The Reaction of Cyanothioformamide with Isocyanates − Formation of a Disulfide by Reduction of a Thiocarbonyl Group[‡]

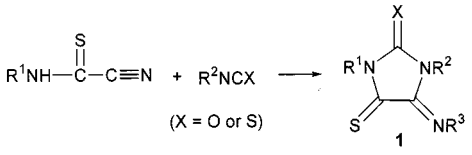
Roger Ketcham,*[a] Ernst Schaumann,*[b] and Gunadi Adiwidjaja[b]

Dedicated to Professor Ralf Miethchen on the occasion of his 60th birthday

Keywords: Thioamides / Isocyanates / Cyclizations / Imidazolidines

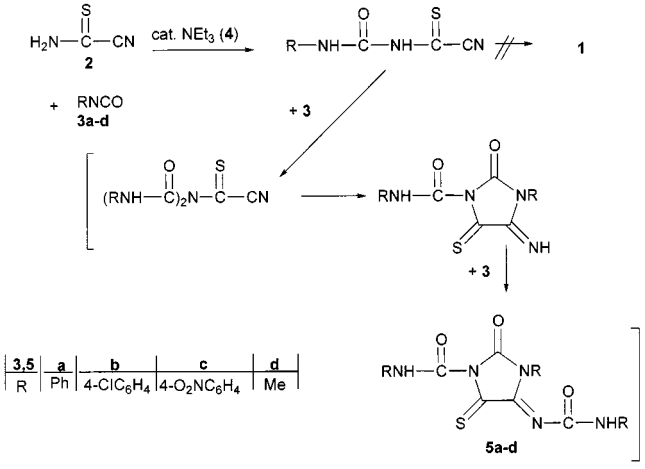
The reactions of the title compounds are governed by sulfur redox chemistry. Thus, cyanothioformamide **2** reacts with aryl isocyanates **3a–c** to give bis[3-aryl-1-(arylcarbamoyl)-2-oxo-4-(arylcarbamoylimino)imidazolidin-5-yl] disulfides **6**, as shown by an X-ray crystallographic investigation of product **6a**. Reaction with methyl isocyanate (**3d**) gives the related trisulfide **7d** along with disulfide **6d**. A desulfurized product, imidazolinone **10**, could also be isolated from the methyl isocyanate reaction and was characterized by X-ray diffraction analysis. In boiling ethanol, **6a** and **7d** undergo reductive desulfurization to give 4-iminoimidazolidin-2-one **11a** and the methyl analog **11d**, respectively.

The reactions of *N*-substituted cyanothioformamides with electrophiles have provided a number of interesting heterocyclic ring closures.[2−5] In particular, their reactions with isocyanates[4] and isothiocyanates[5] give 1,3-disubstituted imidazolidine systems **1** (Scheme 1). In order to determine the scope of these reactions and to evaluate a possible route to the 1-unsubstituted analogs (R^1 = H), it was deemed of interest to study similar reactions using the unsubstituted cyanothioformamide **2**. This compound was first prepared in 1815 by Gay-Lussac[6] from cyanogen and hydrogen sulfide; in fact, it provided one of his examples for establishing the law of combining proportions. In the intervening 185 years, only about 20 references to this compound have appeared in the chemical literature, none of which has explored its synthetic utility. We have found that the conventional synthesis of **2** from 1 equiv. each of cyanogen and hydrogen sulfide[7] can be improved by using diethyl ether as a solvent and by adding triethylamine (**4**) as a catalyst, and that the crude product can best be crystallized from dichloromethane/pentane.



Scheme 1

We first treated **2** with phenyl isocyanate (**3a**) in diethyl ether, using amine **4** as a catalyst. The crude product, obtained in good yield, was found to melt over a wide temperature range. However, repeated recrystallization gradually provided a single, higher melting product, combustion analysis of which was consistent with it being a 3:1 adduct of **3a** and **2**. This composition suggested that the product might have had the imidazole structure **5a**, derived from the sequence of reactions shown in Scheme 2.



Scheme 2

However, that this structure was incorrect was indicated by a signal at δ = 6.6 in the ^{1}H NMR spectrum, by the fact that the mass spectrum showed a peak at *m*/*z* = 2 [M + 1], and by the lack of color of the product, which was inconsistent with the presence of an intact thiocarbonyl group. Thus, we carried out an X-ray crystallographic analysis, which revealed (Figure 1) that the product was apparently derived from **5a** by reduction to the dimer **6a**. The molecule has an almost planar imidazolidine ring and this plane also includes the double-bonded heteroatoms O21 and N51, as

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[a] School of Pharmacy, Department of Pharmaceutical Chemistry, University of California,
San Francisco, CA 94143-0446, USA
[b] Institut für Organische Chemie, Technische Universität Clausthal,
Leibnizstraße 6, 38678 Clausthal-Zellerfeld, Germany
Fax: (internat.) + 49-(0)5323/72-2858
E-mail: ernst.schaumann@tu-clausthal.de
[c] Mineralogisch-Petrographisches Institut, Universität Hamburg, 20146 Hamburg, Germany

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well as the exocyclic phenylcarbamoyl groups; only the benzene ring C11−C16 adopts an almost perpendicular orientation. The bond lengths in the incorporated biuret and urea units correspond to those in a related carbamoyl-substituted imidazolidinedione.[8] The S41−S41′ distance is very close to that in diphenyl disulfide.[9] Moreover, in close analogy to the orthogonal arrangement of the benzene rings in diphenyl disulfide, the dihedral angle C4−S41−S41′−C4′ is 100.7°.

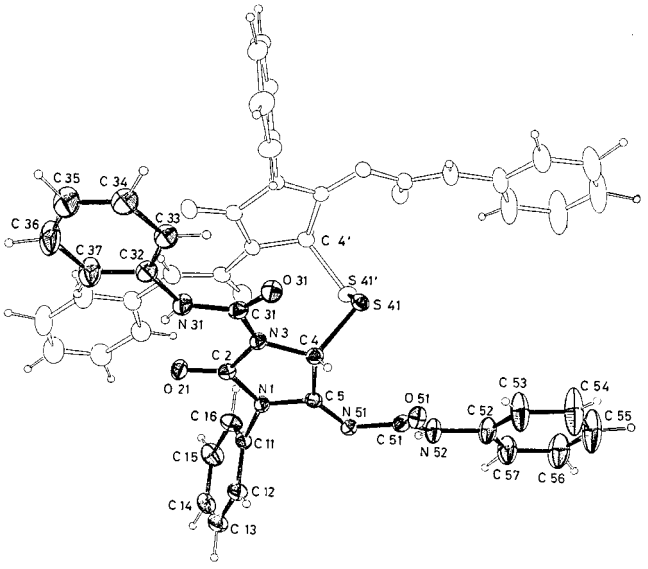
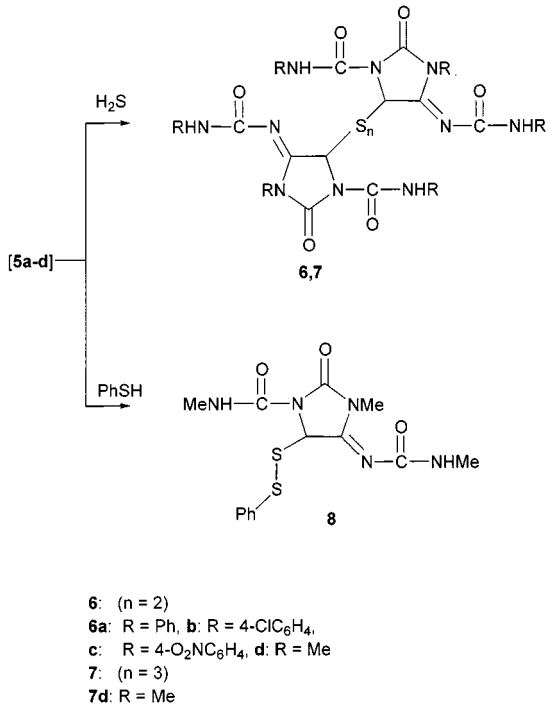


Figure 1. ORTEP drawing of disulfide **6a**; salient bond lengths [Å]: C4−S41 1.820(3), S41−S41′ 2.016(1), N1−C2 1.386(3), N1−C5 1.374(3), N3−C2 1.385(3), N3−C4 1.450(3), N51−C5 1.260(3)

On the basis of the X-ray crystal structure, the NMR peak at δ = 6.6 can be assigned to the hydrogen atom at C-4. The X-ray study (Figure 1) also revealed that the purified product exists in the *meso* form. The racemic form was probably also present in the crude reaction mixture, but it appears to undergo at least partial rearrangement to the higher melting *meso* form via an enamine tautomer. Conversion into the *meso*-disulfide would account for the gradual formation of product **6a** in successive crops upon repeated recrystallization. Sulfur could be isolated from the reaction mixture and the intense color of the reaction solution was suggestive of the formation of some paracyanogen from **2**.[10] The parallel product hydrogen sulfide is the most probable candidate for the reducing agent (Scheme 3). The reduction of a thiocarbonyl group to a sulfide unit is exceptional; thioamides usually serve as thioacylating agents[11] or, in the presence of another adjacent thiocarbonyl group, may be reduced to a methylene group.[12]

p-Chlorophenyl isocyanate (**3b**) and *p*-nitrophenyl isocyanate (**3c**) were found to react quite rapidly with **2** in diethyl ether to provide good crude yields of **6b**,**c**. The MS data of **6b** indicate the presence of a small amount of the trisulfide **7b**. Purification of the products, especially of **6c**, proved difficult because of their low solubilities.

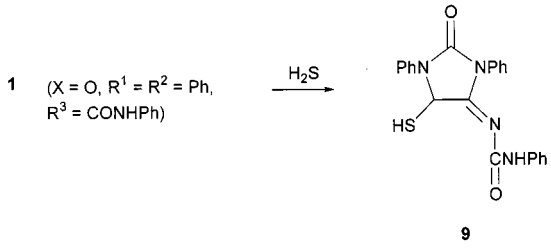
In contrast to its aryl congeners, methyl isocyanate (**3d**) was found to react more slowly with **2** and did not provide disulfide **6d** directly; instead, the main product was trisulfide **7d**, apparently formed by successive thiophilic attacks of hydrogen sulfide on the thiocarbonyl group. Recrystallization of **7d** from $CHCl_3$ resulted in partial extrusion of sulfur to give disulfide **6d**, which was also evident in the MS. The MS also showed the presence of some tetrasulfide.



Scheme 3

The presence of thione **5d** was confirmed by adding thiophenol to the reaction mixture, which gave the mixed disulfide **8**.

Attempts to produce an analogous reduced dimer or a thiophenol adduct from **1** (X = O, R^1 = Ph, R^2 = Me, R^3 = H) were unsuccessful. On the other hand, the 4-N-substituted compound **1** (R^1 = R^2 = Ph, R^3 = CONHPh) was reduced to the thiol **9** with hydrogen sulfide (Scheme 4).



Scheme 4

Besides trisulfide **7d**, work-up of the original mother liquor provided a product formally derived from **2** and 3 mol of **3d** followed by loss of carbonyl sulfide. Its ^1H and ^{13}C NMR spectroscopic data are consistent with the imidazoline structure **10**; this structure assignment was confirmed by an X-ray structural investigation (Figure 2). In view of the apparent catalytic effect of **4**, we assume that the reaction is initiated by the generation of a 1:1 adduct in analogy to thiazolidine formation from *N*-substituted **2** and aryl iso-

thiocyanates.[4] Subsequent loss of carbonyl sulfide yields the intermediate amidine, which can undergo successive reactions with 2 mol of **3d** to give **10**. Alternatively, loss of carbonyl sulfide could follow addition of the second mol of **3d** (Scheme 5).

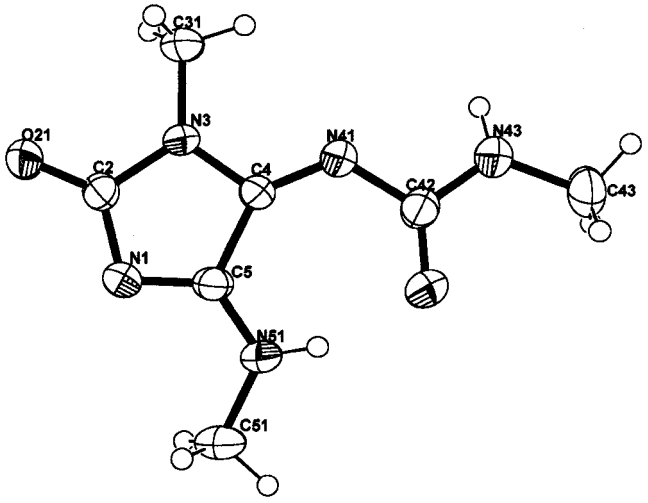
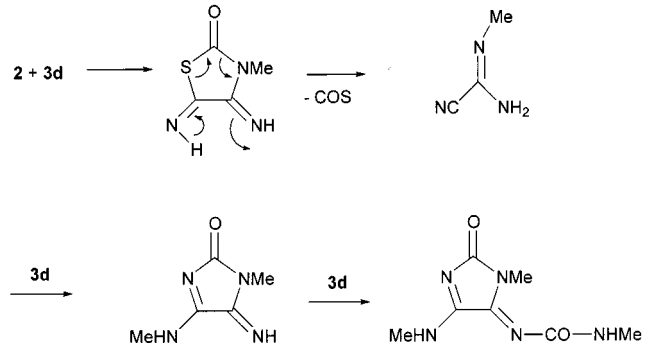
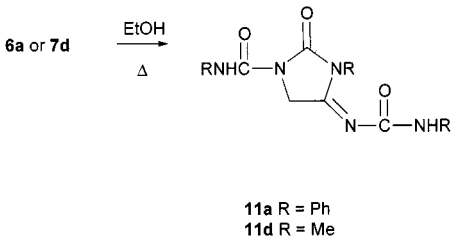


Figure 2. ORTEP drawing of imidazolidinone **10**; salient bond lengths [Å]: N1−C2 1.379(4), N1−C5 1.318(3), C2−N3 1.405(3), N3−C4 1.363(3), C4−C5 1.524(3), C2−O21 1.215(3), C4−N41 1.292(3), C5−N51 1.313(3)



Scheme 5

Finally, attempted recrystallization of the trisulfide **7d** from ethanol resulted in loss of sulfur and reduction to **11d**. The analogous compound **11a** was likewise formed from disulfide **6a** (Scheme 6).



Scheme 6

Experimental Section

General: NMR: Bruker AC 250 P or AMX 400; $CDCl_3$ as solvent unless stated otherwise, with TMS as internal standard; coupling constants *J* are given in Hz. − IR: Perkin−Elmer FT-IR 1720 X or Pye-Unicam SP3-200 spectrometers. − Elemental analyses: Institut für Organische Chemie, TU Braunschweig.

Cyanothioformamide: A stream of H_2S was bubbled into a solution of cyanogen in diethyl ether (120 mL) containing a few drops of triethylamine (**4**) in a 250-mL vessel at −30 °C until a reddish color appeared. The reaction mixture was then concentrated and the residue was recrystallized from dichloromethane/petroleum ether to give yellow prisms; m.p. 88−90 °C (ref.[7] 87−90 °C).

Bis[2-oxo-1-phenyl-3-(phenylcarbamoyl)-5-(phenylcarbamoylimino)-imidazolidin-4-yl] Disulfide (6a): To a mixture of **3a** (1.8 mL, 15 mmol) and **2** (0.43 g, 5 mmol) in diethyl ether was added 1−2 drops of **4**. An exothermic reaction led to a slight warming of the mixture and after 30−50 min a dark oily material separated followed by colorless crystals. After standing at 25 °C for 3 h, the reaction mixture was cooled to 5 °C overnight. The product was collected in several crops; crude yield 60−80%; m.p. 150−180 °C (dec.). After washing with diethyl ether and methanol, the m.p. was 190−193 °C (dec.) − IR (KBr): $\tilde{\nu}$ = 3407.2, 3283.7, 1770.8, 1696.7, 1500.0, 1443.7, 1400.3, 1307.7, 1153.3, 739.6, 684.0 cm^{-1}. − ^1H NMR ([D$_6$]DMSO): δ = 6.6 (s, 1 H, CH), 6.9−7.5 (m, 15 H, ArH), 9.70 (s, 1 H, NH), 9.85 (s, 1 H, NH). − ^{13}C NMR ([D$_6$]DMSO): δ = 158.4, 158.2, 154.8, 147.9 (C=O, C=N), 139.0, 137.1, 131.7 (C-Ar), 129.2, 128.8, 128.3, 124.5, 123.6, 120.2, 120.1 (CH-Ar), 61.9 (CH). − MS (LSIMS): *m/z* = 889.4 [MH^+], 824.4 [M − 64], 294.2 [M/2 − 150]; HRMS: calcd. for $C_{16}H_{14}N_4O_2$ [$M/2^+$ − S − PhNCO + H] 294.111676; found 294.111966. − $C_{46}H_{36}N_{10}O_6S_2$ (888.98): calcd. C 62.29, H 3.86, N 15.79, S 7.23; found C 62.10, H 3.90, N 15.75, S 6.85.

Bis{1-(4-chlorophenyl)-3-[(4-chlorophenyl)carbamoyl]-5-[(4-chlorophenyl)carbamoylimino]-2-oxoimidazolidin-4-yl} Disulfide (6b): To a mixture of **3c** (2.7 g, 17.6 mmol) and **2** (0.43 g, 5.0 mmol) in diethyl ether (10 mL) was added 3 drops of **4**. The temperature rose slightly and a fine, light-yellow precipitate began to form after 15 min. After leaving the mixture to stand for 3 h at 25 °C, the crystals were collected and washed with diethyl ether to give 1.90 g (55%); m.p. 160−165 °C (dec.). The product was found to be sparingly soluble in acetone, dichloromethane, ethyl acetate, or toluene, and only separated again after concentration or dilution with petroleum ether. Products with m.p. ranges from 160−165 °C (dec.) to as high as 190−193 °C (dec.) were obtained, some of which appeared to be solvates. − ^1H NMR: δ = 6.88 (s, 1 H, CH), 7.0−7.5 (m, 12 H, ArH), 9.7 (s, 1 H, NH), 9.75 (s, 1 H, NH); the signals assigned to the NH protons disappeared on dilution with D_2O. − ^{13}C NMR: δ = 157.0, 156.9, 153.2, 153.1, 146.1, 140.0 (C=O), 136.0, 135.9, 135.9, 135.8, 135.6, 135.0, 134.9 (C=N, C-Ar), 129.7, 129.2, 129.1, 129.0, 128.8, 128.6, 121.4, 120.8, 120.1, 120.0 (CH-Ar), 60.6, 59.9 (CH). − MS (LSIMS): *m/z*, MH^+ calcd. for isotopic cluster $C_{46}H_{30}Cl_6N_{10}O_6S_2$ (%) = 1093, 49 (46); 1094, 34 (26); 1095, 100 (100); 1096, 63 (54); 1097, 91 (94); 1098, 51 (48); 1099, 50 (50); 1100, 24 (25); 1101, 17 (17); 1102, 7 (7). − $C_{46}H_{30}Cl_6N_{10}O_6S_2 \cdot 2H_2O$ (1131.69): calcd. C 48.82, Cl 18.81, H 3.01, N 12.38, S 5.68; found C 49.02, Cl 18.70, H 2.72, N 11.98, S 5.70.

Bis{1-(4-nitrophenyl)-3-[(4-nitrophenyl)carbamoyl]-5-[(4-nitrophenyl)carbamoylimino]-2-oxoimidazolidin-4-yl} Disulfide (6c): To a mixture of **3d** (0.82 g, 5 mmol) and **2** (0.22 g, 2.5 mmol) in diethyl ether was added one drop of **4**. The reaction mixture became cloudy within 2−3 min. After 1 h, the fine yellow precipitate was collected to give 0.12 g (13%); m.p. 196−200 °C (dec.). Addition of **4** to the mother liquor gave further product, along with the di-

aryl urea. The initial product dissolved in acetone, but crystallized within a few min to give material with m.p. 195−200 °C. − IR (KBr): $\tilde{\nu}$ = 3271, 3080, 1777, 1672, 1598, 1518, 1413, 1246, 1172, 752, 581 cm^{-1}. − ^1H NMR ([D$_6$]DMSO): δ = 6.5 (s, 1 H, 4-H), 7.4−7.9 (m, 6 H, $H_{2,6}$ of ArH), 8.0−8.5 (m, 6 H, $H_{3,5}$ of ArH), 9.8 (s, 1 H, NH), 10.7 (s, 1 H, NH). − MS: *m/z* (%) = 1159.1 (100) [MH^+], 1160.1 (56.5) [$(MH + 1)^+$], 1161.1 (27.5) [$(MH + 2)^+$], 1162.1 (10.3) [$(MH + 3)^+$], 1163.1 (3.5) [$(MH + 4)^+$]; $C_{46}H_{30}N_{16}O_{18}S_2$ requires 100, 59.87, 30.09, 10.79, and 3.26%, respectively.

Bis[1-methyl-3-(methylcarbamoyl)-5-(methylcarbamoylimino)-2-oxoimidazolidin-4-yl] Disulfide and Trisulfide (6d and 7d): To a solution of **2** (0.40 g, 4.65 mmol) in THF (5 mL) was added **3b** (2 mL, 35 mmol) and 5 drops of a 10% solution of **4** in diethyl ether. An exothermic reaction led to a slight warming of the mixture. The clear solution slowly darkened and after 4 d at room temp. under protection from light, a hard, greyish-white crystalline product had separated on the surface of the flask. The mother liquor was decanted and the crystals were washed with THF and diethyl ether to give 0.33 g (42%) of almost colorless product; m.p. 190−195 °C (dec.). − ^1H NMR ([D$_6$]DMSO): δ = 6.62 (s, 1 H, 4-H), 3.1 (s, 3 H, NCH_3), 2.91 (d, 3 H, *J* = 5, $NHCH_3$), 2.88 (d, 3 H, *J* = 4.5, $NHCH_3$). − ^{13}C NMR ([D$_6$]DMSO): δ = 160.3, 154.0, 149.8, 149.0 (C=O, C=N), 66.9 (CH), 26.5, 25.5, 25.0 (CH_3). − MS (CI): *m/z* (%) of **6d** and/or **7d** = 549 (4) [M + 1], 519 (5), 517 (3), 228 (100). − $C_{16}H_{24}N_{10}O_6S_3 \cdot C_{16}H_{24}N_{10}O_6S_2 \cdot H_2O$ (1083.2): calcd. C 35.48, H 4.65, N 25.86, S 14.80; found C 34.96, H 4.85, N 25.33, S 14.54. − C/N ratio: calcd. 1.372; found 1.380.

Bis[1-methyl-3-(methylcarbamoyl)-5-(methylcarbamoylimino)-2-oxoimidazolidin-4-yl] Trisulfide (7d): In another experiment, the same reactants as above were combined, but after standing overnight the still clear reaction mixture was gently heated for 30 min to remove excess **3d** and some of the solvent. A colorless powder was precipitated (0.12 g); m.p. 185−194 °C (dec.). Heating of the mother liquor for a further 1 h provided an additional 0.12 g of the same product; m.p. 188−194 °C (dec.). − MS (LSIMS): *m/z* + 1 = 581.2 [weak, tetrasulfide], 549.2 [MH^+]. − $C_{16}H_{24}N_{10}O_6S_3$ (548.6): calcd. C 35.04, H 4.38, N 25.55, S 17.52; found C 35.47, H 4.50, N 25.00, S 17.26.

1-Methyl-3-(methylcarbamoyl)-5-(methylcarbamoylimino)-2-oxoimidazolidin-4-yl Phenyl Disulfide (8): To a mixture of **2** (0.43 g, 5 mmol) and **3b** (2.2 mL, 35 mmol) in THF (10 mL) was added one drop of **4**. After leaving the solution to stand for 2 h, the excess MeNCO was removed with a stream of N_2, after which a solution of PhSH (0.55 g, 5 mmol) in THF (5−10 mL) was added. The mixture was chromatographed on silica gel using THF as the eluent. Work-up of the middle fraction gave 40 mg of material with m.p. 155−158 °C. − IR (KBr): $\tilde{\nu}$ = 3393, 3296, 1752, 1678, 1641, 1542, 1351, 1252, 1116, 752 cm^{-1}. − ^1H NMR: δ = 2.65 (d, 3 H, *J* = 4.1, NHMe), 2.86 (d, 3 H, *J* = 3.6, NHMe), 2.93 (s, 3 H, NMe), 5.29 (br., 2 H, NH), 6.61 (s, 1 H, 4-H), 7.1−7.4 (m, 5 H, ArH). − HRMS: calcd. for $C_{14}H_{17}N_5O_3S_2$ [M^+] 367.077283; found 367.078788.

4-Mercapto-1,3-diphenyl-5-(phenylcarbamoylimino)imidazolidin-2-one (9): A stream of H_2S was passed through a suspension of **1** (X = O, R^1 = R^2 = Ph, R^3 = CONHPh) in methanol (10−20 mL). As the brick-red starting material dissolved, a colorless precipitate formed to give a high yield of the dihydro product **9**. Recrystallization from CH_2Cl_2/petroleum ether (35−60 °C) gave a product with m.p. 193−195 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 2341.9, 3275.5, 1766.2, 1669.6, 1603.2, 1530.8, 1500.6, 1379.8, 1319.5, 1301.3, 1174.6, 1138.3, 770.1, 691.6 cm^{-1}. − ^1H NMR ([D$_6$]acetone): δ = 8.34 (s, 1 H, NH; disappears upon addition of D_2O), 7.7−7.0 (m, 15 H, ArH), 7.1 (br., 1 H, SH; disappears upon addition of D_2O), 6.5 (br., 1 H, CH). − ^{13}C NMR ([D$_6$]acetone): δ = 201.5 (C=N), 154.7, 153.5 (C=O), 140.5, 137.8, 135.9 (C^1-Ar), 129.8, 129.7, 129.6, 129.5, 128.6 (C^2-, C^3-Ar), 126.3, 123.0, 119.4 (C^4-Ar), 73.3 (C^4). − HRMS: calcd. for $C_{22}H_{18}N_4O_2S$ [M^+] 402.115048; found 402.114807.

1-Methyl-4-(methylamino)-5-[(*N*-methylcarbamoyl)imino]-imidazolidin-2-one (10): On leaving the mother liquor from the preparation of **7d** to stand overnight, rusty reddish crystals were deposited (0.21 g). Recrystallization from CH_2Cl_2 left a small amount of insoluble off-white crystals; m.p. 238−241 °C (dec.). Evaporation of the solvent from the CH_2Cl_2 solution gave light salmon-colored crystals (0.13 g); m.p. 167−174 °C; R_f (TLC) = 0.3 (EtOAc). − IR (KBr): $\tilde{\nu}$ = 3390, 1772, 1676, 1627, 1531, 1410, 1313, 1241, 1162, 1096, 686, 643 cm^{-1}. − ^1H NMR: δ = 2.92 (d, 3 H, *J* = 5.0, NHMe), 3.08 (s, 3 H, NMe), 3.18 (d, 3 H, *J* = 5.0, NHMe), 6.15 (br. s, 1 H, NH), 11.50 (br. s, 1 H, NH). − ^{13}C NMR: δ = 165.5, 163.3 (C=O), 161.6, 154.3 (C=N), 29.9, 27.5, 26.3 (NMe). − MS: *m/z* (%) = 197 (81) [M^+], 166 (80) [$M - CH_3NH_2$], 83 (100) [$(M - CH_3NH_2)^{2+}$]; HRMS: calcd. for $C_7H_{11}N_5O_2$ [M^+] 197.091275; found 197.091723. − $C_7H_{11}N_5O_2$ (197.2): calcd. C 42.63, H 5.63, N 35.52; found C 42.49, H 5.81, N 35.60.

3-Phenyl-1-(*N*-phenylcarbamoyl)-4-[(*N*-phenylcarbamoyl)-imino]imidazolidin-2-one (11a): Heating of a suspension of **6a** in ethanol under reflux led to slow dissolution. Concentration gave colorless crystals. These were washed with carbon disulfide to remove sulfur and recrystallized from ethanol; m.p. 195 °C. − IR (KBr): $\tilde{\nu}$ = 3279, 1758, 1685, 1637, 1606, 1558, 1507, 1423, 1358, 1314, 1185, 732, 590 cm^{-1}. − ^1H NMR: δ = 5.33 (s, 2 H, CH_2), 7.0−7.6 (m, 16 H, Ph + NH), 9.90 (br. s, 1 H, NH). − ^{13}C NMR: δ = 162.4, 158.4, 154.6, 147.9 (C=O, C=N), 137.8, 136.9, 131.6 (C-Ar), 129.4, 129.1, 129.0, 127.4, 124.4, 124.0, 119.9, 118.9 (CH-Ar), 48.7 (CH_2). − MS: *m/z* (%) = 413 (0.01) [M^+], 321 (0.7), 294 (56), 119 (100); HRMS calcd. for $C_{16}H_{14}N_4O_2$ [M^+ − PhNCO] 294.111676; found 294.111133.

3-Methyl-1-(*N*-methylcarbamoyl)-4-[(*N*-methylcarbamoyl)-imino]imidazolidin-2-one (11d): In an attempt to recrystallize **7d**, a sample (ca. 0.2 g) was suspended in ethanol (10 mL) and heated under reflux until it all dissolved. Subsequent concentration to a volume of 1−2 mL gave 0.1 g of colorless crystals; m.p. 198−201 °C. − IR (KBr): $\tilde{\nu}$ = 3349, 1743, 1697, 1668, 1546, 1534, 1457, 1422, 1361, 1282, 1250, 1204, 1127, 994, 760, 735 cm^{-1}. − ^1H NMR: δ = 2.87 (d, 3 H, *J* = 4.97 Hz, $NHCH_3$), 2.91 (d, 3 H, *J* = 4.02, $NHCH_3$), 3.11 (s, 3 H, NCH_3), 4.97 (s, 2 H, CH_2), 5.50 (br. s, 1 H, NH), 7.65 (br. s, 1 H, NH). − ^{13}C NMR: δ = 162.1, 161.6, 155.3, 151.5 (C=O, C=N), 48.5 (CH_2), 27.1, 26.6, 26.5 (NMe). − HRMS: calcd. for $C_8H_{13}N_5O_3$ [M^+] 227.101839; found 227.102131.

Crystal Structure Determinations of Disulfide 6a and Imidazolidinone 10: Intensity data were collected with a CAD 4-SDP single-crystal diffractometer (Enraf−Nonius) using graphite-monochromated Cu-K_α radiation in the range $2° < \theta < 55°$ for **6a** and in the range $1.5° < \theta < 27.5°$ for **10**. The final refinements were based on 1932 (**6a**) or 1473 (**10**) symmetry-independent reflections with $I > 3\sigma(I)$ for **6a** and $I > 2\sigma(I)$ for **10**. The structures were solved by the direct-methods program MULTAN. The *E* map revealed the positions of all the heavy atoms, while the H atoms were found from a difference Fourier synthesis. Convergence was achieved at R = 0.38 (R_w = 0.36) for **6a** and at R = 0.06 for **10**. − **6a**: $C_{46}H_{36}N_{10}O_6S_2$, M_r = 888.98, monoclinic, a = 17.776(1), b =

15.818(1), c = 16.120(1) Å^3, β = 98.44(1)°; V = 4483 Å, T = room temp., space group C_2/c, Z = 4. − **10**: $C_7H_{11}N_5O_2$, M_r = 197.2, hexagonal, $a = b$ = 15.627(1), c = 6.622(1) Å, γ = 120°, V = 1400.5 Å^3, T = room temp., space group $P6_3$.[13]

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[13] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-146621 (**6a**) and -152950 (**10**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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