

Gas-phase ^{19}F and ^1H High-resolution N.M.R. Spectroscopy: Application to the Study of Unperturbed Conformational Energies of 1,2-Difluoroethane

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The first highly-resolved ^{19}F n.m.r. spectra in the gas-phase have been observed for 1,2-difluoroethane, and the conformational energy difference between the *gauche* and *trans* states has been estimated to be about -0.8 kcal/mol (1 kcal = 4.184 kJ) from the coupling constants observed in the ^{19}F and ^1H n.m.r. spectra.

In previous papers,¹⁻³ we have shown that gas-phase ^1H high-resolution n.m.r. spectroscopy is a useful tool for the structural study of unperturbed states, *i.e.* states free from solvent and intermolecular interactions. We have extended this method to ^{19}F high-resolution n.m.r. spectroscopy and report here the first highly-resolved ^{19}F n.m.r. spectrum obtained at low pressure in the gas-phase.

We have studied the conformational equilibrium of 1,2-difluoroethane through the gas-phase ^{19}F and ^1H n.m.r. coupling constants, hoping to obtain conformational energies which may be compared directly with those predicted by our *ab initio* molecular orbital (MO) calculations⁴ and to settle the

longstanding debate on the wide range of experimental values reported [0 to -1.76 kcal/mol (1 kcal = 4.184 kJ)].⁵

1,2-Difluoroethane was synthesized in a similar way to that of Butcher *et al.*,⁶ and was purified several times by fractional distillation over molecular sieves. Samples at 507, 47, and 104 mmHg (at 27 °C) of 1,2-difluoroethane, tetramethylsilane (TMS), and CFCl_3 , respectively, were introduced by trap-to-trap transfer into a 3 mm outer diameter (o.d.) \times 45 mm long tube and sealed with *ca.* 1 atm nitrogen (at liquid nitrogen temperature). This tube was fixed with a Teflon inner stopper in a 5 mm o.d. standard n.m.r. tube containing $[\text{}^2\text{H}_6]$ dimethyl sulphoxide as lock solvent. N.m.r. spectra were observed on a

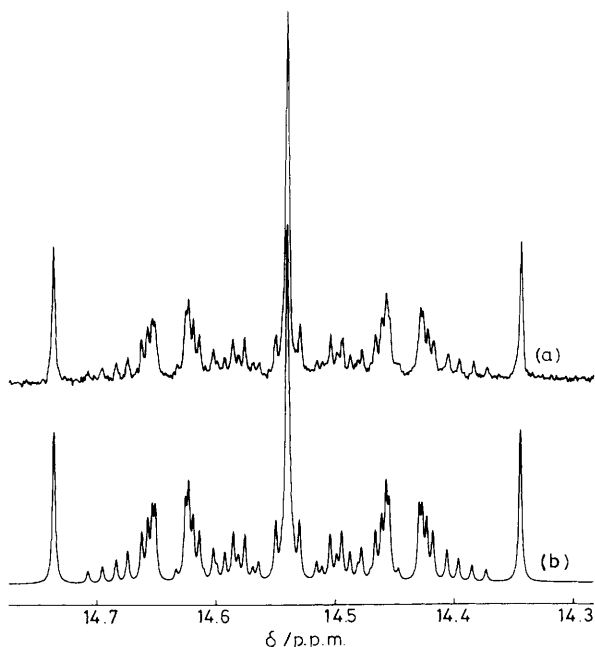


Figure 1. 376 MHz ^{19}F N.m.r. spectra of 1,2-difluoroethane in the gas-phase at 80 °C; (a) observed, (b) simulated.

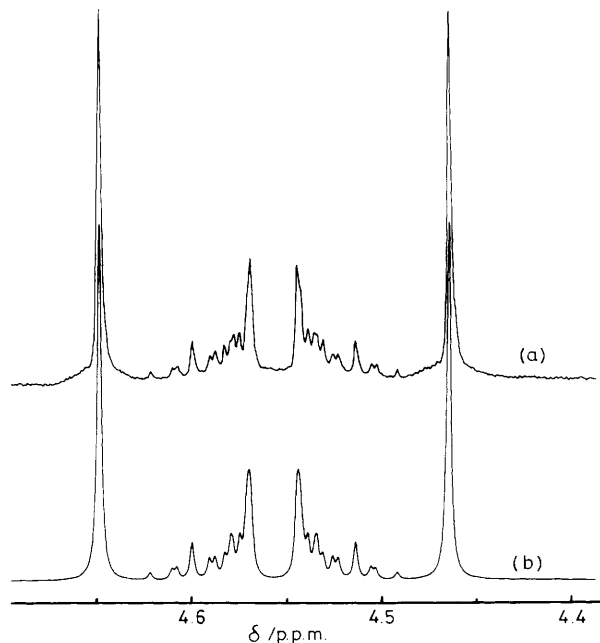


Figure 2. 400 MHz ^1H N.m.r. spectra of 1,2-difluoroethane in the gas-phase at 80 °C; (a) observed, (b) simulated.

JEOL GX-400 for ^{19}F at 376 MHz with 45° flip angle, 3.78 s pulse interval, and 2000–40 000 free induction decay (f.i.d.) accumulations, and for ^1H at 400 MHz with 45° flip angle, 6.28 s pulse interval, and 1000–40 000 f.i.d. accumulations. Chemical shifts are given in p.p.m. downfield from the gaseous internal standards CFCl_3 for ^{19}F and TMS for ^1H .

Figures 1(a) and 2(a) are the ^{19}F and ^1H n.m.r. spectra of 1,2-difluoroethane observed at 80°C in the gas-phase. These spectra as a set were analysed as the AA'A''A'''XX' spin system with the aid of LAOCN3 program.⁷ Under the spin-notation given in Figure 3, the coupling constants $^3J_{1,3}$ ($=^3J_{2,4}$), $^3J_{1,4}$ ($=^3J_{2,3}$), $^3J_{1,6}$ ($=^3J_{2,6} = ^3J_{3,5} = ^3J_{4,5}$), and $^3J_{5,6}$ are determined to be 2.78, 5.63, 25.69, and -12.83 Hz, respectively, and the chemical shifts δ_1 ($=\delta_2 = \delta_3 = \delta_4$) and δ_5 ($=\delta_6$) to be 4.56 and 14.54 p.p.m., respectively. The probable error for each 3J thus determined is less than 0.002 Hz, and the root mean square error between observed and calculated line frequencies is 0.099 Hz. The calculated spectra with these 3J and δ values are given in Figures 1(b) and 2(b) for comparison.

For calculation of the *gauche* and *trans* conformer populations under the rotational isomeric state model, a set of 3J values in each conformer should be known. We tentatively adopted the 3J values given by Abraham *et al.*,⁸ which were determined by extrapolation of the solution data to the gas-phase. With the extrapolated and the observed 3J values, the populations of the *gauche*⁺ ($=$ *gauche*⁻) and *trans* conformers at 80°C are calculated to be 0.43 and 0.14 from

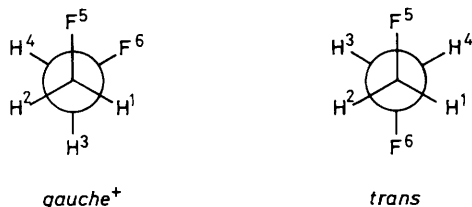


Figure 3. *gauche*⁺ and *trans* Rotational isomeric states of 1,2-difluoroethane, and notation for nuclear spins in the AA'A''A'''XX' spin system.

$^3J_{1,3}$ (H ··· H), 0.43 and 0.14 from $^3J_{1,6}$ (H ··· F), and 0.45 and 0.10 from $^3J_{5,6}$ (F ··· F), respectively. Under the assumption of a Boltzmann distribution, these fractions can be ascribed to the energy difference for *gauche* and *trans* conformers, $\Delta E(gauche - trans)$, of about -0.8 kcal/mol. This $\Delta E(gauche - trans)$ value is in good agreement with those obtained by electron diffraction,^{5a,9} but is slightly lower than that predicted by *ab initio* MO calculations⁴ (-0.31 kcal/mol at 25°C by MP2/6-311G**//HF/6-31G**).

It should be noted that the present determination of $\Delta E(gauche - trans)$ depends entirely on the assumed 3J values in each conformer. For simultaneous determination of the 3J values and $\Delta E(gauche - trans)$, we are continuing the gas-phase ^{19}F and ^1H n.m.r. measurements at various temperatures.

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