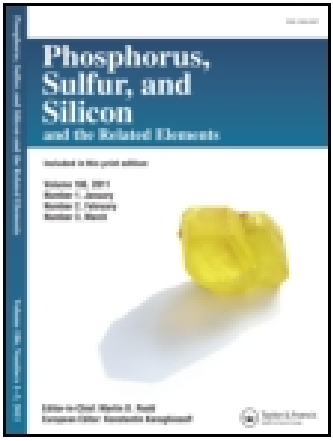

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Electrogenerated Base-Promoted Synthesis of Dithiocarbamate Acid Esters and 3-(N-Substituted-amino)-2-cyanodithiocrotonates from Primary or Secondary Amines and Carbon Disulfide

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Electrogenerated cyanomethyl anion promotes the reaction between primary or secondary amines, carbon disulfide, and alkyl or benzyl halide. Secondary amines are converted to alkyl or benzyl dithiocarbamates, whereas primary amines give N*-substituted alkyl or benzyl 3-amino-2-cyanodithiocrotonates. The mechanisms are discussed.*

Keywords 3-(*N*-substituted-amino)-2-cyanodithiocrotonates; carbon disulfide; cyanomethyl dithiocarbamates; anion; EGBs

INTRODUCTION

In recent years, several articles have been devoted to the synthesis of dithiocarbamates because they are widely used as antibacterial,[1–4] anthelmintic,[5,6] fungicidal,[1,2,4,7–10] and algicidal[11] reagents.

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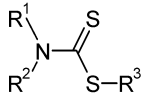
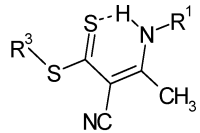
More recently, it was found that brassinin[12] and related compounds[13,14] possess in vitro and in vivo antitumor activity.

The classical synthesis of *N*,*N*-dialkyldithiocarbamates utilizes the reaction of dithiocarbamic acid salts with alkyl halides,[3,15–22] dialkyl phosphates[23] or electron-deficient olefins.[24,25]

Herein we report the synthesis of dithiocarbamates of the general structure**1** and of new *N*-substituted alkyl or benzyl 3-amino-2-cyanodithiocrotonates **3** through the condensation of the electrogenerated cyanomethyl anion at a copper electrode with secondary or primary amines, respectively, and carbon disulfide.



1



3

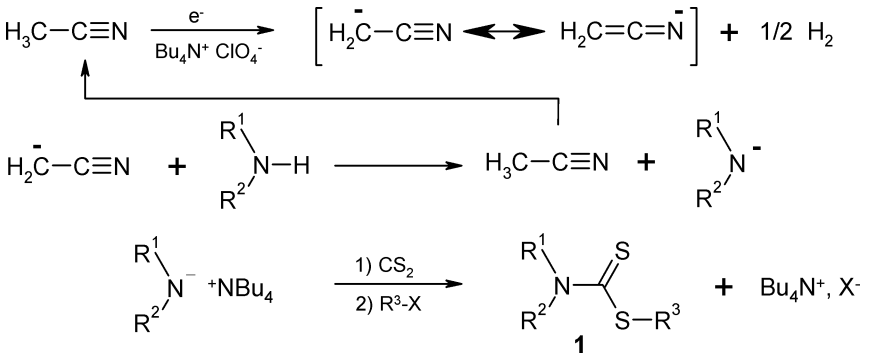
The first aim of this study was the development of an electrochemically induced synthesis of dithiocarbamate derivatives from carbon disulfide and amines without any addition of bases or probases. But, as we shall see below, primary and secondary amines behave differently.

Indeed, Feroci et al. reported the use of electrogenerated cyanomethyl anion to access to the corresponding alkyl carbonates, alkyl carbamates and oxazolone derivatives[26–29] following the condensation of alcohols, amines and 1,4-aminoalcohols, respectively. They also showed a new route to obtain asymmetric oxazolones from α,β-unsaturated nitroalkenes.[30,31]

It is well known, that the electrolysis of acetonitrile at imposed current in the presence or the absence of probases [PBs] such as azobenzene, aromatic aldehydes, ketones and aryl halides,[32–34] leads to the formation of the cyanomethyl anion (Scheme 1). The resulting electrogenerated anion/base [EGB] can induce the deprotonation of primary or secondary amines[35–36] to yield an excellent nucleophilic agent and regenerate acetonitrile.

RESULTS AND DISCUSSION

The electrolysis of acetonitrile under galvanostatic conditions (I = 28–30 mA) in a divided cell in the presence of tetrabutylammonium perchlorate (0.1 mol/L) as supporting electrolyte and a copper plate cathode yields the cyanomethyl carbanion. This anion is a base strong enough



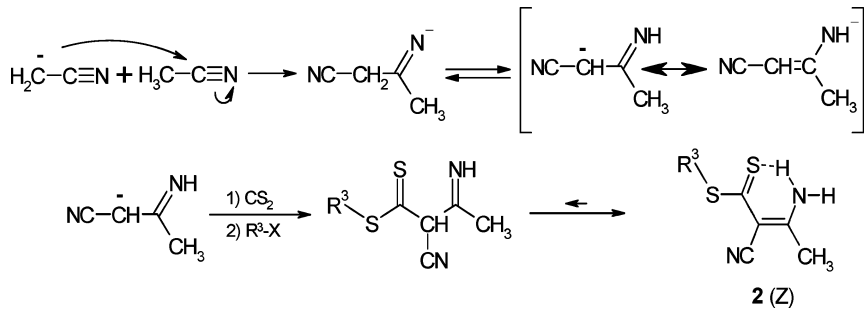
SCHEME 1

(pKa = 31.3 in DMSO[32]) to deprotonate most primary or secondary amines yielding acetonitrile and the amide anion.

When a secondary amine is used, the resulting amide anion acts as a nucleophile towards carbon disulfide allowing the electrochemical synthesis of dithiocarbamates **1** on addition of an alkyl halide such as ethyl iodide, methyl iodide or benzyl iodide (Scheme 1). It should be noted that carbon disulfide (Ep/Hg = −0.99 V vs Hg),[37] which is much more readily reduced than acetonitrile (Ep/Pt = −(3.4 − 3.5) V vs Ag/Ag^+ for MeCN-Bu_4NBF_4 and MeCN-$LiClO_4$),[26a,32] must be added after the end of the electrolysis.

The behavior of the anions formed from the respective amines is in accordance with that reported previously for the reaction with carbon dioxide as electrophile.[26,27,38]

The dithiocarbamate **1** is isolated as the major product along with alkyl or benzyl 3-amino-2-cyanodithiocrotonate **2** as a by-product (Scheme 2, Table I). The latter results from the condensation of the cyanomethyl anion with acetonitrile (Thorpe-like reaction) leading to the stable 3-iminobutanenitrile anion.[26,34] This anion reacts with carbon disulfide. Compound **2** is formed after alkylation of the resulting adduct by the alkyl or benzyl halide (Scheme 2), which is introduced in the cathodic solution. ^1H, ^{13}C NMR and MS spectra are consistent with the formula of **2** shown in Scheme 2 (see Experimental section for **2,** R^3 = Et). Moreover, only one stereoisomer is observed for **2**, which is the *Z*-isomer. This is corroborated by the appearance of two different N-H resonances in the ^1H NMR spectrum, the more deshielded one at 12.6 ppm corresponding to a particularly strong stabilizing intramolecular N−H···S=C hydrogen bond. This structure is in accordance with that previously characterized by spectroscopic data (IR, ^1H, ^{13}C, ^{15}N NMR) and X-ray crystal structure analyses.[39]



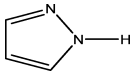
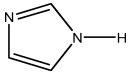
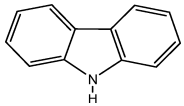
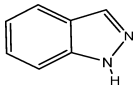
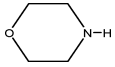
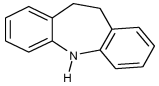
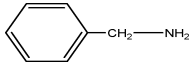
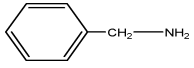
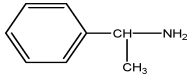
SCHEME 2

Compared to secondary amines, primary amines act differently (Table I). Surprisingly, the electrogenerated $^{(-)}CH_2CN$/primary amine/CS_2 system gives the (*Z*)-3-(*N*-substituted-amino)-2-cyanodithiocrotonates **3** as the major products (Scheme 3).

The structure of **3** is corroborated by the following spectroscopic data, all showing the presence of only one stereoisomer (see also Table I and the Experimental section):

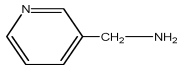
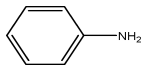
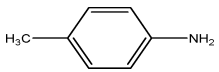
a. **^{1}H NMR**: when $R^3 = PhCH_2$ (in **3a** and **3b**), 3-pyCH_2 (in **3d**) and PhCH(CH_3) (in **3c**), the CH_2 an CH signals appear as a doublet (at 4.65 ppm) and a quintet (at 5.2 ppm), respectively, showing a coupling with one NH proton. Furthermore, the NH signal for all products **3** is extremely deshielded (14 ppm for **3a–3d**, **3g** and 15 ppm when $R^3 = Ar$), which indicates a strong intramolecular N—H···S=C hydrogen bond that stabilizes the *Z* diastereomer.
b. **^{13}C NMR**: all signals fit the structure **3**; in particular the signals at 118 ppm (C≡N), around 94 ppm (C_b) and 167 ppm (C_c) are characteristic of a N—C=C system (e.g. Me_2N—CH=CH_2, $\delta_{CH2} = 91.3$ ppm and $\delta_{CH} = 151.3$ ppm),[40] as well as the signals at 209 ppm (C=S), 127–134 ppm (C_{ar}) and those corresponding to CS_2Et, CS_2Me, and CS_2CH_2Ph, respectively.
c. All **Mass spectra** are consistent with structure **3**.
d. The **IR spectra** of **3c** exhibit a medium broad N-H band at 3150 cm^{-1} corresponding to a strong intramolecular N—H···S=C hydrogen bond and a sharp band at 2195.7 cm^{-1} corresponding to a conjugated C≡N bond.
e. An **X-ray crystal structure analysis** of **3c**, which will be published elsewhere, undoubtedly supports this structure.[41]

TABLE I Preparation of Compounds 1 and 3. Reaction Conditions: Cu Cathode, Graphite Anode; CH_3CN/0.1 M TBAP; Ethyl Iodide as Alkylating Agent (R^3 = Et)

Starting amine	Isolated product	Yield[a](%)	Electricity consumption[b] ($F.mol^{-1}$)
	**1a**	47	1.0
	**1b**	43	1.5
	**1c**	54	1.0
	**1d**	47	1.0
	**1e**	28	1.2
	**1f**[c]	21	1.0
	**2**	[e]	1.1
	**2**	[e]	1.0
	**3a**	60	2.0
	**3b**[d]	54	2.0
	**3c**	47	2.0

(Continued on next page)

TABLE I Preparation of Compounds 1 and 3. Reaction Conditions: Cu Cathode, Graphite Anode; CH_3CN/0.1 M TBAP; Ethyl Iodide as Alkylating Agent (R^3 = Et) *(Continued)*

Starting amine	Isolated product	Yield[a)](%)	Electricity Consumption[b)] ($F.mol^{-1}$)
	**3d**	15	2.0
	**3e**	50	2.0
	**3f**	46	2.0
$C_{12}H_{25}NH_2$	**3g**[c)]	40	2.0

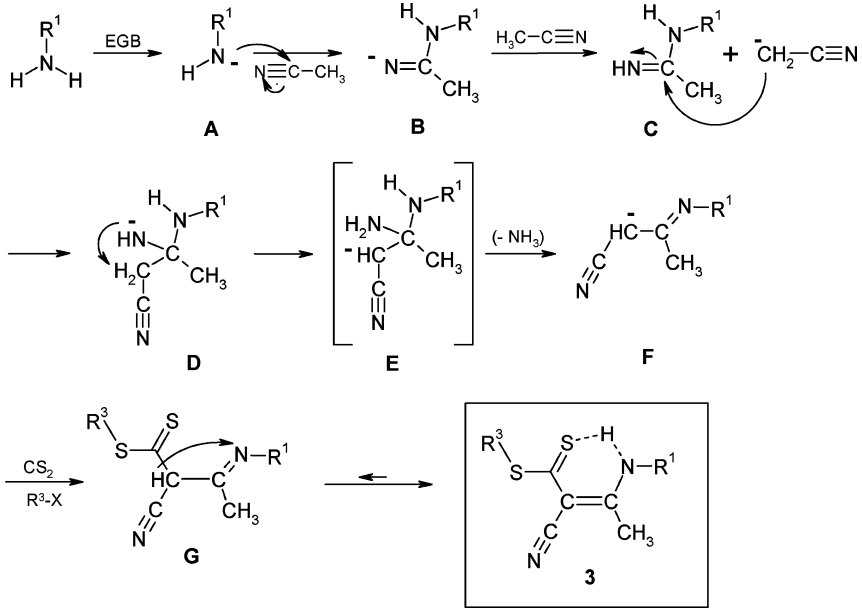
[a)]The yield of isolated dithiocarbamates is based on the starting amine; [b)]The electricity consumption represents the number of Faradays per mole of amines supplied to the electrode. [c)]The alkylating agent R^3X is benzyl bromide; [d)]The alkylating agent R^3X is methyl iodide; [e)]At the end of electrolysis only the compound **2** was isolated. This is certainly in relation with too large pKa values for diisopropylamine (35,7 in THF[42] and DMSO[43]) and iminodibenzyl relatively to that of acetonitrile.

Finally, as for the cyanomethyl anion, the primary amide anions R^1NH^-, less hindered than the secondary ones, form very loose solvent-separated ion pairs with the ammonium cations in the polar solvent MeCN. This renders them sufficiently nucleophilic to add to MeCN molecules.

The following mechanism can thus be proposed to explain the formation of **3** (Scheme 3):

a. the amide anion **A** reacts with acetonitrile to give the intermediate amidine anion **B**; b. acetonitrile exchanges a proton with **B** to form the amidine **C** and the cyanomethyl anion; c. the latter adds to amidine **C** to give the amide anion **D**, which isomerizes into the carbanion **E**; d. spontaneous elimination of ammonia gives the cyanomethylen anion **F**; e. the latter adds to carbon disulfide and the formed dithiocarboxylate anion is trapped by the alkyl halide; f) and finally, the iminocyanodithiocarboxylate isomerizes into the more conjugated (*Z*)-3-(*N*-substituted-amino)-2-cyanocrotonate **3**, which is also stabilized by an intramolecular hydrogen bond.

In summary, the cyanomethyl EGB / amine / carbon disulfide / alkyl or benzyl halide system—easily prepared at room temperature and



SCHEME 3

constant current in a divided cell with TBAP as supporting electrolyte—appears to be convenient for the preparation of dithiocarbamates when starting from secondary amines and (*Z*)-3-(*N*-substituted-amino)-2-cyanocrotonates when starting from primary amines.

EXPERIMENTAL

Apparatus and Materials

Melting points were determined on an Electrothermal 9100 apparatus and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution with a Bruker AC 300 spectrometer operating at 300 MHz for ^{1}H and at 75 MHz for ^{13}C. Chemical shifts are in ppm, with respect to tetramethylsilane (TMS) as internal standard. Mass spectra were recorded with a JEOL MS 700 system in chemical ionization mode using NH_3 or CH_4 and with a MAT Finnigan 90 apparatus for EIMS. Coupled GC/MS analyses were performed in electronic ionization form with a Finnigan integrated spectrometer. The IR spectrum was recorded with a Perkin-Elmer Paragon 1000 FT/IR spectrometer. All reagents were commercially available and were used without further purification.

General Procedure

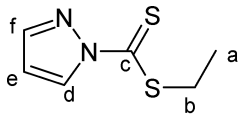
The electrolysis was carried out under galvanostatic conditions (I = 28–30 mA) at a Cu cathode (area: 50 cm^2) and a graphite anode in a divided cell under nitrogen atmosphere at room temperature with 0.1 M TBAP-MeCN as supporting electrolyte. The starting amount of primary and secondary amines was close to 5 mmol. After the consumption of 1 or 2 F/mol with respect to the amine (see Table I), 5 mmol of carbon disulfide was added into the cathodic solution and the reaction mixture was stirred at room temperature for 1 h. The alkylation was then carried out in the presence of an excess (1.1–1.2 equivalent) of alkyl halide R^3-X (X = I, Br) overnight under stirring.

The solvent MeCN was removed under vacuum and the residue extracted with diethyl ether (3 × 30 mL). The organic phase was then washed with 100 mL of water, dried over $MgSO_4$, filtered, and diethyl ether was evaporated. Separation of the products was accomplished by column chromatography (silica gel 60, Fluka) using a 9 : 1 mixture of hexane/AcOEt as eluent.

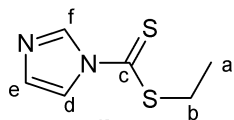
Isolated Products

1a

Yellow oil; ^{1}H NMR ($CDCl_3$): δ 1.40 (t, ^3J = 7 Hz, 3H, H_a); 3.30 (q, ^3J = 7 Hz, 2H, H_b); 6.45 (s, 1H, H_e); 7.78 (s, 1H, H_f); 8.60 (s, 1H, H_d). ^{13}C NMR ($CDCl_3$): δ 12.3 (C_a); 30.6 (C_b); 110.2 (C_e); 129.9 (C_f); 144.5 (C_d); 200.7 (C_c=S). MS (EI): m/z (%): 172 (100) ($M^{+\cdot}$); 139 (40) $(M - HS)^+$; 113 (35); 112 (65); 111 (40) $(M - SC_2H_5)^+$; 105 (20) $(CSSEt)^+$; 104 (35); 103 (25); 84 (35); 77 (40); 69 (40); 68 (95) $(M + H - CS_2C_2H_5)^+$; 60 (45); 59 (35); 57 (20).



1a



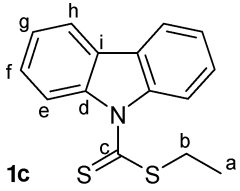
1b

1b

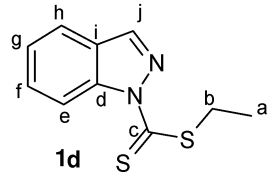
Yellow oil; ^{1}H NMR ($CDCl_3$): δ 1.45 (t, ^3J = 7 Hz, 3H, H_a); 3.35 (q, ^3J = 7 Hz, 2H, H_b); 7.11 (s, 1H, H_e); 7.78 (s, 1H, H_f); 8.50 (s, 1H, H_d). ^{13}C NMR ($CDCl_3$): δ 12.4 (C_a); 31.3 (C_b); 117.7 (C_e); 131.2 (C_f); 135.5 (C_d); 198.0 (C_c=S). MS (EI): m/z (%): 172 (70) ($M+\cdot$); 111 (22) $(M - SC_2H_5)^+$; 105 (100) $(CSSEt)^+$; 84 (35); 77 (60); 68 (20) $(M + H - CS_2C_2H_5)^+$; 60 (10); 57 (15).

1c

Orange, viscous oil; ^{1}H NMR ($CDCl_3$): δ 1.45 (t, $^3J = 7$ Hz, 3H, H_a); 3.40 (q, $^3J = 7$ Hz, 2H, H_b); 7.25 (t, $^3J = 6.5$ Hz, 2H, H_g); 7.40 (t, $^3J = 6.5$ Hz, 2H, H_f); 7.90 (d, $^3J = 6.5$ Hz, 2H, H_e), 8.40 (d, $^3J = 6.5$ Hz, 2H, H_h). ^{13}C NMR ($CDCl_3$): δ 12.9 (C_a); 32.2 (C_b); 115.3 (C_g); 120.0 (C_f); 123.4 (C_e); 125.9 (C_i); 126.8 (C_h); 140.1 (C_d); 202.9 (C_c=S). CI-MS (NH_3): m/z (%): 289 (20) $(M + H + NH_3)^+$; 272 (85) $(M + H)^+$; 212 (80); 210 (25) $(M + H - SC_2H_5)$; 168 (100) $(M + H + 2H - CS_2C_2H_5)$; 167 (25); $(M + H - CS_2C_2H_5)^+$. CI–HRMS (CH_4) m/z (%): 272.0564 $(M+H)^+$.



1c



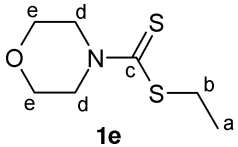
1d

1d

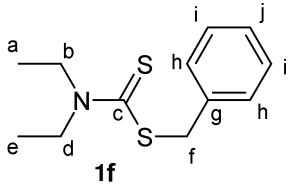
Solid; m.p.: 88–89°C; ^{1}H NMR ($CDCl_3$): δ 1.42 (t, $^3J = 7$ Hz, 3H, H_a); 3.30 (q, $^3J = 7$ Hz, 2H, H_b); 7.37 (t, H_g); 7.57 (t, H_f); 7.72 (d, H_e); 8.17 (s, H_j); 9.12 (d, H_h). ^{13}C NMR ($CDCl_3$): δ 12.5 (C_a); 29.8 (C_b); 116.8 (C_g); 121.4 (C_f); 125.2 (C_e); 127.6 (C_i); 130.3 (C_j); 139.9 (C_h); 140.3 (C_d); 199.7 (C_c=S). MS (EI): m/z (%): 222 (74) $(M^{+\cdot})$; 194 (20) $(M - C_2H_2)^+$; 189 (15); 162 (86); 161 (46) $(M - SC_2H_5)^+$; 134 (28); 129 (30); 118 (100) (M + H − CSSEt); 105 (34) $(CSSEt)^+$; 102 (20); 91 (18); 77 (30); 63 (18); 50 (10).

1e

Solid; m.p.: 40.4°C; ^{1}H NMR (CDCl): δ 1.28 (t, $^3J = 7.2$ Hz, 3H, H_a); 3.23 (q, $^3J = 7.2$ Hz, 2H, H_b); 3.67 (t, br, 4H, H_d); 3.8–4.3 (br, 4H, H_e). ^{13}C NMR ($CDCl_3$): δ 13.7 (C_a); 31.2 (C_b); 50.6 (C_d); 66.1 (C_e); 197.4 (C_c=S). CI–MS (NH_3): m/z (%): 192 (100), $(M + H)^+$; 132 (65); 130 (32) $(M - HSC_2H_5)^+$. CI–HRMS (CH_4): 192.025 (55) $(M+H)^+$.



1e



1f

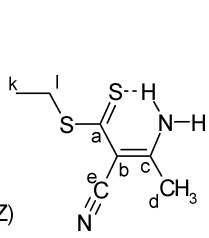
1f

^{1}H NMR ($CDCl_3$): δ 1.25 (t, $^3J = 7$ Hz, 6H, $H_{a,e}$); 3.65 (q, $^3J = 7$ Hz, 2H, $H_{b,d}$); 4.00 (q, $^3J = 7$ Hz, 2H, $H_{b,d}$); 4.52 (s, 2H, H_f); 7.15–7.4 (m, 5H,

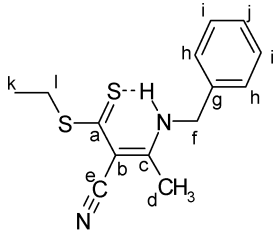
H_{ar}). ^{13}C NMR ($CDCl_3$): δ 11.6 ($C_{a,e}$); 12.5 ($C_{a,e}$); 42.1 (C_f); 46.7 ($C_{b,d}$); 49.4 ($C_{b,d}$); 127.4 (C_j); 128.4 ($C_{h,i}$); 129.5 ($C_{h,i}$); 136.1 (C_g); 195.0 (C_c = S).

2

(R^3 = Et, *Z*-isomer): Yellow solid; m.p.: 147°C; ^1H NMR ($CDCl_3$): δ 1.36 (t, ^3J = 7.3 Hz, 3H, H_k); 2.41 (s, 3H, H_d); 3.23 (q, ^3J = 7.3 Hz, 2H, H_l); 6.6 (br, 1H, NH); 12.6 (br, 1H, intramolecularly bonded NH). ^{13}C NMR ($CDCl_3$, DMSO): 13.0 (C_k); 23.0 (C_d); 27.6 (C_i); 92.7 (C_b); 118.1 (C_e ≡N); 169.4 (C_c); 207.9 (C_a=S). CI–MS (NH_3): m/z (%): 204 (100) (M + H + NH_3)$^+$; 187 (75), (M + H)$^+$; 172 (13), (M + H – CH_3)$^+$; 144 (13), (M – CH_3CNH_3)$^+$; 127 (13) (M – SCH=CH_2)$^+$. CI–HRMS (CH_4): 187.036 (M+H)$^+$.



2 (Z)



3a (Z)

3a

(R^3 = Et, *Z*-isomer): Yellow solid; m.p.: 105°C; ^1H NMR ($CDCl_3$): δ 1.30 (t, ^3J = 7 Hz, 3H, H_k); 2.40 (s, 3H, H_d); 3.20 (q, ^3J = 7 Hz, 2H, H_i); 4.65 (d, J = 6 Hz, 2H, H_f); 7.20–7.40 (m, 5H, H_{ar}); 14.1 (br, 1H, intramolecularly bonded NH). ^{13}C NMR ($CDCl_3$): δ 12.8 (C_k); 19.3 (C_d); 28.6 (C_l); 48.4 (C_f); 94.3 (C_b); 118.7 (C_e ≡N); 127.2 ($C_{h,i}$); 128.3 (C_j); 129.2 ($C_{h,i}$); 134.8 (C_g); 167.5 (C_c); 209.3 (C_a=S). CI–MS (C_4H_{10}): m/z (%): 277 (100), (M + H)$^+$; 243 (4) (M + H – H_2 S)$^+$; 215 (15) (M - EtSH)$^+$; 171 (21) (M + H - CS_2Et)$^+$.

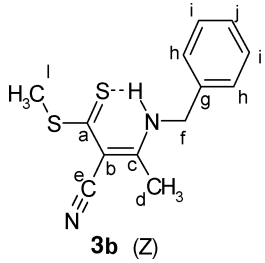
3b

(R^3 = Me, *Z*-isomer): Yellow solid; m.p.: 105.3°C; ^1H NMR ($CDCl_3$): δ 2.40 (s, 3H, H_d); 2.60 (s, 3H, H_l); 4.65 (d, ^3J = 6 Hz, 2H, H_f); 7.20–7.45 (m, 5H, H_{ar}); 14.1 (br, 1H, intra-molecularly bonded NH). ^{13}C NMR ($CDCl_3$, DMSO): δ 17.9 (C_l); 19.3 (C_d); 48.4 (C_f); 101.8 (C_b); 118.7 (C_e ≡N); 127.1 ($C_{h,i,j}$); 128.3 ($C_{h,i,j}$); 129.2 ($C_{h,i,j}$); 134.9 (C_g); 167.0 (C_c); 210.0 (C_a=S). CI–MS (C_4H_{10}): m/z (%): 263 (100), (M + H)$^+$; 236 (4) (M + H – HCN)$^+$; 215 (27), (M + H – MeSH)$^+$; 192 (18); 171 (M + H – CS_2Me)$^+$.

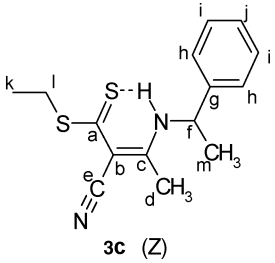
3c

(R^3 = Et, *Z*-isomer): m.p.: 81°C; ^1H NMR ($CDCl_3$): δ 1.30 (t, ^3J = 7 Hz, 3H, H_k); 1.60 (d, ^3J = 6 Hz, 3H, H_m); 2.36 (s, 3H, H_d); 3.20 (q, ^3J = 7

Hz, 2H, H_l); 5.2 (quint, $^3J = 6$ Hz, 1H, H_f); 7.20–7.50 (m, 5H, H_{ar}); 14.1 (br, d, $^3J = 6$ Hz, 1H, intramolecularly bonded NH). ^{13}C NMR ($CDCl_3$+ DMSO): 12.9 (C_k); 19.2 (C_d); 23.3 (C_m); 27.6 (C_l); 54.6 (C_f); 93.5 (C_b); 118.1 ($C_e \equiv N$); 125.9 ($C_{h,i}$); 127.8 (C_j); 129.0 ($C_{h,i}$); 141.3 (C_g); 167.5 (C_c); 206.6 (C_a=S). MS (EI): m/z (%): 290 (10) ($M^{+\cdot}$); 261 (6) $(M - Et)^+$; 229 (18) $(M - SEt)^+$; 196 (4); 185 (14) $(M - CSSEt)^+$; 125(13); 105 (100) $(PhCHCH_3)^+$; 77 (18) $(Ph)^+$; 42 (4). CI–HRMS (CH_4): 291.099 $(M+H)^+$. IR (NaCl): ν (cm^{-1}) = 3150 (m, broad, intramolecularly bonded NH), 3020, 2950, 2925, 2852, 2195 (conjugated C≡N), 1600 (S, conjugated C=C, C_{ar}-C_{ar}), 1447, 1400, 1354, 1324, 1261 (S, conjugated C-N), 1240 (C-N), 1090 (C= S), 1023, 964, 806 (S), 753, 702, 553.



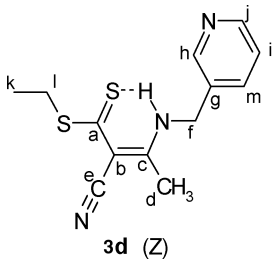
3b (Z)



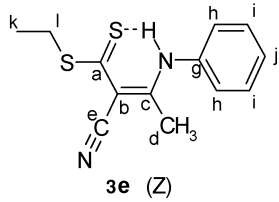
3c (Z)

3d

(R^3 = Et, *Z*-isomer): Solid; m.p.: 153.8°C; ^{1}H NMR ($CDCl_3$): δ 1.30 (t, $^3J = 7$ Hz, 3H, H_k); 2.40 (s, 3H, H_d); 3.10 (q, $^3J = 7$ Hz, 2H, H_l); 4.65 (d, 2H, H_f); 7.20–8.70 (m, 5H, H_{ar}); 14.1 (br, 1H, intramolecularly bonded NH). ^{13}C NMR ($CDCl_3$): δ 12.7 (C_k); 19.4 (C_d); 28.8 (C_l); 49.0 (C_f); 118.5 ($C_e \equiv N$), 128.0 (C_i); 135.0 (C_g); 137.0 (C_m); 148.4 (C_j); 149.0 (C_h); 167.5 (C_c); 210.2 (C_a=S).



3d (Z)



3e (Z)

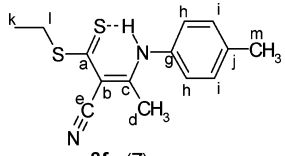
3e

(R^3 = Et, *Z*-isomer): Solid; m.p.: 105°C; ^{1}H NMR ($CDCl_3$): δ 1.35 (t, $^3J = 7$ Hz, 3H, H_k); 2.40 (s, 3H, H_d); 3.25 (q, $^3J = 7$ Hz, 2H, H_l);

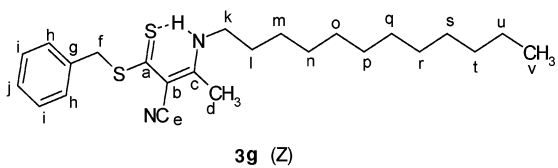
7.30–7.60 (m, 5H, H_{ar}); 15.1 (br, 1H, intra-molecularly bonded NH). ^{13}C NMR ($CDCl_3$, DMSO): δ 12.8 (C_k); 20.3 (C_d); 27.8 (C_l); 94.4 (C_b); 117.7 ($C_e \equiv N$); 125.5 (C_k); 128.1 (C_j); 129.6 (C_i); 135.5 (C_g); 167.3 (C_c); 207.7 (C_a=S).

3f

(R^3 = Et, *Z*-isomer): Solid; m.p.: 101.6°C; ^1H NMR ($CDCl_3$): δ 1.40 (t, $^3J = 7$ Hz, 3H, H_k); 2.35 (s, 3H, $H_{d/m}$); 2.40 (s, 3H, $H_{d/m}$); 3.25 (q, $^3J = 7$ Hz, 2H, H_l); 7.10-7.30 (m, AA'BB', 4H, H_g, H_i); 15.1 (br, 1H, intramolecularly bonded NH). ^{13}C NMR ($CDCl_3$): δ 12.7 (C_k); 20.4 ($C_{d/m}$); 21.1 ($C_{d/m}$); 28.8 (C_l); 94.7 (C_b); 118.4 ($C_e \equiv N$); 125.5 (C_h); 130.3 (C_i); 133.4 (C_j); 138.4 (C_g); 166.2 (C_c); 210.1 (C_a=S). MS (EI): m/z (%): 276 (26) $(M^{+\cdot})$; 247 (45) $(M - Et)^+$; 215 (100) $(M - SEt)^+$; 182 (7); 132 (10); 107(18) $(CH_3C_6H_4NH_2)^+$; 91 (33) $(C_7H_7)^+$; 65 (22).



3f (Z)



3g (Z)

3g

(R^3 = Ph-CH_2, *Z*-isomer): Orange solid; m.p.: 50.3°C; ^1H NMR ($CDCl_3$): 0.90 (t, $^3J = 7$ Hz, 3H, H_n); 1.2 – 1.5 (m, 18H, H_m); 1.72 (quint, $^3J = 7$ Hz, 2H, H_l); 2.40 (s, 3H, H_d); 3.45 (q, $^3J = 7$ Hz, 2H, H_k); 4.50 (s, 2H, H_f); 7.20–7.40 (m, 5H, H_{ar}); 13.7 (br, 1H, intramolecularly bonded NH). ^{13}C NMR ($CDCl_3$): 14.1 (C_v); 19.1 (C_d); 22.7 (C_u); 26.8 (C_t); 28.9 (C_s), 29.1 (C_r); 29.3 (C_p, C_q), 29.5 (C_n, C_o); 29.6 (C_m); 31.9 (C_l); 38.9 (C_f); 45.0 (C_k); 93.7 (C_b); 118.7 ($C_e \equiv N$); 127.4 (C_j); 128.5 ($C_{h,i}$); 129.4 ($C_{h,i}$); 135.6 (C_g); 167.3 (C_c); 207.6 (C_a=S). MS (EI): m/z (%): 416 (5) $(M^{+\cdot})$; 325 (76) $(M - Ph\text{-}CH_2)^+$; 293 (100) $(M - PhCH_2\ S)^+$; 157 (10); 91 (88) $(C_7H_7)^+$; 43 (23). CI–MS (NH_3): m/z (%): 434 (100), $(M + H + NH_3)^+$; 417 (85) $(M + H)^+$; 344 (53); 325 (48) $(M + H - PhCH_2)^+$; 295 (54); 293 (18) $(M + H - PhCH_2\ S)^+$; 251 (15); 200 (22); 186 (68); 108 (35).

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