Analysis of the Multinuclear Magnetic Resonance Spectra of 1,1,1,4,4,4-Hexafluorobutane

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Summary The use of heteronuclear noise decoupling combined with the observation of the ^{13}C and ^{13}C-satellite spectra enable the chemical shifts and coupling constants of all the magnetic nuclei in 1,1,1,4,4-hexafluorobutane to be obtained; these show that the compound exists entirely as the *trans*-rotamer in solution.

Although the use of ^{13}C-satellite spectra to obtain couplings between chemically equivalent nuclei (*e.g.* $CH_2X\cdot CH_2X$) is well established,[1,2] the use of this method combined with heteronuclear decoupling and the observation of the ^{13}C spectrum to analyse more complex spin systems has not been detailed.

We give the complete analysis of the ^1H, ^{19}F, ^{13}C spectra of $CF_3\cdot CH_2\cdot CH_2\cdot CF_3$ (I). This is a strongly coupled ten-spin system with over 2000 allowed transitions and the complexity of the resulting ^1H and ^{19}F spectra lead to extensive overlapping and therefore give many broad and unresolved lines, not suitable for iterative computer analyses.

Observation of the ^{13}C-satellite ^1H spectrum under conditions of ^{19}F noise decoupling gave the characteristic aa′bb′ sub-spectrum of the AA′BB′X system $(CF_3)^{13}CH_2\cdot CH_2(CF_3)$ from which the $^3J_{HH}$ couplings are readily obtained. This spectrum combined with the ^{19}F decoupled ^{13}C spectrum gave the complete analysis of this AA′BB′X system, enabling both the ^1H isotope shift and the relative signs of J_{AX} and J_{BX} to be found. As the $^1J_{CH}$ (J_{AX}) is known to be positive this gives the sign of $^2J_{CH}$ (J_{BX}) as negative.

Again, although the ^{13}C spectrum of the $^{13}CF_3\cdot CH_2$-

Table. *Chemical shifts*[a] *and couplings for* $CF_3\cdot CH_2\cdot CH_2\cdot CF_3$[b]

^1H	$(^{13}C–H)$	2·458	$^3J_{HH}$	4·97	$^1J_{CF}$	$\|274·37\|$
		2·462	$^3J_{HH'}$	11·54	$^2J_{CF}$	$\|30·9\|$
^{19}F	$(^{13}C–F)$	70·14	$^1J_{CH}$	132·24	$^3J_{CF}$	$\|2·4\|$
		70·02	$^2J_{CH}$	$(^{13}CH_2\cdot CH_2)$ — 5·02	$^4J_{CF}$	0·0
^{13}C	CH_2	28·8	$^3J_{HF}$	10·46	$^5J_{FF}$	$\|1·50\|$
	CF_3	127·2	$^4J_{HF}$	−0·55		

[a] ^1H, ^{13}C δ values, ^{19}F ϕ^* values. [b] 30% v/v in $(CD_3)_2CO$.

$\cdot CH_2\cdot CF_3$ species gave a broad unresolved multiplet, a similar analysis of the ^{13}C-satellites of the ^{19}F spectrum with ^1H noise decoupling combined with the observation of the ^{13}C spectrum under the same conditions gave all the ^{13}C–F and F–F couplings in the molecule. As the fluorines are not strongly coupled ($^5J_{FF}$ 1·5 Hz) only the magnitudes of these couplings can be determined.

With this information the complex ^1H and ^{19}F spectrum of the ^{12}C species can be completely analysed to give finally the HF coupling constants. The couplings and chemical shifts thus obtained are given in the Table.

The magnitudes of the $^3J_{HH}$ couplings of 4·97 and 11·54 Hz are consistent with on overwhelming predominance of the *trans*-rotamer. Using the corresponding values of the couplings in the *trans*-rotamer of $CD_3\cdot CH_2\cdot CH_2\cdot CD_3$ of 4·40 and 12·67 Hz[4] combined with the known dependence of such couplings on substituent electronegativity[5] (using the CF_3 group electronegativity of Hagele *et al.*[6]) gives calculated values for the *trans*-rotamer of (I) of 4·94 and 11·92 Hz, in excellent agreement with the observed couplings. The $^5J_{FF}$ coupling of 1·5 Hz is similar to that in perfluorobutane (2·0 Hz)[7] which also exists predominently in the *trans*-conformation.

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