Structure and Intermolecular Interactions of *N*-(3,5-Di-*tert*-butyl-4-hydroxybenzyl)thioureas

S. V. Bukharov, I. A. Litvinov, A. T. Gubaidullin, A. V. Chernova, R. R. Shagidullin, G. N. Nugumanova, and N. A. Mukmeneva

Kazan State Technological University, Kazan, Tatarstan, Russia Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, Kazan, Tatarstan, Russia

Received November 10, 2002

Abstract—The molecular and crystal structure and the hydrogen bonding in crystal and in solutions of N-phenyl-N-(3,5-di-*tert*-butyl-4-hydroxybenzyl)thiourea and N-(3,5-di-*tert*-butyl-4-hydroxybenzyl)thiourea were studied by single crystal X-ray diffraction and IR spectroscopy. The intermolecular interactions of these compounds are essentially different.

Our previous study of 3,5-di-*tert*-butyl-4-hydroxybenzyl acetate I demonstrated the possibility of selfassociation of sterically hindered phenols containing in *p*-positions proton-acceptor functional groups capable of hydrogen bonding [1]. In this work we studied by single crystal X-ray diffraction and IR spectroscopy the molecular and crystal structure of *N*-phenylN-(3,5-di-*tert*-butyl-4-hydroxybenzyl)thiourea II and N-(3,5-di-*tert*-butyl-4-hydroxybenzyl)thiourea III. We also studied the system of hydrogen bonds in the crystals and solutions of these compounds. Compounds II and III were prepared from benzyl acetate I by the following scheme:



R = Ph (II), H (III).

An X-ray diffraction study of a single crystal of **II** showed that, despite the presence of bulky substituents at the N¹ atom, the thiourea moiety remains planar within 0.008(4) Å (Fig. 1). The phenyl substituent at the N¹ atom is virtually out of conjugation with the thiourea moiety: The dihedral angle between the phenyl and thiourea planes is 71.5(2)°. The geometries of the aromatic substituents and thiourea moiety in **II** are usual (the main geometric parameters of **II** in the crystal are linked by the hydrogen bonds O–H…S. The parameters of the hydrogen bond are as follows: $O^8-H^8...S^{1'}$ (1 + x, y, z), O^8-H^8 1.08, $H^8...S^{1'}$ 2.44, $O^8...S^{1'}$ 3.346(3) Å, $\angle O^8-H^8...S^{1'}$ 141°. The chains of hydrogen-bonded molecules are arranged along the 0X

axis (Fig. 2). The amino group is accommodated between the *tert*-butyl substituents of the neighboring molecule and is sterically blocked by them. On the other hand, the NH_2 group is blocked by the phenyl substituent at the N^1 atom. Thus, the absence of hydrogen bonds involving the NH_2 group in **II** is due to its steric shielding.

Single crystal X-ray diffraction data for thioureas substitutes at only one nitrogen atom are scarce. By now, crystal structures have been determined only for 1-thiocarbamoylimidazoline-2-thione [2] and N,N-dimethylthiourea [3]. The molecules of these compounds have a planar conformation stabilized by the N–H…S intramolecular hydrogen bonds in the thio-



Fig. 1. Molecular geometry of II in the crystal.

urea moiety. In crystals, these molecules are linked by intermolecular $N-H\cdots S$ bonds in infinite chains. The absence of hydrogen bonds involving the amino group in the crystal of **II** does not rule out the possibility of their formation in solutions of **II**. This possibility was examined by IR spectroscopy.

Comparison of the IR spectra of crystalline II with the spectra of its solutions reveals characteristic dis-

Table 1. Bond lengths (d, A) in the molecule of II

| Bond | d | Bond | d |
|--------------------------------|----------|--------------------------------|----------|
| $S^{1}-C^{1}$ | 1.685(5) | C ⁷ -C ⁸ | 1.406(5) |
| $O^{8}-C^{7}$ | 1.376(5) | $C^{8}-C^{9}$ | 1.402(6) |
| O ⁸ –H ⁸ | 1.08 | $C^{8}-C^{14}$ | 1.536(6) |
| $N^{1}-C^{1}$ | 1.338(6) | $C^{10}-C^{11}$ | 1.531(7) |
| $N^{1}-C^{3}$ | 1.480(6) | $C^{10}-C^{12}$ | 1.542(7) |
| $N^{1}-C^{18}$ | 1.443(6) | $C^{10}-C^{13}$ | 1.543(7) |
| $N^{2}-C^{1}$ | 1.344(7) | $C^{14}-C^{15}$ | 1.535(7) |
| $N^{2}-H^{1}$ | 1.15 | $C^{14}-C^{16}$ | 1.523(7) |
| $N^2 - H^2$ | 0.98 | $C^{14}-C^{17}$ | 1.537(6) |
| $C^{3}-C^{4}$ | 1.517(6) | $C^{18}-C^{19}$ | 1.383(5) |
| $C^{4}-C^{5}$ | 1.382(5) | $C^{18}-C^{23}$ | 1.388(6) |
| $C^{4}-C^{9}$ | 1.378(6) | $C^{19}-C^{20}$ | 1.390(7) |
| $C^{5}-C^{6}$ | 1.396(6) | $C^{20}-C^{21}$ | 1.372(7) |
| $C^{6}-C^{7}$ | 1.408(6) | $C^{21}-C^{22}$ | 1.371(6) |
| $C^{6}-C^{10}$ | 1.534(5) | $C^{22}-C^{23}$ | 1.391(7) |
| | 1 | 11 | 1 |

Table 2. Selected bond angles (ω , deg) in the molecule of II

| Angle | ω | Angle | 0 | |
|---|--|--|---|--|
| $\begin{array}{c} {} {} {} {} {} {} {} {} {} {} {} {} {}$ | 124 122.9(4) 121.8(4) 115.3(3) 115 120 123 124.4(4) 118.8(3) 116.8(4) 111.2(3) 120.8(4) 119.0(3) 120.2(4) 121.8(4) 116.8(3) 120.8(4) 122.4(4) 122.3(3) 114.9(4) 122.7(4) 117.3(4) 121.9(4) | $\begin{array}{c} C^9 C^8 C^{14} \\ C^4 C^9 C^8 \\ C^6 C^{10} C^{11} \\ C^6 C^{10} C^{12} \\ C^6 C^{10} C^{13} \\ C^{11} C^{10} C^{12} \\ C^{11} C^{10} C^{13} \\ C^{12} C^{10} C^{13} \\ C^{12} C^{10} C^{13} \\ C^8 C^{14} C^{15} \\ C^8 C^{14} C^{15} \\ C^8 C^{14} C^{17} \\ C^{15} C^{14} C^{16} \\ C^{15} C^{14} C^{17} \\ C^{16} C^{14} C^{17} \\ N^1 C^{18} C^{19} \\ N^1 C^{18} C^{23} \\ C^{19} C^{18} C^{23} \\ C^{19} C^{20} C^{21} \\ C^{20} C^{21} C^{22} \\ C^{21} C^{22} C^{23} \\ C^{18} C^{23} C^{22} \end{array}$ | 120.8(3) $121.1(3)$ $111.3(4)$ $110.8(3)$ $110.4(3)$ $106.9(4)$ $111.1(4)$ $106.3(4)$ $110.7(4)$ $109.9(3)$ $110.5(3)$ $110.5(4)$ $107.8(4)$ $107.4(4)$ $118.8(4)$ $119.4(3)$ $121.8(4)$ $118.0(4)$ $120.9(4)$ $120.6(5)$ $120.0(4)$ $118.7(4)$ | |
| | | | | |



Fig. 2. System of hydrogen bonds formed by molecules of II in the crystal.

tinctions (Table 3). In going from solid II to its dilute solutions in CCl_4 or $CHCl_3$, a strong band of irregular shape with maxima at 3510 and 3390 cm⁻¹ transforms into three well-resolved relatively strong bands at 3644, 3522, and 3399 cm⁻¹ (in CCl_4), or at 3639, 3515, and 3393 cm⁻¹ (in $CHCl_3$). Apparently, the high-frequency peak in each triad should be assigned to the vibrations of free OH groups [v(OH free)], and the other two peaks, to v_{as} and v_s of the NH₂ groups, respectively [4–6]. in this case, an asymmetric band with the maximum at 3510 cm⁻¹ in the spectrum of the solid sample can be considered as a superposition of the v_{as}(NH₂) and v(OH) bands. Indeed, this band can be decomposed into two components at 3510 and 3432 cm⁻¹. The spectrum of a concentrated solution of **II** in CHCl₃ (0.3 M) contains, along with the band at 3639 cm⁻¹ [v(OH free)], also a band at 3446 cm⁻¹. This band disappears on further dilution, which allows its assignment to associated OH groups [v(OH bonded)]. It should be noted that, in the spectra of both solid sample and solutions, the frequencies $v_{as}(NH_2)$ and $v_s(NH_2)$ well obey the Puranik relationship for thioamides [7]: $v_s = 1.214v_{as} - 542.5$, which confirms their assignment.

It is noteworthy that both $v(NH_2)$ bands are weakly

Table 3. Frequencies (cm^{-1}) of characteristic vibrations and relative intensities of absorption bands of *N*-phenyl-*N*-(3,5-di*tert*-butyl-4-hydroxybenzyl)thiourea **II**

| Medium | v(OH free) | v(OH bonded) | $v_{as}(NH_2)$ | $v_{s}(NH_{2})$ | δ(NH ₂) | v(C=S) |
|--|-----------------------------|-----------------------|---|----------------------------|-----------------------|----------------------|
| KBr CCl ₄ ^b CHCl ₃ ^c | 3632 vw 3644 s 3639 m | 3432 ^a | 3510 s, 3510 ^a 3522 s 3515 m | 3390 s 3399 s 3393 m | 1580 s 1585 vs | 1108 s 1161 s |

^a Determined by decomposition of the experimental unsymmetrical band with a maximum at 3510 cm⁻¹. ^b C_{II} (1-6) × 10⁻⁴ M. ^c C_{II} 2 × 10⁻²-3 × 10⁻¹ M.

| Medium | v(OH free) | v _{as} (NH ₂) | v _s (NH ₂) | v(NH) | δ(NH ₂) | δ(CNH) | v(C=S) |
|--|---------------------------------------|------------------------------------|-----------------------------------|--------------------------------------|---------------------|-------------------------|-----------------------|
| KBr CCl ₄ ^a CHCl ₃ ^b | 3632 vw, 3610 vs 3642 vs 3637 s | 3453 vs 3515 s 3513 m | 3286 s 3408 s 3401 s | 3191 s 3447/3430 m 3434/3422 m | 1602 vs 1603 vs | 1560 vs - 1511 vs | 1154 s - 1157 s |

Table 4. Frequencies (cm^{-1}) of characteristic vibrations and relative intensities of absorption bands of *N*-(3,5-di-*tert*-butyl-4-hydroxybenzyl)thiourea **III**

^a C_{III} (1-6) × 10⁻⁴ M. ^b C_{III} 3 × 10⁻² M.

sensitive to the state of the substance. The shift of these bands in going from the crystal of **II** to its solution in CCl_4 is 12 (v_{as}) and 9 cm⁻¹ (v_s), which can be accounted for by nonspecific interactions. At the same time, the v(OH) band in going from the crystalline state to solutions is significantly shifted to high frequencies (by 190 cm⁻¹ in CHCl₃), which suggests participation of the OH group in an intermolecular hydrogen bond. The energy of this hydrogen bond, according to the Iogansen frequency rule [8], is 17 kJ mol⁻¹, i.e., it is a medium-strength hydrogen bond.

According to the above single crystal X-ray diffraction data, the second participant of the intermolecular hydrogen bond is the thiocarbonyl group. Correspondingly, the strong band at 1108 cm⁻¹ assignable to v(C=S) [5] shifts to higher frequencies in going from solid II to its solution (Table 3). The shift of this band $[\Delta v(C=S) 53 \text{ cm}^{-1}]$ is abnormally large for such hydrogen bonds {for example, in the spectrum of benzyl acetate I containing the OH…O=C hydrogen bond [1], the shift of v(C=O) is 20 cm⁻¹ at $\Delta v(OH)$ 115 cm⁻¹}. This inconsistency may be caused by the following factors. The break of intermolecular contacts between molecules of **II** may cause certain changes in their electronic structure, e.g., weakening of the conjugation between the lone electron pair of the tertiary nitrogen atom and the C=S group and correspondingly an increase in the multiplicity of the C=S bond, i.e., an increase in the contribution of structure **B**:

$$\sum_{i=1}^{+} N^{-} C^{-} \xrightarrow{i} N^{-} C^{-} S^{-}$$

The thioamide-**II** band $[\delta(NH_2)]$, like the corresponding $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ bands, are weakly sensitive to the phase state of **II** and concentration of its solution (Table 3).

Thus, the IR data for **II** are consistent with single crystal X-ray diffraction data and suggest formation of the intermolecular hydrogen bond OH…S=C. The primary thioamide group remains free.

The IR spectrum of a crystalline sample of III in the range 3650-3000 cm⁻¹ contains five strong bands. The strongest peaks, as in the case of II, are unambiguously assigned to v(OH) (3610 cm⁻¹), $v_{as}(NH_2)$ (3453 cm^{-1}) , and $v_s(NH_2)$ (3286 cm^{-1}) (Table 4)[4-6]. The two remaining bands can be interpreted as follows: the band at 3191 cm⁻¹ with a shoulder at 3174 cm^{-1} is assignable to v(NH), and the band at 3056 $cm^{-1},$ to the overtone $2\delta(NH)$ enhanced by the Fermi resonance. In solutions, the spectral pattern is different. The spectrum of a solution of **III** in CCl_4 contains three strong bands at 3642 (OH), 3515, and 3408 cm^{-1} (NH₂) and a medium-intensity doublet at 3447/3430 cm⁻¹ [v(NH)]. Since the solution concentration did not exceed 6×10^{-4} M, these frequencies refer to the free groups. The $v_{as}(NH_2)$ and $v_{s}(NH_2)$ bands, as in the case of II, obey the Puranik relationship [7].

As seen from Table 4, the band of the secondary thioamide group v(NH) is a doublet both in the solid state and in dilute solutions in inert solvents. This may be due to the conformational nonuniformity of the molecules of **III**, e.g., with the *s*-*cis*-*s*-*trans* isomerism in the NH–C=S moiety.

The frequencies of the free NH₂ group in **III** are close to those in **II**. However, in contrast to **II**, both $v_{as}(NH_2)$ and $v_s(NH_2)$ bands of **III** are appreciably shifted in going from the solid phase to solutions in CCl₄ (by 62 and 122 cm⁻¹, respectively), suggesting participation of the NH₂ group in the hydrogen bonding. The medium exerts a still greater effect on the vibration frequency of the secondary thioamide group in **III**: $\Delta v(NH)$ in CCl₄ is 256 cm⁻¹. The $\delta(NH)$ band also undergoes an appreciable low-frequency shift (by 49 cm⁻¹) in going from solid **III** to its solution in CHCl₃ (Table 4).

These data show that the primary and secondary thioamide groups in **III** are involved in intermolecular hydrogen bonding. Since, as shown above, the thiocarbonyl group in this case does not participate in hydrogen bonding, the most probable proton acceptors in the hydrogen bonds are the nitrogen and oxygen

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 74 No. 11 2004

atoms. The values of Δv of the thioamide groups suggest [4] that the secondary NH groups form cyclic dimers C or cooperative hydrogen bonds D, and the

primary NH_2 groups form linear pairs with the hydroxyl oxygen atoms. Thus, in **III** there is a complex hierarchy of intermolecular hydrogen bonds:



Thus, we revealed essential differences between the patterns of intermolecular interactions in 3,5-di-tertbutyl-4-hydroxybenzyl-substituted thioureas **II** and **III**. Compound **II** in the solid phase and in concentrated solutions forms self-associates through OH…S=C hydrogen bonds, with the primary thioamide groups remaining virtually free. With III, the pattern is opposite: Both primary and secondary thioamide groups participate in intermolecular hydrogen bonding, whereas the hydroxy and thiocarbonyl groups are not bonded with each other. These differences in the pattern of self-association of **III** and **II** may be caused by the above-noted specific features of the crystal packing of **II**. Another cause may be different hybridization of the electron orbitals in the thiourea moiety of II and III (different contribution of structures A and **B**). The phenyl substituent in **II** may increase the contribution of structure A, more active in hydrogen bonding with the sterically shielded hydroxy group.

EXPERIMENTAL

The IR spectra were recorded on a Bruker Vector-22 Fourier spectrometer. The ¹H and ¹³C NMR spectra were taken on a Varian Gemini-200 spectrometer (200 MHz for ¹H, 50 MHz for ¹³C). The residual proton signals of the deuterated solvents were used as references.

Single crystal X-ray diffraction analysis. Crystals of II, $C_{22}H_{30}N_2OS$, are triclinic. At 20°C, *a* 10.100(4), *b* 10.210(9), *c* 10.490(4) Å; α 102.30(6)°, β 99.81(3)°, γ 94.53(5)°; *V* 1034(1) Å³, *d*_{calc} 1.19 g cm⁻³, *Z* 2, space group *P*1. The unit cell parameters and intensi-

ties of 2633 reflections, including 1300 reflections with $I \ge 3\sigma$, were measured at 20°C (Nonius CAD-4 diffractometer, graphite monochromator, Mo K_{α} radiation, ω -scanning, $\theta \le 27^{\circ}$). No decrease in the intensity of three check reflections was observed during the measurements; the absorption (μ Mo 1.6 cm⁻¹) was neglected.

The structure was solved by the direct method using the SIR program [9] and refined first in the isotropic and then in the anisotropic approximation. All the hydrogen atoms were revealed from the differential electron density series, and their contributions to structural amplitudes were taken into account with fixed positional and isotropic thermal parameters $(B_{iso} \ 6 \ Å^2)$. The final divergence factors are as follows: $R \ 0.046$, $R_W \ 0.054$ for 1486 unique reflections with $F^2 \ge 3\sigma$. All the calculations were performed on a DEC AlphaStation-200 computer using the MolEN program package [10]. The PLATON 98 program was used to make the molecular drawings and analyze the crystal packing [11]. The atomic coordinates in the structure of **II** are given in Table 5.

N-Phenyl-*N*-(**3**,**5**-di-*tert*-butyl-**4**-hydroxybenzyl)thiourea II. A solution of 0.3 g of benzyl acetate I and 0.165 g of phenylthiourea in 5 ml of dimethyl sulfoxide was allowed to stand at room temperature for a day. Then the mixture was poured into water, and the precipitate was filtered off, washed with water, dried, and recrystallized from acetone. A colorless crystalline substance was obtained; mp 194.5–196°C, yield 65%. ¹H NMR spectrum (CDCl₃), δ , ppm: 1.34 s (18H, CMe₃), 5.15 s (1H, OH), 5.31 s (2H, CH₂), 6.88–7.08 m (4H, Ar–H), 7.25–7.44 m (3H, Ar–H).

1739

Table 5. Atomic coordinates in the structure of **II**, equivalent isotropic thermal parameters of nonhydrogen atoms $B = 4/3 \sum_{i=1}^{3} \sum_{j=1}^{3} (a_i a_j) B(i, j)$ (Å²), and isotropic thermal parameters of hydrogen atoms

| Atom | x | у | Z | B, B _{iso} | Atom | x | У | Z | B, B _{iso} |
|--|---|---|--|---|---|---|--|---|---|
| Atom S^1 O^8 N^1 N^2 C^1 C^3 C^4 C^5 C^6 C^7 C^8 C^9 C^{10} C^{11} C^{12} C^{13} C^{14} C^{15} C^{16} C^{17} C^{18} C^{19} C^{20} C^{21} C^{22} C^{23} | x 0.7389(1) 1.4275(3) 0.8112(3) 0.7242(4) 0.7599(4) 0.8566(4) 1.0098(4) 1.0835(4) 1.2248(4) 1.2248(4) 1.2889(4) 1.2167(4) 1.3043(4) 1.3918(5) 1.2074(5) 1.3910(5) 1.2887(4) 1.3820(4) 1.3820(4) 1.3690(5) 1.1849(5) 0.8256(4) 0.7287(5) 0.7470(5) 0.8576(5) 0.9376(4) | y 0.7034(1) 0.5356(3) 0.4561(3) 0.5004(3) 0.5440(4) 0.5071(4) 0.6326(4) 0.6499(4) 0.5326(4) 0.4038(4) 0.3947(4) 0.7910(4) 0.8033(4) 0.9002(4) 0.8241(5) 0.2768(4) 0.2549(4) 0.1512(4) 0.3203(4) 0.2165(4) 0.0858(5) 0.0606(5) 0.1644(5) 0.2966(4) | z 0.3487(2) 0.2453(3) 0.2732(3) 0.4629(4) 0.3600(5) 0.1561(4) 0.1752(4) 0.2278(4) 0.2278(4) 0.2211(4) 0.1663(4) 0.1424(4) 0.3041(5) 0.4414(5) 0.3198(6) 0.2048(5) 0.3198(6) 0.2048(5) 0.3173(5) 0.2662(5) 0.0761(6) 0.2878(4) 0.2133(5) 0.2248(5) 0.3080(5) 0.3821(5) 0.3728(5) | $\begin{array}{c} B, \ B_{\rm iso} \\ \hline 4.69(3) \\ 4.54(9) \\ 3.28(9) \\ 4.6(1) \\ 3.5(1) \\ 3.7(1) \\ 3.7(1) \\ 3.1(1) \\ 3.3(1) \\ 3.4(1) \\ 3.1(1) \\ 3.0(1) \\ 3.1(1) \\ 3.8(1) \\ 4.8(1) \\ 5.3(1) \\ 5.2(1) \\ 3.6(1) \\ 4.5(1) \\ 4.2(1) \\ 5.1(1) \\ 3.2(1) \\ 4.2(1) \\ 5.3(1) \\ 5.3(1) \\ 5.3(1) \\ 5.3(1) \\ 5.3(1) \\ 4.9(1) \\ 4.9(1) \end{array}$ | Atom H^1 H^2 H^5 H^8 H^9 H^{19} H^{20} H^{21} H^{22} H^{23} H^{31} H^{32} H^{111} H^{122} H^{123} H^{121} H^{122} H^{123} H^{131} H^{132} H^{133} H^{151} H^{152} H^{153} H^{161} H^{162} | x 0.7155 0.7242 1.0165 1.4972 1.0202 0.6239 0.6652 0.8621 1.0670 1.0185 0.8219 0.8139 1.3145 1.4600 1.4406 1.2791 1.1389 1.1444 1.4681 1.3352 1.4431 1.4218 1.4699 1.3128 1.4433 1.3052 | y 0.5837 0.4050 0.7253 0.6272 0.2801 0.2500 0.0014 -0.0465 0.1501 0.3926 0.5872 0.4018 0.7980 0.8997 0.7089 0.9927 0.8727 0.9028 0.7710 0.8236 0.9106 0.2073 0.3731 0.2792 0.3398 0.2287 | z 0.5528 0.4654 0.2524 0.282 0.1068 0.1431 0.1684 0.3319 0.4510 0.4228 0.1449 0.0611 0.5087 0.4762 0.4602 0.3689 0.3903 0.2212 0.1984 0.1023 0.2250 0.0034 0.0837 -0.0683 0.3299 0.3356 | <i>B</i> , <i>B</i> _{iso} 6 6 6 6 6 6 6 6 6 6 6 6 6 |
| C ²³ | 0.9376(4) | 0.2966(4) | 0.3728(5) | 4.0(1) | H^{102} H^{171} H^{172} H^{173} | 1.3052 1.2244 1.1307 1.1140 | 0.2287 0.0694 0.1667 0.1221 | 0.3356 0.0587 -0.0329 0.1293 | 6 6 6 6 |

N-(**3**,**5**-Di-*tert*-butyl-4-hydroxybenzyl)thiourea III was prepared similarly from 0.3 g of benzyl acetate I and 0.1 g of thiourea in 5 ml of dimethyl sulfoxide. Yield 50%, mp 196–197°C (197–198°C [12]). ¹H NMR spectrum (acetone- d_6), δ, ppm: 1.42 s (18H, CMe₃), 4.62 s (2H, CH₂), 6.03 s (1H, OH), 6.57 s (2H, NH₂), 7.20 s (2H, Ar–H), 7.36 s (1H, NH). ¹³C NMR spectrum (acetone- d_6), δ_C , ppm: 30.34 (CMe₃), 35.12 (CMe₃), 49.68 (CH₂–N), 125.48 (C³), 130.24 (C⁴), 138.32 (C²), 154.06 (C¹), 185.16 (C=S). Found, %: C 65.53; H 9.06; N 9.23; S 10.56. C₁₆H₂₆N₂OS. Calculated, %: C 65.26; H 8.90; N 9.51; S 10.89.

ACKNOWLEDGMENTS

The X-ray diffraction study was performed at the Department of X-ray Diffraction Studies, Center for Collective Use, Russian Foundation for Basic Research (project no. 00-03-40133) on the base of the Laboratory of Diffraction Methods, Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences.

REFERENCES

- Bukharov, S.V., Pod"yachev, S.N., Syakaev, V.V., Litvinov, I.A., and Gubaidullin, A.T., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 10, p. 1658.
- 2. Valle, G., Cojazzi, G., Busetti, V., and Mammi, M., Acta Crystallogr., Sect. B, 1970, vol. 26, no. 5, p. 468.
- Pathirana, H.M.K.K., Weiss, T.J., Reibenspies, J.H., Zingaro, R.A., and Meyers, E.A., Z. Kristallogr., 1994, vol. 209, no. 8, p. 698.
- 4. Bellamy, L.J., Advances in Infrared Group Frequencies, London: Methuen, 1968.

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 74 No. 11 2004

- 5. Rao, C.N.R., *Chemical Applications of Infrared Spectroscopy*, New York: Academic, 1963.
- 6. Nakanishi, K., *Infrared Absorption Spectroscopy*, Tokyo: Nankido, 1962.
- 7. Puranik, R., Nature, 1961, vol. 191, no. 4790, p. 796.
- Iogansen, A.V., Spectrochim. Acta (A), 1999, vol. 55, nos. 7–8, p. 1585.
- 9. Altomare, A., Cascarano, G., Giacovazzo, C., and

Viterbo, D., Acta Crystallogr., Sect. A, 1991, vol. 47, no. 4, p. 744.

- 10. Straver, L.H. and Schierbeek, A.J., *MolEN. Structure Determination System*, Nonius B.V., 1994, vol. 1.
- 11. Spek, A.L., Acta Crystallogr., Sect. A, 1990, vol. 46, no. 1, p. 34.
- 12. Gorbunov, D.B., Voznesenskii, V.N., Ershov, V.V., and Nikiforov, G.A., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1994, no. 1, p. 98.