tonated at N-1 in order to completely eliminate the quadrupolar effects on $J_{2,6}$. The relative size of the errors possible here are such that one cannot entirely rule out the likelihood that the plot of Figure 3 should flatten out near the maximum of J_{HH}.

The observed variations with protonation of the chemical shifts in purine ($\nu_i^+ - \nu_i^0$) are difficult to interpret reliably because of the number and complexity of the factors that can be involved. In the case of pyridine and its cation, Gil and Murrell were able to obtain a reasonable correlation of shifts with π-electron densities only after correcting the former for the paramagnetic and lone-pair dipole contributions of the nitrogen atom.[18] It would appear that similar corrections would be applicable to purine as well. Since in purine there are four different nitrogen atoms (or three, if those in the imidazole ring are considered to exhibit an average behavior), the required calculations,

with appropriate weighting of all the structures, for both the base and its conjugate acid are considerably more involved. Nevertheless, this is a factor which should be incorporated into any comprehensive attempt to interpret and correlate the chemical shift data, which is outside the scope of the present investigation.

The various factors involved in interpreting the n.m.r. parameters suggest that the ^{13}C–H couplings probably provide the least ambiguous basis for a postulated protonation pattern of purine. The distribution of protonated sites deduced above is one which is at least consistent with all of the n.m.r. data. Although it may not necessarily rigorously rule out exclusive protonation at N-1, it provides new grounds for consideration of an alternative such as that presented here.

Nuclear Magnetic Resonance Studies of 1,3-Butadienes. I. The Spectra of Halogenated Butadienes

A. A. Bothner-By and R. K. Harris[1]

Contribution from Mellon Institute, Pittsburgh, Pennsylvania 15213.
Received April 5, 1965

The nuclear magnetic parameters are presented for fluoroprene, chloroprene, and the three isomers of 1,4-dichloro-1,3-butadiene. Comments are made about the mathematical analysis of the spectra. The chemical shifts and H,F coupling constants are discussed.

Introduction

In general there have been few detailed n.m.r. studies of butadiene derivatives, largely because of the complexity of the spectra. Heavily substituted butadienes, which would give simpler spectra, cannot be readily obtained. The only comprehensive study of high accuracy published so far is that of Hobgood and Goldstein,[2] who reported the nuclear magnetic parameters of 1,3-butadiene itself and a number of derivatives. Among these compounds was one halogenated derivative, namely, 2,3-dichlorobutadiene. This report gives the results of investigations on fluoroprene (2-fluoro-1,3-butadiene) and four chlorinated butadienes. The *s-trans* conformations of these molecules are shown in Figure 1, together with the chemical shifts (τ-values) obtained by the present work. Microwave and infrared spectroscopy have shown that the *s-trans* conformation is indeed the stable form in both fluoroprene[3] and chloroprene.[4] There is every reason to suppose this is also true for the three isomeric 1,4-

dichloro-1,3-butadienes.[5] It may be noted that hexachlorobutadiene has been shown to be nonplanar.[4]

Nomenclature

The numbering system for the substituents of 1,3-butadiene used in this paper is illustrated for butadiene itself in Figure 2. This retains the normal numbering for the carbon atoms of the skeleton and extends it to the substituents, using a prime to distinguish between the two substituents bonded to C-1 and to C-4. A new nomenclature has been introduced for the coupling constants in the butadiene molecule in order to facilitate comparisons between molecules. The method of Musher and Corey[6] is used to designate by means of a numerical prefix the number of chemical bonds through which coupling occurs. A subscript c or t indicates that the path of the coupling is through bonds oriented *cis* or *trans*, respectively, about one of the double bonds, ^3J_c and ^3J_t being the usual vicinal vinylic coupling constants. The extension to the ^4J values is self-explanatory. For the long-range coupling through five bonds two suffixes are necessary since the coupling path extends across two double bonds. Thus the symbol $^5J_{tc}$ indicates coupling between protons at positions 1 and 4'. The same symbol is used for the analogous coupling between protons at 1' and 4. Similarly in some molecules there may be two coupling constants each of types ^2J, ^3J_c, ^3J_t, ^4J_c, and ^4J_t. Finally the symbol ^3J_s designates coupling between protons at positions 2 and 3, the s indicating that this is a formal single-bond vicinal coupling.

(1) University of East Anglia, School of Chemical Sciences, Norwich NOR 77H, England.
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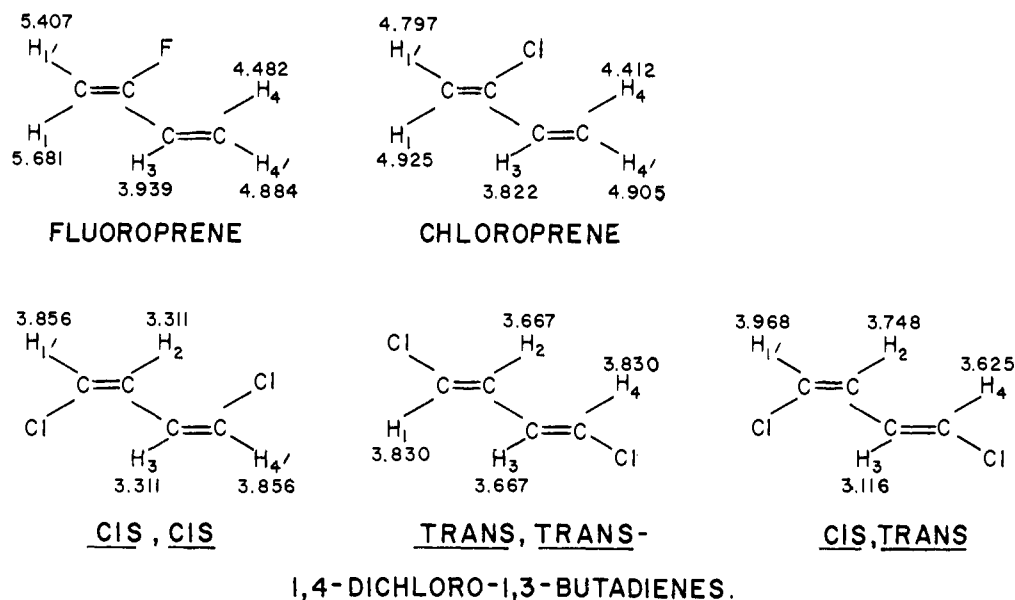(6) J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

Figure 1. The halogenated 1,3-butadienes in the present work, together with the τ-values obtained for the chemical shifts with the solution conditions listed in the Experimental section.
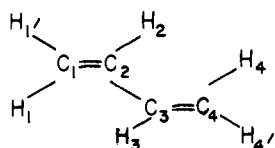
Figure 2. The numbering system used for butadiene derivatives, with the example of butadiene itself.

Experimental

Materials. Fluoroprene was a gift from Dr. D. Lide to whom we are most grateful. Chloroprene was obtained from E. I. du Pont de Nemours and Co. The samples of the three 1,4-dichlorobutadienes were kindly donated by Dr. H. Viehe, to whom we are much indebted.

Sample Preparation. Materials were introduced into 5-mm. o.d. sample tubes, a trace of tetramethylsilane was added to serve as an n.m.r. reference, the mixtures were degassed by freezing and thawing under vacuum, and the tubes were sealed off in the evacuated condition. Fluoroprene and chloroprene were studied in ~50% solution in xylene; the 1,4-dichlorobutadienes were examined neat.

Spectra. Proton n.m.r. spectra at 60 Mc.p.s. were obtained using the Varian A-60 spectrometer. Resolution for proton spectra was about 0.2 c.p.s. Spectra were calibrated with audio side bands generated by a Hewlett-Packard 202-A function generator monitored with a Hewlett-Packard counter. Fluorine spectra were obtained at 56.4 Mc.p.s. using the Varian DP-60 spectrometer.

Spectral Analysis

The compounds shown in Figure 1 fall into four nuclear magnetic systems, namely, in increasing order of complexity, AA'BB' (*cis,cis-* and *trans,trans*-dichloro compounds), ABCD (*cis,trans*-dichloro compound), ABCDE (chloroprene), and ABCDEX (fluoroprene). The observed spectra were in general assigned after

several trial spectra, with estimated nuclear magnetic parameters, had been computed with an IBM 7090 computer using part 1 of the program[7] LAOCOON II. Part 2 of the program was then used to successively iterate to a least-squares error fit of the observed spectrum. Some doubt remains about the uniqueness of the solutions given since it may be quite possible that slightly different trial parameters could lead to an assignment that would "zero-in" to a different solution. It is also frequently plausible to interchange some assignments made after the initial spectrum calculation and thus to change the final parameters (sometimes effecting a sign change in a coupling constant). However, these possibilities are improbable in the present cases (note the discussion of the fluoroprene spectrum). The observed lines were fitted with maximum errors of about 0.06 c.p.s., and this may be taken as an upper limit to the errors in the resulting parameters, since measurements are consistent to about that figure also.

The spectral analysis for the two AA'BB' cases was straightforward. Initial assignments were made utilizing the line-spacing rules and subsequent checks as described by Whitman.[8] The assignments were also checked by increasing the power of the radiofrequency signal and observing the double-quantum spectra.[9] In the case of *trans,trans*-1,4-dichloro-1,3-butadiene no fewer than 13 of the 15 distinguishable double-quantum transitions, and also all four triple-quantum transitions, were observed.

The spectrum of *cis,trans*-1,4-dichloro-1,3-butadiene offered greater difficulties, mainly because of its comparative simplicity (Figure 3); only 24 lines were of sufficient intensity for their positions to be measured accurately. Moreover the lines due to H-3, which occur well to low field of the others, were very nearly symmetrical in position. However, after numerous trial calculations a spectrum was obtained which was

(7) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).
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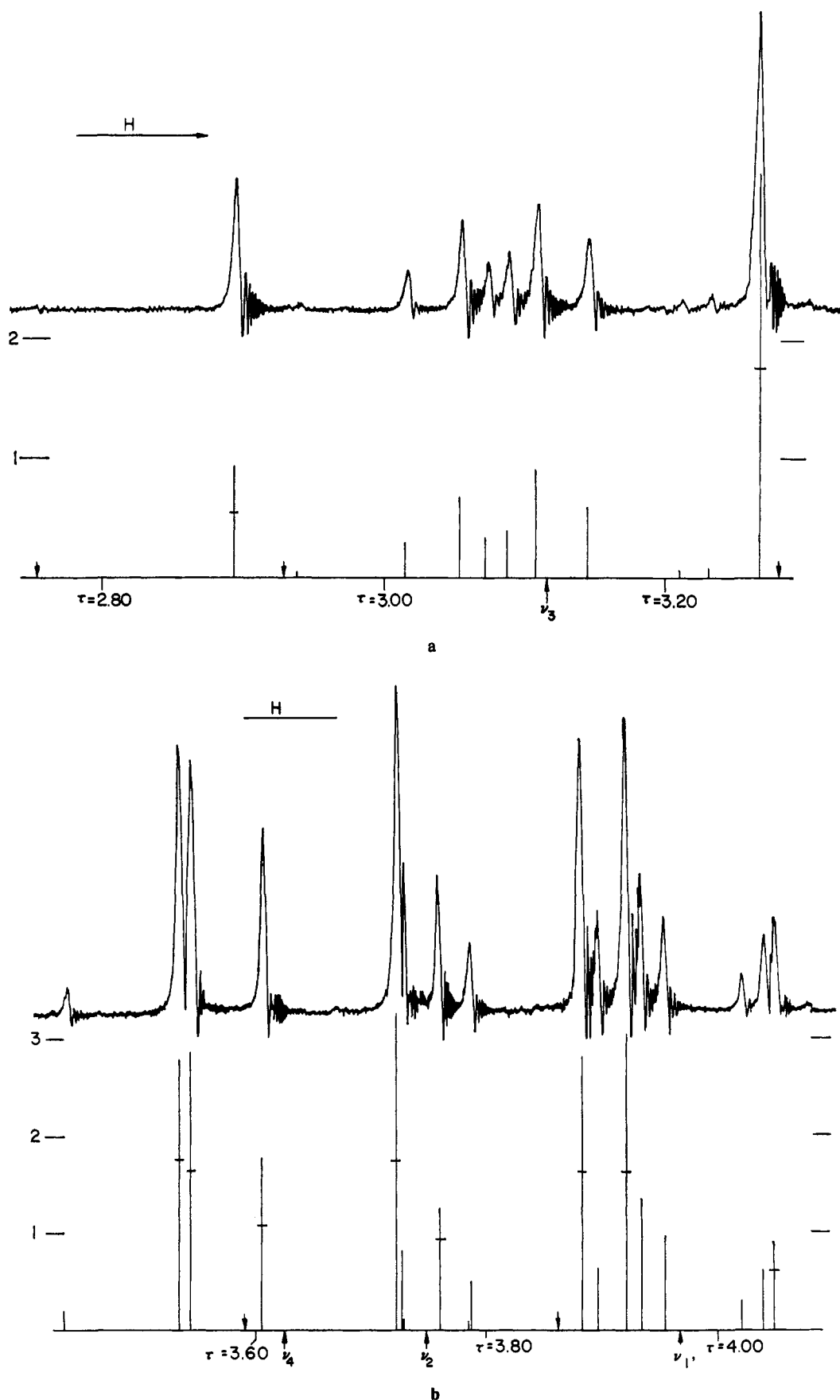(9) J. I. Musher, *ibid.*, **40**, 983 (1964).

Figure 3. (a) The n.m.r. spectrum of *cis,trans*-1,4-dichloro-1,3-butadiene at 60 Mc.p.s. and 30°, with lines assigned to proton H-3. The small horizontal bars on some of the calculated lines indicate that two lines are actually involved, with separations at <0.1 c.p.s. The small vertical arrows above the base line indicate the positions of lines of very low intensity. (b) The n.m.r. spectrum of *cis,trans*-1,4-dichloro-1,3-butadiene at 60 Mc.p.s. and 30°, with lines assigned to protons other than H-3. The small horizontal bars on some of the calculated lines indicate that two lines are actually involved, with separations at <0.1 c.p.s. The small vertical arrows above the base line indicate the positions of lines at very low intensity. Note that the scales of Figures 3a and 3b are different.
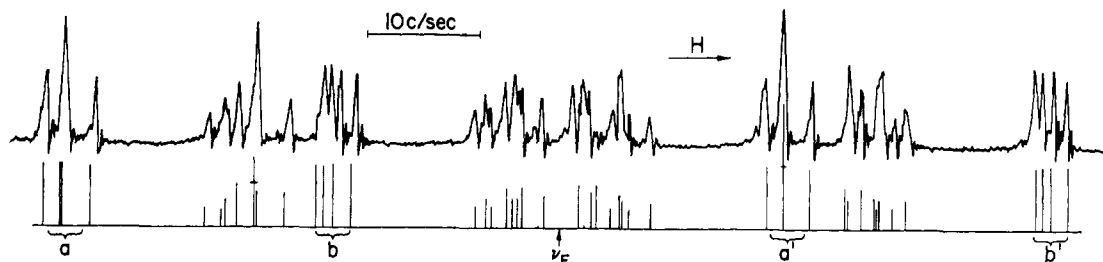
Figure 4. The ^{19}F spectrum of fluoroprene at 56.4 Mc.p.s.: a, observed; b, calculated.

sufficiently similar to the observed one to permit assignment of the lines, and the final fit to the spectrum was very good. It appears that no fewer than ten of the observed lines are in fact very close doublets.

The spectrum of chloroprene also proved rather difficult to assign, principally because the chemical shifts between protons 1, 1', and 4' were relatively small. The final iterations using LAOCOON II were made assigning 47 observed lines, and the result was a very good agreement between the calculated and observed spectra.

The proton spectrum of fluoroprene was first treated as the superposition of two ABCDE subspectra[10] (differing in the spin of the fluorine nucleus) and the initial assignment was relatively simple. This procedure gave two sets of effective proton chemical shifts which differed from one another by the magnitude of the (H,F) coupling constants. The procedure also gave two sets of (H,H) coupling constants which were in good agreement with one another. However, for one of the subspectra the effective chemical shifts of protons 1 and 1', that is $\nu_1 - \frac{1}{2}J_{1F}$ and $\nu_{1'} - \frac{1}{2}J_{1'F}$, were almost exactly equal, and consequently $J(1,1')$ was almost indeterminate from this subspectrum and was held constant during this part of the calculation. The parameters were then refined by carrying out the full, six-spin calculation using LAOCOON II, but the iterative fitting was done assigning proton lines only because their positions were measured more accurately than those of the fluorine lines (since an A-60 spectrometer was used for the measurement of the former and a DP-60 for the latter). Subsequent calculation of the fluorine lines with the parameters derived from fitting the proton lines gave a good fit to the observed ^{19}F spectrum (Figure 4).

One peculiarity of the fluorine spectrum can be seen from Figure 4. Bands a and a' appear almost identical, as do bands b and b'. Moreover calculation shows that the lines in these four bands are about twice as intense as the remaining lines. This situation may be rationalized as follows. Protons 1 and 1' are loosely coupled to all the other nuclei except the fluorine. Thus the nuclear magnetic system is approximately ABCMNX. For calculation of the fluorine spectrum we may consider that there are four spin states of 1 and 1', namely, $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, and $\beta\beta$, and that mixing may occur only between states $\alpha\beta$ and $\beta\alpha$. Thus we have three superimposed subspectra. Moreover the effect of 1 and 1' on the subspectra arising from spin states $\alpha\alpha$ and $\beta\beta$ may be entirely taken into account if we use effective fluorine chemical shifts of (i) $\nu_F +$

(10) J. A. Pople and T. Schaefer, *Mol. Phys.*, 3, 547 (1960); P. Diehl and J. A. Pople, *ibid.*, 3, 557 (1960).

$\frac{1}{2}J_{1'F} + \frac{1}{2}J_{1F}$ for state $\alpha\alpha$ and (ii) $\nu_F - \frac{1}{2}J_{1'F} - \frac{1}{2}J_{1F}$ for state $\beta\beta$. It can be seen that once this approximation is assumed, calculations for the $\alpha\alpha$ and the $\beta\beta$ states will be identical and therefore the two derived subspectra also will be identical. Bands a and b form one subspectrum and bands a' and b' form the other subspectrum. The separation between the centers of the subspectra should be $\approx J_{1'F} + J_{1F}$, as is observed. Furthermore the splitting between bands a and b corresponds to the next largest (H,F) coupling, namely, J_{3F}. The remaining bands are much more complex, as is expected, due to the mixing of states $\alpha\beta$ and $\beta\alpha$ of protons 1 and 1'. Finally for the $\alpha\alpha$ and $\beta\beta$ states, 1 and 1' may be treated as a single magnetic particle. This is not true of the remaining spin states $\alpha\beta$ and $\beta\alpha$. Thus degeneracies lead to the fact that intensities in bands a, a', b, and b' are roughly twice those for the remaining lines.

The point made earlier about the possible interchange of some line assignments is clearly illustrated by the spectrum of fluoroprene, although in this case one such assignment is preferable to the other (see Figure 5). There are two sets of lines for which such alternative assignments are feasible, namely, those of protons 1 and 1' for the α-spin of the fluorine nucleus. In each case the two calculated spectra are obtained by the LAOCOON fitting procedure from alternative assignments, which in fact lead to differing signs (and slightly different magnitudes) for one of the coupling constants. The upper calculated spectrum is obviously the better in each case. Such comparison diagrams are quite common in the literature but the differences shown in Figure 5 are perhaps finer than most, as can be seen from the scale. Significant deviations from the observed pattern were obtained by alteration of the appropriate coupling constants by only 0.05 c.p.s. The values of the coupling constants obtained from the above discussion show that $^4J_c < ^4J_t$, which agrees with the results for the closely related molecule chloroprene.

Results and Discussion

The (H,H) coupling constants are listed in Table I. Since these will be discussed in detail in the second paper[5] of this series, they will not be dealt with here.

Chemical Shifts. The chemical shifts obtained (using solution conditions as stated in the Experimental section) are given in Figure 1. These values do not warrant lengthy discussion for two reasons. Firstly, chloroprene and fluoroprene were studied in solution in xylene, whereas the 1,4-dichlorobutadienes were examined neat. Values for 2,3-dichloro buta-
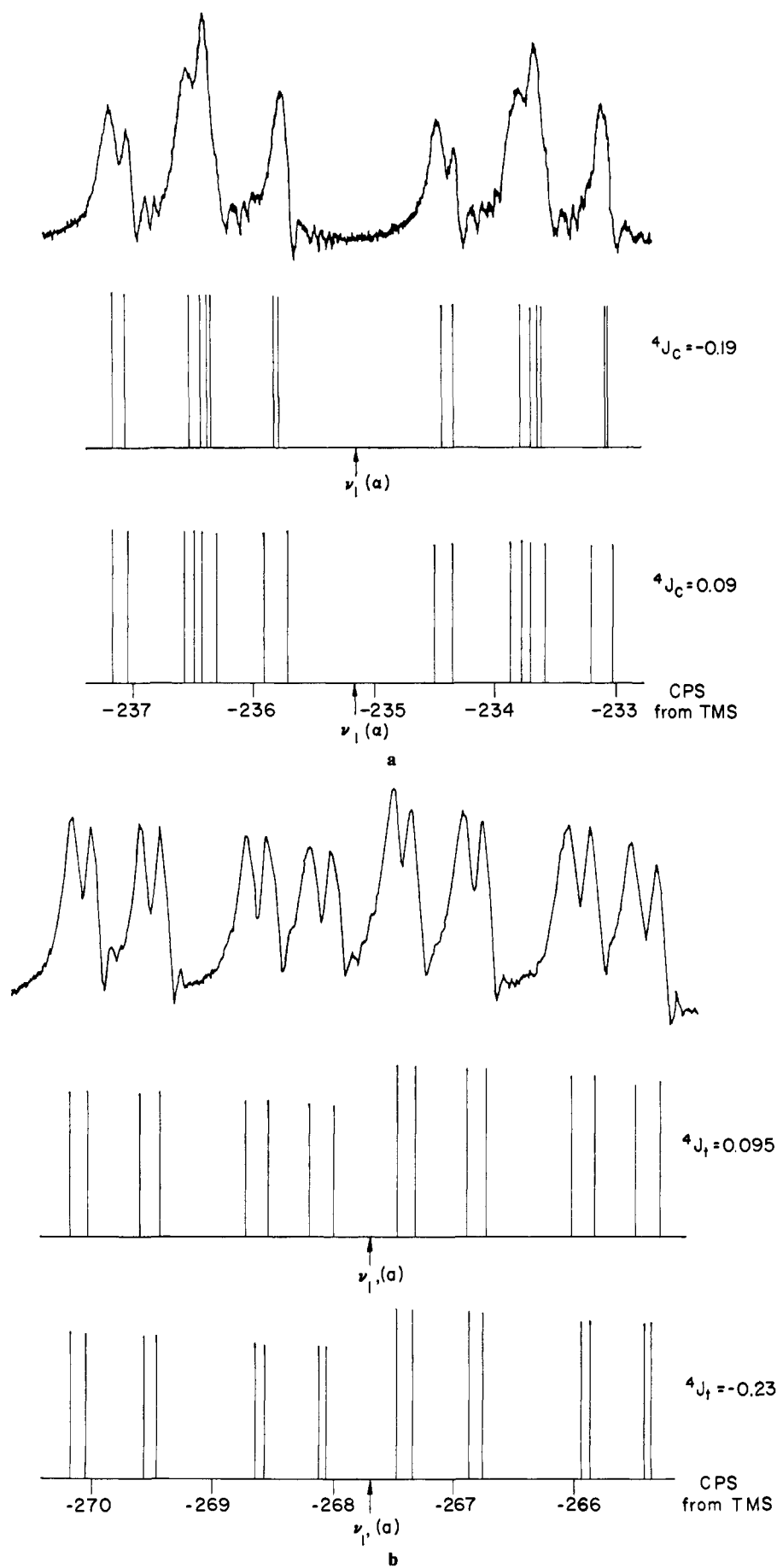
Figure 5. (a) Observed and two calculated proton spectra (for different assignments) of fluoroprene for proton 1. Subspectra for the α spin of the fluorine nucleus only. (b) Observed and two calculated proton spectra (for different assignments) of fluoroprene for proton 1'. Subspectra for the α spin of the fluorine nucleus only.

Table I. (H,H) Coupling Constants[a] for Some Halogenated 1,3-Butadienes

Compd.	^2J	^3J_c	^3J_t	^3J_s	^4J_c	^4J_t	$^5J_{tt}$	$^5J_{cc}$	$^6J_{tc}$
Fluoroprene (2 ≡ F)	−2.74 (1,1') 1.24 (4,4')	11.145	17.32	...	−0.19	0.095	1.49	0.70	0.73 (1,4') 0.62 (1',4)
Chloroprene (2 ≡ Cl)	−1.07 (1,1') 0.95 (4,4')	10.51	16.54	...	−0.60	−0.18	1.42	0.67	0.72 (1,4') 0.61 (1',4)
cis,cis-1,4-Dichloro-1,3-butadiene (1,4 ≡ Cl)	...	7.28	...	10.36	...	−1.17	1.74	...	...
trans,trans-1,4-Dichloro-1,3-butadiene (1',4' ≡ Cl)	...	...	13.12	11.24	−0.69	...	...	0.83	...
cis, trans-1,4-Dichloro-1,3-butadiene (1,4' ≡ Cl)	...	7.24	13.34	10.82	−0.71	−1.19	...	...	0.76
2,3-Dichloro-1,3-butadiene[b] (2,3 ≡ Cl)	−1.70	...	...	...	...	...	1.90	0.59	0.55

[a] In c.p.s. [b] See ref. 2 (solution in CCl_4).

diene[2] and for ethylene derivatives[11,12] have been reported for CCl_4 solutions. The solvent shifts from the neat liquids to CCl_4 are small, but are often large for xylene solutions. Secondly, the major interest lies in the coupling constants. However, it may be said that qualitatively the shifts are as one would expect from comparisons with ethylene derivatives.[11,12]

One interesting feature is that proximity in space of a chlorine or fluorine atom four bonds away (that is, in a 1,3 or 2,4 relation) causes a downfield shift of ≈0.4 p.p.m. Such effects of a spatially proximate C–Cl or C–F group have been noted in a variety of other compounds.[13] Viehe[14] has noted that there may be an attractive interaction between halogen and hydrogen atoms in these positions, thus stabilizing cis-1-fluorobutadiene over trans-1-fluorobutadiene. Such an interaction would also explain the high barrier to internal rotation about the central C–C bonds of chloroprene and fluoroprene as compared to butadiene itself, this resulting from a stabilization of the s-trans form.[15]

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However, if this were the only contribution to the 1,3-chemical shift effect, one might anticipate a larger shift for fluoroprene than for chloroprene, rather than the reverse as actually observed. In any event the downfield shift is not observed, as would be expected, for 1',3 or 2,4' pairs of hydrogen and halogen atoms.

The ^{19}F chemical shift[16] of fluoroprene was found to be $\phi^* = 114.1$ for an approximately 50% solution in CCl_3F. This compares with $\phi^* = +114.4$ for vinyl fluoride.[12]

(H,F) Coupling Constants for Fluoroprene. The vinylic (H,F) coupling constants, $^3J_f(H,F) = 47.93$ c.p.s. and $^3J_c(H,F) = 15.76$ c.p.s. are very close to the analogous values in 2-fluoropropene[17] (+48.6 and +16.6 c.p.s., respectively). There is also very good agreement between the value of ^3J_s in fluoroprene (25.15 c.p.s.) and that deduced[18] for the trans conformation in allyl fluoride ($^3J_t = 22 - 25$ c.p.s.). In contrast with the small negative constants found in allyl fluoride, the long-range H,F coupling constants in fluoroprene are small and positive ($^4J_c = +0.41$, $^4J_t = +1.19$ c.p.s.).

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(17) M. Y. DeWolf and J. D. Baldeschwieler, J. Mol. Spectry., 13, 344 (1964).

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