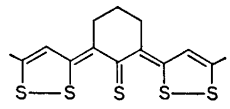
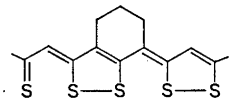
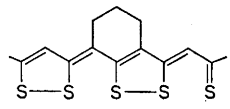


(a)



(b)



(c)

Such a scheme is also in qualitative agreement with the lengths observed for the C – S and the C – C bonds except those of C(5) – C(6) and C(6) – C(7) (Fig. 1). According to the description above these bonds would be expected to be of the same lengths as C(3) – C(4) and C(8) – C(9).

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The Interpretation of the ^{1}H and ^{19}F NMR Spectrum of 1,2-Difluoroethane

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The high resolution ^{1}H and ^{19}F NMR spectrum of 1,2-difluoroethane, given in Fig. 1, are at first sight surprisingly complex. The four protons and the two fluorine atoms in the molecule are chemically equivalent, but due to the different spin-spin interactions, the nuclei are magnetically non-equivalent. The spectra can be classified as AA'A''A'''XX'. The ^{1}H spectrum is symmetrical about ν_{H}, the chemical shift of the protons, and the fine structure is determined by six different coupling constants (*vide infra*). Similarly the ^{19}F spectrum is symmetrical about ν_{F}, the chemical shift of the fluorine nuclei, and the fine structure is determined by the same six coupling constants.

Analogous six spin systems have earlier been studied in 1,1,2,2-tetrafluoroethane [1] and *p*-difluorobenzene.[2] However, the analysis of these spectra was difficult because of heavy overlap between the individual lines in the spectra. The final coupling constants arrived at are therefore uncertain.

We have analysed the spectra in Fig. 1 by using a version of the computer program LAOCOON, written by Castellano and Bothner-By [3] as modified by Aksnes and Albriktsen.[4] The program calculates the position and intensity of all lines in the spectrum from a given set of chemical shifts and coupling constants. The program also fits by the method of least squares the calculated positions to observed positions by changing the coupling constants and chemical shifts. We must therefore start the analysis by estimating reasonable values of the coupling constants.

1,2-difluoroethane exists in two distinct conformers: *gauche* and *trans:*

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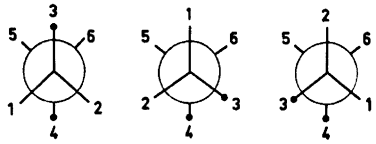

trans *gauche* *gauche*

As the barrier hindering the rotation from one conformer to another will be about 3 kcal/mol, the room temperature NMR spectra will be the averaged spectra where the contribution from each conformer is weighted according to the abundancy of that conformer.[5] In terms of the coupling constants and abundancies of each conformer we can then write down the following average coupling constants:

Geminal:	Type	
$J(1,2)=J(5,6)$	H−H	
$J(1,3)=J(2,3)=J(4,5)=J(4,6)$	H−F	
Vicinal:	**Type**	
$J(1,5)=J(2,6)=n_t J_t^g+\frac{1}{2}n_g(J_g^{g_2}+J_g^t)$	H−H	(1)
$J(1,6)=J(2,5)=n_t J_t^t+n_g J_g^{g_1}$	H−H	(2)
$J(3,5)=J(3,6)=J(1,4)=J(2,4)=n_t J_{tHF}^g+\frac{1}{2}n_g(J_{gHF}^g+J_{gHF}^t)$	H−F	(3)
$J(3,4)=n_t J_{tFF}^t+n_g J_{gFF}^g$	F−F	(4)

n_t and n_g are the abundancy of, respectively, the *trans* and *gauche* conformers and therefore $n_t+n_g=1$. The coupling constant with sub- and superscripts are coupling constants for the individual conformers. The subscript denotes the conformer and the superscript the relative position of the two nuclei. In terms of the numbering given on the Newman projections above, these coupling constants are defined as follows:

$J_t^g=J_{15}$; $J_t^t=J_{16}$; $J_{tHF}^g=J_{35}$; $J_{tFF}^t=J_{34}$.

gauche (left figure):

$J_g^{g_1}=J_{25}$; $J_g^{g_2}=J_{15}$; $J_g^t=J_{26}$; $J_{gHF}^g=J_{36}$; $J_{gHF}^t=J_{14}$; $J_{gFF}^g=J_{34}$.

It is known that the vicinal coupling constant will depend strongly on the conformer abundancy and the geminal coupling constant only slightly.[6] It is therefore much easier to estimate the values of the geminal coupling constants. By looking at closely related fluorinated ethanes reasonable values are found to be: $J(1,2)=-10$ Hz; $J(1,3)=47$ Hz.

As the splitting between the outermost lines in both the ^1H and the ^{19}F spectrum is determined only by the sum of the two H−F coupling constants, we then calculate from the splitting and the estimated value of $J(1,3)$: $J(3,5)=32$ Hz.

To estimate the remaining coupling constants was found to be difficult. Therefore, by trial and error, we now calculated about twenty different ^1H spectra varying the two vicinal H−H coupling constants between 0 and 7 Hz, and the F−F cou-

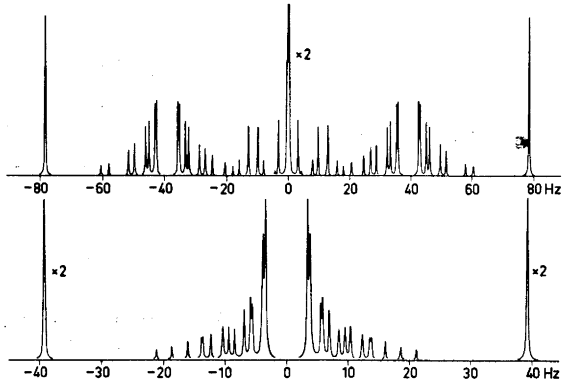

Fig. 1. The ^1H (lower) and ^{19}F (upper) NMR spectrum of neat 1,2-difluoroethane. The spectra are calculated from the final coupling constants. Each line is assumed to be lorentzian with a line width at half height of 1/4 Hz. Note the difference in scale and that three of the strongest lines are given with half amplitude.

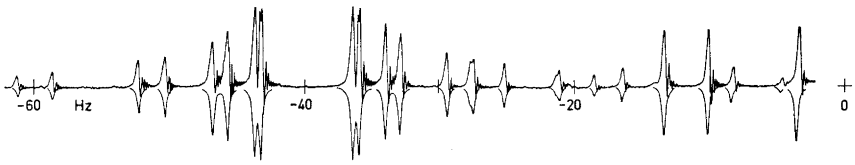

Fig. 2. Part of the observed and calculated ^{19}F NMR spectrum of neat 1,2-difluoroethane. The spectrum was recorded on a Varian HA-100-15 spectrometer. Each line in the calculated spectrum is assumed to be lorentzian with a line width at half height of 1/4 Hz.

pling constant between 0 and −16 Hz, keeping the remaining coupling constants unchanged. The shape of the spetcrum varied remarkably with small changes in the coupling constants.

With 5.6 Hz and 1.6 Hz for the two H−H coupling constants and −10 Hz for the F−F coupling constant the calculated spectrum resembled the observed spectrum. These values were then used as input values for a least square fit and the calculated spectrum converged to the end result drawn in Fig. 1. The intensity distribution in the calculated spectrum is in excellent agreement with the observed spectrum. As the intensity distribution is not used in the least square fitting, this agreement supports the validity of the obtained solution. Furthermore, also the observed fluorine spectrum, recorded later, was found to be in excellent agreement with the X-spectrum calculated on the basis of the coupling constants arrived at from the A-spectrum. Finally, both the ^{1}H- and the ^{19}F-spectra were used as input in a least squares refinement. A part of the ^{19}F-spectrum is shown in Fig. 2. The obtained agreement between the calculated and the observed spectra was excellent with a final r.m.s. error of .077 Hz. The final values of the parameters are (with calculated probable errors in parenthesis):

$J(1,2) = -11.78\ (2)$ Hz
$J(1,3) = 47.88\ (1)$ Hz
$J(1,4) = 30.81\ (1)$ Hz

Vicinal H−H couplings: 5.66 (1) Hz and 1.50 (1) Hz

$J(3,4) = -10.67\ (1)$ Hz

The chemical shift of the protons is 4.55 (1) ppm relative to TMS. The ^{19}F spectrum was recorded without any reference substance added.

The coupling constants in the individual conformers are not known. Therefore we cannot use eqns. (1) to (4) to calculate conformer abundancy. From data presented by Abraham and Cavalle [7] relating the vicinal H−F coupling for $n_t = n_g$ to the electronegativity of the substituents in an ethane fragment it follows that this mean coupling in the compound under study is expected to be 20 Hz. It is known that in general the *trans* coupling is much larger than the *gauche* coupling. Hence, when $J(3,5)$ is found to be 50 % larger than this mean coupling it follows from eqn. (3) that the *gauche* conformer is preferred. Also the relatively small F−F coupling constant of −10.7 Hz points in the same direction. This preference for the *gauche* conformer is supported by electron diffraction data of the molecule in the gas phase.[8,9] Infrared and Raman studies also indicate that the *gauche* conformer is more stable in the liquid state.[10]

The *gauche* preference is further supported by some preliminary investigations of the solvent dependence of the coupling constants. The study of the solvent and temperature dependence of the spectrum will be continued.

Experimental. The sample of 1,2-difluoroethane has previously been used in the vibrational study.[10] It was purified by bulb to bulb distillation, degassed and evaporated into the NMR tubes which were sealed in vacuum.

Note added in proof. Abraham, R. J. and Kemp, R. H. (*J. Chem. Soc.* **B 1971** 1240) have just published a similar interpretation plus a study of the solvent dependence of the coupling constant. The results given above are in agreement with the results of this more extensive investigation.

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2. Petersen, W. G. and Wells, E. J. *J. Mol. Spectry.* **14** (1964) 101.