Determination of the Nuclear Magnetic Resonance Parameters in o-Difluorobenzene

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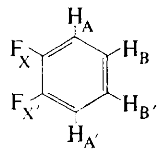
ANALYSES of the n.m.r. spectra of *meta*-[1] and *para*[2]-difluorobenzene have recently been reported; we have now examined and analysed the ^{1}H and ^{19}F spectra of *ortho*-difluorobenzene with the results shown in the Table.

Nuclear magnetic resonance parameters for o-*difluorobenzene*[a]



$\nu_F = -2329\cdot47^{b}$
$\nu_A = -700\cdot77^{c}$
$\nu_B = -693\cdot60$
$J_{XX'} = -20\cdot43$
$J_{AX} = J_{A'X'} = 10\cdot44$
$J_{BX} = J_{B'X'} = 4\cdot33$
$J_{B'X} = J_{BX'} = -1\cdot39$
$J_{A'X} = J_{AX'} = 7\cdot87$
$J_{AB} = J_{A'B'} = 8\cdot30$
$J_{AB'} = J_{A'B} = 1\cdot62$
$J_{AA'} = 0\cdot29$
$J_{BB'} = 7\cdot62$

[a] Ten mole percent solution in tetramethylsilane in Hz;
[b] Relative to internal hexafluorobenzene at 94·077 MHz;
[c] Relative to internal tetramethylsilane at 100 MHz.

The proton and fluorine spectra of *o*-difluorobenzene were recorded at 100 MHz and 94·077 MHz, respectively, on a Varian HA-100 spectrometer. The spectra were analysed as AA′BB′XX′ systems using Prospect-1, a least-squares computer programme modified for an IBM 1620 computer after Laocoon-II.[3] The analysis was simplified somewhat by the availability of the spectral parameters for benzene[4] and fluorobenzene.[5] In the first approximation, the H–H couplings for *o*-difluorobenzene were calculated from these parameters by assuming additivity of substituent effects (*cf.* a series of monosubstituted fluorobenzenes)[6] (Figure 1).

The errors associated with this analysis were quite small, the root-mean-square deviation between the experimental and the calculated frequencies being 0·04 Hz. Probable errors in the parameter sets were no greater than 0·04 Hz.

The parameter which appears to be the least well defined is the *ortho*-F–F coupling. Initially, its magnitude was estimated as 20 Hz from the width of the ^{13}C–^{19}F satellite pattern. This is in accord with the established small range of *ortho*-F–F couplings.[7] The iterative portion of Prospect-I yielded a magnitude of 20·43 Hz for this coupling; however, in keeping with the precedent that has already been established for several fluorinated benzenes,[8] we have taken the sign to be negative in *o*-difluorobenzene.

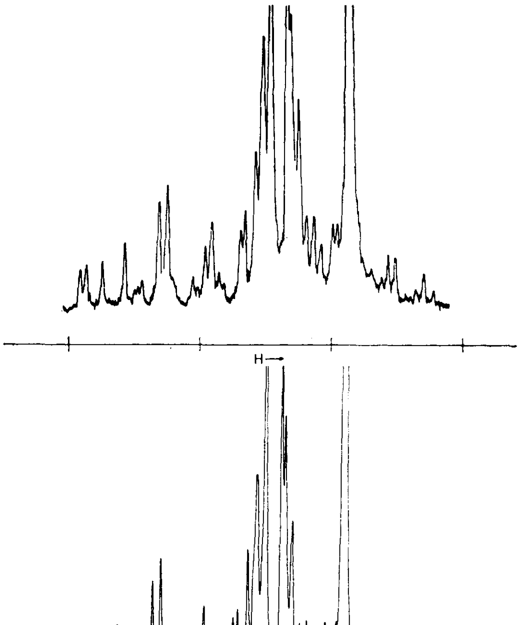


FIGURE. *Observed* (*top*) *and theoretical* (*bottom*) *proton spectra of* o-*difluorobenzene at* 100 *MHz.* (*Two low intensity peaks have been omitted at the downfield end of the scan.*)

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