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DIRECT NMR SPECTROSCOPIC PROOF FOR THE RING-CHAIN TAUTOMERISM IN THE THIAZOLIDINE SYSTEM

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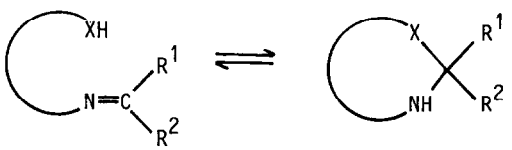
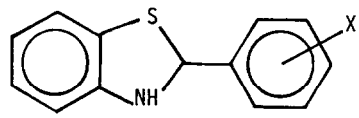
Summary: 2-(2'-Hydroxy-5'-bromophenyl)-benzothiazoline exists as a ring-chain tautomeric mixture in $CDCl_3$ and DMSO-d_6 as proved by NMR spectroscopy.

Within the ring-chain tautomeric processes the intermolecular reversible additions to the C=N group are well known.[1] Because of the enhanced nucleophilicity of the X atom and the reduced steric strain in the sulphur containing heterocycles the ring stability increases in the following order O< NR<S.

In 1,3-oxazolidines and in tetrahydro-1,3-oxazines the ring-chain equilibria can easily be characterized by NMR spectroscopy.[2] In the case of 1,3-thiazolidines only indirect proofs and qualitative approximations support the presence of ring-chain tautomeric mixtures.[3] Utilizing the results obtained previously[1,2] for 1,3-O,N-heterocycles we have been trying to find direct NMR spectroscopic evidence for the ring-chain tautomeric equilibria in the former ring system.[4]



X = O, NR, S



1: X = H; 2: p$N(CH_3)_2$; 3: o-OH

Benzothiazolines[5-8] **1-3** show in $CDCl_3$ and DMSO-d_6 only the presence of ring form. To increase the acidity of the phenolic OH group compound **4** was prepared. It exists both in $CDCl_3$ and DMSO-d_6 as a mixture of the ring and chain tautomers (96.1:3.9 and 96:4, respectively). Compound **5**, a possible oxidation product of **4**, was also prepared[9] to confirm the interpretation of the NMR data.

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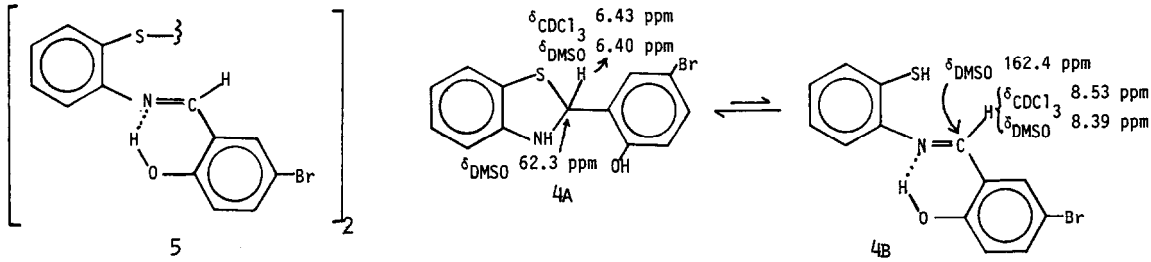

The tautomeric equilibria were determined on a Jeol GX-400 NMR spectrometer by integrating the H-2 signals. Sample concentration was 10 mg/0.5 cm^3. Forty scans was enough to achieve a very good signal to noise ratio for integration.

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4. Together with ring destabilization by the fused benzene ring and electron withdrawing aryl substituent and stabilization of the open-chain form by phenolic -OH and solvent effects.
5. General method for synthesis of **1-5**: 1 mmol 2-aminothiophenol and 1 mmol aldehyde was dissolved under nitrogen atmosphere in 20 ml ethanol and left to stand 4h at room temp. Solvent was evaporated and the product recrystallized (yields 75-90%). **1**: mp 75-77°C (hexane), lit.[6] mp 77°C; **2** 96-100°C (hexane), lit.[7] 98°C; **3** 139-141°C (EtOH), lit.[8] 136-137°C; **4** 157-158°C (EtOH); **5** 162-164°C (EtOH); **5** 162-164°C (EtOH). 400 MHz ^1H NMR and MS data correspond to the structures given.
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