Infrared Carbonyl Absorptions of 2-Oxofurans: Fermi Resonance *versus* Rotational Isomerism as the Cause of Carbonyl Band Doubling in Furan-2-carbaldehyde and Related Aldehydes

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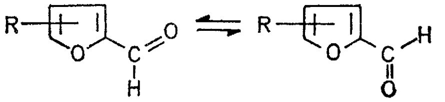
43 2-Oxofurans have been examined at high resolution in the i.r. C=O region. The C=O doublets observed for furan-2-carbaldehyde (and six related aldehydes) originate in Fermi resonance and not rotational isomerism: the C=O stretching bands of the two rotational isomers in these systems must have almost exactly equal wavenumbers.

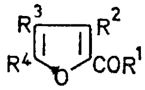
In the last decade there have been many investigations, by physical methods, into the conformational preferences of heterocyclic 2-carbaldehydes under various conditions. The development of the work can be traced from recent papers describing the techniques used (^{1}H n.m.r.,[1] ^{13}C n.m.r.,[2] microwave,[3] and i.r. spectrometry,[4] and dipole moment measurement [5]). Despite some changes of opinion as to the interpretation of the results it is now generally accepted that furan-2-carbaldehyde and a number of analogues substituted in the heterocyclic ring exhibit rotational isomerism; solutions of the aldehydes in non-polar solvents contain *syn*- and *anti*-forms, with the former predominating.



anti *syn*

Our initial work [4a] involved studying the i.r. carbonyl doublet of furan-2-carbaldehyde (1700 and 1681 cm^{-1}; CCl_4 solution at 20°) in solutions of different concentrations over a range of temperature. The results [†] excluded both intramolecular association and the occurrence of a 'hot transition' as the cause of the band splitting. (A hot transition would be identified as the less intense 1681 cm^{-1} band, and, contrary to the observed behaviour, its intensity relative to that of the 1700 cm^{-1} band would be expected to increase as the temperature is raised.) Since there was evidence [6] against the operation of Fermi resonance it seemed very probable that the doublets' components represented characteristic absorptions by the *syn*- and *anti*-forms: on this basis we obtained an apparently reasonable value (3200 J mol^{-1}) for the enthalpy difference between the rotamers,[4a] and the results appeared to harmonise fairly well with those then emerging from ^{1}H n.m.r. work. Later studies,[4b,c] mainly with isotopically labelled aldehydes, showed that the doublet does not reflect the presence of rotational isomers, and, as already adumbrated,[4b] indicated that the splitting does arise from a Fermi resonance effect. The initial object of the present work was to provide unequivocal evidence about the carbonyl doublet's origin; to do this it was necessary to examine a range of 2-oxofurans, and the broader investigation thus occasioned revealed other points of interest concerning the i.r. absorptions of furan aldehydes and ketones.

There does not appear to be any single criterion for deciding whether rotational isomerism or Fermi resonance causes a carbonyl compound to show a doublet C=O absorption. The distinction requires spectroscopic evidence from (i) a comparison of the fundamental and overtone regions,[4c] (ii) a change of solvent dielectric constant,[7] and (iii) a study of closely related compounds. Deuteriated analogues are especially important in the third approach because the position of a putative rotameric equilibrium will not be affected appreciably by deuteriating the substrate; further, replacement of protium by deuterium will produce only a small change in C=O frequency, by a mass effect, and will not introduce complications by altering the polar effects operating in the system. A series of deuteriated furancarbaldehydes was therefore prepared,[8,9] and the detailed investigation into the origin of the C=O doublet of furan-2-carbaldehyde was carried out as shown in Table 1.



(1)-(43)

Evidence from approaches (i) and (ii) was not conclusive. Thus, with rotamers of different dipole moments the equilibrium constant will be influenced by solvent

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[†] The experiments are mentioned briefly in ref. 4*a*: details are described by D. J. Chadwick, D.Phil. Thesis, Oxford, 1972.

[1] (*a*) K.-I. Dahlqvist and S. Forsen, *J. Phys. Chem.*, 1965, **69**, 4062; (*b*) B. P. Roques and S. Combrisson, *Canad. J. Chem.*, 1973, **51**, 573; (*c*) M. L. Martin, J.-C. Roze, G. J. Martin, and P. Fournari, *Tetrahedron Letters*, 1970, 3407; (*d*) S. Nagate, T. Yamabe, K. Yoshikawa, and H. Kato, *Tetrahedron*, 1973, **29**, 2545; (*e*) R. J. Abraham and T. M. Siverns, *ibid.*, 1972, **28**, 3015.

[2] D. J. Chadwick, G. D. Meakins, and E. E. Richards, *Tetrahedron Letters*, 1974, 3183.

[3] F. Mönnig, H. Dreizler, and H. D. Rudolph, *Z. Naturforsch.*, 1966, **21a**, 1633.

[4] (*a*) D. J. Chadwick and G. D. Meakins, *Chem. Comm.*, 1970, 637; (*b*) D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden, *J.C.S. Chem. Comm.*, 1972, 742; (*c*) C. G. Andrieu, C. Chatain-Cathaud, M.-C. Fournie-Zaluski, and B. Roques, *Compt. rend. C*, 1972, **275**, 559.

[5] (*a*) K. Kovalenko, V. I. Minkin, Z. N. Nazarova, and D. V. Kazachenko, *Zhur. obshchei Khim.*, 1962, **32**, 549; (*b*) H. Lumbroso, D. M. Bertin, and P. Cagniant, *Bull. Soc. chim. France*, 1970, 1720.

[6] G. Allen and H. J. Bernstein, *Canad. J. Chem.*, 1955, **33**, 1055.

[7] See, for example, R. J. Abraham, and M. A. Cooper, *Chem. Comm.*, 1966, 588.

[8] D. J. Chadwick, J. Chambers, P. K. G. Hodgson, G. D. Meakins, and R. L. Snowden, *J.C.S. Perkin I*, 1974, 1141.

[9] D. J. Chadwick, J. Chambers, H. E. Hargraves, G. D. Meakins, and R. L. Snowden, *J.C.S. Perkin I*, 1973, 2327.

polarity, and with the aldehyde (1) the observed effects of changing the solvent could be rationalised by assuming that the lower wavenumber form has the higher dipole moment. Again, the variation in the relative absorbances of the doublets' components found on examining the overtone region might result from the rotamers' C=O absorptions having different anharmonicities. The results emphasise also that it is necessary to examine a *range* of analogues. Thus, three of the deuteriated aldehydes, (3), (5), and (9) resemble the protio-aldehyde in showing doublets; this could be construed as favouring rotational isomerism if it were not for the markedly different values of the components' relative absorbances in compounds (3) and (5). The crucial observation is that all the aldehydes deuterated at position 5 show singlets in both carbon tetrachloride and acetonitrile at slightly lower wavenumbers than the higher wavenumber band of furan-2-carbaldehyde. *The* C=O *doublet of furan*-2-*carbaldehyde therefore arises from Fermi resonance* between a ' true ' C=O stretching band (at *ca.* 1694 cm^{-1} in CCl$_4$, from the 5-D analogue) and a nearby interacting absorption: the latter originates in a vibration involving the C(5)-H bond.*

The results in the Tables were obtained by examining solutions, as described previously,[a] at 20° using cells of path lengths 1 cm and 1 mm (for CCl$_4$ fundamental region), and 5 cm (for CCl$_4$, overtone region), and 1 mm and 0·1 mm (for MeCN, fundamental region). Band positions are in cm^{-1}; where more than one absorption is shown the bands' positions are followed, in parentheses, by their relative absorbances.

TABLE 1

Deuteriated aldehydes [b]

Aldehyde	R¹	R²	R³	R⁴	CO Fundamental region CCl$_4$	CO Fundamental region MeCN	CO Overtone region CCl$_4$
(1)	H	H	H	H	1700(1), 1681(0·34)	1692(0·85), 1676(1)	3371(1), 3355(0·58)
(2)	H	D	H	H	1697 *	1690(1), 1672(0·33)	3375(1), 3346(0·36)
(3)	H	H	D	H	1700(0·89), 1691(1)	1690(1), 1682(0·98)	3367
(4)	H	H	H	D	1694	1683	3370
(5)	H	D	D	H	1696(1), 1690(1)	1690(0·43), 1682(1)	†
(6)	H	D	H	D	1697	1684	3372
(7)	H	H	D	D	1695	1685	3370
(8)	H	D	D	D	1694	1682	3370
(9)	D	H	H	H	1682(1), 1672(0·69)	1668	†
(10)	D	H	H	D	1675	1665	†

* Broad band. † Not investigated.

[a] D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden, *J.C.S. Perkin II*, 1972, 1959. [b] Refs. 8 and 9.

This result together with the evidence from other investigations [1-5] requires that the C=O stretching bands of the *syn*- and *anti*-forms of furan-2-carbaldehydes have almost exactly equal wavenumbers. Such an unexpected coincidence is made even more surprising by the comparison with the corresponding esters and acid chlorides where the rotamers absorb at markedly different positions.[4b]

A series of halogenated aldehydes [8,10] is shown in Table 2. Only two exhibit C=O doublets in carbon tetrachloride, and the singlets obtained after deuteriation of these compounds at position 5 establish the occurrence and the origin of Fermi resonance. In all cases examined there is the expected change in position (a decrease of *ca.* 10 cm^{-1}) on passing to the more polar solvent. Comparison of corresponding 3- and 5-halogenated compounds in the senses of isomeric pairs, *e.g.* aldehydes (11) and (18), and of different halogens, *e.g.* aldehydes (17)—(19), indicates that any halogen at either of these positions lowers the position of the C=O absorption by *ca.* 10 cm^{-1} as a result of overall electron donation to the carbonyl group. A halogen substituent at position 4, where mesomerism is inhibited, shows the reverse effect. It is

TABLE 2

Halogenated aldehydes [a]

Aldehyde	R¹	R²	R³	R⁴	CO Region CCl$_4$	CO Region MeCN
(11)	H	Br	H	H	1691 *	1681
(12)	H	I	H	H	1690	1680
(13)	H	H	Br	H	1705·5(1), 1690·5(0·74)	1701 * (0·49), 1686(1)
(14)	H	H	Br	D	1697	1689
(15)	H	H	I	H	1705(1), 1689(0·70)	1699(0·36), 1684(1)
(16)	H	H	I	D	1698	1688
(17)	H	H	H	Cl	1690·5	1683
(18)	H	H	H	Br	1689	1682
(19)	H	H	H	I	1691	1682
(20)	H	H	Br	Cl	1693	1685
(21)	H	H	Br	Br	1694	1687

* Band broadened to high cm^{-1}.

[a] Refs. 8 and 10.

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* We are grateful to a referee for the interesting suggestion that the effect of deuteriation at position 5 might be explained in terms of rotational isomerism as follows. ' It could be argued that the mode corresponding to the " C=O stretch " has some contribution from a C-H motion. Since the extent of the contribution would depend on the relative geometry of the C-H and C=O groups the presence of rotamers would lead to a split carbonyl band. When the C-H motion is removed by deuteriation the difference between the rotamers vanishes and a single band is observed.' However, we feel that this proposal would not account for (i) the extent to which the spectrum of furan-2-carbaldehyde is changed by deuteriation at any nuclear position, and (ii) the marked contrast, with respect to the consequences of 5-deuteriation, between the aldehydes and the furan-2-carboxylates (where the carbonyl doublets, which do arise from rotational isomerism, are unaffected by deuteriation [4b]). Further, the i.r. characteristics of the furan aldehydes are similar to those of the thiophen analogues (which will be described later), and for the latter there is unambiguous n.m.r. evidence against the existence of rotational isomers under the conditions used in the i.r. work.

[10] D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden, *J.C.S. Perkin I*, 1973, 1766.

TABLE 3

Alkyl and aryl substituted aldehydes, and 2-furyl ketones [a]

Compound	R^1	R^2	R^3	R^4	CO Region CCl_4
(22)	H	Me	H	H	1688
(23)	H	Pr^i	H	H	1686
(24)	H	H	Pr^i	H	1687
(25)	H	H	H	Me	1686
(26)	H	H	H	Pr^i	1686
(27)	H	H	Pr^i	Pr^i	1685
(28)	H	H	H	Ph	1683·5
(29)	H	H	H	p-ClC_6H_4	1685
(30)	H	H	H	p-BrC_6H_4	1684
(31)	H	H	H	1-$C_{10}H_7$	1683
(32)	H	H	H	2-$C_{10}H_7$	1681
(33)	Me	H	H	H	1683·5
(34)	Et	H	H	H	1685
(35)	Me	Me	H	H	1677
(36)	Et	Me	H	H	1678·5
(37)	Ph	H	H	H	1656(1), 1650(1)
(38)	Ph	H	H	Br	1656(0·94), 1647·5(1)
(39)	Ph	H	H	I	1654·5(0·71), 1652·5(0·21), 1646·5(1)
(40)	p-$MeOC_6H_4$	H	H	H	1649(0·78), 1641·5(1)
(41)	p-$MeOC_6H_4$	H	H	Br	1643 *
(42)	2,4-$Me_2C_6H_3$	H	H	H	1656 †
(43)	2,4,6-$Me_3C_6H_2$	H	H	H	1663

Band broadened to high * or to low † cm^{-1}.

[a] Refs. 9 and 10.

reasonable that the *syn*-forms of the **3**-halogenated aldehydes and both rotamers of the **5**-halogenated isomers should absorb at similar positions. However, in the *anti*-forms of the 3-halogenated compounds the field effect arising from almost parallel C–Hal and C=O dipoles would be expected to move the bands to higher wavenumbers by *ca.* 20 cm^{-1} (*cf.* α-halogenated ketones [11]). The observation of single bands at normal positions suggests that the 3-halogenated aldehydes resemble 4-bromofuran-2-carbaldehyde (13) [12] in having a marked preference for the *syn*-conformation.

The positions of the CO bands in the aldehydes and ketones (for syntheses see refs. 8 and 10) reported in Table 3 are as expected, the lowest values being found with the *p*-anisoyl compounds (40) and (41). Single bands do not imply marked or exclusive preference for one rotameric form: for example a solution of 2-furyl methyl ketone (33) has one C=O band but almost certainly contains appreciable amounts of both rotational isomers [13] under the conditions used here. The origin of the doublets shown by the aryl 2-furyl ketones (37)—(40) has not been established. Although the doublet of the benzoyl compound (37) is retained in its 5-deuteriated analogue, ^1H n.m.r. examination did not give clear evidence for the existence of rotameric forms.[14]

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[11] L. J. Bellamy, 'Advances in Infrared Group Frequencies,' Methuen, London, 1968.

[12] S. Combrisson, B. Roques, P. Rigny, and J. J. Bassilier, *Canad. J. Chem.*, 1971, **49**, 904.

[13] L. Arlinger, K.-I. Dahlqvist, and S. Forsen, *Acta Chem. Scand.*, 1970, **24**, 662; S. Nagata, T. Yanabe, K. Yoshikawa, and H. Kato, *Tetrahedron*, 1973, **29**, 2545.

[14] R. L. Snowden, D.Phil. Thesis, Oxford, 1973.