Theoretical and Experimental Determination of the Indirect Nuclear Magnetic Fluorine–Fluorine Coupling Anisotropy in *trans*-Difluoroethene

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Summary Theoretical calculations and experimental measurement show that 5% of the anisotropic coupling in *trans*-difluoroethene dissolved in a nematic solvent arises from the indirect (electron-mediated) contribution.

THE anisotropy of indirect nuclear spin–spin coupling tensors is of importance in connection with the determination of geometry from the n.m.r. spectra of solutes dissolved in liquid crystals.[1] Two of us have recently predicted[2] that *trans* $\mathbf{J}_{FF}$ in fluorinated ethenes should manifest substantial anisotropy. We now present results for *trans*-difluoroethene which support these predictions, not only qualitatively but quantitatively.

The calculations used the coupled Hartree–Fock method with INDO wave-functions, as previously indicated.[2] We define the z-axis to be perpendicular to the molecular plane, and the x-axis to be parallel to the CC bond. The calculated $\mathbf{J}_{FF}$ tensor,† which is dominated by the orbital contribution, is given in Table 1. Analysis of spectra yields anisotropic couplings (D^{expt}_{ij} values, between nuclei i and j) which are sums of direct (dipole–dipole) and indirect (electron-mediated) contributions: the former (D^{dir}_{ij}) depend on the orientation parameters C_q and nuclear geometry; the latter, for this molecule of C_{2h} symmetry, are given (in the notation of Snyder[1–3]) by equation (1).

TABLE 1

Calculated $\mathbf{J}_{FF}$/Hz in *trans*-difluoroethene

	x	y	z
x	$-172{\cdot}0$	$-247{\cdot}5$	0
y	$-247{\cdot}5$	$-91{\cdot}0$	0
z	0	0	$-35{\cdot}7$

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† The equality of J_{xy} and J_{yx} in this case derives from a combination of the local C_{2h} symmetry and the retention of only one-centre matrix elements of the perturbation operators.

$$D^{\mathrm{ind}}_{ij} = (1/3\sqrt{5})C_1[2J_{zz} - (J_{xx} + J_{yy})]_{ij} + (1/\sqrt{15})C_2[J_{xx} - J_{yy}]_{ij} + (1/\sqrt{15})C_3[J_{xy} + J_{yx}]_{ij} \quad (1)$$

Seven experiments were performed on *trans*-difluoroethene dissolved in *N*-(*p*-ethoxybenzylidene)-*p*-butylaniline (EBBA), at various concentrations and temperatures. For each experiment, ^{1}H and ^{19}F spectra were obtained and the four D^{expt}_{ij} values deduced;[1] these were interpreted as follows. Anisotropy in $\mathbf{J}_{\mathrm{HH}}$ and $\mathbf{J}_{\mathrm{HF}}$ was neglected,‡ the geometry from recent electron diffraction research[4] was assumed,§ and *three* D_{ij} (HF *gem* and *cis*, and HH) values were used to determine the three C_q values, whence in turn $D^{\mathrm{dir}}_{\mathrm{FF}}$ was calculated. In Table 2 we give, for the most and the least oriented cases, the dominant orientation parameter C_3, and the results of these calculations in columns (2)—(4). Column (5) of Table 2 gives the result of substituting these experimental C_q values and the theoretical $\mathbf{J}_{\mathrm{FF}}$ anisotropies¶ in equation (1); the agreement between columns (4) and (5) is essentially perfect, and in all the seven experiments the largest discrepancy was 0·8 Hz.

Table 2

D_{FF}/Hz for *trans*-difluoroethene dissolved in EBBA

Expt. No.	(1) C_3	(2) $D^{\mathrm{expt}}_{\mathrm{FF}}$	(3) $D^{\mathrm{dir}}_{\mathrm{FF}}$	(4)[a] ΔD_{FF}	(5)[b] $D^{\mathrm{ind}}_{\mathrm{FF}}$
1	−0·30687	−656·9 ± 0·3	−692·9	+36·0	+35·5
7	−0·14039	−311·3 ± 0·1	−327·2	+15·9	$+15{\cdot}9_5$

[a] Column (2) minus column (3). [b] Theoretical, using equation (1).

We have thus shown: (i) that for one *trans* F–F coupling in a fluoroethene the indirect contribution to the anisotropic D_{FF} is substantial, as previously predicted, and amounts to 5%; (ii) that the theoretical method used gives, in this case, quantitative agreement with experiment.

It is highly unlikely that in parallel cases the agreement between theory and experiment would be so excellent, partly because of uncertainty in the one-centre integrals and the inherent limitations of the approximate M.O. method used, partly because of the approximations involved in the interpretation of the experiments. But for *trans* F–F couplings the present results strongly confirm the usefulness of such theoretical calculations.

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‡ The calculations were also repeated by taking into account our (not very reliable) theoretical $\mathbf{J}_{\mathrm{HF}}$ anisotropies: the agreement with experiment was very marginally improved.

§ $r_{\mathrm{CC}} = 1{\cdot}320$, $r_{\mathrm{CH}} = 1{\cdot}088$, $r_{\mathrm{CF}} = 1{\cdot}338$ Å; $\angle$CCH = 124·7, $\angle$CCF = 119·8°. The internal consistency of the global results for this molecule indicate that transfer of geometry from the gas-phase electron-diffraction results was legitimate in this case (see also ref. 5). The INDO calculations actually used a standard geometry;[6] it seems likely that the differences would have little effect on $\mathbf{J}_{\mathrm{FF}}$ (though $\mathbf{J}_{\mathrm{HF}}$ would be markedly affected).

¶ It is interesting to observe that the *uncoupled* Hartree-Fock INDO calculations of ref. 7 predict an indirect contribution only about half as great.

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