SOME ASPECTS OF THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF COMPOUNDS CONTAINING C-METHYL GROUPS¹

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ABSTRACT

The N.M.R. spectra of compounds containing various types of C-methyl groups are discussed with special reference to the effects of spin coupling. Particular attention is given to compounds containing the CHCH₃ group in saturated systems. It is pointed out that the observed splitting of the methyl band is not always equal to the coupling constant between the methyl protons and the adjacent proton, even when the chemical shift between the two groups of protons is large.

The detection and differentiation of C-methyl groups in organic compounds is of importance, particularly in natural product chemistry. The standard (Kuhn-Roth) method of estimating C-methyl groups consists of oxidizing the compound with chromic acid and determining the acetic acid (and(or) higher homologue(s)) produced. By suitable modifications (1) it is possible to analyze for each acid separately and so to find out whether the group is a simple C-methyl group, or a C-ethyl group, etc. Infrared spectroscopy (2) has been used to detect and to determine C-methyl groups, and also to differentiate between isopropyl, *tert*-butyl, and other C-methyl groups.

Both of the above methods have limitations for the differentiation of C-methyl groups. Proton nuclear magnetic resonance (N.M.R.) has already been applied to the problem (3) but little discussion of the scope and limitations of the method has been published. In the present paper the effect of coupling of a methyl group to other protons in a molecule is considered in detail.

The detection of C-methyl groups by means of N.M.R. spectroscopy is especially favorable for two reasons. In the first place, a strong signal is usually obtained because of the complete magnetic equivalence of the three protons as a result of the rapid internal rotation of the methyl group. Secondly, when the methyl group is attached to a saturated carbon atom, the chemical shift of the methyl group, which is about 1 p.p.m. downfield from tetramethylsilane, is usually different from that of other protons in the molecule. Exceptions occur in compounds containing certain structural features such as cyclopropane rings. *trans*-1,1-Dichloro-2,3-dimethylcyclopropane (4), for example, has an N.M.R. spectrum which is essentially a single line at 8.78 τ .

The N.M.R. spectra of compounds containing C-methyl groups attached to unsaturated carbon atoms have been discussed in some detail by several authors (5, 6, 7, 8, 9, 10) and will not be considered here.

When the methyl group is attached to a saturated carbon atom we may consider three separate cases, depending on whether the saturated carbon atom also carries (a) no hydrogen atom, (b) one hydrogen atom, or (c) two hydrogen atoms.

In class (*a*), when there is no hydrogen atom on the adjacent carbon atom, the methyl group generally gives rise to a single sharp line. Since all the intensity is concentrated in one line there is no difficulty in observing such a signal in a spectrum. Typical examples are the 18- and 19-methyl groups of steroids (11) and the methyl groups in camphane derivatives (12). In exceptional cases, the methyl group may show very weak coupling to

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other protons in the molecule, thus (4) the two non-equivalent gem-methyl groups of (I) are coupled together to the extent of 0.5 c.p.s. Roberts (13) has reported a value of 0.75 c.p.s. for the coupling constant of the C-methyl group to one of the protons of the methylene group in methyl 2-bromo-2-methylpropionate. In general, it may be anticipated that this type of coupling will be very small (<1 c.p.s.) and can be neglected for practical purposes.



The second class is that of compounds containing the CHCH₃ group. The spectrum to be expected from such a system, in the absence of other magnetically active nuclei, has been dealt with in several places (cf. ref. 14). The simplest case, usually designated (15) by the symbols AX_3 , occurs when the chemical shift of the two groups of protons is large compared with the coupling constant between them. The methyl group then gives rise to a doublet, and the separation is equal to the coupling constant. It may be mentioned here that the coupling constants of methyl groups to adjacent protons generally lie in the range of 6–8 c.p.s.

We may also place in this class the isopropyl group. If the two methyl groups are chemically identical and are well shifted from the CH proton, the situation is analogous to that just described. If the two methyl groups are not chemically identical, usually (but not necessarily) because of the presence of an asymmetric center in the molecule, two different methyl doublets, which may overlap, are obtained (16, 17). The non-equivalence of methyl groups in such systems is similar to that of two protons of a methylene group in certain molecules (18, 19).

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When the chemical shift in the CHCH₃ group is not very large, the spectrum becomes an AB_3 type (15) and contains more lines. However, when the ratio of coupling constant to chemical shift is not more than about 0.25, the spectrum of the methyl group is still approximately a doublet. More exactly, each "line" of the doublet is now split into a number of lines, and the high-field component is split more and also is of lower intensity than the low-field component (assuming the CH group to be at low field of the methyl group). When the chemical shift is much less, a doublet is no longer recognizable. Jackman (3) has tried to rationalize the spectra of certain compounds (e.g. methylcyclohexane) containing CHCH₃ groups simply in terms of AB₃ systems. However, closer inspection shows that the observed and calculated spectra of the methyl groups cannot be made to agree completely, no matter what combination of chemical shifts and coupling constants are used. In each case there are other protons in the molecule which are appreciably coupled to, but only slightly chemically shifted from, the tertiary proton of the CHCH₃ group. These protons *must* be included in the analysis in order to obtain correct results. This is so even if, as is generally true, the methyl group is coupled only to the tertiary proton and not to the other protons of the molecule.

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We shall first examine the spectrum to be expected for the methyl group in a molecule such as (II), where the R's are not involved in coupling with the system under consideration. We will assume that the methyl group is well chemically shifted from H(1) and



H(2) and that $J_{CH_3,H(2)}$ is zero. This is actually a special case of the X_3AB system, which has been treated by Fessenden and Waugh (9). Figure 1 shows the calculated spectra due



FIG. 1. Calculated spectra for compounds of type (II) for various values of the chemical shift (ν) between H(1) and H(2) and with $J_{CH_3, H(1)} = J_{H(1), H(2)} = 8$ c.p.s. and $J_{CH_3, H(2)} = 0$.

to the CH₃ group for various values of the chemical shift $(\nu_{H(1),H(2)})$ between H(1) and H(2), and, for simplicity, with $J_{CH_3,H(1)} = J_{H(1),H(2)} = 8.0$ c.p.s. Although the coupling constants are not generally equal, this does not affect the general conclusions drawn from the calculations.

When the chemical shift, $\nu_{\rm H(1), H(2)}$, is very large the spectrum of the methyl group is a doublet, the lines being at $+1/2J_{\rm CH_3, H(1)}$ and $-1/2J_{\rm CH_3, H(1)}$ from the position of the methyl band in the absence of coupling. This is, of course, just the result expected from a first-order treatment. When the chemical shift is *not* large, only half of the intensity of the methyl band resides in the two lines at positions mentioned above. Most of the

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remaining intensity is situated *between* these two lines, the exact distribution depending very markedly on the value of $\nu_{H(1),H(2)}$ (Fig. 1). The effect of H(2) is most pronounced when $\nu_{H(1),H(2)}$ is no greater than $J_{H(1),H(2)}$ and is negligible when $\nu_{H(1),H(2)} > 2J_{H(1),H(2)}$.

It can easily be understood why half of the intensity is in the lines at $\pm 1/2J_{\text{CH}_3, \text{H}(1)}$. There are four spin states for the protons H(1) and H(2), and the wave functions of the states with both protons having a spin of $\pm 1/2$ or with both protons having a spin of -1/2 will not mix with any other functions, whereas the pairs of wave functions associated with one proton having a spin of $\pm 1/2$ and the other a spin of -1/2 and vice versa do mix as they have the same total spin (15). From similar considerations it can be seen that if there are two protons similar to H(2), then only one quarter of the intensity of the methyl group lies in the "unperturbed" lines at $\pm 1/2J_{\text{CH}_3, \text{H}(1)}$. For three and four protons these fractions fall to 1/8 and 1/16 respectively. Complete solutions in these cases would be very laborious but it can be surnised that most of the remaining intensity, in the form of many lines, will be situated, as before, between the pair of unperturbed lines.

Therefore, the CHCH₃ group in a complex molecule may be expected to be a doublet or a doublet showing some additional lines, or in extreme cases, just a wide band with little resolved structure. This is the situation where the chemical shift between the CH₃ group and the adjacent proton is large compared with the coupling constant. When the chemical shift is not large, a similar effect is to be expected. The spectrum of the methyl group will correspond to the B_3 part of an AB_3 system only when A is not coupled to any protons other than the B protons. If the effects described above for the AX_3 system are important, a much more complex spectrum may be expected, which in extreme cases may reduce to a structureless wide band.

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It should be noted that the observed splitting of the methyl band will not always be equal to the coupling constant. The splitting will usually be less because most of the intensity of the extra lines lies inside the two unperturbed lines whose separation gives the true coupling constant. This is probably the explanation for the wide variation in the "coupling constants"* of the methyl groups of 6α - and 6β -methyl steroids found by Slomp and McGarvey (20). In particular, for certain compounds some quite small splittings were found for which no explanation was presented. It would be expected that the coupling constant of the methyl group to the adjacent proton would not vary greatly in such a series of compounds. In agreement with the arguments presented in this paper is the fact that small splittings were not observed whenever the tertiary proton on C6 was likely to be chemically shifted (generally to low field) from the protons on C7, such as by the presence of a $\Delta^{4,5}$ double bond, or by the C6 proton being equatorial rather than axial (21). Unfortunately, the chemical shifts of the significant protons in such complex molecules cannot be observed directly, because the bands of a large number of other protons interfere.

Similar effects are found in the dimethylcyclohexanes examined recently by Musher (22). From the 40 Mc/sec N.M.R. spectra of the cis and trans isomers of 1,2-, 1,3-, and 1,4-dimethylcyclohexanes, Musher concluded that the coupling constants of equatorial methyl groups to the adjacent axial protons were zero or small (2.7 c.p.s.). In the alternative case of axial methyl groups and adjacent equatorial protons, appreciable (ca. 5 c.p.s.) coupling constants were observed. However, these "coupling constants" were merely the observed splittings of the methyl bands. Since the compounds used should be particularly liable to the effects discussed in this paper, the conclusions of Musher

*In cases of this type the term "splitting" would seem to be preferable to the term "coupling constant".

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regarding coupling constants cannot be regarded as correct. The correct constants could no doubt be obtained by preparing suitably deuterated derivatives, which is, unfortunately, not an easy task, but which has been achieved in the present work for some compounds discussed later in this paper. It may be noted that where zero splittings were observed by Musher, the methyl bands were in fact broad and not sharp as they should be if the coupling constants were zero. In order to obtain experimental confirmation of the deductions made, the N.M.R. spectra of a number of suitable compounds containing C-methyl groups have been examined.

A very simple spectrum (Fig. 2) is given by the 3,5-dinitrobenzoate of erythro-3-bromo-2-butanol. The spectrum shows two different methyl bands, each a well-defined doublet



FIG. 2. A. Spectrum of 3,5-dinitrobenzoate and *erythro*-3-bromo-2-butanol, in chloroform solution. The sharp band at the extreme left is that of $C^{13}HCl_3$. The two parts of the spectrum were taken at different recorder gain. B.

Methyl band of meso-2,3-dibromobutane (pure liquid).

in accordance with the X_3 part of an AX_3 system. It should be noted that protons on C2 and C3 are well chemically shifted from one another and from the methyl groups and occur at low fields as doublets of quartets. In contrast to this case is the spectrum of the closely related meso-2,3-dibromobutane, where the chemical shift between the protons

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on C2 and C3 is zero. The methyl groups here have the same chemical shift so only one methyl band is observed, but this is not a simple doublet (Fig. 2), for other lines appear. The spectrum of this molecule has already been discussed briefly (23) and fuller details will be published in a separate paper.

The spectra of methylsuccinic acid and β -methylglutaric acid are shown in Fig. 3.



FIG. 3. Spectra of methylsuccinic acid and β -methylglutaric acid in trifluoroacetic acid. The bands of the carboxyl protons are not shown. The methyl bands at slow sweep are shown on the right.

These structurally related compounds give quite different bands for the methyl group. In methylsuccinic acid there is a distinct, though not large, chemical shift between the α and the two α' protons and, as expected, the methyl group is a fairly good doublet. The coupling constant $J_{CH_3,H(2)}$ is probably a little larger than the observed splitting (6.6 c.p.s.) of the methyl band. In β -methylglutaric acid the α, α' and β -protons must be only slightly chemically shifted from one another as they give rise to a single, slightly broad band. The result is that the methyl group does not give rise to a doublet at all, but to a wide band which obviously contains many lines.

Other examples of this type are the N.M.R. spectra of 2- and 3-methylcyclohexanone. The band of the methyl group of 2-methylcyclohexanone is a fairly good doublet, as expected, since the 2-proton should be chemically shifted from the 3-methylene protons by the proximity of the carbonyl group. On the other hand, in 3-methylcyclohexanone

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the methyl group gives a very poor "doublet" (Fig. 4) which is a result of the carbonyl group shifting the position of the 2-methylene protons so that these are only slightly separated from the 3-proton. Support of this explanation was obtained by deuteration at position 2 (and incidentally at 6 also since an exchange method was used). The deuterated isomer gives a good doublet (Fig. 4) for the methyl group. This also shows that 1,3-coupling of the methyl group is not important as one methylene group (at C4) remains



FIG. 4. Spectra of 3-methylcyclohexanone and of 2,2,6,6-tetradeuterio-3-methylcyclohexanone.

in the deuterated isomer. The methyl splitting for the deuterated isomer is 6.1 c.p.s. The splitting of the methyl band in 3-methylcyclohexanone itself depends very markedly on the resolution and sweep rate, owing to the asymmetry of the band. At very high resolution and slow sweep rate the splitting is 5.0 c.p.s., but at lower resolution or faster sweep the observed splitting is only ca. 4.0 c.p.s. Even in the deuterated isomer, the splitting is probably not quite equal to the true coupling constant, as there are still protons on C4 which are not strongly chemically shifted from the proton on C3.

In all the examples described above the chemical shift between the methyl group and the adjacent proton is reasonably large. In methylcyclohexane this shift is much smaller, resulting in a strong skewness in the intensity of the methyl band (Fig. 5) which is an extremely poor doublet with a separation of 4.7 c.p.s. However, this band does not agree with the B_3 part of an AB_3 spectrum. Methylcyclohexane is known to exist largely with the methyl group equatorial (24). It is also known (21) that axial protons are found at slightly higher field than equatorial protons, and that tertiary protons are at slightly lower field than methylene protons, other things being equal (3). These shifts should largely cancel out and the axial proton adjacent to the methyl group should be very close in chemical shift to the protons (especially the equatorial ones) on C2 and C6.

The spectrum (Fig. 5) of 2,2,6,6-tetradeuteriomethylcyclohexane (for isotopic purity see Experimental), on the other hand, gives a methyl band whose structure is consistent with the B_3 part of an AB_3 system. Calculation shows that J = 6.8 c.p.s. and that J/ν is about 0.25. It should again be noted that the value of the coupling constant is appreciably greater than the observed splitting in undeuterated methylcyclohexane.

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FIG. 5. Spectra of methylcyclohexane and 2,2,6,6-tetradeuteriomethylcyclohexane. The methyl bands at slow sweep are shown on the right. The sharp band at the left of the methylcyclohexane spectrum is a side band of tetramethylsilane.

The Lycopodium alkaloid lycodine (IIIa) (25) presents a good example of a natural product showing some of the effects discussed in this paper. In the first publication (26) on this alkaloid, the N.M.R. spectrum (40 Mc/sec) was taken as evidence that the methyl group, which was known to be present, was attached to a quaternary carbon atom, as the methyl band was unsplit. However, spectra (Fig. 6) taken (27) at 60 Mc/sec and under somewhat better resolution showed that the methyl band was quite broad and, in fact, could just be resolved as a doublet of separation 1.9 c.p.s. This splitting undoubtedly does not represent the coupling constant. In N-acetyllycodine (IIIb), the methyl band of the lycodine part of the molecule cannot even be resolved into a doublet under the best possible resolution. The band (Fig. 6) is nevertheless broad and does show an inflection on the high-field side. In contrast, the band of the methyl protons of the N-acetyl group is quite sharp and therefore also of much greater height. These effects can be ascribed to the smallness of the chemical shift of the CH proton to the adjacent pairs of methylene protons, partly as a result of the CH proton being shifted upfield from

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FIG. 6. Methyl bands of (A) lycodine and (B) N-acetyllycodine. The two methyl bands of B were taken under the same instrumental conditions. The magnetic field increases from left to right.

its normal position by the pyridine ring. Molecular models show that the CH proton lies in the region above the plane of the pyridine ring where the circulating π electrons cause a diamagnetic shift. The related alkaloids α - and β -obscurine (28) show the same apparently abnormal methyl band shown by lycodine. Further discussion on the spectra of these alkaloids will be published in a paper dealing with these compounds.



Another example of "abnormal" behavior is found in $1-\beta(3,5\text{-dinitrobenzoyloxy})-2\alpha\text{-iodo-}3\alpha\text{-methylcyclohexane}$ prepared recently by Lemieux and Kavadias. The N.M.R. spectrum taken at a comparatively fast sweep (29) shows only a single, somewhat broad line for the methyl group. This can be understood if the proton on C3 is only slightly chemically shifted from the protons on C4. In agreement with this interpretation, the proton on C2 gives a broad line, instead of the doublet of doublets expected. In other isomers of the above compound the methyl group is a doublet and the C2 proton shows the expected fine structure.

The spectrum of compounds containing ethyl groups can be expected to show the same behavior as that of compounds containing the CHCH₃ group. The methyl group will only be a good triplet when it is well chemically shifted from the methylene protons, *and*

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ANET: N.M.R. SPECTRA

the methylene protons are chemically shifted from other protons to which they are coupled. When the ethyl group is attached to a saturated carbon atom not bearing a strongly electronegative or strongly electropositive substituent, neither of these conditions will generally be fulfilled. Thus valeric acid (3) gives rise to a methyl band which is wide and fairly shapeless. In fact, it is not too easy to differentiate this type of ethyl group from the "abnormal" CHCH₃ group discussed previously. *n*-Butyraldehyde (3), where the second condition above is fairly well fulfilled, gives a recognizable, if poor, triplet. Diethyl ketone fulfills both the conditions and indeed gives (3) a good triplet for the methyl group. It should be noted that in molecules containing an asymmetric carbon atom, the two methylene protons of an ethyl group are not identical and may have slightly different coupling constants to the methyl group. The ethyl group of some small molecules have been analyzed as A_3B_2 or A_3B_2X systems (30, 31), and during the course of the present work Cavanaugh and Dailey have investigated the spectra of propyl derivatives (32).

In this paper, the only magnetically active nuclei present have been assumed to be protons. However, the arguments presented can be extended readily to cases where fluorine, phosphorus, etc. occur in an organic compound.

EXPERIMENTAL

The spectra were taken at a frequency of 60 Mc/sec on a Varian V-4302 high-resolution spectrometer. The compounds were dissolved in carbon tetrachloride (except where otherwise stated) containing about 1% tetramethylsilane to make 10–15% solutions. Chemical shifts are reported on Tiers' τ scale (33) (i.e. in p.p.m. increasing to high field, with tetramethylsilane given the value of 10.00). Calibration of the spectra was carried out by the side-band technique. The frequency of the audio-oscillator was monitored on a Hewlett–Packard frequency counter, model 521C. In all cases a number of spectra were taken with increasing as well as with decreasing magnetic fields. The tetramethylsilane peak was always observed as a single, very sharp band. Coupling constants are estimated to be accurate to 0.15 c.p.s.

Preparation of 2,2,6,6-Tetradeuteriomethylcyclohexane

Cyclohexanone (10 g), deuterium oxide (15 ml, 99.7%), and anhydrous potassium carbonate (0.5 g) were refluxed for 2 hours. The cyclohexanone, recovered by ether extraction, was submitted to two more such treatments. The 2,2,6,6-tetradeuteriocyclohexanone was finally distilled through a small column, b.p. 93–96° (142 mm) (4 g), and was free of isomers containing protons α to the carbonyl group, as shown by the N.M.R. spectrum. Treatment of the deuterated cyclohexanone with triphenylphosphinemethylene according to the procedure described in Organic Syntheses (34) gave crude methylenecyclohexane, ca. 2 g, b.p. 80-100°. The only impurity was found to be benzene, both by gas chromatography and by the N.M.R. spectrum. The N.M.R. spectrum (bands at 5.52τ and 8.48τ only) also showed that the methylenecyclohexane was fully deuterated at positions 2 and 6. The above fraction was hydrogenated at room temperature and pressure in the presence of platinum oxide catalyst (10 mg). The product was shaken with concentrated sulphuric acid at 60° until gas chromatography showed that all the benzene was removed. The product gave a single peak with the same retention time as methylcyclohexane on gas chromatography using a silicone oil column at 110°. The mass spectrum (kindly taken by Dr. F. Lossing of the National Research Council, Ottawa) showed the presence of 65% tetradeuterated, 11% undeuterated, 10% pentadeuterated, 9% trideuterated, 3% monodeuterated, and 2% dideuterated methylcyclohexane. The

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presence of unexpectedly large amounts of the undeuterated isomer can be explained most simply if some isomerization (35, 36) to 1-methylcyclohexene took place. This compound could then undergo an exchange of its allylic deuterium atoms prior to hydrogenation. Indeed, gas chromatography of the hydrogenation mixture contained a small peak, not present in the initial product, with a retention time consistent with that expected for 1-methylcyclohexene. This product disappeared, as expected, on treatment with sulphuric acid. Although the final product was only 65% isotopically pure, this should not affect the N.M.R. spectrum too much.

2,2,6,6-Tetradeuterio-3-methylcyclohexanone

3-Methylcyclohexanone was deuterated as described above for cyclohexanone.

3,5-Dinitrobenzoate of Erythro-3-bromo-2-butanol

The compound had m.p. 85° (lit. (37) m.p. 85°). In the N.M.R. spectrum (Fig. 2) the bands centered at 4.68 τ and 5.60 τ can be assigned to the protons on C2 and C3 respectively, and the doublets at 8.44 τ and 8.19 τ can be assigned to the 4- and 1-methyl groups respectively. The coupling constants are $J_{12} = 6.4$, $J_{34} = 6.9$, and $J_{23} = 4.2$ c.p.s. The assignments are consistent with the chemical-shift effects of bromine and oxygen atoms (38).

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