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^{1}H and ^{19}F NMR Study of *p*-Chlorobenzylidyne Trifluoride Partially Oriented in a Nematic Phase

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The ^{1}H and ^{19}F NMR spectra of *p*-chlorobenzylidyne trifluoride dissolved in a nematic phase of EBBA have been analyzed, and the structure of the proton and fluorine skeleton has been determined. No presice information about the anisotropy of the indirect F-F coupling can be given.

Since Saupe and Englert first observed the NMR spectra in liquid crystals, many studies have been reported in this area.[1–4] The method has also been applied to the molecules with internal rotation.[5–10] There are few studies, however, about the molecules containing ^{19}F nuclei with internal rotation.[11] We have analyzed the ^{1}H and ^{19}F NMR spectra of *p*-chlorobenzylidyne trifluoride in a nematic phase of EBBA (*N*-(*p*-ethoxybenzylidene)-*p*-butylaniline), and obtained the relative internuclear distances and the orientation parameters of this molecule in EBBA.

Experimental

The sample studied consisted of a 14 mol% solution of commercially available *p*-chlorobenzylidyne trifluoride in EBBA. It was contained in a 5-mm NMR sample tube and degassed by repeated freeze-pump-thaw cycles and then sealed *in vacuo*. The ^{1}H NMR spectra were observed with a Hitachi R-20B spectrometer operated at 60 MHz in the field sweep mode without locking. The ^{19}F NMR spectra were observed with the same spectrometer equipped with a R-203F-B attachment at 56.45 MHz in the frequency sweep mode with an external lock. The ^{1}H and ^{19}F spectra extended over about 9.7 and 11.5 kHz, respectively, and contained 40 and 25 resolved lines; all resolvable lines were used for the determination of the spectral parameters. In both cases the spectra were obtained at 31.0±0.5 °C and accumulated on a Hitachi Al600-A signal averaging analyzer; the line width of each signal was about 20 Hz. The resonance position of the signal was determined on each recording chart by interpolation: the sweep width was calibrated by either the frequency counter or the side-band method; the error was about 5 Hz. The calculation of spectral and structural analyses was made by a HITAC-8450 computer system located in this Institute or a FACOM-230-75 system located in the Computer Center of Nagoya University.

Results and Discussion

Analyses of the Spectra. The ^{1}H and ^{19}F spectra of the sample are center-symmetric and divided into two and three parts, respectively. The observed upfield ^{1}H and ^{19}F spectra consisted of 20 and 10 resolved lines, and are shown in Figs. 1-a and 1-b. The central part of the observed ^{19}F spectrum consisted of 5 strong lines. Analyses of the spectra were followed by a program LAOCN3+D, which includes the direct coupling constants as the spectral parameters. This was slightly modified from the original LAOCN3,[12] described by Diehl *et al.*[13] The indirect coupling constants were kept constant in the iteration calculation and the values were estimated by means of an additivity.[14,15] The spectral parameters thus obtained are shown in Table 1. The numberings of the nuclei are shown in Fig. 2.

TABLE 1. SPECTRAL PARAMETERS FOR *p*-CHLOROBENZYLIDYNE TRIFLUORIDE IN Hz[a)]

Direct coupling[b)]		Indirect coupling[c)]	
D_{23}	−2282.74±0.16	J_{23}	8.40
D_{25}	28.29±0.17	J_{25}	0.38
D_{26}	204.60±0.70	J_{26}	2.31
D_{35}	203.97±0.69	J_{35}	2.19
D_{27}	−494.63±0.34	J_{27}	−0.74
D_{37}	−169.00±0.34	J_{37}	0.82
D_{78}	1480.46±0.14		

a) The numberings of the nuclei are given in Fig. 2. b) The errors shown in the Table are the probable program output errors. The differences between the D_{26} and D_{35} and between W(2) and W(3) are small and within the experimental error; they are not important. c) The parameters are taken from Refs. 14 and 15.

Analyses of the Molecular Structure. The parameters obtained in Table 1 were used to obtain the geometrical information about the sample. The following assumptions were made: 1. The trifluoromethyl group rotates freely around the C_1–C_7 bond; 2. The benzene ring forms a hexagonal plane and the C–C and C–H bond lengths can be taken as 1.397 and 1.084 Å;[16] 3. The molecular vibrations need not be taken into consideration; 4. Anisotropies of the proton-fluorine and proton-proton indirect couplings are negligible. Relations between the ratios of the inter-proton distances and the direct couplings are given by the following equations:

$$r_{35}/r_{26} = (D_{26}/D_{35})^{1/3}, \tag{1}$$

$$D_{23}(r_{23}/r_{26}) - D_{25}\{(D_{26}/D_{35})^{1/3} + (r_{23}/r_{26})^2\}^{5/2} = -D_{26}(D_{26}/D_{35})^{1/3}, \tag{2}$$

$$(r_{25}/r_{26})^2 = (D_{26}/D_{35})^{1/3} + (r_{23}/r_{26})^2. \tag{3}$$

The orientation parameters S_{xx} and S_{zz} are related to the D's and r's by[3)]

$$S_{\mathrm{xx}} = -(4\pi^2/h\gamma_{\mathrm{H}}^2)D_{26}r_{26}^3, \tag{4}$$

$$S_{\mathrm{zz}} = -(4\pi^2/h\gamma_{\mathrm{H}}^2)r_{23}^3[D_{23} - (D_{26}/4)(r_{23}/r_{26})^{-5} \times \{(D_{26}/D_{35})^{1/3} - 1\}^2]/[1 - (1/4)(r_{23}/r_{26})^{-2} \times \{(D_{26}/D_{35})^{1/3} - 1\}^2]. \tag{5}$$

By means of these equations, the inter-proton distances

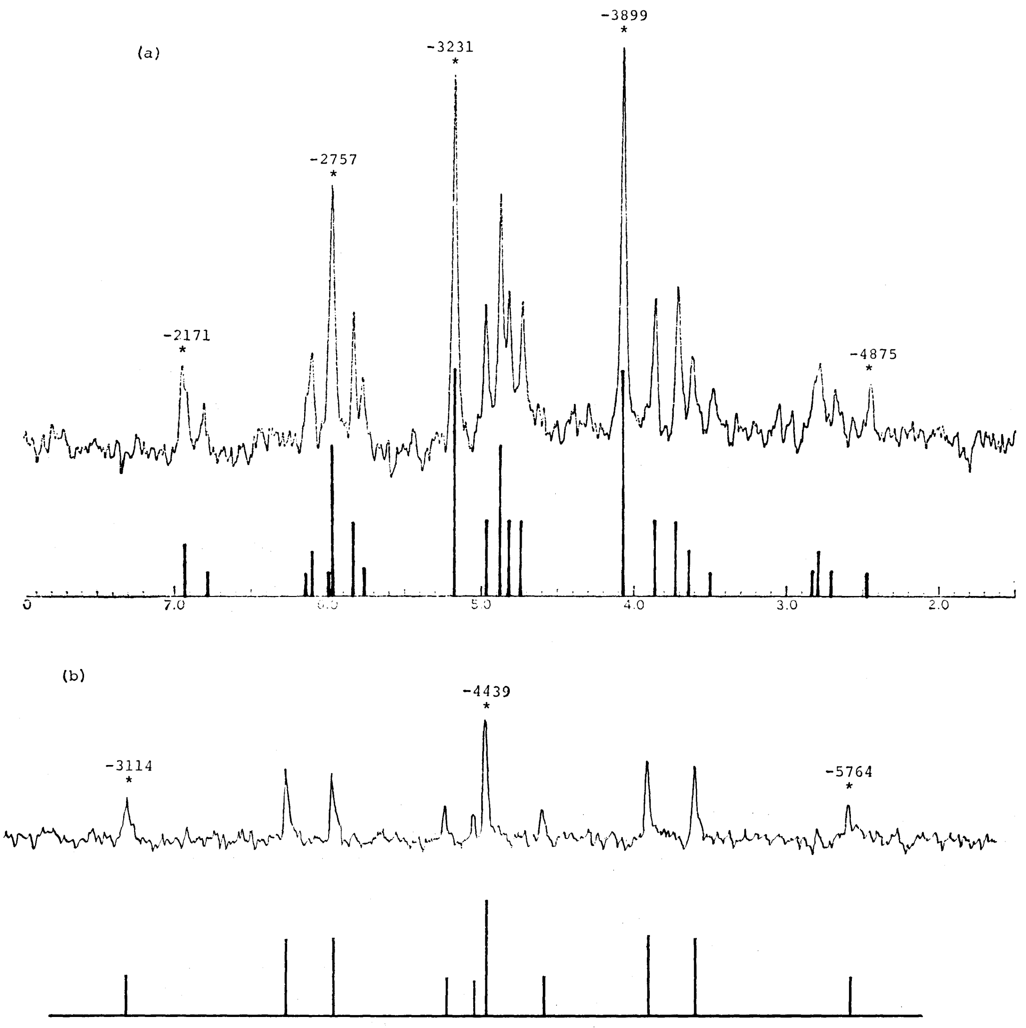

Fig. 1. Observed ^1H and ^{19}F NMR spectra of *p*-chlorobenzylidyne trifluoride dissolved in EBBA. Several peak positions are given in Hz with asterisk. Calculated stick spectra are also given under the observed one; (a) An upfield ^1H spectrum, accumulated 36 scans, (b) an upfield ^{19}F spectrum, accumulated 25 scans.

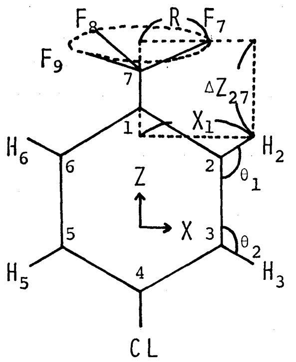

Fig. 2. Numbering system for *p*-chlorobenzylidyne trifluoride.

and the orientation parameters are determined as given in Table 2. The distances between the rotating trifluoromethyl fluorines and the protons are determined by the method used in Ref. 7. These values are also given in Table 2. The inter-proton distances obtained for the sample are similar to those obtained for benzene[16] (r_{23}=2.481, and r_{26}=4.297 Å)and a little different from those obtained for chlorobenzen[17] (r_{23}=2.509—2.465, r_{26}=4.297, and r_{35}=4.350—4.230) and benzylidyne trifluoride[11] (r_{23}=2.482, r_{26}=4.324, and r_{35}=4.298). The interfluorine distance obtained is smaller than that of benzylidyne trifluoride (r_{78}=2.165 Å).[11] Thus the radius of the circle formed by three fluorine nuclei is 1.228 Å, which is smaller than that of benzylidyne trifluoride (1.250 Å).[11]

TABLE 2. STRUCTURAL AND ORIENTATION PARAMETERS DERIVED FROM THE ^1H AND ^{19}F SPECTRA

r_{23}	2.481 ±0.003 Å
r_{26}	4.295 ±0.005 Å
r_{35}	4.300 ±0.005 Å
θ_1	120°06′±17′
θ_2	119°52′±17′
r_{78}	2.126 ±0.024 Å
R	1.228 ±0.014 Å
ΔZ_{27}	2.168 ±0.011 Å
S_{xx}	−0.1350 ±0.0004
S_{zz}	0.2902 ±0.0009

The Anisotropy of the Indirect Coupling. The D_{78} (or D_{FF}) coupling constant may contain a contribution from the anisotropy of the indirect coupling between the geminal fluorine nuclei. In the case of a trifluoromethyl group having a C_3 symmetry axis, the following relation has been reported:[3]

$$D_{78}^{\mathrm{exp}} = D_{78}^{\mathrm{dir}} + D_{78}^{\mathrm{ind}}, \tag{6}$$

$$D_{78}^{\mathrm{ind}} = S_{zz}\Delta J_{78}/3, \tag{7}$$

where

$$\Delta J_{78} = |J_{zz} - (J_{xx}+J_{yy})/2|_{78}.$$

J_{zz}, J_{xx}, and J_{yy} are the diagonal elements of the J-tensor. Due to the low accuracy of the determined r_{FF} distance in Table 2, the ΔJ_{FF} value can not be obtained uniquely. The anisotropy of J_{FF} is given as a function of r_{FF} in Table 3. The ΔJ_{FF} value shown in Table 3 is negative and this agrees with other reported values for CF_2 and CF_3 groups.[11,18,19]

Table 3. The anisotropy ΔJ_{FF} of the F-F indirect coupling as a function of the internuclear distance r_{FF}

r_{FF}, Å	D_{FF}^{dir}, Hz	D_{FF}^{ind}, Hz	ΔJ_{FF}, Hz
2.102	1660.2±5.2	−179.7±5.3	−1858±61
2.114	1632.1±5.1	−151.6±5.2	−1567±59
2.126	1604.6±5.0	−124.1±5.1	−1283±57
2.138	1577.7±4.9	−97.3±5.0	−1006±55
2.150	1551.5±4.8	−71.0±5.0	−734±53
2.167	1515.2±4.7	−34.8±4.8	−360±51

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