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Conformational Asymmetry of a Linear Perfluoroalkyl Chain in Solution. Dynamic Fluorine-19 NMR Spectroscopy of the Perfluoro-*n*-alkanes Carrying a Chiral End-Group as a Probe of Magnetic Nonequivalence

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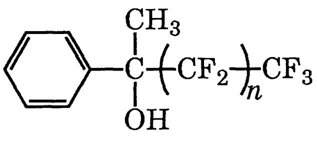
The 470 MHz ^{19}F NMR spectra of 1-perfluorohexyl-1-phenylethanol (**1a**) were measured in toluene-d_8. At 0 °C and the lower temperatures, magnetic nonequivalence was observed for the two fluorine nuclei in the CF_2 group adjacent to the asymmetric carbon atom and for those in the subsequent four CF_2 groups. The extent of the nonequivalence was highly dependent on temperature. **1a** and the perfluorooctyl- and perfluorodecyl-homologues were optically resolved and specific rotation of the pure (−)-isomers were examined from the viewpoint of the conformational asymmetry induced on the perfluoroalkyl chain.

Poly(tetrafluoroethylene) is known to adopt helical structure in the crystalline state,$^{1)}$ and is insoluble in any organic solvent at room temperature. The lack of solubility is partly due to the low flexibility of the polymer chain. Conformational properties of soluble perfluoro-*n*-alkanes in solution are of great interest. However, several recent studies on perfluoro-*n*-alkanes$^{2-5)}$ have been focused on the solid-state structures. In the present communication, we report the dynamic ^{19}F NMR studies in solution of a perfluoro-*n*-alkane carrying a chiral end-group, which is expected to introduce asymme try on the perfluoroalkyl chain. ^{19}F NMR spectroscopy exhibits a great range of chemical shifts exceeding 400 ppm, and this great range often makes it possible to discriminate rather subtle environmental differences in polymer chains.


$C_6H_5-\overset{CH_3}{\underset{OH}{C}}-(CF_2)_n-CF_3$

n=5, **1a**; *n*=7, **1b**; *n*=9, **1c**

1-Perfluorohexyl-1-phenylethanol (**1a**) and the perfluorooctyl- (**1b**) and perfluorodecyl-homologues (**1c**) were prepared from the corresponding perfluoroalkyl iodide and acetophenone according to the procedure described in the literature.[6)] ^{19}F NMR spectra were recorded in toluene-d_8 on a JEOL JNM-GX500 spectrometer operated at 470.5 MHz. The concentration of the solution of **1a** was 1.8 w/v%. Chemical shifts of the ^{19}F NMR signals referred to $CFCl_3$ used as an internal standard.

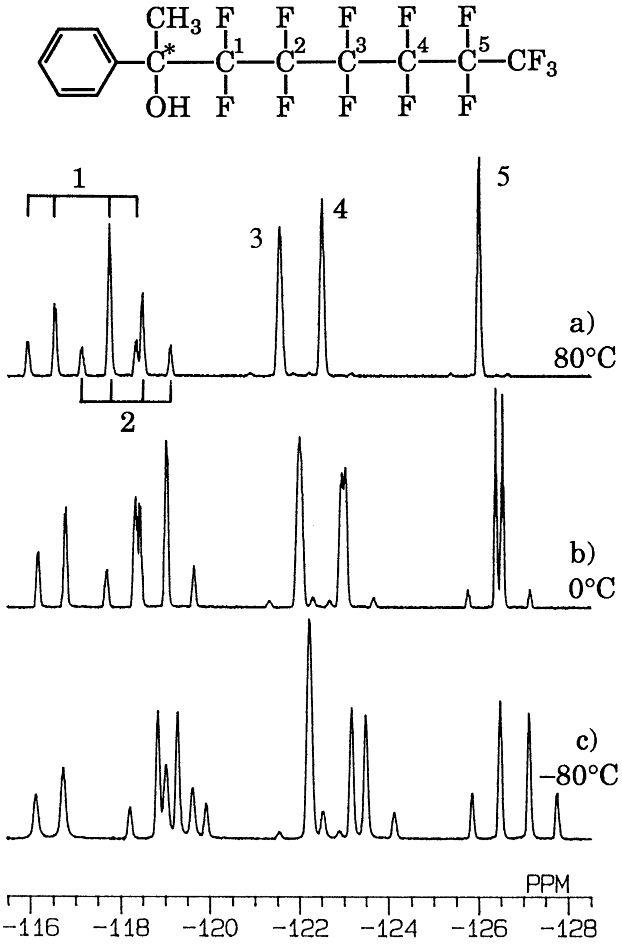


Fig. 1. ^{19}F NMR spectra of 1-perfluorohexyl-1-phenylethanol (**1a**) recorded at 80 (a), 0 (b), and −80 °C (c). (toluene-d_8, 470 MHz).

Figure 1 shows the CF_2 region ^{19}F NMR spectra of **1a**. Assignment of the signals was made by the homonuclear spin-decoupling and NOE experiments.[7)] In the spectrum measured at 80 °C (Fig. 1a), two fluorine nuclei in the CF_2 group (C^1F_2) adjacent to the asymmetric carbon atom (C^*) were nonequivalent (diastereotopic), and showed an AB quartet. The penultimate CF_2 group (C^2F_2) also showed an AB quartet, while the subsequent CF_2 groups (C^3F_2, C^4F_2, and C^5F_2) gave singlet peaks. At 0 °C, the nonequivalence was also observed for C^4F_2 and C^5F_2 (Fig. 1b), and the nonequivalence became larger at −80 °C (Fig. 1c). The singlet signal due to C^3F_2 had small satellite signals at 0 and −80 °C, exhibiting a sign of the nonequivalence, too. The signals due to C^1F_2, C^2F_2, C^6F_2, and C^7F_2 of **1b** also appeared as AB quartets at low temperatures (≤ 0 °C). However, measurements below −60 °C became difficult because of low solubility of this compound.

C^1F_2 group showed the largest chemical shift difference ($\Delta\delta$) between the two nonequivalent fluorine nuclei, and the $\Delta\delta$ values for C^1F_2, C^2F_2, C^5F_2, and C^4F_2 decreased in this order. Figure 2 displays the temperature dependence of the $\Delta\delta$ values for **1a**. The $\Delta\delta$ values for C^1F_2, C^4F_2, and C^5F_2 groups increased with decreasing temperature, whereas that for C^2F_2 showed the opposite tendency. At −80 °C, C^5F_2 exceeded C^2F_2 in $\Delta\delta$. The values of $\Delta\delta$ for C^4F_2 and C^5F_2 could not be determined above 20 °C since the values were comparable to the line width of the CF_2 signals. The coupling constants, $^2J_{FF}$, were independent of temperature, and gave the values, −281.8±1.3, −297.0±2.0, −302.0±0.2, −292.5±1.7 Hz, for C^1F_2, C^2F_2, C^4F_2, and C^5F_2, respectively. The natural line width of the signals did not change throughout the experiment.

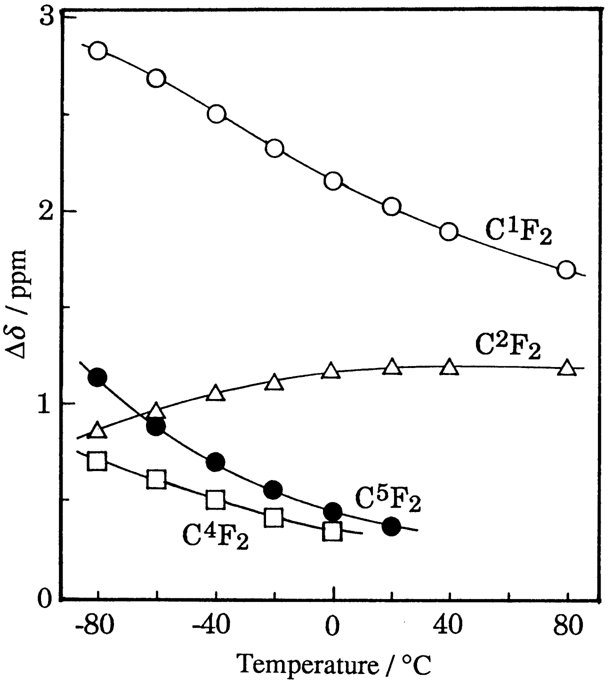


Fig. 2. Temperature dependence of the chemical shift difference, Δδ, of the two fluorine nuclei in the CF_2 groups of **1a**.

The nonequivalence observed for C^4F_2 and C^5F_2, which are apart from C^* by four carbon-carbon bonds or more, should be attributed not only to the asymmetric center but also to an asymmetric structure introduced on the perfluorohexyl chain itself, probably the helical conformation with a one-handed screw sense. As the temperature decreases, the fraction of the conformer assuming the one-handed helix increases, resulting in the increase in the extent of the observed magnetic nonequivalence of the CF_2 groups along the chain from C^* to the CF_3-terminal. The one-handed helical conformation of the perfluoroalkyl chain of **1b** and **1c** also seems to persist to the CF_3-terminal from C^*.

If asymmetry is induced on the perfluoroalkyl chain, the optical isomers of these compounds may show optical activity contributed from the conformational asymmetry to some extent. Recently, the optical activity arising from one-handed helicity was found to exist even in the linear, low molecular weight oligomers such as chloral oligomers.[8,9]

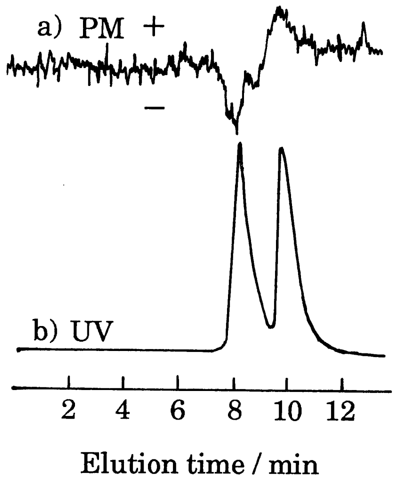


Fig. 3. Optical resolution of **1a** by HPLC; the chromatograms recorded by polarimetric (a) and UV (254 nm) detectors (b).

1a, **1b**, and **1c** were optically resolved into the two enantiomers, respectively, by the HPLC[10,11] equipped with a chiral stationary phase; the (−)-isomer eluted faster than the (+)-isomer for each racemate (Fig. 3). The isomers obtained were optically pure (>99%), according to the HPLC analysis.[12] CD spectra of the (−)-isomers (positive absorbtion observed around 235-270 nm based on π-π* transition) showed that the (–)-isomers had the same absolute configuration with respect to C*. Specific rotation, $[\alpha]_{365}^{25}$, of the (–)-isomers in ethanol are given in Table 1. The absolute values for **1b** and **1c** were larger than that of **1a**, suggesting that the one-handed helicity of the longer perfluoroalkyl groups may enlarge the specific rotation of the whole molecule. However, the values were not significantly dependent on the chain length, *n*, of the perfluoroalkyl group. Measurements of $[\alpha]_{365}^{25}$ at low temperatures may be more informative if any solvent dissolving these compounds sufficiently at low temperatures is available.

Table 1. $[\alpha]_{365}^{25}$ values of (–)-**1a**, (–)-**1b** and (–)-**1c** in ethanol[a)]

	n	$[\alpha]_{365}^{25}$	c / g·dL^{-1}
1a	5	–1.43	4.350
1b	7	–4.21	2.984
1c	9	–3.54	3.006

a) Measured in a 10 mm cell.

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7) $\delta(CF_3) = -81.26$ ppm, $^3J_{FF}(CF_3/C^5F_2) = 2.7$ Hz, $^4J_{FF}(CF_3/C^4F_2) = 10.2$ Hz, $^3J_{FF}(C^4F_2/C^5F_2) = 5$ Hz, $^4J_{FF}(C^3F_2/C^5F_2) = 16$ Hz.

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10) Stationary phase, cellulose tris(3,5-dimethylphenyl)carbamate;[11)] mobile phase: hexane / isopropyl alcohol = 90 / 10. A 2.0 mm *i.d.* x 500 mm column was used for the isolation of the optical isomers.

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12) Melting points of **1b**, **1c**, (–)-**1b**, and (–)-**1c** were 53.0, 80.4, 28.9, and 70.0 °C, respectively, by differential scanning calorimetry (a Rigaku DSC-8230 apparatus was used). (–)-**1b** and (–)-**1c** also showed small endotherm due to a phase transition other than melting at –47.7 and –79.7 °C, respectively.

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