

Rotational Isomerism. Part XX.† Relative Conformational Stabilities of some Chlorofluoropropanes

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A combination of classical conformational-energy calculations and variable-temperature n.m.r. analysis was used to determine the relative conformational stabilities of $\text{CFCl}_2\cdot\text{CHCl}\cdot\text{CCl}_3$, $\text{CFCl}_2\cdot\text{CHCl}\cdot\text{CFCl}_2$, and $\text{CF}_2\text{Cl}\cdot\text{CHCl}\cdot\text{CFCl}_2$. The analysis of the variable-temperature data was carried out using a specially written least-mean-squares routine considering explicitly uncertainties in both the coupling constant and temperature measurements. Although 1,3-interactions play an important role in determining conformational stability in these systems, the attractive polar interactions between fluorine and carbon and hydrogen atoms are also found to play an important and sometimes dominant role.

ALTHOUGH conformational isomerism in substituted ethanes has been extensively studied by n.m.r. spectro-

† Part XIX, R. J. Abraham and P. Loftus, *J.C.S. Perkin II*, 1975, 535.

¹ L. Cavalli, *J. Magnetic Resonance*, 1972, **6**, 298.

² T. D. Alger, H. S. Gutowsky, and R. Vold, *J. Chem. Phys.*, 1967, **47**, 3130.

³ F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 1968, **90**, 3577.

scopy,¹⁻⁶ the next higher homologues, the propanes, have received much less attention. One reason for this is the marked increase in conformational complexity en-

⁴ F. J. Weigert, M. B. Winstead, J. I. Garrels, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 7359.

⁵ B. L. Hawkins, W. Bremser, S. Borcic, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1971, **93**, 4472.

⁶ R. A. Newmark and C. H. Sederholm, *J. Chem. Phys.*, 1963, **39**, 3131.

countered on going from a substituted ethane (a maximum of three conformations), to a substituted propane (a maximum of nine conformations).

Despite the difficulties inherent in their treatment, the substituted propanes constitute a very important class of chemical compounds, since they are the simplest molecules in which the possibility of 1,3- as well as 1,2-interactions arise. 1,3-Interactions have been shown to play an important role in determining relative conformational stabilities⁷ and, consequently, it was decided to undertake a study of some fluorinated chloropropanes using the

All spectra were obtained at 60 MHz for protons and 56.45 MHz for fluorine using a Varian Associates A56/60A spectrometer equipped with a V6040 variable-temperature accessory. Spectral calibration was accomplished by generating sidebands from the SiMe₄ reference for ¹H and CF₃·CCl₃ for ¹⁹F using a Hewlett Packard 4204A oscillator, calibrated by counting the frequency in the reciprocal mode on a Hewlett Packard 5212A electronic counter.

Room-temperature spectra of all three compounds were recorded as neat liquids. Variable-temperature studies on compounds (1) and (3) were carried out on the neat liquid, while compound (2) was studied as 10% (v/v) solutions in

TABLE I
Calculated conformational stabilities

Form	CFCl ₂ ·CHCl·CCl ₃ (1)					CFCl ₂ ·CHCl·CFCl ₂ (2)				CF ₂ Cl·CHCl·CFCl ₂ (3)			
	θ	φ	Energy (kcal mol ⁻¹)	Rel. energy (kcal mol ⁻¹)	Statistical wt.	θ	φ	Energy (kcal mol ⁻¹)	Rel. energy (kcal mol ⁻¹)	θ	φ	Energy (kcal mol ⁻¹)	Rel. energy (kcal mol ⁻¹)
(A)	30 (34)	48 (52)	0.61 (-4.89)	0.00 (0.00)	2	42 (50)	44 (54)	-20.80 (-23.53)	0.00 (0.10)	90 (86)	68 (68)	-32.10 (-33.21)	3.48 (3.65)
(B)	202 (200)	82 (80)	9.82 (-0.75)	9.21 (4.14)	2	32 (36)	168 (170)	-18.58 (-22.74)	2.22 (0.89)	92 (86)	190 (188)	-30.09 (-32.40)	5.49 (4.46)
(C)	328 (324)	74 (72)	2.98 (-1.76)	2.38 (3.13)	1	64 (56)	328 (320)	-19.50 (-23.63)	1.30 (0.00)	78 (72)	316 (312)	-34.02 (-35.50)	1.56 (1.36)
(D)					2	202 (200)	74 (74)	-15.36 (-21.05)	5.44 (2.58)	168 (174)	48 (56)	-33.83 (-34.55)	1.75 (2.32)
(E)					1	202 (200)	200 (198)	-9.50 (-17.26)	11.30 (6.37)	158 (162)	168 (172)	-34.35 (-35.96)	1.23 (0.91)
(F)					1	326 (320)	68 (66)	-16.31 (-18.71)	4.49 (4.92)	162 (168)	298 (304)	-35.58 (-36.86)	0.00 (0.00)
(G)										310 (306)	74 (72)	-31.52 (-34.97)	4.07 (1.90)
(H)										274 (278)	168 (174)	-28.33 (-31.86)	7.25 (5.01)
(I)										304 (298)	326 (322)	-30.89 (-34.03)	4.69 (2.83)

temperature variation of coupling-constant technique.^{1,2,8}

It is not possible, however, to apply an analysis of the temperature variation of couplings to a nine component system. Consequently, it is necessary to be able to establish which are the significant conformations. This was accomplished by means of a theoretical study employing the classical molecular mechanics approach.⁹

EXPERIMENTAL

The compounds studied consisted of 1,1,2,3,3,3-hexachloro-1-fluoropropane (1), 1,1,2,3,3-pentachloro-1,3-difluoropropane (2), and 1,2,3,3-tetrachloro-1,1,3-trifluoropropane (3).

All three compounds were prepared by Mr. H. Cooper, from the condensation of carbon tetrachloride and trichloroethylene in the presence of aluminium trichloride.¹⁰ The mixture was then fluorinated using a mixture of antimony trifluoride-antimony pentafluoride, again using literature procedures,¹⁰ to give a mixture of fluorinated compounds which were separated by fractional distillation. The trifluoro-compound (3), had not been reported previously.

⁷ C. Kingsbury and D. Best, *J. Org. Chem.*, 1967, **32**, 6.

⁸ G. M. Whitesides, J. P. Sevenair, and R. W. Galtz, *J. Amer. Chem. Soc.*, 1966, **89**, 1135.

CF₂Cl₂ and CF₂ClBr. All studies were carried out using sealed n.m.r. tubes, which had been degassed, prior to sealing on a vacuum line. All measurements are the average of at least three spectra, apart from the variable-temperature studies on compound (2) which are averaged over four spectra and the ¹³C satellite spectra of (2), which, due to poor signal-to-noise, are averaged over six spectra.

Temperature measurements were made using an ethylene glycol sample (from 200 to 40 °C), a methanol sample (from 40 to -100 °C) and, below -100 °C, using a precalibrated thermocouple in a non-spinning sample tube containing CF₂ClBr as solvent. Temperature measurements were taken before and after the spectra and the quoted values are the average of the two measurements.

The 'frozen out' spectra of compound (2) at -160 °C were integrated by tracing over the spectra on to plain paper, cutting out the peaks and weighing them. The results were averaged over thirteen spectra.

Conformational Energy Calculations.—In order to establish their significant conformations the theoretical rotamer stabilities were calculated using the computer program

⁹ R. J. Abraham and K. Parry, *J. Chem. Soc. (B)*, 1970, 539.

¹⁰ A. L. Henne and E. C. Ladd, *J. Amer. Chem. Soc.*, 1938, **60**, 2491.

CONTOUR.* The results obtained are given in Table 1 and the individual conformations shown in Figure 1. The output from the program appears in the form of a conformational energy profile and a typical result is shown in Figure 2.

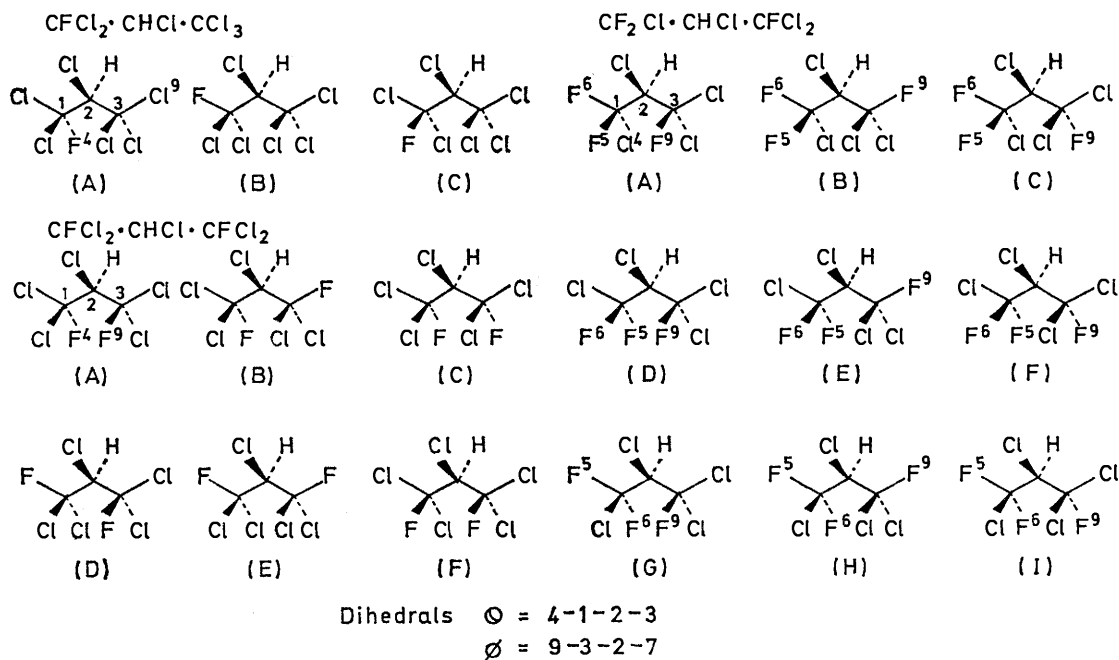


FIGURE 1 Molecular conformations

The results given were obtained using the standard⁹ C-C-C bond angle of 112.50°. In the case of a propane, however, the 1,3-interactions can be considerably reduced by a slight opening out of this bond angle and to take account of this possibility the calculations were also performed using a C-C-C bond angle of 117°; these results are given in brackets. This deformation requires only *ca.* 1 kcal mol⁻¹ of strain energy.¹² As can be seen from a comparison of the relevant conformational energies, the reduction in overall energy is normally considerably greater than 1 kcal mol⁻¹ making this deformation energetically advantageous.

The calculations for compound (1), using the normal bond angle, indicate that there are only two significant conformations (A) and (C). It is interesting to note that an increase in the C-C-C bond angle leads to a reduction in the stability of (C) relative to both (A) and (B).

The importance of the role played by the C-C-C bond angle is demonstrated quite clearly by compound (2). In both cases (A), (B), and (C) are predicted to be the three significant conformations but, as can be seen, the relative stabilities of the two most stable forms, (A) and (C), are reversed on opening out the C-C-C bond angle. In contrast to this, the two sets of results for compound (3) are very similar and, in both cases, (C), (D), (E), and (F) are predicted to be the significant conformations with (F) being the most stable form.

* The CONTOUR program and associated MODELS 2 program are revised and re-parameterised molecular-mechanics calculations based on the MODELS program.⁹ Full details are available elsewhere.^{11,12}

¹¹ R. J. Abraham and P. Loftus, to be submitted.

¹² P. Loftus, Ph.D. Thesis, Liverpool University, 1974.

Spectral Analysis.—Compound (1) gives rise to an AX spectrum so that the coupling can be obtained directly from the spectrum and, similarly, compound (2) gives rise to an AX₂ spectrum. Compound (3), however, gives rise to an ABCX spectrum which cannot be analysed explicitly. The

low-temperature spectrum of this compound at -33 °C approximates to an AMRX spectrum and was analysed on a

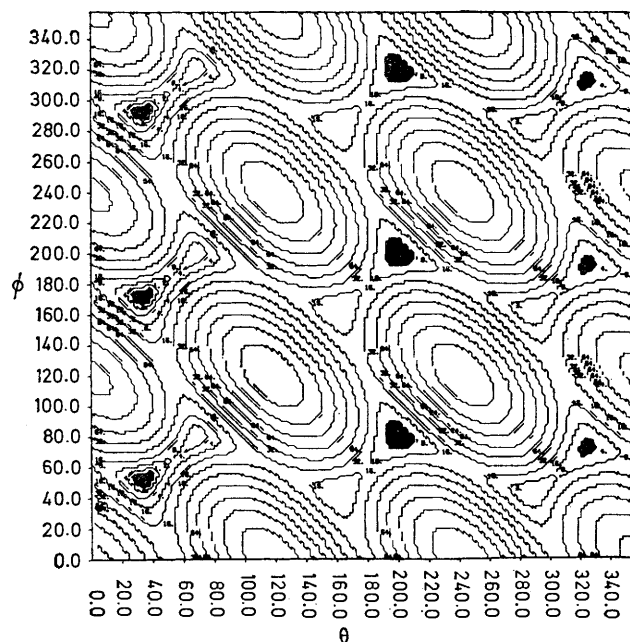


FIGURE 2 Conformational energy profile for $\text{CFCl}_2 \cdot \text{CHCl} \cdot \text{CCl}_3$

first-order basis to give trial parameters used as initial input for a LAOCOON3A¹³ analysis. An analysis of the room-
¹³ S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, 1964, **41**, 3863.

temperature ABCX spectrum permits a determination of the relative signs of the coupling constants.¹⁴ The results obtained assume $^2J_{FF}$ to be positive.¹⁵

The values obtained for all three compounds studied as neat liquids are shown in Table 2. Variable-temperature measurements were performed on compounds (1) and (3) as the neat liquid and on compound (2) as a 10% solution in CF_2Cl_2 ; the results are given in Table 3.

CONTOUR Calculations on compound (1) indicate that

The normal procedure^{2,17} is to perform a least-mean-square (l.m.s.) fit of the experimental data assuming that the temperature measurements can be considered as 'error free'. The accuracy with which vicinal couplings can be measured (better than 0.05 Hz), however, compared with the accuracy of the temperature measurement ($\pm 2^\circ C$) and the temperature gradients encountered within the sample itself cast considerable uncertainty upon the validity of this assumption. This question poses a considerable difficulty

TABLE 2
Room-temperature spectral parameters

$CFCl_2 \cdot CHCl \cdot CCl_3$			$CFCl_2 \cdot CHCl \cdot CFCl_2$			$CF_2Cl \cdot CHCl \cdot CFCl_2$			Probable error (Hz) ^{e, f}
Parameter	Hz	p.p.m.	Parameter	Hz ^e	p.p.m.	Parameter	Hz	p.p.m.	
ν_H^a	306.41	5.11	ν_H^a	296.41	4.94	ν_H^a	289.17	4.82	0.03
ν_F^b	1 816.77	32.19	ν_F^b	1 565.42	27.73	ν_F^{5b}	1 660.68	29.42	0.04
$^3J_{HF}$	2.67	—	$^3J_{HF}$	4.93	—	ν_F^{6b}	1 438.03	25.48	0.06
			$^4J_{FF}^d$	20.9	—	ν_F^{9b}	1 474.00	26.11	0.04
						$^3J_{HF}^5$	3.83	—	0.04
						$^3J_{HF}^6$	9.27	—	0.05
						$^3J_{HF}^9$	5.43	—	0.04
						$^2J_{F^5F^6}$	196.06	—	0.06
						$^4J_{F^5F^9}$	19.03	—	0.08
						$^4J_{F^6F^9}$	12.33	—	0.05

^a Downfield from $SiMe_4$. ^b Downfield from CF_3CCl_3 ; ϕ^* value 82.27¹⁶ p.p.m. ^c R.m.s. error in line positions 0.014 Hz. ^d Measured from the carbon-13 satellite spectra. ^e From LAOCOON3A. ^f R.m.s. error 0.1 Hz.

TABLE 3
Variable-temperature spectral parameters

$CFCl_2 \cdot CHCl \cdot CCl_3$ (1)				$CFCl_2 \cdot CHCl \cdot CFCl_2$ (2)				$CF_2Cl \cdot CHCl \cdot CFCl_2$ (3)				R.m.s. error							
$\theta_c/^\circ C$	$^3J_{HF}^e$	ν_H^a	ν_F^b	$\theta_c/^\circ C$	$^3J_{HF}^e$	ν_H^a	ν_F^b	$\theta_c/^\circ C$	ν_F^{5b}	ν_F^{6b}	ν_F^{9b}		ν_H^a	J_{HF}^5	J_{HF}^6	J_{HF}^9	$J_{F^5F^6}$	$J_{F^5F^9}$	$J_{F^6F^9}$
-68	1.23	311.07	—	-96	3.87	298.85	1 470.6	92	1 669.5	1 471.3	1 484.8	287.8	4.2	8.9	5.7	169.8	17.4	12.9	0.12
-61	1.52	310.63	—	-77	4.05	297.92	1 491.3	40	1 655.9	1 433.7	1 470.9	—	3.6	9.3	5.2	167.5	18.7	12.3	0.42
-51	1.66	310.00	—	-33	4.49	—	1 524.8	32	1 653.7	1 428.2	1 469.0	—	3.5	9.3	5.4	167.6	18.9	12.1	0.17
-16	2.11	308.26	—	—	4.61	295.75	1 537.5	9	1 650.7	1 408.4	1 466.3	—	3.5	9.5	5.2	168.3	20.8	11.8	0.32
-1	2.25	307.35	1 810.52	13	4.73	295.46	1 547.0	—	1 643.6	1 397.1	1 461.2	—	3.3	9.6	5.0	167.2	20.6	11.8	0.23
45	2.71	306.62	1 814.79	36	4.80	295.19	1 558.5	-18	1 641.9	1 390.6	1 460.2	—	3.2	9.6	4.9	167.2	20.8	11.8	0.22
64	2.74	306.62	1 818.13	92	5.28	—	1 585.8	-33	1 637.0	1 373.6	1 458.2	292.4	2.9	10.1	4.7	168.0	22.0	11.6	0.13
82	3.14	305.92	1 821.42	—	—	—	—	-39	1 634.1	1 369.1	1 457.1	—	2.7	10.1	4.2	167.0	22.1	11.3	0.25
100	3.37	305.73	—	—	—	—	—	-58	1 623.9	1 348.3	1 452.9	—	2.6	10.9	4.5	166.3	23.4	10.9	0.25
192	3.79	—	—	—	—	—	—	-61	1 620.4	1 340.5	1 452.2	—	2.7	10.6	4.5	166.4	23.9	10.8	0.09
				98.5	—	18.9	—	—	—	—	—	—	—	—	—	—	—	—	—
				36.0	—	20.3	—	—	—	—	—	—	—	—	—	—	—	—	—
				-28.5	—	23.4	—	—	—	—	—	—	—	—	—	—	—	—	—

^aIn Hz downfield from $SiMe_4$. ^bIn Hz downfield from $CF_3 \cdot CCl_3$; ϕ^* value 82.27¹⁶ p.p.m. ^c From LAOCOON3A. ^d Non-iterated parameter. ^e All couplings in Hz.

TABLE 4
Derived energy differences and coupling constants

Compound	ΔE	$J_{\alpha\alpha}/Hz$	$J_{\beta\beta}/Hz$	ϕ/Hz
	$(E_{\beta} - E_{\alpha})/kcal\ mol^{-1}$			
$CFCl_2 \cdot CHCl \cdot CCl_3$	0.7 ± 0.2^a	-1 ± 0.8	14.0 ± 1.6	0.097
$CFCl_2 \cdot CHCl \cdot CFCl_2$	1.1 ± 0.2^b	3.3 ± 0.3	9.4 ± 0.6	0.060
$CF_2Cl \cdot CHCl \cdot CFCl_2$	1.0^c	1.4	16.3	0.104
	1.1^d	3.4	18.1	0.191

^a $E_C - E_A$. ^b $E_A - E_C$. ^c From $^3J_{HF}^5$, $E_C - \langle E_{D,F} \rangle$. ^d From $^3J_{HF}^9$, $E_D - \langle E_{C,F} \rangle$.

there are only two significant conformations for this compound, (A) and (C). The data in Table 3 were analysed accordingly using the computer program OPTIMUM¹² to fit the experimental data to the relationship (1) where $J_{\alpha\alpha}$

$$J_{obs} = J_{\beta} + (J_{\alpha} - J_{\beta})/[1 + (Z_{\alpha}/Z_{\beta}) \exp(-\Delta E/RT)] \quad (1)$$

and J_{β} are the couplings in the individual conformers, Z_{α} and Z_{β} are their respective statistical weights and ΔE is the energy difference between them ($E_{\beta} - E_{\alpha}$) in kcal mol⁻¹.

¹⁴ C. N. Banwell, N. Sheppard, and J. J. Turner, *Spectrochim. Acta*, 1960, **16**, 796.

¹⁵ J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon Press, New York, 1965.

since the error function ϕ is somewhat insensitive to the fitting routine employed (the principal weakness of the temperature variation of coupling technique), and thus the final values of $J_{\alpha\alpha}$ and $J_{\beta\beta}$ obtained by different methods can show considerable discrepancies.

Accordingly, a separate l.m.s. routine has been devised and incorporated into OPTIMUM which considers equal uncertainties in both sets of parameters. This is the technique which has been used to obtain all the results presented here.

The data for compound (1) were analysed in this manner taking $Z_{\alpha} = Z_{\beta} = 1$ to give the results shown in Table 4.

¹⁶ R. J. Abraham, D. F. Wileman, and G. R. Bedford, *J.C.S. Perkin II*, 1973, 1027.

¹⁷ H. S. Gutowsky, G. G. Belford, and P. E. McMahon, *J. Chem. Phys.*, 1962, **36**, 3353.

The uncertainties were determined by obtaining the root-mean-square (r.m.s.) deviation in the data E' (taken as the r.m.s. deviation of the experimental data from a smooth curve), plotting the OPTIMUM results as a function of the error parameter ϕ and considering any value for which $\phi < E'$ to be a possible solution [the individual plots for compound (2) are shown in Figure 3 where parameters

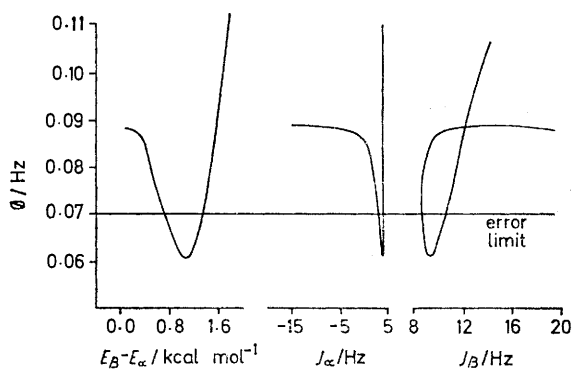


FIGURE 3 Correlation of molecular parameters and ϕ for compound (2)

corresponding to any value of ϕ below E' (0.07 Hz) are considered acceptable]. The uncertainties quoted in Table 4 are the r.m.s. deviations taken over all acceptable solutions.

The effect of a possible contribution from (B) was studied by determining the effect of an increase in Z_{α} on ϕ . (B) contains a *gauche* coupling similar to that in (A) and, consequently, the presence of an appreciable contribution from (B) would lead to an increase in the proportion of molecules in the *gauche* conformation [(A) or (B)]. This effect can be taken into consideration by increasing the statistical weight of Z_{α} . The analysis was repeated for a number of values of Z_{α} in the range 1.0–1.4, but in no case did this lead to any improvement in ϕ . Consequently, this result lends further support to the CONTOUR prediction that the contribution from form (B) is unimportant.

The calculations for compound (2) are somewhat less clear. Three significant conformations (A), (B), and (C) are predicted, with (A) and (C) being more stable than (B), but the relative stabilities of (A) and (C) themselves depend on the C–C–C angle used (Table 1).

Conformation (A) contains a *trans* and a *gauche* vicinal HF coupling and so the observed coupling will be given by their average, whereas (B) and (C) both contain two *gauche* couplings. The observed coupling of 3.87 Hz at -96°C is somewhat small to be the average of a *gauche* and a *trans*-coupling, demonstrating that (B) or (C) must be the most stable conformation or, alternatively, that the contribution of (B) and (C) together must be greater than that of (A).

Unfortunately, the two *gauche* conformations (B) and (C) cannot be distinguished by the magnitude of their vicinal coupling constants and, in order to establish their relative stabilities, the ^{13}C satellite spectra of $^{13}\text{CFCl}_2\cdot\text{CHCl}\cdot\text{CFCl}_2$ were measured as a function of temperature; the results obtained are given in Table 3.

It has been shown previously¹⁸ that in heavily fluorinated propanes the values of the four-bond coupling constants have the orders of magnitude shown in Figure 4. The results in Table 3 show that as the temperature decreases the value of ${}^4J_{\text{FF}}$ increases, attaining a value of 23.4 Hz at -28.5°C . This is very close to the value of 26 Hz given

above for J_e and indicates that (C) is the predominant conformation for this molecule. In (B) ${}^4J_{\text{FF}}$ corresponds to J_{tg} and would be expected to have a magnitude of 0 Hz.

In order to investigate the possibility of a small contribution from (B) the analysis of the results in Table 3 was carried out using a value of $Z_{\beta} = 2.0$ and $Z_{\alpha} = 1.0$ to 1.4. In no case did an increase in Z_{α} lead to an improvement in ϕ and, consequently, it was concluded that the system was best described as a direct equilibrium between (A) and (C). The results of the OPTIMUM analysis using $Z_{\alpha} = 1.0$ and $Z_{\beta} = 2.0$ are given in Table 4. The accuracy of the parameters was determined in an identical manner to that employed for compound (1) and a plot of the individual parameters against ϕ is shown in Figure 3.

In the case of this compound it also proved possible to obtain spectra at sufficiently low temperatures for the individual rotamers to be observed. Unfortunately, the separation only took place below -155°C and the high viscosity of the sample at this temperature resulted in broadening of the peaks so that no coupling information could be obtained. The ratios of the peak areas corresponded to an energy difference of $0.8 \pm 0.1 \text{ kcal mol}^{-1}$, in reasonable agreement with the value obtained from the temperature variation of the coupling constant of $1.1 \pm 0.2 \text{ kcal mol}^{-1}$. It did not prove possible to obtain the corresponding 'frozen out' spectra for compounds (1) and (3), even at these low temperatures.

Compound (3) is the most complicated, having a total of nine non-equivalent conformations. CONTOUR calculations on this compound indicated the presence of four

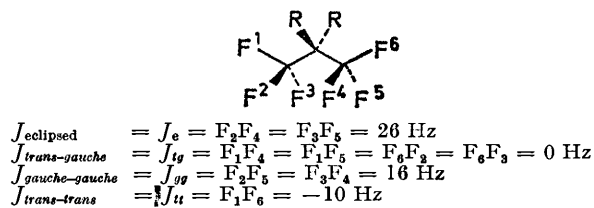


FIGURE 4 Four-bond couplings in fluorinated propanes¹⁸

significant forms (C), (D), (E), and (F), with (F) being more stable than (C), (D), and (E) by *ca.* 1 kcal mol⁻¹.

As can be seen from Figure 1, the $\text{CF}_2\text{Cl}\cdot\text{CHCl}$ fragments of conformations (C), (D), (E), and (F) each contain a *trans* and a *gauche* vicinal HF coupling. Consequently, if these are the only important forms, then, making the assumption that there is only one *gauche* and one *trans* vicinal coupling in this fragment, the sum of these two couplings ${}^3J_{\text{HF}^*} + {}^3J_{\text{HF}^*}$ should be constant and equal to $J_{\text{trans}} + J_{\text{gauche}}$. The results in Table 3 show that the sum of these two couplings is indeed constant to within the experimental error.

An examination of the four-bond coupling constants given in Table 3 shows that ${}^4J_{\text{FF}}$ increases as the temperature decreases, attaining a value of 23.9 Hz at -60.5°C . The large magnitude of this value provides strong evidence that form (F) in which these two fluorines are eclipsed is the most stable conformation.

The reduction in magnitude of this coupling with increasing temperature can be rationalized in terms of increased contributions from forms (C) and (D) (corresponding to a *gauche-gauche* coupling), and (E) (corresponding to a *trans-gauche* coupling). The large magnitude of ${}^4J_{\text{FF}}$ at -61°C

¹⁸ R. J. Abraham, *J. Chem. Soc. (B)*, 1969, 1022.

does, however, preclude an appreciable contribution from (E), since this would be expected to give rise to two four-bond fluorine-fluorine couplings of zero.

Similarly, ${}^4J_{\text{F}^*\text{F}}$ is found to increase with increasing temperature going from 10.8 Hz at -61°C to 12.9 Hz at 92°C . This can be rationalized in terms of an increased contribution from form (D) since ${}^4J_{\text{F}^*\text{F}}$ corresponds to an eclipsed coupling in (D) as opposed to a *gauche-gauche* coupling in (F). Increased contributions from (C) and (E), in which ${}^4J_{\text{F}^*\text{F}}$ corresponds to a *trans-gauche* coupling, would be expected to lead to a reduction in the observed coupling.

For the vicinal couplings ${}^3J_{\text{HF}}$ increases with temperature, indicating a contribution from form (D), corresponding to a *trans*-coupling, whereas (C), (E), and (F) all correspond to *gauche*-couplings. If the contribution from (C) was insignificant, then ${}^3J_{\text{HF}}$ and ${}^3J_{\text{HF}}$ would be expected to be temperature independent, except for a small effect due to the change in orientation of the substituents.^{19,20} The observed increase in ${}^3J_{\text{HF}}$ and decrease in ${}^3J_{\text{HF}}$ with increasing temperature, demonstrate quite clearly the significant contribution made by form (C). Consequently, the variations in coupling with temperature are in qualitative agreement with the CONTOUR calculations, indicating that (F) is the most stable conformation, with significant contributions from (C) and (D) and a possible small contribution from (E).

The analysis of ${}^3J_{\text{HF}}$ was carried out using $Z_\beta = 1.0$ and values of Z_α in the range 1.0–1.4. This is because conformations (D), (F), and (E) all contain *gauche*-coupling constants for ${}^3J_{\text{HF}}$ whereas only (C) contains a *trans*-coupling. The minimum values of ϕ were obtained for values of Z_α of 1.0, 1.1, and 1.2, the value of ϕ increasing for higher values. In all cases the optimum value for ΔE was 1.0 kcal mol⁻¹.

A similar analysis of ${}^3J_{\text{HF}}$ was also carried out again using $Z_\beta = 1$ and values of Z_α in the range 1.0–1.4. In this case forms (C), (E), and (F) all correspond to a *gauche*-coupling whereas (D) now corresponds to a *trans*-coupling. Once again the minimum values of ϕ were obtained for $Z_\alpha = 1.0$ and 1.1.

The previous calculated energy difference $E_D - E_F$ of 1 kcal mol⁻¹ corresponds to an increase in Z_α due to the contribution made by (C) of *ca.* 0.1. Accordingly, the results obtained from the analysis of ${}^3J_{\text{HF}}$ are in complete agreement with the *gauche*-component corresponding to the contributions made by (F) and (C) and, consequently, support the idea that (E) does not make a significant contribution. In an analogous manner, the OPTIMUM energy difference obtained for ${}^3J_{\text{HF}}$ was 1.1 kcal mol⁻¹, again corresponding to an increase in Z_α of 0.1 in the analysis of ${}^3J_{\text{HF}}$ in complete agreement with the results presented above.

Accordingly, the final analysis was carried out on the basis of three significant conformations, (C), (D), and (F), using values of $Z_\alpha = 1.1$ and $Z_\beta = 1.0$. These results are also included in Table 4.

Because of the uncertainties inherent in an analysis of this kind, no attempt to evaluate the accuracy of the results was made, since it was felt that they would give an unrealistic estimate of the uncertainties present in the parameters.

An attempt to analyse ${}^3J_{\text{HF}}$ in an analogous manner to ${}^3J_{\text{HF}}$ did not meet with any success, the programme failing to reach a realistic solution. One possible reason for this is

the small percentage variation in ${}^3J_{\text{HF}}$, 17% as opposed to 47 and 24% for ${}^3J_{\text{HF}}$ and ${}^3J_{\text{HF}}$ respectively.

DISCUSSION

The values of J_α and J_β obtained for compound (1) correspond directly to the *gauche*- and *trans*-couplings in that compound giving $J_{\text{gauche}} = -1 \pm 0.8$ and $J_{\text{trans}} = 14 \pm 1.6$ Hz. At first sight, the value of J_{gauche} appears to be somewhat small and to possess a sign opposite to that which would have been expected.²¹ This abnormal value can, however, be rationalized by considering the results of the CONTOUR calculations. These indicate that the HF dihedral in the *gauche*-conformation is *ca.* 90° and, if ${}^3J_{\text{HF}}$ obeys a Karplus-type relationship^{22,23} then it would be expected to be a minimum when the dihedral angle is 90° . Consequently, the value of -1.0 Hz is not unreasonable and means that the Karplus curve²⁴ for this compound crosses the negative axis at its minimum giving

$${}^3J_{\text{HF}} = A \cos^2 \theta - 1 \quad (2)$$

The *trans*-coupling is predicted to correspond to a dihedral angle of *ca.* 152° . Substituting this value in equation (2) gives $A = 19.2$ and ${}^3J_{\text{HF}(180)} = 18 \pm 1.6$ Hz.

The vicinal-coupling constants ${}^3J_{\text{HF}}$ obtained for compound (2) are $J_\alpha = 3.3$ Hz and $J_\beta = 9.4$ Hz. Form (A) contains two *gauche*-coupling constants and so $J_\alpha = J_{\text{gauche}} = 3.3 \pm 0.3$ Hz. In the case of (B), however, J_β corresponds to the average of a *trans*- and a *gauche*-coupling. Making the assumption that J_{gauche} is the same in the two conformations gives $J_{\text{trans}} = 15.5$ Hz. The HF dihedral in (A) corresponds to *ca.* 164° and, making the assumption that the vicinal coupling in equation (2) also obeys equation (2), the value of J_{180} can be calculated as being 17 ± 0.6 Hz, in good agreement with the corresponding value of 18 Hz obtained for compound (1).

The analysis of ${}^3J_{\text{HF}}$ for compound (3) gives values of $J_\alpha = 1.4$ and $J_\beta = 16.3$ Hz. These two values correspond to $J_{\text{HF}^*\text{-gauche}}$ and $J_{\text{HF}^*\text{-trans}}$ respectively. Similarly, the analysis of ${}^3J_{\text{HF}}$ gave $J_\alpha = 3.4$ Hz and $J_\beta = 18.1$ Hz, again corresponding to $J_{\text{HF}^*\text{-gauche}}$ and $J_{\text{HF}^*\text{-trans}}$ respectively. At first sight there appears to be a considerable discrepancy between these two sets of values but an examination of the calculated geometries shows that the HF dihedral corresponding to $J_{\text{HF}^*\text{-gauche}}$ is *ca.* 78° while that corresponding to $J_{\text{HF}^*\text{-gauche}}$ is *ca.* 58° . Consequently, J_{HF^*} would be expected to exhibit a normal *gauche*-coupling, ${}^3J_{\text{HF}^*\text{-gauche}} = 3.4$ Hz [cf. ${}^3J_{\text{HF}^*\text{-gauche}}$ in compound (2) of 3.3 Hz], whereas ${}^3J_{\text{HF}^*\text{-gauche}}$ corresponds to a dihedral angle of almost 80° , so that, in this case, a much smaller value of the coupling would be expected. Similarly, the values for ${}^3J_{\text{HF}^*\text{-trans}}$ and ${}^3J_{\text{HF}^*\text{-trans}}$ correspond to dihedral angles of *ca.* 162°

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and 168° respectively. If the assumption is made, as before, that the coupling in these two fragments obeys equation (2), values for ${}^3J_{\text{HF}^*(180)}$ and ${}^3J_{\text{HF}^*(180)}$ of 18 and 19 Hz respectively are obtained.

On this basis the results obtained for compounds (1), (2), and (3) show a marked consistency, the *gauche*-couplings in (2) and (3), which represent reasonable staggered conformations being 3.3 and 3.4 Hz respectively and the corrected couplings ${}^3J_{180}$ being 18, 17, 18, and 19 Hz respectively. This result is very pleasing since the fragments in all these molecules possess very similar electronegativities and, consequently, would be expected to give rise to similar couplings.

On the basis of 1,3-chlorine-chlorine interactions conformations (A) and (C) of compound (1) would be predicted to be considerably more stable than (B). However, the application of simple steric considerations to the relative stabilities of (A) and (C) would lead to the conclusion that (C) should be more stable than (A), since it contains an F-Cl and an H-Cl *gauche*-interaction compared with an H-F and a Cl-Cl interaction in (A).

Both the CONTOUR calculations and the experimental results show that this is not the case, however, and that (A) is more stable than (C). A breakdown of the interaction energies obtained by CONTOUR indicates that a considerable factor contributing to the stability of (A) is the substantial attractive polar interaction present between the *gauche* hydrogen and fluorine atoms, but the large deviations from a staggered geometry present in these molecules means that a direct comparison of a single interaction in two different conformations is not strictly valid.

The most favourable conformation of compound (2), in terms of 1,3-interactions is (A), since this is the only form

which is free from 1,3-chlorine-chlorine interactions. Experimentally, however, the preferred conformation is not (A) but (C), in which the two fluorine atoms are *gauche* to the hydrogen. The two fluorines are also *gauche* to the hydrogen in (B) but, in this case, a 1,3-fluorine-fluorine interaction has been replaced by a less favourable fluorine-chlorine interaction. Also, there is a strong attractive polar interaction between C¹ and F⁹ in (C) (which have a *gauche*-relationship to one another); this is substantially reduced in (B) (where C¹ and F⁹ are now *trans*).

The most stable conformations of compound (3) would have been predicted to be (D) and (F) which have the minimum 1,3-interactions. The experimentally preferred conformation is, however, (F) where, once again, there is a *gauche*-relationship between H⁷ and F⁹ in the most stable form.

In summary, although 1,3-interactions play an important role in determining conformational stabilities in these compounds, they are not always the decisive factor. Conformational stability in these systems appears to be determined by a combination of two factors, the minimization of 1,3-interactions and, secondly, the optimization of the number of F-H and F-C polar interactions. This second factor is not always of minor importance, however, and is directly responsible for the conformational preferences of (A) over (C) for compound (1) and (C) over (A) for compound (2).

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