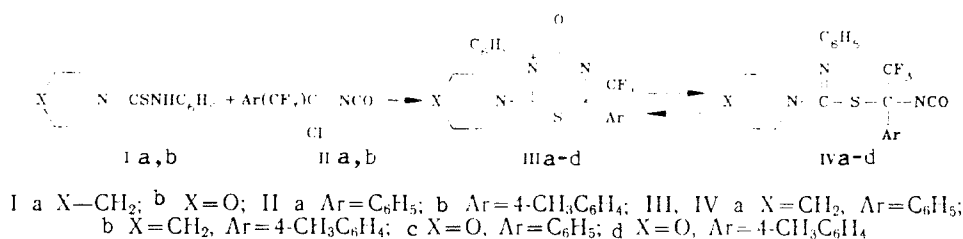


EXAMPLE OF RING-CHAIN TAUTOMERISM IN 2H-1,3,5-THIADIAZIN-5-IO-4-OLATES

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UDC 547.876'867.4'822:541.023

The reaction of trisubstituted thioureas (Ia, b) with 1-chloroalkyl isocyanates (IIa, b) has been found to give the cyclic mesoionic compounds (2-H-1,3,5-thiadiazin-5-io-4-olates) (IIIa-d) (cf. [1]). According to IR and ^{19}F NMR spectroscopy, the compounds (III) exist in the solid state and in nonpolar solvents (benzene and carbon tetrachloride) as mesoionic compounds. In polar solvents (acetone, chloroform, and acetonitrile) they exist as tautomeric mixtures with the S-(1-isocyanatoalkyl)isothioureas (IV).



To a solution of 0.01 mole of the isocyanate (IIa, b) in 25 ml of benzene was added 0.01 mole of the thiourea (Ia, b), followed with stirring by a solution of 0.01 mole of triethylamine in 10 ml of benzene. The mixture was stirred for 2 h, filtered, the filtrate evaporated, and the residue purified by crystallization.

6-Piperidino-2-trifluoromethyl-2,5-diphenyl-2H-1,3,5-thiadiazin-5-io-4-olate (IIIa). Yield 72%, mp 86-87°C (hexane-benzene, 4:1). IR spectrum (in KBr): 1685 cm⁻¹ (C=O); (in benzene): 1690 cm⁻¹ (C=O); (in chloroform): 2265 (N=C=O), 1685 (C=O), 1620 cm⁻¹ (C=N). PMR spectrum [(CD₃)₂CO]: 7.65-7.28 (10H, m, C₆H₅); 4.10-3.91 (4H, m, NCH₂); 1.65-1.44 ppm (6H, m, CH₂). ^{19}F NMR spectrum (in C₆D₆): 68.62 ppm [in (CD₃)₂CO]: 69.40, 68.56 ppm.

2-(4-Methylphenyl)-6-piperidino-2-trifluoromethyl-5-phenyl-2H-1,3,5-thiadiazin-5-io-4-olate (IIIb). Yield 76%, mp 127-128°C (hexane-benzene, 2:1). IR spectrum (in KBr): 1675 cm⁻¹ (C=O); (in C₆H₆): 1685 cm⁻¹ (C=O); (in CHCl₃): 2260 (N=C=O), 1680 (C=O), 1610 cm⁻¹ (C=N). PMR spectrum [(CD₃)₂CO]: 7.35-7.28 (9H, m, H_{arom}); 4.10-3.98 (4H, m, NCH₂); 2.35 (3H, s, CH₃); 1.65 ppm (6H, br.s, CH₂). ^{19}F NMR spectrum (in C₆D₆): 68.46 ppm [in (CD₃)₂CO]: 68.94, 68.11 ppm.

6-Morpholino-2-trifluoromethyl-2,5-diphenyl-2H-1,3,5-thiadiazin-5-io-4-olate (IIIc). Yield 86%, mp 115-116°C (hexane-benzene, 1:1). IR spectrum (in KBr): 1675 cm⁻¹ (C=O); (in C₆H₆): 1690 cm⁻¹ (C=O); (in CDCl₃): 2260 (N=C=O), 1685 (C=O), 1615 cm⁻¹ (C=N). PMR spectrum [(CD₃)₂CO]: 7.56-7.21 (10H, m, C₆H₅); 4.18-4.05 (4H, m, NCH₂); 3.87-3.61 ppm (4H, m, OCH₂). ^{19}F NMR spectrum (in C₆D₆): 68.85 ppm [in (CD₃)₂CO]: 69.37, 68.39 ppm.

2-(4-Methylphenyl)-6-morpholino-2-trifluoromethyl-5-phenyl-2H-1,3,5-thiadiazin-5-io-4-olate (III d). Yield 69%, mp 123-124°C (hexane-benzene, 2:1). IR spectrum (in KBr): 1670 cm⁻¹ (C=O); (in C₆H₆): 1690 cm⁻¹ (C=O); (in CHCl₃): 2270 (N=C=O), 1675 (C=O), 1605 cm⁻¹ (C=N). PMR spectrum [(CD₃)₂CO]: 7.44-7.28 (9H, m, H_{arom}); 4.15 (4H, br.s, NCH₂); 3.73 (4H, br.s, OCH₂); 2.37 ppm (3H, s, CH₃). ^{19}F NMR spectrum (in C₆D₆): 68.47 [in (CD₃)₂CO]: 68.08, 68.96 ppm.

The elemental analyses for (IIIa-d) were in agreement with the calculated values.

LITERATURE CITED

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