A Nuclear Magnetic Resonance Study of the Conformational Equilibrium in Fluorosulphonylethanes

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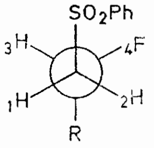
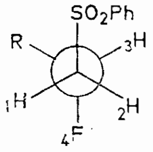
The dependence of the coupling constants on the temperature has been studied for fluorosulphonylethanes (I)—(IV) and with the aid of some simplifying assumptions quantitative information on the population of rotamers (a)—(c) has been obtained. In each case the conformation having the bulkiest substituents in the antiperiplanar position predominates with a fractional population in the range 0.6—1. In the series of compounds investigated $^3J_{HF}$ increases and $^2J_{HF}$ decreases with increasing electronegativity of substituents, thus showing an unusual trend. For these couplings a modest but significant solvent dependence has been also observed. The INDOR technique has proved to be a useful tool for the separation of overlapping spectra of diastereoisomeric pairs.

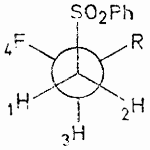
In a recent paper[1] n.m.r. data were reported which suggested that in 1-fluoro-2-phenylsulphonyl-1-phenylthioethane (I) the most highly populated conformation is that with the two sulphur substituents in the antiperiplanar position. In connection with stereochemical and kinetic work [2] on the dehydrohalogenation of similar substrates we undertook a quantitative study on the conformational equilibrium involving (I) and the related compounds (II)—(IV).



(a)



(b)



(c)

(I) R = SPh

(II) R = SOPh

(III) R = SO_2Ph

(IV) R = Br

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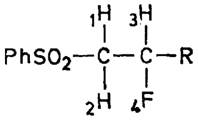
[1] G. Marchese, F. Naso, L. Schenetti, and O. Sciacovelli, *Chimica e Industria*, 1971, **53**, 843.

[2] V. Fiandanese, G. Marchese, F. Naso, and O. Sciacovelli, *J.C.S. Perkin II*, 1973, 1336; V. Fiandanese, G. Marchese, and F. Naso, *ibid.*, p. 1538; *J.C.S. Chem. Comm.*, 1972, 250.

RESULTS AND DISCUSSION

The n.m.r. spectra were interpreted for ethane fragments only. The spin system was treated as an ABCX case (A, B, C =H; X=F) using the notation (A). For



$$\mathrm{PhSO_2-\underset{{}_2H}{\overset{{}_1H}{C}}-\underset{{}_4F}{\overset{{}_3H}{C}}-R}$$

(A)

the iterative calculation only proton spectra were used with the aid of a hypothetical fluorine signal necessary to close the iterative loops.[3]

The spectra showed magnetic non-equivalence of H(1) and H(2) due to the diastereotopic nature of the methylene group. The coupling pattern permitted an unambiguous assignment even if the spectra contain second-order features. In the case of compound (II) the presence of the sulphur and carbon chiral centres give rise to two diastereoisomeric products A and B which were obtained in a 2 : 1 ratio (see Experimental section). The related n.m.r. spectra consist of two superimposed ABC systems within which the sixteen line signal of H(3) is clearly distinguished (see Figure 1) whereas in the region of the H(1) and H(2) signals, marked overlap does not permit attribution of the signals. Since similar compounds are dehydrohalogenated [2] easily and their purification is not without difficulty, rather than attempting to separate the diastereoisomers the use of the INDOR [4] technique was preferred since it gives the possibility of overcoming this difficulty. Consequently, monitoring all lines due to H(3) a series of intensity spectra were obtained which showed the position and the character (progressive or regressive) of the connected transitions (see Figure 2). Through this connection the correct energy level diagram was built up and the n.m.r. parameters were iterated using all the experimental transitions for the diastereoisomeric pair. Referred to $^3J_{23}$ taken as positive $^3J_{13}$, $^3J_{14}$, $^3J_{24}$, and $^2J_{34}$ are positive whereas $^2J_{12}$ is negative. The same trend was assumed to be valid for the other compounds. Indeed, this sign combination proved to give the lowest root mean square values.

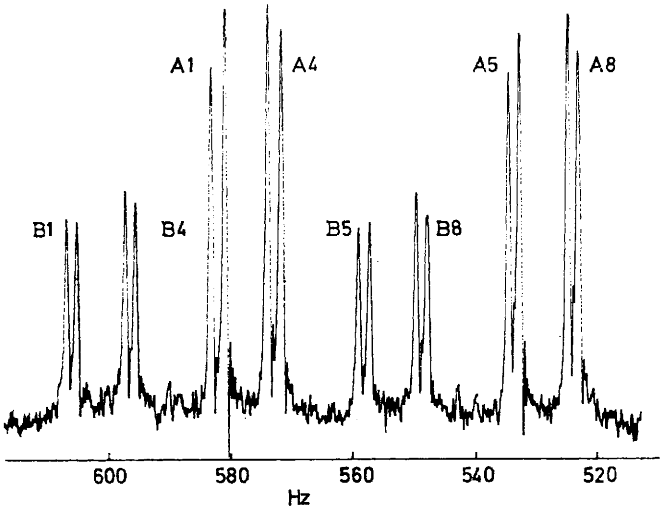


FIGURE 1 Spectrum of H-3. The higher peaks are due to the isomer A

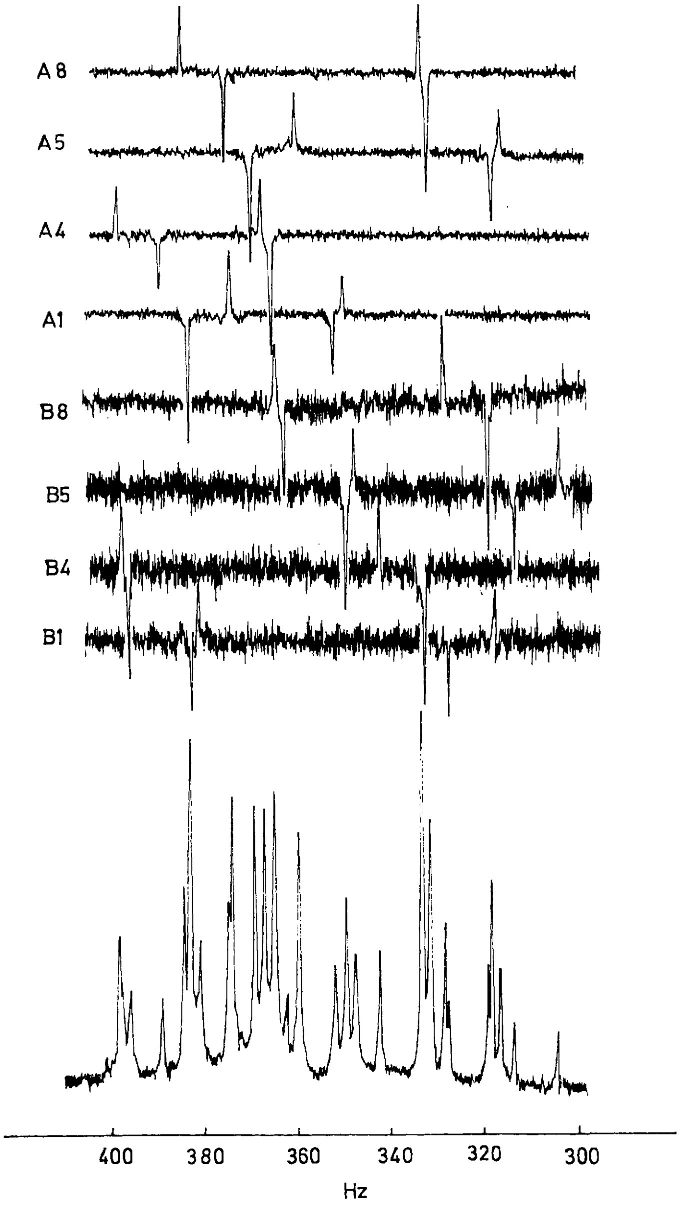


FIGURE 2 Spectrum of compound (II) showing the absorption region of H-1 and -2 and the sequence of intensity spectra necessary to locate all the individual lines of H-1 and -2 for both isomers (only eight of the 16 INDOR experiments performed are shown)

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[3] S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, 1964, **41**, 3863.

[4] E. B. Baker, *J. Chem. Phys.*, 1966, **45**, 609.

Table 1

Coupling constants (Hz) and conformer populations for compound (I)

T/°C	$^3J_{13}$	$^3J_{23}$	$^3J_{24}$	$^3J_{14}$	$J_{13} + J_{23}$	$\frac{1}{3}(2J_{24} + J_{14})$	x_a	$x_b + x_c$
Solvent $(CD_3)_2CO$								
−50	2.2_1	9.9_8	9.5_7	29.8_5	12.1_9	16.3	0.84—0.87	0.13—0.16
−40	2.3_5	9.7_3	9.6_8	29.2_6	12.0_8	16.2	0.81—0.85	0.15—0.19
−30	2.4_6	9.6_1	9.8_5	28.7_3	12.0_7	16.1	0.79—0.83	0.17—0.21
−20	2.5_7	9.5_3	10.0_6	28.1_6	12.1_0	16.1	0.78—0.83	0.17—0.22
−10	2.6_5	9.3_4	10.2_7	27.7_4	11.9_9	16.1	0.76—0.81	0.19—0.24
−3	2.7_3	9.3_2	10.4_9	27.4_0	12.0_5	16.1	0.76—0.81	0.19—0.24
17	2.9_9	9.0_4	10.9_2	26.7_4	12.0_3	16.2	0.73—0.78	0.22—0.27
30	3.0_5	8.8_6	11.0_0	26.0_5	11.9_1	16.0	0.70—0.76	0.24—0.30
37	3.1_0	8.7_6	11.1_2	25.5_6	11.8_6	15.9	0.69—0.75	0.25—0.31
Solvent $(CD_3)_2SO$								
40	2.9_2	9.0_9	11.8_1	26.0_5	12.0_1	16.6	0.73—0.78	0.22—0.27
60	3.0_9	8.8_3	12.1_0	25.4_3	11.9_1	16.5	0.70—0.76	0.24—0.30
80	3.1_9	8.6_1	12.3_9	24.7_5	11.8_0	16.5	0.67—0.74	0.26—0.33
100	3.3_4	8.4_4	12.5_7	24.1_8	11.7_8	16.4	0.65—0.72	0.28—0.35
120	3.3_9	8.2_0	12.9_4	23.5_0	11.5_9	16.5	0.63—0.70	0.30—0.37
140	3.5_2	8.0_7	13.2_1	23.1_9	11.5_9	16.5	0.61—0.68	0.32—0.39

Table 2

Coupling constants (Hz) and conformer populations for compound (IIA) *

T/°C	$^3J_{13}$	$^3J_{23}$	$^3J_{24}$	$^3J_{14}$	$J_{13} + J_{23}$	$\frac{1}{3}(2J_{23} + J_{14})$	x_a	$x_b + x_c$
Solvent $CDCl_3$								
−17	1.3_2	10.3_3	11.7_6	36.7_3	11.6_5	20.1	0.89—0.92	0.08—0.11
−9	1.3_5	10.2_2	11.8_8	36.6_3	11.5_5	20.1	0.88—0.91	0.09—0.12
−6	1.3_8	10.1_7	12.0_7	36.5_5	11.5_5	20.2	0.87—0.91	0.09—0.13
5	1.4_2	10.0_7	12.4_7	35.9_4	11.4_9	20.3	0.86—0.90	0.10—0.14
17	1.4_6	10.0_3	12.80	35.6_3	11.4_9	20.4	0.86—0.89	0.11—0.14
41	1.5_1	9.7_8	13.6_0	34.9_5	11.2_9	20.7	0.83—0.87	0.13—0.17
49	1.5_8	9.7_5	13.6_7	34.7_1	11.3_3	20.7	0.82—0.87	0.13—0.18
Solvent $(CD_3)_2SO$								
40	1.5_0	9.5_1	15.3_9	34.2_4	11.0_1	21.7	0.79—0.85	0.15—0.21
50	1.5_7	9.5_0	15.3_5	34.2_1	11.0_7	21.6	0.79—0.85	0.15—0.21
60	1.5_2	9.4_1	15.7_8	34.0_8	10.9_3	21.9	0.78—0.84	0.16—0.22
70	1.6_0	9.2_8	15.6_7	33.9_7	10.8_8	21.8	0.77—0.83	0.17—0.23
80	1.6_4	9.2_0	15.8_5	33.7_8	10.8_4	21.8	0.76—0.82	0.18—0.24

* See text.

Table 3

Coupling constants (Hz) and conformer populations for compound (IIB) *

T/°C	$^3J_{13}$	$^3J_{23}$	$^3J_{24}$	$^3J_{14}$	$J_{13} + J_{23}$	$\frac{1}{3}(2J_{24} + J_{14})$	x_a	$x_b + x_c$
Solvent $CDCl_3$								
−17	1.1_7	10.0_6	13.0_3	35.7_1	11.2_3	20.6	0.86—0.90	0.10—0.14
−9	1.2_3	10.0_5	13.0_9	35.3_9	11.2_9	20.5	0.86—0.90	0.10—0.14
−6	1.2_5	9.9_8	13.1_5	35.4_6	11.2_3	20.6	0.85—0.89	0.11—0.15
5	1.3_6	9.9_5	13.2_7	35.0_8	11.3_1	20.5	0.85—0.89	0.11—0.15
17	1.4_4	9.8_5	13.4_0	34.6_1	11.2_9	20.5	0.83—0.88	0.12—0.17
41	1.6_6	9.5_9	13.7_7	33.9_7	11.2_5	20.5	0.80—0.86	0.14—0.20
49	1.7_2	9.5_6	13.9_5	33.5_6	11.2_8	20.5	0.80—0.85	0.15—0.20
Solvent $(CD_3)_2SO$								
40	1.6_9	10.1_0	13.5_0	35.7_0	11.7_9	20.9	0.86—0.90	0.10—0.14
50	1.7_2	9.9_0	13.6_8	35.2_2	11.6_2	20.9	0.84—0.88	0.12—0.16
60	1.7_8	9.7_8	13.8_2	35.1_5	11.5_6	20.9	0.83—0.87	0.13—0.17
70	1.9_2	9.6_6	14.0_7	34.7_3	11.5_8	21.0	0.81—0.86	0.14—0.19
80	1.9_6	9.6_2	13.9_4	34.6_0	11.5_8	20.8	0.81—0.86	0.14—0.19

* See text.

TABLE 4

Coupling constants (Hz) and conformer populations for compound (III)

T/°C	${}^3J_{13}$	${}^3J_{23}$	${}^3J_{24}$	${}^3J_{14}$	$J_{13} + J_{23}$	$\frac{1}{3}(2J_{24} + J_{14})$	x_a	$x_b + x_c$
Solvent $CDCl_3$								
-59	0.9_2	10.8_4	11.2_7	37.2_8	11.7_6	19.9	~0.99	~0.01
-52	0.9_0	10.8_3	11.3_0	37.0_8	11.7_3	19.9	~0.99	~0.01
-45	0.9_7	10.7_8	11.4_7	37.0_7	11.7_5	20.0	~0.98	~0.02
-37	0.9_7	10.7_7	11.6_0	36.9_5	11.7_4	20.0	~0.98	~0.02
-23	1.0_8	10.6_6	11.8_6	36.7_0	11.7_4	20.1	~0.97	~0.03
-12	1.0_9	10.6_8	12.0_1	36.5_9	11.7_7	20.2	~0.97	~0.03
-2	1.1_1	10.5_3	12.1_6	36.3_2	11.7_4	20.2	0.95—0.96	0.04—0.05
-2	1.1_3	10.6_1	12.1_8	36.3_9	11.6_4	20.2	0.96—0.97	0.03—0.04
11	1.1_2	10.5_3	12.3_3	36.1_5	11.6_5	20.3	0.95—0.96	0.04—0.05
30	1.2_2	10.3_3	12.6_7	35.9_1	11.5_5	20.4	0.93—0.94	0.06—0.07
40	1.1_9	10.3_7	12.7_4	35.6_8	11.5_6	20.4	0.93—0.94	0.06—0.07
50	1.3_2	10.2_6	12.9_0	35.6_1	11.5_8	20.5	0.92—0.94	0.06—0.08
Solvent $(CD_3)_2SO$								
30	1.2_9	10.0_9	14.4_7	36.2_8	11.3_8	21.7	0.89—0.92	0.08—0.11
42	1.3_4	10.0_0	14.5_5	35.9_9	11.3_4	21.7	0.88—0.91	0.09—0.12
50	1.4_1	9.9_6	14.5_0	35.8_7	11.3_7	21.6	0.88—0.91	0.09—0.12
55	1.4_3	9.9_7	14.5_6	35.7_5	11.4_0	21.6	0.88—0.91	0.09—0.12
61	1.4_6	9.9_3	14.6_7	35.6_1	11.3_9	21.6	0.87—0.90	0.10—0.13
84	1.5_3	9.7_7	14.6_3	35.1_7	11.3_0	21.5	0.85—0.89	0.11—0.15
90	1.5_6	9.8_1	14.6_6	34.9_6	11.3_7	21.4	0.86—0.89	0.11—0.14
100	1.6_2	9.6_7	14.6_7	34.8_1	11.2_9	21.4	0.84—0.88	0.12—0.16
110	1.6_5	9.7_3	14.8_9	34.5_3	11.3_8	21.4	0.85—0.89	0.11—0.15
120	1.7_3	9.6_2	14.7_5	34.3_2	11.3_5	21.4	0.83—0.88	0.12—0.17

TABLE 5

Coupling constants (Hz) and conformer populations for compound (IV)

T/°C	${}^3J_{13}$	${}^3J_{23}$	${}^3J_{24}$	${}^3J_{14}$	$J_{13} + J_{23}$	$\frac{1}{3}(2J_{24} + J_{14})$	x_a	$x_b + x_c$
Solvent $CDCl_3$								
-58	1.6_3	9.9_0	9.7_7	35.3_7	11.5_3	18.3	0.86—0.90	0.10—0.14
-50	1.7_3	9.8_1	9.9_1	35.0_0	11.5_4	18.3	0.85—0.89	0.11—0.15
-41	1.8_0	9.6_8	10.1_0	34.4_0	11.4_8	18.2	0.83—0.88	0.12—0.17
-32	1.8_8	9.6_7	10.3_0	33.8_6	11.5_5	18.2	0.83—0.88	0.12—0.17
-21	1.9_5	9.5_6	10.4_9	33.6_6	11.5_1	18.2	0.82—0.87	0.13—0.18
-11	2.0_1	9.4_0	10.5_9	33.1_2	11.4_1	18.1	0.80—0.85	0.15—0.20
1	2.0_9	9.2_9	10.7_5	32.6_9	11.3_8	18.1	0.78—0.84	0.16—0.22
11	2.1_5	9.1_4	10.8_7	32.0_0	11.2_9	17.9	0.77—0.83	0.17—0.23
36	2.3_2	8.9_6	11.3_4	30.9_3	11.2_8	17.9	0.74—0.81	0.19—0.26
44	2.3_9	8.8_2	11.5_3	30.4_8	11.2_1	17.9	0.73—0.80	0.20—0.27
Solvent $(CD_3)_2SO$								
60	2.4_5	8.7_1	11.9_3	30.8_1	11.1_6	18.2	0.71—0.79	0.21—0.29
70	2.5_3	8.6_6	12.1_0	30.3_6	11.1_9	18.2	0.71—0.79	0.21—0.29
80	2.5_8	8.5_0	12.2_5	30.0_0	11.0_8	18.2	0.69—0.77	0.23—0.31
90	2.6_5	8.4_5	12.5_2	29.6_3	11.1_0	18.2	0.68—0.77	0.23—0.32

TABLE 6

Chemical shift (p.p.m. from Me_4Si *) ranges of H-1, -2, and -3 for compounds (I)—(IV)

Compound	Solvent	ν_1	ν_2	ν_3
(I)	$(CD_3)_2CO$	4.05_1—3.84_0	4.08_3—3.89_2	6.40_5—6.27_8
	$(CD_3)_2SO$	4.57_1—4.42_7	4.56_7—4.46_1	6.78_4—6.74_6
(IIA)	$CDCl_3$	3.43_1—3.50_3	3.90_0—3.79_2	5.58_6—5.50_9
	$(CD_3)_2SO$	3.51_2—3.53_7	4.04_6—3.97_9	5.89_8—5.80_5
(IIB)	$CDCl_3$	3.80_4—3.74_9	3.31_8—3.27_4	5.82_8—5.74_8
	$(CD_3)_2SO$	4.16_2—4.05_2	3.89_8—3.80_5	5.98_6—5.90_8
(III)	$CDCl_3$	4.02_3—3.91_4	3.83_0—3.68_2	5.78_0—5.65_7
	$(CD_3)_2SO$	4.16_4—3.95_6	4.10_6—3.85_8	6.20_4—5.90_2
(IV)	$CDCl_3$	4.38_9—4.11_6	4.73_9—4.38_1	7.22_0—6.99_3
	$(CD_3)_2SO$	4.32_0—4.20_4	4.56_9—4.43_0	7.00_8—6.86_4

* The data refer to the temperature ranges in Tables 1—5. The dependence was not linear.

The n.m.r. parameters of the compounds investigated are reported in Tables 1—7.

TABLE 7

Coupling constant ranges (Hz) for geminal H–H and H–F

Compound	Solvent	$^2J_{12}$	$^2J_{34}$
(I)	$(CD_3)_2CO$	-15.0_4 to -15.2_2	53.4_2—54.0_9
	$(CD_3)_2SO$	-15.1_6 to -15.2_3	53.3_1—54.0_4
(IIA)	$CDCl_3$	-15.3_1 to -15.4_2	48.3_1—48.9_0
	$(CD_3)_2SO$	-15.5_7 to -15.7_1	47.8_5—48.0_5
(IIB)	$CDCl_3$	-15.0_0 to -15.1_4	47.5_2—47.8_1
	$(CD_3)_2SO$	-15.1_7 to -15.3_0	48.2_4—48.4_6
(III)	$CDCl_3$	-14.8_6 to -15.2_9	48.4_8—48.8_7
	$(CD_8)_2SO$	-15.2_4 to -15.3_7	47.7_1—48.1_3
(IV)	$CDCl_3$	-15.0_8 to -15.1_9	49.9_6—50.3_5
	$(CD_3)_2SO$	-15.1_6 to -15.2_8	49.7_5—49.9_1

By examining the values of the vicinal coupling constants and their temperature dependence the following information on the conformational behaviour can be obtained. Rotational averaging occurs and for all compounds, in the range of temperature investigated, the conformer having the two groups with the highest steric requirements in an antiperiplanar position is much preferred. Therefore, the observed vicinal couplings are the weighted mean of those in the individual rotamers (a)—(c) [equations (1) and (2) where x_a—x_c designate the

$$J_{13} = x_a(J_g)^a{}_{13} + x_b(J_t)^b{}_{13} + x_c(J_g)^c{}_{13} \qquad (1)$$

$$J_{23} = x_a(J_t)^a{}_{23} + x_b(J_g)^b{}_{23} + x_c(J_g)^c{}_{23} \qquad (2)$$

fractions of population of conformers (a)—(c) respectively]. Obviously equation (3) holds. Therefore in

$$x_a + x_b + x_c = 1 \qquad (3)$$

order to get information on fractional populations, knowledge of the J values is needed and this cannot be obtained without a few simplifying assumptions.

Coupling Constant J_t.—We can set $(J_t)_{13} = (J_t)_{23}$, as the Karplus equation in the simple original form [5] and in the subsequent formulations [6-10] shows that $J_{180°}$ is relatively insensitive to small changes in the dihedral angle. On the other hand, the electronegativity of the substituents would be expected to effect both J_t values [7,11] to a similar extent. We find that for a series of selected data for a variety of open chain and some cyclic compounds (see Table 8), within experimental error, J_t has a linear dependence on the Huggins electronegativity [12] according to equation (4). Therefore by using known

$$J_t = 25.00—1.16 \sum_{n=1}^{4} e_i \qquad (4)$$

electronegativity values [12,13] equation (4) allows us to calculate the following J_t values: (I), 11.33; (II), 11.21; (III), 10.96; (IV), 11.09 Hz.

Coupling Constant J_g.—A survey of literature data for compounds having S, SO, and SO_2 groups as substituents [14] and an electronegativity sum comparable with that for compounds (I)—(IV) gives J_g values in the range 1.2—2.9 Hz. However, treatment similar to that performed for J_t is not possible since J_g values are sensitive to small variations in the dihedral angle and, particularly, to the orientation [6,7,15-17] of substituents. At this point it is worth noting that the available data [14] refer to cyclic systems with some degree of flexibility. In spite of this difficulty we can show that even enlarging the above range to include the limiting case where $J_g \simeq 0$ a valid approach is still possible.

TABLE 8

J_t Values and the sum of the electronegativities of the substituents [a]

Compound	J_t/Hz	$\sum_{n=1}^{4} e_i$	Ref.
$Bu^tCH_2CH_2Li$	15.5 ± 0.3	8.0	*d*
$Bu^tCH_2CH_2CN$	13.9 ± 0.4	9.6	*e*
$Bu^tCH_2CH_2SPh$	14.2 ± 0.4	9.6	*e*
2-t-Butyl-1,3-dithian 1-oxide	13.0 [b]	9.6	*f*
Cyclohexane	13.1 ± 0.05	9.6	*g*
$Bu^tCH_2CH_2I$	14.5 ± 0.3	9.6_5	*e*
CH_2ICH_2I	14.0 ± 0.1	9.7	15
$Bu^tCH_2CH_2Ph$	13.7 ± 0.3	9.7_5	*e*
2-t-Butyl-1,3-dithian 1-oxide	13.0 [c]	9.7_8	*f*
$Bu^tCH_2CH_2Br$	14.1 ± 0.3	9.9_5	*e*
CH_2BrCH_2Br	13.4 ± 0.1	10.3	15
CH_2ClCH_2Br	13.0 ± 0.4	10.5	15
CH_2ClCH_2Cl	12.5 ± 0.5	10.7	15
CH_2FCH_2Br	12.1 ± 0.4	11.2_5	15
$MeOCH_2CH_2OMe$	11.9	11.4	20
2,3-Dimethyl-1,4-dioxan	11.5	11.8	*h*
$CHBr_2CHF_2$	9.0 ± 0.5	13.7	16
$CHCl_2CHF_2$	8.4 ± 0.5	14.1	16
CHF_2CHF_2	6.9 ± 0.3	15.6	16
CH_2FCH_2Cl	11.5 ± 0.5	11.4_5	15

[a] r.m.s. = ±0.40; [b] $J_{4ax,5ax}$; [c] $J_{5ax,6ax}$. [d] M. Witanowski and J. D. Roberts, *J. Amer. Chem. Soc.*, 1966, **88**, 737. [e] G. M. Whitesides, J. P. Sevenair, and R. W. Goetz, *J. Amer. Chem. Soc.*, 1967, **89**, 1135. [f] M. J. Cook and A. P. Tonge, *J.C.S. Perkin II*, 1974, 767. [g] E. W. Garbisch and M. G. Griffith, *J. Amer. Chem. Soc.*, 1968, **90**, 6543. [h] G. Gatti, A. L. Segre, and C. Morandi, *Tetrahedron*, 1967, **23**, 4385.

Indeed, the sum of the population of conformers (b) and (c) can be evaluated by transforming equations (2) and (3) into (5) and (6). From the J_{23} values reported in

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Tables 1—5 it can be seen that, due to the predominance of isomer (*a*), in our compounds $(J_t - J_{23})$ ranges

$$J_{23} = J_t - x_b[J_t - (J_g)^b{}_{23}] - x_c[J_t - (J_g)^c{}_{23}] \quad (5)$$

$$J_t - J_{23} = x_b[J_t - (J_g)^b{}_{23}] + x_c[J_t - (J_g)^c{}_{23}] \quad (6)$$

between 0.1 and 3.3 the lower and the higher limits being valid, respectively, for (III) at −59° and for (I) at 140°. If we take $[J_t - (J_g)^b{}_{23}] = [J_t - (J_g)^c{}_{23}] = (J_t - J_g)$, an assumption which will be justified *a posteriori*, equation (6) simplifies to (7). Equation (7) allows us to

$$J_t - J_{23} = (x_b + x_c)(J_t - J_g) \quad (7)$$

calculate $x_b + x_c$ and, consequently x_a. The data are reported in Tables 1—5.

The validity of the above assumption can now be easily shown if we take into account that $J_t - J_g \simeq 10$ Hz and that a difference of 1 Hz in this value would lead to a maximum variation of 0.03 in the fraction of population.

The x_a values at a given temperature show that within the series of sulphur substituted compounds (I)—(III) the steric requirements of the R group govern the relative conformation stability.[18]

Partition of $x_b + x_c$ between the two components is not possible. By combining equations (1) and (3) we obtain (8). If in a simplifying attempt we assume

$$J_{13} = (J_g)^a{}_{13} + x_b[J_t - (J_g)^a{}_{13}] + x_c[(J_g)^c{}_{13} - (J_g)^a{}_{13}] \quad (8)$$

$(J_g)^c{}_{13} \simeq (J_g)^a{}_{13} \simeq (J_g)_{13}$ equation (9) is obtained. Now

$$J_{13} - (J_g)_{13} = x_b(J_t - J_{13}) \quad (9)$$

it can be realized that the choice of a value for $(J_g)_{13}$ is crucial in calculating x_b. Indeed, recalling that $J_t - (J_g)_{13} \simeq 10$ Hz an uncertainty of 1 Hz in the J_g values leads to an uncertainty of 0.1 in the value of x_b. If we consider that the highest value for $x_b + x_c$ is 0.4 (see Table 1) this would amount to at best an error of 25%. Therefore equations (8) and (9) are of little help.

On the other hand some useful information on the relative population can be obtained by a different approach.[19] By adding equations (1) and (2) we obtain (10). The data for compounds (IIB) and (III) (see Tables 3 and 4) show that this sum is constant in the two solvents over a wide range of temperature. In principle, this insensitivity to the temperature changes could arise for a variety of reasons.

$$J_{13} + J_{23} = x_a[J_t + (J_g)^a{}_{13}] + x_b[J_t + (J_g)^b{}_{23}] + x_c[(J_g)^c{}_{13} + (J_g)^c{}_{23}] \quad (10)$$

(i) A fortuitous compensation of effects in the right hand terms of equation (10) could occur. Actually, increase in temperature leads to a decrease of x_a and to a corresponding increase of $x_b + x_c$. However, it seems highly unlikely that over a wide temperature range and for two solvents a decrease in the product $x_a[J_t + (J_g)^a{}_{13}]$ would be perfectly balanced [±0.02 Hz for (III) in $CDCl_3$; ±0.05 Hz for (III) Me_2SO; ±0.04 for compound (IIB) in $CDCl_3$] by the sum $x_b[J_t + (J_g)^b{}_{13}] + x_c[(J_g)^c{}_{13} + (J_g)^c{}_{23}]$.

(ii) $x_a \simeq 1$. When conformer (a) is practically the only one present both J_{13} and J_{23} should be constant with temperature according to equations (1) and (2). This seems likely to occur for compound (III) in $CDCl_3$ at low temperature (−59 to −37°) (see Table 4).

(iii) $x_c \simeq 0$. This seems likely to occur for compound (III) in Me_2SO and for compound (IIB) in $CDCl_3$ and in Me_2SO. The high energy of rotamer (c) should be due to steric and dipolar repulsion between the C–F, C–SOPh, and C–SO_2Ph groups. In these conditions equation (10) becomes (11). The insensivity of the sum $J_{13} + J_{23}$ to the temperature would also require that $[J_t + (J_g)^b{}_{23}] \simeq [J_t + (J_g)^a{}_{13}]$ and with $x_a + x_b = 1$ equation (11) simplifies to (12).

$$J_{13} + J_{23} = x_a[J_t + (J_g)^a{}_{13}] + x_b[J_t + (J_g)^b{}_{23}] \quad (11)$$

$$J_{13} + J_{23} = J_t + J_g \quad (12)$$

It is worth noting that for compound (IIB) $(J_t + J_g)Me_2SO \neq (J_t + J_g)$ $CDCl_3$. This variation could be due mainly to changes[20,21] of molecular geometry induced by solvent in the most highly populated conformer (a).

Besides the above cases no other quantitative information on the relative population of x_b and x_c is given by our data. It can be only said that for all the other compounds the decrease of $J_{13} + J_{23}$ with increasing temperature suggests the presence of a small but definite amount of conformer (c).

On the basis of theoretical[6-9,22] and experimental[23,24] work it is known that $^3J_{HF}$ depends upon the dihedral angle between the coupling nuclei in the same manner of $^3J_{HH}$. However, no rotamers population analysis can be performed starting from vicinal H–F couplings because of their intrinsic solvent[25-27] and, occasionally, concentration dependence.[25] Nevertheless, the $^3J_{HF}$ values show some interesting features.

The values of $^3J_{24}$, particularly for compounds (IIA) and (III) (see Tables 2 and 4) apparently suggest that the population of conformer (c) increases with respect to the population of conformer (b) on going from $CDCl_3$ to Me_2SO. In effect in molecules having polar groups the population of the more polar conformer is expected to

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increase with the dielectric constants of the solvent.[28] Indeed, inspection of the Newman projections of conformer (c) reveals that the groups are oriented in a favourable position for producing high polarity.

On the other hand the observation that the values of $\frac{1}{3}(2{}^3J_{13} + {}^3J_{23})$ are practically constant in the two solvents,[10c,29] ranging between 4.2 and 4.3, indicates that this effect is not of great relevance. In conclusion, the trend in ${}^3J_{24}$ values and the difference $\frac{1}{3}(2{}^3J_{24} + {}^3J_{14})_{\mathrm{Me_2SO}} - \frac{1}{3}(2{}^3J_{24} + {}^3J_{14})_{\mathrm{CDCl_3}}$ should be mostly due to a solvent effect arising from solvent-induced electronic changes in solute molecules.[27] Furthermore, the hypothesis is corroborated by the observation that this difference is higher for the more polar molecules.

In any case these results suggest that equations relating the H–F vicinal coupling constants with the electronegativities of the substituent [23,30] should be based on systematic studies performed in solvents of different polarity and over a sufficiently wide temperature range. This is also valid in the light of the unusual trend of the $\frac{1}{3}(2{}^3J_{24} + {}^3J_{14})$ values in the series of compounds investigated. In fact, an increase with the electronegativity of the substituents is observed for this parameter. A theoretical study performed by Chandra and Narasimhan [10a] in fragments of the type H–X–Y–H (X, Y = C, N, or O) predicts a positive sign for the *B* coefficient when the coupling constant increases with the electronegativity of the substituent. It is worth noting that in our systems at low temperature the relation $4{}^3J_{24} > {}^3J_{14}$ is valid.

${}^2J_{34}$ (see Table 7) shows an unusual trend since it decreases with increasing electronegativity of the substituent in contrast with the situation for several substituted fluoroalkanes.[25,31,32] Furthermore, this constant shows a small but well defined solvent dependence, which should be caused by electronic rather than by conformational factors. In fact, when R = SPh the ${}^2J_{\mathrm{HF}}$ values are very close in $\mathrm{Me_2SO}$ and in $(\mathrm{CD_3})_2\mathrm{CO}$, both solvents being polar. On the other hand for all the other compounds the difference ${}^2J_{34}$ ($\mathrm{CDCl_3}$) $-$ ${}^2J_{34}$ ($\mathrm{Me_2SO}$) increases with the C–R dipole and different behaviour is observed within the diasteroisomeric pair.[27]

EXPERIMENTAL

Synthesis of Compounds (I)—(IV).—1-Fluoro-1-phenylthio-2-phenylsulphonylethane (I), m.p. 75—76° (from ethanol), was prepared by a procedure described elsewhere.[1] Diastereoisomers of 1-*fluoro*-1-*phenylsulphinyl*-2-*phenylsulphonylethane* (II) were obtained by oxidation of compound (I) with the required amount of perbenzoic acid in chloroform at −20°. After completion of the oxidation the resulting solution was washed with $\mathrm{NaHCO_3}$ (5%) and water and dried ($\mathrm{Na_2SO_4}$). The solvent was removed and the residue washed with ethyl ether. The resulting 2 : 1 mixture of diastereoisomers had m.p. 107—116° (Found C, 53.5; H, 4.1; F, 6.0; S, 20.3. $\mathrm{C_{14}H_{13}FO_3S_2}$ requires C, 53.8; H, 4.2; F, 6.1; S, 20.5%). Oxidation of (I) with an excess of peracetic acid in a steam-bath gave 1-*fluoro*-1,2-*bisphenylsulphonylethane* (III), m.p. 163—164° (from ethanol) (Found C, 50.6; H, 4.2; F, 5.8; S, 19.4. $\mathrm{C_{14}H_{13}FO_4S_2}$ requires C, 51.2; H, 4.0; F, 5.8; S, 19.5%). 1-*Bromo*-1-*fluoro*-2-*phenylsulphonylethane* (IV) was obtained by refluxing a solution of 48% HBr (20 ml) containing phenyl *cis*-2-fluorovinyl sulphone (0.5 g,),[1] m.p. 87—88° (from ethanol) (Found C, 35.7; H, 3.0; Br, 29.4; F, 7.0; S, 12.0 $\mathrm{C_8H_8BrFO_2S}$ requires C, 36.0; H, 3.1; Br, 29.1; F, 7.1; S, 12.0%).

^{1}H *N.m.r. Spectra*.—Spectra were recorded at −60 to 140°. For each compound the higher limit was determined by the start of decomposition and the lower by precipitation from solution. Since the solubility of the compounds in the solvents used is not high, experiments were performed close to saturation. For the spectra at higher temperature $(\mathrm{CD_3})_2\mathrm{SO}$ was used as solvent. Lower temperature spectra were taken in $\mathrm{CDCl_3}$, except for one case which required $(\mathrm{CD_3})_2\mathrm{CO}$. The spectra were recorded at 100 MHz using a Varian HA100 spectrometer with the following conditions: recording scale 2 Hz cm^{-1}, sweep rate 0.2 Hz s^{-1}. Calibration at 10 Hz intervals was made by a Hewlett–Packard 5521 frequency counter. For INDOR spectra the instrument was modified following the Varian publication VKZ 4354–001. The observing frequency was obtained with a Hewlett-Packard 4204 audio-oscillator. The scan rate and the intensity of saturating frequency were adjusted to obtain a new equilibrium distribution of the spin population. The temperature of the sample was checked before and after recording the spectra. The experimental spectra were analysed with the aid of LAOCOON 3 program on a IBM 360/65 computer. The root mean square deviations between calculated and observed transitions have a mean value of 0.034.

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