities of 915 independent reflections with $I \geq 3\sigma(I)$ were measured on an automated four-circle RED-4 diffractometer (Cu-$K\alpha$, ω-θ/2θ scanning technique, graphite monochromator, θ < 60°). The structure was solved by the direct method; atomic coordinates of nonhydrogen atoms were refined anisotropically by the least-squares method; atomic coordinates of H atoms were located from the difference electron density series and refined isotropically using the AREN-90 program.[11] The final R factor was 0.07. Atomic coordinates are given in Table 1; bond lengths and bond angles are listed in Table 2.

We thank I. P. Yakovlev for help in recording and interpreting the IR spectra.

References

1. K. A. Petrov and L. A. Andreev, *Usp. Khim.*, 1971, **XI**, 1014 [*Russ. Chem. Rev.*, 1971, No. 6 (Engl. Transl.)].
2. B. Milligan and J. M. Swan, *J. Chem. Soc.*, 1961, 1194.
3. R. Taylor, O. Kennard, and W. Versichel, *Acta Crystallogr., Sect. B*, 1984, **40**, 280.
4. L. N. Kuleshova and P. M. Zorkii, *Acta Crystallogr., Sect. B*, 1981, **37**, 1363.
5. Yu. V. Zefirov and P. M. Zorkii, *Zh. Strukt. Khim.*, 1976, **17**, 994 [*J. Struct. Chem.*, 1976, **17** (Engl. Transl.)].
6. H. W. Roesky, H. Hofmann, M. Noltemeyer, and G. M. Sheldrick, *Z. Naturforsch., Teil B*, 1985, **40**, 124.
7. G. Adiwidjaja and J. Voss, *Chem. Ber.*, 1977, **110**, 1159.
8. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, **12**, S1.
9. R. E. Carter and J. Sandström, *J. Phys. Chem.*, 1972, **76**, 642.
10. B. Persson and J. Sandström, *Acta Chem. Scand.*, 1964, **18**, 1059.
11. V. I. Andrianov, *Kristallografiya*, 1987, **32**, No. 1, 228 [*Sov. Phys. Crystallogr.*, 1987, **32**, No. 1 (Engl. Transl.)].

Received July 3, 1995