solution of *n*-butyllithium in hexane (8.12 mL, 13.0 mmol) was added to a stirred solution of diisopropylamine (1.98 mL, 1.43 g, 14.2 mmol) in dry THF (100 mL) at −78 °C. After 10 min, a solution of the amino nitrile **9** (0.88 g, 5.9 mmol) in THF (10 mL) was added and the solution was stirred at −78 °C for 2 h. At this time, 1-iodooctane (1.17 mL, 1.56 g, 6.50 mmol) was added and after 15 min at −78 °C and 15 min at 0 °C, the solution was poured into an ice/aqueous ammonium chloride mixture. The product was extracted into ether, and the extract was washed with saturated sodium chloride solution, dried over potassium carbonate, and evaporated in vacuo. The residual heavy oil was dissolved in methanol (30 mL), 10 wt % aqueous sodium hydroxide solution (30 mL) was added, and the solution was stirred at room temperature for 1 h. The solution was diluted with water (150 mL), the product was extracted into ether, and the extract was washed with saturated sodium chloride solution and then dried over magnesium sulfate. The ether solution was evaporated in vacuo and the residue (1.5 g) was purified by flash chromatography on silica gel using hexane–ethyl acetate (3:1) as the eluting solvent. The pure ketone **12a** was obtained as a crystalline solid (1.01 g, 83% yield). ^{1}H NMR ($CDCl_3$): δ 0.87 (t, CH_3), 1.29 (m, $(CH_2)_5$), 1.71 (m, CH_2CH_3), 2.76 (t, CH_2CO), 6.65 (dd, $J_{2,4}$ = 1.51, $J_{4,5}$ = 2.93, H-4), 6.78 (dd, $J_{2,5}$ = 1.92, $J_{4,5}$ = 2.93, H-5), 7.43 (t, $J_{2,4}$ = 1.51, $J_{2,5}$ = 1.92, H-2), 9.38 (NH).

Compounds **12b** and **12c** were prepared as described above except that the crude product was purified by crystallization.

The alkylation of **8a** with benzyl chloride or 2-iodobutane was effected as described for the synthesis of **12a** but the product mixtures were separated by column chromatography on activity II neutral alumina using 4:1 and 5:1 hexane–ethyl acetate mixtures for the benzyl bromide and 2-iodobutane reactions, respectively. The alkylation of **8a** with α-methylbenzyl bromide was carried out in the same way as when benzyl bromide was used except that the reaction was maintained at −78 °C for 0.5 h and 0 °C for 0.5 h after the addition of the alkyl halide. The product mixture (**15d** and **16d**) was separated by flash chromatography on silica gel using hexane–ethyl acetate (4:1) as the eluting solvent.

Alkylation of α-(Dimethylamino)-α-(1-methylpyrrol-2-yl)acetonitrile. Synthesis of *N*-Methyl-2-(2-methylbutyroyl)pyrrole (18c). The synthesis of this compound exemplifies the general procedure. The synthesis of the monoanion of **6** was effected in the usual way by using LDA, generated with 1.6 M *n*-butyllithium in hexane (4.20 mL, 6.75 mmol) and diisopropylamine (1.03 mL, 0.74, g, 7.36 mmol) in THF (100 mL). After being stirred at −78 °C for 10 min, the amino nitrile **8b** (1.00 g, 6.13 mmol) was added, stirring was continued for 1 h at the same temperature, and then 2-iodobutane (1.24 g, 6.75 mmol) in THF (10 mL) was added. The reaction mixture was agitated magnetically for 15 min at −78 °C and 15 min at 0 °C and thereafter it was worked up as described above for the synthesis of **12a**. The crude product was purified by column chromatography on activity II neutral alumina by using hexane–ethyl acetate (6:1) as the eluting solvent. The product (0.67 g, 67% yield) was obtained as an oil. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, CH_3), 1.34 (m, $(CH_2)_5$), 1.69 (m, CH_2CH_3), 2.75 (t, CH_2CO), 3.93 (s, NMe), 6.11 (dd, $J_{3,4}$ = 4.08, $J_{4,5}$ = 2.48, H-4), 6.78 (m, $J_{3,5}$ = 1.69, $J_{4,5}$ = 2.68, H-5), 6.94 (dd, $J_{3,4}$ = 4.08, $J_{3,5}$ = 1.69, H-3).

Acknowledgment. We thank Dr. M. L. Maddox for helpful discussion of various aspects of the ^{1}H NMR spectra. We are also grateful to L. Guzzo, L. Kurz, and J. Nelson for their extra effort on our behalf in measuring the ^{1}H NMR spectra.

Registry No. **1a**, 109-97-7; **1b**, 96-54-8; **2**, 3724-43-4; **3a**, 75866-92-1; **3b**, 117068-08-3; **4**, 87630-35-1; **6**, 117067-97-7; **8a**, 117067-98-8; **8b**, 117068-07-2; **9**, 117067-99-9; **12a**, 117068-00-5; **12b**, 96999-24-5; **12c**, 117068-01-6; **14a**, 89631-85-6; **14b**, 13169-74-9; **14c**, 117068-03-8; **15b**, 117068-02-7; **15c**, 117068-04-9; **15d**, 117068-05-0; **16d**, 117068-06-1; **18a**, 117068-09-4; **18c**, 115045-72-2; DMF, 68-12-2; 1-iodooctane, 629-27-6; benzyl chloride, 100-44-7; 2-iodobutane, 513-48-4.

Supplementary Material Available: Table I containing the ^{1}H NMR spectra of the pyrrole derivatives (3 pages). Ordering information is given on any current masthead page.

Synthesis of a Novel Tetrahydrothieno[2,3-*b*]pyrrole[1]

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Esters of 1-[4′-(carboxy)phenyl]-3-pyrrolidinone (**1**)[2] have proven to be versatile intermediates for the preparation of a number of different types of fused heterocycles.[3,4] Although **1a** condenses normally under Knoevenagel conditions with cyanoacetamide (**2**) to give **4**,[5] an attempt to utilize cyanothioacetamide (**3**) as the active methylene partner with **1a** under the normal condensation conditions (reflux in benzene with added β-alanine and acetic acid) did not give the anticipated Knoevenagel product analogous to **4**, but instead yielded a compound whose spectral and chemical properties showed it to be the novel tetrahydrothieno[2,3-*b*]pyrrole **5a** (Scheme I). Analogous results were obtained with the ethyl and *tert*-butyl esters of **1**, leading to the bicyclic products **5b** and **5c**, respectively.

The presence of an *o*-aminonitrile functionality in **5** was indicated by IR absorptions at 3400, 3320, 3220, and 2170 cm^{-1} and confirmed by the conversion of **5a–c** with triethyl orthoformate or diethoxymethyl acetate to ethoxymethyleneamino derivatives **6**, which were then cyclized with ammonia to the fused 4-aminopyrimidine derivatives **8**.[6] The bicyclic tetrahydrothieno[2,3-*b*]pyrrole structure present in **5** was also evident from the NMR spectra of all three derivatives; the bridgehead hydrogen at C-3a appeared as a multiplet at ca. δ 4 and the bridgehead C-6a hydrogen as a doublet at ca. δ 6.0. A homonuclear decoupling experiment on the extremely soluble (dimethylamino)methylene derivative **7a** (prepared from **5a** with dimethylformamide dimethylacetal in the usual manner) also confirmed this structural assignment; irradiation at δ 2.3 (for the H-4 proton) resulted in conversion of the C-3a multiplet at δ 4.1 to a doublet, while irradiation at δ 4.1 resulted in collapse of the H-6a doublet at δ 6.0 to a sharp singlet.

(1) Presented in part at the 10th International Congress of Heterocyclic Chemistry, Waterloo, Ontario, Canada, August 11–16, 1985 (Abstract P5-158).

(2) (a) Taylor, E. C.; McDaniel, K. F.; Skotnicki, J. S. *J. Org. Chem.* **1984**, *49*, 2500. (b) Taylor, E. C.; Ahmed, Z.; Kempton, R. J., manuscript in preparation.

(3) For a review of the preparation and utilization of 3-pyrrolidinols (from which pyrrolidinones are readily prepared), see: Flanagan, D. M.; Joullie, M. M. *Heterocycles* **1987**, *26*, 2247.

(4) For the conversion of the pyrrolidine enamine of **1a** to a "tied-back" deaza analogue of Methotrexate, see: Taylor, E. C.; Fletcher, S. R.; Fitzjohn, S. *J. Org. Chem.* **1985**, *40*, 1010.

(5) Taylor, E. C.; Fletcher, S. R.; Kempter, P., manuscript in preparation.

(6) These properties and reactions are characteristic of the *o*-aminonitrile functionality; see: Taylor, E. C.; McKillop, A. *The Chemistry of Cyclic Enaminonitriles and o-Aminonitriles*; Interscience: New York, 1970.

0022-3263/88/1953-6118$01.50/0

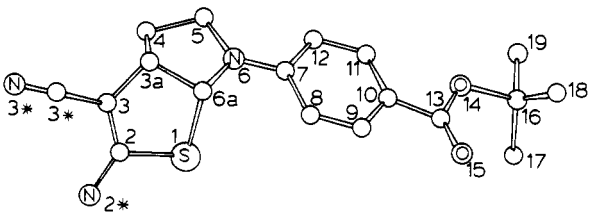
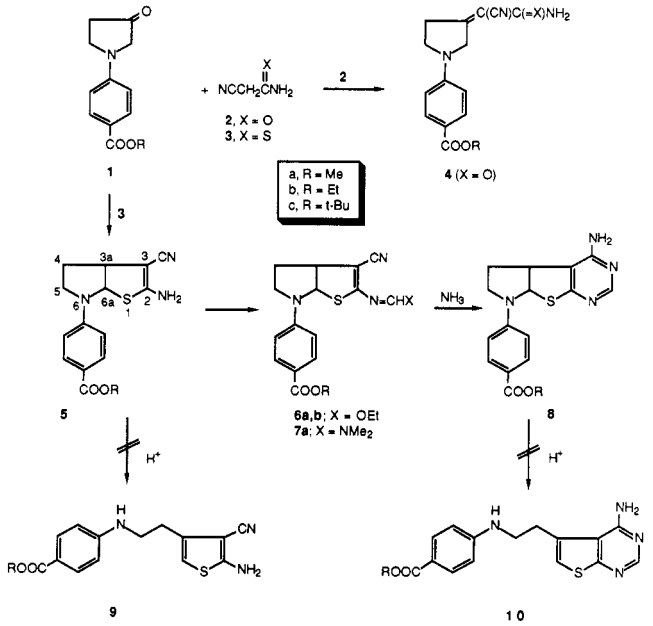


Figure 1. Crystal molecular structure of **5c**. Asterisks distinguish substituent atoms from ring atoms.

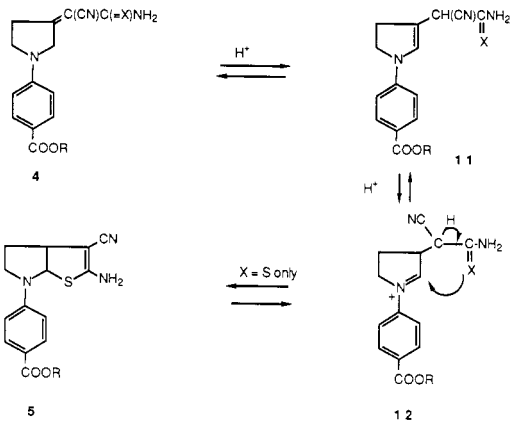
Scheme I



Final confirmation of structure **5** for these cyanothioacetamide condensation products with **1** was obtained by a single-crystal X-ray analysis on the *tert*-butyl ester **5c** (Figure 1). The ring junction between the two heterocyclic rings is cis, with the rings folded 93° with respect to one another. The aryl ring is essentially coplanar with the tetrahydropyrrole ring (−1.2°) and with the carbalkoxy group (−5.1°). The S1–C6a bond length (1.88 Å) is much longer than that normally observed in other cyclic sulfides (1.80 Å). The amino group forms intermolecular hydrogen-bond contacts both with the carbonyl oxygen of the ester grouping (2.87 Å) and with the nitrile group (3.08 Å).

The different behavior of cyanoacetamide and cyanothioacetamide in the above reaction with the pyrrolidinones **1a–c** is striking. The normal Knoevenagel product **4** is certainly formed initially with both active methylene compounds and is the isolated product from cyanoacetamide. The prototropic shifts that interconvert **4**, **11**, and **12** (depicted in Scheme II) are certainly reversible; the observed ring closure of the cyanothioacetamide-derived penultimate precursor **12** (X = S) to the tetrahydrothienopyrrole **5** is most probably a consequence of the much greater nucleophilicity of sulfur as contrasted to oxygen. We have noted that **5a–c** all melt with decomposition accompanied by vigorous evolution of ammonia; mass spectral analysis also indicates loss of alkoxy and a 17 mass unit fragment. This observation can be rationalized by assuming that the final ring closure (**12** → **5**) is also reversible and that ammonia is then lost from intermediate **12**. It is worth noting that neither **5** nor **8** (both of which are cyclic thioaminals) could be converted to aromatic thiophene derivatives (**9** and **10**, respectively) by acid-catalyzed elimination of the (arylamino)ethyl substituent; **5** was converted to an intractable mixture of

Scheme II



compounds with acid, while **8** was stable to acid.

Experimental Section

General Procedures. All reactions were run under an atmosphere of nitrogen. Melting points were taken on a Thomas-Hoover instrument and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 1320 spectrophotometer. Proton NMR spectra were recorded either on a Perkin-Elmer R-32 90 MHz instrument or a JEOL FX 90-Q instrument. Mass spectra were obtained on an AIE MS-9 instrument. All analytical thin layer chromatograms were performed on Baker-flex silica gel 1B2-F sheets. Preparative thin layer chromatograms were performed on Analtech silica gel GF, 1500, 20 × 20 cm plates, and all column chromatography was carried out on 230–400-mesh silica gel.

6-[4′-(Methoxycarbonyl)phenyl]-2-amino-3-cyano-3a,4,5,6a-tetrahydrothieno[2,3-*b*]pyrrole (5a). A solution of 1-[4′-(methoxycarbonyl)phenyl]-3-pyrrolidinone (**1a**) (1.0 g, 4.75 mmol), cyanothioacetamide (0.74 g, 7.4 mmol), β-alanine (0.1 g), and glacial acetic acid (1 mL) in 75 mL of benzene was refluxed through a water separator for 1 h. Benzene was removed by rotary evaporation and the crude product was applied to a silica gel column and eluted with $CHCl_3$–CH_3OH (95:5). The product separated cleanly from the slower moving cyanothioacetamide. A total of 0.8 g (58%) of colorless crystals was isolated: mp 197–198 °C dec (with vigorous gas evolution); IR (Nujol) 3400, 3320, 3220 (NH_2), 2170 (CN), 1705 (C=O), 1630, 1605, 1570, 1545 cm^{-1}; LRMS, *m/z* 301 (M^+), 284, 270, 241, 202, 164, 135, 120; ^1H NMR (Me_2SO-d_6) δ 2.45 (m, 2 H, H-4), 3.5 (m, 2 H, H-5), 3.76 (s, 3 H, OCH_3), 3.9 (m, 1 H, H-3a), 6.0 (d, 1 H, J = 7.03 Hz, H-6a), 6.9 (br s, 2 H, NH_2), 6.7 and 7.9 (AB q, 4 H, J = 9 Hz, aromatic CH); ^{13}C NMR (Me_2SO-d_6) δ 175, 162, 147, 130, 118, 113, 72, 51, 49, 45, 30; HRMS, calcd for $C_{15}H_{15}N_3O_2S$ *m/z* 301.0885, found *m/z* 301.0870.

6-[4′-(Ethoxycarbonyl)phenyl]-2-amino-3-cyano-3a,4,5,6a-tetrahydrothieno[2,3-*b*]pyrrole (5b). A mixture of the pyrrolidinone **1b** (0.8 g, 3.5 mmol) and cyanothioacetamide (0.4 g, 4.0 mmol) was taken up in benzene (50 mL) and β-alanine (0.1 g) and glacial acetic acid (1 mL) were added. The mixture, which formed a clear solution upon heating, was refluxed through a water separator for 18 h. The contents of the flask were cooled and petroleum ether (10 mL) was added. The tan product that separated was collected by filtration and purified by column chromatography (silica gel; $CHCl_3$–petroleum ether, 9:1). The yield of colorless product was 0.53 g (49%): mp 192–194 °C dec (with vigorous gas evolution); IR (KBr) 3400, 3320, 3220 (NH_2), 2170 (CN), 1695 (C=O), 1630, 1602 cm^{-1}; ^1H NMR [$CDCl_3$–Me_2SO-d_6 (2:1)] δ 1.39 (t, 3 H, J = 8 Hz), 2.25 (m, 2 H, H-4), 3.55 (m, 2 H, H-5), 4.07 (m, 1 H, H-3a), 4.30 (q, 2 H, J = 8 Hz), 5.95 (d, 1 H, J = 8 Hz, H-6a), 6.29 (br s, 2 H, NH_2), 6.61 and 7.92 (AB q, 4 H, J = 9 Hz); LRMS, *m/z* 315 (M^+), 298, 270, 255, 183, 135, 120; HRMS, calcd for $C_{16}H_{17}N_3O_2S$ *m/z* 315.1041, found *m/z* 315.1033.

6-[4′-(*tert*-Butoxycarbonyl)phenyl]-2-amino-3-cyano-3a,4,5,6a-tetrahydrothieno[2,3-*b*]pyrrole (5c). A mixture of 1-[4′-(*tert*-butoxycarbonyl)phenyl]-3-pyrrolidinone (**1c**) (0.46 g, 1.75 mmol), cyanothioacetamide (0.22 g, 2.2 mmol), β-alanine (0.05

g), glacial acetic acid (1 mL), and dry benzene (30 mL) was refluxed through a water separator half filled with dry benzene. After 1.5 h there was no evidence of starting material by TLC. The reaction mixture was cooled and the solvent removed by rotary evaporation. The crude product was purified by column chromatography (silica gel, $CHCl_3$). The yield of pure, colorless product was 0.47 g (77%): mp 200–201 °C dec (with vigorous gas evolution); IR (KBr) 3400, 3320, 3220 (NH_2), 2170 (CN), 1692 (C=O), 1630, 1603 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.59 (s, 9 H), 2.3 (m, 2 H, H-4), 3.6 (m, 2 H, H-5), 4.1 (m, 1 H, H-3a), 4.72 (br s, 2 H, NH_2), 6.03 (d, 1 H, J = 8 Hz, H-6a), 6.57 and 7.92 (AB q, 4 H); LRMS, m/z 343 (M^+), 326, 287, 270, 150, 105; HRMS, calcd for $C_{18}H_{21}N_3O_2S$ m/z 343.1354, found m/z 343.1325.

6-[4′-(Methoxycarbonyl)phenyl]-3-cyano-2-[[(dimethylamino)methylene]amino]-3a,4,5,6a-tetrahydrothieno[2,3-*b*]pyrrole (7a). A suspension of **5a** (0.11 g, 0.36 mmol) in absolute ethanol (5 mL) was treated with dimethylformamide dimethyl acetal (0.44 g, 3.7 mmol), and the mixture was refluxed for 1 h. The contents of the flask were cooled and the ethanol was removed by rotary evaporation. The light brown residue was taken up in a small (1–2 mL) volume of $CHCl_3$ and run through a Pasteur pipette filled with silica gel. The colorless product moved away from the colored impurities, which remained at the top of the column. The yield of **7a** was 0.12 g (92%): mp 199–201 °C dec; IR (Nujol) 2190 (CN), 1700 (C=O), 1620, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.3 (m, 2 H, H-4), 3.0 (s, 3 H, N-methyl), 3.1 (s, 3 H, *N*-methyl), 3.5 (m, 2 H, H-5), 3.8 (s, 3 H, OCH_3), 4.1 (m, 1 H, H-3a), 6.0 (d, 1 H, J = 7.3 Hz, H-6a), 6.6 and 8.0 (AB q, 4 H, J = 9 Hz, aromatic CH), 7.5 (s, 1 H, vinylic H); LRMS, m/z 356 (M^+), 325, 284, 267, 240, 178, 162, 135, 115, 90; HRMS, calcd for $C_{18}H_{20}N_4O_2S$ m/z 356.1296, found m/z 356.1307.

6-[4′-(Methoxycarbonyl)phenyl]-3-cyano-2-[(ethoxymethylene)amino]-3a,4,5,6a-tetrahydrothieno[2,3-*b*]pyrrole (6a). A mixture of 6-[4′-(methoxycarbonyl)phenyl]-2-amino-3-cyano-3a,4,5,6a-tetrahydrothieno[2,3-*b*]pyrrole (**5a**) (0.30 g, 1.0 mmol), diethoxymethyl acetate (0.55 g, 3.0 mmol), and toluene (15 mL) was refluxed for 18 h. The toluene was removed by rotary evaporation and the residue was chromatographed on silica gel (CH_2Cl_2). Homogeneous fractions were pooled, the solvent was removed, and the residue was triturated with hexanes to yield colorless crystals; yield 0.19 g (53%): mp 135–140 °C; IR (Nujol) 2200 (CN), 1720 (C=O), 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (t, 3 H, OCH_2CH_3), 2.3 (m, 2 H, H-4), 3.7 (m, 2 H, H-5), 3.9 (s, 3 H, OCH_3), 4.1 (m, 1 H, H-3a), 4.3 (q, 2 H, OCH_2CH_3), 6.0 (d, 1 H, J = 7 Hz, H-6a), 6.6 and 8.0 (AB q, 4 H, J = 7.8 Hz, aromatic H), 7.7 (s, 1 H, vinylic H); HRMS, calcd for $C_{18}H_{19}N_3O_3S$ m/z 357.1147, found m/z 357.1131.

6-[4′-(Ethoxycarbonyl)phenyl]-3-cyano-2-[(ethoxymethylene)amino]-3a,4,5,6a-tetrahydrothieno[2,3-*b*]pyrrole (6b). 6-[4′-(Ethoxycarbonyl)phenyl]-2-amino-3-cyano-3a,4,5,6a-tetrahydrothieno[2,3-*b*]pyrrole (**5b**) (0.115 g, 0.36 mmol) was dissolved in 9 mL of triethyl orthoformate, and one drop (Pasteur pipette) of H_2SO_4 (concentrated) was added with stirring. The solution was refluxed for 25 min (oil bath temperature 140 °C), cooled, diluted with ethyl acetate, and washed once with 10% aqueous $NaHCO_3$ and 3 times with water. The organic layer was dried ($MgSO_4$) and filtered, and the solvent was removed on a rotary evaporator. Traces of triethyl orthoformate that remained were removed in vacuo at 50 °C. The residue was purified by column chromatography (silica gel, $CHCl_3$–petroleum ether (88:12)). The product crystallized as colorless flakes; yield 0.10 g (74%), mp 139–143 °C: IR (thin film) 2200 (CN), 1705 (C=O), 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (two overlapping triplets, 6 H, CH_3), 2.4 (m, 2 H, H-4), 3.6 (m, 2 H, H-5), 4.1 (m, 1 H, H-3a), 4.38 (two overlapping quartets, 4 H, OCH_2), 6.10 (d, 1 H, J = 8 Hz, H-6a), 6.61 and 7.97 (AB q, 4 H, J = 9 Hz, aromatic CH), 7.72 (s, 1 H, vinylic H); LRMS, m/z 371 (M^+), 326, 315, 298, 269, 225, 217, 171; HRMS, calcd for $C_{19}H_{21}N_3O_3S$ m/z 371.1303, found m/z 371.1282.

7-[4′-(Ethoxycarbonyl)phenyl]-4-amino-4b,5,6,7a-tetrahydropyrrolo[3′,2′:4,5]thieno[2,3-*d*]pyrimidine (8b). A mixture of 6-[4′-(ethoxycarbonyl)phenyl]-3-cyano-2-[(ethoxymethylene)amino]-3a,4,5,6a-tetrahydrothieno[2,3-*b*]pyrrole (**6b**) (85 mg, 0.23 mmol) was suspended in absolute ethanol (15 mL) in a pressure vessel and saturated with dry ammonia. The vessel was then sealed and stirred at room temperature for 18 h. The ethanol was removed under reduced pressure and the crude product was purified by preparative TLC (silica gel, $CHCl_3$/methanol (97:3)). The yield of colorless product was 36 mg (46%): mp 190–192.5 °C dec; IR (KBr) 3330, 3160, 1708, 1605, 1568, 1273, 1182, 1110 cm^{-1}; LRMS, m/z 342 (M^+), 297, 178, 165, 120, 105; HRMS, calcd for $C_{17}H_{18}N_4O_2S$ m/z 342.1150, found m/z 342.1123.

7-[4′-(*tert*-Butoxycarbonyl)phenyl]-4-amino-4b,5,6,7a-tetrahydropyrrolo[3′,2′:4,5]thieno[2,3-*d*]pyrimidine (8c). A mixture of 6-[4′-(*tert*-butoxycarbonyl)phenyl]-2-amino-3-cyano-3a,4,5,6a-tetrahydrothieno[2,3-*b*]pyrrole (**5c**) (0.2 g, 0.6 mmol), triethyl orthoformate (8.5 mL), and *p*-toluenesulfonic acid (3 mg) was placed in a small round-bottomed flask fitted with a short-path distillation head, and the flask was immersed in an oil bath preheated to 145 °C. After 1 h, about 1 mL of distillate boiling at ca. 60 °C had been collected. Excess triethyl orthoformate was removed under high vacuum at 60 °C, and the residue was immediately chilled and taken up in cold absolute ethanol (20 mL) that had been saturated with ammonia. The resulting homogeneous reaction mixture was allowed to stand at 0 °C for 24 h and then at room temperature for an additional 24 h. The ethanol was removed by rotary evaporation and the product was isolated by preparative TLC (silica gel, $CHCl_3/CH_3OH$ (97:3)). The yield of colorless product was 120 mg (55%): mp 215–217 °C dec (with gas evolution); LRMS, m/z 370 (M^+), 314, 313, 189, 178, 165, 150, 137, 120; HRMS, calcd for $C_{19}H_{22}N_4O_2S$ m/z 370.1463, found m/z 370.1453.

Single-Crystal X-ray Analysis of 5c ($C_{18}H_{21}N_3O_2S \cdot {}^1/_2CH_2Cl_2$). Crystals suitable for X-ray diffraction were grown from petroleum ether/methylene chloride. The crystal used for data collection was a prism measuring 0.1 × 0.1 × 0.8 mm. Lattice constants and intensity data were measured at 298 K and λ = 0.71073 Å (Mo Kα) on a Nicolet P3 automated diffractometer. Data were collected from $4° < 2\phi < 55°$. A total of 4738 reflections were collected, yielding 2750 reflections with $I > 4.0\sigma(I)$. Data included corrections for background, Lorentz, and polarization effects but not absorption. The cell data are as follows: space group $C2/c$, a = 24.362 (5), b = 10.992 (2), and c = 17.459 (3) Å, β = 119.12 (2)°, V = 4084 Å^3, Z = 8, d_c = 1.27 g/cm, μ = 1.62.

The structure was solved by use of the direct methods programs MULTAN and NQEST.[7,8] Subsequent least-squares difference Fourier maps revealed the hydrogen positions. In the final cycle of least-squares analysis, all non-hydrogen atom positions were varied with anisotropic coefficients and all hydrogen atoms were held fixed in their theoretical positions. The dichloromethane molecule is positioned on a 2-fold axis in the lattice and was held fixed at half occupancy. Refinement converged at R = 0.12 (R_w = 0.15) for 2270 data. Refinement of the data in a Cc lattice showed that the molecules were related by a 2-fold axis and that the solvent was disordered near the 2-fold axis. Therefore, the final refinement was carried out in the centrosymmetric space group $C2/c$. All calculations were performed on a DEC VAX 11/780 computer system.

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Registry No. **1a**, 90030-20-9; **1b**, 117098-11-0; **1c**, 94930-27-5; **5a**, 117098-09-6; **5b**, 117098-10-9; **5c**, 117098-12-1; **5c**·1/2CH_2Cl_2, 117098-17-6; **6a**, 117098-13-2; **6b**, 117098-14-3; **7a**, 117120-41-9; **8b**, 117098-15-4; **8c**, 117098-16-5; $NCCH_2C(NH_2)$=S, 7357-70-2; dimethylformamide dimethyl acetal, 4637-24-5; diethoxymethyl acetate, 14036-06-7; triethyl orthoformate, 122-51-0.

Supplementary Material Available: Tables of atomic coordinates and bond distances and angles for compound **5c** (2 pages). Ordering information is given on any current masthead page.

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(8) DeTitta, G. T.; Edmonds, J. W.; Langs, D. A.; Hauptman, H. A. *Acta Crystallogr., Sect. A* **1975**, *31*, 472.