Rotational Isomerism. Part XIX.[1] Nuclear Magnetic Resonance Spectral Analysis and Conformation of 1,1,1,4,4,4-Hexafluorobutane

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The combined techniques of heteronuclear noise decoupling and carbon-13 satellite analysis were used to provide initial parameters for a complete analysis of the ten-spin system of $CF_3 \cdot CH_2 \cdot CH_2 \cdot CF_3$. The results demonstrate clearly that the compound exists predominantly in the *trans*-conformation, both as the neat liquid and in acetone solution. ^1H, ^{19}F, and ^{13}C spectra were observed and the significance of the couplings, particularly the ^{13}C couplings, is discussed.

THE technique of high power heteronuclear noise de-coupling, when used in conjunction with carbon-13 satellite analysis, is a powerful tool for the investigation of complex spin systems consisting of equivalent groups of nuclei. In order to investigate the potential of this technique a study of 1,1,1,4,4,4-hexafluorobutane (HFB) was undertaken. This constitutes a strongly coupled ten-spin system containing well in excess of two thousand significant transitions, and is consequently not amenable to normal iterative methods of analysis.

EXPERIMENTAL

HFB was prepared by hydrogenation of 1,1,1,4,4,4-hexafluorobut-2-yne, using a standard literature procedure.[2] The sample was studied both as a neat liquid and as a 30% v/v solution in [$^2H_6$]acetone. The samples were contained in 5 mm diam. tubes, which were degassed prior

to sealing on a vacuum line. For proton and carbon-13 chemical shifts internal Me_4Si was used as reference; for fluorine chemical shifts external 1,1,1-trifluoro-2,2,2-trichloroethane was employed.

Spectra were obtained with a Varian XL-100-15 spectrometer, operating at 100 and 94·1 MHz in the CW frequency-swept mode for hydrogen and fluorine nuclei, respectively, and at 25·2 MHz in the pulse fourier transform (PFT) mode for carbon-13.

The probe temperature of the instrument was *ca.* 30 °C for the undecoupled spectra, but increased to *ca.* 37 °C with the use of high-power decoupling. Heteronuclear decoupling experiments were carried out using maximum high-power noise decoupling with a bandwidth of 4000 Hz.

Carbon-13 spectra were transformed unweighted to give

[1] Part XVIII, R. J. Abraham and J. R. Monasterios, *J.C.S. Perkin II*, in the press.

[2] R. N. Haszeldine, *J. Chem. Soc.*, 1952, 2504.

frequency domain spectra containing 2048 real data points, giving an accuracy of between $\pm2\cdot5$ and $\pm0\cdot1$ Hz depending on the spectral window employed.

RESULTS

HFB corresponds to an $[\text{AA}'\text{X}_3]_2$ spin system; consequently, any attempt to decouple one nucleus while simultaneously observing the other will result in the collapse of the spectrum into a single line, from which no information other than the chemical shift can be obtained. In order to overcome this problem it is necessary to decouple one nucleus while simultaneously observing the carbon-13 satellite spectrum of the other.

Although the six fluorine atoms are isochronous, their multiplet structure covers an appreciable range of frequency (ca. 60 Hz). In the case of the carbon-13 satellite spectra, this multiplet structure will be even broader, since it is now the fluorine spectrum of the $\text{CF}_3\cdot{}^{13}\text{CH}_2\cdot\text{CH}_2\cdot\text{CF}_3$ species which must be considered, in which the two trifluoromethyl groups are no longer
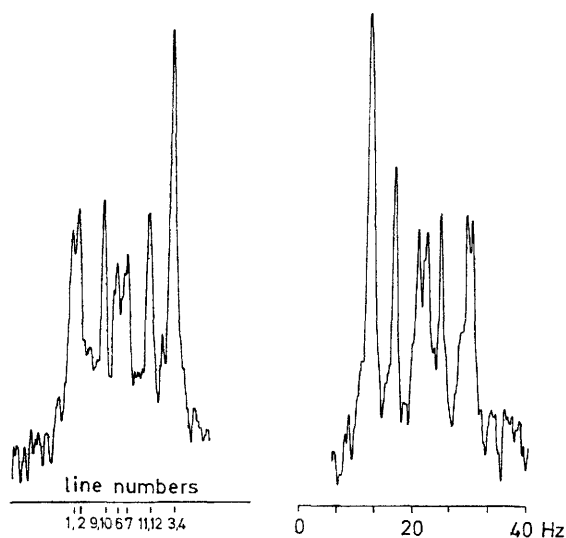

FIGURE 1   Outer ¹³C satellite 100 MHz ¹H–{¹⁹F} spectrum of HFB (pure liquid)

equivalent, so that $^2J(^{13}\text{CF})$, $^3J(^{13}\text{CF})$, and $^5J_{\text{FF}}$ (where the superscripts to J indicate the number of intervening bonds) are now involved in determining the fluorine spectrum. Consequently, in order to ensure complete decoupling it proved necessary to employ maximum power noise decoupling (a 4000 Hz bandwidth being used).

The fluorine noise-decoupled carbon-13 proton satellite spectrum of HFB corresponds to an AA'BB'X system, the outer satellites of which, obtained from the neat liquid, are shown in Figure 1. (The inner satellites for this compound were not observed.) The two multiplets are mirror images of one another, contain seven resolved lines, and can be analysed straightforwardly,[3,4] making the simplifying assumption $J_{\text{AA}'} = J_{\text{MM}'}$ (since the

³ R. M. Lynden-Bell and N. Sheppard, Proc. Roy. Soc., 1962, 269, 385.
⁴ R. J. Abraham, 'Analysis of High Resolution N.M.R. Spectra,' Elsevier, Amsterdam, 1971.

presence of a carbon-13 nucleus would not be expected to alter significantly the geminal proton coupling constants), to give the ¹H coupling constants and chemical shifts.

The fluorine noise-decoupled carbon-13 spectrum of this molecule was also observed. This corresponds to the X region of the AA'BB'X spectrum and can be combined with the above satellite spectra to give the complete spectrum. (The signal corresponding to CF_3 in this spectrum appeared as a broad hump at 123·9 p.p.m., from which no coupling information could be obtained.) This was then analysed by using the computer program LAOCOON III[5] (taking the ¹H parameters outlined above) to give the final results shown in Table 1.

TABLE 1

AA'BB'X Analysis of the fluorine noise-decoupled spectra of HFB ($R^{13}CH_2\cdot CH_2R$)

	Neat liquid		30% v/v Solution in [²H₆]acetone	
Parameter	Value (Hz)	Probable error ᵃ (Hz)	Value (Hz)	Probable error ᵃ (Hz)
ν_A, $\nu_{\text{A}'}$ ᵇ	231·05	0·02	244·88	0·01
ν_B, $\nu_{\text{B}'}$ ᵇ,ᶜ	231·50		245·30	
ν_X ᵇ	725 ᵈ		716 ᵈ	
$J_{\text{AA}'}$, $J_{\text{BB}'}$	−17·03	1·47	−17·16	1·28
J_{AB}	4·64	0·05	4·97	0·03
$J_{\text{AB}'}$	12·50	0·05	11·54	0·03
J_{AX}	132·01	0·03	132·24	0·02
J_{BX}	−4·92	0·04	−5·02	0·02

ᵃ From LAOCOON III.   ᵇ Downfield from Me₄Si.   ᶜ Position of proton ¹²C centre-band.   ᵈ δ 28·8 and 28·4 p.p.m.

Since the inner proton satellite spectra were not observed, the chemical shift of H_B was assigned as the proton centre-band frequency and this parameter was omitted from the iteration.

Unlike the AA'MM'X spectrum, the AA'BB'X spectrum is dependent on the signs of the coupling constants and so the relative signs of many of the individual couplings can be determined. The analysis was carried out assuming J_{AX} and J_{BX} to be either the same or opposite in sign, and the results demonstrated that the two couplings are in fact opposite, in agreement with previous sign determinations.[3]

The value of the geminal coupling given by $J_{\text{AA}'}$ and $J_{\text{BB}'}$ is not well-determined as can be seen from the large probable error, and, as will be seen later, its numerical value is essentially undefined. The analysis also fails to establish the relative sign of this coupling and the negative value has been assumed.[6]

The experiment was repeated, this time employing proton noise decoupling and observing the carbon-13 fluorine satellite spectra, corresponding to the $^{13}CF_3\cdot CH_2\cdot CH_2\cdot CF_3$ spin system. This gives rise to an A_3B_3X spectrum, which, owing to the large magnitude of the $^1J(^{13}CF)$ coupling, approximates to an A_3M_3X spectrum. This was analysed, on a first order basis, to

⁵ S. Castellano and A. A. Bothner-By, J. Chem. Phys., 1964, 3863.
⁶ F. A. L. Anet, J. Amer. Chem. Soc., 1962, 84, 3767.

give the results shown in Table 2, where ν_M is once again taken as the position of the ^{12}C fluorine centre-band.

The proton noise-decoupled carbon-13 spectrum of this compound consisted of two quartets. The low-field quartet, corresponding to CF_3, comprised four sharp

TABLE 2

A_3M_3X Analysis of the proton noise-decoupled spectra of HFB

$(F_A)_3{}^{13}C_X$—C—C—C$(F_M)_3$

Parameter	Neat liquid value		30% v/v Solution in [²H₆]acetone value	
	Hz	p.p.m.	Hz	p.p.m.
ν_A [a]	997·1	71·61	1134·8	70·144
ν_M [a,b]	1008·9	71·484	1146·5	70·02
$^1J_{AX}$	274·0		274·4	
$^5J_{AM}$	1·1		1·5	

[a] Downfield from CF_3CCl_3 ($\phi*$ 82·27; see footnote b to Table 3). [b] Position of fluorine ^{12}C centre-band.

lines separated by the one bond $^1J(^{13}CF)$ coupling of $274·0 \pm 0·5$ Hz; the high-field quartet, corresponding to CH_2, comprised four broad lines, separated by $31·4 \pm 0·15$ Hz [geminal $^2J(CF)$ coupling].

These studies were repeated with a 30% solution in [²H₆]acetone; the results are also given in Tables 1 and 2. The fluorine noise-decoupled carbon-13 spectrum, besides providing the X region for the AA'BB'X analysis, again gave a broad multiplet at $127·3 \pm 0·1$ p.p.m. for the trifluoromethyl group. In this case, however, it proved possible to resolve this peak into a five-line multiplet. In this particular instance, however, the A and B effective chemical shifts are very similar and the spectrum is deceptively simple, resembling the A_4X case. Consequently, only the average of the two coupling constants can be obtained and this is given as $2·2 \pm 0·15$ Hz.

The proton-decoupled carbon-13 spectrum again consists of two quartets. As in the previous case, the low-field quartet consists of four sharp lines separated by $^1J(^{13}CF)$. Consequently, the four-bond $^4J(^{13}CF)$ coupling in this molecule must be $0 \pm 0·5$ Hz. Expansion of the high-field quartet, however, showed that each line was itself composed of a second quartet. This gives values for $^2J(^{13}CF)$ of $30·9 \pm 0·15$ and $^3J(^{13}CF)$ of $5·15 \pm 0·15$ Hz, the assignment being made by comparison with the analogous couplings in hexyl fluoride of $19·9$ and $5·25$ Hz, respectively.[7]

The carbon-13 satellite studies furnish values of all the couplings involved in the undecoupled spectrum, apart from the two HF couplings, making it possible to undertake an iterative analysis of the complete, undecoupled spectrum. The only distinguishing feature of this spectrum is the presence of a sharp quartet in the proton region, and a correspondingly sharp triplet in the fluorine region. The line separation in both these

[7] F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 1971, **93**, 2361.

[8] P. Diehl, R. K. Harris, and R. Jones, *Progr. N.M.R. Spectroscopy*, 1967, **3**, ch.1.

[9] D. R. Whitman, L. Onsager, M. Saunders, and H. T. Dubb, *J. Chem. Phys.*, 1960, **32**, 67.

regions is the same (9·9 Hz) and corresponds to $^3J_{HF} + {}^4J_{HF}$.[8,9]

The magnitude of $^4J_{HF}$ would be expected to be quite small, by analogy with the corresponding couplings in $CF_3\cdot CH_2\cdot CH_3$ where $^3J_{HF} = 10·6$ and $^4J_{HF} = 0·4$ Hz.[10] Consequently, two possibilities were considered, the first being $^3J_{HF} = 9·4$ while $^4J_{HF} = 0·5$ Hz, and the second $^3J_{HF} = 10·4$ while $^4J_{HF} = -0·5$ Hz, and the analysis was carried out by considering both these alternatives. The $[AA'X_3]_2$ analysis establishes the relative signs of the majority of the coupling constants,[11] the signs of the two AX couplings being determined relative to one another, but not relative to the AA' coupling.

The observed spectrum consisted of 48 resolved lines in the proton region and 55 resolved lines in the fluorine region. An iterative analysis of the spectrum was carried out by using the computer program LAME,[12] with all 103 observed lines assigned, and the results are given in Table 3. Because of the similarity between the

TABLE 3

$[AA'X_3]_2$ Analysis of HFB as a 30% v/v solution in [²H₆]acetone

Parameter	Value		Standard deviation [a]
	Hz	p.p.m.	(Hz)
ν_{HA}, ν_{HB} [b]	$245·3 \pm 0·1$	2·453	
ν_{FA}, ν_{FB} [c]	$1146·5 \pm 0·1$	70·00	
$^2J_{HAHA'}, {}^2J_{HBHB'}$	$-11·16$		0·12
$^3J_{HAHB}$	5·03		0·02
$^3J_{HAHB'}$	11·46		0·02
$^3J_{HAFA}$	10·46		0·01
$^4J_{HAFB}$	$-0·54$		0·01
$^5J_{FAFB}$	1·51		0·01

[a] From LAME. [b] Downfield from Me_4Si. [c] Downfield from CF_3CCl_3 ($\phi*$ 82·27, see R. J. Abraham, D. F. Wileman, and G. R. Bedford, *J.C.S. Perkin II*, 1973, 1027).

two sets of results obtained from the carbon-13 proton satellite spectra, the complete analysis was only performed on the sample as a 30% solution in [²H₆]acetone, this sample being chosen since it gave slightly higher resolution than the neat liquid.

The observed and calculated spectra corresponding to these parameters are shown in Figures 2 and 3. Calculated spectra were obtained for the two alternatives of $^3J_{HF}$ and $^4J_{HF}$ of the same and opposite sign, as described above, and a comparison of these with the observed spectrum showed clearly that the two couplings are opposite in sign.

A close comparison of the observed and calculated spectra shows that there are still slight discrepancies. These are mainly attributed to an apparently increased resolution in the calculated spectrum. That this is not

[10] D. D. Elleman, L. C. Brown, and D. Williams, *J. Mol. Spectroscopy*, 1961, **7**, 322.

[11] R. M. Lynden-Bell, *Mol. Phys.*, 1963, **6**, 601.

[12] C. W. Haigh and J. M. Williams, *J. Mol. Spectroscopy*, 1969, **32**, 398.

the case, however, is demonstrated quite clearly by the line-widths of the sharp quartet in the proton region
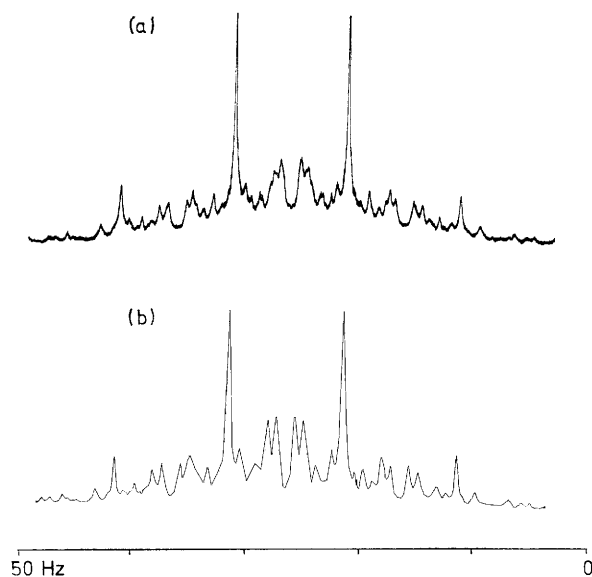

FIGURE 2 Observed (a) and calculated (b) 100 MHz ^{1}H spectra of HFB (30% solution in acetone)
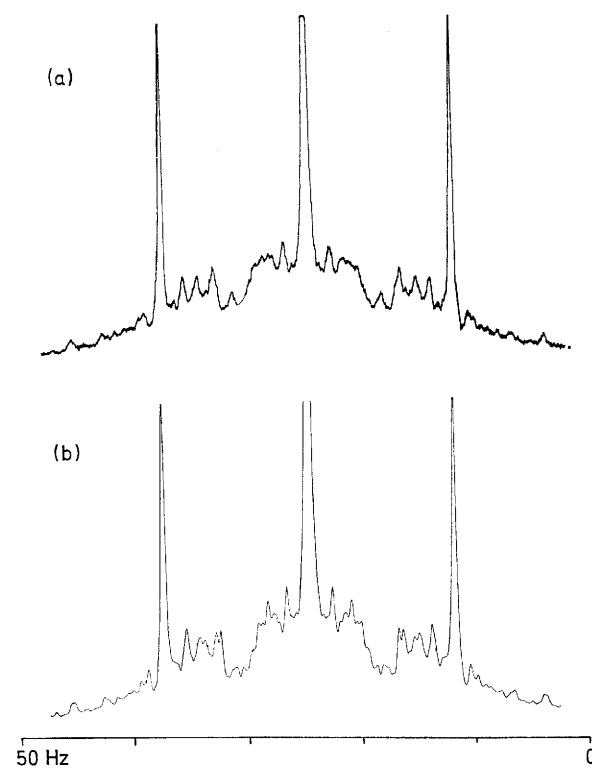

FIGURE 3 Observed (a) and calculated (b) 96·4 MHz ^{19}F spectra of HFB (30% solution in acetone)

and the analogous triplet in the fluorine region, which correspond quite accurately with the observed spectrum.

The real reason for this discrepancy lies in the complexity of the spectrum itself. In order to reduce

the theoretical spectrum to manageable proportions it was necessary to increase the minimum intensity threshold from its normal value of 0·01 to 0·1; even then the spectrum still contained in excess of two thousand theoretical transitions. Reducing this parameter to 0·01 introduces many thousand of additional lines, rendering an analysis of the spectrum impossible.

Although these excluded lines are of negligible individual importance, their number is such that, overall, they exert a significant effect on the appearance of the spectrum. This effect is to increase the width of the resonance bands (virtually no lines in either region correspond to a single transition), causing the spectrum to appear appreciably broadened. Taking this effect into account, the agreement between the observed and calculated spectra appears reasonable.

DISCUSSION

One of the noteworthy features of the parameters obtained from the undecoupled analysis is that the value of $^2J_{AA'}$ is now much better defined, giving a reasonable value of $-11·2$ Hz as opposed to the unrealistic values of $-17·0$ and $-17·2$ Hz obtained from the carbon-13 proton satellite analyses. (The relative sign of this coupling is still undetermined and, as before, the negative value has been assumed.[6])

The observed values of the vicinal proton couplings in the undecoupled spectrum ($^3J_{AB}$ 5·0, $^3J_{AB'}$ 11·5 Hz) demonstrate clearly that the preferred conformation of this molecule in [$^2H_6$]acetone solution is the trans-form. The close similarity of the analogous couplings obtained from the AA'BB'X analysis of the neat liquid sample ($^3J_{AB}$ 4·6, $^3J_{AB'}$ 12·5 Hz) shows that this situation is also present in the neat liquid. The slight decrease in $^3J_{AB'}$ and the corresponding increase in $^3J_{AB}$ on going from the neat liquid to [$^2H_6$]acetone solution would be expected, since the highly polar gauche conformation would be stabilized by polar solvents such as acetone.

The magnitudes of the proton couplings are, in fact, very similar to the results obtained by Waller and Garbisch,[13] who determined the coupling constants in the trans-form of 1,1,1,4,4,4-hexadeuteriobutane to be 12·7 and 4·4 Hz. These results are very close to the analogous values of 12·5 and 4·6 Hz obtained for HFB as the neat liquid. This close agreement is, however, unexpected, since the two compounds differ by the replacement of the essentially neutral CD_3 groups with two highly electronegative CF_3 groups. This would have been expected[14] to result in an increase in $^3J_{AB}$ and a decrease in $^3J_{AB'}$, but, as can be seen, these differences are not supported by the experimental results, which are almost identical in the two cases.

Further support for the trans-conformation for HFB comes from the magnitude of the five-bond $^5J_{FF}$ coupling in [$^2H_6$]acetone of 1·5 Hz. This is very similar to the value of 2·0 Hz found by Harris and Woodman[15] in the

[13] P. B. Waller and E. W. Garbisch, J. Amer. Chem. Soc., 1972, 94, 5310.

[14] G. Hagele, R. K. Harris, and P. Satori, Org. Magnetic Resonance, 1971, 3, 463.

[15] R. K. Harris and C. M. Woodman, J. Mol. Spectroscopy, 1968, 26, 432.

case of perfluorobutane, which was also found to exist predominantly in the *trans*-conformation.

The value of the vicinal hydrogen–fluorine coupling $^3J_{FF}$ can be compared with the corresponding value obtained by De Marco and Gatti [16] from an analysis of the spectrum of 1,1,1,3,3-pentafluorobutane (PBF). This compound contains a $CF_3 \cdot CH_2$ fragment identical to that in HFB. Because of the three-fold symmetry of the trifluoromethyl group, the observed coupling will be rotationally averaged, and is, consequently, independent of the molecular conformation. The value obtained of 10·2 Hz for PFB in $CFCl_3$ solution, is very close to the value of 10·5 Hz obtained for HFB.

The close similarity of the two results is once again surprising, since in the case of HFB the $CF_3 \cdot CH_2$ group is adjacent to a further CH_2, whereas in PFB the adjacent group is CF_2. Accordingly, it appears that the replacement of a CH_3 substituent by CF_3, or of CH_2 by CF_2, appears to have little effect on the magnitude of the vicinal HH and HF couplings.

The carbon-13 coupling constants obtained from HFB as a 30% v/v solution in $[^2H_6]$acetone can also be compared with the corresponding couplings obtained for PFB [17] as follows:

	CF_3—CH$_2$—CH$_2$—CF$_3$				CF_3—CH$_3$—CF$_2$—CH$_3$			
$J(CF)$	274·4,	30·9,	5·2,	0·0	274·0,	29·4,	3·5,	1·8
$J(CH)$	(2·2),	132·2,	−5·0,	(2·2)	7·2,	130·0,	5·2,	1·8

The value of $^1J_{CF}$ in PFB of 274·0 Hz is very close to the corresponding value in HFB of 274·4 Hz, as is the value of $^2J_{CF}$ of 29·4 *vs.* 30·9 Hz. On moving further down the chain differences between the two sets of values begin to appear ($^3J_{CF}$ 3·5 and 5·2 Hz, respectively),

and the four-bond $^4J_{CF}$ values (1·8 and 0) are appreciably different.

A similar situation is also observed for the CH couplings: once again the values of $^1J_{CH}$ (130·0 and 132·2 Hz, respectively) and $^2J_{CH}$ [5·2 and −5·0 Hz, respectively for C(3)H(2)] are again very close. The sign of the coupling in PFB was not established; presumably it should be negative, similar to that in HFB. The value of $^2J_{C(1)H(2)}$ in HFB is very poorly defined (only an averaged value was observed), but even allowing for this effect the values of 2·2 and 7·2 Hz for HFB and PFB, respectively, show a considerable difference. Unlike the case of the CF coupling the correlation between the two compounds does not appear to deteriorate in proportion to the number of intervening bonds and the values of the three bond $^3J_{CH}$ couplings of 2·2 and 1·8 Hz in HFB and PFB, respectively, still show close agreement, although the value of 2·2 Hz in HFB is somewhat uncertain.

The most noticeable feature of all these comparisons is the close similarity of the coupling constants, despite considerable changes in the substitution patterns. Consequently, it appears that the carbon couplings (with the exception of the one-bond couplings [18]) in saturated molecules exhibit relatively small substituent effects, rendering them potentially powerful tools for spectral assignment.

[16] A. De Marco and G. Gatti, *Org. Magnetic Resonance*, 1971, **3**, 599.

[17] A. De Marco and G. Gatti, *Spectrochim. Acta*, 1972, **28**, 2295.
[18] E. R. Malinowski, *J. Amer. Chem. Soc.*, 1961, **83**, 4479.