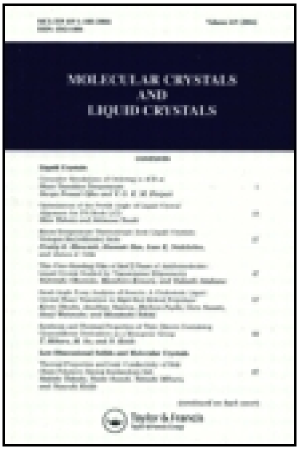

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NMR Spectra of 1,2-Difluorobenzene and 1,1-Difluoroethene in Nematic Solvents. Anisotropy of Indirect Fluorine Couplings and Molecular Geometry†

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Abstract—The interpretation of the NMR spectra of 1,2-difluorobenzene, partially oriented in nematic solvents, leads to a very small anisotropy in the indirect coupling between the fluorine nuclei. A geometrical model of this molecule is given.

In 1,1-difluoroethene, a strong anistropy in J_{FF} is found. Taking $\langle 1/r^3_{HH}\rangle / \langle 1/r^3_{FF}\rangle = 0.6691$, the tensor elements obtained are

$$\begin{aligned} J_{xx} &= -720 \pm 39\,\text{Hz} \\ J_{yy} &= +339 \pm 39 \\ J_{zz} &= +478 \pm 26 \end{aligned}$$

if the x-axis is chosen along the C=C bond and the z-axis perpendicular to the molecular plane.

1. Introduction

The NMR spectra of partially orientated molecules can be described in terms of the Hamiltonian⁽¹⁾:

$$\begin{aligned} \mathscr{H} = & -\frac{1}{2\pi}\sum_i \gamma_i(1-\sigma_i) H_0 I_{zi} \\ & + \sum_{i>j} (D^{dd}_{ij} + D^{\text{ind}}_{ij}) \{I_{zi}I_{zj} - \tfrac{1}{4}(I_{+i}I_{-j} + I_{-i}I_{+j})\} \\ & + \sum_{i>j} J_{ij}\{I_{zi}I_{zj} + \tfrac{1}{2}(I_{+i}I_{-j} + I_{-i}I_{+j})\} \end{aligned}$$

The experimentally determined anisotropic coupling D^{exp}_{ij} is composed of two parts. One contribution, D^{ind}_{ij}, arises from the anisotropic

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part of the indirect coupling J and the other contribution, D_{ij}^{dd}, is the averaged dipole–dipole interaction. These two contributions can not be separated experimentally:

$$D_{ij}^{\mathrm{exp}} = D_{ij}^{dd} + D_{ij}^{\mathrm{ind}}$$

There is evidence that D_{ij}^{ind} for proton–proton couplings is zero.(2) The aim of this study is to investigate to what extent indirect interactions between fluorine nuclei are anisotropic. If $D_{ij}^{\mathrm{ind}} = 0$ then

$$D_{ij}^{\mathrm{exp}} = D_{ij}^{dd}$$

The dipole–dipole couplings and the molecular geometry are related by

$$D_{ij}^{dd} = K_{ij}\left\langle \frac{3\cos^2\theta_{ij} - 1}{r_{ij}^3} \right\rangle$$

where K_{ij} is a constant, θ_{ij} the angle between the magnetic field direction and the axis connecting the nuclei i and j, separated by a distance r_{ij}; the average is taken over all motions. A generally accepted assumption in liquid crystal NMR work is, that there is no correlation between the orientation of a rigid molecule and the distances within it, so that these can be separated. This means that

$$D_{ij}^{dd} = K_{ij}\,\overline{(3\cos^2\theta_{ij} - 1)} \cdot \left\langle \frac{1}{r_{ij}^3} \right\rangle$$

2. Anisotropy of J_{FF}

In order to decide whether D_{FF}^{ind} is zero or non-zero, use can be made of the fact that in some molecules an axis connecting fluorine nuclei is parallel to an axis connecting protons. In the case of 1,1-difluoroethene, for example, the ratio

$$\frac{D_{FF}^{dd}}{D_{HH}^{dd}} = \frac{K_{FF}}{K_{HH}} \cdot \frac{\langle 1/r_{FF}^3 \rangle}{\langle 1/r_{HH}^3 \rangle}$$

is a constant. The ratio of the corresponding experimental couplings is given by

$$\frac{D_{FF}^{\mathrm{exp}}}{D_{HH}^{\mathrm{exp}}} = \frac{D_{FF}^{dd} + D_{FF}^{\mathrm{ind}}}{D_{HH}^{dd}} = \frac{K_{FF}}{K_{HH}} \cdot \frac{\langle 1/r_{FF}^3 \rangle}{\langle 1/r_{HH}^3 \rangle} + \frac{D_{FF}^{\mathrm{ind}}}{D_{HH}^{dd}}$$

If this ratio varies in experiments with essentially different orientations, one can conclude that $D_{FF}^{\mathrm{ind}} \neq 0$. The change of this ratio is most significant in the region where D_{HH}^{dd} is comparatively small. The criterion for the existence of anisotropy in indirect couplings given here can be used for all ratios of direct couplings, arising from pairs of nuclei whose interconnecting axes are parallel.

Once the existence of D_{FF}^{ind} has been established, it is of interest to evaluate its value from the experimental data. In 1,2-difluorobenzene, nine anisotropic couplings are measured. The four proton–proton couplings are purely dipolar. If we now assume that the same holds true for the four anisotropic proton–fluorine couplings, the eight proton–proton and proton–fluorine couplings can be used to calculate the four geometrical unknowns and the two parameters that describe the orientation of this molecule. From the geometrical and orientational parameters calculated in this way, D_{FF}^{dd} can be deduced. D_{FF}^{ind} can then be obtained, using the relation $D_{FF}^{\text{ind}} = D_{FF}^{\text{exp}} - D_{FF}^{dd,\text{ calc}}$.

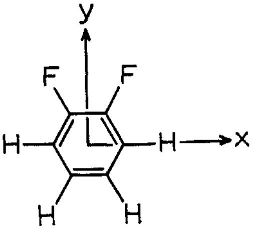
In 1,1-difluoroethene, the geometry can not be obtained from the three proton–proton and proton–fluorine couplings, because the number of unknowns (two geometrical and two orientational parameters) exceeds the number of dipolar couplings. In this case, the microwave geometry was used, without any vibrational corrections.

3. Results

The experimental data for 1,2-difluorobenzene are collected in Table 1. The orientational parameters are given in the notation of Snyder.(1) From the figures in Table 1 one can conclude that D_{FF}^{ind} is very small in this molecule. Although the orientation varied significantly, the ratio of $D_{FF}^{\text{exp}}/D_{45}^{\text{exp}}$ is nearly constant. Furthermore, the values of D_{FF}^{ind}, calculated along the lines mentioned above, are also small. In combination with microwave data(3,4), a molecular geometry was computed (Table 2). Details of these experiments will be reported elsewhere.(5)

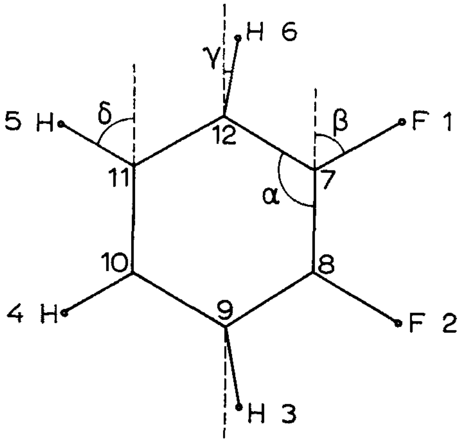
Comparison of the experiments of orientated 1,1-difluorethene by Buckingham *et al.*(6) and by Spiesecke and Saupe(7) already suggests the existence of an anisotropy in J_{FF}. In Table 3 our data of 1,1-difluoroethene are given. Indeed the change in $D_{FF}^{\text{exp}}/D_{HH}^{\text{exp}}$ with varying orientation is appreciable. In each experiment, D_{FF}^{ind} can be calculated using data from the microwave geometry.(8)

Table 1 Final Results for 1, 2-difluorobenzene



exp.	$C_{x^2-y^2}/C_{3z^2-r^2}$	$D_{FF}^{\mathrm{exp}}/D_{45}^{\mathrm{exp}}$	$D_{FF}^{\mathrm{ind}} = D_{FF}^{\mathrm{exp}} - D_{FF}^{dd,\,\mathrm{calc}}$
1	0.382	0.713	0.9 ± 2.4 Hz
2	0.341	0.705	2.9 ± 3.0
3	0.333	0.707	2.4 ± 2.6
4	0.550	0.702	0.5 ± 0.5

Table 2 A possible geometry of 1,2-difluorobenzene, consistent both with Microwave- and NMR data. All *C–C* distances are taken equal and no corrections for vibrations have been made



$r_{CC} = 1.400\,\dagger\text{Å}$

$r_{6,12} = 1.084\,\dagger\text{Å}$

$r_{CF} = 1.316 \pm 0.002\,\text{Å}$

$r_{5,11} = 1.090 \pm 0.009\,\text{Å}$

$\alpha = 120°17' \pm 4'$

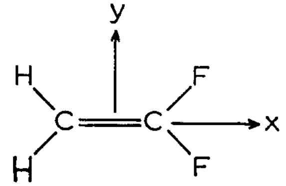
$\beta = 60°52' \pm 7'$

$\gamma = 1°22' \pm 18'$

$\delta = 59°50' \pm 14'$

† assumed values

TABLE 3 Final Results for 1, 1-difluoroethene



exp.	$C_{x^2-y^2}/C_{3z^2-r^2}$	$D^{exp}_{FF}/D^{exp}_{HH}$	$D^{ind}_{FF}/C_{3z^2-r^2}$
1	−0.440	0.756	311
2	−0.489	0.875	343
3	−0.613	−0.129	365
4	−0.715	0.382	405
5	−0.895	0.493	438
6	−0.392	0.687	244
$D^{dd}_{HH}=0$	−0.577		

The relation between D^{ind}_{FF} and the tensor components of J_{FF} is given by⁽¹⁾

$$\frac{D^{ind}_{FF}}{C_{3z^2-r^2}} = \frac{2}{3\sqrt{5}}\left\{J_{zz} - \tfrac{1}{2}(J_{xx}+J_{yy})\right\}_{FF} + \frac{C_{x^2-y^2}}{C_{3z^2-r^2}}\,\frac{1}{\sqrt{15}}\left\{J_{xx}-J_{yy}\right\}_{FF}$$

In Fig. 1, $D^{ind}_{FF}/C_{3z^2-r^2}$ is plotted against $C_{x^2-y^2}/C_{3z^2-r^2}$. Using the relation

$$J_{FF} = \tfrac{1}{3}(J_{xx}+J_{yy}+J_{zz}) = +32.5\,\text{Hz},$$

the separate components of the J tensor can be calculated:

$$J_{xx} = -720 \pm 39\ \text{Hz}$$
$$J_{yy} = +339 \pm 39$$
$$J_{zz} = +478 \pm 26$$

taking $\langle 1/r^3_{HH}\rangle/\langle 1/r^3_{FF}\rangle = 0.6691$. The margins of error given, are probable errors based on the accuracy of the fit.

4. Discussion

The reported values of the tensor components of J_{FF} in 1,1-difluoroethene are highly dependent on the choice of $\langle 1/r^3_{HH}\rangle/\langle 1/r^3_{FF}\rangle$.

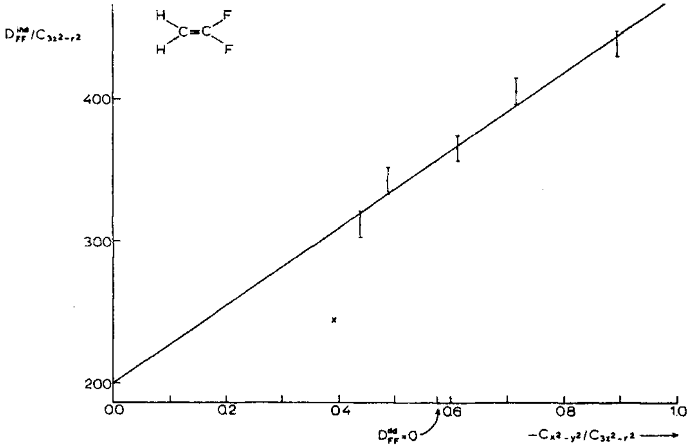


Figure 1. Least squares adaptation of experimental parameters in 1,1-difluoroethene.

However, for all reasonable ratios, the components are large compared to the isotropic value of J_{FF}.

The experiments 1–5 (Table 3) were performed in ethoxybenzylidene-butyl-aniline, where experiment 6 was done in a mixture of azo compounds. Experiment 6 is indicated as a cross in Fig. 1. These experiments show that the tensor components of J_{FF} are different in these two nematic solvents, which indicates that these tensor components are solvent dependent, a result which is physically reasonable.

Recent calculations of the anisotropy in indirect couplings[9–12] are in disagreement with the experimental values, but these calculations are highly approximate in nature and are far from decisive up to now.

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