^{19}F High-Resolution Nuclear Magnetic Resonance Study of Structure and Properties of Crystalline *sym*-$C_6Cl_3F_3$

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Dedicated to Professor Dr. Alarich Weiss on the Occasion of his 60th Birthday

From the high-resolution ^{19}F NMR spectrum of single crystal *sym*-$C_6Cl_3F_3$ its chemical shift shielding tensor is determined. The most shielded direction lies perpendicular to the molecular plane and the least shielded one in the molecular plane perpendicular to the C-F bond. The most (σ_{33}) and least (σ_{11}) shielded components change significantly in going from *sym*-$C_6H_3F_3$ and *sym*-$C_6Cl_3F_3$ to C_6F_6 whereas the component in the C-F bond direction (σ_{22}) changes little. It is concluded that the π-electron density distribution varies little but the σ-electron density is changed when other substituents are introduced. At 20 °C the *sym*-$C_6Cl_3F_3$ molecule rotates about its figure axis and its motion averages out the shielding tensor components within the molecular plane. The mode of the molecular motion does not change at the phase transition point (296 K) and up to the melting point in the time scale of ^{19}F high-resolution spectra.

Introduction

The chemical shift tensor of a nucleus depends on the electron distribution around it, and therefore its determination provides information about the structure and the properties of the chemical bonds in which the atom of the nucleus participates. However, in gaseous, liquid, and plastic phases, the rapid three-dimensional molecular motion averages out the anisotropic part of the chemical shift tensor ($\underset{\sim}{\sigma}$), leaving only the isotropic part

$$\sigma_i = (1/3)\ \mathrm{Tr}\ (\underset{\sim}{\sigma}) = (1/3)\ (\sigma_{11} + \sigma_{22} + \sigma_{33})\ , \quad (1)$$

where σ_{11}, σ_{22}, and σ_{33} are the principal components of the chemical shift tensor. Therefore information about the anisotropy in the chemical shift, which is very important for detailed studies of chemical bonds, is completely lost in experiments on gases, liquids, and special solids like plastic crystals [1].

In an ordinary solid, in which no rapid molecular rotation is excited, the chemical shift tensor is not, in principle, averaged out. Therefore measurements of the angular dependence of the resonance frequency by use of high-resolution technique allow one to determine the anisotropy in the chemical shift tensor $\underset{\sim}{\sigma}$ in the solid and to get information about the local symmetry of the electron cloud around the resonant nucleus and the chemical bonding within the molecule in the crystal. If substantial molecular motion is excited in the crystal, the chemical shift tensor is partially averaged and its analysis will disclose the type and correlation time of the molecular motion [2].

We applied a multiple-pulse high-resolution NMR method to *sym*-$C_6Cl_3F_3$ (1,3,5-trichloro-2,4,6-trifluorobenzene) in order to obtain the complete chemical shift tensor of ^{19}F in the crystalline state. It was thought that *sym*-$C_6Cl_3F_3$ will provide a good example to demonstrate the type of information one could obtain from such studies because the molecular and crystal structures are highly symmetrical and all fluorine atoms may be considered to be crystallographically equivalent from the fact that the all chlorine atoms are equivalent [3].

Experimental

A sample of *sym*-$C_6Cl_3F_3$ was purchased from Alfa Chemical Co. Ltd. Single crystal were grown from its heptane solution by evaporation at 30 °C and/or 5 °C. The crystals were trigonal bipyramidal, colorless and transparent. A single crystal with the dimension 3 mm × 3 mm × 2 mm was used for the high-resolution NMR experiments.

The apparatus was a home-built coherent pulsed spectrometer which operates at 40 MHz. The MREV-8 pulse sequence [4] was used to obtain the

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time-domain signal, the pulse intervals of which were adjusted to obtain the optimum condition of the spectrometer: Its shortest value was 6.7 μs. The resolution of the spectrum was examined by observing the ^{19}F signal in a single crystal of CaF_2. It was revealed that the half-height width of the resonance line was about 300 Hz which corresponds to 8 ppm. In order to attain a good stabilization of the static magnetic field we employed a frequency-modulated field-locking system. Its details will be described elsewhere [5].

We applied this NMR spectrometer system to collect the rotational patterns of the ^{19}F chemical shifts in *sym*-$C_6Cl_3F_3$ at 20 °C. The single crystal was placed between two thin polystyrene plates and set into the sample coil. The time-domain signal was accumulated 10 ~ 20 times every 20 min and the Fast Fourier Transform (FFT) was performed on 1024 data points to obtain the frequency spectrum by use of a NOVA-01 minicomputer system. In most cases the initial 100 actual data points were used for FFT and the rest was set to be zero to reduce the undesirable low-frequency spurious signal due to the noise in the spectrometer: The line distortion due to such a data truncation was confirmed to be negligible. One of the spectra thus obtained is shown in Fig. 1, in which the half-height width, 30 ppm (1.2 kHz), is seen. The chemical shift in this study was measured from the ^{19}F signal of liquid C_6H_5F and converted to the standard chemical shift value by multiplying with a scaling factor 1.6*. The estimated error in the chemical shift was less than ± 1.5 ppm.

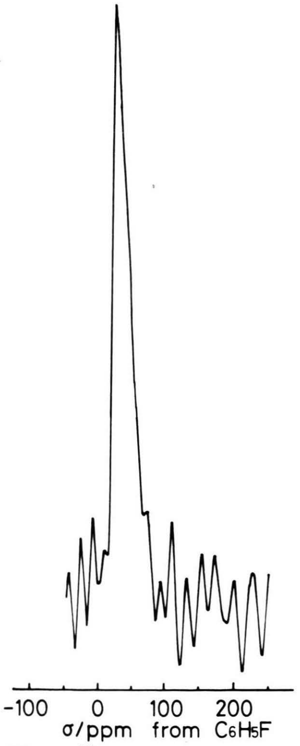

Fig. 1. ^{19}F NMR spectrum of *sym*-$C_6Cl_3F_3$ single crystal obtained at the crystal orientation as marked by *a** in Figure 2.

Results and Discussion

Sym-$C_6Cl_3F_3$ is a molecule having the D_{3d} symmetry. An early NQR (nuclear quadrupole resonance) study reported a single resonance line at 39.312 MHz at 77 K [3], showing that all chlorine atoms in the crystal are crystallographically equivalent. Therefore all fluorine atoms in the crystal should also be crystallographically equivalent. This and the trigonal bipyramidal shape of the crystal suggests that this substance has trigonal or hexagonal symmetry.

One can thus expect that the ^{19}F spectrum consists of three lines of the same intensity when the Zeeman field is in a general orientation with respect to the crystalline axes. However, as can be seen in Fig. 1, only one ^{19}F resonance line was observed at 20 °C, and it gives the rotational patterns shown in Fig. 2; when the crystal was rotated about the hexagonal axis, i.e., the Zeeman field was rotated in the *c*-plane, a rotational pattern shown on the r.h.s. of Fig. 2 was obtained. The ^{19}F chemical shift now remains constant at -43 ppm (assigned to the average value of σ_{11} and σ_{22}) within the experimental error. On the other hand, the rotational pattern on the l.h.s. was obtained when the Zeeman field was rotated in a plane which contains the *c*-axis. It shows a distinct angular dependence, and the maximum value of the chemical shift σ_{33}, $+85$ ppm, was obtained when the field was directed along the *c*-axis.

Since only one resonance line was observed at any field direction and the two components of the

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* The theoretical scaling factor for the MREV-8 method is $3/\sqrt{2}$, but it depends slightly on experimental conditions. We then determined the experimental scaling factor by measuring the chemical shift at several values of the carrier frequency.

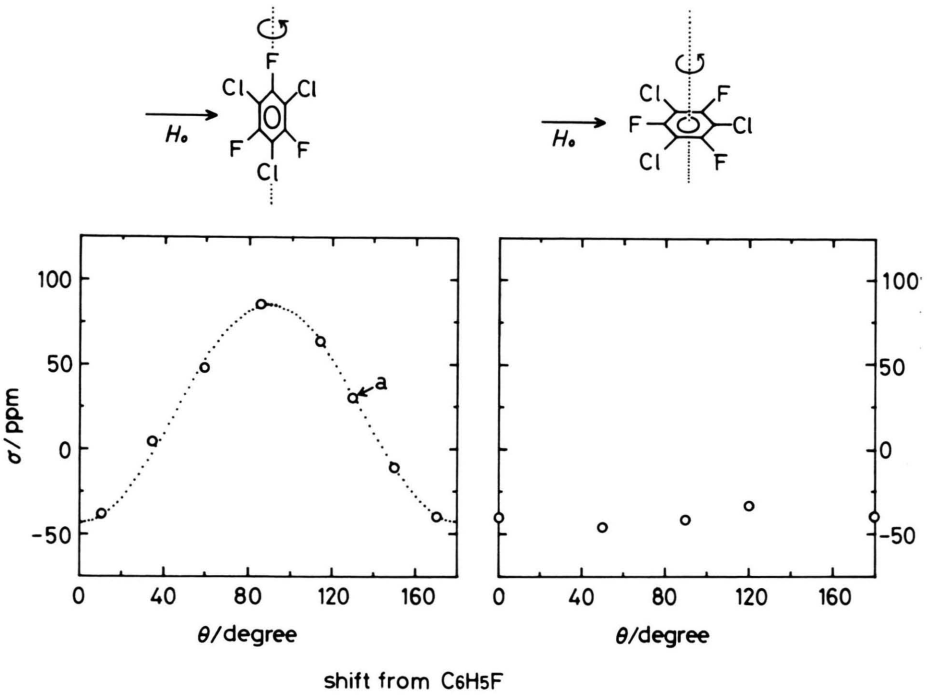

Fig. 2. Angular dependence of the ^{19}F chemical shift in *sym*-$C_6Cl_3F_3$ single crystal at 20 °C. The rotational pattern on the right hand side was obtained by rotating the Zeeman field in the crystallographic *c*-plane and the pattern on the left was obtained when the Zeeman field was rotated in a plane containing the *c*-axis.

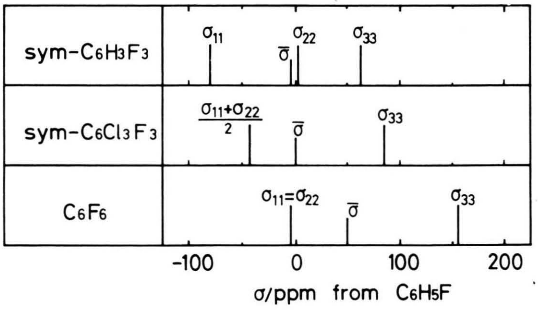

Fig. 3. Principal elements of the ^{19}F chemical shielding tensor in symmetrically substituted benzenes. The data for *sym*-$C_6H_3F_3$ and C_6F_6 were taken from [7].

Table 1. ^{19}F chemical shielding tensors in benzene derivatives. The principal values in ppm relative to an external reference of liquid C_6H_5F.

Substance	σ_{11}	σ_{22}	σ_{33}	Reference
sym-$C_6H_3F_3$	−79	2	63	[7]
sym-$C_6Cl_3F_3$	$(\sigma_{11}+\sigma_{22})/2 =$	−43	85	this work
C_6F_6	−3	−3	155	[7]

chemical shift tensor in the *c*-plane are equivalent, some molecular motion in this plane must averages partially the chemical shift tensor components. Now, the value of the most shielded component σ_{33}, which is for the direction of the *c*-axis, is comparable to the values assigned to the component perpendicular to the benzene ring in other aromatic compounds (see in Table 1) [6]. Therefore, the present experimental results lead definitly to the conclusion that the molecular plane of *sym*-$C_6Cl_3F_3$ is parallel to the trigonal or hexagonal *c*-plane and the molecular in-plane reorientation is excited to the extent capable to average the two chemical shift components within the molecular plane. Hence, the *sym*-$C_6Cl_3F_3$ crystal is necessarily trigonal or hexagonal.

Next we will turn to discuss the chemical shift values in the $C_6Cl_3F_3$ molecule in relation to its electronic structure. Raber and Mehring measured the shielding tensor values in an analogous compound [7]. Their values together with ours are listed in Table 1 and shown schematically in Figure 3. Our value of $(\sigma_{11}+\sigma_{22})/2$ in Table 1 and Fig. 3 indicates the motionally averaged value of the two directions in the molecular plane. According to Raber and Mehring the least shielded direction of the F nucleus is perpendicular to the C-F bond and lies within the benzene ring plane, and σ_{22}, which assumes a medium value, is almost constant irrespective of the functional groups which substitute other positions of the benzene ring [7].

The chemical shift tensor can generally be separated into two terms according to Ramsey [8] as

$$\underline{\sigma} = \underline{\sigma}^{(d)} + \underline{\sigma}^{(p)}\,, \tag{2}$$

where $\underline{\sigma}^{(d)}$ and $\underline{\sigma}^{(p)}$ are the diamagnetic and the paramagnetic contributions, respectively. Ramsey obtained $\underline{\sigma}^{(d)}$ and $\underline{\sigma}^{(p)}$ by first-order and second-order perturbation theory, respectively. A variational treatment gives similar results to Ramsey's [9]. In the case of ^{19}F resonance the paramagnetic contribution usually dominates the chemical shift [10], and so we may take account of only the paramagnetic parts $\sigma_{ii}^{(p)}$ ($i = x$, y, and z) to examine the electronic structure of *sym*-$C_6Cl_3F_3$.

Now we consider the following simple relation presented by Karplus and Das [10]

$$\sigma_{xx}^{(p)} = (3/2)\,\sigma_0\,(P_{yy} + P_{zz} - P_{yy}\,P_{zz})\,, \tag{3}$$

where P_{ii} represent the populations of the fluorine 2p orbitals and the cross terms P_{ij} are neglected. σ_0 is a semiempirical parameter as defined by Karplus and Das. $\sigma_{yy}^{(p)}$ and $\sigma_{zz}^{(p)}$ can be obtained by cyclic permutation of the subscripts.

For a closed shell ion or atom all the P_{ii} should be 2, giving rise to zero paramagnetic shift. Thus the degree of inbalance of the electron population in the fluorine 2p-orbitals can in principle be estimated from the experimental chemical shift anisotropy. We now write the p-orbital populations as

$$P_{xx} = 2 - \varrho_x\,,$$
$$P_{yy} = 2 - \varrho_y\,,$$
$$P_{zz} = 2 - \varepsilon\,, \tag{4}$$

where ϱ_x and ϱ_y represent the π-bond character of the C-F bond and

$$\varepsilon = 1 - (I + s - I s)\,. \tag{5}$$

In (5) I is the ionic character and s the degree of the sp-hybridization of the C-F σ-bond. Introduction of (4) and (5) in (3) gives

$$\sigma_{xx}^{(p)} = (3/2)\,\sigma_0\,\{\varepsilon + \varrho_y\,(1-\varepsilon)\}\,, \tag{6a}$$

$$\sigma_{yy}^{(p)} = (3/2)\,\sigma_0\,\{\varepsilon + \varrho_x\,(1-\varepsilon)\}\,, \tag{6b}$$

$$\sigma_{zz}^{(p)} = (3/2)\,\sigma_0\,(\varrho_x + \varrho_y - \varrho_x\,\varrho_y)\,. \tag{6c}$$

Here we assume for the *sym*-$C_6Cl_3F_3$ molecule that the x-axis is perpendicular to the benzene ring plane, the y-axis lies in the plane and is perpendicular to the C-F bond, and the z-axis coincides with the C-F bond. The assumption that only the p_x-orbital can form a double bond with the carbon π-orbitals on the ring leads to $\varrho_y = 0$ and so we obtain from (6)

$$\sigma_{xx}^{(p)} = (3/2)\,\sigma_0\,\varepsilon\,, \tag{7a}$$

$$\sigma_{yy}^{(p)} = (3/2)\,\sigma_0\,\{\varepsilon + \varrho_x\,(1-\varepsilon)\}\,, \tag{7b}$$

$$\sigma_{zz}^{(p)} = (3/2)\,\sigma_0\,\varrho_x\,. \tag{7c}$$

Since the most shielded direction is in the x-axis direction, σ_{xx} is equal to σ_{33}. The bond direction component (σ_{zz}) is σ_{22}, and σ_{yy} corresponds to σ_{11}. Table 1 and Fig. 3 show that the z-components ($\sigma_{zz} = \sigma_{22}$) in the three benzene derivatives are virtually insensitive to substitution. This indicates that ϱ_x is nearly constant, i.e., the π-electron density on the ϱ_x orbital in the fluorine atom is little affected by the substitution. The component σ_{xx} is increased from *sym*-$C_6H_3F_3$ to C_6F_6. This implies that ε changes significantly on substitution. As the decrease in ε can be attributed to an increase of the ionic character I in (5), it may be considered that the ionicity in a C-F bond is increased on going from *sym*-$C_6H_3F_3$ and *sym*-$C_6Cl_3F_3$ and to C_6F_6. Therefore, according to the semi-empirical simple molecular orbital theory due to Karplus and Das [10], the ionic character of the C-F bond is influenced by substitution of the other bonds significantly whereas the π-bond nature of the C-F bond remains unchanged.

As was mentioned above, it was found during the analysis of the ^{19}F chemical shift rotational patterns that the molecules undergo reorientation about the figure axis at room temperature. In order to examine this motion in more detail the spin-lattice relaxation time T_1 and the spin-spin relaxation time T_2 of ^{35}Cl were measured [11]. We found that the correlation time, τ_c, for the three-fold reorientation of the molecule is about 5×10^{-4} s at 300 K, which is just the order of magnitude sufficient to average out the components of the ^{19}F shielding tensor in the benzene ring plane.

Paukov and Glukhikh [12] and Andon and Martin [13] measured the heat capacity of *sym*-$C_6Cl_3F_3$ and found a higher-order phase transition at 296 K with an enthalpy change of only 18 J mol^{-1}. It is possible that the transition is related to some change in the motional mode of the molecules. We then measured the ^{19}F high-resolution NMR spectra on a powdered specimen from 293 K to 337 K (up to immediately above the melting point) to examine the relation of the molecular motion and this phase transition. The spectra showed no discernible change between 293 K and the melting point. This indicates that no other kind of molecular motion than the three-fold molecular reorientation is excited in the high-temperature phase in the time scale of ^{19}F high-resolution spectra. We also collected Raman spectral data with a single crystal at 289 K and 308 K. No detectable change in the spectra, however, was observed in the frequency range between 10 and 1000 cm^{-1}. Further studies are necessary to elucidate the mechanism of the phase transition at 296 K in this material.

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