# Substituted *N*-Cyanomethyl-2-halo-*N*-methylarenecarboxamides as Precursors of 1,4-Benzothiazepines



Wolfgang Dölling*

Institute of Organic Chemistry, Department of Chemistry, Martin-Luther University Halle-Wittenberg, 06120 Halle (Saale), Germany

Alexander Perjéssy

Department of Organic Chemistry, Faculty of Natural Sciences, Comenius University, 84215 Bratislava, Slovak Republic

Ingrid Schaller and Alfred Kolbe

Institute of Physical Chemistry, Department of Chemistry, Martin-Luther University Halle-Wittenberg, 06120 Halle (Saale), Germany

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2-Halogeno substituted *N*-cyanomethyl-*N*-methylbenzamides **1a-1i** were investigated in a correlation analysis by ir spectroscopy to determine the conformational behavior. Compound **1h** gives 4-methyl-2-methylthio-8-nitro-5-oxo-4,5-dihydro-1,4-benzothiazepine-3-carbonitrile **3** by dithiocarboxylation procedure whereas **1b** was not able to react to heterocyclic seven-membered ring system.

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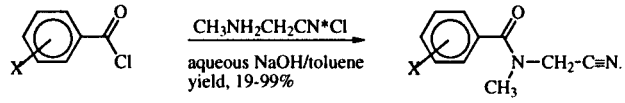
## Introduction.

It is the purpose of this paper to outline the results of investigations in the field of dithiocarboxylation of α-aza-*C*-nucleophiles derived from title amides. A preliminary investigation using this new thiazepine formation method of heterocyclization by nucleophilic aromatic substitution has been performed [1]. This paper describes the principle on which our studies have been carried out, gives some examples of application for heterocyclic two heteroatom containing seven-membered ring or ketene dithioacetal formation and presents new amides with a discussion of the ir spectra and conformation of the rotamers.

## Results and Discussion.

The *N*-cyanomethyl-*N*-methylamides of 2-chloronicotinic acid or substituted 2-halobenzoic acids **1** were obtained in a conventional manner by treating the appropriate acids with thionyl chloride followed by distillation and reaction of the intermediate acid chloride (2-chloronicotinoyl chloride [2,3,4,5]) with methylaminoacetonitrile hydrochloride in a 10% sodium hydroxide solution/-toluene two phase system. These new compounds were obtained in good to excellent yields with the exception of the new derivative of 2-chloronicotinic acid which was obtained only in 19% yield. Only the 2-chloro-*N*-(cyanomethyl)-*N*-methyl-4-pyridinecarboxamide is described in literature [6,7] in the pyridine series and 4-chloro-*N*-(cyanomethyl)-*N*-methylbenzamide [8], nitrosubstituted [9,10] and the unsubstituted one [11,12] in carbocyclic series. The syntheses of several known compounds have been given in detail in the Experimental, since no spectroscopic data of these substances were available. Amides are known to exist as *syn*- and *anti*- rotamers. Therefore, nmr spectra of these unsymmetrical substituted amides show a double set of signals (see Experimental). They were prepared according to the following scheme:

Scheme 1




## Infrared Spectra and Conformation of Substituted *N*-Cyanomethyl-*N*-methylbenzamides.

The infrared spectral data for series of substituted *N*-cyanomethyl-*N*-methylbenzamides **1a-1i** measured in trichloromethane are given in Table 1. The wave numbers of the carbonyl stretching vibration are observed in the region of 1672-1648 $cm^{-1}$ (in chloroform solution) and are strongly dependent on the substituents on the benzene ring. The above dependence can be quantitatively expressed for all compounds **1a-1i** by the following linear correlation:

$$\nu_{(C=O)} = (11.50 \pm 1.35)\,\sigma + 1651.2 \quad (1)$$

$r = 0.955$, $s = 2.32$, $F = 72.6$

Table 1

Infrared Spectral Data [$cm^{-1}$] for a Series of Substituted *N*-Cyanomethyl-*N*-methylbenzamides **1a-1i** in Trichloromethane

| Compound | ν(C=O) | ν(C≡N) |
|---|---|---|
| **1a** | 1649 | 2251 |
| **1b** | 1654 | 2253 |
| **1c** | 1656 | 2252 |
| **1d** | 1651 | 2252 |
| **1e** | 1656 | 2252 |
| **1f** | 1664 | 2257 |
| **1g** | 1659 | 2253 |
| **1h** | 1664 | 2255 |
| **1i** | 1672 | [a] |

[a] Low solubility.

In the above correlation all *ortho*-substituted compounds have been approximated as *para*-substituted isomers using $\sigma_p$ Hammett substituent constants. For compound **1g** the σ value has been calculated by approximation of the 3-pyridyl ring by the 3-nitrophenyl isomer. The linear dependence is illustrated in Figure 1.

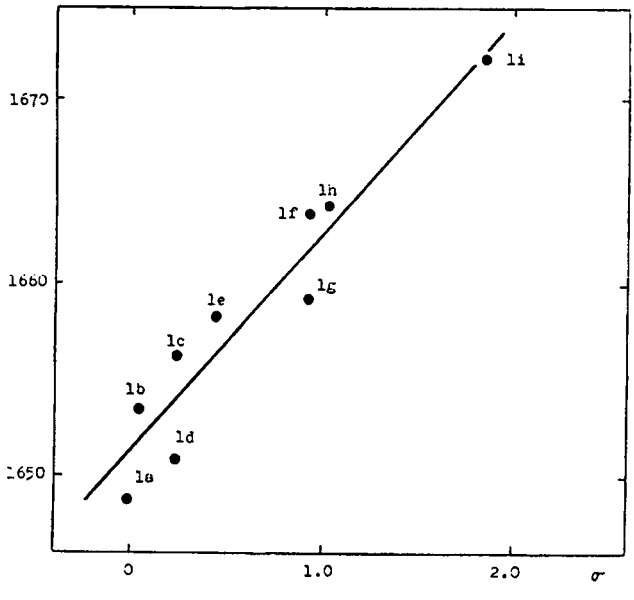
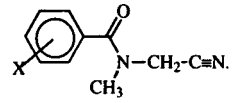



Figure 1. Plot of the wave numbers of C=O stretching vibration of compounds **1a-1i** on Hammett σ values.

It follows from the comparison with similar series of substituted *N,N*-dimethylbenzamides [13] that the ν(C=O), absorption band of compounds **1a-1i** are observed at *ca* 20 $cm^{-1}$ higher wave numbers. This indicates that the cyano group has an extremely strong electron-withdrawing effect on the amide carbonyl group. Such an increase of the carbonyl stretching wave number can be explained as a consequence of the superposition of both the inductive and the field effects of the cyano group and is connected with the preference of conformation **2a**, which will be discussed later.




| No. | X | lit |
|---|---|---|
| **1a** | H | [11,12] |
| **1b** | 2-F | |
| **1c** | 2-Cl | [1] |
| **1d** | 4-Cl | [8] |
| **1e** | 2,4-$Cl_2$ | [1] |
| **1f** | 2-Cl, 5-$NO_2$ | [10,9] |
| **1g** | 2-Cl, 3-N [a] | |
| **1h** | 2-Cl, 4-$NO_2$ | [10,9] |
| **1i** | 2,4-$Cl_2$, 3,5-$(NO_2)_2$ | [10,9] |

[a] 3-Pyridyl instead of phenyl.

Comparing the slope of ν(C=O) *vs.* σ correlation for compounds **1a-1i**, ρ = 11.50 $cm^{-1}$ (Equation 1) with that of a similar correlation for substituted *N,N*-dimethylbenzamides ρ = 17.74 [13], it can be ascertained that the strong electron-withdrawing effect of the cyano group significantly diminishes the substituent effect sensitivity of the *N,N*-dimethylbenzamide carbonyl group. The wave numbers of the nitrile stretching vibration are observed in the region of 2251-2258 $cm^{-1}$ and are less dependent on the effects of substituents in the benzene ring than the carbonyl vibrational bands.

The measurements with compound **1c** in chloroform showed that by increasing the temperature from 25° up to 68° only a moderate change occurs in the range of ν(C=O) values (3.5 $cm^{-1}$), however a significant change is observed in the region of the ν(C≡N) values (45.3 $cm^{-1}$). This is probably connected with the equilibrium between two conformations **2a** and **2b**:


**2a** **2b**

In conformation **2a** (existing at room temperature), owing to the strong field effect interaction between the two polar groups: C=O and C≡N, the ν(C≡N) absorption band is observed at higher wave numbers: 2252 $cm^{-1}$. At increased temperature a new absorption band occurs at 2207 $cm^{-1}$ belonging to conformation **2b** in which the

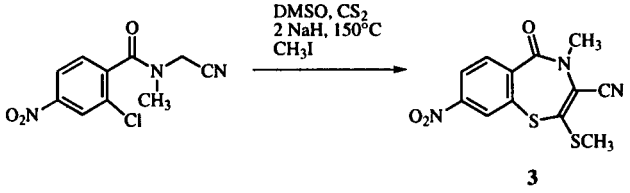
$CH_2$-C≡N group is twisted out of the vicinity of the C=O group and there is no field effect between the two polar groups.

On the basis of the above results it can be concluded that substituted *N*-cyanomethyl-*N*-methylbenzamides **1a-1i** at room temperature preferably exist in conformation **2a**, stabilized by a strong field interaction between the two polar groups C=O and C≡N. At higher temperatures the equilibrium is shifted to structure **2b**, where the field effect between C=O and C≡N groups is absent.

Examples of Dithiocarboxylation Studies at Different Reaction Temperatures.

Having dealt at some length with the structure of amides **1**, we may now consider results of dithiocarboxylation experiments. Surprisingly, starting with compound **1b** we were not able to isolate the seven-membered ring as a result of the reaction with carbon disulfide and a base. However, compound **1h** gives 4-methyl-2-methylthio-8-nitro-5-oxo-4,5-dihydro-1,4-benzothiazepine-3-carbonitrile **3** on treatment with carbon disulfide in dimethyl sulfoxide and sodium hydride first at rt and then several hours at 150° followed after cooling to rt by adding methyl iodide (Scheme 2). During our study it was noted that no reaction took place at a lower temperature. The structure of the product was proofed by analytical and spectroscopical data.

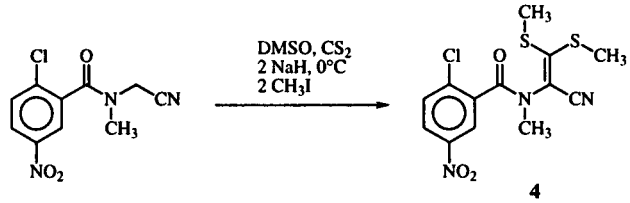
Scheme 2




**3**

We obtained in the case of reacting **1f** at 0° with carbon disulfide in the above described manner in good yield the corresponding ketene dithioacetal **4** (Scheme 3).

Scheme 3




**4**

In conclusion, recent results obtained during our study of the reactivity of α-heteroatom substituted carbanionic species with carbon disulfide or phenyl isothiocyanate show, that new 1,4-benzothiazepines **3** can be synthesized by dithiocarboxylation procedure (dimethyl sulfoxide/carbon disulfide/sodium hydride) starting with appropriate nitrogen containing *C*-nucleophiles derived of 2-halo-substituted *N*-cyanomethyl-*N*-methylarenecarboxamides.

## EXPERIMENTAL

All dithiocarboxylation reactions were carried out under argon atmosphere. Melting points were determined on a Kofler hot stage microscope and are uncorrected. The infrared spectra (ir) were measured with an infrared spectrophotometer Specord Carl Zeiss Jena or FTIR-spectrometer 1000 from Perkin-Elmer. The infrared spectra of trichloromethane solutions of the compounds **1a-1i** in the regions of 2300-2100 $cm^{-1}$ and 1750-1600 $cm^{-1}$ were measured on a Bruker IFS 25 FTIR-spectrometer using sodium chloride cells of 0.1 cm thickness. Solution concentrations were 6-20 mg/ml. The measurements were carried out for compound **1c** at temperatures 25° and 68° in trichloromethane and 25° and 80° in toluene, respectively. The peak positions were determined with an accuracy of ±0.2 $cm^{-1}$.

The $^1H$ and $^{13}C$ nmr spectra were recorded on either a Bruker WP 200 or AC 80 or a Varian Gemini 200 or Unity 500 spectrometer in deuteriochloroform. Mass spectra were measured on an AMD 402 of the AMD Intectra GmbH. Reactions were monitored by tlc using Merck DC Alufolien Kieselgel 60 $F_{254}$ plates and were visualized under uv irradiation. Column chromatography was performed with Kieselgel 60 (Merck, practical size 0.063-0.2 mm). The elemental analyses were obtained on elemental analyser Vario El Foss Heraeus of Elementar Analysen Systeme GmbH.

*N*-Cyanomethyl-2-fluoro-*N*-methylbenzamide **1b**.

Methylaminoacetonitrile hydrochloride (10.56 g, 0.1 mole) was dissolved in water (40 ml). 2-Fluorobenzoyl chloride, prepared by refluxing 2-fluorobenzoic acid (14.01 g, 0.1 mole) and thionyl chloride, in toluene (40 ml) was added. A sodium hydroxide solution was added with cooling and vigorous stirring until the reaction mixture was alkaline. After stirring one hour the phases were separated and the aqueous layer was extracted several times with toluene. The solution was dried with sodium sulfate and evaporated in a rotary evaporator under diminished pressure to afford 16.89 g of a colorless oil, $R_f$ = 0.42 (ethyl acetate/*n*-hexane 1:1). This liquid was distilled under reduced pressure, yield 13.89 g (72%), bp 133-135°, 17 Pa, mp 39-43°; ir (neat): ν 2929, 2250, 1651, 1616, 1584, 1495, 1480, 1455, 1397, 1345, 1298, 1229, 1182, 1156, 1109, 1070, 1031, 920, 891, 823, 773, 758, 647, 632, 611, 538, 497, 452 $cm^{-1}$; $^1H$-nmr (deuteriochloroform): δ 3.02 (s, 2.8H) and 3.19 (s, 0.2H, $CH_3$), 4.12 (s, 0.18H) and 4.48 (s, 1.82H, $NCH_2$), 7.02-7.24 (m, 2H, arom), 7.35-7.48 (m, 2H, arom) ppm; $^{13}C$-nmr (deuteriochloroform): δ 166.6 (CO), 160.3 and 155.3 (C-2) $^1J$ ($^{13}C$,$^{19}F$) = -249 Hz, 132.0 and 131.8 (C-4), 128.8 and 128.7 (C-6), 124.5 and 124.4 (C-5), 122.3 and 121.9 (C-1), 115.8 and 115.3 (C-3), 114.8 (CN), 36.0 and 35.9 ($NCH_2$), 34.7 ($NCH_3$) ppm; $^{19}F$-nmr (188.1 MHz) δ -116.2 (0.19F), -116.4 (0.81 F) ppm; ms: (70 eV): m/z 192 (12), 173 (3), 123 (100), 95 (43), 75 (24).

*Anal.* Calcd. for $C_{10}H_9FN_2O$ (192.19): C, 62.49; H, 4.72; N, 14.58. Found: C, 62.23; H, 4.75; N, 14.69.

2-Chloro-*N*-cyanomethyl-*N*-methyl-5-nitrobenzamide **1f**.

Methylaminoacetonitrile hydrochloride (10.56 g, 0.1 mole) was dissolved in water (40 ml). 2-Chloro-5-nitrobenzoyl chloride (prepared by refluxing 2-chloro-5-nitrobenzoic acid (20.16 g, 0.1 mole) and thionyl chloride) in toluene (40 ml) was added. With cooling and vigorous stirring a sodium hydroxide solution was added until the reaction mixture was alkaline. After stirring one hour the product which precipitated was separated by filtration to give 25.21 g (99% yield) of a colorless solid, mp 121°; ir (potassium bromide): ν 3099, 3075, 3036, 2995, 2951, 2864, 2403, 2347, 2245, 1920, 1641, 1593, 1527, 1497, 1467, 1404, 1349, 1299, 1261, 1221, 1185, 1142, 1121, 1088, 1043, 989, 961, 924, 911, 876, 839, 773, 750, 727, 697, 655, 608, 540, 486, 417 $cm^{-1}$; $^1$H-nmr (deuteriochloroform): δ 2.99 (s, 2.6H) and 3.26 (s, 0.4H, $CH_3$), 4.03 (s, 0.28H) and 4.54 (s, 1.72H, $NCH_2$). 7.52 (d. H, $^3J$ = 8.4 Hz, arom, H-3), 8.211 (dd, H, $^3J$ = 8.4 Hz, $^4J$ = 2.15 Hz, arom, H-4), 8.307 (d, H, $^4J$ = 2.15 Hz, arom, H-6) ppm; ms: (70 eV) m/z (%) = 253 (11), 218 (13), 184 (100), 168 (5), 154 (8), 138 (32), 126 (15), 110 (15), 75 (19).

*Anal.* Calcd. for $C_{10}H_8ClN_3O_3$ (253.65): C, 47.35; H, 3.18; N, 16.57. Found: C, 47.44; H, 3.17; N, 16.36.

2-Chloro-*N*-cyanomethyl-*N*-methylnicotinamide **1g**.

Methylaminoacetonitrile hydrochloride (10.56 g, 0.1 mole) was dissolved in water (60 ml). 2-Chloronicotinoyl chloride, [prepared by reacting 2-chloronicotinic acid (15.76 g, 0.1 mole) in thiolyl chloride (70 ml) and distillation of the excess thionyl chloride] dissolved in toluene (60 ml) was added. With cooling and vigorous stirring a sodium hydroxide solution was added until the reaction mixture was alkaline. After one hour stirring the layers were separated. The organic layer was washed three times with water, dried with anhydrous sodium sulfate and concentrated to give 4 g (yield, 19%) of a colorless solid which may be purified by recrystallization from water, mp 78-81°; ir (potassium bromide): ν = 3064, 3026, 2994, 2965, 2935, 2253, 1642, 1605, 1580, 1561, 1499, 1491, 1449, 1437, 1405, 1397, 1339, 1296, 1263, 1237, 1205, 1134, 1107, 1061, 1047, 985, 961, 927, 889, 825, 774, 761, 736, 682, 638, 617 $cm^{-1}$; $^1$H-nmr (deuteriochloroform): δ 3.02 (s, 2.57H, $NCH_3$), 3.25 (s, 0.43H, $NCH_3$), 4.07 (s, 0.3H, $NCH_2$), 4.53 (s, 1.7H, $NCH_2$), 7.36 (dd, H, H-4, $^3J$ = 7.62 Hz, $^4J$ = 4.88 Hz), 7.69 (dd, H, H-5, $^3J$ = 7.62 Hz, $^4J$ = 1.95 Hz), 8.48 (dd, H, H-6, $^3J$ = 4.88 Hz, $^4J$ = 1.95 Hz) ppm; ms: (70 eV): m/z (%) = 209 ($M^+$, 7), 174 (16), 140 (100), 112 (46), 85 (7), 76 (29).

*Anal.* Calcd. for $C_9H_8ClN_3O$ (209.64): C, 51.55; H, 3.85; N, 20.04; Cl, 16.91. Found: C, 51.53; H, 3.90; N, 20.22; Cl, 16.89.

2-Chloro-*N*-cyanomethyl-*N*-methyl-4-nitrobenzamide **1h**.

Methylaminoacetonitrile hydrochloride (10.56 g, 0.1 mole) was dissolved in water (40 ml). 2-Chloro-4-nitrobenzoyl chloride (prepared by refluxing of 20.16 g, 0.1 mole of 2-chloro-4-nitrobenzoic acid and thionyl chloride) in toluene (40 ml) was added. With cooling and vigorous stirring a sodium hydroxide solution was added until the reaction mixture was alkaline. After stirring one hour the product which precipitated was separated by filtration to give 25.02 g (yield, 98%) of a colorless solid, which was dissolved in acetic acid and precipitated by adding water, mp 116-118° (lit 116-118° [9, 10]); ir (potassium bromide): ν = 3107, 3076, 1993, 2946, 2862, 2251, 1658, 1640, 1599, 1593, 1525, 1492, 1467, 1447, 1404, 1351, 1287, 1221, 1182, 1135, 1121, 1087, 1043, 985, 973, 961, 925, 911, 895, 877, 48, 841, 773, 761, 748, 723, 698, 658, 609, 562, 495, 466, 419 $cm^{-1}$; $^1$H-nmr (deuteriochloroform): δ 2.99 (s, 2.6H) and 3.27 (s, 0.4H, $CH_3$), 4.02 (s, 0.28H) and 4.54 (s, 1.82H, $NCH_2$), 7.52 (d, H, $^3J$ = 8.4 Hz, arom, H-6), 8.22 (dd, H, $^3J$ = 8.4 Hz, $^4J$ = 2.15 Hz, arom, H-5), 8.32 (d, H, $^4J$ = 2.15 Hz, arom, H-3) ppm; ms: (70 eV): m/z (%) = 253 (11), 218 (13), 184 (100), 168 (5), 154 (8), 138 (32), 126 (15), 110 (15), 75 (19).

*Anal.* Calcd. for $C_{10}H_8ClN_3O_3$:(253.65): C, 47.35, H, 3.18; N, 16.5. Found: C, 47.43; H, 2.91; N, 16.51.

2,4-Dichloro-*N*-cyanomethyl-*N*-methyl-3,5-dinitrobenzamide **1i**.

Methylaminoacetonitrile hydrochloride (5.28 g, 0.05 mole) was dissolved in water (40 ml). 2,4-Dichloro-3,5-dinitrobenzoyl chloride (prepared by refluxing of 14.05 g, 0.05 mole 2,4-dichloro-3,5-dinitrobenzoic acid and thionyl chloride) in toluene (40 ml) was added. With cooling and vigorous stirring a sodium hydroxide solution was added until the reaction mixture was alkaline. After stirring one hour the product which precipitated was separated by filtration to give 16.02 g of a yellow solid material, which was dissolved in acetic acid and precipitated by adding water, yield, 15.02 g (90%), mp 171-173° (lit 178-180° [9,10]); ir (potassium bromide): ν = 3079, 2986, 2947, 1705, 1659, 1599, 1561, 1540, 1490, 1434, 1404, 1376, 1358, 1342, 1287, 1191, 1125, 1098, 948, 931, 910, 861, 819, 788, 760, 741, 729, 684, 624, 582, 558, 535 $cm^{-1}$; $^1$H-nmr (deuteriochloroform): δ 3.10 (s, 2.8H) and 3.31 (s, 0.2H, $CH_3$), 4.12 (s, 0.1H) and 4.55 (s, 1.9H, $NCH_2$), 8.07 (s, 0.9H, arom, H-6), 8.09 (2, 0.1H, arom, H-6) ppm; ms: (70 eV): m/z (%) = 332 ($M^+$, 8), 315 (6), 297 (16), 267 (11), 266 (6), 265 (65), 264 (10), 263 (100), 247 (5), 217 (30), 171 (18), 143 (20), 108 (11).

4-Methyl-2-methylthio-8-nitro-5-oxo-4,5-dihydro-1,4-benzothiazepine-3-carbonitrile **3**.

Sodium hydride (0.5 g 80% in paraffin oil, 10 mmoles) was added to a solution of 2-chloro-*N*-cyanomethyl-*N*-methyl-4-nitrobenzamide **1h** (1.27 g, 5 mmoles) and carbon disulfide (0.38 g, 0.3 ml 5 mmoles) in dry dimethyl sulfoxide (20 ml) at -10°. After the addition, the mixture was warmed to room temperature and stirred for 6 hours at 100°. After this time it was cooled to -10°. Iodomethane (1.53 g, 0.66 ml, 10 mmoles) was added and the resulting mixture was stirred for 1 hour at rt. Then the solution was poured into ice water. The precipitate was filtered and dried. The material (2.12 g) obtained was dissolved in dichloromethane and was purified by column chromatography on silica gel (Merck 60, eluent ethyl acetate/*n*-hexane 1:1) to afford 0.3 g of an pale yellow solid. Recrystallization from ethanol gave the pure sample (0.29 g, yield, 19%) as colorless needles, mp 156 ° (ethanol); ir (potassium bromide): ν = 3098, 3076, 2989, 2928, 2856, 2212, 1929, 1812, 1655, 1594, 1583, 1521, 1466, 1443, 1423, 1394, 1352, 1303, 1291, 1246, 1166, 1121, 1061, 1033, 981, 955, 926, 909, 874, 848, 788, 766 $cm^{-1}$; $^1$H-nmr (deuteriochloroform): δ 2.63 (s, 3H, $SCH_3$), 3.38 (s, 3H, $NCH_3$), 7.99 (d, H, $^3J$ = 8.4 Hz, arom, H-6) 8.23 (d, H, $^4J$ = 2.3 Hz, arom, H-9), 8.27 (dd, H, $^3J$ = 8.4 Hz, $^4J$ = 2.3 Hz, arom, H-7), ppm; $^{13}$C-nmr (deuteriochloroform): δ 166.2 (C=O), 154.6 (C-2), 148.8 (C-8), 142.6 (C-5a), 138.6 (C-9a), 133.7 (C-6), 126.2 (C-7), 124.5 (C-9), 114.1 (CN), 113.1 (C-3), 35.8 ($N-CH_3$), 18.3 ($SCH_3$) ppm; ms: (70 eV): m/z (%) = 307 (75), 260 (84), 240 (36), 234 (12), 224 (11), 214 (13), 196 (26), 179 (24), 150 (12), 135 (6), 103 (11), 91 (32), 75 (29), 67 (100).

*Anal.* Calcd. for $C_{12}H_9N_3O_3S_2$ (307.35): C, 46.90; H, 2.95; N, 13.67; S, 20.80. Found: C, 47.22; H, 2.84; N, 13.43; S, 20.73.

3,3-Bis(methylthio)-2-[*N*-(2-chloro-5-nitrobenzoyl)-*N*-methylamino]acrylonitrile **4**.

Sodium hydride (0.5 g 80% suspension in paraffin oil, 10 mmoles) was added with stirring and in an argon atmosphere to a solution of 2-chloro-*N*-cyanomethyl-*N*-methyl-5-nitrobenzamide **1f** (1.27 g, 5 mmoles) and carbon disulfide (0.38 g, 0.3 ml 5 mmoles) in dimethylformamide (30 ml, dried over calcium hydride and stored over molecular sieves) at 0°. After the addition, the mixture was stirred for 2 hours. Methyl iodide (1.53 g, 0.66 ml, 10 mmoles) was added and the resulting mixture was stirred for 1 hour at rt. Then the solution was poured into ice water and acidified by adding hydrochloric acid. The precipitate was extracted with ethyl acetate. This material (2.07 g) obtained after evaporation was purified by column chromatography on silica gel (Merck 60, eluent ethyl acetate/*n*-hexane 1:1) to afford 0.96 g of a yellow oil. Recrystallization from ethanol gave the pure sample (0.86 g, yield, 48%) as yellow crystals ($R_f$ = 0.44, ethyl acetate/*n*-hexane 1:1), mp 91-109° (ethanol); ir (potassium bromide): ν = 3094, 2928, 2204, 1669, 1597, 1530, 1477, 1424, 1347, 1292, 1255, 1186, 1139, 1121, 1108, 1075, 1055, 1029, 974, 928, 895, 874, 838, 780, 760, 745, 721, 661, 490, 413 $cm^{-1}$; $^1$H-nmr (deuteriochloroform): δ 2.23 (s, 2.4H, $SCH_3$), 2.43 (s, 2.4H, $SCH_3$), 2.51 (s, 0.6H, $SCH_3$), 2.57 (s, 0.6H, $SCH_3$), 3.00 (s, 0.6H, $NCH_3$), 3.28 (s, 2.4H, $NCH_3$), 8.1 (dd, 0.8H, $^4J$ = 2.15 Hz, $^3J$ = 8.5 Hz, H-4, arom), 7.56 (d, 0.2H, $^3J$ = 8.5 Hz, H-3, arom), 7.63 (d, 0.8H, $^3J$ = 8.5 Hz, H-3, arom), 8.21 (dd, 0.2H, $^4J$ = 2.15 Hz, $^3J$ = 8.5 Hz, H-4, arom), 8.27 (d, 0.8H, $^4J$ = 2.15 Hz, H-6, arom), 8.31 (d, 0.2H, $^4J$ = 2.15 Hz, H-6, arom) ppm; ms: (70 eV): m/z (%) = 310 (M-$SCH_3$, 100), 264 (9), 184 (13), 173, (18), 138 (13), 91 (25).

*Anal.* Calcd. for $C_{13}H_{12}ClN_3O_3S_2$ (357.84): C, 43.64; H, 3.38; N, 11.74. Found: C, 43.54; H, 3.03; N, 11.85.

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* To whom correspondence may be addressed.

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