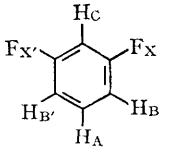
The Nuclear Magnetic Resonance Spectrum of *m*-Difluorobenzene

By D. B. MACDONALD

(*Mellon Institute, Pittsburgh, Pennsylvania* 15213)

THE analysis of the n.m.r. spectra of a number of fluorinated benzenes has recently been reported.[1-3] By virtue of the symmetry of these molecules and large fluorine chemical shifts, group theoretical methods[1] and sub-spectral analysis[2] have been of great value in analysing the spectra. *m*-Difluorobenzene (I) is an example of the ABB'CXX' system which cannot be analysed completely by these direct means. The proton and fluorine resonance spectra have now been analysed by computer methods and are reported here.



(I)

Despite simplification achieved by making use of the symmetry of this molecule and the *X*-approximation, the energy matrix contains many sub-determinants of higher order than two which cannot be solved explicitly. A partial analysis, however, can be obtained by application of these principles. The secular determinant will factorise into twelve single elements, two 2×2 determinants and twelve higher order determinants. The off-diagonal elements of both 2×2 determinants are equal to $\frac{1}{2}J_{AC}$, the *para* H–H coupling constant, which is very small compared with ν_{AC}, the chemical shift between nuclei A and C and which may safely be neglected. The energies of ten transitions (plus a number of combination transitions) may be calculated explicitly thus: two X transitions of energy $\nu_X \pm (\frac{1}{2}J_{AX} + \frac{1}{2}J_{BX} + \frac{1}{2}J'_{BX} + \frac{1}{2}J_{CX})$, four A transitions of energy $\nu_A \pm \frac{1}{2}J_{AC} \pm J_{AX}$ and four C transitions of energy $\nu_C \pm \frac{1}{2}J_{AC} \pm J_{CX}$.

The parameters: ν_A, ν_X, ν_C, J_{AX}, J_{CX}, and the sum $J_{BX} + J'_{BX}$ were obtained from the experimental spectrum. Of the remaining six parameters a fairly reliable estimate of the *meta* H–H coupling constant, J_{BC}, was obtained from the repeated spacing in the high-field part of the C-proton spectrum. In order to obtain values of the remaining parameters, use was made of the iterative computer program LAOCN3.† The initial trial values of the remaining coupling constants were estimated from the trends observed in the series of 1-substituted-2,6-difluorobenzenes previously analysed.[5]

The initial guesses were good enough for the

† An improved version of the program LAOCOON II in reference 4.

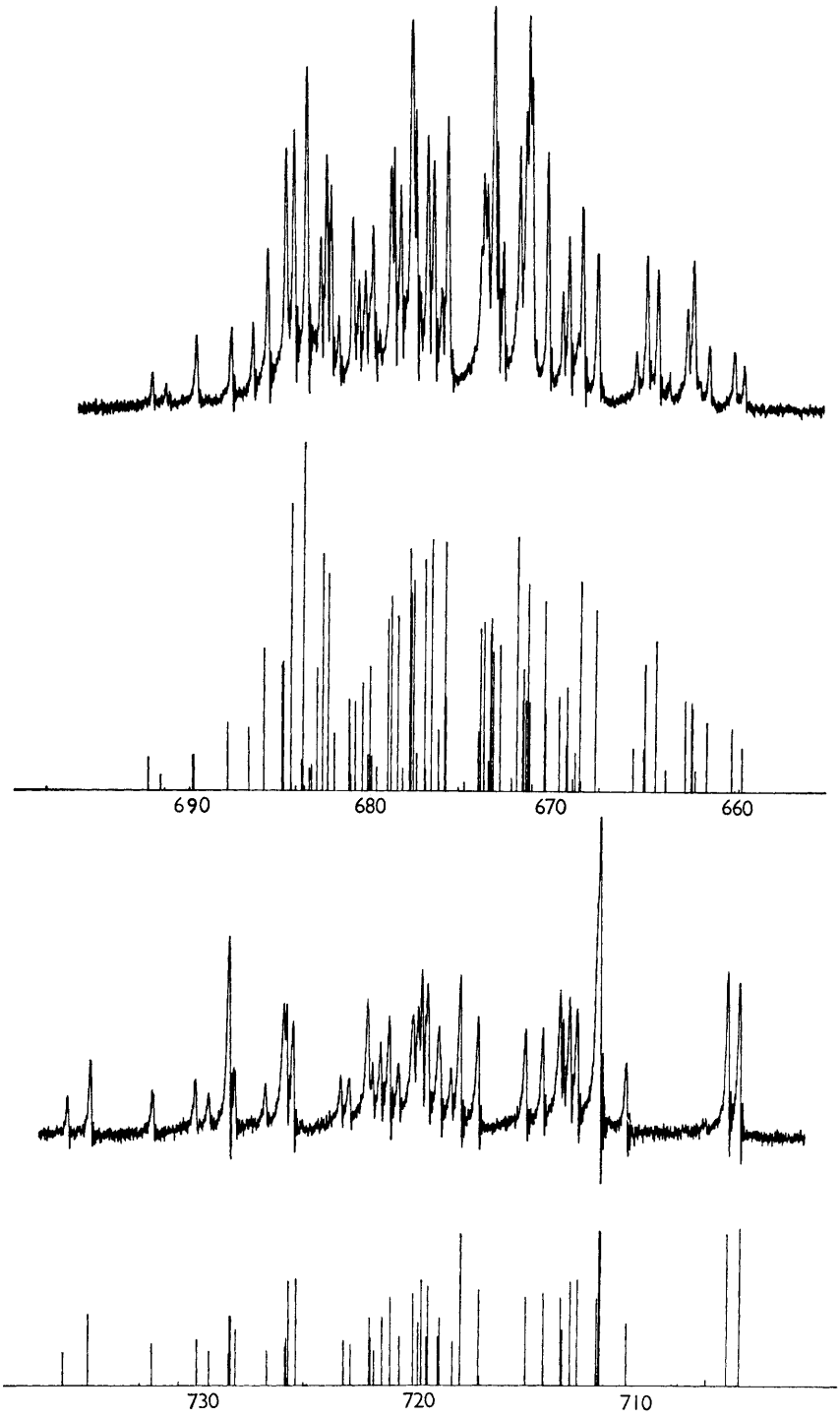


FIGURE. *The observed and calculated* 100 Mc./sec. *proton resonance spectra of* m-*difluorobenzene*. Upper trace: *High-field* (*B and C proton*) *spectrum*. Lower trace: *Low-field* (*A proton*) *spectrum*.

computer to converge to a solution which gave a good fit (r.m.s. error of 0·05 c./sec.) over ninety observed lines and the calculated spectrum. The observed and calculated proton resonance spectra are shown in the Figure. The best values of the coupling constants and chemical shifts obtained by this procedure are given in the Table. The spectrum is sensitive to the relative signs of all the coupling constants and these are indicated in the Table also.

Of particular interest in this molecule is the coupling constant between the two fluorine nuclei. In a recent Communication[5] it was shown how the *meta* F–F coupling constants in fluorobenzenes varied with the substituents. The contributions of the substituents to this coupling were shown to be additive, making it possible to predict both the sign and magnitude of the *meta* F–F coupling constant in any fluorobenzene. In this way the coupling between the two fluorine nuclei in *meta*-difluorobenzene was predicted to be $+6{\cdot}3 \pm 0{\cdot}3$ c./sec. The measured value of $+6{\cdot}57$ (*cf.*, Table) is in excellent agreement with these earlier predictions. This provides strong support for the validity of the additive substituent contributions.

TABLE

N.m.r. parameters for m-*difluorobenzene* (30% v/v in CCl_4)

τ_A	2·805 p.p.m.
τ_B	3·226 "
τ_C	3·281 "
ϕ_X‡	103·557 "
J_{AB}	+8·40 c./sec.
J_{AC}	+0·33 "
J_{AX}	+6·46 "
J_{BC}	+2·45 "
J_{BX}	+8·19 "
J'_{BX}	−0·86 "
J_{BB}	+0·86 "
J_{CX}	+9·23 "
J_{XX}	+6·57 "

‡ Relative to internal $CFCl_3$

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