Title
NMR FLUORINE-FLUORINE COUPLING CONSTANTS II SATURATED ORGANIC COMPOUNDS

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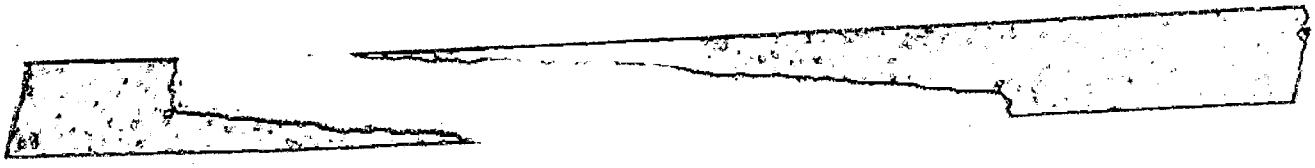

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The spectra of fluorine substituted saturated organic compounds have been investigated. It has been found that the coupling constants between 1,2 fluorine atoms are usually near zero. The coupling constants between 1,3 fluorine atoms in a free chain are usually between 7 and 10 cps if all of the intermediate skeletal atoms are carbon atoms. If one of the intermediate skeletal atoms is a nitrogen atom, these coupling constants go up to between 10 and 17 cps. The coupling constants between 1,4 fluorine atoms are usually in the range 2 to 7 cps when a nitrogen atom is in the intermediate skeletal chain. Rings usually reduce all coupling constants below the above stated values.

Several exceptions are found to these generalizations. These generalizations with their exceptions lead the authors to believe that in the case of coupling constants between fluorine atoms, the main effect is not a through-the-bond effect as has been formerly assumed, but rather a direct-through-space effect. The approximate order of magnitude of this through-space coupling is given by $D > 2.73$ Å, $J = 0$ cps;

$D < 2.73$ Å, $J = (2.73 \text{ Å} - D)$ 507 cps where J is the coupling constant and D is the distance between the fluorine atoms. It is demonstrated that the restricted rotation about the carbon-carbon bonds has little to do with the near-zero coupling constants, but that these are readily explained on the basis of through-space coupling.

Introduction

In 1956 Saika and Gutowsky[1] reported a near-zero coupling constant between the fluorine atoms on adjacent carbon atoms in the NMR spectrum of $CF_3CF_2N(CF_3)_2$. This appeared anomalous to them since fluorine-fluorine coupling constants were known to be large, and in particular, since the coupling constant between the fluorine atoms in the two nonequivalent perfluoromethyl groups was found to be 6 cps. Since that time several other similar cases have been reported in the literature.[2,3,4,5] Furthermore, it has been assumed that the restrictions upon rotation are responsible for these near-zero coupling constants. This idea was presented in the literature by Crapo and Sederholm.[2]

Theoretically, not much headway has been made toward prediction of fluorine-fluorine coupling constants due to the complexity of the problem. However, it is clear from the work of McConnell[6] that there are several types of terms which may give sizeable contributions.

Little has been said explicitly in the literature concerning the mechanism for fluorine-fluorine coupling constants; however, it seems to be generally assumed that, as in the hydrogen case,[7] the fluorine-fluorine coupling takes place through the bonds. The discussion herein, examines the validity of this assumption.

Experimental and Interpretation

The spectra were run on a Varian spectrometer at 56 Mcs. All of the compounds listed gave first order spectra with the exception of small second order perturbations of some of the intensities. The samples were sufficiently pure so that no extraneous lines appeared. Coupling constants[8] are tabulated in Table I. The interpretation of all spectra was straight forward except for perfluorodiethylmethylamine,[9] compound 1. In this compound the multiplicity and overlap of lines made the interpretation somewhat complex. In Fig. 1 the observed spectrum is compared with the calculated spectrum based on the values of the coupling constants listed in Table I.

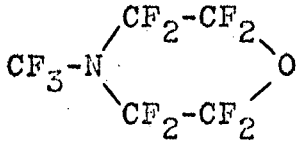
The spectrum of compound 2 consists of two lines, one containing seven equally spaced components, the other containing ten equally spaced components. Likewise, the spectrum of compound 3 consists of two lines, one containing five equally spaced components, the other containing seven equally spaced components. Although very surprising, the analysis of these spectra was unambiguous and yielded the values of J listed in Table I.

Table I

Serial Number	Compound	Coupling Constants (cps)
1	CF_3-CF_2 $\quad\quad\quad\quad N-CF_3$ CF_3-CF_2 a b c	$J_{ab} = 5.1$ $J'_{ab} = 5.1$ $J_{ac} = 6.8$ $J_{bc} = 15.8$
2	CF_3-CF_2 $\quad\quad\quad\quad N-CF_2-CF_3$ CF_3-CF_2 a b b a	$J_{ab} = 6.8$ $J'_{ab} = 6.8$
3	$CF_3-CF_2-O-CF_2-CF_3$ a b b a	$J_{ab} = 1.7$ $J'_{ab} = 1.7$
4[a)]	CF_3-CF_2-COOH a b	$J_{ab} = 1.38$
5[b)]	$CF_3-CF_2-N(CF_3)_2$ a b c	$J_{ab} \leq 1$ $J_{ac} = 6$ $J_{bc} = 16$
6	$CF_3-CF_2-CF_2-NF_2$ a b c d	$J_{ab} \leq 1$ $J_{ac} = 8.6$ $J_{ad} = 2.2$ $J_{bc} \leq 1$ $J_{bd} = 10.5$ $J_{cd} \leq 1$

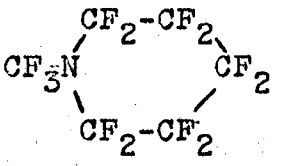
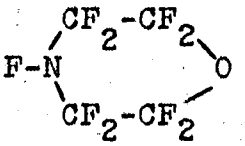
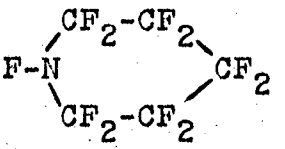
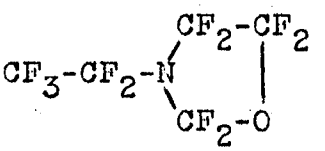
(Continued)

Table I (Continued)

Serial Number	Compound	Coupling Constants (cps)
7	CF_3-CF_2-CF_2-COOH a b c	$J_{ab} \leq 1$ $J_{ac} = 9.9$ $J_{bc} \leq 1$
8	CF_3-CF_2-CF_2-$COOCH_3$ a b c	$J_{ab} \leq 1$ $J_{ac} = 9.0$ $J_{bc} \leq 1$
9	CF_3-CF_2-CFClI a b c	$J_{ab} \leq 1$ $J_{ac} = 10.8$ $J_{bb'} = 270.4$ $J_{bc} = 14.6$
10	$(CF_3)_3$=CF a b	$J_{ab} = 4.0$
11	CF_3-CF_2-CF_2H (D) a b c	$J_{ab} \leq 1$ $J_{ac} \leq 1$ $J_{bc} = 4.0$-4.5
12	 a b c	$J_{ab} = 13.6$ $J_{ac} \leq 2$ $J_{bc} \leq 2$ $J'_{bc} \leq 2$

(Continued)

Table I (Continued)

Serial Number	Compound	Coupling Constants (cps)
13	 a b c d	$J_{ab} = 16.4$ $J_{ac} \leq 2$ $J_{ad} \leq 2$ $J_{bc} \leq 2$ $J_{bc} \leq 2$ $J_{bd} \leq 2$ $J_{cd} \leq 2$
14	 a b c	$J_{ab} \leq 2$ $J_{ac} \leq 2$ $J_{bc} \leq 2$ $J'_{bc} \leq 2$
15	 a b c d	$J_{ab} \leq 2$ $J_{ac} \leq 2$ $J_{ad} \leq 2$ $J_{bc} \leq 2$ $J'_{bc} \leq 2$ $J_{bd} \leq 2$ $J_{cd} \leq 2$
16	 a b c d e	$J_{ab} \leq 1$ $J_{ac} = 6.5$ $J_{ad} = 6.5$ $J_{ae} \leq 1$ $J_{bc} = 9.9$ $J_{bd} = 9.9$ $J_{be} \leq 1$ $J_{cd} \leq 1$ $J_{ce} \leq 1$ $J_{de} = 3.5$

(Continued)

Table I (Continued)

Serial Number	Compounds	Coupling Constants (cps)
17[c)]	C_6H_5-CH — CH_2 | | CF_2-CF_2 a b	$J_{ab} \leq 1$ $J_{ab'} \leq 1$
18[d)]	CF_2Br-CFBrCl a b c	$J_{ab} = 159$ $J_{ac} = 13$ $J_{bc} = 14$
19[e)]	CF_2Br-CFHCl a b c	$J_{ab} = 175$ $J_{ac} = 18$ $J_{bc} = 18$

a) See Reference 3 in text.

b) See Reference 1 in text.

c) See Reference 5 in text.

d) See Reference 10 in text.

e) See Reference 11 in text.

Discussion

Let us first examine the near-zero coupling constants. They appear in many cases between fluorine atoms on adjacent, saturated carbon atoms. These cases fall into two classes, one where relatively free rotation is allowed around the carbon-carbon bond, and another where rings limit the free rotation about the carbon-carbon bond. Near-zero coupling constants occur in both of these cases. However, there seems to be no set type of molecule which always yields a near-zero coupling constant. For instance, in compounds 1, 2, 3, and 4 the coupling constants between the CF_3 group and the adjacent CF_2 group are nonvanishing, whereas the coupling constants between the CF_3 group and the adjacent CF_2 group are nearly zero in a whole host of compounds. It has been assumed that the near-zero coupling constants come about as a result of averaging nonzero coupling constants over the three stable configurations with respect to rotation about the connecting carbon-carbon bond. Due to the common occurrence of this phenomenon, if this explanation is valid, one must assume that the coupling constant does not vary much from compound to compound but is only a function of the dihedral angle, as in the case of hydrogen.[7] However, this would lead one to predict that the coupling constants in all compounds having the CF_3-CF_2- group would be nearly zero which is not the case. Hence, it appears that the near-zero coupling is not explained by any accidental, mutual cancellation of the coupling constants averaged over three staggered configurations.

One readily accounts for all fluorine-fluorine coupling constants in saturated compounds thus far investigated if one assumes that the major contribution to the coupling constants comes about as a direct-through-space effect rather than a through-the-bonds effect. The large excursions of the p electrons in fluorine atoms make it reasonable to assume that such an effect could be significant in the case of fluorine-fluorine coupling constants and not significant in the case of hydrogen-hydrogen coupling constants. In the latter case it has already been well established[7] that the coupling is mainly a through-the-bond interaction; however, Roberts[12] has suggested the possibility of through-space coupling to explain long range hydrogen-hydrogen and hydrogen-fluorine coupling constants. Qualitatively, through-space coupling explains the near-zero coupling constants in many of the fluorocarbons. These near-zero coupling constants always occur between fluorine atoms on adjacent carbon atoms. Such fluorine atoms are held apart in space by the bonding. Assuming all bonding to be tetrahedral, the carbon-carbon bond distance to be 1.54 Å and the carbon-fluorine bond distance to be 1.33 Å, and assuming that the staggered configurations are the favored ones, the closest fluorine-fluorine approach between the two sets of fluorine atoms in the $R\text{-}CF_2\text{-}CF_2\text{-}R'$ group is 2.73 Å. We propose that the coupling through bonds is small as is the case in the hydrogen analogs; that 2.73 Å is too great a distance to result in any through-space contribution; and that 2.73 Å is just outside the radius at which through-space coupling becomes

important. This is quite reasonable since the sum of the van der Waal radii for two fluorine atoms is 2.70 Å. One can then readily see that a small change in the C-C-R bond angle would result in closer stable distances between the adjacent fluorine atoms and thus in a larger coupling constant. This opening of the C-C-R angle can be brought on by steric hindrance, if R is sufficiently bulky.

The large coupling constants between 1,3 fluorines (fluorines on skeletal atoms which are β to each other) can be explained on this basis. If coupling through the bonds is small between 1,2 fluorines (fluorines on adjacent skeletal atoms) it is certainly negligible in the 1,3 case. In two of the nine possible staggered configurations of the $-CF_2-CF_2-CF_2-$ group the 1,3 fluorines are closer to each other than the closest stable distance between 1,2 fluorines. Again, calculating on the basis of the staggered configurations and the above bond distances and angles, the 1,3 fluorine-fluorine distance in these two configurations is 2.51 Å. There is some evidence[13] that these configurations are not the stable ones, but the structural data are not sufficient to warrant their use over the tetrahedral assumption.

The fluorine-fluorine distance between gem-fluorine atoms in perfluorocyclohexane, again assuming tetrahedral angles and normal bond distances, is 2.17 Å. In this case, the coupling constant is 284 cps. Here we again propose that the contribution from the through-bond coupling is small, and most of the

284 cps comes about through space as might be expected from the fluorine-fluorine distance which is much smaller than the sum of the van der Waal radii.

Several other compounds exist in which the fluorine-fluorine distances and coupling constants have been measured. However, in all of these cases, π electrons are involved in the bonding. Certainly, in this model one would expect the injection of π electrons into the space between the two fluorine atoms to substantially alter the coupling constants.

One can make a crude calculation of the coupling constant to be expected on the basis of this model for 1,3 fluorine atoms. From the gem-fluorines in cyclohexane one assigns 284 cps to the coupling constant at 2.17 Å. The near-zero coupling between 1,2 fluorine atoms which are separated by approximately 2.73 Å in two of the three possible staggered configurations, leads one to assign a value of zero to J for fluorine atoms separated by this distance. It is also noted that a slight decrease in this distance seems to cause J to increase to several cycles. Certainly a plot of through-space coupling constants as a function of distance should increase somewhat more rapidly as the distance decreases. However, as a first approximation, we assume that a straight line connecting these two points should give a proper order of magnitude. We would expect this approximation to give a slightly high value for the coupling constant. The equation for a straight line through these points is $J = (2.73\ \text{Å} - D)507$ cps. The coupling constant at 2.51 Å is then approximately 111 cps.

However, only two of the nine possible configurations result in this distance, and the other seven configurations yield fluorine-fluorine distances greater than the 2.73 Å corresponding to zero coupling. We weight all nine of these possible configurations equally, although there may be some small barrier against the configurations which do not correspond to a zigzag carbon skeleton. Likewise, the 2.51 Å figure is probably smaller than the actual distance, which would result in too large a coupling constant. On this basis, the coupling constant between 1,3 fluorine atoms is calculated to be (2/9) x 111 cps = 24.5 cps. This is large as expected and can readily be accounted for by the curvature of J vs. D and by the error in the assumed geometric configuration.

One may extend this calculation with less precision to the 1,4 fluorine coupling constants. These fluorine atoms are separated by five bonds and probably are essentially not coupled through the bonds. In as crude a calculation as this, one cannot hope to tell the difference between a nitrogen atom in the chain with 90° bond angles, and a carbon atom in the chain with 109-1/2° bond angles. The calculation is again made for an all carbon chain with tetrahedral angles, but it should be about the same if a nitrogen takes the place of one of the chain carbon atoms. Again, taking the staggered configurations as the stable ones, there are 27 different relative positions for a pair of fluorines on the 1 and 4 carbon atoms. All of the distances between the fluorines are greater than 2.75 Å except for four configurations in which the distances are 1.76 Å

(two cases) and 2.46 Å (two cases). Certainly, the two configurations corresponding to the 1.76 Å cannot exist as preferred configurations because of the close fluorine-fluorine approach. In order to increase this distance, one must rotate about some of the carbon-carbon bonds which should be relatively easy to do. It seems reasonable that rotation will occur about the carbon-carbon bonds until the fluorine atoms come to a distance of approximately 2.5 Å, 0.2 Å less than the van der Waal radii. This rotation lengthens the 2.46 Å fluorine-fluorine distance to a distance greater than 2.73 Å and therefore these configurations can be neglected in the calculation. The coupling constant associated with 2.5 Å again assuming a linear J vs. D function is 111 cps. These two configurations have a weight of 2/27, and therefore the coupling constant expected for the 1,4 fluorine atom case is (2/27) x 111 = 8 cps. Again, this is a little above the observed value and is readily explained on the basis of a nonlinear J vs. D and on the basis of errors in the assumed amount of twist of the carbon-carbon dihedral angle.

This model is also capable of explaining why the two coupling constants between the gem-fluorine and the third fluorine atom are the same in compounds with the general form CF_2X-CFYZ where X, Y, and Z are halogens or hydrogen. The coupling constant between trans fluorine atoms is zero on this model, and the coupling constant between gauche fluorine atoms would be a small, constant Jg. An equal population of the

three rotational forms would then result in equal coupling constants, as observed, equal to (2/3) Jg. At room temperature, the difference in depths of the three potential minima is probably small enough so that equal population of the three rotational isomers is a good assumption.

In compound 5, the coupling constants are what would be expected on the basis of the model presented, the 1,2 fluorine atoms being coupled by less than one cycle, the 1,3 fluorine atoms being coupled by 16 cps, and the 1,4 fluorines being coupled by 6 cps in reasonable agreement with the calculated values. In compound 1 which is very similar to 5, the coupling constants are also similar except for the coupling between the 1,2 fluorine atoms. Here, that coupling has gone up to 5.1 cps. This might be expected from a model of the compound since there are a large number of atoms crowded around the central nitrogen atom. This tends to increase the C-C-N bond angle, thus throwing the 1,2 fluorine atoms closer to each other, and increasing the coupling constant. One might expect this effect to be more pronounced in compound 2 where another perfluoroethyl group is taking the place of a perfluoromethyl, and indeed this is the case. Here, the 1,2 fluorine coupling constant has gone up to 6.8 cps which would imply a further increase in the C-C-N angle, as is expected.

In compound 3, the 1,2 coupling constant is again non-vanishing because of opening of the C-C-O bond angle due to steric hindrance between the two ends of the molecule. Note that here the 1,2 coupling constant is less than in compound 1

since the extra perfluoromethyl group is absent, thus not yielding as great an amount of steric hindrance. Also, the 1,4 coupling constant is about what it is in compound 6 and less than in compounds 1 and 2. A tertiary nitrogen in the chain certainly throws the 1,4 carbon atoms closer together than a secondary oxygen in the chain.

In compound 4 the coupling constant is small, but nonzero. The main contribution to this coupling constant may come about through the bonds, although there may also be a small opening of the C-C-C bond angle due to the steric repulsion between the methyl group and the carboxyl group. Compound 7 gives very similar results to this with the 1,3 fluorine coupling constant being slightly less than the 1,3 fluorine coupling constants in compounds 1 and 5. This is what is expected since in compounds 1 and 5 an intermediate chain atom is a nitrogen atom with approximately 90° bond angles, whereas in this compound all intermediate chain atoms are carbon atoms with 109-1/2° bond angles, thus throwing the 1,3 fluorine atoms further apart. It is not readily apparent why the 1,2 coupling constant in this compound is smaller than in compound 4; however, this difference is minor and the electronic structure has changed substantially in this area of the molecule. In compound 8 the coupling constants are very similar to compound 7. The decrease in the 1,3 fluorine atom interaction is reasonable since the added methyl group will interfere with the perfluoromethyl group, partially opening up the bond angle

between the α, β and γ carbon atoms, thus taking the 1,3 fluorine atoms further apart. Compound 6 gives very similar results. Again, it should be noted that the 1,3 fluorine atom coupling constant is smaller when all of the intermediate atoms are carbon atoms, than when one of them is a nitrogen atom.

Compound 9 again shows two different kinds of 1,2 coupling constants, a near-zero one which results from normal bond angles; and one which is equal to 14.6 cps probably resulting from the steric repulsion between the Cl and I atoms and the adjacent CF_2 group, thus throwing the two sets of fluorine atoms closer together. The 1,3 coupling constant is quite normal. Compound 10 shows a large 1,2 coupling, again due to the steric repulsion of the three CF_3 groups, thus bringing each of them closer to the lone fluorine atom.

The spectra of compounds 11 were reported by G. V. D. Tiers in connection with an isotopic substitution investigation. The two near-zero coupling constants were inferred from his paper. The near-zero coupling assigned to the 1,2 coupling is quite reasonable; however, on the basis of the other compounds we have investigated the near-zero coupling between the 1,3 fluorine atoms seems highly unlikely.

A six-membered ring, assuming it to be in the chair form, would hold 1,3 fluorine atoms apart sufficiently so that one would expect a near-zero coupling constant between them. Likewise, one would also expect a near-zero coupling constant for

the 1,2 case. This is observed in compound 12 where the only large coupling constant is between the nonring CF_2 group and the two CF_2 groups β to it. This coupling constant is 13.6 cps as one would expect with an intermediate N atom. It should be noted that the ring structure keeps the CF_3 group far away from the CF_2 group γ to it thus resulting in a near-zero coupling constant between these two sets of fluorine atoms.

This phenomenon is likewise observed in compound 13 where again the only large coupling constant is between the nonring CF_3 group and the two CF_2 groups β to it. Since a nitrogen is in the intermediate chain, the coupling constant is in the range 12-17 cps. Again in this compound one finds a near-zero coupling constant between the CF_3 group and the CF_2 groups γ to it because of the forced geometry of the ring system.

In compounds 14 and 15 all coupling constants are nearly zero since the ring structure prevents any pair of fluorine atoms from getting within 2.73 Å of each other except for gem-fluorine atoms which are nearly equivalent; hence the splitting is not observable.

When the ring is reduced to five members such as in compound 16, fluorine atoms which are on adjacent carbon atoms are still not coupled, but fluorine atoms removed by one more bond are capable of getting closer together and therefore are slightly coupled. The 1,4 coupling constants across the nitrogen atom between the side chain and ring are quite normal. The 1,3 coupling constants across the nitrogen atom between the

side chain and ring are somewhat smaller than usual, but the geometry of the strained ring system may keep these two sets fo atoms further apart than they would be in an unrestrained linear chain. It is reassuring to note that the coupling constants across the nitrogen atom are the same to each of the two sets of ring fluorines which are adjacent to the nitrogen atom. This would be expected if it is indeed a through-space coupling since these two sets of atoms occupy similar positions in space with respect to the perfluoroethyl group. However, the electronic structure in the two N-C bonds should be somewhat different due to the asymmetrically placed oxygen atom and hence if the coupling were through-the-bonds, one would expect a different coupling constant between the nonring fluorines and these two sets of ring fluorines.

In compound 17, the four-membered ring certainly holds the two sets of fluorine atoms far enough apart to yield a near-zero coupling constant which is observed. It is to be noted that in this case, the fluorines are probably locked into the eclipsed configuration whereas in the six-membered rings, the fluorine atoms are restrained to two of the three staggered configurations. All of these cases result in near-zero coupling constants. It is almost impossible to imagine any kind of function of J vs. dihedral angle such that the average of the three staggered configurations would yield zero, the average over the two gauche staggered configurations would yield zero, and the value of the coupling constants corresponding to eclipsed and 120° would be

zero, expect for the trivial case where the coupling constant equals zero for all dihedral angles. Therefore, this set of examples implies again that averaging over various dihedral angles has little to do with the near-zero coupling constants.

In compounds 18 and 19 the 1,2 coupling constants are nonzero probably because of shortening of the fluorine-fluorine distance due to steric effects caused by the other halogens present. As presented earlier, in each compound, the two different 1,2 coupling constants are nearly equal which implies nearly equal residence time in the three rotational configurations.

Conclusions

The coupling constants between fluorine atoms in saturated, organic compounds can be explained if one assumes that the major portion of the coupling constant comes about as a direct coupling through space, rather than a coupling through the bonds. A reasonable order of magnitude for this coupling constant can be predicted from the equation $J = (2.73\ \text{Å} - D)507$ cps where D is less than 2.73 Å, and from the assumption that all staggered configurations of a molecule are equally probable unless they result in interatomic distances less than the van der Waal radii. The coupling constants between 1,2 fluorine atoms are usually nearly zero unless some shortening of the fluorine-fluorine distance occurs due to steric hindrance caused by atoms nearby. The coupling constants between 1,3 fluorine

atoms in a free chain are usually between 7 and 10 cps if all the intermediate skeletal atoms are carbon atoms. If one of the intermediate atoms is a nitrogen atom, these coupling constants go up to the range 10 to 17 cps due to the smaller nitrogen bond angles. The coupling constants between 1,4 fluorine atoms are usually in the range 2-7 cps if a nitrogen atom is in the intermediate skeletal chain. Rings usually hold the molecules more firmly, reducing all of the coupling constants.

Acknowledgements

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Figure Caption

Fig. 1 Experimental and theoretical fluorine resonance spectrum of $(CF_3-CF_2)_2-N-CF_3$:

a) $(CF_3)_2$ group

b) $(CF_2)_2$ group

c) CF_3.

Fig. 1a

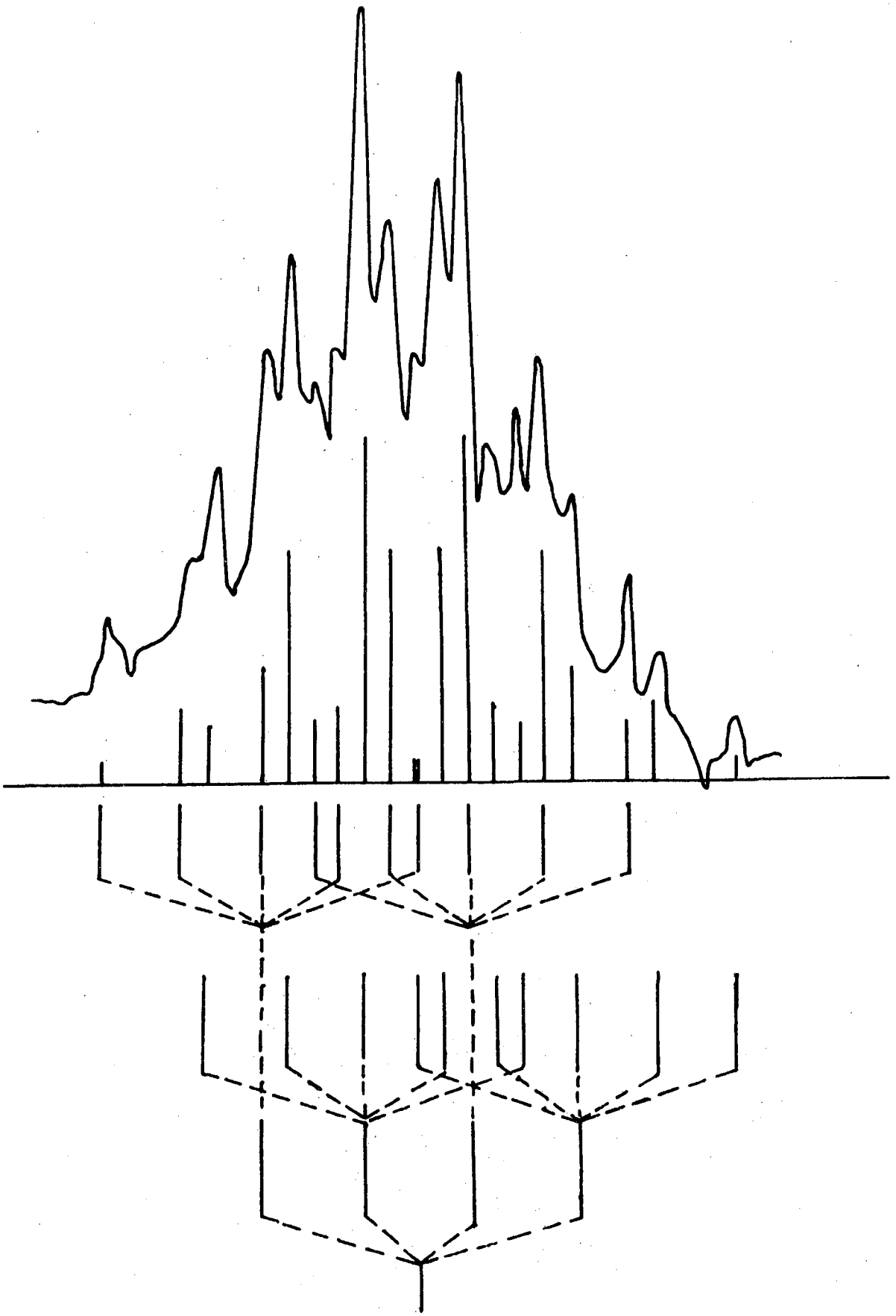

Fig 16

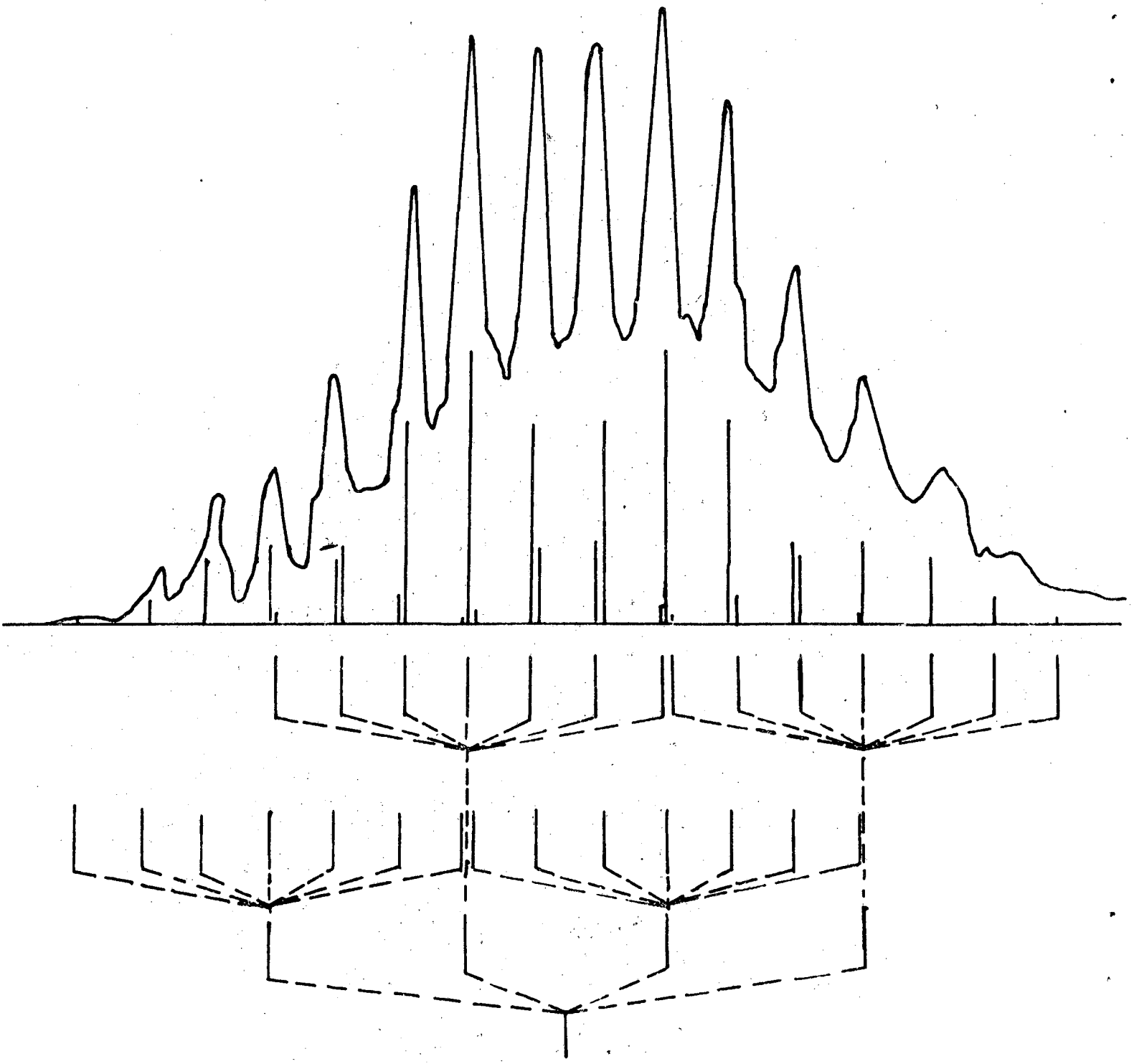

Fig 1c