Rotational Isomerism in the Esters of Furan-2- and Thiophen-2-carboxylic Acids

By D. J. CHADWICK, J. CHAMBERS, G. D. MEAKINS,* and R. L. SNOWDEN
(*Dyson Perrins Laboratory, Oxford University, Oxford* OX1 3QY)

Summary In carbon tetrachloride solution at 303 K the rotational isomers of the esters of furan-2- and thiophen-2-carboxylic acids are tentatively correlated with the *syn-s-trans* and the *anti-s-trans* conformations.

RECENT work on rotational isomerism has been concerned with identification of the conformations adopted by ester groups[1,2] and by aldehyde groups[3] in compounds such as 2-furaldehyde.[4] We report that the i.r. spectra of many furan-2- and thiophen-2-carboxylic esters have well defined carbonyl doublets; study of these involves features common to the two stereochemical topics.

TABLE 1

Thermodynamic results (using band areas in CCl_4 *of higher frequency form* $\rightleftharpoons$ *lower frequency form)*

	$\Delta H°$(J mol^{-1})	$\Delta S°$(J K^{-1} mol^{-1})	$\Delta G°$(J mol^{-1} at 303 K)	K (at 303 K)
(Ia)	-1153 ± 250	$-5·0 \pm 1·7$	$+303 \pm 250$	0·887
(Ib)	-2142 ± 250	$-9·8 \pm 1·7$	$+813 \pm 250$	0·725
(Ic)	-2483 ± 250	$-7·3 \pm 1·7$	-264 ± 250	1·27

TABLE 2

$C{=}O$ *Stretching bands*[a]

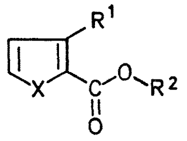
No.	Solvent	ν_{max}	Conformation
(Ia)	CCl_4	1740·5(1·1) 1726(1)	A B
„	$CHCl_3$	1730·5* 1725	A B
„	CCl_4–MeCN[b]	1736·5(1·2) 1725(1)	A B
(Ib)	CCl_4	1733·5(1) 1718(1·1)	A B
„	$CHCl_3$	1725* 1716	A B
„	CCl_4–MeCN	1729·5(1·1) 1717·5(1)	A B
(Ic)	CCl_4	1729·5(1) 1711·5(1·2)	A B
„	$CHCl_3$	1719* 1708	A B
„	CCl_4–MeCN	1725·5(1) 1711(1)	A B
(IIa)	CCl_4	1732(1) 1714·5(1·5)	A B
„	$CHCl_3$	1723·5(1) 1711·5(1·9)	A B
(IIc)	CCl_4	1721·5(1) 1705·5(1·7)	A B
„	$CHCl_3$	1710* 1701·5	A B
(IIIa)	CCl_4	1721·5	A
„	$CHCl_3$	1709	A
(IIIc)	CCl_4	1710	A
„	$CHCl_3$	1698·5	A
(IVa)	CCl_4	1714	A
„	$CHCl_3$	1706·5 1693*	A B
(IVb)	CCl_4	1710	A
„	$CHCl_3$	1702·5(2·3) 1690·5(1)	A B
(IVc)	CCl_4	1706·5(3·2) 1692(1)	A B
„	$CHCl_3$	1697·5(1·3) 1684(1)	A B
(Va)	CCl_4	1727·5(1·7) 1701·5(1)	A B
„	$CHCl_3$	1720(2·3) 1698(1)	A B
(Vb)	CCl_4	1723·5(1·2) 1698(1)	A B
„	$CHCl_3$	1713·5(1·3) 1692(1)	A B
(Vc)	CCl_4	1720·5(1) 1695(1·5)	A B
„	$CHCl_3$	1710·5(1) 1683(1·3)	A B
(VIb)	CCl_4	1722·5(1·7) 1696·5(1)	A B
„	$CHCl_3$	1713·5(1·7) 1687(1)	A B
(VIIa)	CCl_4	1719·5	—
„	$CHCl_3$	1710	—

[a] The ν_{max} values (cm^{-1}), obtained at a spectral slit-width of 1·7 cm^{-1}, refer to 303 K. For satisfactorily resolved doublets the relative optical densities of the components are given in parentheses; in other cases the components marked * are shoulders on the neighbouring main bands. [b] Mixture with dielectric constant of 6.

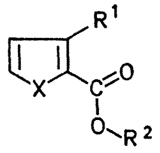
The spectrometric results, and the main conclusions are set out in Tables 1 and 2. All samples were shown to be pure by g.l.c. and t.l.c. examination. Compounds (Ia—c), (IIa), (IIIa and c), (IVa and b), and (Va and b) had constants close to the literature values; the structures of the other esters, which are new compounds, follow from their methods of preparation and n.m.r. spectra. For brevity, only the relative optical densities of the doublets' components are shown; quantitative treatment of the intensities and of the doublets' temperature dependence[5] will be given in full later.

Esters of the type studied here could adopt four planar conformations, A—D. It is believed that forms A and B are the forms principally involved because (i) an *s-trans*–*s-cis* pair, *e.g.* A and C, would not explain the relatively large frequency separations in the doublets,[1,2] (ii) the separations are similar to those observed with *syn–anti* pairs of furan- and thiophen-2-carbaldehydes,[4,6] (iii) the esters do not have any of the special structural features which lead to the adoption of *s-cis* forms,[1,7] and (iv) with all the t-butyl esters form D involves an unfavourable

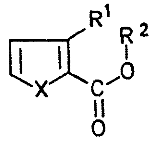
Planar conformations



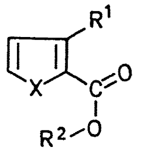
A, *syn-s-trans*



B, *anti-s-trans*

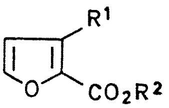


C, *syn-s-cis*

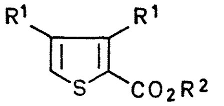


D, *anti-s-cis*

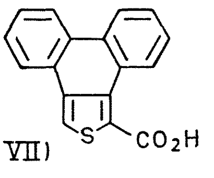
Esters with a; R^2=Me, b; R^2=Et, c; R^2=Bu^t, derived from:-



	R^1
(I)	H
(II)	Me



	R^1
(III)	H
(IV)	Me
(V)	Ph
(VI)	p-MeO·C_6H_4



(VII)

X · · · · · R^2 interaction, and when a 3-substituent is present the R^1· · · · · · · R^2 repulsion in form C is prohibitive.

Assignment of the higher frequency (h.f.) and lower frequency (l.f.) components of doublets to particular conformations is hampered by the lack of regular solvent effects. With 2-furaldehydes an increase in the dielectric constant of the medium (*i.e.*, addition of acetonitrile to the carbon tetrachloride, or use of chloroform as solvent) leads to a relative intensification of the l.f. bands, which have been rigorously correlated with the *syn* conformation.[4] In contrast, the behaviour of the esters is much more complicated, as shown by comparing the various series of esters and the corresponding esters in different series, and little can be deduced from it. The tentative correlations in the Tables (h.f.–*syn*, l.f.–*anti*) are based on a steric effect. Detailed examination of esters (Ia—c) in carbon tetrachloride, as described previously,[6] established that the h.f. bands arise from the thermochemically less stable forms. With the methyl ester and (to a greater extent) the ethyl ester this form is thermodynamically more stable at 303 K than the l.f. form, but the situation is reversed in the t-butyl ester. Correspondingly, in the series of esters (IV) only the t-butyl compound (IVc) exhibits a doublet in carbon tetrachloride. [The frequency of the stronger band (1706·5 cm^{-1}) shows it to arise from the conformation which gives single bands in the ethyl ester (IVb, 1710 cm^{-1}) and the methyl ester (IVc, 1714 cm^{-1})]. This relatively higher proportion of the l.f. form with the larger alkyl group may arise from increased R^1 · · · · · · OR^2 repulsion in form A; the l.f. form would then correspond to the form (B) in which this unfavourable interaction is relieved.

Replacement of the nuclear methyl groups in compounds (IV) by phenyl groups [compounds (V)] raises (*sic*) the C=O frequencies, suggesting that the aromatic substituents are twisted out of plane. When aromatic rings are constrained to lie in the plane of the heterocyclic nucleus [compound (VII)] the ester group is forced into a nonplanar conformation (single band at 1719·5 cm^{-1}).

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