The moisture-sensitive title compounds were obtained in good yields by treating the corresponding silver salts AgN(SO₂R)₂ with the thiocarbamoyl chloride Me₂NC(S)Cl in acetonitrile. In the NMR solution spectra of the novel thioureas, as recorded at room temperature for ¹³C and up to 120 °C for ¹H, the Me₂N group invariably gives rise to two distinct resonances, reflecting unusually high barriers to rotation about the C(S)–NMe₂ bond. The crystal structure of the ditosyl compound (triclinic, space group P₁, X-ray diffraction at −130 °C) contains two independent molecules A and B, in which the bond lengths and angles are nearly identical, whereas the conformations exhibit pronounced discrepancies. The amide N and thiocarbonyl C atoms have trigonal-planar environments, but the S–N–S planes are strikingly rotated into approximately perpendicular orientations relative to the planar C₅N–C(S)–N moieties. Other remarkable features of the molecular structures are the exceedingly long C(S)–NS₂ bonds [mean: 145.4(3) pm] and the concomitantly short C–S and C(S)–NC₂ bonds [mean values: 164.8(2), 132.6(3) pm]. The packing is governed by a three-dimensional system of weak hydrogen bonds and may be viewed as a self-clathrate, in which (B)₂ dimers constructed from C–H····S=C interactions are inserted as guest species into parallel tunnels between (A)ₓ tapes based upon short C–H····O=S contacts.