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Preliminary communication

DIASTEREOTOPY OF EQUATORIAL FLUORINES AT THE TRIGONAL-BIPYRAMIDAL SILICON ATOM IN ORGANYL [β-(TRIFLUOROSILYL)ETHYL]SULFOXIDE MOLECULES

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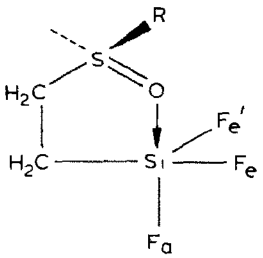
Summary

The low temperature ^{19}F NMR spectra of $RS(O)CH_2CH_2SiF_3$ ($R = CH_3$, C_2H_5 or $C_6H_5CH_2$) display a non-equivalence of all the fluorine atoms in their molecules. This is caused by both the trigonal-bipyramidal structure of the silicon atom involved in the intramolecular Si←O coordination and the chirality of the sulfur atom. The F_e—F'_e coupling constants have been determined to be lower than the F_e—F_a values.

The ^{19}F NMR spectra of some Si-fluoro-substituted pentacoordinate silicon derivatives display a non-equivalence of the axial and equatorial fluorine atoms at low temperature [1—3]. The two bond $^{19}F_a$—$^{19}F_e$ spin—spin coupling constant is 40—50 Hz [2,3]. The non-equivalence of equatorial fluorine atoms and the coupling between their nuclei ($^2J(F_e$—$F_e)$ 15 Hz) was observed only recently with [α-(*N*-pyrrolidono-2)ethyl]trifluorosilane (I) [4]. Diastereotopy of the equatorial fluorine nuclei is caused by slow rotation of the pentacoordinate (due to intramolecular Si←O bonding) silicon atom and chirality of the C-atom attached to silicon in molecule I.

We have shown that the non-equivalence of all the fluorine atoms is also revealed at low temperature (<—100°C) in the ^{19}F NMR spectra of a new type of pentacoordinate silicon compounds, organyl [β-(trifluorosilyl)ethyl]sulfoxides (II—IV). The anisotopism of the equatorial fluorines in these compounds upon slow inversion of the trigonal-bipyramidal silicon atom is caused by the asymmetry of the sulfur atom. At —120 to —130°C intramolecular exchange between the fluorines in molecule III is slow enough to allow observation of all the two bond ^{19}F—^{19}F spin—spin couplings (Fig. 1). As with com-



(II, R = CH_3;
III, R = C_2H_5;
IV, R = $C_6H_5CH_2$)

pound I, the value of the coupling constant between the equatorial fluorines in III, $^2J(F_e—F_e)$ 19.5 Hz, is lower than that for the axial—equatorial interaction, $^2J(F_a—F_e)$ 36.6 Hz. Under these conditions, inversion of the trigonal-bipyramidal silicon atom in molecule III is still too fast for small ^{19}F NMR signal splittings (5 Hz) caused by vicinal $^1H—^{19}F$ coupling to be observed.

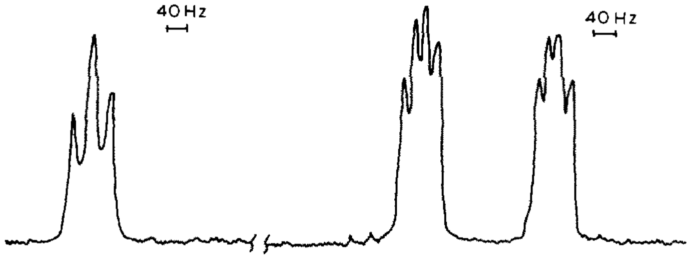


Fig. 1. The ^{19}F NMR spectra of $C_2H_5S(O)CH_2CH_2SiF_3$ at —120° C.

The limited solubility of compound II at low temperature does not permit measurement of the value of the $^{19}F_e—^{19}F_e$ coupling constant. In the ^{19}F NMR spectrum of sulfoxide IV no signal splitting due to coupling between the three non-equivalent fluorines occurs, even at temperatures close to the freezing point.

Increasing the temperature of solutions of organosilicon sulfoxides II—IV results in an increase of the silicon atom inversion rate and ^{19}F NMR signal coalescence in the spectra of these compounds. Coalescence of the signals of non-equivalent F_e nuclei for compounds II, III and IV occurs at —90, —95 and —105° C, respectively, whereas the F_e and F_a atoms coalesce at —80, —85 and —95° C, respectively.

TABLE 1

^{19}F AND ^{29}Si NMR SPECTRAL PARAMETERS OF ORGANYL [β-(TRIFLUOROSILYL)ETHYL]-SULFOXIDES II—IV

Compound	$\delta(Si)^a$	$\delta(F)^a$	$J(SiF)^a$	$\delta(F_a)^b$	$\delta(F_e)^b$	$\delta(F_e')^b$
II	—86.4 ^{c}	—124.7	226.4	—110.9	—128.4	—132.8
III	—85.7	—126.9	230.7	—113.1	—131.4	—133.9
IV	—83.6	—127.4	233.1	—113.0	—128.8	—133.4

^{a} At room temperature. ^{b} At —102° C. ^{c} At —80° C.

The pentacoordination of silicon in molecules II—IV at room temperature is confirmed by the considerable high-field shifts of the ^{29}Si NMR signal and by low-field shifts of the ^{19}F nuclei (Table 1) relative to those of the tetracoordinate silicon model derivative, methyltrifluorosilanes (δ(Si) −51.8 ppm [5] and δ(F) −135 ppm [6]). This is also demonstrated by the lower ^{19}F—^{29}Si spin—spin coupling values in II—IV as compared to methyltrifluorosilanes (^1J(Si—F) 267.9 Hz [6]).

At 25°C the difference in the NMR spectra of methyltrifluorosilane and compounds II—IV increases on going from IV to III and II. Judging by the coalescence temperatures of the ^{19}F NMR signals the free energies of activation of trigonal-bipyramidal silicon pseudo-rotation in the molecules of the compounds mentioned above increase in the same sequence. It may be suggested, therefore, that the intramolecular Si←O interaction in the organyl [β-(trifluorosilyl)ethyl]sulfoxides studied strengthens in the following order: IV < III < II. This seems to reflect the same order of decreasing steric interaction of substituents at the trigonal-bipyramidal silicon atom in the compounds studied, which evidently should weaken the intramolecular Si←O bond and enhance the stereodynamic mobility of molecules II—IV.

The weaker the intramolecular Si←O bond in II—IV, the stronger the temperature effect on the ^{29}Si NMR chemical shifts and the values of the ^{29}Si—^{19}F spin—spin coupling constant. Thus, a 100°C temperature drop increases the ^{29}Si shielding and decreases the ^{29}Si—^{19}F spin—spin coupling constants by 0.9 ppm and 2.3 Hz, and 2.0 ppm and 4.7 Hz for III and IV, respectively. A similar relationship between the sensitivity of the spectral parameters of pentacoordinate silicon derivatives to variations in external conditions and the strength of intramolecular interaction has previously been observed for (aroyloxymethyl)trifluorosilanes [3].

The intramolecular character of coordination in compounds II—IV has been confirmed by the fact that the NMR spectral parameters of solutions of these compounds are independent of the concentration.

Compounds II—IV were synthesized by oxidation of the corresponding organyl [(β-trifluorosilyl)ethyl]sulfides with 70—80% hydrogen peroxide in diethyl ether at 10—15°C. These are colorless crystalline substances, readily soluble in water (with subsequent hydrolysis) and other polar solvents (acetonitrile, DMSO).

Methyl [(β-trifluorosilyl)ethyl]sulfoxide, $CH_3S(O)CH_2CH_2SiF_3$, *(II)*. Colorless needles recrystallized from acetonitrile solution with a 50/50 mixture of diethyl ether and hexane, m.p. 115—116°C. Found: C, 20.41; H, 3.95; F, 31.84; S, 18.12; Si, 15.80. $C_3H_7F_3OSSi$ calcd.: C, 20.45; H, 4.01; F, 32.36; S, 18.16; Si, 15.94%.

Ethyl [(β-trifluorosilyl)ethyl]sulfoxide, $C_2H_5S(O)CH_2CH_2SiF_3$ *(III)*. Colorless scales recrystallized from chloroform, m.p. 44—45°C. Found: C, 25.17; H, 4.61; F, 29.87; S, 16.67; Si, 14.54. $C_4H_9F_3OSSi$ calcd.: C, 25.26; H, 9.77; F, 29.97; S, 16.83; Si, 14.77%.

Benzyl [(β-trifluorosilyl)ethyl]sulfoxide, $C_6H_5CH_2S(O)CH_2CH_2SiF_3$ *(IV)*. Colorless needles, m.p. 126—127°C, recrystallized from acetonitrile solution with a 50/50 diethyl ether/hexane mixture. Found: C, 42.70; H, 4.28; F, 22.36; S, 12.32; Si, 10.51. $C_2H_{11}F_3OSSi$ calcd.: C, 42.86; H, 4.40; F, 22.60; S, 12.70; Si, 11.14%.

NMR spectra were obtained with a JEOL FX 90Q spectrometer. The ^{19}F nuclei signals (84.25 MHz) were observed without ^{1}H-decoupling. The ^{29}Si NMR spectra (17.75 MHz) were recorded using the INEPT technique upon complete ^{1}H-decoupling. The accuracy of the measurements of the ^{19}F NMR chemical shifts relative to CCl_3F was 0.01 ppm, that for ^{29}Si relative to TMS being 0.1 ppm. The compounds were studied in 0.1—0.5 *M* solutions in a mixture of CCl_4, CH_2Cl_2 and $CDCl_3$ (13/60/27) in 5 mm tubes. The ^{2}H NMR peak of the latter was used as the internal lock signal.

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