Tetrahedron. 1967. Vol. 23, pp. 709 to 714. Pergamon Press Ltd. Printed in Northern Ireland

cis-1H,1H,4H-TRIFLUOROBUTA-1,3-DIENE

THE CHARACTERISATION OF A NEW CONJUGATED DIENE BY NMR SPECTROSCOPIC ANALYSIS

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(*Received* 22 *June* 1966)

Abstract—A new isolated diene has been shown by analysis of the ^1H and ^{19}F resonance spectra to be the named compound. The chemical shifts and coupling constants have been evaluated and confirmed by comparison of observed and theoretical spectra.

INTRODUCTION

Recent publications dealing with fluorinated dienes[1-3] prompt us to publish our results of an NMR investigation of a new diene.[4] Analysis showed that the diene was a trifluorobutadiene and mol. wt. 108 (mass spectroscopy) concurred with this conclusion.

EXPERIMENTAL

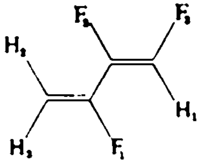
The ^1H and ^{19}F spectra: at 60 and 56·4 Mc/s. respectively using a Perkin–Elmer R.10.NMR spectrometer. A 40% soln. of the diene in trichlorofluoromethane (standard for ^{19}F shifts) with TMS added as an internal standard was used. The ^{19}F chemical shifts were determined with precision by using the calibrated decade-field shift facility of the R.10.

Preliminary analysis of the complex multiplets was facilitated by the use of a 1st order NMR program developed by one of us (T.N.H.) and the final assignment of lines was made by compilation of the complete spectrum using a 6-spin version of Freqint IV[5] adapted for use on the Birmingham University English-Electric KDF-9 computer by the authors.

RESULTS

The ^1H spectrum showed two distinct absorptions with integrated intensities of 2:1, the more intense signal being the AB part of an ABX system, while the weaker signal, from its position and structure,[6] arises from the vinylic proton of a HFC= group. The ^{19}F spectrum consisted of three equally intense signals.

The numbering of atoms is shown in I, and the signals from H_2, H_3, and F_1



I

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[1] K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.* **87**, 1339 (1965).

[2] A. A. Bothner-By and R. K. Harris, *J. Amer. Chem. Soc.* **87**, 3445 (1965).

[3] P. L. Bladon, D. W. A. Sharp and J. M. Winfield, *Spectrochim. Acta* **22**, 343 (1966).

[4] T. N. Huckerby and R. Stephens, Unpublished work.

[5] A. A. Bothner-By, Mellon Institute.

[6] N. Bowden, J. W. Emsley, J. Feeney and L. H. Sutcliffe, *Proc. Roy. Soc.* **282A**, 559 (1964).

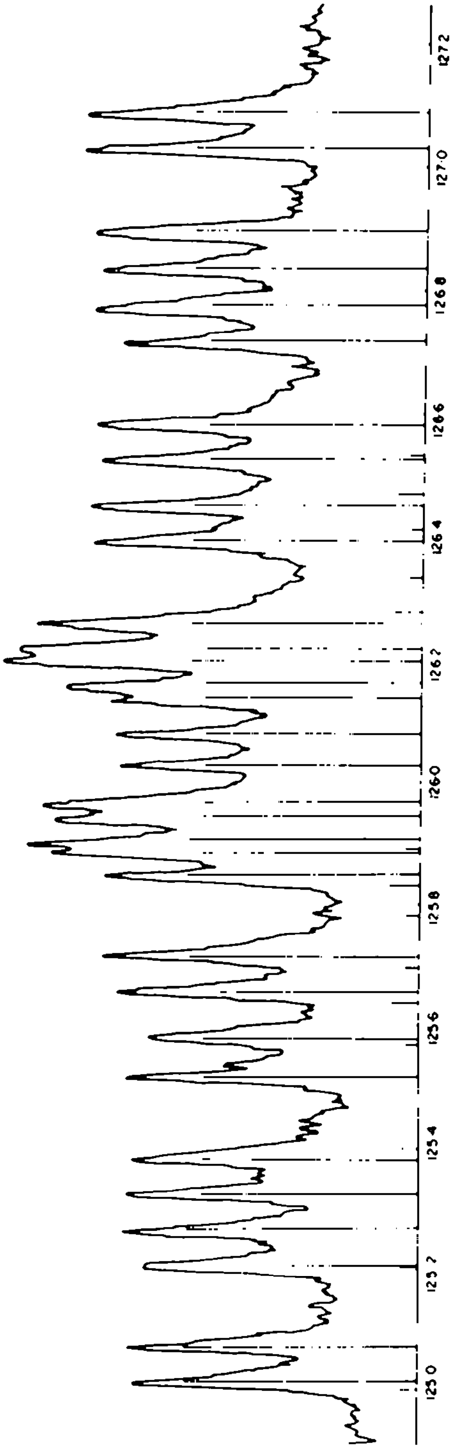


Fig. 1 ^{19}F Signal of F_1.

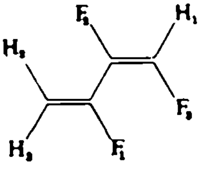
TABLE 1. OBSERVED AND CALCULATED FREQUENCIES OF THE PROTON SIGNALS (IN C/S FROM TMS)

	Calculated	Observed		Calculated	Observed
H_1	453·0	−453·1	H_2 and H_3	−320·8	−320·9
	−449·7	449·7		316·9	−317·0
	437·0	−437·0		313·0	313·0
	−433·7	−433·7		303·5	−303·5
	−381·5	381·3		−299·6	−299·5
	378·2	−378·1		−295·7	−295·6
	365·5	−365·4		−285·9	−285·8
	362·2	−362·2		−282·0	282·0
				278·1	−278·0
				−271·9	−271·9
				−268·0	268·0
				−264·1	264·1

constituted the ABX part of the spectrum which was initially analysed[7] to permit a number of reliable parameters to be used in the final calculations using the modified Freqint IV program. The calculated and experimental line frequencies of the protons are shown in Table 1 and, because of the complexity of the fluorine spectrum the actual experimental and theoretical spectra are reproduced in Figs. 1–3. The NMR parameters thus derived are shown in Tables 2 and 3. The sign of coupling of H_2 and H_3 is unknown, since there was no change in the calculated spectrum on changing the sign, and our "tickling" experiments were inconclusive. This coupling has been found to be negative.[2]

DISCUSSION

While it is generally assumed that butadienes exist in the *transoid* conformation the corresponding *cisoid* conformation cannot be ignored in substituted butadienes.[8] Consequently in addition to structure I, which is of the *transoid* conformation with *cis* F_2F_3, we must also consider II, *transoid* but with *trans* F_2F_3, and III and IV, both *cisoid* with F_2F_3 *cis* and *trans* respectively.



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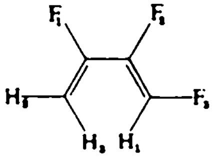

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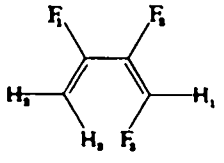

IV

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[7] J. D. Roberts, *An Introduction to the Analysis of Spin-Spin Splitting in High Resolution Nuclear Magnetic Resonance Spectra* p. 61. Benjamin, New York (1961).

[8] A. A. Bothner-By and R. K. Harris, *J. Amer. Chem. Soc.* 87, 3451 (1965).

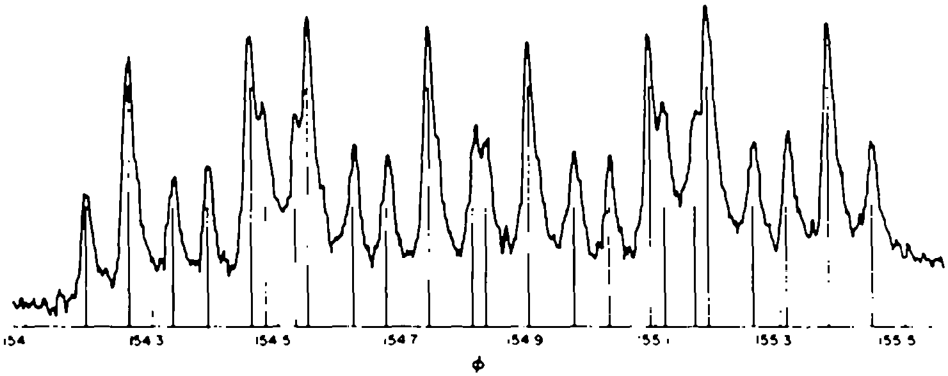

Fig. 2. ^{19}F Signal of F_2

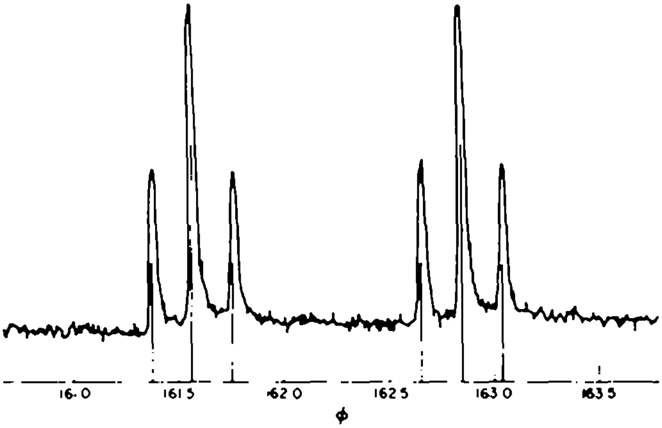

Fig. 3. ^{19}F Signal of F_3

Table 2. Chemical shift values of *cis*-1H,1H,4H-trifluorobuta-1,3-diene

Nucleus	Shift	Notes
H_1	3·21 τ	
H_2	5·106 τ	Constitute the AB part
H_3	5·134 τ	of an ABX system
F_1	+126·07 φ	X part of ABX spectrum
F_2	+154·82 φ	
F_3	+162·21 φ	

* $\delta_A - \delta_B$ found to be 1·7 c/s, ie. 0·028 ppm at 60 Mc/s.

The relative orientation of the hydrogen and fluorine atoms about the double bonds is readily determined from the coupling constants as the value of $J(H_2F_1)$ of 48·4 c/s is typical of the *trans* HF coupling of a $H_2C{=}CF$— group, and the value of $J(H_1F_2)$ of 16·0 c/s is typical of the *trans* HF coupling of a HFC=CF— group;[9] further the value for $J(F_2F_3)$ of 10·9 c/s is typical of *cis* FF coupling. It is thus evident

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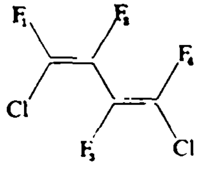
[9] L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry* p. 86. Pergamon Press, London (1959).

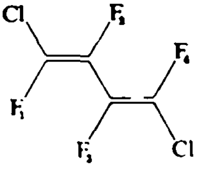
TABLE 3. COUPLING CONSTANTS (IN c/s) OF *cis*-1H,1H,4H-TRIFLUOROBUTA-1,3-DIENE

$J(H_1F_1) = 3{\cdot}3$	$J(H_2F_1) = 48{\cdot}4$	$J(F_1F_2) = 35{\cdot}9$
$J(H_1F_2) = 16{\cdot}0$	$J(H_2F_2) = 3{\cdot}9$	$J(F_1F_3) = 10{\cdot}9$
$J(H_1F_3) = 71{\cdot}5$	$J(H_3F_1) = 18{\cdot}1$	$J(F_2F_3) = 10{\cdot}9$
$J(H_2H_3) = 3{\cdot}9$	$J(H_3F_2) = 3{\cdot}9$	

that structures II and IV may be excluded, and the structure I chosen in favour of III on the basis of the magnitude of the coupling between F_1 and F_2. This assignment is supported by recent work[3] in which the isomeric 1,4-dichlorotetrafluorobuta-1,3-dienes were studied, and the corresponding FF coupling (i.e. between F_2F_3) in the *cis-trans* isomer (V) and *trans-trans* isomer (VI) found to be 34·1 and 34·4 c/s respectively.

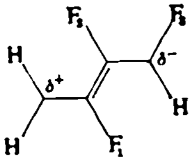


V



VI

The chemical shifts of the olefinic fluorine atoms of I warrants some discussion. In ^{19}F resonance the anisotropic effects of double bonds must be of less importance than in ^{1}H resonances as, e.g. CF_3 groups are to lower field than those of olefinic fluorine atoms. On the basis of π-orbital anisotropy both F_1 and F_2 would be expected to be at lower field than F_3, but from Table 2 it is clearly seen that the ϕ values of F_1 and F_2 are very different (28·8 ppm). We would suggest that there is extensive delocalization of the π-electrons, and C_2—C_3 has considerable double bond character, as indeed is reflected in the value of $J(F_1F_2)$ and thus the canonical form VII is of importance. There is thus a dipolar gradient from C_1 to C_4 and the chemical shifts



VII

are in the order of this dipolar interaction i.e. F_1 at lower field being nearest +ve dipole and F_3 being to highest field being at −ve end of dipole. It must however be remembered that the chemical shift of the fluorine atoms is dependent upon the nature of the other substituent groups.

We hope that further studies of olefinic fluorine resonances, and correlation with photo-ionization data and MO treatment will clarify these anomalous chemical shifts; it has already been suggested that the difference of ^{19}F chemical shifts in two similar conjugated molecules is dependent upon both the fluorine electron charge densities and the carbon-fluorine π-electron bond orders.[10]

Acknowledgements—One of us (T. N. H.) wishes to acknowledge the award of a Medical Research Council Grant. Thanks are expressed to the Director (Mr. K. A. Redish) and Staff of Birmingham University Computing Services for valuable advice and assistance, and also to Professor J. C. Tatlow for his continued interest.

[10] F. Prosser and L. Goodman, *J. Chem. Phys.* **38**, 374 (1963).