A new stereoselective synthesis of 2-amino-4,5-dihydrothiophene-3-carbonitrile derivatives

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A new stereoselective method for the synthesis of *trans*-isomers of 2-amino-4-aryl-5-benzoyl-4,5-dihydrothiophene-3-carbonitriles was proposed. The method involves base-catalyzed reactions of phenacyl thiocyanate with 3-(het)aryl-2-cyanoprop-2-enethioamides. (4*R*,5*S*/4*S*,5*R*)-2-Amino-5-benzoyl-4-(2-chlorophenyl)-4,5-dihydrothiophene-3-carbonitrile was structurally characterized by X-ray diffraction analysis.

Key words: phenacyl thiocyanate, 3-(het)aryl-2-cyanoprop-2-enethioamides, cyanothioacetamide, the Michael reaction, cyclocondensation, X-ray diffraction analysis, *trans*-2-amino-4-(het)aryl-5-benzoyl-4,5-dihydrothiophene-3-carbonitriles.

2-Aminothiophene derivatives most commonly synthesized by the Gewald reaction[1—3] exhibit a broad spectrum of useful properties and are convenient synthons for the synthesis of various heterocyclic compounds.[4—6] Partially hydrogenated 2-aminothiophene derivatives (*e.g.*, dihydrothiophenes) are much less studied. Nevertheless, 2-amino-4,5-dihydrothiophenes are of interest as starting materials for the synthesis of not easily accessible partially hydrogenated thieno[2,3-*b*]pyridines[7] and -pyrimidines.[8] Earlier, it has been shown that *trans*-4,5-disubstituted 2-amino-4,5-dihydrothiophene-3-carbonitriles can be obtained by stereoselective tandem Michael addition—1,5-cycloelimination (Ad_N—$E_{1,5}$) between 3-(het)aryl-2-cyanoprop-2-enethioamides **1** and stabilized pyridinium[9—14] or sulfonium ylides.[14—16] Known modifications of this synthesis are based on three-component cyclocondensation of cyanothioacetamide, an aldehyde, and an appropriate ylide[9—13] and recyclization of 5-pyridinio-1,4,5,6-tetrahydropyridine-2-thiolate derivatives.[11] In the case of pyridinium ylides, the regiodirectivity of the reaction is temperature-dependent;[11,17] in the case of sulfonium ylides, the yields of the target dihydrothiophenes are usually low and the reactions are accompanied by the formation of by-products, including dimethyl sulfide,[14—16] which presents some preparative difficulties. 2-Amino-4,5-dihydrothiophene derivatives can also be obtained in moderate yields by base-catalyzed cyclocondensation of chalcone and ethyl cyanoacetate (or their adduct) with elemental sulfur.[18] All this creates prerequisites for further investigations of selective and preparatively convenient methods for the synthesis of dihydrothiophene derivatives. The stereochemistry of the aforementioned *trans*-4,5-disubstituted dihydrothiophenes is quite interesting. Mutual *trans*-arrangement of the substituents in positions 4 and 5 is undoubted and confirmed by both X-ray diffraction[14,15] and spectroscopic data (the corresponding coupling constant is $^3J_{C(4)H,C(5)H} = 0.8$—5.2 Hz).[11—16]

Proceeding further in our investigations of the chemistry of cyanothioacetamide,[17,19] we studied reactions of 3-(het)aryl-2-cyanoprop-2-enethioamides **1** with phenacyl thiocyanate (**2**).[20] Earlier, this promising reagent has been successfully used for the synthesis of functionalized thiazole[21—26] and pyridine derivatives.[27] It has been found that thioamides **1** easily react with thiocyanate **2** in the presence of tertiary amines (triethylamine or *N*-methylmorpholine) to give 2-amino-4,5-dihydrothiophene-3-carbonitriles **3** (Scheme 1, method *A*). The catalyst nature has no appreciable effect on the yields of the target dihydrothiophenes (52—54%); however, the

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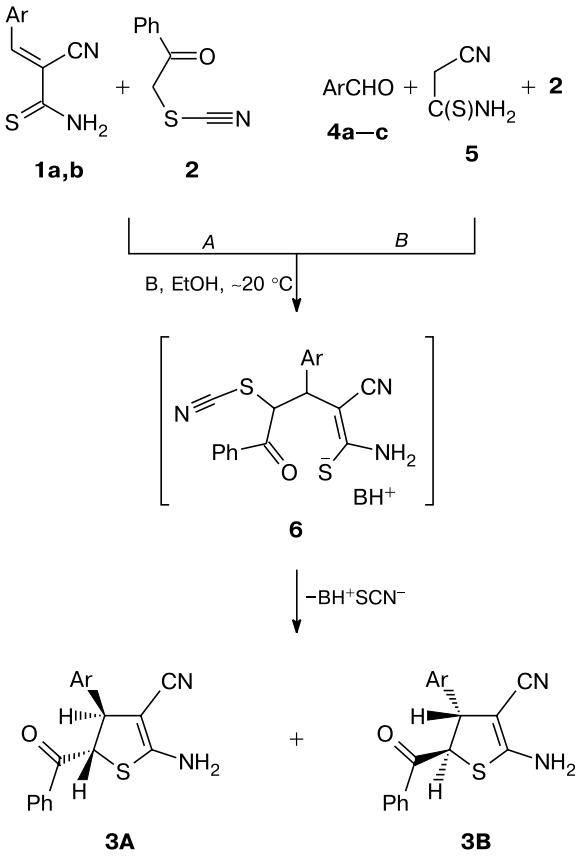
Et_3N-catalyzed reactions proceed much more rapidly. Compounds **3a—c** are obtained in comparable yields (37—50%) *via* multicomponent cyclocondensation of appropriate aldehydes **4a—c**, cyanothioacetamide (**5**), and thiocyanate **2**; in this case, unsaturated thioamides **1** are formed *in situ* (see Scheme 1, method *B*). The reaction is stereoselective but not stereospecific, giving only two configurational isomers **3A** and **3B** with the 4,5-*trans*-arrangement of the substituents out of four possible diastereomeric products.

Scheme 1



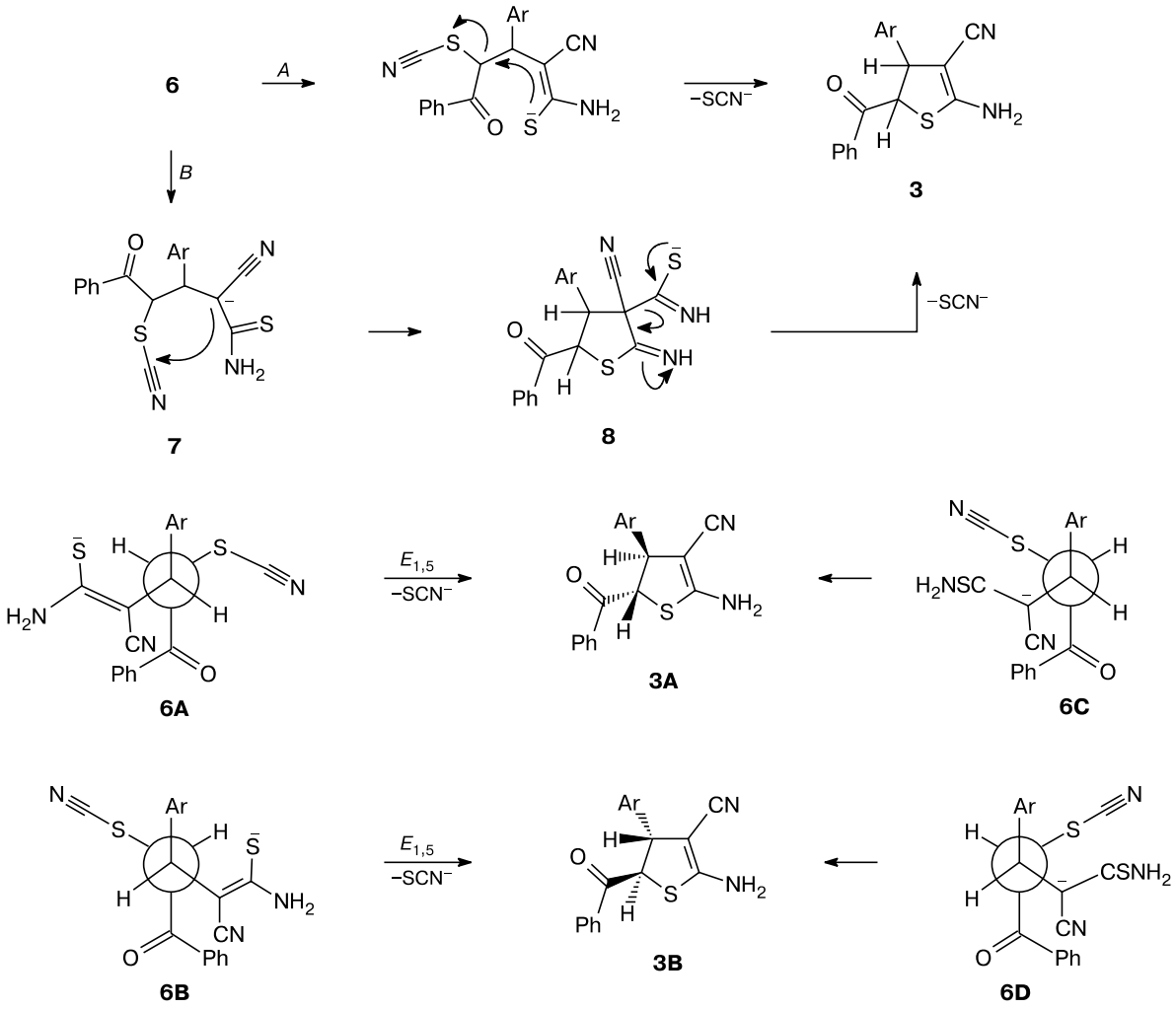
1, 3, 4: Ar = 2-ClC_6H_4 (**a**), 2-furyl (**b**), Ph (**c**);
B = *N*-methylmorpholine, Et_3N

Presumably, the first step of the reaction is the formation of the Michael adduct **6**. It should be noted that (*E*)-2-cyano-3-[4-(dimethylamino)phenyl]prop-2-enethioamide (**1**, Ar = 4-$Me_2NC_6H_4$), which is inert to nucleophiles in the Michael reaction because of the strong donating effect of the Me_2N group, does not enter into this reaction. Undoubtedly, the key step that determines the stereochemistry of products is the formation of adduct **6**. It is obvious that bulky benzoyl and (het)aryl substituents will be *trans* to each other, which is sterically favorable. Thus, adducts with the *anti*-periplanar arrangement of (het)aryl and benzoyl fragments are most stable. Two pairs of diastereomeric adducts (**6A**, **6B** and **6C**, **6D**) meet this requirement (Scheme 2). Apparently, when the formation of the diastereomeric pair **6A** and **6B** is preferred, the reaction occurs as intramolecular nucleophilic substitution with retention of the adduct configuration. Elimination of the thiocyanate ion gives enantiomers **3A** and **3B** (see Scheme 2, pathway *A*). The possibility of nucleophilic displacement of the thiocyanate seems to be rather unusual, although a number of reactions of this type have been described earlier (*e.g.*, see Refs 28—30). The presence of the thiocyanate ion in the reaction mixture was unambiguously confirmed by an analytical test: several seconds after the addition of a base to a mixture of compounds **1** and **2**, a sample was withdrawn from the mixture and showed a positive reaction toward a solution of $FeCl_3$. Neither the starting reagents, nor products, nor catalysts form blood-red complexes with iron(III). However, an alternative pathway cannot be completely excluded: intramolecular cyclization of structure **7** (carbanionic tautomer of the Michael adduct **6**) is followed by dethiocarbamoylation of intermediate tetrahydrothiophene **8** (see Scheme 2, pathway *B*). In this case, isomeric dihydrothiophenes **3A** and **3B** are formed from adducts **6C** and **6D**, respectively, with the *syn*-clinal arrangement of the thiocyanato and α-cyano-α-thiocarbamoylmethylide groups. Evidence for the possible cyclization **7** → **8** is provided by numerous examples of reactions of active methylene compounds with organic thiocyanates,[23—27] occurring through an attack of the carbanionic intermediate on the electrophilic C atom of the N≡C—S group. Thus, the question of the mechanism of the described transformation remains open.

The structures of dihydrothiophenes **3** were confirmed by elemental analysis and spectroscopic data. For instance, the IR spectra of the reaction products contain absorption bands due to amino, cyano (ν = 2200—2195 cm^{-1}), and carbonyl groups (ν = 1675—1670 cm^{-1}) and show no bands at 2170—2130 cm^{-1} (S—C≡N). The ^1H NMR spectra of dihydrothiophenes **3** exhibit signals at δ 4.80—4.87 and 5.18—5.20 (C(4) and C(5)H, respectively) as multiplets or broadened doublets ($^3J_{C(4)H,C(5)H}$ = 2.9—3.2 Hz) resulting from overlap of the signals for the protons in isomeric structures **3A** and **3B**. Another distinctive feature of the spectra of compounds **3** is the presence of a broadened singlet for the NH_2 protons (δ 7.01—6.93).

To elucidate the stereochemical aspects of the reaction and the spatial structures of dihydrothiophenes **3**, we examined compound **3a** by X-ray diffraction analysis. We found that the crystal of compound **3a** consists of two crystallographically independent molecules **A** and **B** with very close geometrical parameters. The general view of structure **3aA** with selected geometrical parameters is shown in Fig. 1. The central five-membered S(1)C(1)—C(4) ring is nonplanar (deviations of the atoms

Scheme 2



from the root-mean-square plane are 0.138 Å) and exists in the half-chair conformation: in both molecules, the S(1)C(1)—C(3) atoms are coplanar to within 0.011 Å, and the fragment S(1)—C(3)—C(4) makes with this plane a dihedral angle of 21.0°. For steric hindrances, the benzene rings C(6)—C(11) and C(13)—C(18) are rotated relative to the five-membered ring through 74.5° and 72.5° in molecule **A** and through 66.5° and 74.5° in molecule **B**, respectively. In the crystal, the five-membered rings of molecules **A** and **B** make a dihedral angle of 66.5°. The N(1) atom has a trigonal planar bond configuration (the sum of the bond angles at this atom is 360° to within the experimental error). The amino $N(1)H_2$ group is virtually coplanar with the five-membered ring (the corresponding dihedral angle in molecules **A** and **B** does not exceed 2.3°). This conformation is very favorable for conjugation of the lone electron pair of the N(1) atom with the π-system of the double C(1)=C(2) bond. Indeed, the N(1)—C(1) bond (1.342(4) Å in molecule **A** and 1.339(4) Å in molecule **B**) is substantially shorter than the single $N(sp^2)$—$C(sp^2)$ bond with characteristic values of 1.43—1.45 Å.[31,32] In the crystal, molecules **3a** are united into infinite chains through the hydrogen bonds:[33] N(1B)—H···O(1A) (N—H 0.89(4) Å, N···O 2.858(4) Å, H···O 2.04(4) Å; angle N—H—O 152(3)°) and N(1A)—H···O(1B) (N—H 0.86(4) Å, N···O 2.856(4) Å, H···O 2.08(4) Å; angle N—H—O 149(3)°) (Fig. 2).

To sum up, base-catalyzed reactions of phenacyl thiocyanate with 3-(het)aryl-2-cyanoprop-2-enethioamides are a novel and accessible stereoselective route to 4-(het)aryl-5-benzoyl-4,5-dihydrothiophene-3-carbonitrile derivatives obtained as a pair of *trans*-diastereomers.

Experimental

^{1}H NMR spectra were recorded on a Varian Gemini 200 instrument (200 MHz) in DMSO-d_6 with Me_4Si as the internal standard. IR spectra were recorded on an IKS-29 spectropho-

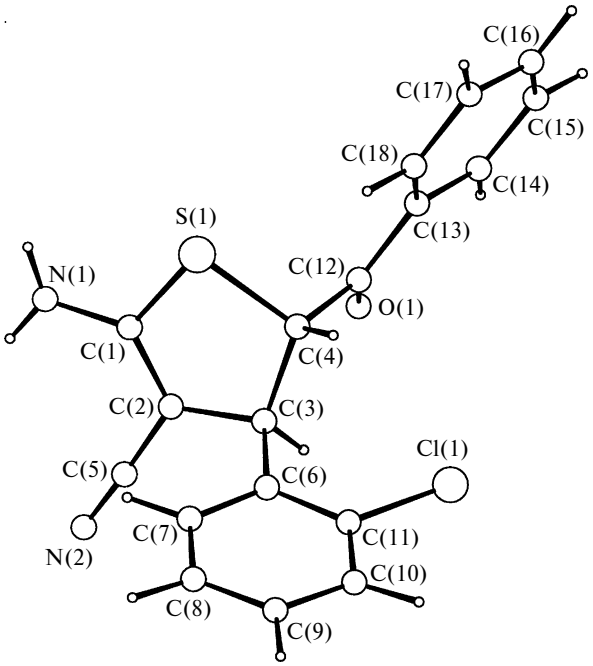


Fig. 1. General view of structure **3aA**. Selected bond lengths: S(1)—C(1) 1.759(3) Å, S(1)—C(4) 1.759(3) Å, C(1)—C(2) 1.348(4) Å, C(2)—C(3) 1.509(4) Å, and C(3)—C(4) 1.557(4) Å; and bond angles: C(1)—S(1)—C(4) 91.9(2)°, S(1)—C(1)—C(2) 113.6(2)°, C(1)—C(2)—C(3) 116.7(3)°, C(2)—C(3)—C(4) 105.9(2)°, and S(1)—C(4)—C(3) 107.6(2)°.

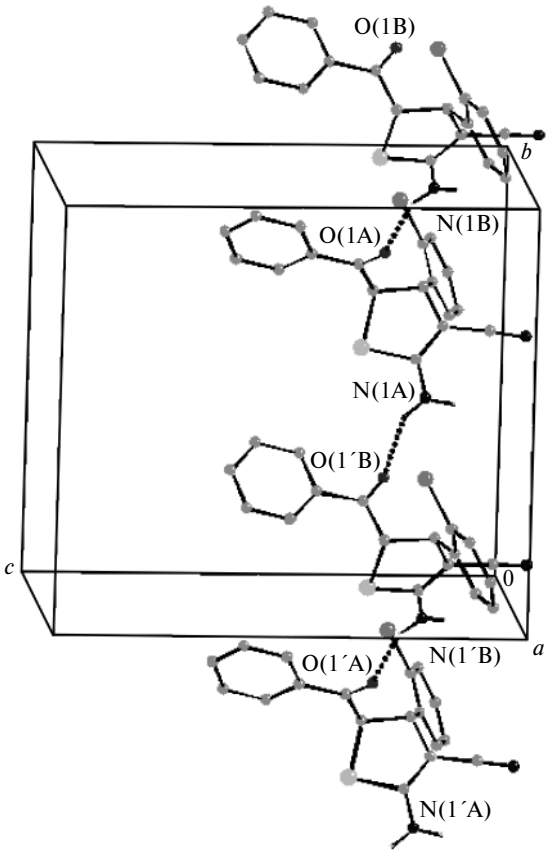


Fig. 2. Crystal packing of compound **3a**. Intermolecular N—H···O hydrogen bonds are indicated with dashed lines; primed atoms are obtained from the initial atoms *via* the symmetry operation code (x, $y-1$, z).

tometer (in Nujol). Elemental analysis was carried out on a Perkin—Elmer C,H,N-Analyser instrument. The course of the reaction was monitored and the purity of the compounds obtained was checked by TLC on Silufol UV 254 plates in acetone—heptane (1 : 1). Spots were visualized in the iodine vapor or under UV light. Melting points were determined on a Kofler hot stage and are given uncorrected.

3-(Het)aryl-2-cyanoprop-2-enethioamides **1** and cyanothioacetamide (**5**) were prepared according to known procedures.[34]

Phenacyl thiocyanate (2) was prepared according to a modified procedure.[22] Acetone (70 mL) was added to a mixture of phenacyl bromide (23.5 g, 0.118 mol) and potassium thiocyanate (12.6 g, 0.13 mol). The mixture was refluxed with vigorous stirring for 1 h, concentrated to half the initial volume, and cooled to ~20 °C. Water (50 mL) was added. The precipitate that formed was filtered off, washed with water and twice with cooled 50% EtOH. The yield of compound **2** was 20.6 g (98.5%), colorless crystals, m.p. 74—75 °C (*cf.* Ref. 22: m.p. 75—77 °C).

2-Amino-4-(het)aryl-5-benzoyl-4,5-dihydrothiophene-3-carbonitriles 3 (general procedure). ***Method A.*** Triethylamine (0.94 mL, 6.75 mmol) or *N*-methylmorpholine (0.75 mL, 6.75 mmol) was added to a stirred suspension of unsaturated thioamide **1a,b** (4.5 mmol) and thiocyanate **2** (0.8 g, 4.5 mmol) in EtOH (15 mL). The reaction mixture was stirred to homogenization and left at ~20 °C for 24 h (in the case of **3b**, for 1.5 h). The precipitate of dihydrothiophene **3a,b** was filtered off and recrystallized from an appropriate solvent.

Method B. An appropriate aldehyde **4a—c** (5 mmol) and a drop of a tertiary amine (Et_3N or *N*-methylmorpholine) were successively added to a stirred suspension of cyanothioacetamide (**5**) (0.5 g, 5 mmol) in EtOH (10 mL). After 0.5-h stirring, thiocyanate **2** (0.89 g) and Et_3N (1.04 mL, 7.5 mmol) or *N*-methylmorpholine (0.83 mL, 7.5 mmol) were added. The reaction mixture was stirred to complete homogenization and kept at ~20 °C for 24 h (in the case of **3b**, for 1.5 h). The precipitate of dihydrothiophene **3a—c** was filtered off and recrystallized from an appropriate solvent.

(4*R*,5*S*/4*S*,5*R*)-2-Amino-5-benzoyl-4-(2-chlorophenyl)-4,5-dihydrothiophene-3-carbonitrile (3a). Yield 52% (method *A*) and 49% (*B*), bright yellow crystals, m.p. 243—245 °C (decomp.) (Me_2CO—EtOH (1 : 1)). Found (%): C, 63.01; H, 3.88; N, 8.18. $C_{18}H_{13}ClN_2OS$. Calculated (%): C, 63.43; H, 3.84; N, 8.22. IR, ν/cm^{-1}: 3415, 3310, 3200 (NH_2); 2195 (C≡N); 1675 (C=O); 1645 ($\delta(NH_2)$). ^1H NMR, δ: 4.80 (br.d, 1 H, C(4)H, ^3J = 2.9 Hz); 5.18 (m, 1 H, C(5)H); 7.01 (br.s, 2 H, NH_2); 7.21—7.57 (m, 7 H, 4-$ClC_6\underline{H}_4$, $C(3)H_{Ph}$—$C(5)H_{Ph}$); 7.85 (br.d, 2 H, $C(2)H_{Ph}$, $C(6)H_{Ph}$, ^3J = 7.1 Hz).

(4*R*,5*S*/4*S*,5*R*)-2-Amino-5-benzoyl-4-(2-furyl)-4,5-dihydrothiophene-3-carbonitrile (3b). Yield 54% (method *A*) and 50% (*B*), light brown crystals, m.p. 208—210 °C (EtOH—dioxane (1 : 1)). Found (%): C, 64.64; H, 4.10; N, 9.53. $C_{16}H_{12}N_2O_2S$. Calculated (%): C, 64.85; H, 4.08; N, 9.45. IR, ν/cm^{-1}: 3405, 3290, 3170 (NH_2); 2200 (C≡N); 1670 (C=O); 1640 ($\delta(NH_2)$). ^1H NMR, δ: 4.87 (br.d, 1 H, C(4)H, ^3J = 3.0 Hz); 5.20 (br.d, 1 H, C(5)H, ^3J = 3.0 Hz); 6.29 and 6.35

(both m, 1 H each, C(3)H_{fur}, C(4)H_{fur} (hereafter, fur stands for furyl)); 6.98 (br.s, 2 H, NH_2); 7.45—7.65 (m, 4 H, C(5)H_{fur}, C(3)H_{Ph}—C(5)H_{Ph}); 7.94 (br.d, 2 H, C(2)H_{Ph}, C(6)H_{Ph}, ^3J = 7.1 Hz).

(4*S*,5*S*/4*R*,5*R*)-2-Amino-5-benzoyl-4-phenyl-4,5-dihydrothiophene-3-carbonitrile (3c). Yield 37% (method *B*), yellow crystals, m.p. 207—209 °C (Me_2CO—EtOH (1 : 1)) (*cf.* Ref. 15: for the (4*R*,5*R*)-isomer, m.p. 206—207 °C (from Me_2CO)). Found (%): C, 70.29; H, 4.65; N, 9.11. $C_{21}H_{18}N_4O_2S$. Calculated (%): C, 70.56; H, 4.61; N, 9.14. IR, ν/cm^{-1}: 3400, 3285, 3175 (NH_2); 2200 (C≡N); 1675 (C=O); 1640 (δ(NH_2)). ^{1}H NMR, δ: 4.84 (br.d, 1 H, C(4)H, ^3J = 3.2 Hz); 5.18 (m, 1 H, C(5)H); 6.93 (br.s, 2 H, NH_2); 7.26—7.59 (m, 8 H, Ar); 7.90 (br.d, 2 H, C(2)H_b, C(6)H_b (b stands for benzoyl), ^3J = 8.0 Hz).

X-ray diffraction analysis of compound **3a** was carried out at ~20 °C for a single crystal (0.35×0.42×0.49 mm) on an Enraf—Nonius CAD-4 automatic four-circle diffractometer (Mo-Kα radiation, λ = 1.71069 Å, 2θ/ω = 1.2, θ_{max} = 25°, sphere segment $-17 \le h \le 10$, $0 \le k \le 16$, $-17 \le l \le 16$). The total number of reflections was 6408 (5984 symmetrically independent reflections, the averaging factor R_{int} = 0.013). Crystals of compound **3a** are triclinic: a = 8.880(3) Å, b = 13.585(4) Å, c = 14.805(4) Å, α = 93.56(2)°, β = 107.44(2)°, γ = 90.01(2)°, V = 1700.3(9) Å^3, M = 681.7, Z = 4 (two independent molecules), d_{calc} = 1.33 g cm^{-3}, μ = 3.52 cm^{-1}, F(000) = 704, space group $P\bar{1}$ (No. 2). The structure was solved by the direct method and refined by the least-squares method in the full-matrix anisotropic approximation with the CRYSTALS program package.[35] In refinement, 3382 reflections with $I > 3\sigma(I)$ were used (431 parameters refined, the number of reflections per parameter was 7.8). All hydrogen atoms were located from the electron density difference map. All hydrogen atoms were refined with fixed coordinates and thermal parameters (only the H atoms in the amino group were refined isotropically). The Chebyshev weighting scheme[36] with five parameters (1.04, 0.24, 0.68, −0.14, and 0.14) was used in refinement. Final residuals were R = 0.051 and R_w = 0.053, GOF = 0.903. The residual electron densities were 0.35 and −0.31 e Å^{-3}. Absorption correction was applied by azimuthal scanning.[37] Comprehensive X-ray diffraction data for compound **3a** have been deposited with the Cambridge Crystallographic Data Center (CCDC 609934; CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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