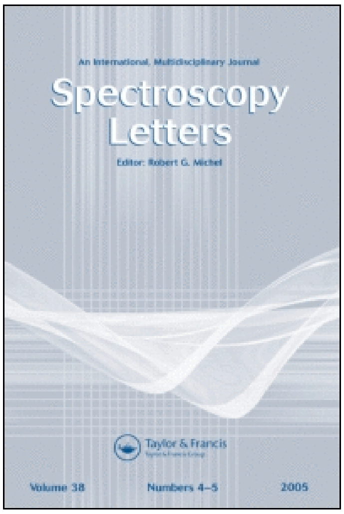

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Nuclear Spin-Spin Couplings via Nonbonded Fluorine-Fluorine Interactions in 1-Methyl-3,7,10-This- and 1-Methyl-3,7-bis-(Trifluoromethyl) Silatranes

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NUCLEAR SPIN-SPIN COUPLINGS VIA NONBONDED FLUORINE-FLUORINE INTERACTIONS IN 1-METHYL-3,7,10-TRIS- AND 1-METHYL-3,7-BIS-(TRIFLUOROMETHYL)SILATRANES

KEYWORDS: ^{19}F NMR, Through-Space Coupling, Conformation, Silatranes.

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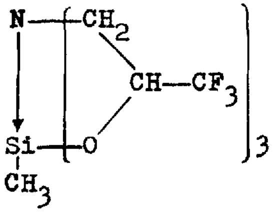
ABSTRACT: Through space spin-spin coupling between 8-bonded fluorine nuclei has been found in the title silatranes spectra and the conformations derived from these constants.

Through-space interactions are believed to be chiefly responsible for the especially large long-range fluorine-fluorine nuclear spin-spin coupling constants.[1-4] No more than 7 bonds[2] along the shortest pathway through the molecular framework that connect the two coupled fluorines were found in the extensive literature survey of nmr data. The 8-bonded F-F coupling constant ($^8J_{FF}$ = 1,6 Hz) for 1-methyl-3,7,10-tris-(trifluoromethyl)silatrane



has been determined for its B diastereoisomer (Fig.1).

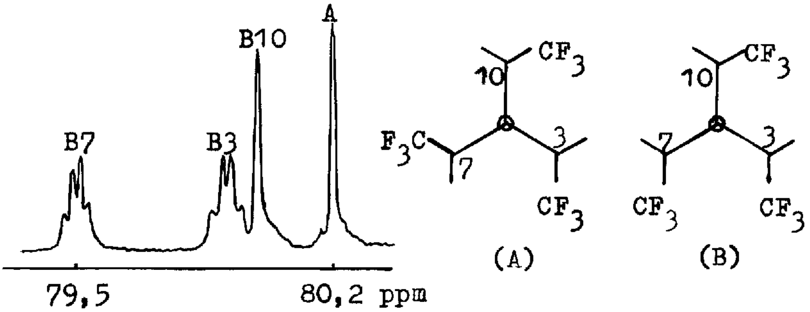


FIG.1

^{19}F-(^1H) nmr spectrum of the stereoisomeric mixture of $CH_3\overline{Si[OCH(CF_3)CH_2]_3N}$.

"Through-space" spin-spin interactions between ^{19}F nuclei depend strongly on the distance between the nuclei[4] and the 1,6 Hz coupling is inferred for 4,2 Å.

Assuming that the rotationally-averaged coupling may be considered as being made up of the averaged sum of the individual couplings of each 3-CF_3 fluorine to each 7-CF_3 fluorine in the B stereoisomer the real shortest distance should be lower than 4,2 Å. The temperature-independency of proton-proton couplings should be explained by the fact that both the A and B molecules exist in a single frozen conformation.

Model examination of 3-7 F-F intramolecular distances for the B isomer led to an agreement with the calculated value 4,2 Å only when any Si(O-C-C)$_3$N skeletal deformation preserves the C_3 symmetry. Taking account of the half-chair conformation of each five-membered bridging ring determined by X-ray diffraction,[5,6] the 3- and 10-CF_3 groups should occupy equatorial positions and the 7-CF_3 group - axial one

There are four uncoupled singlets (C, D3, D7 and E) in the $^{19}F-(^1H)$ nmr spectrum of 1-methyl-3,7-bis-(trifluoromethyl)silatrane (Fig.2). As the fluorine

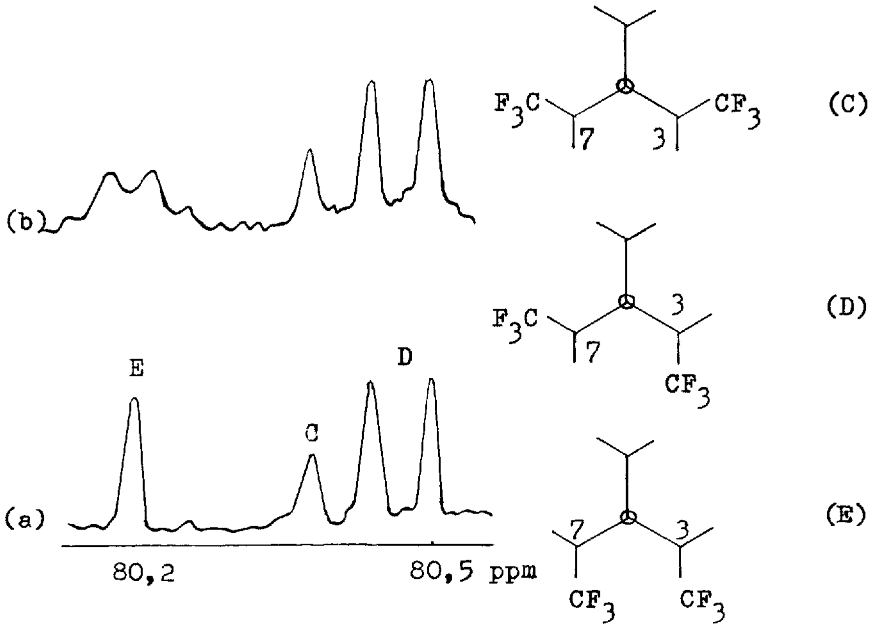


FIG.2

$^{19}F-(^1H)$ nmr spectrum of the stereoisomeric mixture of $CH_3\overline{Si[OCH(CF_3)CH_2]_2(OCH_2CH_2)N}$. (a)Normal fluorine spectrum. (b)High-field ^{13}C satellites.

nuclei are very sensitive to environmental effects the 3,7-equivalences of the CF_3 groups in the C and E diastereoisomers are due to fast, on the nmr time scale, convertion of their five-membered rings at normal temperature that is an exchange process between two equally strained states of different shape where each group occupies alternately equatorial and axial positions.

However the through space coupling constant for the E isomer was distinguished ($^8J_{FF}$ = 1,6 Hz) in the ^{13}C satellites signals of the CF_3 groups (Fig.2). It is due to magnetic nonequivalence of the $3\text{-}^{13}CF_3$ and $7\text{-}^{12}CF_3$ fluorine nuclei (or $3\text{-}^{12}CF_3$ and $7\text{-}^{13}CF_3$) in the E molecule, the average distance between them being the same as in the B isomer. The isotop shift of the fluorine resonance, $\delta(F\text{-}^{13}C;\ F\text{-}^{12}C) = 0{,}12$ ppm, and the ^{13}C-F spin-spin coupling constant, J_{CF}=280,3Hz, for the C, D and E isomers are held by Frankiss relationship[7]: $\delta(F\text{-}^{13}C;\ F\text{-}^{12}C) = 0{,}007 + 4{,}36 \times 10^{-4} J_{CF}$.

The spectra were recorded on a Varian XL-100/12 spectrometer by the total ^1H-decoupling technique using $CDCl_3$ as solvent and $C_6H_5CF_3$ as internal standard, $\delta(CFCl_3) = \delta(C_6H_5CF_3) + 64$ppm.

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