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Investigation of Rotational Isomerism in Thiophen- and Furan-2-carbonyl Halides by Nuclear Magnetic Resonance and Infrared Spectrometry

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The possible occurrence of rotational isomerism in 35 thiophen- and furan-2-carbonyl fluorides and chlorides has been investigated by n.m.r. and i.r. spectrometry. At room temperature, solutions of the fluorides in trichlorofluoromethane, carbon tetrachloride, and acetonitrile contain appreciable amounts of the *syn*- and *anti*-rotamers. With furan-2-carbonyl fluoride, the compound investigated in most detail, the rotamer giving the higher field ^{19}F signal in non-polar solvents at low temperature corresponds to the rotamer of the 5-deuterio-analogue which has the higher wavenumber C=O band; these are the predominant forms (*ca.* 70% in trichlorofluoromethane) and are thought to be the *syn*-rotamers. It is probable that the chlorides also exhibit rotational isomerism, but the absence of halogen n.m.r. evidence makes the interpretation less certain.

OUR studies of heterocyclic compounds containing a C=O group originated in the observation that many heterocyclic aldehydes show two or more bands in the i.r. carbonyl region. Detailed examination of furan-[1a] and thiophen-2-carbaldehydes[1b] revealed a situation more complicated than that expected at the outset. In general the furancarbaldehydes, as dilute solutions in non-polar solvents below *ca.* 30° contain appreciable amounts of the *syn*- and *anti*-rotamers, but the thiophen derivatives exist under these conditions either mainly or exclusively in one form,† and to demonstrate the occurrence of rotational isomerism in the thiophens required low-temperature ^{13}C n.m.r. examination.[1c] While the i.r. carbonyl region doublets of the furans might have represented the individual bands of the rotamers this explanation could not be applied to the similar doublets of the thiophens; in the event Fermi resonance proved to be the cause of the multiple absorptions in both cases.[1a,b]

The present spectrometric investigation of heterocyclic acid halides is concerned particularly with the possibility that these compounds might exhibit rotational isomerism. (Systematic work on the spectra of acid halides appears to be confined to the early i.r. studies of benzoyl bromides[2] and the recent examinations of a few heterocyclic chlorides[3] and fluorides.[4]) Although the fluorides are extremely sensitive to moisture they can be purified by distillation and stored, for varying times, under suitable conditions. Table 3 (Experimental section) shows the characteristics of the new halides studied here.

Data from the i.r. and n.m.r. spectra of the chlorides and fluorides (and one bromide) at about room temperature are presented in Table 1, and the results of examining selected compounds over a temperature range are collected in Table 2. In view of the detailed nature of the Tables only the main points require discussion; the various possible interpretations of obscure features are not rehearsed.

^{19}F *N.m.r. Results*.—The ^{19}F n.m.r. signals of the fluorides (Table 2) provide the clearest evidence for the occurrence of rotational isomerism. As the temperature is lowered the signals broaden gradually and, at certain temperatures, become so broad that they are no longer visible. With five of the six fluorides examined a further decrease in temperature results in the appearance of *two* ^{19}F signals;‡ with the sixth compound (35) the

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† References to the definitive ^{1}H n.m.r. work are given in refs. 1*a* and *b*.

‡ These effects were not revealed by the previous examinations of thiophen-2-carbonyl fluoride[4a] (at temperatures down to −40°) and furan-2-carbonyl fluoride[4b] (at 32°). Evidence for the occurrence of rotational isomerism was adduced from comparisons of the observed coupling constants with those calculated for the separate isomers. Nevertheless it is difficult to see why the furan fluoride was assumed[4b] to exist as a 1 : 1 mixture of rotamers. For the thiophen analogue the proportions of rotamers were obtained, ' by assuming a Boltzmann distribution between two planar configurations for which energies are calculated in the CNDO/2 approximation.'[4a]

[1] D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden (*a*) *J.C.S. Perkin II*, 1975, 13; (*b*) *ibid.*, p. 604; (*c*) D. J. Chadwick, G. D. Meakins, and E. E. Richards, *Tetrahedron Letters*, 1974, 3183

[2] L. J. Bellamy, 'Advances in Infrared Group Frequencies,' Methuen, London, 1968, p. 127.

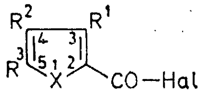
[3] A. Arcoria, S. Fisichella, and D. Sciotto, *Tetrahedron Letters*, 1973, 2907.

[4] K. Schaumberg, (*a*) *Canad. J. Chem.*, 1971, **49**, 1146; (*b*) *J. Magnetic Resonance*, 1972, **7**, 177.

TABLE 1

I.r. and n.m.r. spectra of furan- and thiophen-2-carbonyl halides

References are given to known compounds; the rest are new. The i.r. curves of the fundamental region were resolved to give symmetrical component bands; those of the overtone region were not resolved. The positions of i.r. bands (components or apparent maxima) are given in cm^{-1} and where more than one band is shown the positions are followed, in parentheses, by relative absorbances. Very weak i.r. bands ($<5\%$ of the total absorption in a particular region) are not listed. For n.m.r. signals other than singlets (s), doublets (d), triplets (t), and multiplets (m) the number of lines is indicated by an italicised number, and where appropriate the descriptions are followed by *J* values (Hz) or apparent *J* values as described earlier [a]



Compound	X	Hal	R^1	R^2	R^3	I.r. bands (303K), CO fundamental region		^{1}H N.m.r. signals (308 K), CCl_4			
						CCl_4	MeCN	τ	Form	*J*	Assignment
(1) [b]	O	Cl	H	H	H	1 797(0.40), 1 780(0.84), 1 756 (0.57), 1 744(1)	1 778 (0.33), 1 749(1)	2.26	*4*	1.7, 0.9	5-H
								2.55	*4*	3.6, 0.9	3-H
			(overtones)			3 524(0.92), 3 501(1), 3 476(0.70)		3.38	*4*	3.6, 1.7	4-H
(2) [b]	O	Br	H	H	H	1 780(1), 1 769(0.68), 1 746(0.23)		2.16	*4*	1.8, 0.8	5-H
								2.51	*4*	3.1, 0.8	3-H
								3.39	*4*	3.1, 1.8	4-H
(3)	O	Cl	D	H	H	1 787 (0.44), 1 755(1)	1 781(0.28), 1 746(1)	2.29	d	1.8	5-H
			(overtones)			3 522(0.84), 3 495(1)		3.40	d	1.8	4-H
(4)	O	Cl	H	D	H	1 794(0.25), 1 766(1), 1 749(0.58)	1 759(1), 1 749(0.83)	2.29	d	0.8	5-H
			(overtones)			3 513(1), 3 480(0.83)		2.59	d	0.8	3-H
(5)	O	Cl	H	H	D	1 768(1), 1 753(0.60)	1 760(1), 1 753(0.72)	2.59	d	3.8	3-H
			(overtones)			3 513(1), 3 470(0.44)		3.41	d	3.8	4-H
(6)	O	Cl	D	D	H	1 795(0.17), 1 765(1), 1 748(0.62)	1 759(1), 1 746(0.92)	2.29	s		5-H
(7)	O	Cl	D	H	D	1 792(0.12), 1 768(1), 1 752(0.60)	1 759(1), 1 748(0.86)	3.42	s		4-H
(8)	O	Cl	H	D	D	1 792(0.12), 1 770(1), 1 755(0.59)	1 759(1), 1 749(0.84)	2.60	s		3-H
			(overtones)			3 518(1), 3 488(0.78)					
(9)	O	Cl	D	D	D	1 767(1), 1 753(0.63)	1 759(1), 1 749(0.90)				
			(overtones)			3 510(1), 3 475(0.68)					
(10)	O	Cl	Br	H	H	1 755	1 749	2.36	d	1.9	5-H
			(overtones)			3 495(1), 3 473(0.71)		3.28	d	1.9	4-H
(11)	O	Cl	I	H	H	1 750	1 745	2.37	d	1.8	5-H
								3.17	d	1.8	4-H
(12)	O	Cl	H	Br	H	1 795(0.26), 1 764(1), 1 747(0.50)	1 793(0.14), 1 756(1), 1 746(0.31)	2.25	d	0.9	5-H
			(overtones)			3 516(1), 3 478(0.67)		2.54	d	0.9	3-H
(13)	O	Cl	H	Br	D	1 812(0.13), 1 795(0.19), 1 768(1), 1 755(0.43)	1 761(1), 1 748(0.19)	2.57	s		3-H
			(overtones)			3 518(1), 3 480(0.48)					
(14)	O	Cl	H	I	H	1 794(0.30), 1 765(1), 1 748(0.52)	1 793(0.20), 1 755(1), 1 745(0.34)	2.28	d	0.8	5-H
			(overtones)			3 520(1), 3 484(0.56)		2.50	d	0.8	3-H
(15)	O	Cl	H	I	D	1 768(1), 1 755(0·57), 1 738(0·12)	1 761(1), 1 747(0.12)	2.51	s		3-H
			(overtones)			3 519(1), 3 482(0.56)					
(16) [c]	O	Cl	H	H	Cl	1 807(0.13), 1 762(1), 1 745(0.62)	1 752	2.50	d	3.6	3-H
			(overtones)			3 506(1), 3 474(0.52)		3.59	d	3.6	4-H
(17) [c]	O	Cl	H	H	Br	1 804(0.16), 1 762(1), 1 752(0.20), 1 744(0.55)	1 801(0.09), 1 759(0.38), 1 748(1)	2.66	d	3.8	3-H
			(overtones)			3 555(0.26), 3 505(1), 3 475(0.56)		3.46	d	3.8	4-H
(18)	O	Cl	D	D	Br	1 776(0.39), 1 761(1), 1 746(0.73)	1 758(0.70), 1 748(1)				
			(overtones)			3 530(0.94), 3 509(1), 3 475(0.59)					
(19) [d]	O	Cl	H	H	I	1 802(0.22), 1 762(1), 1 745(0.78)	1 800(0.11), 1 754(1), 1 744(0.85)	2.75	d	3.5	3-H
								3.26	d	3.5	4-H
			(overtones)			3 510(1), 3 476(0.77)					
(20) [c]	O	Cl	H	H	NO_2	1 768(1), 1 750(0.66)	1 752(1), 1 742(0.65)	2.41	d	3.8	3-H
			(overtones)			3 521(1), 3 486(0.74)		2.59	d	3.8	4-H
(21)	O	Cl	Br	H	Br	1 750	1 746	3.35	s		4-H
			(overtone)			3 482					
(22)	O	Cl	H	Br	Br	1 766(1), 1 747(0.60)	1 758(1), 1 746(0.61)	2.57	s		3-H
			(overtones)			3 512(1), 3 476(0.58)					
(23)	O	Cl	H	Br	Cl	1 767(1), 1 748(0.64)	1 758(1), 1 748(0.66)	2.54	s		3-H
			(overtones)			3 512(1), 3 478(0.61)					
(24) [e]	S	Cl	H	H	H	1 759(0.45), 1 750(1)	1 757(0.51), 1 743(1)	2.07	*4*	4.0, 1.5	3-H
			(overtones)			3 511(0.42), 3 483(1), 3 450(0.23)		2.17	*4*	5.0, 1.5	5-H
								2.82	*4*	5.0, 4.0	4-H
(25)	S	Cl	H	Br	H	1 764(0.22), 1 751(1)	1 762(0.28), 1 749(1)	2.08	d	1.6	5-H
								2.27	d	1.6	3-H
(26) [f]	S	Cl	H	H	Br	1 760(0.56), 1 746(1)	1 757(0.54), 1 744(1)	2.37	d	4.0	3-H
								2.90	d	4.0	4-H
(27)	S	Cl	Br	H	Br	1 768(1), 1 750(0.29)	1 766(1), 1 748(0.67)	2.77	s		4-H

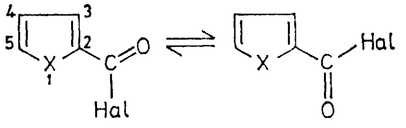
TABLE 1 (*Continued*)

Compound	X	Hal	R^1	R^2	R^3	I.r. bands (303K), CO fundamental region		^{1}H N.m.r. signals (308 K), CCl_4			
						CCl_4	MeCN	τ	Form	*J*	Assignment
(28)[g,*]	O	F	H	H	H	1 828(1), 1 816(0.54), 1 807(0.12)	1 821(1), 1 812(0.77)	2.26	*8*	2,5. 1.6, 0.8	5-H
			(overtones)			3 630(1), 3 610(0.82)		2.62	*8*	3.6, 0.8, 0.6	3-H
								3.39	*8*	3.6, 1.6, 0.8	4-H
(29)	O	F	H	H	D	1 828(1), 1 816(0.64)	1 818(1), 1 812(-) †	2.65	*4*	3.8, 0.6	3-H
			(overtones)			3 637(1), 3 614(0.70)		3.41	*4*	3.8, 0.9	4-H
(30)	O	F	D	D	D	1 830(1), 1 822(0.71), 1 814(0.72)	1 824(-), 1 815(1) †				
			(overtones)			3 633(1), 3 609(0.72)					
(31)	O	F	H	H	Br	1 828(1), 1 813(0.61)	1 819(1), 1 811(0.63)	2.67 †	d	3.7	3-H
								3.46 †	*4*	3.7, 0.8	4-H
(32)[g,*]	S	F	H	H	H	1 813(0.39), 1 807(1)	1 808(0.43), 1 799(1)	2.10	m		? 5-H
								2.23	m		? 3-H
								2.72	*8*	4.8, 3.9, 2.1	4-H
(33) *	S	F	H	Br	H	1 818(-), 1 810(1) †	1 813(-), 1 803(1) †	2.12	d	1.7	3-H
								2.25	*4*	2.3, 1.7	5-H
(34) *	S	F	H	H	Br	1 814(0.48), 1 805(1)	1 809(0.75), 1 797(1)	2.25	d	4.1	3-H
								2.74	*4*	4.1, 2.0	4-H
(35) *	S	F	Br	H	Br	1 817(1), 1 793(0.53)	1 810(1), 1 788(0.40)	2.75	d	3.0	4-H

* Positions (Φ* values, see Table 2) and form of ^{19}F signals (CCl_4 solutions at 308 K): (28), −15.2, broad d, *J* 2.2; (32), −23.5, distorted t, *J* 2.9 and 2.8; (33), −23.3, d, *J* 2.0; (34), −22.4, d, *J* 2.15; and (35), −32.0, d, *J* 3.0. † The closeness of the components prevents accurate curve resolution.[h] ‡ In $CDCl_3$.

[a] M. G. Combe, W. A. Denny, G. D. Meakins, Y. Morisawa, and E. E. Richards, *J. Chem. Soc.* (*C*), 1971, 2300. [b] T. Reichstein and H. J. Morsman, *Helv. Chim. Acta*, 1934, **17**, 1119. [c] Ref. 7. [d] Z. N. Nazarova and I. G. Gakh, *Zhur. obshchei Khim.*, 1960, **32**, 2322. [e] R. Nahnsen, *Ber.*, 1884, **17**, 2192. [f] N. Buu-Hoi and X. Nguyen-Hoan, *Rec. Trav. chim.*, 1949, **68**, 5. [g] Ref. 4. [h] Ref. 6*a*.

disappearance occurs only at the lowest attainable temperature. The energy barrier to rotation in the fluorides must be low, and success in detecting the individual forms stems from the large differences (up to *ca.* 10 p.p.m.) between their ^{19}F chemical shifts (*cf.* the CHO difference of *ca.* 0.18 p.p.m. for the *syn*- and *anti*-forms of furan-2-carbaldehyde[5]). Thus it is not surprising that the ring protons' signals of fluorides are not observed to coalesce. (The ^{1}H n.m.r. data for one compound, furan-2-carbonyl fluoride, are included in Table 2 and illustrate this point.) The ^{19}F results establish that solutions of the fluorides in trichlorofluoromethane at 293 K contain appreciable amounts of each rotamer.



anti *syn*

I.r. Results.—Carbon tetrachloride solutions of the fluorides show multiple i.r. absorptions (mostly doublets) in the carbonyl region (Table 1). Although experience with heterocyclic aldehydes[1a,b] enjoins caution in ascribing the doublets' components to rotational isomers, support for such an interpretation here is provided by other evidence. Shifts (usually of 5—10 cm^{-1}) of the bands to lower wavenumbers occur with all the fluorides when the solvent is changed from carbon tetrachloride to the more polar acetonitrile. Examination of three fluorides in the overtone region revealed doublets with the expected wavenumber separations. Further, the intensity values found in variable temperature i.r. studies with five of the fluorides in carbon tetrachloride and in trichlorofluoromethane (Table 2) are consistent with the occurrence of equilibria between forms having only small enthalpy differences. Nevertheless Fermi resonance is not entirely dormant; it is manifest for example in the presence of a third band (at 1 807 cm^{-1}) in the spectrum of furan-2-carbonyl fluoride (28), and presumably influences the intensity of the 1 816 cm^{-1} band [*cf.* the 5-deuterio-analogue (29)].

The proposal by other workers[3] that 5-substituted thiophen-2-carbonyl chlorides adopt one form exclusively in carbon tetrachloride was based solely on the observation of only one C=O band in the i.r. spectra; solvent shift studies of the ^{1}H n.m.r. signals then led to identification of the favoured form as the *syn*-rotamer. These conclusions are invalidated by the present results which include two compounds, (24) and (26), examined previously: in both cases the spectra (*i.e.* the experimental traces before band resolution) show clear doublets whose wavenumbers bracket those of the supposed single bands[3] which were probably recorded at too large a spectral slit-width. Although the occurrence of rotational isomerism has been established[1c] with one chloride, the furan compound (1), neither rotational isomerism nor Fermi resonance alone provides a satisfactory basis for interpreting the i.r. spectra of all the chlorides in Table 1. The simplest explanation of the four bands shown by furan-2-carbonyl chloride (1) is that rotamers are present, and give separate bands which are each split by the resonance effect. Deuteriation, notably at position 5,[1a] may be expected to inhibit or remove the resonance, and the doublets of compounds (3) and (5) would then be ascribed to rotamers. However, certain

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[5] K.-I. Dahlqvist and S. Forsén, *J. Phys. Chem.*, 1965, **69**, 4062.

TABLE 2

Examinations over a range of temperatures

N.m.r. signals. The positions (Φ^* values) of ^{19}F signals are shifts in p.p.m. relative to CCl_3F. The coupling constants (J) and hal intensity widths ($w_{\frac{1}{2}}$) are in Hz. The form of resolved signals is shown (in parentheses) after the Φ^* value; the multiplicity of tl other signals (broad and/or weak) is uncertain

Compound (28) in $MeCHCl_2$

Values from ^{1}H n.m.r. spectra						
Temp. (K)	$J_{3,4}$	$J_{3,5}$	$J_{4,5}$	$J_{3,F}$	$J_{4,F}$	$J_{5,F}$
308	3.62	0.78	1.74	0.47	0.75	2.39
273	3.62	0.78	1.76	0.47	0.60	2.47
243	3.62	0.78	1.76	0.46	0.49	2.62
223	3.63	0.80	1.76	†	0.30	2.90
188	3.64	†	1.77	†	<0.2	†

^{19}F spectra *			
Temp. (K)	Φ *	J	$W_{\frac{1}{2}}$
303	−14.7 (d)	2.18	4.3
243	−14.5 ‡		16.0
218			
203	−13.3		18.0
183	−13.2 (d) §	3.4	6.3
	−17.5		6.6

Compound (28), ^{19}F spectra (pulsed Fourier transform)

in CD_2Cl_2			
Temp. (K)	Φ *	J	$\omega_{\frac{1}{2}}$
298	−14.6 (d)	2.05	4.4
258	−14.4		12.4
203	−13.3		10.2
	−17.8		28.6
183	−13.2 (d) §	3.42	5.5
	−17.8 (d)	3.08	5.5

in CCl_3F			
Temp. (K)	Φ *	J	$\omega_{\frac{1}{2}}$
297	−14.7 (d)	2.91	4.5
193	−13.4		9.8
	−17.9		25.0
183	−13.4 (d) §	3.32	6.9
	−17.9		6.9

Compounds (31)—(35), ^{19}F spectra *

	Temp. (K)	Φ *	$\omega_{\frac{1}{2}}$
(31) in $MeCHCl_2$	293	−13.5	2.8
	253	−13.0	30
	233 ‡		
	193	−11.1 §	5
		−17.7	17
	183	−11.1 §	2.3
		−17.7	8
(33) in CCl_3F	293	−23.0 (d, J 2.0)	3
	223	−22.9	13
	193 ‡		
	173	−21.0 §	30
		−25.8	45
	ca. 168	−21.0 §	15
		−25.8	20
(35) in CCl_3F	293	−32.3 (d, J 2.4)	3.5
	253	32.6 (d, J 2.3)	7
	223	−33.0	9
	203	−33.2	18
	173 ‡		

	Temp. (K)	Φ *	$\omega_{\frac{1}{2}}$
(32) in CCl_3F	283	−23.8 (t, J *ca.* 2.7)	4.5
	273	−23.8	7
	223	−23.9	45
	193 ‡		
	173	−20.5 §	13.5
		−28.2	18
(34) in CCl_3F	293	−22.3	4.5
	243	−22.2	27
	193 ‡		
	ca. 168	−18.0 §	7
		−28.5	9

* Continuous wave spectra (see text). † Line broadening prevented measurement of J (but no coalescence implied). ‡ Signal t broad to be located. § The stronger of the two signals at this temperature.

I. r. C=O *bands*. The areas of the higher and lower wavenumber bands (A_h and A_l respectively) are based on $(A_h + A_l) = 10$(at the lowest temperature shown for each solution [a]

		(25)		(26)		(27)		(29)		(32)		(33) ¶		(34)		(35)	
	Temp. (K)	A_h	A_l	A_h	A_l	A_h	A_l	A_h	A_l	A_h	A_l	A_h	A_l	A_h	A_l	A_h	A
in CCl_4	258	15	85	34	66	72	28	73	27	40	60	~40	~60	32	68	69	3
	303	16	78	35	63	69	21	65	26	44	53	~35	~55	30	62	59	3
	348	18	71	35	61	66	14	54	29	46	47	~33	~50	33	52	55	3
in CCl_3F	173							80	20	41	59	~40	~60	35	65	77	2
	258							70	25	42	55	~35	~55	32	55	60	2
	303 ‖							58	24	46	49	~33	~50	30	45	55	2

¶ The closeness of the components prevents accurate curve resolution.[b] ‖ Wavenumbers of components: (29), 1 829, 1 8 (32), 1 814, 1 808; (33), 1 819, 1 812; (34), 1 816, 1 807; and (35), 1 818, 1 795.

Percentages of rotamers. ν_h is the form with the higher wavenumber C=O band (i.r. results), and Φ_h^* that with the higher field signal (nmr. results)

Compound	Solvent	Temp. (K)	ν_h	ν_l	Φ_h *	Φ_l *
(28) and (29) (see text)	CCl_3F	183	78	22	72	28
	CD_2Cl_2	183			84	16
	$MeCHCl_2$	183			80	20
(32)	CCl_3F	173	41	59	57	43
(33)	CCl_3F	173	~40	~60	63	37
(34)	CCl_3F	173	35	65	61	59

[a] Ref. 6*b*. [b] Ref. 6*a*.

features are not easily rationalised by this interpretation: 4-bromo-5-deuteriofuran-2-carbonyl chloride (13) has four bands, the positions of the higher wavenumber bands of the deuterio-compounds (3)—(9) are surprisingly different, and while 3,5-dibromothiophen-2-carbonyl chloride (27) shows a doublet the corresponding furan compound (21) has only one band. (It may also be noted [2] that benzoyl chloride and all three monobromo-derivatives give doublets, at least some of which must arise from Fermi resonance.) With most of the chlorides changing the solvent from carbon tetrachloride to acetonitrile causes a decrease in the relative intensities of the lower wavenumber bands which, assuming rotational isomerism, would then be attributed to the rotamers having the lower dipole moments; there are, however, several chlorides which show the opposite behaviour.

Despite the complications caused by the unpredictable incursion of Fermi resonance certain trends emerge: corresponding pairs of chlorides and fluorides (both within one heterocyclic series, and from the two series) show fairly consistent differences in band positions, the wavenumber shifts caused by changing the solvent are general, and substitution of halogen atoms at different ring positions produces changes in band positions similar to those observed (and discussed) previously with heterocyclic aldehydes.[1a,b]

Correlation of N.m.r. and I.r. Results, Identification of Rotamers.—In order to correlate the spectrometric results and to associate certain absorptions with particular rotamers it is desirable to use one solvent for all types of spectra. Unfortunately only with the least polar solvents are the i.r. doublets' components sufficiently well separated for accurate curve resolution; [6] since the halides are only sparingly soluble in such solvents at low temperature, detailed examination of weak signals using conventional (continuous wave) n.m.r. spectrometers is hampered by the low signal-to-noise ratio. It emerged that trichlorofluoromethane is the best solvent for direct comparison of a fluoride's i.r. and ^{1}H and ^{19}F n.m.r. characteristics, and although technical considerations made it necessary to use other solvents for some of the variable temperature n.m.r. work all the results can be related to the spectra in trichlorofluoromethane.

Interpretation of the spectra may be illustrated with furan-2-carbonyl fluoride (28), the key compound which was examined in most detail. The critical features of the ^{1}H n.m.r. spectra (in 1,1-dichloroethane, Table 2) are the gradual decrease of the 4-H–F coupling and the gradual increase of the 5-H–F coupling as the temperature is lowered. Thus, the equilibrium shifts in favour of the rotamer in which the main fluorine coupling is to 5-H. That this isomer is already predominant at room temperature is established by comparing the $J_{\mathrm{H,F}}$ values at 308 K with those of the individual rotamers at low temperature (the latter being obtained from the ^{19}F spectra, since, as noted earlier, there is no coalescence in the ^{1}H n.m.r. spectra). The variable temperature ^{19}F spectra (also in 1,1-dichloroethane) then show that this predominant rotamer is the one having the higher field (stronger) ^{19}F signal; at room temperature the chemical shift of the weighted average signal is close to that of this rotamer. Although the main ^{19}F signal of the low temperature spectra is a doublet, examination by the continuous wave n.m.r. method did not reveal the form of the weaker signal. The compound was therefore studied using pulsed Fourier-transform n.m.r. (which gives a more favourable signal-to-noise ratio), and in one solvent (dichlorodideuteriomethane) both ^{19}F signals appeared as doublets. (For further development of the interpretation it is important to note that the three non-polar solvents used for the n.m.r. work led to similar values for the rotamer proportions at low temperature as shown in Table 2. In dideuteriodichloromethane the F–H coupling observed as a weighted average in the room temperature ^{19}F spectrum is significantly lower than either of the individual rotamers' F–H couplings determined at low temperature. It may be that this situation arises from the intrinsic temperature dependence of coupling constants; alternatively, the individual $J_{\mathrm{F,H}}$ values may be of opposite sign.) If, as has been suggested,[7] the **W** rule established for H–H coupling in heterocyclic systems [8] also applies to H–F couplings, the predominant isomer (with the 5-H–F coupling) must be the *syn*-rotamer. In the minor (*anti*) rotamer the zig-zag couples 4-H–F, the lower J value here showing that transmission through the **W** system is less effective when the heteroatom is not involved. These correlations do not necessarily hold with the other acid fluorides in Table 2 (examined by continuous wave n.m.r. only, and consequently with uncertain multiplicities for their low temperature ^{19}F signals), but the overall resemblance in n.m.r. behaviour between these compounds and the key fluoride (28) suggests a common pattern of rotational isomerism.

Since Fermi resonance renders furan-2-carbonyl fluoride (28) unsuitable for detailed i.r. work, the 5-deuterio-analogue (29), which has a well resolved doublet, was used for variable temperature work. (There can be little, if any, difference between the conformational preferences of these two compounds.) The variation in the relative intensities of the components shows that the rotamer with the higher wavenumber C=O band is the one which [in compound (28)] has the higher field ^{19}F signal. However this does not apply generally; with three fluorides in Table 2 the higher wavenumber C=O rotamer has the lower field ^{19}F signal.

The gratifying agreement in the proportions of rotamers as determined for several fluorides by ^{19}F n.m.r. and i.r. techniques (shown in the last section of Table 2) may be fortuitous in view of the experimental difficulties

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[6] (*a*) D. J. Chadwick, J. Chambers, and R. L. Snowden, *J.C.S. Perkin II*, 1974, 1181; (*b*) D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden, *ibid.*, 1972, 1959.

[7] R. D. Schuetz and G. R. Nilles, *J. Org. Chem.*, 1971, **36**, 2188.

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and the assumption made in the i.r. calculations that pairs of rotamers have equal integrated absorption coefficients.[6b]

EXPERIMENTAL

Spectrometric Work.—The infrared spectra were recorded on a Perkin-Elmer 521 spectrometer purged continuously with dry air at a spectral slit width of 1—2 cm^{-1}, and resolved into symmetrical components as described in ref.[6a] The cells and solutions used generally [window material, path length in cm, solvent, carbonyl region examined, temp. or temp. range (K)] were: NaCl, 0.1 and 1, CCl_4, fundamental, 303; NaCl, 1 and 5, CCl_4, overtone, 303; AgCl, 0.1 and 1, CCl_4, fundamental, 258—348; NaCl, 0.01, MeCN, fundamental, 303; and AgCl, 0.01 and 0.1, CCl_3F, fundamental, 173—295. In most of the n.m.r. work, carried out with Perkin-Elmer R14 and R32 spectrometers, the resonating nuclei, the irradiating frequencies (MHz), solvents, temperatures or temperature ranges (K) were: ^1H, 100 or 90, CCl_4, 308; ^1H, 90, CCl_3F, 180—300; ^{19}F, 84.6, CCl_4, 308; and ^{19}F, 84.6, CCl_3F, 180—300. Solutions used for variable temperature continuous wave ^{19}F spectra contained PhCOF (Φ^* −17.1); the spectrometer (the R32 instrument) was 'locked' to the sharp ^{19}F resonance of this compound.

TABLE 3

Characterisation of new acid chlorides and fluorides

-2-Carbonyl chloride	B.p. (bath temp). (°C) [M.p.] (°C)		Analytical figures (%) C	H	Hal	Abundance (%) of M^+
3-Deuteriofuran (3)	90—92/12 mmHg	Found	45.3	21.0 *	27.3	21
		$C_5H_2ClDO_2$ requires	45.6	21.3 *	27.0	
4-Deuteriofuran (4)	98—100/14 mmHg	Found	45.5	21.2 *	27.1	15
5-Deuteriofuran (5)	90—92/12 mmHg	Found	45.3	21.5 *	27.2	28
3,4-Dideuteriofuran (6)	97—99/14 mmHg	Found	45.0		27.2	
		$C_5HClD_2O_2$ requires	45.3		26.8	25
3,5-Dideuteriofuran (7)	94—96/13 mmHg	Found	45.1		26.9	19
4,5-Dideuteriofuran (8)	91—93/12 mmHg	Found	45.0		27.2	
3,4,5-Trideuteriofuran (9)	84—86/10 mmHg	Found	45.1	4.3 †	26.8	21
		$C_5ClD_3O_2$ requires	45.0	4.5 †	26.6	
3-Bromofuran (10)	[38—40]	Found	28.9	1.1	38.4 (Br)	15
		$C_5H_2BrClO_2$ requires	28.7	1.0	38.2 (Br)	(*m/e* 210)
3-Iodofuran (11)	80—82/0.4 mmHg	Found	23.5	1.0		29
		$C_5H_2ClIO_2$ requires	23.4	0.8		
4-Bromofuran (12)	70—71/0.5 mmHg	Found	28.8	1.0	38.4 (Br)	36
		$C_5H_2BrClO_2$	28.7	1.0	38.2 (Br)	(*m/e* 210)
4-Bromo-5-deuteriofuran (13)	68—70/0.5 mmHg	Found	28.5		38.1 (Br)	38
		$C_5HBrClDO_2$ requires	28.5		38.0 (Br)	(*m/e* 211)
4-Iodofuran (14)	78—80/0.1 mmHg	Found	23.5	0.9	49.6 (I)	27
		$C_5H_2ClIO_2$ requires	23.4	0.8	49.9 (I)	
5-Deuterio-4-iodofuran (15)	79—81/0.1 mmHg	Found	23.4	7.1 *	49.7 (I)	37
		$C_5HClDIO_2$ requires	23.3	7.4 *	49.5 (I)	
5-Bromo-3,4-dideuteriofuran (18)	[55—56]	Found	28.5	1.7 †	38.0 (Br)	19
		$C_5BrClD_2O_2$ requires	28.4	1.9 †	37.8 (Br)	(*m/e* 212)
4,5-Dibromofuran (22)	[29—30]	Found	20.9	0.4	55.3 (Br)	30
		$C_5HBr_2ClO_2$ requires	20.8	0.35	55.5 (Br)	(*m/e* 288)
4-Bromo-5-chlorofuran (23)	70—72/0.02 mmHg	Found	24.8	0.5	33.0 (Br)	18
		$C_5HBrCl_2O_2$ requires	24.6	0.4	32.8 (Br)	(*m/e* 244)
4-Bromothiophen (25)	82—84/0.4 mmHg	Found		M^+ 223.870		24
		$C_5H_2{}^{79}Br^{35}ClOS$ requires		M^+ 223.870		(*m/e* 226)
3,5-Dibromothiophen (27)	126—128/0.1 mmHg	Found	19.8	0.3	52.2 (Br)	17
		C_5HBr_2ClOS requires	19.7	0.3	52.5 (Br)	(*m/e* 304)
-2-Carbonyl fluoride						
Furan (28) ‡	45—47/15 mmHg	Found	52.8	2.9	17.0	100
		$C_5H_3FO_2$ requires	52.6	2.6	16.7	
5-Deuteriofuran (29)	45—47/15 mmHg	Found	52.0		16.3 (F)	100
		$C_5H_2DFO_2$ requires	52.2		16.5 (F)	
3,4,5-Trideuteriofuran (30)	45—47/15 mmHg	Found	50.9		16.3 (F)	100
		$C_5D_3FO_2$ requires	51.2		16.2 (F)	
5-Bromofuran (31)	24—26/0.2 mmHg	Found	30.9	0.8		96
		$C_5H_2BrFO_2$ requires	31.1	1.0		(*m/e* 194)
Thiophen (32) ‡	75—78/14 mmHg	Found		M^+ 129.990		58
		C_5H_3FOS requires		M^+ 129.990		
4-Bromothiophen (33)	25—25/0.1 mm Hg	Found	28.8	0.9		93
		C_5H_2BrFOS requires	28.7	1.0		(*m/e* 210)
5-Bromothiophen (34)	42—45/0.1 mmHg	Found	28.6	1.0		96
		C_5H_2BrFOS requires	28.7	1.0		(*m/e* 210)
3,5-Dibromothiophen (35)	90—92/5 mmHg	Found		M^+ 287.808		12
		$C_5H^{79}Br^{81}BrFOS$ requires		M^+ 287.808		(*m/e* 288)

* Values are combined ($H_2O + D_2O$) percentages. † Values are D percentages. ‡ The characterisation of these compounds is no reported in the papers (ref. 4) describing their ^{19}F n.m.r. spectra.

Compound (28) was also examined on a Bruker WH9 pulsed Fourier-transform instrument using solutions i CCl_3F with $(CD_3)_2CO$ as external field lock, and in CD_2Cl which served also as internal deuterium lock.

Solvents were dried and kept over molecular sieves Samples were distilled before spectrometric examinations and their purity checked by g.l.c.[7] Solutions were prepared and cells and tubes filled, in a dry-box.

Preparative Work.—The acid chlorides were prepared b treating the corresponding acids with $SOCl_2$; the acids apart from the well known furan- and thiophen-2-carboxylic acids and 5-nitrofuran-2-carboxylic acid,[9] are described in, or can be found from, ref. 10. The chlorides were converted into the fluorides by heating with KHF_2, the technique being varied according to the scale as illustrated in the following sections. For acid halides not shown in Table 3 the values of the constants agreed with the literature values contained in the references at the foot of Table 1.

5-*Bromothiophen*-2-*carbonyl Fluoride* (34).—A mixture of 5-bromothiophen-2-carboxylic acid (5.2 g) and $SOCl_2$ (purified immediately before use; 16.5 g) was heated under reflux for 15 min. Evaporation at 100° and 15 mmHg and fractional distillation of the residue gave 5-bromothiophen-2-carbonyl chloride (24) (4.9 g), b.p. (bath temp.) 72—74° at 0.5 mmHg (lit., see ref. *f* in Table 1, 126—130° at 4 mmHg). A paste of the chloride (2.6 g) and KHF_2 (commercial material used as supplied; 3 g) was placed in a three-necked flask fitted with two condensers (which served also as N_2 inlet and outlet) and glass cup apparatus. (This device consisted of a cup sealed to the bottom of a short cold finger.) The mixture was heated at 165° under N_2 for 10 min, during which time water was not passed through the cooling apparatus, and for a further 30 min with the water running through. A colourless liquid (860 mg) collected in the cup and a solid [identified by its m.p., 141—142° (lit.,[11] 141—142°), and comparison with authentic material as 5-bromothiophen-2-carboxylic acid; *ca.* 1 g] formed on the walls of the flask. The liquid was distilled in a short-path apparatus (the cold finger of which contained Me_2CO–solid CO_2) at 42—45° (bath temp.) and 0.1 mmHg. 5-*Bromothiophen*-2-*carbonyl fluoride* (34) (710 mg) was collected as a solid which melted below room temperature.

Repetition of the experiment using KHF_2 which had been heated at 100° for 2 days before use gave volatile material (1.2 g) shown by i.r. to be a mixture of the chloride (26) (main component) and the fluoride (34).

Furan-2-*carbonyl Fluoride* (28).—Furan-2-carbonyl chloride (1) (15 g) and KHF_2 (18 g) were mixed and placed in a conventional distillation apparatus, at atmospheric pressure, which was continuously purged with N_2. The temperature of the mixture was gradually raised to 160°; a vigorous reaction occurred. After 45 min the pressure was reduced gradually to 15 mmHg. Furan-2-carbonyl fluoride (8.1 ml) was collected as a colourless liquid, and purified by fractional distillation at 45—47° (bath temp.) and 15 mmHg.

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