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SYNTHESIS AND ALKYLATION OF N-METHYLMORPHOLINIUM 4-ARYL-3,5-DICYANO-6-OXO-1,4,5,6-TETRAHYDRO-2-PYRIDINETHIOLATES. MOLECULAR AND CRYSTAL STRUCTURE OF 4,5-*trans*-3,5-DICYANO-4-(2-METHOXYPHENYL)-2-METHYLTHIO-6-OXO-1,4,5,6-TETRAHYDROPYRIDINE

S. G. Krivokolysko[1], V. D. Dyachenko[1], E. B. Rusanov[2], and V. P. Litvinov[3]

The reaction of aromatic aldehydes with cyanothioacetamide and ethyl cyanoacetate in the presence of N-methylmorpholine gives N-methylmorpholinium 4-aryl-3,5-dicyano-6-oxo-1,4,5,6-tetrahydro-2-pyridinethiolates, which are used in the synthesis of substituted 2-alkylthiotetrahydropyridines. X-ray diffraction analysis was used to study the structure of 4,5-trans-3,5-dicyano-4-(2-methoxyphenyl)-2-methylthio-6-oxo-1,4,5,6-tetrahydropyridine.

Keywords: aromatic aldehydes, substituted N-methylmorpholinium 1,4,5,6-tetrahydro-2-pyridinethiolates, cyanothioacetamide, ethyl cyanoacetate, X-ray diffraction analysis.

Cyanothioacetamide, ethyl cyanoacetate, and ethyl cyanoacetate derivatives may be used as convenient reagents in the synthesis of 4-spiro-1'-cyclopentane-, 4-spiro-1'-cyclohexane- [1, 2], and 4-alkyl-3,5-dicyano-6-oxo-1,4,5,6-tetrahydro-2-pyridinethiolates [3,4]. Furthermore, 4-aryl-3,5-dicyano-6-hydroxy-2(1H)-pyridinethiones, which are precursors of compounds with high antimicrobial activity [5], may be prepared by the reaction of arylmethylenecyanothioacetamides with ethyl cyanoacetate or of ethyl arylmethylenecyanoacetates with cyanothioacetamide [6-9] as well as by the recyclization of the corresponding 2,6-diamino-4-aryl-3,5-dicyano-4H-pyrans [6, 9]. There is no information in the literature on the synthesis of the hydrogenated analogs of these compounds [10].

We have found that the consecutive reactions of aromatic aldehydes **1a-c** with cyanothioacetamide **2** and ethyl cyanoacetate **3** in the presence of N-methylmorpholine gives substituted N-methylmorpholinium tetrahydropyridinethiolates **4a-c**. Brief heating of salts **4a** and **4b** with equimolar amounts of halides **5a-d** leads to sulfides **6a-d**.

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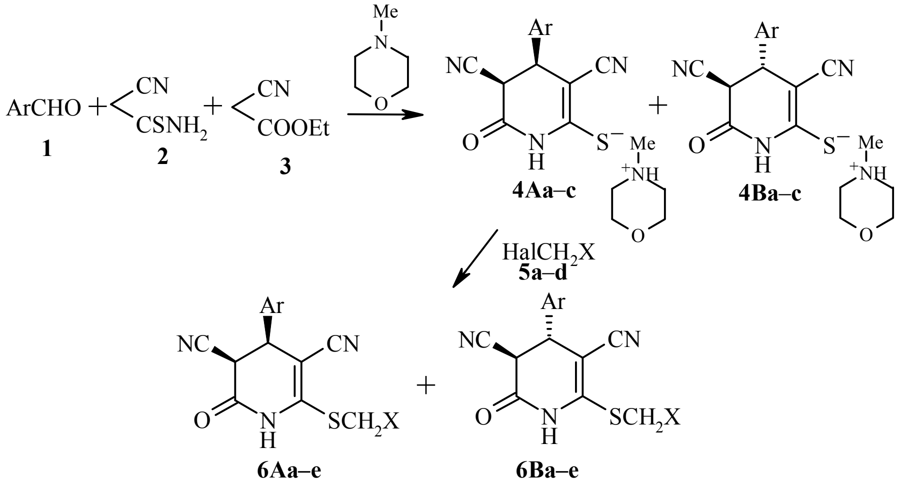
[1] Taras Shevchenko Lugansk State Pedagogical University, 348011 Lugansk, Ukraine; e-mail: kgb@gpi.lgans.ua. [2] Institute of Organic Chemistry, National Academy of Sciences of Ukraine, 253660 Kiev. [3] N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 117913 Moscow, Russia; e-mail: vpl@cacr.ioc.ac.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 525-531, April, 2001. Original article submitted May 18, 1999.

^{1}H NMR spectroscopy indicates that compounds **4** and **6** exist in DMSO solution as mixtures of *cis* (A) and *trans* (B) stereoisomers in different ratios (see Experimental). The vicinal coupling constants of protons 4-H_A and 5-H_A are 7.6-8.1 Hz in salts **4** and 6.7-8.1 Hz in sulfides **6**, while these constants for 4-H_B and 5-H_B are 10.5-15.2 Hz in **4** and **6**. This isomerization is probably a consequence of the enolization of the amide fragments of these compounds upon dissolution in DMSO as has been noted for isostructural analogs of such pyridones [11].



1, **4** **a** Ar = 2-ClC_6H_4, **b** Ar = 2-$MeOC_6H_4$, **c** Ar = Ph. **5** **a** Hal = I, X =H; **b** Hal = Cl, X = MeOOC;
c Hal = Cl, X = 4-BrC_6H_4NHCO; **d** Hal = Cl, X = NH_2CO. **6** **a** Ar = 2-ClC_6H_4, X = H; **b** Ar = 2-ClC_6H_4, X = MeOOC;
c Ar = 2-ClC_6H_4, X = 4-BrC_6H_4NHCO; **d** Ar = 2-$MeOC_6H_4$, X = H; **e** Ar = 2-$MeOC_6H_4$, X = NH_2CO

An X-ray diffraction analysis was carried out for refinement of the structures of pyridines **4** and **6** (Fig. 1 and Table 1). Heterocycle $N_{(1)}C_{(1)}C_{(2)}C_{(3)}C_{(4)}C_{(5)}$ is markedly nonplanar (the average extrusion of the atoms from the mean-square plane is 0.215 Å) and has compressed half-chair conformation [12]: $N_{(1)}$, $C_{(1)}$, $C_{(2)}$,

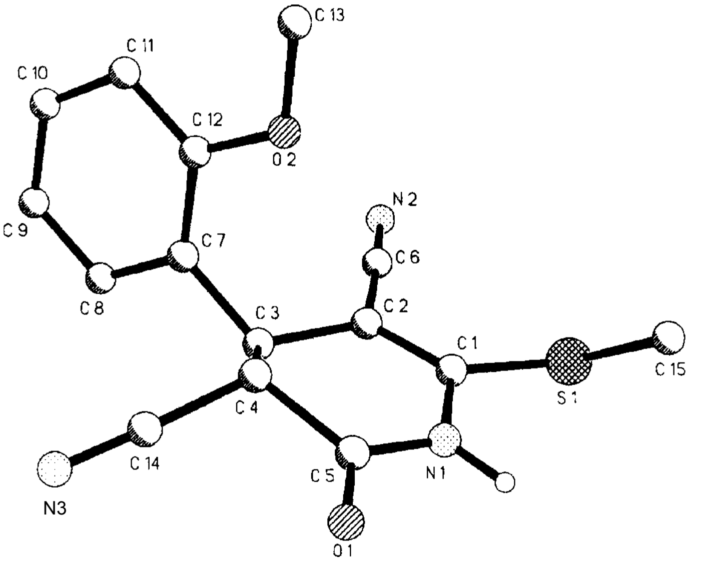


Fig. 1. General view of molecule of compound **6d** with the numbering of the atoms ($H_{(1)}$ is the only hydrogen atom shown).

TABLE 1. Bond Lengths (*d*) and Bond Angles (ω) in Molecule of Compound **6d**

Bond	*d*, Å	Angle	ω, deg.
$O_{(2)}–C_{(12)}$	1.381(4)	$C_{(1)}–S_{(1)}–C_{(15)}$	102.4(2)
$S_{(1)}–C_{(1)}$	1.737(3)	$C_{(1)}–N_{(1)}–C_{(5)}$	125.7(2)
$S_{(1)}–C_{(15)}$	1.803(4)	$S_{(1)}–C_{(1)}–N_{(1)}$	117.8(2)
$O_{(1)}–C_{(5)}$	1.221(3)	$S_{(1)}–C_{(1)}–C_{(2)}$	122.2(2)
$N_{(1)}–C_{(1)}$	1.392(4)	$N_{(1)}–C_{(1)}–C_{(2)}$	119.8(3)
$N_{(1)}–C(5)$	1.344(4)	$C_{(1)}–C_{(2)}–C_{(3)}$	122.1(3)
$N_{(2)}–C_{(6)}$	1.142(4)	$C_{(1)}–C_{(2)}–C_{(6)}$	119.9(3)
$C_{(1)}–C_{(2)}$	1.353(4)	$C_{(3)}–C_{(2)}–C_{(6)}$	117.8(2)
$C_{(2)}–C_{(3)}$	1.506(4)	$C_{(2)}–C_{(3)}–C_{(4)}$	109.7(2)
$C_{(2)}–C_{(6)}$	1.427(4)	$C_{(2)}–C_{(3)}–C_{(7)}$	115.3(2)
$C_{(3)}–C_{(4)}$	1.549(4)	$C_{(4)}–C_{(3)}–C_{(7)}$	110.2(2)
$C_{(3)}–C_{(7)}$	1.507(4)	$C_{(3)}–C_{(4)}–C_{(5)}$	115.0(2)
$C_{(4)}–C_{(5)}$	1.524(4)	$O_{(1)}–C_{(5)}–N_{(1)}$	122.9(3)
$N_{(3)}–C_{(14)}$	1.128(4)	$O_{(1)}–C_{(5)}–C_{(4)}$	120.8(3)
$C_{(4)}–C_{(14)}$	1.452(4)	$N_{(1)}–C_{(5)}–C_{(4)}$	116.2(2)
		$N_{(2)}–C_{(6)}–C_{(2)}$	176.9(3)
		$N_{(3)}–C_{(14)}–C_{(4)}$	175.7(3)
		$C_{(12)}–O_{(2)}–C_{(13)}$	118.2(3)

and $C_{(3)}$ are coplanar within ±0.022 Å, while $C_{(4)}$ and $C_{(5)}$ extrude from this plane by 0.67 and 0.27 Å, respectively. The torsion angles are 5.1° for $N_{(1)}C_{(1)}C_{(2)}C_{(3)}$, 28.7° for $C_{(1)}C_{(2)}C_{(3)}C_{(4)}$, 38.9° for $C_{(2)}C_{(3)}C_{(4)}C_{(5)}$, 28.0° for $C_{(3)}C_{(4)}C_{(5)}N_{(1)}$, 2.5° for $C_{(4)}C_{(5)}N_{(1)}C_{(1)}$, 10.1° for $C_{(5)}N_{(1)}C_{(1)}C_{(2)}$, 67.8° for $C_{(7)}C_{(3)}C_{(4)}C_{(14)}$, and 165.5° for $H_{(3)}C_{(3)}C_{(4)}H_{(4)}$.

The twist angle ψ [12], i.e., the pseudotorsion angle between bonds $C_{(1)}–C_{(2)}$ and $C_{(4)}–C_{(5)}$, which characterizes the non-planarity of the heterocycle, is only 11.2°. The benzene ring is virtually orthogonal to the mean-square plane of the heterocycle and the corresponding dihedral angle is 85.0°. The bonds at $N_{(1)}$ atom have plane-trigonal configuration and the sum of the bond angles at this atom is 360°. The unshared electron pair of this atom has virtually parallel orientation relative to the π-system of the $C_{(1)}=C_{(2)}$ and $O_{(1)}=C_{(5)}$ double bonds, which is favorable for $n(N_{(1)})$-$\pi^*(C_{(1)}=C_{(2)})$ conjugation; the corresponding torsion angles are ~9 and 2°, respectively. Not only the marked contraction of the formal single bonds $N_{(1)}–C_{(1)}$ (1.392(4) Å) and $N_{(1)}–C_{(5)}$ (1.344(4) Å) (the standard range for $N_{(sp^2)}–C_{(sp^2)}$ bonds is 1.43-1.45 Å [13, 14]) but also the significant compression of the $N_{(1)}C_{(1)}C_{(2)}C_{(3)}C_{(4)}C_{(5)}$ heterocycle relative to ordinary cyclohexene systems [12] are probably a consequence of this conjugation. The $S_{(1)}–C_{(1)}$ (1.737(3) Å) and $S_{(1)}–C_{(15)}$ (1.803(4) Å) bond lengths and $C_{(1)}–S_{(1)}–C_{(15)}$ bond angle (102.4(2)°) are similar to the corresponding values found for Ph–S–Me ($S–C_{(sp^2)}$ 1.749(4) Å; $S–C_{(sp^3)}$ 1.803(4) Å; CSC 105.6(7)°) [4] and $H_2C=CH–S–Me$ ($S–C_{(sp^2)}$ 1.759(18) Å; $S–C_{(sp^3)}$ 1.795(8) Å; CSC 102.1(5)°) molecules [16].

The molecules in the crystal of compound **6d** are bound in centrosymmetric dimers by means of medium-strength $N_{(1)}–H_{(1)}\cdots O_{(1)}$ hydrogen bonds (Fig. 2). The major geometric parameters of these hydrogen bonds are $N_{(1)}–H_{(1)}$ 0.90(4) Å; $N_{(1)}\cdots O_{(1)}$ 2.915(4) Å; $O_{(1)}\cdots H_{(1)}$ 2.03(4) Å, $N_{(1)}H_{(1)}\cdots O_{(1)}$ 167.7(2.4)° (the mean N···O distance for N–H···O hydrogen bonds is 2.89 Å) [17]).

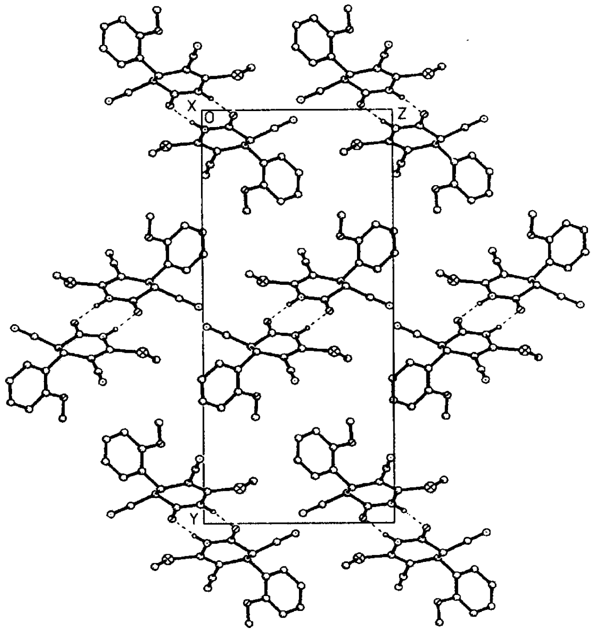


Fig. 2. Projection *bc* of the crystal structure of compound **6d**
(the intermolecular hydrogen bonds $N_{(1)}H_{(1)}\cdots O_{(1)}$ are shown by dashed lines).

TABLE 2. Atomic Coordinates and Equivalent Isotropic Temperature Parameters in the Structure of Compound **6d**

Atom	x	y	z	U_{eq}
1	2	3	4	5
$S_{(1)}$	0.46668(15)	0.08531(4)	-0.18737(8)	0.0675
$O_{(1)}$	0.9924(3)	0.01258(9)	0.1651(2)	0.0571
$O_{(2)}$	0.6198(4)	0.19318(9)	0.2230(3)	0.0729
$N_{(1)}$	0.7318(4)	0.0464(1)	0.0163(3)	0.0477
$N_{(2)}$	0.0717(5)	0.15632(12)	0.0195(3)	0.0723
$N_{(3)}$	0.7660(5)	0.02433(14)	0.4796(3)	0.0759
$C_{(1)}$	0.5446(4)	0.07807(11)	-0.0186(3)	0.0466
$C_{(2)}$	0.4218(4)	0.09881(11)	0.0780(3)	0.0454
$C_{(3)}$	0.4697(4)	0.08501(12)	0.2233(3)	0.0447
$C_{(4)}$	0.7197(5)	0.07262(12)	0.2502(3)	0.0462
$C_{(5)}$	0.8252(4)	0.04010(11)	0.1405(3)	0.0445
$C_{(6)}$	0.2292(5)	0.13107(12)	0.0424(3)	0.0523
$C_{(7)}$	0.3959(5)	0.12794(12)	0.3204(3)	0.0491
$C_{(8)}$	0.2499(5)	0.11324(16)	0.4155(3)	0.0602
$C_{(9)}$	0.1818(7)	0.1519(2)	0.5070(4)	0.0815
$C_{(10)}$	0.2586(8)	0.2048(2)	0.5022(5)	0.0933
$C_{(11)}$	0.4056(7)	0.22127(16)	0.4091(4)	0.0776
$C_{(12)}$	0.4729(5)	0.18200(12)	0.3194(3)	0.0582
$C_{(13)}$	0.7366(11)	0.2441(2)	0.2305(7)	0.0989
$C_{(14)}$	0.7528(5)	0.04479(13)	0.3783(3)	0.0520
$C_{(15)}$	0.7250(8)	0.10278(19)	-0.2574(5)	0.0729
$H_{(1)}$	0.800(6)	0.0289(15)	-0.049(4)	0.085(12)
$H_{(3)}$	0.396(5)	0.0491(13)	0.241(3)	0.062(9)

TABLE 2 (continued)

1	2	3	4	5
$H_{(4)}$	0.804(5)	0.1103(13)	0.258(3)	0.060(9)
$H_{(8)}$	0.194(6)	0.0735(15)	0.416(3)	0.075(11)
$H_{(9)}$	0.088(7)	0.1390(17)	0.571(4)	0.101(14)
$H_{(10)}$	0.209(7)	0.2347(18)	0.567(5)	0.110(14)
$H_{(11)}$	0.479(7)	0.2597(18)	0.411(4)	0.101(13)
$H_{(131)}$	0.630(8)	0.2720(19)	0.225(5)	0.106(17)
$H_{(132)}$	0.826(8)	0.2470(19)	0.324(5)	0.110(17)
$H_{(133)}$	0.845(8)	0.2463(19)	0.161(5)	0.123(17)
$H_{(151)}$	0.802(6)	0.1332(17)	-0.194(4)	0.093(13)
$H_{(152)}$	0.816(7)	0.0716(19)	-0.263(4)	0.103(14)
$H_{(153)}$	0.671(7)	0.1156(18)	-0.344(5)	0.105(15)

Thus, the aryl substituent and corresponding cyano group in compounds **4** and **6** in the crystal lie exclusively in a *trans*-diequatorial arrangement, while protons 4-H and 5-H lie in a *trans*-diaxial arrangement. In DMSO solution, a partial isomerization of *trans*-pyridones **4** and **6** to the *cis* isomers through enolization of the amide fragment takes place.

EXPERIMENTAL

The ^{1}H NMR spectra were taken for compound **4a** on a Bruker AM-300 spectrometer, for compounds **6a-e** on a Bruker WM-250 spectrometer, for compounds **4b,c** on a Bruker 100-SY spectrometer in DMSO-d_6 with TMS as the internal standard. The IR spectra were recorded on an IKS-29 spectrophotometer for suspensions in vaseline oil. The course of the reactions and purity of the reagents were monitored by thin-layer chromatography on Silufol UV-254 plates using 3:5 acetone–hexane as the eluent.

N-Methylmorpholinium 4-Aryl-3,5-dicyano-6-oxo-1,4,5,6-tetrahydro-2-pyridinethiolates (4a-c). Sample of ethyl cyanoacetate **3** (2.13 ml, 20 mmol) and N-methylmorpholine (2.53 ml, 25 mmol) was added to a stirred mixture of aldehyde **1a-c** (20 mmol), cyanothioacetamide **2** (2.00 g, 20 mmol), and three drops of N-methylmorpholine in ethanol (25 ml) at 20°C. After 3 h, the precipitate of salt **4** was filtered off and washed with acetone.

Salt 4a was obtained in 73% yield; mp 210-212°C. IR spectrum, ν, cm^{-1}: 3300-3450 (NH), 2178, 2210 sh, 2250 (CN), 1680-1712 (CO). ^{1}H NMR spectrum (the integral intensity of the signals in the spectra of **4a-c** and **6a-e** corresponds to the proposed formulas and stereoisomer ratio) (A:B = 1:1), δ, ppm, J (Hz): 2.78 (s, NMe); 3.16 (br. s, CH_2NCH_2); 3.77 (br. s, CH_2OCH_2); 4.42 (m, 4-H_A, 4-H_B, 5-H_B); 4.87 (d, ^3J = 7.7, 5-H_A); 7.17-7.61 (m, Ar); 9.57 (br. s, NH), 9.61 (br. s, NH_A). Found, %: C 55.40; H 4.71; Cl 9.18; N 14.54; S 8.07. $C_{18}H_{19}ClN_4O_2S$. Calculated, %: C 55.31; H 4.90; Cl 9.07; N 14.33; S 8.20.

Salt 4b was obtained in 68% yield; mp 181-183°C. IR spectrum, ν, cm^{-1}: 3320, 3435 (NH), 2178, 2260 (CN), 1700 (CO). ^{1}H NMR spectrum (A:B = 1:1), δ, ppm, J (Hz): 2.75 (s, NMe); 3.12 (t, CH_2NCH_2); 3.74 (s, OMe_B); 3.78 (CH_2OCH_2); 3.82 (s, OMe_A); 4.15 (d, ^3J = 7.6, 4-H_A); 4.18 (d, ^3J = 15.2, 4-H_B); 4.42 (d, ^3J = 15.2, 5-H_B); 4.67 (d, ^3J = 7.6, 5-H_A); 6.80-7.40 (m, Ar); 9.20 (br. s, NH_B); 9.42 (br. s, NH_A). Found, %: C 59.25; H 5.91; N 14.63; S 8.48. $C_{19}H_{22}N_4O_3S$. Calculated, %: C 59.05; H 5.74; N 14.50, S 8.30.

Salt 4c was obtained in 70% yield; mp 133-135°C. IR spectrum, ν, cm^{-1}: 3140, 3250, 3350 (NH), 2170, 2260 (CN), 1725 (CO). ^{1}H NMR spectrum (A:B = 1:1), δ, ppm, J (Hz): 2.74 (s, NMe); 3.10 (t, CH_2NCH_2); 3.76 (m, CH_2OCH_2 and 4-H_A); 3.96 (d, ^3J = 10.5, 4-H_B); 4.36 (d, ^3J = 10.5, 4-H_B); 4.77 (d, ^3J = 10.5, 4-H_B); 7.05-7.61 (m, Ar); 9.53 (br. s, NH). Found, %: C 60.81; H 5.47; N 15.84; S 9.13. $C_{18}H_{20}N_4O_2S$. Calculated, %: C 60.65; H 5.66; N 15.72; S 9.00.

4-Aryl-3,5-dicyano-2-X-methylthio-6-oxo-1,4,5,6-tetrahydropyridines (6a-e). Mixture of salt **4a,b** (10 mmol) and halide **5a-d** (10 mmol) in 80% aq. ethanol (30 ml) was heated until the starting reagents dissolved and then filtered. The filtrate was maintained at room temperature for 12 h. The precipitate formed was filtered off and washed with ethanol and hexane. The products obtained did not require further purification.

Sulfide 6a was obtained in 77% yield; mp 208-210°C. IR spectrum, ν, cm^{-1}: 3360-3450, 3510 (NH), 2210, 2250 (CN), 1710 (CO). ^{1}H NMR spectrum (A:B = 1:2), δ, ppm, *J* (Hz): 2.57 (s, SMe); 4.73 (d, ^3J = 7.8, 4-H$_A$); 4.87 (d, ^3J = 14.3, 4-H$_B$); 4.98 (d, ^3J = 14.3, 4-H$_B$); 5.10 (d, ^3J = 7.8, 4-H$_A$); 7.15-7.62 (m, Ar); 11.12 (br. s, NH$_B$); 11.16 (br. s, NH$_A$). Found, %: C 55.48; H 3.51; Cl 11.52; N 13.61; S 10.64. $C_{14}H_{10}ClN_3OS$. Calculated, %: C 55.36; H 3.32; Cl 11.67; N 13.83; S 10.56.

Sulfide 6b was obtained in 75% yield; mp 155-157°C. IR spectrum, ν, cm^{-1}: 3430 (NH), 2202, 2260 (CN), 1725 (CO). ^{1}H NMR spectrum (A:B = 1:2), δ, ppm, *J* (Hz): 3.72 and 3.75 (two s, OMe); 3.92 and 4.05 (two d, ^2J = 17, SCH$_2$); 4.88 (m, 4-H$_A$, 4-H$_B$, and 5-H$_B$); 5.04 (d, ^3J = 7.9, 5-H$_A$); 7.22-7.60 (m, Ar); 11.17 (br. s, NH$_B$); 11.24 (br. s, NH$_A$). Found, %: C 53.31; H 3.12; Cl 9.97; N 11.79; S 8.64. $C_{16}H_{12}ClN_3O_3S$. Calculated, %: C 53.12; H 3.34; Cl 9.80; N 11.61; S 8.86.

Sulfide 6c was obtained in 78% yield; mp 152-155°C. IR spectrum, ν, cm^{-1}: 3430 (NH), 2210, 2263 (CN), 1720 (CO). ^{1}H NMR spectrum (A:B = 1:2), δ, ppm, *J* (Hz): 3.98 (m, SCH$_2$); 4.82 (d, ^3J = 7.8, 4-H$_A$); 4.85 (d, ^3J = 14.5, 4-H$_B$); 4.94 (d, ^3J = 14.5, 4-H$_B$); 5.07 (d, ^3J = 7.8, 5-H$_A$); 7.25-7.61 (m, 2Ar); 10.43 (br. s, CONH); 11.31 (br. s, NH$_B$); 11.38 (br. s, NH$_A$). Found, %: C 50.10; H 2.98; Cl 7.28; N 11.05; S 6.51. $C_{21}H_{14}BrClN_4O_2S$. Calculated, %: C 50.27; H 2.81; Cl 7.07; N 11.17; S 6.39.

Sulfide 6d was obtained in 68% yield; mp 178-180°C. IR spectrum, ν, cm^{-1}: 3390, 3450, 3390 (NH), 2212, 2270 (CN), 1690 (CO). ^{1}H NMR spectrum (A:B = 5:6), δ, ppm, *J* (Hz): 2.54 (s, SMe); 3.78 (s, OMe$_B$); 3.88 (s, OMe$_A$); 4.40 (d, ^3J = 8.1, 4-H$_A$); 4.54 (d, ^3J = 13.1, 4-H$_B$); 4.73 (d, ^3J = 13.1, 5-H$_B$); 4.92 (d, ^3J = 8.1, 5-H$_A$); 6.94-7.42 (m, Ar); 10.85 (br. s, NH$_B$); 10.98 (br. s, NH$_A$). Found, %: C 60.03; H 4.52; N 14.18; S 10.92. $C_{15}H_{13}N_3O_2S$. Calculated, %: C 60.19; H 4.38; N 14.04; S 10.71.

Sulfide 6e was obtained in 72% yield; mp 182-184°C. IR spectrum, ν, cm^{-1}: 3330-3400 (NH), 2212, 2260 (CN), 1710 (CO). ^{1}H NMR spectrum (A:B = 11:12), δ, ppm, *J* (Hz): 3.70 (m, SCH$_2$); 3.78 (s, OMe$_B$); 3.88 (s, OMe$_A$); 4.44 (d, ^3J = 8.1, 4-H$_A$); 4.54 (d, ^3J = 13.9, 4-H$_B$); 4.68 (d, ^3J = 31.9, 5-H$_B$); 4.88 (d, ^3J = 8.1, 5-H$_A$); 6.92-7.42 (m, Ar); 7.51 (br. s, CONH$_2$); 7.85 (br. s, CONH$_2$); 11.62 (br. s, NH). Found, %: C 56.32; H 4.25; N 16.13; S 9.50. $C_{16}J_{14}N_4O_3S$. Calculated, %: C 56.13; H 4.12; N 16.36; S 9.37.

X-ray Diffraction Analysis of Compound 6d was carried out on a 0.09×0.22×0.38-mm crystal at 18°C on an Enraf-Nonius CAD-4 automatic four-circle diffractometer using CuKα radiation, scan rate ratio $\omega/2\theta = 1.2$, $\theta_{max} = 70°$, sphere segment $0 \leq h \leq 8$, $0 \leq k \leq 30$, $-13 \leq l \leq 13$) for a total of 3126 reflections, of which 2768 were symmetrically independent, $R = 0.025$. The unit cell parameters of the monoclinic crystals of compound **6d** were as follows: $a = 6.050(3)$, $b = 24.093(9)$, $c = 20.033(3)$ Å; $\beta = 93.61(3)°$; $V = 1459.4$ Å^3; M = 299.35; $Z = 4$; $d_{calc} = 1.36$ g/cm^3; $\mu = 19.96$ cm^{-1}; space group $P2_1/c$. The structure was solved by the direct method and refined anisotropically by the least-squares method in the full-matrix approximation using the CRYSTALS program package [18]. In the refinement, we used 1724 reflections with $I > 3\sigma(I)$; 242 refined parameters, the number of reflections per parameter was 7.1. All the hydrogen atoms were found from the differential map and refined isotropically. Absorption in the crystal was taken into account by azimuthal scanning [19]. The Chebyshev weighting scheme [20] was used with parameters 1.55, 0.43, 1.25; 0.05, and 0.37. The final values of the divergence factors $R = 0.046$, $R_w = 0.049$. GoF = 1.022. The residual electronic density from the Fourier differential map was 0.21 and -0.30 e/Å^3. The atomic coordinates are given in Table 1.

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