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HIGHLY FLUORINATED HETEROCYCLES—VIII

NMR SPECTRA AND STRUCTURES OF POLYFLUORO-1,4-DIOXANS, -1,4-OXATHIANS, AND -1,4-DITHIANS. AN ANOMERIC EFFECT IN POLYFLUOROHETEROCYCLES

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Abstract—The structures of a large number of polyfluoro-1,4-dioxans, and -1,4-oxathians are deduced from their ^{19}F NMR spectra by means of a chemical shift parameter scheme. The shapes of the molecules are discussed, together with possible reasons for distortions to flexible forms in some cases. An anomeric effect, or its equivalent, operates both α to oxygen and α to sulphur. The NMR parameters used are compared with literature values for related systems.

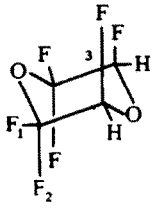
THE PREVIOUS paper[1] described the fluorinations of 1,4-dioxan and 1,4-oxathian; the fluorination of 1,4-dithian has also been reported.[2] These papers concerned themselves primarily with the fluorination process and left consideration of the detailed structures of the products isolated to the present one. This paper now assigns structures to all the dioxans and oxathians isolated by means of a chemical shift parameter scheme.

At least one example of a successful, extensive scheme of ^{19}F chemical shift parameters has been put forward previously, for the fairly closely related case of polyfluorocyclohexanes,[3] and a number of less comprehensive, or less successful examples have also been put forward. Also, several fluoro-sugars have had their ^{19}F NMR spectra measured and shift parameters have been derived from them.[4] These parameters might have been employed as checks on the overall accuracy of the present scheme; unfortunately, this is probably not possible because the carbohydrate systems are too different structurally from ours. It should be pointed out that the present exercise is more difficult than any of the cases mentioned, since these all imposed systems of chemical shift parameters onto a series of known compounds, having at the worst to assign conformations, whereas in the present case the structures must be deduced from the best—internally most consistent—fit of experimental shifts to parameters; this was done by trial and error.

It is, of course, true that we were not working wholly in the dark; the structures of several of the compounds were known with certainty, and some were almost surely right. For example, the hexafluorodioxans had been classified into *cis/trans* isomeric pairs by chemical means;[1] and mass spectroscopy had allowed assignment of the relevant compounds as 2H, 3H-hexafluoro-dioxans and -oxathians.[1] The geminal F-F coupling constants gave unambiguously the positions of the CF_2 groups in oxathians,[1] and glc retention times were also suggestive. By synthesising all the above information it was, for most of the compounds, clear that each one must be one of a given pair, or at worst of a given four structures.

In drawing up the parameter scheme, it has been assumed that the polyfluorodioxans and oxathians adopt chair forms, and that axial fluorines resonate to low field of equatorial, as they do in polyfluorocyclohexanes. These assumptions will be discussed in more detail later.

The final, successful, parameter scheme is given in Tables 4 and 5 for $-CF_2-$ and $-CFH-$ type fluorines respectively. 81 chemical shifts of fluorine atoms in 26 molecules can be correlated very well (*ca.* ± 3 ppm) by means of these parameters. The calculation of shifts for a given chair conformation (see later) is a simple matter; the environment of each fluorine in turn is examined, and the proper corrections made for the existence of hydrogen atoms, which are regarded as substituents for this purpose, in the molecule. Thus, for 2H,6H/-hexafluorodioxan the calculation proceeds as shown in Fig. 1.



For F_1; base value = 90
correction reqd. for α Heq. = −4
∴ calc. value = 86

For F_2; base value = 82
correction reqd. for α Heq. = −7
∴ calc. value = 75

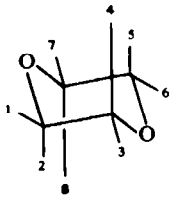
For F_3; base value = 140
correction reqd. for β Heq = 0
∴ calc. value = 140

FIG 1

Tables 1 and 2 list the experimental and calculated values for all the shifts from all the polyfluoro-dioxans and oxathians. The experimental shifts are probably accurate only to ± 2–3 ppm, because no attempt has been made to make all the measurements at the same concentration, or to allow for inconsistencies in instrument performance over the 12 month period during which this work was carried out. Furthermore, some CF_2-group signals have been analysed as AB-systems, although they are clearly more complex than this. There is good reason to suppose that the five molecules which do not fit the scheme adopt flexible conformations (see later). We therefore claim that the excellence of the overall fit, and the resemblance of the parameters to those of Homer and Thomas,[3] as well as to each other (in the different ring systems) are powerful arguments for the accuracy of the structural assignments. Furthermore, we wish to make the point most strongly that the assigned structures are supported by all the available evidence (NMR, mass spec., chemical, glc retention time). The total agreement of all these pieces of evidence makes it almost certain that those compounds (26) whose calculated spectra fit the experimental ones have been assigned the correct structures.

Overall, the fit is much better for the polyfluorodioxans than for the polyfluoro-oxathians. This could be due to more consistent ring shapes in the dioxans than in the oxathians, where some distortion of the shape predicted by Dreiding-type models—which show the axial substituents all toeing in, the ones α to oxygen by a lesser amount than those α to sulphur— will almost certainly occur. This is because the energy required to distort bond angles is relatively small, and this will certainly permit axial F-F interactions to reduce themselves by flattening the rings. Such distortions could be expected to be different for different polyfluoro-oxathians.

TABLE 1. COMPARISON OF CALCULATED AND EXPERIMENTAL ^{19}F CHEMICAL SHIFTS IN POLYFLUORO-1,4-DIOXANS.

ALL COMPOUNDS NUMBERED AS IN 

^{19}F SHIFTS IN ϕ; ^{1}H SHIFTS IN τ

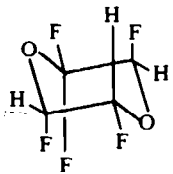
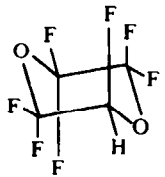
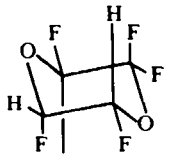
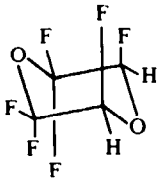
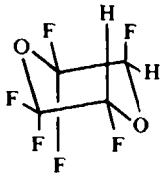
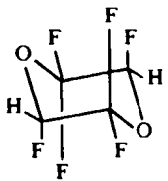
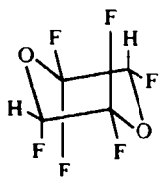
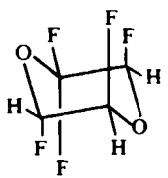
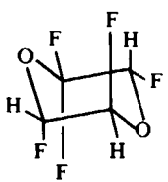
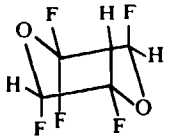
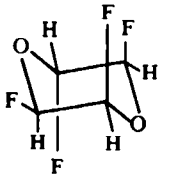
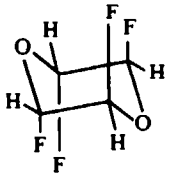
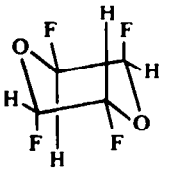
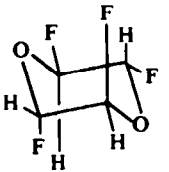
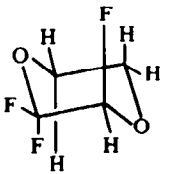
Compound Number	Structure		Position No. 1	2	3	4	5	6	7	8	Coupling Constants and Remarks
I		A				140					J_{34} = 51 Hz. Other shifts not straightforwardly available.
		B			4·27	141·9					
		C				−1·9					
II		A		134		134	82	94	94	82	$J_{12} - J_{34}$ − 51Hz. *d*
		B	4·28	135·3	4·28	135·3	81·9	93·9	93·9	81·9	$J_{56} = J_{78}$ = 139 Hz.
		C		−1·3		−1·3	+0·1	+0·1	+0·1	+0·1	
III		*A		152·5	152·5		90·5	86	86	90·5	$J_{12} = J_{34}$ = 51 Hz.
		B	*e*	152·3	152·3	*e*	90·4	85·3	85·3	90·4	$J_{56} = J_{78}$ = 154 Hz.
		C		+0·2	+0·2		+0·1	+0·7	+0·7	+0·1	
IV		A	86	75		140	140		86	75	$J_{12} = J_{78}$ = 168 Hz.
		B	86·9	76·2	*e*	139·5	139·5	*e*	86·9	76·2	$J_{34} = J_{56}$ = 51 Hz.
		C	−0·9	−1·2		+0·5	+0·5		−0·9	−1·2	(J_{34} unreliable, due to admixture).

TABLE 1—*continued*

Compound Number	Structure		Position 1	2	3	4	5	6	7	8	Coupling Constants and Remarks
V		*A	86·5	77·5	152·5		152·5		77·5	86·5	$J_{12} = J_{78} = 160$ Hz.
		B	88·3	79·8	150·9	4·23	150·9	4·23	79·8	88·3	$J_{34} = J_{56} = 47$ Hz.
		C	−1·8	−2·3	+1·6		+1·6		−2·3	−1·8	
VI		A		139	90	75	139		90	75	$J_{12} = J_{56} = 51$ Hz.
		B	[e]	139·0	91·5	73·8	139·0	[e]	91·5	73·8	$J_{34} = J_{78} = 168$ Hz.
		C		0·0	−1·5	+1·2	0·0		−1·5	+1·2	
VII		*A		149	86·5	82·5		149	82·5	86·5	$J_{12} = J_{56} = 51$ Hz.
		B	[e]	141·0	81·0	76·4	[e]	141·0	76·4	81·0	$J_{34} = J_{78} = 167$ Hz.
		†C		+8·0	+5·5	+6·1		+8·0	+6·1	+5·5	
VIII		A		134		134	140		90	75	$J_{12} = 49$ Hz; $J_{34} = 49$ Hz.
		B	4·50	135·4	4·30	133·7	139·2	4·30	89·2	73·9	
		C		−1·4		+0·3	+0·8		+0·8	+1·1	$J_{56} = 51$ Hz; $J_{78} = 167$ Hz. Arbitary assignment of ^{1}H values to positions.
IX		A		134		139		160	87	84	$J_{12} = 51$ Hz; $J_{34} = 52$ Hz.
		B	4·34	135·4	4·34	140·2	4·30	150·3	85·3	82·1	
		†C		−1·4		−1·2		+9·7	+1·8	+1·9	$J_{56} = 53$ Hz; $J_{78} = 155$ Hz.

X		A		151	158		145		90	75	J_{12} = 49 Hz; J_{34} = 50 Hz.	
		B	[e]	153·1	161·2	[e]	147·1	[e]	90·6	74·3		
		C		−2·0	−3·2		−2·1		−0·6	+0·7	J_{56} = 53 Hz; J_{78} = 166 Hz. external references.	
XI		A	160			151	139			134	^{1}H spectrum is complex multiplet centred at 4·1.	
		B	157·6			151·3	140·9			132·3		
		C	+2·4			−0·3	−2·9			+1·7	J_{12} = 59 Hz; J_{34} = 53 Hz; J_{56} = 51 Hz; J_{78} = 51 Hz.	
XII		A		134		134	134			134	J_{APP} = 53 Hz.	[g]
		B	4·17	133·0	4·17	133·0	133·0	4·17	4·17	133·0		
		C		+1·0		+1·0	+1·0			+1·0		
XIII		*A		157	157		157		157		J_{APP} = 48 Hz.	[g]
		B	4·10	155·9	155·9	4·10	155·9	4·10	155·9	4·10		
		C		+1·1	+1·1		+1·1		+1·1			
XIV		*A		141·5		141·5		141·5	141·5		J_{APP} = 53 Hz.	[g]
		B	[e]	141·2	[e]	141·2	[e]	141·2	141·2	[e]		
		C		+0·3		+0·3		+0·3	+0·3			
XV		A	90	80		145					J_{12} = 162 Hz.	
		B	88·7	84·5	4·65	148·9	Complex multiplet between 5·4 and 6·6.				J_{34} = 52 Hz.	
		C	−1·3	−4·5		−3·9						

For footnotes see Table 3.

On the subject of ring shapes, it may be pointed out that the shapes of our ring systems are not the same as for cyclohexane; this is not normally well brought out in discussions of these rings, but it may well be very important in the present case, where differing molecular shapes give rise to differing magnitudes of ^{19}F substituent parameters—although the signs always remain the same as for cyclohexanes. For the same reason, it is not too surprising that different base values have to be used for fluorines α to oxygen in dioxans and oxathians; the different molecular shapes would be expected to alter the environment significantly.

The assumption that axial fluorines resonate to low field of equatorial, whilst in line with the polyfluoro-literature, appears to be in contradiction to results in the carbohydrate field,[4] where the opposite assignment has been correctly made. This contradiction is not, however, necessarily real; in the polyfluoro-field the base values for —CFH— fluorines, say, are those shown by these fluorines in an otherwise completely fluorinated molecule, whereas, in the carbohydrate case, the base values

2

FIG 2

refer to completely hydrogen containing molecules. Indeed, application of our parameters to the carbohydrate system will in fact invert the base values, so that our parameters predict F_{ax} to high field in these systems. It is, of course, possible to fit the spectra and structures of the polyfluoro-dioxans and oxathians just as well if the reverse assumption (axial fluorine to *high* field) is made—and the final structures would be *exactly the same*, albeit in reversed conformations—but this would be against all our previous experience.

The 'theoretical' spectra can only be calculated if an *a priori* assumption as to the preferred conformations of the molecules, is made. The best and most consistent fit (that given in Tables 1 and 2) is obtained on the assumption that a molecule will adopt the conformation having the most —CFH— fluorines axial—*i.e.* that a strong anomeric effect, or its equivalent, prevails over any other effects in deciding the conformation of these rings.

The anomeric effect is well documented in carbohydrates, where in its simplest form the effect produces a preference for conformation A over B (Fig. 2): X here is a strongly electronegative group, such as halogen, OH or OMe.

This effect contrasts with the normal steric control which should favour B; there is ample precedent for such an effect operating for fluorine α to oxygen.[4]

The cause of the anomeric effect seems clear; in simple terms it is due to a favourable interaction between the positive end of the C_6-O dipole and the negative end of the C_2-X dipole, which only occurs in the X-axial conformation. This simple explanation of the classical anomeric effect is illustrated in Fig. 2.

The strength of the anomeric effect is predicted to be less in sulphur rings, for two reasons: firstly because C-S bonds (1·84 Å) are longer than C-O bonds (1·43 Å), which

decreases the favourable interaction; secondly, and more importantly, because the electronegativity of sulphur (2·5) is less than that of oxygen (3·5), being indeed the same as that of carbon (2·5) on the Pauling scale, so that only very small C-S dipoles may be expected. Thus, there seems to be no good reason why there should be an anomeric effect α to sulphur, and indeed there appear to be no good examples of it in the literature.

Anomeric effects in rings with more than one hetero-atom are more complex than would be indicated by the simple outline of the previous two paragraphs, and with our compounds the situation is made even more difficult since, quite apart from the anomeric effects α to hetero-atoms, the powerful C-F dipoles are expected to give rise to anomeric-type effects of their own. These fall into two categories. Firstly, the presence of a C-F bond will produce an anomeric type effect at the β-position (Fig.3).

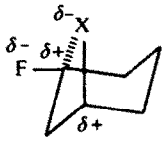


FIG 3

This will probably not be very effective if the inducing fluorine is part of a $-CF_2-$ group, since this will certainly produce a strong 1-3 diaxial repulsion probably only partly compensated for by the 'anomeric' effect. Secondly, for the usual electrostatic reasons, the powerful C-F dipoles will tend to drive the molecule into conformations where adjacent C-F bonds are opposed; *i.e.* where they occupy *trans* positions in the Newmann projection (Fig. 4). These two factors, especially the second, are expected to operate so as to put as many —CFH— fluorines axial as possible (there can be no difference for $-CF_2-$).

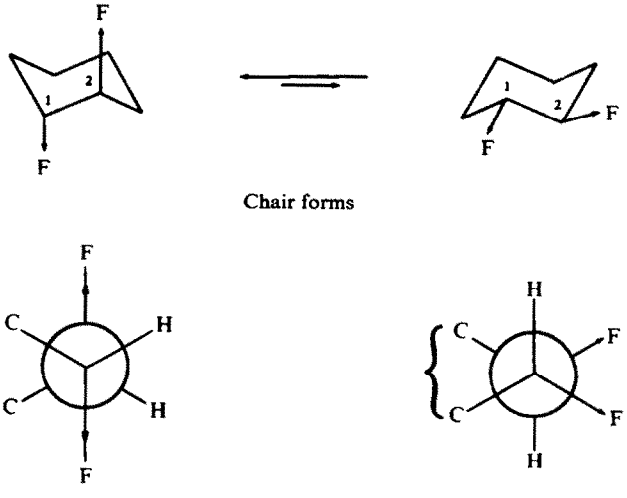
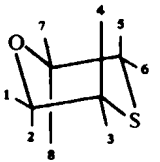
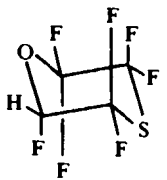
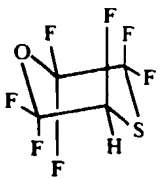
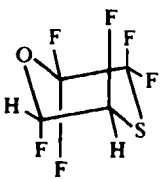


FIG 4

TABLE 2. COMPARISON OF CALCULATED AND EXPERIMENTAL ^{19}F CHEMICAL SHIFTS IN POLYFLUORO-1,4-OXATHIANS

ALL COMPOUNDS NUMBERED AS IN 

^{19}F SHIFTS IN ϕ; ^{1}H SHIFTS IN τ

No.	Compound Structure		Position No. 1	2	3	4	5	6	7	8	Coupling Constants and Remarks
XVI		A		139							
		B	*	140·8		Too complex for analysis					J_{12} = 50 Hz.
		C		−1·8							
XVII		A	76	73		166	82	104	88	78	J_{12} = 166 Hz; J_{34} = 47 Hz;
		B	79·1	75·4	4·22	167·8	81·7	106·4	90·1	83·9	J_{56} = 241 Hz; J_{78} = 154 Hz.
		C	−3·1	−2·4		−1·8	+0·3	−2·4	−2·1	−5·9	
XVIII		A		134		162	82	104	93	78	J_{12} = 45 Hz; J_{34} = 45Hz;
		B	4·07	134·0	4·27	162·7	82·3	104·2	93·9	80·4	J_{56} = 242 Hz; J_{78} = 156 Hz.
		C		0·0		−0·7	−0·3	−0·2	−0·9	−2·4	

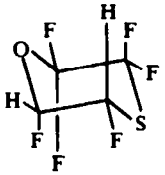
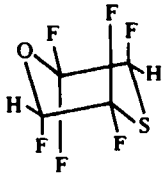
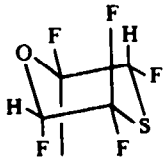
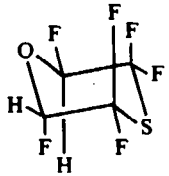
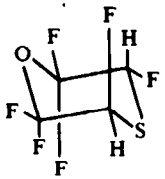
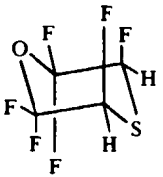
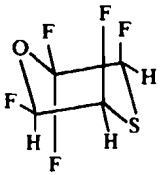
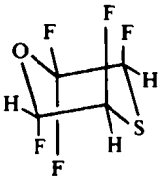
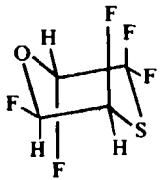
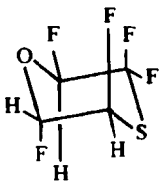
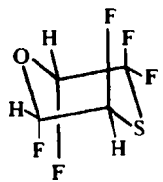
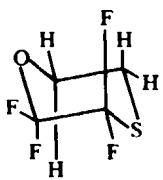
XIX		*A		144	167		91	97	93	78	J_{12} = 47 Hz; J_{34} = 47 Hz;
		B	4·02	139·1	181·5	4·34	80·4	105·1	90·3	90·3	J_{56} = 245 Hz; J_{78} not observed since AB collapsed
		†C		+4·9	−14·5		+10·6	−8·1	+2·7	−12·3	
											2H, 5H/– fits the NMR better, but is incompatible with the mass. spec.
XX		A		139	99	73	166		81	73	J_{12} = 51 Hz; J_{34} = 260 Hz;
		B	4.25	137·7	96·6	74·2	166·9	4·73	82·8	71·3	J_{56} = 46 Hz; J_{78} = 170 Hz.
		C		+1·3	+2·4	−1·2	−0·9		−1·8	−1·7	
XXI		*A		139	93	82		178	92	82	J_{12} = 51 Hz; J_{34} = 222 Hz;
		B	4·22	144·3	91·2	95·8	4·34	165·5	80·1	79·0	J_{56} = 48 Hz; J_{78} = 160 Hz.
		†C		−5·3	+1·8	−13·8		+12·5	+11·9	+3·0	2H, 3H/– fits the NMR better, but is incompatible with the mass. spec.
XXII		*A		150	93	82	82	93	150		$J_{12} = J_{78}$ = 51 Hz;
		B	4·14	151·1	94·3	84·5	84·5	94·3	151·1	4·14	$J_{34} = J_{56}$ = 238 Hz.
		C		−1·1	−1·3	−2·5	−2·5	−1·3	−1·1		
XXIII		*A	79	72		173·5		173·5	72	79	$J_{12} = J_{78}$ = 140 Hz;
		B	76·8	71·7	4·15	172·3	4·15	172·3	71·7	76·8	$J_{34} = J_{56}$ = 51 Hz.
		C	+2·2	+0·3		+1·2		+1·2	+0·3	+2·2	

TABLE 2—*continued*

No.	Compound Structure		Position No. 1	2	3	4	5	6	7	8	Coupling Constants and Rekarks
XXIV		A	76	73		166	166		76	73	$J_{12} = J_{78} = 169$ Hz;
		B	77·5	75·6	4·47	167·1	167·1	4·47	77·5	75·6	$J_{34} = J_{56} = 45$ Hz.
		C	−1·5	−2·6		−1·1	−1·1		−1·5	−2·6	
XXV		A	143		169		166		76	78	$J_{12} = 47$ Hz; $J_{34} = 48$ Hz;
		B	135·8	4·15	181·2	4·50	163·2	4·50	76·4	81·5	$J_{56} = 48$ Hz; $J_{78} = 165$ Hz.
		†C	+7·2		−12·2		+2·8		−0·4	−3·5	
XXVI		A		133		162	166		81	73	$J_{12} = 47$ Hz; $J_{34} = 45$ Hz;
		B	4·05	132·1	4·55	160·6	164·4	4·55	79·7	71·5	$J_{56} = 45$ Hz; $J_{78} = 166$ Hz.
		C		+0·9		+1·4	+1·6		+1·3	+1·5	

XXVII		A	146			169	99	73		144	J_{12} = 47 Hz; J_{34} = 49 Hz;
		B	145·9			168·8	99·2	71·2		144·9	J_{56} = 251 Hz; J_{78} = 47 Hz.
		C	−0·1			+0·2	−0·2	+1·8		−0·9	^{1}H spectrum is a complex doublet centred at *ca.* 4·1.
XXVIII		A		138		162	98	94	156		J_{12} = 49 Hz; J_{34} = 45 Hz;
		B		138·7		161·2	97·1	92·5	153·6		J_{56} = 227 Hz; J_{78} = 50 Hz.
		C		−0·7		+0·8	+0·9	+1·5	+2·4		^{1}H spectrum is a complex doublet centred at *ca.* 4·1.
XXIX		A		133		162	99	73		139	J_{12} = 54 Hz; J_{34} = 49 Hz;
		B		129·5		161·5	96·6	74·2		135·5	J_{56} = 254 Hz; J_{78} = 50 Hz.
		C		+3·5		+0·5	+2·4	−1·2		+3·5	^{1}H spectrum is a complex doublet centred at *ca.* 4·5.
XXX		*A	86	86	97	97					
		B	92·5	92·5	97·8	97·8	7·00	7·00	5·61	5·61	Tentative structural assignment.
		C	−6·5	−6·5	−0·8	−0·8					

For footnotes, see table 3.

It is perfectly possible, therefore, that the apparent anomeric effect in our compounds arises not at all, or not predominantly, from the same cause—the ring oxygen or sulphur—as the classical anomeric effect; the preference for —CHF— axial conformers might well be due almost entirely to the C-F dipole/dipole interactions.

The observed preference for —CHF— axial conformers may also owe something to the lack of a second 1-3 diaxial interaction (Fig. 5), although this will be to some extent compensated for by the lack of 1-2 interactions in the —CHF— equatorial conformer of the heterocycles. (Note here that the chair/flexible form energy difference in 1,4-dioxan is about 2·2 kcal/mole, as compared to 5·5 kcal/mole in cyclohexane[5]). The nett result of these two opposing effects should be in favour of the F_{ax} form, and since it would require only a small extra push to lock the conformations of polyfluoroalicyclics into the CHF_{ax} form (undecafluorocyclohexane is only 65:35 in favour of the CHF_{eq} conformer, and 1H,3H/-decafluorocyclohexane favours the CHF_{ax} form by 60:40[3]) this effect alone would amply suffice to produce the observed result.

Missing 1,3 diaxial interactions (—CHF—axial)

Missing 1,2 interactions (—CHF— equatorial)

FIG 5

We therefore do not feel wholly certain as to the cause of our 'anomeric' effect, but the effect itself is well established in our systems.

The predicted conformations are therefore arrived at quite straightforwardly in most cases; we have simply chosen the chair form with the most axial —CHF— groupings, and calculated the shifts for that. In cases where there are two equally favourable possibilities we have calculated a 50/50 time-averaged shift for each fluorine, and where there is a competition between CHF_{ax} α to oxygen and α to sulphur (2H,3H/- and 2H,5H/-hexafluoro-oxathians) we have calculated both extreme possibilities and a 50/50 average. (Neither of these two compounds fits any of these calculated sets of shifts, and we therefore postulate that these molecules exist primarily as flexible forms—see later). For example, 2H,6H/-hexafluorodioxan should exist primarily in conformation C; whereas the 2H/6H-isomer is expected to flip rapidly between E and G (Fig. 6).

Two rather lightly fluorinated compounds, 2,2,3-trifluoro-1,4-dioxan and 2,2,3,3-tetrafluoro-1,4-oxathian, have been included in the tables, the fit is not so good for these as for the other chair forms, but the different electron distributions in these (as compared with the highly fluorinated compounds) may go far to explain this.

There are five compounds that do not fit the parameter scheme; these have been assigned structures on other grounds (by elimination, glc retention time, mass spec., gross structures from NMR). These structures are all of types which have relatively favourable flexible forms available to them, and we therefore postulate that these compounds do, in fact, adopt flexible conformations for relatively large percentages of

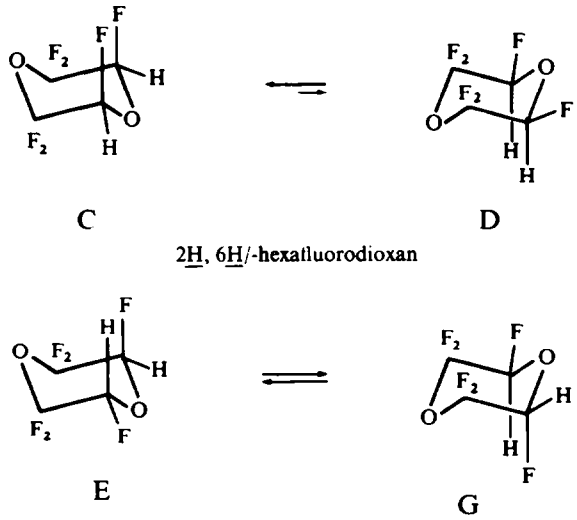


FIG 6

the time. These compounds are 2H,5H/-hexafluoro-dioxan and -oxathian, 2H,5H/3H-pentafluoro-dioxan, 2H,3H/-hexafluoro-oxathian and 2H,3H,5H/-pentafluoro-oxathian; in all of these there is no chair form where all the —CHF— fluorines are axial, and model studies indicate favourable flexible forms for all of them, with all the —CHF— fluorines pseudo-axial and somewhat lined up against each other, and where steric interactions are somewhat reduced by pushing fluorines closer to the β-heteroatom. It might be thought that the 2H/6H-hexafluoro-isomers and 2H,3H/-hexafluorodioxan should also adopt flexible forms, and indeed it is not wholly clear why they do not; in the case of the 2H/6H- (and 3H/5H-) isomers the chair forms may be stabilised by favourable 1-3 diaxial F-H interactions, and by anomeric effects enhanced by an equatorial fluorine on the inducing carbon (Fig. 3), whereas no such stabilising factor exists for the 2H,5H/-isomers, where these interactions would employ $—CF_2—$ groups. As an explanation of the discrepancy between the two 2H,3H/-hexafluoro-isomers, we clutch at the straw that the energy difference between the chair and flexible forms should be larger for dioxans than for oxathians. Of course, this may be only a difference in degree; and indeed, all the compounds may spend some time in flexible conformations, some more than others; the fit of all the compounds could probably be improved if a way could be devised to calculate both the chemical shifts and percentages of flexible forms, and the present scheme certainly does not rule out small (<10%) amounts of flexible forms, even for well-fitted compounds.

A certain amount of comment on the parameters employed is in order; their signs follow closely those found for polyfluorocyclohexanes, and their magnitudes, although often larger than those of Homer and Thomas,[3] are not unreasonable. The detailed reasons for the observed variations in magnitude cannot be profitably discussed without a detailed knowledge of the ring shapes, and this is almost wholly lacking for similar systems in solution; we therefore make no comment on these variations here.

TABLE 3. SPECTRAL PARAMETERS OF SOME POLYFLUORO-1,4-DITHIANS
(^{19}F SHIFTS IN ϕ, ^{1}H SHIFTS IN τ)

Compound	Resonating Nucleus				Couplings	
	CHF	CHF	CF_2		J_{HF} (Hz)	J_{FF} (Hz)
2H-Heptafluoro 1,4-dithian	163·7	4·29	Too complex to estimate		45	
Hexafluoro-1,4-dithians Isomer 1	174·9	4·10	88·4	76·5	48	237
Isomer 2	170·2	3·90	96·2	85·8	60	226
Isomer 3	162·0	4·60	79·4	74·6	48	255
Isomer 4	162·8	4·35	90·6	71·1	45	249
Isomer 5	156·8	4·04	101·4	80·8	30,45[h]	231[h]

A – Value calculated from parameters of tables 4 and 5.
B – Experimental value.
C – Difference.
[e] – Compound only isolated in admixture; no ^{1}H values.
[f] – Couplings unreliable, owing to tendencies towards A_2X_2 spectrum.
[g] – A_4X_4 spectrum; J's not directly available.
[h] – Spectrum is heavily coupled $A_2X_2M_4$ type. Shifts should be reasonably accurate, but the coupling constants may be in serious error.
* – Calculated values are for 50/50 time averaged mixture of the two equivalent chairs.
† – Compound thought to adopt a flexible conformation—see text.

The tables also list geminal coupling constants; the J_{FF} values are useful structurally, being unambiguously characteristic of α-oxygen (140–170 Hz) or α-sulphur (220–260 Hz). We had hoped that these geminal coupling constants might also give useful information as to which compounds are in flexible forms and which in chairs, but there seems to be no useful correlation here. The non-geminal couplings have been studied (although, not being germane to the argument, they are not included here) but they also appear not to be consistent; for instance; in the dioxans 1,3 diaxial F-F couplings appear to vary from about 22 Hz to 3 Hz. Because of this lack of consistency we have not thought it necessary to perform complete coupling analyses; also we have no computer available capable of handling eight non-degenerate spins, which also militated against this undertaking. Finally, the uncertainty over the precise molecular shapes makes the drawing of any conclusions in this area extremely hazardous.

Table 3 shows the spectral parameters of certain polyfluoro-1,4-dithians;[2] we assign no definite structures to the hexafluoro-dithian isomers, because of the lack of enough compounds to really substantiate any assignments; it is in fact possible to fit the shifts to more than one parameter scheme. These compounds contribute to the structural problem in the 1,4-oxathians by demonstrating what values may be expected for the geminal F-F coupling constants α to sulphur.

In conclusion, we have attempted to assign structures to all the polyfluoro-dioxans and -oxathians previously described, by means of a chemical shift parameter scheme. This approach has been reasonably successful, and leads to a high degree of internal consistency, which we argue is powerful evidence for the correctness of our structures. We do not claim absolute certainty, however, since the fit is reasonable rather than excellent, with a margin for error of about ±3 ppm being required. We have assigned the majority of the compounds to chair conformations, with a strong anomeric effect

TABLE 4. ^{19}F CHEMICAL SHIFT PARAMETERS FOR $\underline{CHF}$ NUCLEI

Position of nucleus	F_{ax} α H_{ax}	α H_{eq}	β H_{ax}	β H_{eq}	Base value	F_{eq} α H_{ax}	α H_{eq}	β H_{ax}	β H_{eq}	Base value
α to oxygen in dioxans	+11	−6	+5	0	140	−16	−2	0	+2	158
α to oxygen in oxathians	+5	−6	+5	0	139	−9	−10	[c]	+3	153
α to sulphur in oxathians	+3	−4	0	0	166	[c]	−11	[c]	+3	178
In polyfluorocyclohexanes [b]	+4·5	[c]	[c]	[c]	212·2	−11	−7·6	[c]	[c]	233·2

For footnotes – see Table 5.

TABLE 5. ^{19}F CHEMICAL SHIFT PARAMETERS FOR $\underline{CF_2}$ NUCLEI

Position of nucleus	F_{ax} α H_{ax}	α H_{eq}	β H_{ax}	β H_{eq}	Base value	F_{eq} α H_{ax}	α H_{eq}	β H_{ax}	β H_{eq}	Base value
α to oxygen in dioxans	+5	−7	+5	0	82	−9	−4	0	+4	90
α to oxygen in oxathians	+4	−5	[c]	0	78	−17	−12	0	+5	88
α to sulphur in oxathians	+12	−9	+9	0	82	−6	−5	0	+7	97
In polyfluorocyclohexanes [b]	+2·3	−4·3	[c]	[c]	124·2	−15	−10·5	+4	[c]	142·1

[a] Parameters in p.p.m. upfield from internal CCl_3F
[b] Taken from ref. 4. Base values calculated on the basis that their reference (external CF_3COOH) is at 77 on our scale
[c] No examples requiring this parameter

dominating the conformations, but we are not certain either how accurate this assignment (to pure chairs) is, or how best to explain the preference for axial fluorine. Indeed, if F_{ax} were to resonate to high field of F_{eq}, then, although the structural assignment would be unaffected, the anomeric effect would no longer be apparent.

TABLE 6. COMPOUNDS WHOSE STRUCTURES ARE ASSIGNED IN THIS PAPER

Compound	Number in Tables 1 and 2
2H-Heptafluoro-1,4-dioxan	I
2H/3H-Hexafluoro-1,4-dioxan	II
2H, 3H-Hexafluoro-1,4-dioxan	III
2H, 6H-Hexafluoro-1,4-dioxan	IV
2H/6H Hexafluoro-1,4-dioxan	V
2H/5H-Hexafluoro-1,4-dioxan	VI
2H, 5H-Hexafluoro-1,4-dioxan	VII
2H/3H-Pentafluoro-1,4-dioxan	VIII
2H/3H,5H-Pentafluoro-1,4-dioxan	IX
2H,3H/5H-Pentafluoro-1,4-dioxan	X
2H/3H,5H,6H-Tetrafluoro-1,4-dioxan	XI
2H,6H/3H,5H-Tetrafluoro-1,4-dioxan	XII
2H,3H/5H,6H-Tetrafluoro-1,4-dioxan	XIII
2H,5H/3H,6H-Tetrafluoro-1,4-dioxan	XIV
2,2,3-Trifluoro-1,4-dioxan	XV
2H-Heptafluoro-1,4-oxathian	XVI
3H-Heptafluoro-1,4-oxathian	XVII
2H/3H-Hexafluoro-1,4-oxathian	XVIII
2H,3H/-Hexafluoro-1,4-oxathian	XIX
2H/5H-Hexafluoro-1,4-oxathian	XX
2H,5H/-Hexafluoro-1,4-oxathian	XXI
2H/6H-Hexafluoro-1,4-oxathian	XXII
3H/5H-Hexafluoro-1,4-oxathian	XXIII
3H,5H/-Hexafluoro-1,4-oxathian	XXIV
2H,3H,5H/-Pentafluoro-1,4-oxathian	XXV
2H,3H,5H-Pentafluoro-1,4-oxathian	XXVI
2H,3H/6H-Pentafluoro-1,4-oxathian	XXVII
2H/3H,6H-Pentafluoro-1,4-oxathian	XXVIII
2H,6H/3H-Pentafluoro-1,4-oxathian	XXIX
2,2,3,3-Tetrafluoro-1,4-oxathian	XXX

RESULTS

All NMR spectra were measured in CCl_4 solution, using a Perkin Elmer R10 machine operating at 60 MHz for ^1H spectra and 56·4 MHz for ^{19}F spectra. Chemical shifts were measured using the decade shift facility, and are in ppm upfield from internal CCl_3F (ϕ) and τ from internal TMS. No attempt has been made to extrapolate the shifts to infinite dilution; all the spectra were recorded at 35°.

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REFERENCES

[1] Part VII, J. Burdon and I. W. Parsons, *Tetrahedron* **27**, 4533 (1971)
[2] J. Burdon and I. W. Parsons, *J. Chem. Soc. C*, 355 (1971)
[3] J. Homer and L. F. Thomas, *Trans. Faraday Soc.* **59**, 2431 (1963)
[4] L. D. Hall and J. R. Manville, *Canad. J. Chem.* **47**, 1 and 19, (1969)
[5] E. L. Eliel, N. J. Allinger, S. J. Angyal and G. A. Morrison, *Conformational Analysis*, Interscience, New York, (1965)