The Synthesis of 2-Cyano-cyanothioformanilides from 2-(4-Chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitriles Using DBU

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Abstract: A series of 2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitriles were fully characterized. Cyanothioformanilides (thiooxanilonitriles) demonstrate herbicidal activity, and have been used extensively for the preparation of various heterocycles including pyroles, imidazoles, oxazoles, thiazoles, and other fused heterocycles. Furthermore, cyanothioformanilides participate in Diels–Alder and ene-reactions, and can be N-aroylated and, upon addition of water, hydrogen sulfide or hydroxylamine to the nitrile, afford aminooxothioacetylanilines, respectively. Reaction of the 1,2,3-dithiazolines with DBU (3 equiv) at –5 °C gave the corresponding 2-cyano-cyanothioformanilides in near quantitative yields. Treatment of 2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitrile with DBU (4 equiv) at –5 to +20 °C gave 2-isothiocyanatobenzonitrile in 96% yield. The latter compound was also formed directly from 2-cyanothioformanilide on treatment with DBU (1 equiv) in 95% yield. A tentative mechanism for the DBU-mediated dithiazole to cyanothioformanilide transformation is proposed and all compounds were fully characterized.

Key words: Appel salt, DBU, Cyanothioformanilide, isothiocyanate

Cyanothioformanilides (thiooxanilonitriles) demonstrate herbicidal activity, and have been used extensively for the preparation of various heterocycles including pyroles, imidazoles, oxazoles, thiazoles, and other fused heterocycles. Furthermore, cyanothioformanilides participate in Diels–Alder and ene-reactions, and can be N-aroylated and, upon addition of water, hydrogen sulfide or hydroxylamine to the nitrile, afford aminooxothioacetylanilines, aminothiooxacycylanilines (N-arylthiooxamides) or amidinothioformylanilines, respectively.

Cyanothioformanilides are traditionally prepared by the reaction of N-aryl isothiocyanates with cyanide, bis(dialkylamino)acetonitriles and also via dethiohydration of N-arylthiooxamides, thionation–dehydration of N-aryltiooxalamides and thionation–dehydration of aryloxalamides. More recent methods involve treating 2-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)benzenes with either the oxidizing agent m-chloroperbenzoic acid (MCPBA), or with nucleophilic (thiophilic) reagents such as aqueous sodium hydroxide, hydroxyamine, tert-butylamine, tryptamine, o-aminophenethylamine and o-phenylenediamine, triphenylphosphine in moist dichloromethane, and through the use of ethylmagnesium bromide (1 equiv). While the use of triphenylphosphine (2 equiv) was reported to give good yields of the cyanothioformanilides, it was not possible to obtain 2-cyano-cyanothioformanilide (2a) from the reaction of 2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitrile (1a) despite the preparation of the 4,5-dimethoxy analogue in high yield. Nevertheless Kim et al. successfully isolated 2-cyano-cyanothioformanilide (2a) from the reaction of the dithiazolimine 1a with either NH4OH·HCl (4 equiv) in pyridine at ~20 °C for 4 h (27%) or as a by-product from reaction with phosphoranylenedine in low yield (8%). As part of our ongoing investigations of 4,5-dichloro-1,2,3-dithiazolium chloride (Appel salt) and our desire to study the chemistry of 2-cyano-cyanothioformanilides, we required an efficient synthesis that tolerated a range of aryl substituents. Here, we describe the reaction of 2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitriles 1 with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), which affords the desired 2-cyano-cyanothioformanilides 2 in near quantitative yields.

Treatment of 2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitrile (1a) with only DBU (3 equiv) in dichloromethane at ca. –5 °C gave near quantitative conversion of dithiazolimine 1a into 2-cyano-cyanothioformanilide (2a) and no sulfur formation could be observed by TLC. The use of an additional equivalent of DBU led to the clean formation of 2-isothiocyanatobenzonitrile (3), which could also be formed directly from a pure sample of 2-cyano-cyanothioformanilide (1a; Scheme 1). No reaction occurred between the dithiazolimine 1a and three equivalents of either pyridine, 1,4-diazabicyclo[2.2.2]octane (DABCO), or 4-(N,N-dimethylamino)pyridine (DMAP) or triethylamine in dichloromethane at ~20 °C.

The high-yielding formation of the isothiocyanate 3 is worthy of note; since 1995, only four reports have appeared on the conversion of 2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitrile (1a) with only DBU (3 equiv) in dichloromethane at ca. –5 °C. The reaction afforded the desired 2-cyano-cyanothioformanilide (2a) in 96% yield.

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Scheme 1 Reagents and conditions: (i) DBU (3 equiv), CH2Cl2, –5 °C, 5 min, 93%; (ii) DBU (1 equiv), 20 °C, 0.5 h, 95%; (iii) DBU (4 equiv), CH2Cl2, –5 to +20 °C, 0.5 h, 96%.
These have involved the use of either MCPBA, \(^\text{16}\) ethylmagnesium bromide (2 equiv) in hot anhydrous THF under an argon atmosphere, \(^\text{24h,25}\) or sodium hydride (2.2 equiv) in anhydrous THF at 67 °C for 18 hours.\(^\text{24h}\) Furthermore, only two methods have appeared on the conversion of cyanothioformanilides into \(N\)-aryl isothiocyanates using either ethylmagnesium bromide (2 equiv) in hot, anhydrous THF under an argon atmosphere, \(^\text{24h,25}\) or in neat 2,6-lutidine using microwave irradiation.\(^\text{24h}\) Despite this, the conversion of the cyanothioformanilide (2a) into isothiocyanate (3) in the presence of DBU (1 equiv) was not surprising. A quick screen of alternative 3° amine bases (1 equiv) in dichloromethane at ~20 °C showed that pyridine was unreactive, whereas the use of DABCO or DMAP led to incomplete conversion after two days, and that triethylamine could effect the conversion slowly (10 h) to give the isothiocyanate (3) in 65% yield. The unusual reactivity of dithiazole towards DBU was, however, at first unclear. None of the alternative bases screened (pyridine, DABCO, DMAP, and Et₃N) under similar reaction conditions (3 equiv base at ~20 °C in CH₂Cl₂) showed any reactivity.

DBU and DBN are commonly used to effect base-induced dehydrohalogenations and other eliminations to produce carbon–carbon and carbon–heteroatom multiple bonds.\(^\text{27}\) As such, these bicyclic amidines are often referred to as non-nucleophilic strong bases.\(^\text{28}\) Nevertheless, a careful search of the literature revealed multiple reports of nucleophilic behavior for both DBU and DBN, notably in reactions with either phosphorus\(^\text{29}\) or carbon\(^\text{30}\) electrophiles. In search of the literature revealed multiple reports of nucleophilic attack via the DBU cleophilic behavior for both DBU and DBN, notably in reactions with either phosphorus\(^\text{29}\) or carbon\(^\text{30}\) electrophiles. In search of the literature revealed multiple reports of nucleophilic attack via the DBU

A tentative mechanistic rationale for the reaction can be proposed as follows. Nucleophilic attack via the DBU amide nitrogen at the dithiazole S(2) ring sulfur and subsequent ring-opening can afford the disulfide (6). A second equivalent of DBU could then abstract HCl to give the neutral disulfide (7). Further nucleophilic attack by a third equivalent of DBU could cleave the disulfide S–S bond to ultimately give the cyanothioformanilide and the neutral sulfane (8) (Scheme 2).

### Table 1: Reaction of Anthranilonitriles 4 with 4,5-Dichloro-1,2,3-dithiazolium Chloride (5) Followed by Treatment with Pyridine

<table>
<thead>
<tr>
<th>R</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1a</td>
<td>92</td>
</tr>
<tr>
<td>6-Me</td>
<td>1b</td>
<td>91</td>
</tr>
<tr>
<td>5-O₂N</td>
<td>1c</td>
<td>80</td>
</tr>
<tr>
<td>4-Cl</td>
<td>1d</td>
<td>87</td>
</tr>
<tr>
<td>5-Cl</td>
<td>1e</td>
<td>86</td>
</tr>
<tr>
<td>4-MeO</td>
<td>1f</td>
<td>74</td>
</tr>
<tr>
<td>4,5-(MeO)₂</td>
<td>1g</td>
<td>76</td>
</tr>
</tbody>
</table>

\(^\text{a}\) Reaction conditions: 4 (0.65 mmol), 5 (1 equiv), CH₂Cl₂, ~20 °C, 1 h then pyridine (2 equiv), ~20 °C, 2 h.

### Table 2: Reaction of 2-(4-Chloro-5-H-1,2,3-dithiazol-5-ylideneamino)benzonitriles 1 with DBU

<table>
<thead>
<tr>
<th>R</th>
<th>Temp (°C)</th>
<th>Time (min)</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
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<td>−5</td>
<td>5</td>
<td>2a</td>
<td>93</td>
</tr>
<tr>
<td>6-Me</td>
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</tr>
<tr>
<td>5-O₂N</td>
<td>−5</td>
<td>10</td>
<td>2c</td>
<td>69</td>
</tr>
<tr>
<td>5-O₂N</td>
<td>−78 to 20</td>
<td>45</td>
<td>2c</td>
<td>93</td>
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<tr>
<td>4-Cl</td>
<td>−5</td>
<td>15</td>
<td>2d</td>
<td>82</td>
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<tr>
<td>4-Cl</td>
<td>−78 to 20</td>
<td>35</td>
<td>2d</td>
<td>91</td>
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<td>5-Cl</td>
<td>−5</td>
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<td>87</td>
</tr>
<tr>
<td>4-MeO</td>
<td>−5</td>
<td>15</td>
<td>2f</td>
<td>95</td>
</tr>
<tr>
<td>4,5-(MeO)₂</td>
<td>−5</td>
<td>15</td>
<td>2g</td>
<td>88</td>
</tr>
</tbody>
</table>

\(^\text{a}\) Reaction conditions: 1 (0.40 mmol), DBU (3 equiv), anhyd CH₂Cl₂ (2 mL).
cyanothioformanilides found to date. Reactions provide the most efficient route to this class of isothiocyanatobenzonitrile (1). 2- (4-Chloro-5H-1,2,3-dithiazol-5-ylidene)benzonitrile (1a); Typical Procedure
To a stirred solution of 4,5-dichloro-1,2,3-dithiazolium chloride (5; 352.4 mg, 1.69 mmol) in CH2Cl2 (4 mL) at ~20 °C and protected with CaCl2 drying tube, was added 2-aminobenzonitrile (4a; 200 mg, 1.69 mmol). After 1 h, pyridine (273.4 µL, 3.38 mmol, 2 equiv) was added dropwise, and the reaction mixture was stirred at ~20 °C for an additional 2 h. The reaction mixture was adsorbed onto silica and chromatography (hexane) gave S8 (traces). Further elution (hexane–CH2Cl2, 8:2) gave 4-chloro-5H-1,2,3-dithiazole-5-thione (9; 10 mg, 6%) and (hexane–CH2Cl2, 2:8) gave the title compound 1a.

Yield: 395 mg (92%); yellow crystals; mp 125–126 °C (Lit. 21 128 °C) (cyclohexane–CH2Cl2).

IR: 3088 (w), 3025 (w; ArCH), 2238 (m; C≡N), 1593 (s), 1562 (s), 1461 (m), 1149 (s), 961 (s), 750 (s), 730 (s). MS (EI): [M+ + 2] = 255 (35) [M+], 192 (99), 160 (71), 134 (10), 75 (33), 64 (100), 51 (31). UV/Vis (CH2Cl2): λmax (log ε) = 231 (3.33), 268 (inf; 2.79), 302 (2.65), 379 (2.92), 398 (inf; 2.85), 423 nm (inf; 2.56); identical to an authentic sample.

Scheme 2
It is worthy of note that the sulfane sulfur could migrate from N to C(6) and similar N–P to C(6)–P migrations have been reported with DBU adducts.29i While isolation from N to C(6) and similar N–P to C(6)–P migrations of less than this amount gave incomplete conversion of the anticipated sulfane, it is worthy of note that the sulfane sulfur could migrate from the reaction mixture tentatively added support to the entrapment of the sulfur, possibly as the sulfane.

Treatment of 2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitriles 1a–g with DBU (3 equiv) in dichloromethane at ambient or sub-ambient temperatures provides a simple and high-yielding protocol for the preparation of 2-cyano-cyanothioformanilides 2a–g. In one case, 2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitrile (1a) was reacted with DBU (4 equiv) to afford 2-isothiocyanatobenzonitrile (3) in high yield. These conditions provide the most efficient route to this class of cyanothioformanilides found to date.

CH2Cl2 was freshly distilled from CaH2 under argon. Reactions were protected from atmospheric moisture by CaCl2 drying tubes. Anhydrous Na2SO4 was used for drying organic extracts, and all volatiles were removed under reduced pressure. All reaction mixtures and column eluents were monitored by thin-layer chromatography using commercial glass-backed TLC plates (Merck Kieselgel 60 F254); the plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography was used throughout for all non-TLC-scale chromatographic separations using Merck Silica Gel 60 (0.063 mm). Melting points were determined using a PolyTherm-A, Wagner & Munz, Koefler-Hotstage Microscope apparatus. Solvents used for recrystallization are indicated after the melting point. UV spectra were obtained using a Perkin-Elmer Lambda-25 UV/Vis spectrophotometer; inflections are identified by the abbreviation ‘inf’. IR spectra were recorded on a Shimadzu FTIR-NIR Prestige-21 spectrometer with a Pike Miracle Ge ATR accessory; strong (s), medium (m) and weak (w) peaks are abbreviated. 1H and 13C NMR spectra were recorded on a Bruker Avance 300 instrument (300 and 75 MHz, respectively). Deuterated solvents were used for homonuclear lock and the signals are referenced to the deuterated solvent peaks. Low resolution (EI) mass spectra were recorded on a Shimadzu QP2010 GCMS with direct inlet probe. 4,5-Dichloro-1,2,3-dithiazole chloride 1b was prepared according to the literature procedure.33

2-(4-Chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitrile (1a); Typical Procedure
To a stirred solution of 4,5-dichloro-1,2,3-dithiazolium chloride (5; 352.4 mg, 1.69 mmol) in CH2Cl2 (4 mL) at ~20 °C and protected with CaCl2 drying tube, was added 2-aminobenzonitrile (4a; 200 mg, 1.69 mmol). After 1 h, pyridine (273.4 µL, 3.38 mmol, 2 equiv) was added dropwise, and the reaction mixture was stirred at ~20 °C for an additional 2 h. The reaction mixture was adsorbed onto silica and chromatography (hexane) gave S8 (traces). Further elution (hexane–CH2Cl2, 8:2) gave 4-chloro-5H-1,2,3-dithiazole-5-thione (9; 10 mg, 6%) and (hexane–CH2Cl2, 2:8) gave the title compound 1a.

Yield: 395 mg (92%); yellow crystals; mp 125–126 °C (Lit.21 128 °C) (cyclohexane–CH2Cl2).

IR: 3088 (w), 3025 (w; ArCH), 2238 (m; C≡N), 1593 (s), 1562 (s), 1461 (m), 1149 (s), 961 (s), 750 (s), 730 (s). MS (EI): [M+ + 2] = 255 (35) [M+], 192 (99), 160 (71), 134 (10), 75 (33), 64 (100), 51 (31). UV/Vis (CH2Cl2): λmax (log ε) = 231 (3.33), 268 (inf; 2.79), 302 (2.65), 379 (2.92), 398 (inf; 2.85), 423 nm (inf; 2.56); identical to an authentic sample.

2-(4-Chloro-5H-1,2,3-dithiazol-5-ylideneamino)-6-methylbenzonitrile (1b) Similar treatment of 2-amino-6-methylbenzonitrile (4b; 200 mg, 1.52 mmol), 4,5-dichloro-1,2,3-dithiazolium chloride (5; 315.9 mg, 1.52 mmol) and pyridine (245.9 µL, 3.04 mmol, 2 equiv) in CH2Cl2 (4 mL) gave the title compound 1b.

Yield: 369.3 mg (91%); yellow cotton fibers; mp 109–110 °C (cyclohexane–CH2Cl2).

IR: 3088 (w), 3025 (w; ArCH), 2238 (m; C≡N), 1593 (s), 1562 (s), 1461 (m), 1149 (s), 961 (s), 750 (s), 730 (s). MS (EI): [M+ + 2] = 255 (35) [M+], 192 (99), 160 (71), 134 (10), 75 (33), 64 (100), 51 (31). UV/Vis (CH2Cl2): λmax (log ε) = 231 (3.33), 268 (inf; 2.79), 302 (2.65), 379 (2.92), 398 (inf; 2.85), 423 nm (inf; 2.56); identical to an authentic sample.
5-Chloro-2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitrile (1e)
Similar treatment of 2-amino-5-chlorobenzonitrile (4c; 200 mg, 1.31 mmol), 4,5-dichloro-1,2,3-dithiazolium chloride (5; 283.1 mg, 1.31 mmol) and pyridine (212 µL, 2.62 mmol, 2 equiv) in CH₂Cl₂ (4 mL) gave the title compound 1e.

Yield: 323.3 mg (86%); yellow cotton fibers; mp 147–148 °C (cyclohexane–CH₂Cl₂).

IR: 3071 (w; ArCH), 2237 (w; C≡N), 1568 (s), 1492 (s), 876 (s), 865 (s), 816 (s), 769 (s) cm⁻¹.

1H NMR (300 MHz, DMSO-d₆): δ = 8.09 (d, J = 2.4 Hz, 1 H, ArH-6), 7.85 (dd, J = 8.8, 2.4 Hz, 1 H, ArH-4), 7.51 (d, J = 8.8 Hz, 1 H, ArH-3).

13C NMR (75 MHz, DMSO-d₆): δ = 163.5, 152.0, 146.7, 135.3 (ArCH), 133.5 (ArCH), 129.9, 119.7 (ArCH), 115.4 (C≡N), 106.9 (C≡N).

UV/Vis (CH₂Cl₂): λₘₐₓ (log ε) = 378 nm (1.0), 308 (2.76), 265 (2.81), 218 (2.81), 237 (2.39), 247 (2.96), 229 nm (3.07).

Anal. Calc'd for C₂₁H₁₄ClN₄O₂S: C, 56.6; H, 2.9; N, 13.0. Found: C, 56.5; H, 3.1; N, 13.0.

4-Chloro-2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitrile (1f)
Similar treatment of 2-amino-4,5-dimethoxybenzonitrile (4f; 200 mg, 1.35 mmol), 4,5-dichloro-1,2,3-dithiazolium chloride (5; 281.8 mg, 1.35 mmol) and pyridine (218 µL, 2.70 mmol, 2 equiv) in CH₂Cl₂ (4 mL) gave the title compound 1f.

Yield: 282.7 mg (74%); orange needles; mp 163–164 °C (cyclohexane–CH₂Cl₂).

IR: 2965 (w) and 2835 (w; CH₃), 2221 (s; C≡N), 1589 (s), 1495 (s), 1249 (s), 1095 (s), 1022 (s), 871 (s), 821 (s), 756 (s) cm⁻¹.

1H NMR (300 MHz, CDCl₃): δ = 7.66 (d, J = 8.7 Hz, 1 H, ArH-6), 6.81 (dd, J = 8.7, 2.4 Hz, 1 H, ArH-5), 6.75 (d, J = 2.4 Hz, 1 H, ArH-3), 3.88 (s, 3 H, CH₃).

13C NMR (75 MHz, DMSO-d₆): δ = 164.3, 163.6, 156.0, 146.3, 135.7 (ArCH), 116.9 (C≡N), 112.4 (ArCH), 103.4 (ArCH), 95.7 (C≡N), 56.1 (CH₃).

UV/Vis (CH₂Cl₂): λₘₐₓ (log ε) = 270 nm (2.81), 210 (2.81), 240 (2.81), 270 (2.81), 302 (2.53), 367 (2.75), 411 nm (inf; 2.51).

Anal. Calc'd for C₁₉H₁₄ClN₄O₂S: C, 42.3; H, 2.1; N, 14.8. Found: C, 42.4; H, 2.0; N, 14.8.

2-(4-Chloro-5H-1,2,3-dithiazol-5-ylideneamino)-4,5-dimethoxybenzonitrile (1g)
Similar treatment of 2-amino-4,5-dimethoxybenzonitrile (4g; 200 mg, 1.12 mmol), 4,5-dichloro-1,2,3-dithiazolium chloride (5; 233.5 mg, 1.12 mmol) and pyridine (181 µL, 2.24 mmol, 2 equiv) in CH₂Cl₂ (4 mL) gave the title compound 1g.

Yield: 266.4 mg (76%); orange crystals; mp 156–157 °C (cyclohexane–EtOH).
To a stirred solution of 2-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)amino)benzonitrile (1a; 100 mg, 0.39 mmol) in distilled CH₂Cl₂ (2 mL) cooled to ca. −5 °C and protected with a CaCl₂ drying tube, was added in one portion. DBU (175 µL, 1.17 mmol, 3 equiv.) After 5 min at ca. −5 °C, no starting material remained (TLC) and the reaction mixture was adsorbed onto silica. Chromatography (CH₂Cl₂) gave the title compound 2a.

Yield: 67.8 mg (93%); orange powder; mp 100–101 °C (Lit.19 104–105 °C (pentane–CH₂Cl₂)).

IR: 3113 (w) and 3036 (w; ArCH), 2241 (m; C≡N), 1681 (s), 1590 (m), 1536 (m), 1517 (s), 1418 (m), 1374 (s), 1307 (m), 1278 (s), 1234 (m), 1172 (s), 1125 (s), 1052 (w), 990 (m), 893 (m), 779 (s) cm⁻¹.

UV/Vis (CH₂Cl₂): \( \lambda_{\text{max}} \) (log \( e \)) = 350 (inf; 2.59), 379 (inf; 2.68), 398 (2.72), 418 (inf; 2.69), 443 nm (inf; 2.48).


colorless crystalline solid; mp 173–174 °C (Lit.19 173–175 °C (pentane–CH₂Cl₂)).

Yield: 7.94 mg (95%); red powder; mp >300 °C (pentane–CH₂Cl₂).

IR: 3611 (w), 3399 (w; NH), 3053 (w; CH₃), 2236 (w; C≡N), 1597 (m), 1483 (s), 1443 (s), 1346 (s), 1261 (m), 1177 (m), 843 (m), 733 (m) cm⁻¹.

H NMR (300 MHz, DMSO-d₆): \( \delta = 8.58 \) (d, \( J = 7.2 \) Hz, 1 H, ArH-6), 8.33 (dd, \( J = 7.2, 9.0 \) Hz, 1 H, ArH-4), 7.64 (d, \( J = 9.0 \) Hz, 1 H, ArH-3); NH missing.

1C NMR (75 MHz, DMSO-d₆): \( \delta = 162.7, 160.75, 141.5, 128.85 \) (ArCH), 128.0 (ArCH), 117.7 (CsN), 116.1 (CsN), 105.7 (CsN).

MS (E): \( m/z \) (%) = 232 (19) [M⁺], 205 (100), 199 (8), 186 (6), 175 (36), 159 (37), 147 (24), 132 (14), 115 (26), 99 (7), 94 (14), 88 (17), 75 (21), 64 (21), 57 (14), 50 (13).

UV/Vis (CH₂Cl₂): \( \lambda_{\text{max}} \) (log \( e \)) = 228 (3.10), 254 (2.97), 283 (2.75), 332 (2.79), 348 nm (2.85).

Anal. Calcd for C₁₇H₁₃N₅S₂: C, 46.5; H, 1.7; N, 24.1. Found: C, 46.5; H, 1.8; N, 24.1.

1H NMR (300 MHz, CD₃OD): \( \delta = 8.75 \) (d, \( J = 9.0 \) Hz, 1 H, ArH-3) and 8.28 (d, \( J = 9.0 \) Hz, 1 H, ArH-2); ArCl-1, C≡N).

13C NMR (75 MHz, CD₃OD): \( \delta = 162.4 \) (CsS), 154.6 (ArC), 137.4 (ArC), 134.2 (ArCH), 123.4 (ArCH), 117.6 (CaN), 117.1 (CsN), 104.7 (CsN).

UV/Vis (CH₂Cl₂): \( \lambda_{\text{max}} \) (log \( e \)) = 230 (3.60), 250 (3.45), 333 nm (3.57); identical to an authentic sample.

1H NMR (300 MHz, CDCl₃): \( \delta = 8.75 \) (d, \( J = 9.0 \) Hz, 1 H, ArH-3) and 8.28 (d, \( J = 9.0 \) Hz, 1 H, ArH-2); ArCl-1, C≡N).

13C NMR (75 MHz, CDCl₃): \( \delta = 162.4 \) (CsS), 154.6 (ArC), 137.4 (ArC), 134.2 (ArCH), 123.4 (ArCH), 117.6 (CaN), 117.1 (CsN), 104.7 (CsN).

UV/Vis (CH₂Cl₂): \( \lambda_{\text{max}} \) (log \( e \)) = 230 (3.60), 250 (3.45), 333 nm (3.57); identical to an authentic sample.

1H NMR (300 MHz, CDCl₃): \( \delta = 8.75 \) (d, \( J = 9.0 \) Hz, 1 H, ArH-3) and 8.28 (d, \( J = 9.0 \) Hz, 1 H, ArH-2); ArCl-1, C≡N).

13C NMR (75 MHz, CDCl₃): \( \delta = 162.4 \) (CsS), 154.6 (ArC), 137.4 (ArC), 134.2 (ArCH), 123.4 (ArCH), 117.6 (CaN), 117.1 (CsN), 104.7 (CsN).

UV/Vis (CH₂Cl₂): \( \lambda_{\text{max}} \) (log \( e \)) = 230 (3.60), 250 (3.45), 333 nm (3.57); identical to an authentic sample.
5-Chloro-2-(cyanothioformamido)benzonitrile (2e)

Similarly, treatment of 2-(4-chloro-5H-1,2,3-dithiazol-5-yldieneamino)-5-chlorobenzonitrile (1e) 100 mg, 0.35 mmol) cooled to ca. –5 °C with DBU gave, after chromatography (CH2Cl2), the title compound 2e.

Yield: 73.7 mg (88%); orange crystals; mp 145–146 °C (cyclohexane–EtOH).

IR: 3198 (w), 3103 (w; NH), 2230 (m; C≡N), 1516 (s), 1534 (s), 1271 (s), 1236 (s), 983 (s), 866 (s), 779 (s) cm⁻¹.

1H NMR (300 MHz, CDCl3): δ = 7.83 (s, 1 H, Ar-H-3), 7.16 (s, 1 H, Ar-H-5), 3.97 (s, 3 H, CH3O), 3.96 (3 H, CH3O); NH missing.

13C NMR (75 MHz, DMSO-d6): δ = 165.3 (C=S), 153.0 (ArC), 148.4 (ArC), 133.5 (ArC), 116.1 (C≡N), 114.6 (ArC), 113.5 (C≡N), 110.4 (ArC), 100.5 (CC≡N), 56.3 (CH3O), 56.2 (CH2O).

UV/Vis (75 MHz, DEPT-135, DMSO-d6): δ = 114.65 (ArC), 110.4 (ArC), 56.3 (CH3O), 56.2 (CH2O).

MS (EI): m/z (δ) = 247 (100) [M+], 232 (7), 220 (50), 214 (15), 205 (27), 195 (35), 180 (21), 177 (28), 162 (13), 150 (10), 134 (13), 119 (17), 104 (13), 90 (7), 83 (7), 76 (15), 70 (23), 50 (11).

UV/Vis (CH3Cl2): λmax (log ε) = 230 (3.56), 265 (3.48), 277 (inf; 3.51), 287 (3.56), 331 (inf; 3.07), 347 (3.11), 375 (3.16), 395 nm (inf; 3.07).

Anal. Calcd for C16H13N3O3S: C, 53.4; H, 3.7; N, 17.0. Found: C, 53.4; H, 3.8; N, 16.9.

2-Isothiocyanatobenzonitrile (3) from 2-(Cyanothioformamido)benzonitrile (2a)

To a stirred solution of 2-(cyanothioformamido)benzonitrile (2a) 100 mg, 0.32 mmol) cooled to –5 °C, and protected with a CaCl2 drying tube, was added dropwise, DBU (79.3 μL, 0.53 mmol, 1 equiv). The mixture was then allowed to stir at 20 °C, until no starting material remained (TLC). The reaction mixture was adsorbed onto silica and purified by chromatography (CH2Cl2–tert-butyl methyl ether, 9:1) to give the title compound 3.

Yield: 81.4 mg (96%); colorless needles; mp 66–67 °C (Lit. 24h 64 °C) (cyclohexane).

IR: 2232m (C≡N), 1624 (m), 1597 (m), 1493 (s), 1319 (s), 1099 (m), 752 (s).

1H NMR (300 MHz, CDCl3): δ = 8.26 (d, J = 7.8 Hz, 1 H, Ar-H), 7.80 (d, J = 7.8 Hz, 1 H, Ar-H), 7.73 (dd, J = 7.8, 7.8 Hz, 1 H, Ar-H), 7.50 (dd, J = 7.35, 7.35 Hz, 1 H, Ar-H).

MS (EI): m/z (δ) = 161 (12) [M+ + 1], 160 (100) [M+], 133 (7), 116 (10), 102 (41), 91 (4), 76 (36) [C6H4], 75 (25), 70 (8), 64 (10), 51 (17), 50 (12), 44 (75), 43 (10); identical to an authentic sample.

2-Isothiocyanatobenzonitrile (3) from 2-(4-Chloro-5H-1,2,3-dithiazol-5-yldieneamino)benzonitrile (1a)

To a stirred solution of 2-(4-chloro-5H-1,2,3-dithiazol-5-yldieneamino)benzonitrile (1a) 100 mg, 0.39 mmol) in distilled CH2Cl2 (2 mL) at ~20 °C and protected with a CaCl2 drying tube, was added dropwise, DBU (79.3 μL, 0.53 mmol, 1 equiv). The mixture was then allowed to stir at ~20 °C, until no starting material remained (TLC). The reaction mixture was adsorbed onto silica and purified by chromatography (CH2Cl2–tert-butyl methyl ether, 9:1) to give the title compound 3.

Yield: 59.3 mg (95%); colorless needles; mp 66–67 °C (Lit. 24h 64 °C) (cyclohexane); identical to that described above.

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References