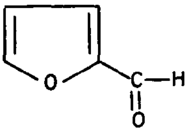
Tetrahedron Letters No.19, pp. 1381-1384, 1965. Pergamon Press Ltd.
Printed in Great Britain.

STUDIES IN FURAN CHEMISTRY (1). ROTATIONAL ISOMERISM

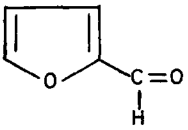
R. Grigg and M. V. Sargent
The University Chemical Laboratory, Cambridge,
England.
J. A. Knight
The Chemistry Department, The University,
Nottingham, England.

(Received 15 March 1965)

The Raman and infrared spectra of furfural show two carbonyl absorptions. Early workers (2) ascribed the doublet to molecular association. More recent cryoscopic and spectral investigations (3,4) have shown that the two carbonyl absorptions are due to the existence of rotational isomers (I-II). Infrared studies on pyrrole-2-esters have shown that these compounds exhibit rotational isomerism (5,6). 2-Formylthiophen has also been reported (7) to have two carbonyl absorptions.



(I)



(II)

TABLE

Carbonyl Absorptions of Substituted Furans

Substituents				Carbonyl Stretching Frequencies (cm.$^{-1}$)		
2	3	4	5			
CHO	H	H	Me	1686		1710
CHO	H	H	I	1694		1719
CHO	H	H	Br	1691		1718
CHO	H	H	NO_2	1704	1716 sh	1722
COC_6H_5	H	H	H	1654		1660
COC_6H_5	H	H	I	1650		1659
COC_6H_5	H	H	Br	1653		1661
$COCH_3$	H	H	H	1689		1717
CO_2Me	H	H	Me	1730		1742
CO_2Me	H	H	CH_2Cl	1729		1743
CO_2Et	H	H	CH_2Cl	1726		1741
CO_2Me	H	H	I	1735		1751
CO_2Me	H	H	Br	1723		1736
CO_2Me	Me	H	Br	1721		1738
CO_2Me	H	Br	Me	1730		1744
CO_2Me	H	i-Pr	Br	1726		1741

The recent report by Forsen and his co-workers (8) that the presence of two rotational isomers can be detected in the n.m.r. spectrum of furfural at -80°, prompts us to publish our preliminary observations on the infrared spectra of a series of furans with carbonyl substituents at the 2-position. All of these furans exhibited two carbonyl absorptions in carbon tetrachloride solution (Table), and dilution studies on several of these furans indicates that the relative intensities of the two carbonyl absorptions are concentration dependent. Studies in chloroform and carbon disulphide have shown that the relative intensities of the two carbonyl absorptions are also solvent dependent. The solvent and concentration dependence of the carbonyl absorptions is in agreement with the earlier observations on furfural (2-4).

We suggest our data indicate the presence of rotational isomerism in these compounds. Studies are in progress to provide further evidence on this point.

REFERENCES

1. R. Grigg, J. A. Knight and M. V. Sargent, Part I, J. Chem. Soc., in the press.
2. P. Mirone, Atti Accad. nazl. Lincei, Rend. Classe sci. fis. mat. e nat., **16**. 483, (1954).
3. G. Allen and H. J. Bernstein, Canad. J. Chem., **33**, 1055, (1955).

4. N. Claverie, C. Garrigou-Lagrange, and J. Domingues Dos Santos, J. Chim. Phys., 59, 1046, (1962).

5. R. Grigg, J. Chem. Soc., in the press.

6. R. A. Jones and A. G. Moritz, Spectrochim. Acta, 21, 295, (1965).

7. P. Chiorbili and A. M. Drusiani, Atti Accad. natzl. Lincei Rend. Classe sci. fis. mat. e nat., 12, 309, (1952).

8. S. Forsen, B. Akermark, and T. Alm, Acta Chem. Scand., 18, 2313, (1964).