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SYNTHESIS AND PROPERTIES OF AMMONIUM 5-BENZOYL-4-(2-CHLOROPHENYL)-3-CYANO-6-HYDROXY-6-PHENYL-1,4,5,6-TETRAHYDROPYRIDINE-2-THIOLATES

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The reaction of 2-chlorobenzaldehyde with cyanothioacetamide and dibenzoylmethane in the presence of piperidine or N-methylmorpholine gave the corresponding 5-benzoyl-4-(2-chlorophenyl)-3-cyano-6-hydroxy-6-phenyl-1,4,5,6-tetrahydropyridine-2-thiolates, used in the synthesis of 1-alkylthio-4-benzoyl-1-benzoylamino-3-(2-chlorophenyl)-2-cyanobut-1-enes.

Keywords: substituted 1,4,5,6-tetrahydropyridine-2-thiolates, ring opening under the effect of aminating agents.

Piperidinium 3-cyano-6-hydroxy-6-methyl-5-(2-methylphenyl)carbamoyl-4-(2-thienyl)-1,4,5,6-tetrahydropyridine-2-thiolate was converted to 2-(4-phenylthiazol-2-yl)-3-(2-thienyl)acrylonitrile on reaction with phenacyl bromide [1]. No other examples of ring opening of sulfur-containing tetrahydropyridines are known.

We have established that condensation of 2-chlorobenzaldehyde (**1**) with cyanothioacetamide (**2**) and dibenzoylmethane (**3**) in ethanol in the presence of piperidine or N-methylmorpholine (~20°C) occurs with the formation of the corresponding substituted tetrahydropyridine-2-thiolates **4,5**. The piperidinium salt **4** is transformed into the thiolate **6** on maintaining the reaction mixture for 12 h at room temperature. The N-methylmorpholinium salt **5** did not undergo further transformations, but was readily dehydrated in DMSO solution during the ^{1}H NMR experiment permitting registration of proton signals of the dihydropyridine **7**.

According to the ^{1}H NMR spectrum, thiolate **6** is formed as a mixture of major (A) and minor (B) conformational isomers with a ratio A:B = 2:1 (see experimental). The sulfides **9a,b** formed from alkylation of the salt **6** with the halides **8a,b** are in the similar ratio.

Reaction of the salt **5** with the halides **8c,d** in the presence of KOH occurs regioselectively with simultaneous opening of the tetrahydropyridine ring to give compounds **9c,d** as a single conformer of type B. It is interesting that conformers of this type are the minor forms for compounds **6,9a,b**.

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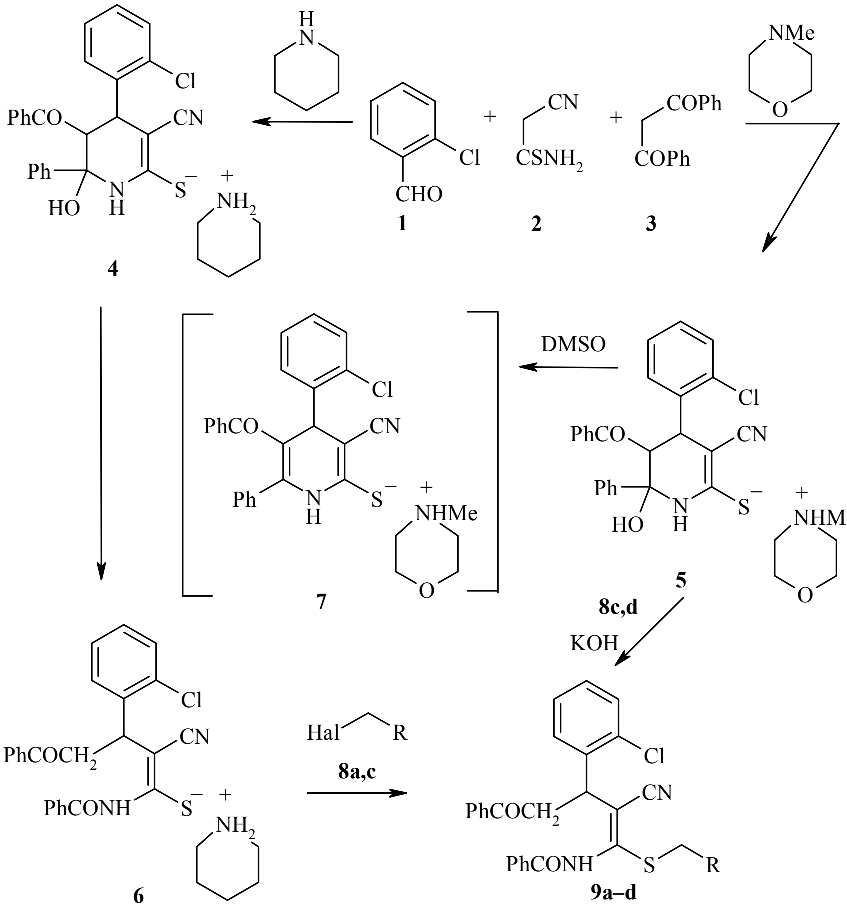

8 a,c Hal = I**; 8 b, d** Hal = Cl;
8, **9a** R = H; **b** R = 4-BrC_6H_4NHCO; **c** R = Me; **d** R = Ph

The structure of compound **9c** was determined by X-ray crystallography. The general view of the molecule of **9c** is shown in Fig. 1 and the basic geometric parameters are presented in Table 1.

TABLE 1. Principal Bond Lengths (*d*) and Bond Angles (ω) in the Molecule of Compound **9c**

Bond	*d*, Å	Angle	ω, deg
$Cl_{(1)}–C_{(8)}$	1.725(4)	$C_{(1)}–S_{(1)}–C_{(19)}$	103.4(2)
$S_{(1)}–C_{(1)}$	1.748(4)	$C_{(1)}–N_{(1)}–C_{(21)}$	126.3(4)
$S_{(1)}–C_{(19)}$	1.807(5)	$S_{(1)}–C_{(1)}–N_{(1)}$	119.6(3)
$O_{(1)}–C_{(5)}$	1.214(4)	$S_{(1)}–C_{(1)}–C_{(2)}$	120.3(3)
$O_{(2)}–C_{(21)}$	1.206(4)	$N_{(1)}–C_{(1)}–C_{(2)}$	120.1(3)
$N_{(1)}–C_{(1)}$	1.394(5)	$C_{(1)}–C_{(2)}–C_{(3)}$	126.1(3)
$N_{(1)}–C_{(21)}$	1.369(5)	$C_{(1)}–C_{(2)}–C_{(6)}$	118.7(4)
$N_{(2)}–C_{(6)}$	1.138(4)	$C_{(1)}–C_{(2)}–C_{(5)}$	130.3(4)
$C_{(1)}–C_{(2)}$	1.344(5)	$C_{(2)}–C_{(3)}–C_{(4)}$	111.2(3)
$C_{(2)}–C_{(6)}$	1.436(5)	$C_{(2)}–C_{(3)}–C_{(7)}$	109.1(3)
$C_{(4)}–C_{(5)}$	1.351(6)	$C_{(4)}–C_{(3)}–C_{(7)}$	114.3(3)
		$N_{(2)}–C_{(6)}–C_{(2)}$	176.2(5)

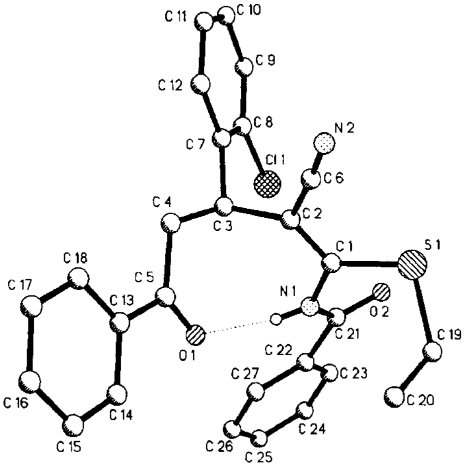

Fig. 1. General view of the molecule of **9c** with numbering of the atoms
(of the hydrogen atoms, only $H_{(1)}$ is shown; the dotted line represents a hydrogen bond).

A characteristic of the structure of compound **9c** is the intramolecular hydrogen bond $O_{(1)}\cdots H_{(1)}–N_{(1)}$ ($O_{(1)}\cdots N_{(1)}$ 2.90(4), $O_{(1)}–H_{(1)}$ 2.19(3), $N_{(1)}–H_{(1)}$ 0.79(3) Å, angle $O_{(1)}–H_{(1)}–N_{(1)}$ 149(2)°), closing the eight-membered ring $O_{(1)}H_{(1)}N_{(1)}C_{(1\text{-}5)}$. The geometrical parameters of this bond correspond to an H-bond of medium strength, while the $O_{(1)}\cdots N_{(1)}$ distance is close to the statistical average of 2.89 Å for N–H···O bonds [2, 3]. The $N_{(1)}$ atom has a planar trigonal configuration – the sum of the bond angles at this atom is 358.9°. The lengths of the bonds $S–C_{(2)}$ are 1.748(4) and $S–C_{(19)}$ 1.807(5) Å and the magnitude of the bond angle $C_{(2)}–S_{(1)}–C_{(19)}$ 103.4(2)° coincide within the limits of experimental error with the corresponding values of 1.759(8), 1.795(18) Å and 102.1(5)° found in the molecule $H_2C=CH–S–Me$ [4].

The molecules of compound **9c** are linked in the crystal by van der Waals forces: no short intermolecular distances were observed. The crystal packing of compound **9c** is shown in Fig. 2.

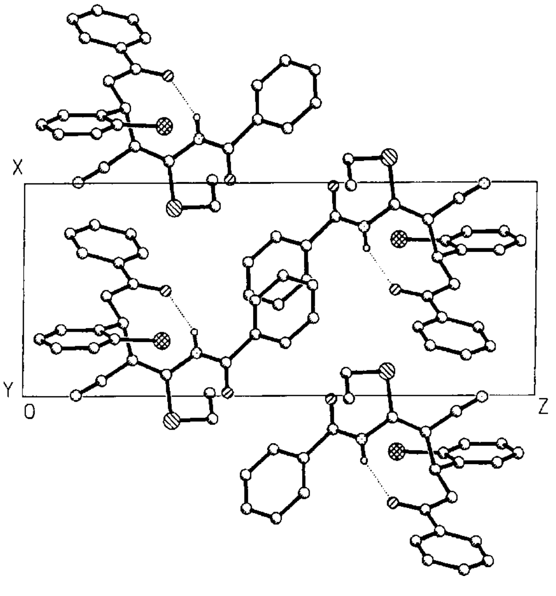

Fig 2. Crystal packing (*ac* projection) of compound **9c**.

TABLE 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters U_{eq} in the Structure of **9c**

Atom	*x*	*y*	*z*	U_{eq}, Å^2
Cl$_{(1)}$	0.2621(2)	0.61028(15)	0.26880(7)	0.0995
S$_{(1)}$	-0.11532(14)	0.17480(16)	0.29021(7)	0.0779
O$_{(1)}$	0.4985(3)	0.0426(3)	0.27517(14)	0.0661
O$_{(2)}$	0.0158(4)	0.3844(4)	0.39889(17)	0.0959
N$_{(1)}$	0.2037(5)	0.2253(4)	0.33802(17)	0.0569
N$_{(2)}$	0.0052(5)	0.1883(5)	0.1032(2)	0.0868
C$_{(1)}$	0.1016(5)	0.2207(4)	0.2784(2)	0.0548
C$_{(2)}$	0.1710(5)	0.2475(4)	0.2122(2)	0.0494
C$_{(3)}$	0.3461(5)	0.3128(5)	0.19305(18)	0.0520
C$_{(4)}$	0.4738(5)	0.1895(5)	0.16000(19)	0.0588
C$_{(5)}$	0.5313(5)	0.0442(5)	0.2117(2)	0.0535
C$_{(6)}$	0.0739(5)	0.2138(5)	0.1527(2)	0.0577
C$_{(7)}$	0.3133(5)	0.4731(5)	0.1471(2)	0.0545
C$_{(8)}$	0.2703(5)	0.6129(5)	0.1771(2)	0.0652
C$_{(9)}$	0.2287(6)	0.7587(6)	0.1367(3)	0.0823
C$_{(10)}$	0.2277(6)	0.7675(6)	0.0639(3)	0.0919
C$_{(11)}$	0.2710(6)	0.6321(7)	0.0317(2)	0.0836
C$_{(12)}$	0.3147(5)	0.4870(5)	0.0728(2)	0.0669
C$_{(13)}$	0.6301(5)	-0.0971(5)	0.1833(2)	0.0556
C$_{(14)}$	0.6755(6)	-0.2321(6)	0.2298(2)	0.0784
C$_{(15)}$	0.7640(7)	-0.3670(6)	0.2056(4)	0.0988
C$_{(16)}$	0.8083(7)	-0.3668(7)	0.1354(4)	0.1041
C$_{(17)}$	0.7680(7)	-0.2332(8)	0.0885(3)	0.0957
C$_{(18)}$	0.6775(6)	-0.0968(5)	0.1121(2)	0.0746
C$_{(19)}$	-0.1068(6)	0.0322(6)	0.3702(3)	0.0873
C$_{(20)}$	0.0139(7)	-0.1158(7)	0.3643(3)	0.1209
C$_{(21)}$	0.1578(6)	0.3084(5)	0.3949(2)	0.0639
C$_{(22)}$	0.2915(5)	0.2960(5)	0.4517(2)	0.0612
C$_{(23)}$	0.2505(6)	0.3752(6)	0.5101(2)	0.0825
C$_{(24)}$	0.3681(8)	0.3698(7)	0.5642(2)	0.0944
C$_{(25)}$	0.5229(8)	0.2861(7)	0.5619(3)	0.1063
C$_{(26)}$	0.5679(8)	0.212(1)	0.5041(4)	0.1790
C$_{(27)}$	0.4518(7)	0.2148(8)	0.4500(3)	0.1400
H$_{(1)}$	0.303(4)	0.190(4)	0.3330(17)	0.041(11)

EXPERIMENTAL

^{1}H NMR spectra of DMSO-d$_6$ solutions with TMS as internal standard were recorded on a Bruker AM-300 (300.13 MHz) spectrometer, IR spectra in nujol mulls on an IRS-29 spectrophotometer, EI mass spectra (70 eV) on a Kratos MS-30 machine with direct injection of the sample into the source. The course of the reaction and the purity of substances were monitored by TLC on Silufol UV-254 plates with acetone–hexane 3:5 as eluent.

Piperidinium 5-Benzoyl-4-(2-chlorophenyl)-3-cyano-6-hydroxy-6-phenyl-1,4,5,6-tetrahydropyridine-2-thiolate (4). Cyanothioacetamide **2** (2 g) was added with stirring at room temperature to a mixture of 2-chlorobenzaldehyde **1** (2.25 g, 20 mmol) and piperidine (3 drops) in ethanol (30 ml), then over 5 min dibenzoylmethane **3** (4.48 g, 20 mmol) and more piperidine (2.47 ml, 25 mmol).The precipitate of **4**, which formed over 20 min, was filtered off and washed with ethanol and hexane. Yield 8.41 g (79%); mp 117-119°C. IR spectrum, ν, cm^{-1}: 3150-3270 (NH, OH), 2170 (CN), 1695 CO). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 1.58 (6H, br. s, 3CH$_2$); 2.96 (4H, br. s, CH$_2$NCH$_2$); 4.28 (1H, d, ^3J = 9.3, 5-H); 4.85 (1H, d, ^3J = 9.3, 4-H); 5.50 (1H, s, OH); 7.09-8.18 (15H, m, 14H$_{arom}$ + NH). Found, %: C 67.94; H 5.89; N 7.71; S 6.18. $C_{30}H_{30}ClN_3O_2S$. Calculated, %: C 67.72; H 5.68; N 7.90; S 6.03. Mass spectrum *m/z* (*I*$_{rel}$, %): 69 (43), 77 (43), 84 (38), 105 (46), 147 (38), 187 (45), 224 (99). The molecular ion peak [M$^+$] was absent.

N-Methylmorpholinium 5-Benzoyl-4-(2-chlorophenyl)-3-cyano-6-hydroxy-6-phenyl-1,4,5,6-tetrahydropyidine-2-thiolate (5). To a mixture of 2-chlorobenzaldehyde **1** (2.25 g, 20 mmol) and N-methylmorpholine (3 drops) in ethanol (30 ml) cyanothioacetamide **2** (2 g) was added with stirring at room temperature. After 5 min, dibenzoylmethane **3** (4.48 g, 20 mmol) and then N-methylmorpholine (2.52 ml, 25 mmol) were added. After the reagents had dissolved, the reaction mixture was maintained at room temperature for 12 h. The precipitate formed was filtered off and washed with acetone to give **5** (8.1 g, 74%); mp 127-129°C. IR spectrum, ν, cm^{-1}: 3300-3365 (NH, OH), 2170 (CN), 1680 (CO). Found, %: C 65.96; H 5.82; N 7.43; S 5.93. $C_{30}H_{30}ClN_3O_3S$. Calculated, %: C 65.74; H 5.52; N 7.67; S 5.85. Mass spectrum, *m/z* (*I*$_{rel}$, %): 43 (100), 51 (21), 71 (24), 77 (63), 105 (43), 391 (38). The [M$^+$] peak was absent. Because of the rapid dehydration of thiolate **5** in DMSO solution, the spectrum of the 1,4-dihydropyridine-2-thiolate **7**, was recorded: δ, ppm, *J* (Hz): 2.51 (3H, s, NMe); 2.77 (4H, br. s, CH$_2$NCH$_2$); 3.70 (4H, br. s, CH$_2$OCH$_2$); 5.10 (1H, s, 4-H); 6.95-8.27 (15H, m, 14H$_{arom}$ + NH).

Piperidinium 4-Benzoyl-1-benzoylamino-3-(2-chlorophenyl)-2-cyanobut-1-en-1-thiolate (6) was obtained analogously to compound **4**, but the reaction mixture was kept at room temperature for 12 h. Yield 8.81 g (83%); mp 131-133°C. IR spectrum, ν, cm^{-1}: 3145-3210 (NH), 2170 (CN), 1620, 1695 (2CO). ^{1}H NMR spectrum (A:B 2:1), δ, ppm, *J* (Hz): 1.58 (6H, m , 3CH$_2$); 3.00 (4H, t, ^3J = 6.8, CH$_2$NCH$_2$); 3.30-3.91 (2H, m 4,4-H$_2$); 4.67 (dd, ^3J = 5.2, ^3J = 9.1, 3-H); 5,32 (t, ^3J = 7, 3-H$_A$, sum of the intensities of the 3-H$_A$ and 3-H$_B$ signals corresponds to 1H); 7.15-7.65, m, 7.87, m, and 8.03, d (^3J = 7.2) (14H, H$_{arom}$); 9.06 (1H, br. s, NH). Found, %: C 67.88; H 5.92; N 7.77; S 6.22. $C_{30}H_{30}ClN_3O_2S$. Calculated, %: C 67.72; H 5.68; M 7.90; S 6.03. Mass spectrum, *m/z* (*I*$_{rel}$, %): 51 (58), 56 (41), 77 (79), 84 (68), 85 (47), 105 (100), 207 (72). The [M$^+$] peak was absent.

4-Benzoyl-1-benzoylamino-3-(2-chlorophenyl)-2-cyano-1-methylthiobut-1-ene (9a). A mixture of salt **6** (2.66 g, 5 mmol) and methyl iodide **8a** (0.31 ml, 5 mmol) in 80% ethanol (30 ml) was heated until the starting reagents dissolved and the solution was then filtered through filter paper. The precipitate formed in the filtrate over 12 h was separated and washed with ethanol and hexane to give **9a** (1.89 g, 82%); mp 161-163°C. IR spectrum, ν, cm^{-1}: 3285 (NH), 2205 (CN), 1685, 1710 (2CO). ^{1}H NMR spectrum (A:B, 2:1), δ, ppm, *J* (Hz): 2.26 (s, SMe$_A$); 2.31 (s, SMe$_B$); 3.66 (m, 4,4-H$_2$ conformer A); 3.76 (dd, ^2J = 16, ^3J = 5.4, 4-H); 3.94 (dd, ^2J = 16, ^3J = 9, 4-H$_B$); 4.84 (dd, ^3J = 5.4, ^3J = 9, 3-H$_B$); 4.96 (t, ^3J = 7.2, 3-H$_A$). The total intensity of the signals for SMe$_A$ and SMe$_B$ corresponds to 3H, 4-H$_A$ and 4-H$_B$ to 2H, and 3-H$_A$ and 3-H$_B$ to 1H; 7.25-7.68 and 7.90-8.05 (14H, two m, H$_{arom}$); 10.42 (1H, br. s, NH). Found, %: C 67.95; H 4.33; N 6.18; S 7.07. $C_{26}H_{21}ClN_2O_2S$. Calculated, %: C 67.74; H 4.59; N 6.08; S 6.96. Mass spectrum, *m/z* (*I*$_{rel}$, %): 77 (90), 78 (49), 105 (100), 106 (92), 122 (35), 207 (46), 292 (50), 355 (31), 413 (21), 460 [M$^+$] (6).

4-Benzoyl-1-benzoylamino-1-(4-bromophenyl)carbamoylmethylthio-3-(2-chlorophenyl)-2-cyanobut-1-ene (9b) was obtaining analogously to compound **9a**, using the corresponding chloride **8b**. Yield 2.89 g (88%); mp 219-221°C. IR spectrum, ν, cm^{-1}: 3210-3285 (2NH), 2200 (CN), 1650, 1710 (3CO). ^{1}H NMR spectrum (A:B, 5:3), δ, ppm, *J* (Hz): 3.66-3.86 (4H, SCH$_2$ and 4,4-H$_2$); 4.82 (dd, ^3J = 5.5, ^3J = 8.9, 3-H$_B$); 5.08 (t, ^3J = 6.7, 3-H$_A$); 7.25-7.65, 7.98 (18H, two m, H$_{arom}$); 10.17 and 10.53 (two s, 2NH$_A$); 10.23 and 10.56 (two s, 2NH$_B$). The total integrals of the 3-H signals and also the two NH groups for conformers A and B are equal to the intensities of one and two protons respectively. Found, %: C 60.26; H 4.03; N 6.25; S 4.95. $C_{33}H_{25}BrClN_3O_3S$. Calculated, %: C 60.15; H 3.82; N 6.38; S 4.87. Mass spectrum, *m/z* (*I*$_{rel}$, %): 77 (60), 89 (17), 105 (100), 133 (23), 173 (21), 207 (30), 227 (29). The [M$^+$] peak was absent.

4-Benzoyl-1-benzoylamino-3-(2-chlorophenyl)-2-cyano-1-ethylthiobut-1-ene (9c). 10% Aqueous potassium hydroxide (2.8 ml, 5 mmol) was added at room temperature with stirring to a suspension of salt **5** (2.73 g, 5 mmol) in ethanol (30 ml 80%), then ethyl iodide (0.4 ml, 5 mmol) was added over 5 min. After the starting materials had dissolved the solution was filtered through paper filter. The precipitate which formed in the filtrate over 12 h was isolated and washed with ethanol and hexane to give **9c** (1.92 g, 81%); mp 145-147°C. IR spectrum, ν, cm^{-1}: 3300 (NH), 2195 (CN), 1680 (2CO). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 1.20 (3H, t, $^3J = 7.2$, Me); 2.84 (2H, m, SCH_2); 3.78 (1H, dd, $^2J = 17.8$, $^3J = 5.9$, 4-H); 3.97 (1H, dd, $^2J = 17.8$, $^3J = 9$, 4-H); 4.84 (1H, dd, $^3J = 5.9$, $^3J = 9$, 3-H); 7.25-7.64, 7.86-7.98 (14H, two m, H_{arom}); 10.47 (1H, br. s NH). Found, %: C 68.36; H 4.92; N 6.03; S 6.84. $C_{27}H_{23}ClN_2O_2S$. Calculated, %: C 68.27; H 4.88; N 5.90; S 6.75. Mass spectrum, *m/z* (I_{rel}, %): 77 (75), 78 (62), 105 (100), 106 (82), 122 (48), 207 (68), 292 (61), 294 (28), 369 (51), 474 [M$^+$] (3).

4-Benzoyl-1-benzoylamino-1-benzylthio-3-(2-chlorophenyl)-2-cyanobut-1-ene (9d) was prepared analogously to **9c** using the corresponding chloride **8d**. Yield 2.06 g (77%); mp 126-129°C. IR spectrum, ν, cm^{-1}: 3295 (NH), 2195 (CN), 1670 (2CO). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 3.74 (1H, dd, $^2J = 18.1$, $^3J = 5.6$, 4-H); 3.94 (1H, dd, $^2J = 18.1$, $^3J = 8.8$, 4-H); 4.11 (2H, s, SCH_2); 4.81 (1H, dd, $^3J = 5.6$, $^3J = 8.8$, 3-H); 7.23-7.64, 7.91-7.98 (19H, two m, H_{arom}); 10.57 (1H, br. s, NH). Found, %: C 71.72, H 4.92, N 5.21, S 6.04. $C_{32}H_{25}ClN_2O_2S$. Calculated, %: C 71.56; H 4.69; N 5.22; S 5.97. Mass spectrum, *m/z* (I_{rel}, %): 58 (19), 65 (22), 77 (100), 78 (19), 91 (90), 105 (81), 106(48), 207 (33), 324 (17), 427 (16). The [M$^+$] was absent.

An X-ray Crystallographic Investigation of a Monocrystal of Compound 9c with dimensions 0.24 × 0.30 × 0.34 mm was carried out at 18°C on automatic four-circle Enraf-Nonius CAD-4 diffractometer (Mo$K\alpha$ radiation, relative scanning ratio $\omega/2\theta = 1.2$, $\theta_{max} = 25°$, sphere segment with $0 \le h \le 10$, $-11 \le k \le 11$, $-23 \le l \le 23$). A total of 4309 reflexions were collected, of which 3979 were symmetrically independent ($R_{int} = 0.013$). Crystals of compound **9c** are triclinic, $a = 7.657(2)$, $b = 8.434(2)$, $c = 18.841(3)$, $\alpha = 82.97(1)$, $\beta = 88.38(2)$, $\gamma = 83.76(2)°$; $V = 1200.7$ Å^3; M = 475.01; $Z = 2$; $d_{calc} = 1.31$ g/cm^3; $\mu = 2.66$ cm^{-1}; space group P-1. The structure was solved by direct method and refined by the least-squares method in the full matrix anisotropic approximation using the CRYSTALS package of programs [5]. For the refinement 2091 reflexions with $I > 3\sigma(I)$ were used (302 refined parameters with 6.9 reflexions per parameter). All H atoms were found by difference synthesis of electron density and included in the refinement procedure with fixed positional and thermal parameters. Only the atom $H_{(1)}$, linked to atom $N_{(1)}$, was refined isotopically. Absorption correction in the crystal was carried out by the azimuthal scanning method [6]. The pseudostatistical weighting scheme $w = 1/[0.01F_0^2 + 12.0\sigma(|F_0|)^2 + 1.00]$ was used for the refinement. The final values of the divergence factors were $R = 0.044$ and $R_w = 0.043$. The residual electron density from the difference Fourier synthesis was 0.22 and -0.16 e/Å^3. Atomic coordinates are given in Table 2.

REFERENCES

1. S. G Krivolysko, V. D. Dyachenko, and V. P. Litvinov. *Khim. Geterotsikl. Soedin.,* 1425 (1998).
2. L. Kuleshova and P. M. Zorkii. *Acta crystallogr. (B)*, **37**, 1363 (1981).
3. V. Bertolasi, P. Gilli, V. Ferretti, and G. Gilli. *Acta Crystallogr. (B)*, **51**, 1004 (1995).
4. S. Samdal, H. M. Seip, and T. Torgrimsen. *J. Mol. Struct.,* **57**, 105 (1979).
5. D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge. *Crystals*, Issue No. 10, Chemical Crystallography Laboratory, Univ. Oxford, 1996.
6. C. T. North, D. C. Phillips, F. Scott, and F. S. Mathews. *Acta Crystallographica (A)*, **24**, 351 (1968).