The Infrared Bands of Thiophen-2-carbaldehydes in the Carbonyl Region: Multiple Absorption caused by Fermi Resonance

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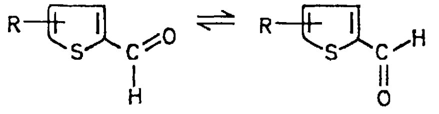
Thiophen-2-carbaldehyde and 19 related aldehydes have been examined under high resolution in the i.r. C=O region. It has been established that the multiple absorptions shown by many of the aldehydes are caused by Fermi resonance. Deuteriation of an aldehyde may lead to an increase in the complexity of its spectrum; bromination is also often effective in diagnosing the occurrence of Fermi resonance.

THIOPHEN-2-CARBALDEHYDE has been examined by several physical methods in attempts to define its conformation under various conditions. The observation of twin carbonyl bands in the Raman spectrum of the neat liquid was ascribed to intermolecular association,[1] whereas the results of ultrasonic studies were interpreted in terms of an equilibrium between rotational isomers.[2] Dipole moment measurements of a solution in benzene suggested the presence of only one form, the *syn*-rotamer,[3] but microwave examination of the aldehyde in the vapour phase indicated an exclusive preference for the *anti*-conformation.[4] (The apparent conflict between these claims may be illusory, as explained in a similar case.[5]) The gradual accumulation of results from ^{1}H n.m.r. studies [6] has proved conclusively that solutions in solvents such as acetone and deuteriochloroform contain exclusively, or very predominantly, the *syn*-form of the aldehyde. While the *anti*-form could not be detected in the ^{1}H n.m.r. work, the occurrence of an equilibrium between rotamers has been established subsequently by ^{13}C n.m.r. spectrometry.[7]



anti *syn*

Solutions of thiophen-2-carbaldehyde show multiple absorptions in the i.r. carbonyl region.[8] Our initial work,[8a] in which the doublet of solutions in carbon tetrachloride was studied over a range of temperatures, excluded intermolecular association and the occurrence of a ' hot transition ' as the cause of the band splitting.[9] At that time, before the definitive n.m.r. investigations, it seemed reasonable to correlate the components of the doublet with two rotameric forms although the supposed enthalpy difference between these (7400 J mol^{-1}) was surprisingly high. Soon afterwards, Andrieu *et al.*[8b] concluded, from examinations of the derived 2-[^{2}H]- and ^{18}O-aldehydes, that the doublet arises from the operation of Fermi resonance, and acceptable resonance parameters were calculated on this basis.[8c] However, there were some disturbing aspects (*e.g.* the doublet nature of the ^{18}O-aldehyde's absorption [8b]) and it seemed desirable to obtain conclusive evidence for the Fermi resonance explanation. This was the initial object of the present study,[8d] but in the event points of more general interest emerged.

The basic feature of our investigation, as in the similar work on furan-2-carbaldehyde,[10] is the examination of a series of deuteriated and halogenated analogues prepared for this purpose.[11] In the following account the i.r. background discussed earlier [10] is assumed, and only the main results are presented; full details, including the temperature dependence of the spectra (255—350 K) in various solvents, are recorded elsewhere.[9]

Although rigorous analysis of the absorption of thiophen-2-carbaldehyde (1) in carbon tetrachloride reveals five bands in the C=O fundamental region (Figure 1), two (listed under ' other bands ' in the Table) are very weak and in essence the spectrum comprises three bands, A, B, and C; of these the more intense components, A and B, constitute the ' doublet ' described in the literature.[8] The spectra of the 3-, 4-, and 5-deuterio-compounds [aldehydes (2)—(4)] are much simpler (Figure 2), each having a main absorption (band A) with lower wavenumber components whose intensities decrease markedly as the temperature is raised. Increasing the dielectric constant of the solvent has a dramatic effect with aldehydes (1)—(5); the main

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absorptions are at lower wavenumbers (bands B or C) and the spectra of the deuterio-compounds become more complex. These results by themselves establish that the multiplet of the parent aldehyde (1) originates in Fermi resonance. Further, since deuteriation in the thiophen ring will not have an appreciable effect on the position of an aldehyde's C=O stretching vibration,[10] the ' true ' C=O band of thiophen-2-carbaldehyde in carbon tetrachloride solution is at *ca.* 1687 cm^{-1}. Inspection of the deuterio-compounds' spectra shows that the resonance is most effectively inhibited by deuteriation at position 5, though the differences between the effects of deuteriation at different ring positions is less marked than is the case with furan-2-carbaldehydes.[10] The overtone region of thiophen-2-carbaldehyde (1) shows two bands (*cf.* the reported single band[8b]), of which only the higher wavenumber band (3355 cm^{-1}) can be related to the fundamental (1688 cm^{-1}) if an acceptable anharmonicity constant (0·0061) is to be obtained.

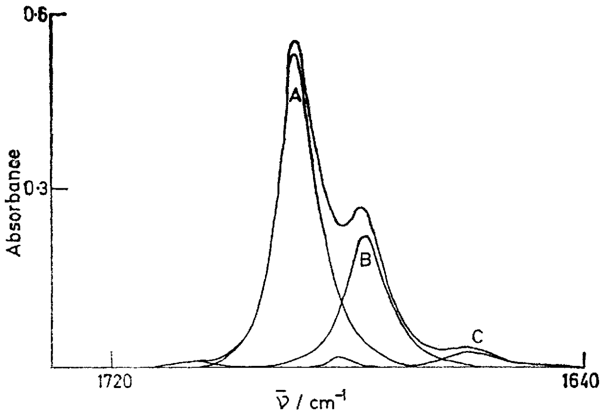


FIGURE 1 Thiophen-2-carbaldehyde (1) in CCl_4 at 303 K

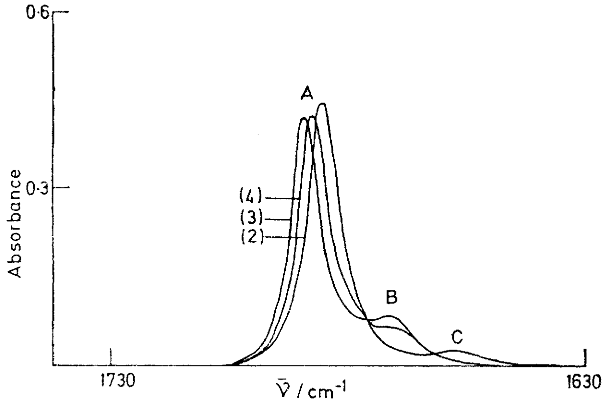


FIGURE 2 3-Deuterio-(2), 4-deuterio-(3), and 5-deuterio-thiophen-2-carbaldehydes (4) in CCl_4 at 303 K

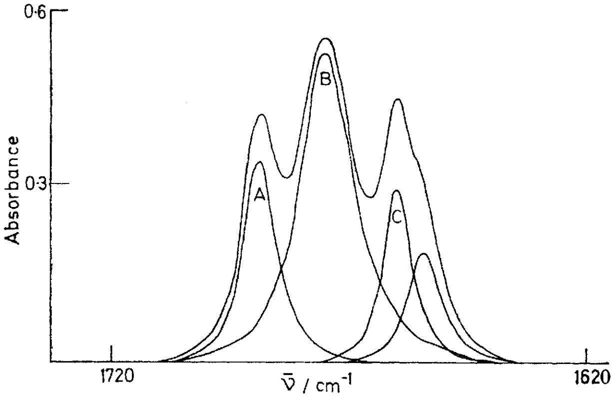


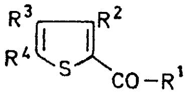
FIGURE 3 Thiophen-2-[^{2}H]carbaldehyde (5) in CCl_4 at 303 K

Although deuteriation of a compound exhibiting Fermi resonance often simplifies the spectrum (this is generally regarded as a criterion for detecting the resonance effect) the i.r. C=O absorption of the 2-[^{2}H]aldehyde (5) is compounded of four bands (Figure 3). Deuteriation in the aldehyde group is expected to lower the ' true ' C=O stretching frequency by *ca.* 15 cm^{-1}: this has the effect of bringing the C=O band into a position suitable for more extensive resonance involving at least two other modes. Correlation of the fundamental (*ca.* 1673 cm^{-1} in carbon tetrachloride) with the higher wavenumber overtone (3320 cm^{-1}) gives an anharmonicity constant of 0·0076.

Since five of the halogenated aldehydes in the Table [(6), (9), (10), (12), and (13)] are known from ^{1}H n.m.r. work[6c,d] to have a marked preference for the *syn*-conformation under a range of conditions, the observed multiple absorptions cannot be ascribed to rotational isomerism. Comparisons within the various structural types provide independent evidence against such an interpretation and establish that Fermi resonance is again the cause. Thus, for example, the 5-bromo-aldehyde (13) has two C=O bands at 303 K (A and B, Table), the 5-bromo-2-[^{2}H]aldehyde (15) has two bands whose intensities do not exactly parallel those observed in the protio-compound, and the 5-bromo-3-deuterio-aldehyde (14) has three bands. Also, although the 4-bromo-aldehyde (10) has two C=O bands, the 5-deuteriated analogue (11) has only a single band.

The notion that deuteriation does not necessarily simplify a spectrum is further illustrated by comparing, for example, the 3,5-dibromo-aldehyde (17) with its 2-deuteriated companion (18). Indeed with thiophen-2-carbaldehydes bromination is sometimes more effective than deuteriation for spectrum simplification. When two or three bromine substituents are present Fermi resonance is no longer rampant; the C=O vibrations are seen clearly and their positions can be interpreted along the usual lines. The results, together with those of the monobrominated compounds, show that the position (in cm^{-1}) of the C=O stretch is appreciably decreased, slightly decreased, and slightly increased by a bromine substituent at positions 3, 5, and 4 respectively. These trends are in agreement with the expected variations in the inductive and mesomeric effects of bromine at different sites: there is also the implication that, at least in the 3-bromo-aldehydes, there are no significant proportions of the *anti*-forms since these would

Solutions were examined, as described previously,[a] using cells of path lengths 1 cm and 1 mm (for CCl$_4$, fundamental region), 5 cm (for CCl$_4$, overtone region), and 1 and 0·1 mm (for MeCN and CHCl$_3$, fundamental region). The curves of the fundamental region were resolved[a] to give symmetrical bands; the positions (cm^{-1}) of these are followed, in parentheses, by their areas expressed as percentages of the total absorption at a particular temperature. The curves of the overtone region were not resolved; where more than one absorption is shown the bands' positions are followed, in parentheses, by their relative absorbances. The groupings of bands under the headings A, B, and C are made on the basis of their wavenumbers, and are not intended to imply common vibrational origins



Aldehyde	R¹	R²	R³	R⁴	Solvent	Temp. (K)	Fundamental region				
							Band A	Band B	Band C	Other bands	
(1)	H	H	H	H	CCl$_4$	258	1687 (49·5)	1676 (35)	1659 (7)	1707 (2·5)	1683 (6)
					CCl$_4$	303	1688 (62)	1677 (29)	1659 (5·5)	1708 (2·5)	1683 (1)
					MeCN	303	1688 (23·5)	1676 (50)	1663 (26·5)		
(2)	H	D	H	H	CCl$_4$	258	1685 (80)		1669 (20)		
					CCl$_4$	303	1687·5 (80)	1679 (6)	1669·5 (14)		
					MeCN	303	1682 (37·5)	1677 (3·5)	1670 (59)		
(3)	H	H	D	H	CCl$_4$	258	1687 (64)	1680 (13)	1670 (23)		
					CCl$_4$	303	1689 (74)	1681 (7·5)	1670·5 (19·5)		
					MeCN	303	1684 (42)	1677 (8·5)	1668 (49·5)		
(4)	H	H	H	D	CCl$_4$	258	1683·5 (86)	1670 (8)	1659·5 (6)		
					CCl$_4$	303	1685·5 (88)	1671·5 (6·5)	1657·5 (8·5)		
					MeCN	303		1678 (70·5)	1660·5 (29·5)		
(5)	D	H	H	H	CCl$_4$	258	1687·5 (20)	1672·5 (42)	1659·5 (22)	1653·5 (16)	
					CCl$_4$	303	1687 (21)	1673 (52)	1659 (16)	1653·5 (11)	
					MeCN	303		1673·5 (22)	1657·5 (36)	1645·5 (36)	
(6)	H	Br	H	H	CCl$_4$	258	1690 (24·5)	1672·5 (75·5)			
					CCl$_4$	303	1690·5 (31)	1673 (69)			
					CHCl$_3$	303	1690 (15)	1667·5 (85)			
(7)	H	Br	H	D	CCl$_4$	258	1688·5 (26)	1671 (74)			
					CCl$_4$	303	1687 (37)	1672 (63)			
					MeCN	303	1688 (16)	1666 (84)			
(8)	D	Br	H	H	CCl$_4$	258		1654 (100)			
					CCl$_4$	303		1655 (100)			
					MeCN	303		1649·5 (100)			
(9)	H	I	H	H	CCl$_4$	258	1685 (39)	1669·5 (61)			
					CCl$_4$	303	1685 (52·5)	1670·5 (47·5)			
					MeCN	303	1685·5 (18)	1665 (82)			
(10)	H	H	Br	H	CCl$_4$	258	1689 (73)	1673 (27)			
					CCl$_4$	303	1690 (80)	1673·5 (20)			
					MeCN	303	1686 (47)	1673 (44·5)		1712 (8·5)	
(11)	H	H	Br	D	CCl$_4$	258	1690 (100)				
					CCl$_4$	303	1691·5 (100)				
					MeCN	303	1681 (100)				
(12)	H	H	I	H	CCl$_4$	258	1687 (82)	1671 (18)			
					CCl$_4$	303	1689 (87)	1671·5 (13)			
					MeCN	303	1682·5 (60)	1670 (40)			
(13)	H	H	H	Br	CCl$_4$	258		1678 (100)			
					CCl$_4$	303	1687 (13)	1680·5 (87)			
					CHCl$_3$	303	1677·5 (4)	1670·5 (96)			
(14)	H	D	H	Br	CCl$_4$	258	1689·5 (3)	1678 (82·5)		1699·5 (14·5)	
					CCl$_4$	303	1690·5 (5·5)	1680 (77)		1698·5 (17·5)	
					MeCN	303		1671 (100)			
(15)	D	H	H	Br	CCl$_4$	258	1682 (18)	1662 (82)			
					CCl$_4$	303	1682·5 (21)	1663 (79)			
					MeCN	303		1655 (100)			
(16)	H	H	H	I	CCl$_4$	258	1684·5 (26)	1676 (74)			
					CCl$_4$	303	1685·5 (39)	1677·5 (61)			
					CHCl$_3$	303		1670 (100)			
(17)	H	Br	H	Br	CCl$_4$	258		1673 (100)			
					CCl$_4$	303		1674 (100)			
					MeCN	303		1668 (100)			
(18)	D	Br	H	Br	CCl$_4$	258	1686 (11)	1670 (10)	1650 (79)		
					CCl$_4$	303	1686 (12)	1670 (9)	1651·5 (79)		
					MeCN	303	1685 (9)	1669 (6)	1648 (85)		
(19)	H	H	Br	Br	CCl$_4$	258		1684 (100)			
					CCl$_4$	303		1685 (100)			
					MeCN	303		1676 (100)			
(20)	H	Br	Br	Br	CCl$_4$	258		1675 (100)			
					CCl$_4$	303		1676·5 (100)			
					MeCN	303		1670·5 (100)			
								Overtone region			
(1)	H	H	H	H	CCl$_4$	303		3355 (0·87)	3343 (1)		
(5)	D	H	H	H	CCl$_4$	303		3320 (1)	3305 (0·88)		
(8)	D	Br	H	H	CCl$_4$	303		3294			
(15)	D	H	H	Br	CCl$_4$	303		3333 (0·50)	3310 (1)		
(18)	D	Br	H	Br	CCl$_4$	303		3319 (0·45)	3289 (1)		
(20)	H	Br	Br	Br	CCl$_4$	303		3336			

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

lead to higher C=O wavenumbers by a dipolar field effect.[12]

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