The NMR Spectrum of a Conjugated Aldehyde:
Sorbaldehyde

P. ALBRIKTSEN[a] and R. K. HARRIS[b]

[a] Chemical Institute, University of Bergen, N-5000 Bergen, Norway and
[b] School of Chemical Sciences, University of East Anglia, Norwich NOR 88C, England

The NMR spectrum of *trans*-sorbaldehyde has been fully analysed and is consistent with an all-*trans*-conformation. Coupling constants to the aldehyde proton are measurable for up to four bonds between the coupled nuclei, and there is some indication of more extensive coupling. The coupling constants to the methyl group are measurable for nuclei separated by up to six bonds. The values of the coupling constant are discussed in relation to those for acroleins and for *trans*-penta- and hexa-dienes.

Several NMR investigations of α-β-unsaturated aldehydes have been reported.[1-4] Hoffman and Gronowitz[1] analysed the NMR spectrum of crotonaldehyde in order to explain the long-range coupling mechanism in unsaturated compounds. Moreover, the NMR analysis of acrolein has been published twice.[2,3] Klinck and Stothers[4] reported the chemical shift of the formyl proton in various aldehydes. Benzene-induced solvent shifts[5] have been used as an aid to the determination of stereochemistry for some α,β-unsaturated compounds. Crotonic acid derivatives,[6] *trans*-2,4-pentadienoic acid,[7] and *trans*-2,4-hexadienoic esters[8] have been analysed in detail by NMR. No highly conjugated aldehydes have, however, been completely analysed by NMR. This is partly because the unsaturated aldehydes are reactive and hence it is difficult to obtain spectra of the monomers, and partly because of the number of coupled protons in the molecules. The *trans*-sorbaldehyde studied in this work has eight coupled nuclei, which is too large a spin system for many computers programs to handle. This investigation was undertaken to obtain information about configuration and long-range (H,H) coupling constants in highly unsaturated aldehydes. It is of special interest to compare the NMR parameters obtained with those found for buta- and penta-dienes.[9]

EXPERIMENTAL

The 2,4-hexadienal, sorbaldehyde, was commercially available from Aldrich. The NMR spectrum of this compound showed two doublets in the aldehyde region with

intensities in the ratio *ca.* 1:20. The sorbaldehyde was purified by the following procedure: The crude mixture was cooled to *ca.* − 60°C, transferred to a pre-cooled filter funnel and allowed to warm up to *ca.* − 40°C. The mixture was then cooled to − 60°C again. The non-crystalline compounds or isomers were continuously sucked off. The cooling and heating cycle was repeated three times. The crystalline compound was allowed to melt and was collected. The NMR spectrum showed only one CHO doublet, which was taken as evidence of isomeric purity. The purified sorbaldehyde was assumed to be the all-*trans* isomer (see Fig. 1), as this isomer should show the higher melting point; this is confirmed by the NMR spectral analysis.

The sorbaldehyde (neat liquid) was introduced into a 5 mm O. D. sample tube, and a small quantity of TMS was added to serve as NMR locking and reference substance. The sample was degassed by the freeze, pump, thaw technique and sealed in the evacuated condition.

The spectra were recorded using a Varian Associates HA-100 spectrometer operating at 100 MHz. The spectra were recorded at ambient temperature (*ca.* 35°C) in the field-frequency lock mode with frequency sweep. The spectra for detailed measurement were recorded at 50 Hz sweep width and scan rate 0.02 Hz s^{-1}; they were calibrated every 5 Hz using a Hewlett-Packard 5212A frequency counter.

The computations were carried out using the IBM 360/50 computer at the University of Bergen and, in part, the Atlas Computer at the Science Research Council Atlas Laboratory, Chilton, Didcot, England. The results were plotted with a Calcomp Plotter.

SPECTRAL ANALYSIS

The NMR spectrum of the all-*trans* sorbaldehyde gave well-separated bands for each of the nuclei involved except for protons A and B. The spectrum is therefore of the $ABKMXY_3$ type (see Fig. 1), with only one pair, AB, of
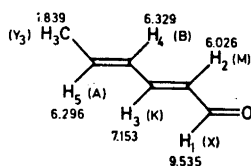

Fig. 1. trans-Sorbaldehyde: Notation, and chemical shifts in ppm from TMS.

tightly-coupled nuclei. Considerable second-order splittings were, however, observed. The high frequency doublet is easily assigned to the aldehyde proton, and the low-frequency band (Fig. 2) to the CH_3-group. The olefinic nuclei, with $\delta \sim 5.8$ to 7.5, can be assigned as follows: Assuming negligible or small coupling between the proton K and protons X or Y_3 and with the M nucleus in either the α or β spin state, the spectrum of nucleus K should resemble the K part of an ABK spin system. In fact, the high frequency multiplet of the olefinic region looks like the K part of two ABK spin systems (Fig. 3). Therefore this multiplet is assigned to H_K, the separation of the two sub-spectra being ^3J_t, *ca.* 15 Hz. The separation of certain strong pairs of lines in these abk-subspectra arising from H_K gives an estimate of $|J_{AK} + J_{BK}| \simeq 10$ Hz. Moreover, each line in the K multiplet (Fig. 3) is further split due to the aldehyde proton and the methyl group. The low-frequency part of the olefinic signals (Fig. 4), a doublet of doublets with splittings of *ca.* 7.9 Hz and 15.3 Hz, is assigned to H_M with coupling constants $J_{KM} \simeq 7.9$ Hz and $J_{KM} \simeq 15.3$ Hz. Each signal is further split into a complex pattern due to long-range coupling. The remaining signals are assigned to H_A and H_B (Fig. 5).
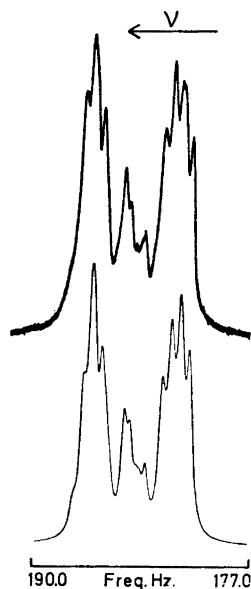
Fig. 2. Spectrum of the methyl protons: Upper, observed spectrum; lower, spectrum computed with the parameters of Table 1, with a linewidth of 0.2 Hz.
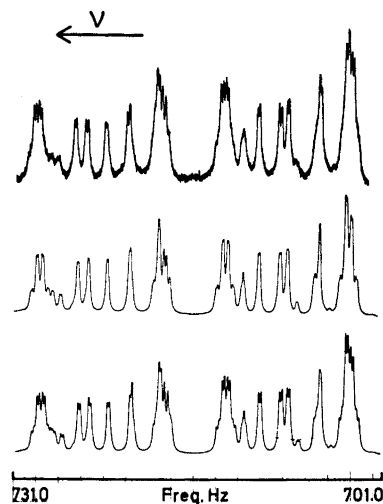
Fig. 3. Spectrum of H_K: Upper, observed spectrum; middle, spectrum computed with the parameters obtained from the iterative computations, *i.e.* $^4J_{KX} = -0.19$ Hz; lower, spectrum computed with the parameters of Table 1, *i.e.* with the parameters obtained from the iterative calculations apart from $^4J_{KX}$, which is changed to -0.25 Hz. The linewidth of the computed spectra is 0.2 Hz.

The coupling constants (Table 1) and chemical shifts (Fig. 1) were obtained using a modified version [10] of LAOCN3 [11] which accommodates eight spins. The final RMS error was 0.068 when 20 parameters were allowed to vary. The computed probable errors on the coupling constants are 0.01 to 0.02 Hz when 325 computed transitions were fitted to 125 observed lines. The figures show a good correlation between the theoretical spectrum, obtained for the parameters of Table 1, and the experimental spectrum. A better visual fit of

Table 1. Coupling constants for sorbaldehyde.[a,b,c,d]

$^3J_s(M,X) = 7.96$ Hz	$^4J_c(B,M) = -0.72$ Hz	$^3J(A,Y) = 6.89$ Hz
$^3J_s(B,K) = 10.96$ Hz	$^4J_c(A,K) = -9.92$ Hz	$^4J_c'(B,Y) = -1.55$ Hz
$^3J_t(K,M) = 15.34$ Hz	$^4J_c(K,X) = -0.25$ Hz[e]	$^5J_t'(K,Y) = 0.48$ Hz
$^3J_t(A,B) = 15.23$ Hz	$^5J_{cc}(A,M) = 0.66$ Hz	$^6J_{ct}'(M,Y) = -0.67$ Hz

[a] Errors in the coupling constants are estimated to be ± 0.08 Hz. [b] See Fig. 1. [c] $^5J(B,X)$, $^6J(A,X)$, and $^7J(X,Y)$ are all unobservable (≤ 0.1 Hz). [d] For the notation see Ref. 9. [e] The value obtained during the iterative calculation was $^4J_c = -0.19$ Hz (see the text and Fig. 3).
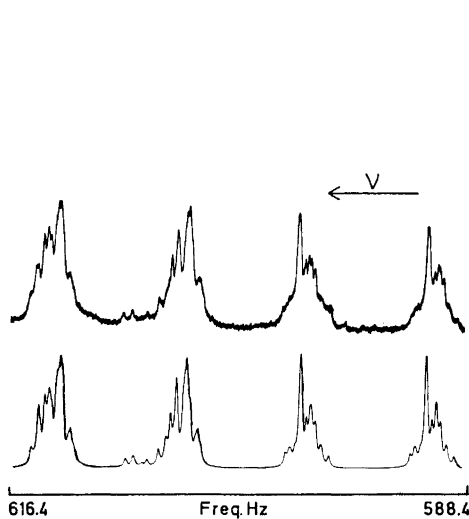
Fig. 4. Spectrum of H_M: Upper, experimental spectrum; lower, spectrum computed with the parameters if Table 1, with a linewidth of 0.2 Hz.
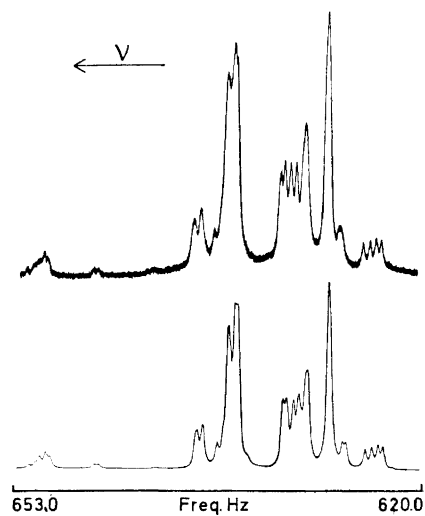

Fig. 5. Spectrum of H_A and H_B: Upper, experimental spectrum; lower, spectrum computed with the parameters of Table 1, with a linewidth of 0.4 Hz.

observed and calculated spectra was obtained for H_K (Fig. 3) with the value of -0.25 Hz for $^4J_{KX}$ instead of the value, -0.19 Hz, obtained during the iterative calculations.

RESULTS AND DISCUSSION

The data for *trans*-sorbaldehyde (Table 1) are consistent with an all-*trans* configuration and an all-*trans* conformation of the molecule. It is unlikely that there is a significant population of other conformations. This statement is based on a comparison of the coupling constants with those for butadiene and acrolein derivatives. In making comparisons of coupling constants (see below) we have restricted our choice of model compounds to cases without steric hindrance, *i.e.* to molecules with all-*trans* configurations and with no side-chains. The chemical shifts for sorbaldehyde (Fig. 1) are unremarkable and in view of uncertainty due to solvent and concentration effects, we do not propose to make quantitative conclusions from the available data. Certain trends are, however, apparent. The chemical shift of the aldehyde proton, $\delta = 9.535$, lies within the range found for other conjugated aldehydes [2,3,12] (9.48 to 9.58 ppm). The *trans*-terminal methyl group is little affected (< 0.2 ppm) by the interposition of a $C = C$ double bond. The effect of a $C = O$ group on the olefinic protons shows the same trend as observed for acroleins, with the α-proton shifted to low frequency and the *cis*-β-proton shifted to high frequency as compared to the remaining olefinic protons of the sorbaldehyde.

Table 2. Coupling constants for *trans*-substituted acroleins, $XCH = CH - CHO$.

Molecule	X	^3J_s/Hz	^4J_c/Hz	Reference
Sorbaldehyde	[a]	7.96	− 0.25	this work
Acrolein	H	7.49 to 8.11[b]	[c]	3
Crotonaldehyde	Me	$\begin{cases} 7.57 \\ 7.61 \text{ to } 7.85^b \end{cases}$	− 0.25 (−)0.32	2 12
Cinnamaldehyde	Ph	$\begin{cases} 7.5 \\ 7.17 \text{ to } 7.90^b \end{cases}$	− 0.3 [d]	13 12
2-Furylacrolein	[e]	7.7 ± 0.1	0.0 ± 0.1	14
2-Thienylacrolein	[f]	7.43 ± 0.1	− 0.11 ± 0.1	15
4-Ketohex-2-enal	COEt	7.14	0.04	16
N,N-Dimethylamino-propenal	NMe$_2$	7.26 to 7.72[b]	[c]	17
Ethoxyacrolein	OEt	8.12	[c]	18

[a] See Fig. 1. [b] Solvent and temperature dependent. [c] Not relevant to the present discussion. [d] Not obtained. [e] Structure I. [f] Structure II.

I   II
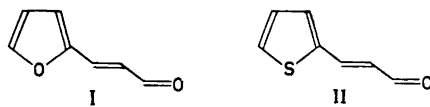
The value of ^3J_s to the aldehyde proton (7.96 Hz) lies within the rather narrow range (7.1 to 8.2 Hz) found for other *trans-β*-substituted acroleins, $X - CH = CH - CHO$, for which results are quoted in Table 2. There are several possible influences on ^3J_s in this series of compounds:

(i) Direct substituent effects; these appear to be small, presumably because the site of substitution is fairly remote from the coupled protons.

(ii) The effect of extended conjugation. This would be expected to influence principally the π-contributions to coupling (though the σ-contribution may be affected indirectly if the $C - C$ formal single bond is changed in length). Cunliffe, Grinter and Harris [19] have presented theoretical results for ^3J_s in the butadiene-hexatriene-octatetraene series which suggest the effects of extended conjugation are small (≤ 0.2 Hz). In any case several of the values quoted above for acrolein derivatives are for compounds where extended conjugation is possible; there is no indication that this has a marked effect.

(iii) Rotational isomerism about the $C_1 - C_2$ bond. It is possible that sorbaldehyde contains small amounts of *s-cis* or *s-gauche* forms. It has been estimated from a microwave study [20] that at 30°C acrolein may contain about 3 % of the *s-cis* form, and that there is an energy difference of about 10 kJ mol^{-1} between the *s-cis* and *s-trans* isomers. The effect of isomerism on the NMR spectrum of acrolein has been investigated by Davies.[3] He tentatively attributed the small increase of ^3J_s as temperature decreased to the increased proportion of the predominant *s-trans* form. Similar comments have been made for cinnamaldehyde and crotonaldehyde.[12] The influence of isomerism has been

Table 3. Coupling constants for *trans,trans*-disubstituted butadienes, $XCH=CH-CH=CHY$.

Molecule	X	Y		^3J_s/Hz	^4J_c/Hz	$^5J_{cc}$/Hz	Reference
Sorbaldehyde	Me	CHO		10.96	-0.92^a -0.72^b	0.66	this work
Methyl sorbate	Me	CO_2Me		10.5	c	c	24
Hexadiene	Me	Me		10.30	-0.84	0.68	9
Muconates	CO_2R	CO_2R	R=H	11.7	-0.71	~ 0.5	25
			R=Me	11.4	-0.7	0.8	8
			R=Et	11.3	-0.8	0.8	8
			R=t-Bu	11.5	-0.8	0.7	8
Diphenylbutadiene	Ph	Ph		10.80	-0.94	0.90	26
Dicyanobutadiene	CN	CN		$\begin{cases} 10.3^d \\ 11.1^e \\ 11.11^f \end{cases}$	-1.0 -0.7 -0.64	1.4 0.9 0.81	27 8 28
Pentadiene	Me	H		$\begin{cases} 10.30 \\ 10.33 \text{ to } 10.52^h \end{cases}$	-0.78^a -0.77 to $-0.80^{a,h}$	g g	9 29
t-Butylbutadiene	t-Bu	H		10.16	-0.78^a	g	29
2,4-Pentadienoic acid	CO_2H	H		11.05	-0.71^a	g	7
Butadiene	H	H		$\begin{cases} 10.41 \\ 10.20 \text{ to } 10.65^h \end{cases}$	g g	g g	30 29
Methoxybutadiene	OMe	H		10.49 to 10.57^h	g	g	31
Dichlorobutadiene	Cl	Cl		11.24	g	g	32

^{a} ^4J_c for the group $XCH=CH-CH$. ^{b} ^4J_c for the group $CH-CH=CHY$. ^{c} Not given. ^{d} $CDCl_3$ solution. ^{e} MeCN solution. ^{f} Me_2SO solution. ^{g} Not relevant to the present discussion. ^{h} Solvent- and/or temperature-dependent.

Table 4. Coupling constants involving the methyl protons for sorbaldehyde and related compounds.

Compound	$^3J'$/Hz	$^4J_c'$/Hz	$^5J_t'$/Hz	$^6J_{ct}'$/Hz	Reference
Sorbaldehyde	6.89	-1.55	0.48	-0.67	this work
Pentadiene	$\begin{cases} 6.69 \\ 6.58 \text{ to } 6.71^a \end{cases}$	-1.70 -1.61 to -1.66^a	0.45 0.37 to 0.46^a	-0.76 -0.69 to -0.70^a	9 29
Hexadiene	6.84	-1.71	0.42	-0.84	9
Methyl sorbate	6.5	-1.6	b	b	24

^{a} Solvent-and/or temperature-dependent. ^{b} Not given.

discussed for the butadiene series by Bothner-By and Moser.[21] Kozerski and Dabrowski[22] have shown by direct NMR measurement of spectra showing separate bands for *s-cis* and *s-trans* isomers of protonated *N,N*-dimethyl-aminopropenal that this compound exists to 86 % in the *s-trans* form. In so far as our result for ^3J_s to the aldehyde proton of sorbaldehyde is on the high side for such compounds it may be assumed that the compound is predominantly *s-trans*. Rotational isomerism about the C_3-C_4 bond will affect ^3J_s (M,X) much less than ^3J_s(B,K); see below.

(iv) *Molecular deformations.* For the butadiene series these have been discussed theoretically by Bacon and Maciel [23] and from experimental results by Albriktsen, Cunliffe and Harris.[9] There is no suggestion of appreciable effects of this type for *trans*-substituted systems.

Reported values of ^3J_s across the central single bond of all-*trans* 1,3-dienes (see Table 3) also fall in a narrow range (10.1 to 11.7 Hz); our result for sorbaldehyde (10.96 Hz) is in the middle of this range. The influences of extended conjugation and substituent electronegativity are clearly not large and are difficult to analyse in any detail, particularly in view of the variable accuracy of the data quoted in Table 3 and of small variations with temperature and solvent. However it seems that both factors tend to increase ^3J_s. It may be noted that when both substituents are alkyl groups or hydrogen, values of ^3J_s are in the lower part of the range. There is no evidence to suggest any appreciable population of conformations other than *s-trans* for sorbaldehyde.

The magnitude of ^3J_t for the MeCH = CH group of sorbaldehyde (15.23 Hz) is similar to the corresponding values for *trans*-pentadiene (15.00 to 15.06 Hz [9,29]), *trans,trans*-hexadiene (15.01 Hz[9]) and methyl sorbate (15.1 Hz [2]). The value of ^3J_t for the CH = CHCHO group of sorbaldehyde (15.34 Hz) should be compared to the data for methyl sorbate (15.8 Hz [24]), *trans,trans*-muconic acid and its esters (15.79 to 16.0 Hz [8,25]), *trans*-2,4-pentadienoic acid (15.41 Hz [7]) and cinnamaldehyde (15.71 to 15.93 Hz, [12] 15.9 Hz [13]). The fact that for sorbaldehyde ^3J_t is slightly larger for the CH = CHCHO group (*i.e.* for the "central" double bond) than for the MeCH = CH group is consistent with the results for methyl sorbate.[24]

Long-range coupling between the diene protons follows the pattern shown by *trans,trans*-hexadiene [9] and related compounds (see Table 3). However, the two values of ^4J_c differ by 0.2 Hz, the result for J_{AK} being algebraically lower than for the other compounds of Table 3. Coupling constants to the methyl protons (Table 4) are measurable for up to six bonds between the nuclei concerned; the values are closely comparable with those for related molecules. In contrast long-range coupling to the aldehyde proton is small; in fact only for ^4J_c is it detectable (-0.25 Hz), as obtained by full analysis of the K region, though the linewidth of the aldehyde doublet, 0.7 Hz, gives some indication of more extensive coupling. The small magnitude of ^4J_c to aldehyde protons is well-known (see Table 2). The negative sign gave a better correlation of both line positions and intensities than a positive sign; this is consistent with signs for the diene series [9] and for acrolein.[3] We believe the magnitude of ^4J_c to the aldehyde proton to be accurate to 0.08 Hz. The lack of longer-range coupling to the aldehyde proton of sorbaldehyde is in contrast to the situation for hexatriene and its derivatives, for which both experimental [33,34] and theoretical [19] data have been reported.

REFERENCES

1. Hoffman, R. A. and Gronowitz, S. *Acta Chem. Scand.* **13** (1959) 1377; *Arkiv Kemi* **16** (1961) 471.
2. Douglas, A. W. and Goldstein, J. H. *J. Mol. Spectry.* **16** (1965) 1.
3. Davies, J. E. D. *J. Mol. Spectry.* **29** (1969) 499.
4. Klinck, D. E. and Stothers, J. B. *Can. J. Chem.* **44** (1966) 45.

5. Ronayne, I. and Williams, D. H. *J. Chem. Soc.* **C 1967** 2642.
6. Collin, P. J. and Sternhell, S. *Aust. J. Chem.* **19** (1966) 317.
7. Kelly, D. P. *J. Mol. Spectry.* **28** (1968) 204.
8. Elvidge, J. A. and Ralph, P. D. *J. Chem. Soc.* **C 1966** 387.
9. Albriktsen, P., Cunliffe, A. V. and Harris, R. K. *J. Magn. Resonance* **2** (1970) 150, and references therein.
10. Albriktsen, P. *Unpublished work.*
11. Castellano, S. and Bothner-By, A. A. *J. Chem. Phys.* **41** (1964) 3863.
12. Scrimshaw, G. F. *M. Sc. Thesis*, University of East Anglia 1967.
13. Hoffman, R. A., Gestblom, B. and Rodmar, S. *J. Chem. Phys.* **42** (1965) 1695.
14. Schaefer, T. *Can. J. Chem.* **40** (1962) 1678.
15. Bothner-By, A. A. and Harris, R. K. *Unpublished work.*
16. Gilby, A. R. and Waterhouse, D. F. *Aust. J. Chem.* **17** (1964) 1311.
17. Dabrowski, J. and Kozerski, L. *Org. Magn. Resonance* **4** (1972) 137.
18. Bothner-By, A. A. and Harris, R. K. *J. Org. Chem.* **30** (1965) 254.
19. Cunliffe, A. V., Grinter, R. and Harris, R. K. *J. Magn. Resonance* **3** (1970) 299.
20. Wagner, R., Fine, J., Simmons, J. W. and Goldstein, J. H. *J. Chem. Phys.* **26** (1957) 634.
21. Bothner-By, A. A. and Moser, E. *J. Am. Chem. Soc.* **90** (1968) 2347.
22. Kozerski, L. and Dabrowski, J. *Org. Magn. Resonance* **4** (1972) 253.
23. Bacon, M. and Maciel, G. E. *Mol. Phys.* **21** (1971) 257.
24. Elvidge, J. A. and Ralph, P. D. *J. Chem. Soc.* **B 1966** 243.
25. Bishop, E. O. and Musher, J. I. *Mol. Phys.* **6** (1963) 621.
26. Bothner-By, A. A. and Harris, R. K. *J. Am. Chem. Soc.* **87** (1965) 3451.
27. Hall, J. H. and Patterson, E. *J. Am. Chem. Soc.* **89** (1967) 5856.
28. Wendisch, D. and Kurtz, P. *Z. Naturforsch.* **22b** (1967) 599.
29. Segre, A. I., Zetta, L. and DiCorato, A. *J. Mol. Spectry.* **32** (1969) 296.
30. Hobgood, R. T. and Goldstein, J. H. *J. Mol. Spectry.* **12** (1964) 76.
31. Diez, E. and Rico, M. *J. Mol. Spectry.* **37** (1971) 131.
32. Bothner-By, A. A. and Harris, R. K. *J. Am. Chem. Soc.* **87** (1965) 3445.
33. Albriktsen, P. and Harris, R. K. *Acta Chem. Scand.* **27** (1973) 1875.
34. Cunliffe, A. V., Grinter, R. and Harris, R. K. *J. Magn. Resonance* **2** (1970) 200.