The Relative Stabilities of the *syn* and *anti* Forms of 2-Furaldehyde in Carbon Tetrachloride Solution

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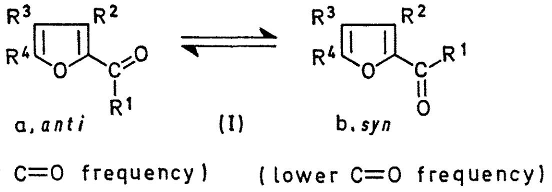
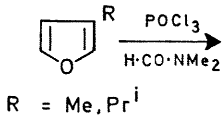
Summary I.r. measurements show that the *anti* form of furan-2-carbaldehyde is thermodynamically more stable than the *syn* form in carbon tetrachloride at 303 K.

IT is generally accepted[1-5] that 2-furaldehyde, as a dilute solution in a non-polar solvent, exists in the *anti* (Ia) and the *syn* (Ib) forms, but there is disagreement about the relative stabilities of these rotational isomers. Below *ca.* 200 K the rate of interconversion is sufficiently slow for the n.m.r. signals of the forms to be observed separately. The *anti* form was originally thought to be the more abundant isomer in dimethyl ether at low temperature[2]; later work[3] left the question open, and recent observations[4] suggest that the predominant conformation is the *syn* form. At higher temperatures the equilibrium is more readily studied by i.r. spectrometry. The i.r. C=O doublet ν_{max} (CCl_4) 1700 and 1681 cm^{-1}, showed 2-furaldehyde to be mainly in the thermochemically less stable form (ν_{max} 1700 cm^{-1}) at temperatures around 303 K, but the structures of the forms remained in doubt.[5] The basis of the present work is a comparison of 3-, 4-, and 5-alkylfuran-2-carbaldehydes. On purely steric grounds the 4- and 5-alkyl compounds should resemble the parent aldehyde: molecular models of the 3-alkyl compounds show that the *anti* forms involve a repulsion, whose magnitude is not easily predicted, between the 3-alkyl group and the aldehyde oxygen.





		τ(4-H)	τ(5-H)	$J_{4,5}$(Hz)
(II)	95%^{a}	3·60	2·45	1·6
(III)	92%	3·53	2·55	1·8

I.r. results, obtained with samples rigorously purified by t.l.c. or g.l.c., and the main conclusions are summarised in the Table. For brevity only the relative optical densities of doublets' components are given; band areas and the temperature dependence of the doublets[6] will be discussed in full later. All the aldehydes and ketones except (III), (VII), and (XI) are known compounds. 3-Alkylfuran-2-carbaldehydes are not readily accessible, and for the present purpose it was essential to establish the structures of the materials used. Vilsmeier formylation of 3-alkylfurans is expected on mechanistic grounds to give the required 2-carbaldehydes, and this was confirmed by n.m.r. examination of the major products (Table). [The 3-methyl aldehyde (II) has been prepared previously by a different route.[7]]

All the 4- and 5-alkyl-2-carbaldehydes show single carbonyl absorptions, at about 1685 cm^{-1} in CCl_4 and at a frequency lower by the expected figure of *ca.* 10 cm^{-1} in $CHCl_3$.† Therefore in these solvents at 303 K the 4- and 5-alkyl compounds exist very largely in one conformation.

While the 3-alkyl-2-carbaldehydes (II) and (III) have single bands in carbon tetrachloride, they exhibit *doublets* in chloroform. The frequencies are such that the new bands in $CHCl_3$ must be those at 1667 cm^{-1} and 1673 cm.$^{-1}$ Considerations of steric hindrance indicate that the conformation associated with the lower frequency component is the one (the *syn* form, b) which is relatively more favoured by the presence of a 3-alkyl group. Comparison with

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† With one compound, 5-methylfuran-2-carbaldehyde (IV), this conflicts with the report[8] of two bands, attributed to rotational isomers, at 1710 and 1686 cm^{-1}. Our spectrum shows that the 1710 cm^{-1} band is very weak, accounting for less than 2% of the combined area: further, the absorptions do not exhibit the temperature dependence expected[5] for those of rotational isomers, and, as already noted,[8] their relative intensities are concentration dependent. The 1710 cm^{-1} band is similar to the weak adventitious bands of unknown origin observed with other heterocyclic aldehydes.[5]

2-furaldehyde, bearing in mind the expected lowering in frequency of a particular band by the inductive effect of alkyl groups, shows that the correlation applies also to the conversion –CHO → –CO·Me to *increase* the C=O frequency, the *anti* form of the aldehyde is the one absorbing at higher frequency (1700 cm^{-1}) than the ketone.

C=O Stretching bands[b] and conformations

No.	R^1	R^2	R^3	R^4	CCl$_4$ ν_{max}	CCl$_4$ Form	CHCl$_3$ ν_{max}	CHCl$_3$ Form
(I)	H	H	H	H	1700(1)	a	1693(1)	a
					1681(0·34)	b	1676(1·4)	b
(II)	H	Me	H	H	1688	a	1680·5(1)	a
							1673(0·91)	b
(III)	H	Pr^i	H	H	1686	a	1678(1)	a
							1667(1·2)	b
(IV)	H	H	H	Me	1686	a	1672	a
(V)	H	H	H	Pr^i	1686	a	1672·5	a
(VI)	H	H	Pr^i	H	1687	a	1677	a
(VII)	H	H	Pr^i	Pr^i	1685	a	1672	a
(VIII)	Me	H	H	H	1683·5	a	1674	a
(IX)	Et	H	H	H	1685	a	1674	a
(X)	Me	Me	H	H	1677	a	1667·5	a
(XI)	Et	Me	H	H	1678·5	a	1667·5	a

[a] Of total 3-*R*-plus 4-*R*-2-carbaldehydes. [b] The ν_{max} values (cm^{-1}), obtained at a spectral slit-width of 1·7 cm^{-1}, refer to 303 K For doublets the relative optical densities of the components are given in parentheses.

parent aldehyde. Thus, the thermodynamically more stable form of 2-furaldehyde in CCl$_4$ at 303 K, that giving the 1700 cm^{-1} band,[5] is now identified as the *anti* conformation (Ia). (This is the reverse of our earlier tentative proposal.[5])

The results with the 2-ketones support the conformational assignments. All these compounds, in hexane solution, have u.v. absorptions near 263 nm, ϵ *ca.* 14,000, indicating that non-planar conformations make little contribution. In the more heavily substituted members steric effects would render the *syn* forms very unfavourable. It is likely that the single carbonyl bands are associated with *anti* conformations. One band of 2-furaldehyde must correspond to the *anti* form of 2-acetylfuran (II), ν_{max} 1683·5 cm^{-1}. Since it would be unprecedented for the

Two effects, which are not directly involved in the main arguments, emerge from the results. (i) It was not expected that the alkylfuran-2-carbaldehydes and the unhindered 2-ketones would show such a marked preference for the *anti* form. The cause, which must be electronic in origin, is not understood. (ii) With 2-furaldehyde the use of chloroform, or a mixture of acetonitrile and carbon tetrachloride,[5] instead of carbon tetrachloride as solvent increases the proportion of the *syn* form. This change, with chloroform, is general for the aldehydes and ketones studied here. Despite complications in the literature[9] we consider that the *syn* forms should have higher dipole moments, and, for this reason, should be favoured by an increase in solvent polarity.

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[1] See, *e.g.*, G. Allen and H. J. Bernstein, *Canad. J. Chem.*, 1955, **33**, 1055.
[2] K-I. Dahlqvist, and S. Forsen, *J. Phys. Chem.*, 1965, **69**, 4062.
[3] L. Arlinger, K-I. Dahlqvist, and S. Forsen, *Acta Chem. Scand.*, 1970, **24**, 662.
[4] M. L. Martin, J.-C. Roze, G. J. Martin, and P. Fournari, *Tetrahedron Letters*, 1970, 3407.
[5] D. J. Chadwick and G. D. Meakins, *Chem. Comm.*, 1970, 637.
[6] J. Chambers, Part II Thesis, Oxford, 1971.
[7] T. Reichstein, H. Zschokke, and A. Goerg, *Helv. Chim. Acta*, 1931, **14**, 1277.
[8] R. Grigg, J. A. Knight, and M. V. Sargent, *Tetrahedron Letters*, 1965, 1381.
[9] K. Kovalenko, V. I. Minkin, Z. N. Nazarova, and D. V. Kazachenko, *Zhur. obshchei Khim.*, 1962, **32**, 549; H. Lumbroso, D. M. Bertin, and P. Cagniant, *Bull. Soc. chim. France*, 1970, 1720, and earlier paper; F. Mönnig, H. Dreizler, and H. D. Rudolph, *Z. Naturforsch.*, 1965, **20a**, 1323; 1966, **21a**, 1633.