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EVIDENCE FOR s-*TRANS* CONFORMATION OF SOME 5-SUBSTITUTED 2-THENOYL CHLORIDES

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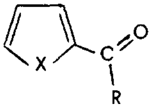
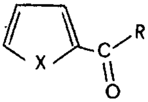
The 2-thienyl carbonyl compounds exist exclusively in the s-*trans* conformation as supported by NMR studies (1-3), X-ray analysis (1,4) and dipole moment measurements (5-7), whereas in the 2-analogous furan derivatives the presence of both s-*cis* and s-*trans* conformational isomers (1,8-12) has been established.



s-*cis*

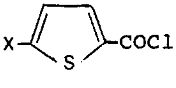


s-*trans*

X = O, S

Many conformational studies are reported for 2-thienyl and 2-furan carbonyl compounds, whereas nothing exists concerning 3-analogous derivatives and the acid chlorides of these heterocyclic molecules.

In order to provide insight on conformational preferences, we have undertaken a study on 2- and 3-thenoyl and -furoyl chlorides. In this preliminary note we report data for some 5-substituted 2-thenoyl chlorides.



X = H, CH_3, Cl, Br, NO_2

The NMR spectra of 5-substituted 2-thenoyl chlorides do not change when the samples are cooled down to -100°, suggesting the presence of only one rotational isomer. In fact all the 5-substituted 2-thenoyl chlorides show only one carbonyl stretching frequency when dissolved in CCl_4, except the 5-nitro derivative where one band (1757 cm^{-1}) of the doublet is caused by Fermi resonance (TABLE I)

TABLE I

IR SPECTRA OF 5-SUBSTITUTED 2-THENOYL CHLORIDES IN CCl_4

Substituent	$\nu_{C=O}$ (cm^{-1})
H (13)	1753
CH_3 (14)	1750
Br (14)	1750
Cl (14)	1750
NO_2 (14)	1767

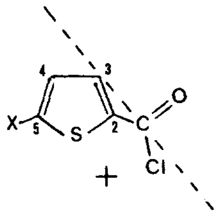
In order to establish whether the conformation is the s-*cis* or the s-*trans*, we have made use of the ASIS technique. The proton chemical shifts of these compounds in benzene are greatly different from those measured in CCl_4.

Recently many workers have investigated the specific shielding effect in NMR shown by aromatic solvents on polar solutes (15-17). The interaction between the aromatic molecules and the polar sites of the solute will cause a diamagnetic effect on the protons located near the positive end of the dipole axis of the solute molecules.

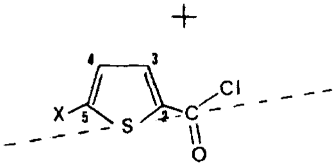
The induced shifts on carbonyl compounds can be explained by the Connolly and McCrindle model (18). If a reference plane is drawn through the carbonyl carbon atom at right angles to the C=O bond, since benzene complexes preferentially on the opposite side to the carbonyl oxygen atom, the protons in this region should be subject to shielding effect (indicated in the figure as +) and the solvent shift

$$\Delta_{(ppm)} = \delta_{CCl_4} - \delta_{C_6D_6}$$

should be positive.



s-*cis*



s-*trans*

The s-*trans* conformation of 5-substituted 2-thenoyl chlorides will give a positive △ value for the protons in the 3- and 4-positions, on the other hand the s-*cis* conformation will give a positive △ value for the proton in the 4-position and a small shift (close to zero) for the 3-proton. The 5-substituent (X = H, CH_3) is also subject to its characteristic solvent shift depending on the conformation, but in both the cases it will be positive.

From the obtained results, listed in TABLE II, it can be noted that both the 3- and 4-protons show large positive solvent shift values. The same effect is observed for the 5-proton and the methyl group in the compounds where X = H, CH_3 respectively. The differences in △ values in the 5-substituted 2-thenoyl chlorides are due mainly to steric or dipole interactions of the substituents in the thienyl ring and the benzene molecules. From these results we can conclude that the 5-substituted 2-thenoyl chloride molecules occur exclusively in the s-*trans* conformation.

TABLE II

CHEMICAL SHIFTS AND SOLVENT SHIFTS (△) OF THE 5-SUBSTITUTED 2-THENOYL CHLORIDES

Substituent X	Solvent	δ_3 (ppm)	Δ_3	δ_4 (ppm)	Δ_4	δ_X (ppm)	Δ_X
	CCl_4	7.98		7.20		7.81	
H			+0.50		+0.77		+0.93
	C_6D_6	7.48		6.43		6.88	
	CCl_4	7.73		6.87		2.60	
CH_3			+0.31		+0.67		+0.73
	C_6D_6	7.47		6.20		1.87	
	CCl_4	7.71		7.17			
Br			+0.67		+0.80		
	C_6D_6	7.04		6.37			
	CCl_4	7.82		7.07			
Cl			+0.73		+0.86		
	C_6D_6	7.09		6.21			
	CCl_4	7.93		7.93			
NO_2			+0.99		+1.06		
	C_6D_6	6.94		6.87			

Solutions were 1 molar in both the solvents.

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References

1) R. Roques, S. Combrisson, C. Riche and C. Pascard -Billy, Tetrahedron **26** , 3555 (1970).
2) M. L. Martin, C. Andrieu and G. L. Martin, Bull. Soc. Chim. Fr. , 698 (1968)
3) L. Kaper and Th. J. De Boer, Rec. Trav. Chim. Pays Bas, , **89**, 825 (1970).
4) H. J. Streurman and H. Schenk, ibid, **89**, 392 (1970).
5) H. Lumbroso and P. Pastour, C. R. Acad. Sc., Paris**261**, 1279 (1965).
6) H. Lumbroso, D. M. Bertin, M. Robba and B. Roques, ibid, **262** c, 36 (1966).
7) H. Lumbroso, M. M. Bertin and P. Cagniant, Bull. Soc. Chim. Fr., 1720 (1970)
8) K. I. Dahlqvist and S. Forsen, J. Phys. Chem,**69**, 1760 (1965).
9) L.Arlinger, K. I. Dahlqvist and S. Forsen, Acta Chem. Scand., **24**, 2, 662 (1970).
10) D. J. Chadwick and G. D. Meakins, Chem. Comm., 637(1970).
11) G. J. Karabatsos and F. F. Vane, J. Amer. Chem. Soc.,**85**, 3886 (1963).
12) M. L. Martin, J. C. Roze, G. J. Martin and P. Fournari, Tetrahedron Letters, **39**, 3407 (1970).
13) J. J. Peron and P. Saumagne, Spectrochim. Acta, **26A**, 1651 (1970).
14) This work.
15) T. Ledaal, Tetrahedron Letters, 1683 (1968) and refs therein.
16) K. M. Baker and R.G. Wilson, J. Chem. Soc.,236 (1970).
17) F. H. A. Rummens and R. H. Krystynak, J. Amer. Chem. Soc.,**94**, 6914 (1972).
18) J. D. Connolly and R. McCrindle, Chem. Ind. London,379 (1965)