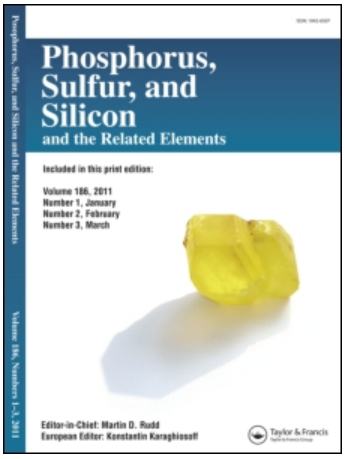

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Structural Dynamics of 4-Hydroxy-6-Mercaptothiopyran-2-Thiones

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STRUCTURAL DYNAMICS OF 4-HYDROXY-6-MERCAPTOTHIOPYRAN-2-THIONES

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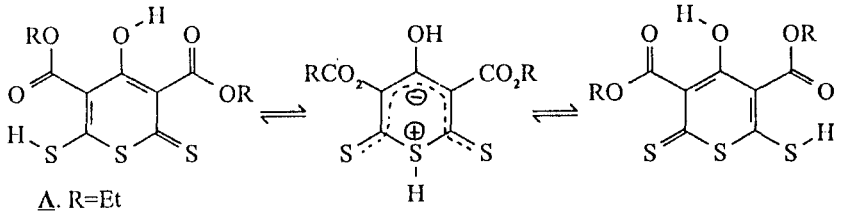
Abstract 4-hydroxy-6-mercaptothiopyran-2-thiones in solution exhibit structural dynamics owing to occurrence of intramolecular degenerated tautomerism.

Variable temperature ^{1}H NMR studies of two 3,5-dialkoxycarbonyl-4-hydroxy-6-mercaptothiopyran-2-thiones (A,B) have demonstrated that these compounds in solution exist as a degenerated tautomeric equilibrium system.
Information about the mechanism for this interconversion can be obtained through the standard activation parameters $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. These parameters are derived from the rate constants obtained by complete bandshape analysis of the variable temperature ^{1}H-NMR series.

Tabel 1. Activation Parameters for Compounds A and B.

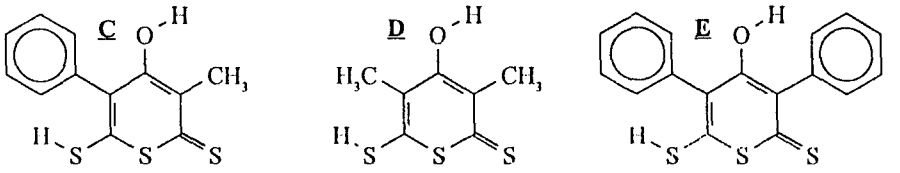
Run	solvent	$\Delta G^{\ddagger}_{300K}$ (kJ mol^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1}K^{-1})
A.1	Toluen-d_8	53.1	23.3 ±0.78	- 99.2 ±3.6
A.2	CD_2Cl_2 (15mM)	57.7	21.5 ±0.79	- 120.3 ±3.2
A.3	CD_2Cl_2 (3mM)	57.7	22.8 ±1.0	- 115.7 ±4.2
B.1	CD_2Cl_2	47.1	33.5 ±0.9	- 45.4 ±3.5

The large negative entropy of activation determinated for the interconversion points to a proton transfer mechanism involving a highly arranged transition state, possessing a high degree of symmetry. The concentration runs (A.2,A.3) exclude a second-order mechanism. Alltogether the experimental observations are best rationalized in terms of a mechanism involving intermolecular proton-sliding over the lone pair orbital of the ring-sulphur atom.



A. R=Et
B. R=Me

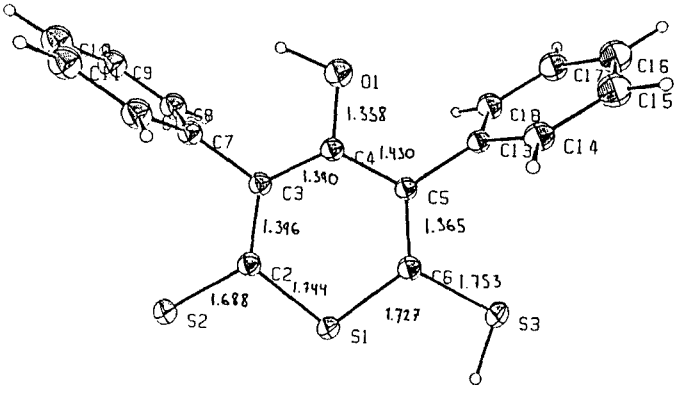
To clarify whether the observed structural dynamics is a characteristic feature for the entire class of these compounds, we have prepared a series of 2H-thiopyran-thiones with different sidegroups in the 3 and 5 positions (C-E).



The ^{1}H NMR spectra of the symmetric molecules, recorded at 300K, all display equivalent sidegroup-protons, and the hydroxy- and mercapto-proton signals are hardly observable. On lowering the temperature to ~200K, the mercapto-proton signals as well as and the hydroxy-proton signal appears in the spectra.

^{13}C-NMR spectra recorded at 300K in general display only signals of the sidegroup carbons, i. e. the ring-carbon signals are not observable. Both of these phenomena can be explained by existence of a degenerated tautomeric interchange system like that described above.

The crystal structures of the compounds A and E have been determined by X-ray diffractometry. Both compounds exhibit a molecular structure characterized by a central planar 6-membered ring, which is apparently structurally very little affected by the nature of the substituents at the position 3 and 5.



E