

## Derivatives of Hydrazine

### IV. Second Order Approach to $A_6B$ $^1H$ NMR Spectra

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The  $A_6B$   $^1H$  NMR spectrum of isopropyl groups showing only small second order splittings are analysed to give the chemical shifts of the protons and the coupling constant  $J$ . It is demonstrated that the spacing between the two highest peaks on each side of the central peak of the methine septuplet is very close to  $2J$ . To explain the origin of this relationship a conceptually simple picture of the spectrum is developed by taking into account the magnetic equivalence of the six A protons. It is shown that the peaks in question correspond to the two outermost lines of the triplet subspectrum of the equivalence-factored  $A_6B$  system. The value of the splitting ( $2J$ ) is the result of an accidental compensation of second order terms. The doublet from the A protons shows a separation of the maxima somewhat less than  $J$ . The reason for this is concluded to be that both peaks of the doublet are shifted away from the septuplet, but the innermost signal to the highest degree.

The  $^1H$  NMR spectrum originating from the protons of the isopropyl group usually appears as an  $A_6X$  spectrum if recorded on a 60 MHz apparatus. If second order effects are neglected, the coupling constant  $J$  can be measured directly as the separation between the signals of the doublet (at high field) or of the septuplet (at low field). In this approximation the difference in chemical shift,  $\Delta\nu$ , is the distance between the centers of the two multiplets.

The second order effects depend only upon the ratio  $\alpha = |J/\Delta\nu|$ . Ranft<sup>1</sup> gave numerical results for the isopropyl group for  $\alpha > 0.09$ , however, in modern spectrometers operating at high field strength these highly perturbed situations rarely will occur. The present paper presents an extension of these results to lower  $\alpha$ -values, *i.e.* to  $A_6B$ -systems with small second order effects.

Our interest was directed towards second order splitting in <sup>1</sup>H NMR signals from isopropyl groups by the observation<sup>2</sup> that the methine septuplet of isobutyrylhydrazines with  $\alpha$ -values near 0.08 was always followed by three extra bands on the low-field side of the three central signals. This phenomenon is clearly visible on Fig. 1, which is a typical spectrum of the methine septuplet of the isobutyryl group of isobutyryl *N,N*-diisopropylhydrazine in CD<sub>3</sub>OD. A change of solvent left the three extra peaks unaffected. This observation excludes the possibility that they may arise from a tautomeric form. On recording the same spectrum on a 100 MHz instrument (Fig. 2) the three extra peaks appeared to have moved towards the main peaks. This experi-

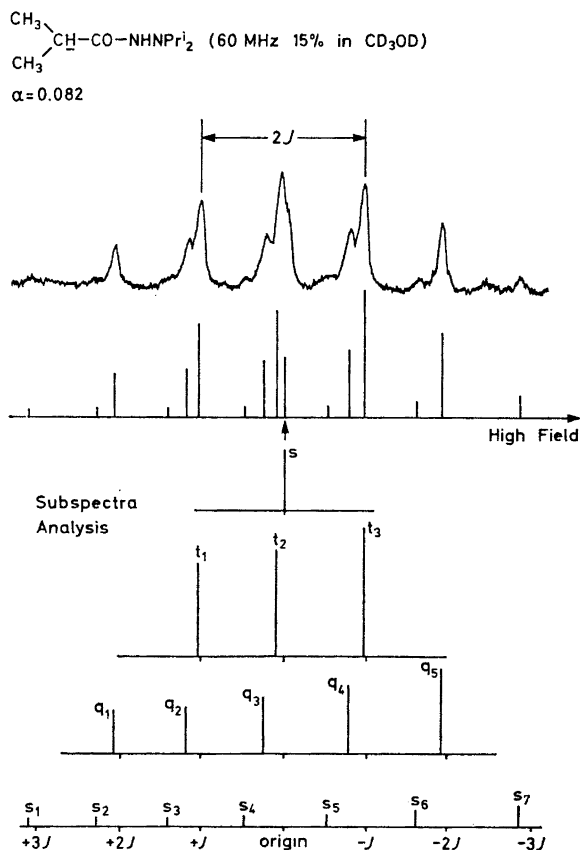


Fig. 1.

ment excludes that they arise from an impurity (including a tautomeric form) and, in addition, establishes that they are not due to a long-range coupling. A long-range coupling with the NH proton is also excluded by the observation that the three extra bands were unaffected by deuteration (exchange of hydrogen with deuterium using  $\text{CD}_3\text{OD}$ , cf. Fig. 1).

Since the phenomenon appeared to be general for compounds containing isopropyl groups<sup>2</sup> the only remaining possibility was that of a second order effect. A series of calculations was therefore carried out by computer, using the method described by Ferguson and Marquardt.<sup>3</sup> The  $\alpha$ - and  $J$ -values were varied until the calculated spectra, shown below the experimental spectra in Figs. 1 and 2, showed the best fit.

#### COMPUTER ANALYSIS

Consider first the methine septuplet of Fig. 1 consisting of seven line groups. The calculated spacings between the strongest peaks of each of the groups are from the high-field end of the septuplet: 6.39, 6.46, 7.07, 6.51, 7.03, and 7.00 Hz. These values are quite irregular and with no simple relation to the coupling constant  $J=6.8$  Hz. However, for small  $\alpha$ -values as in the present case, it was noted that *the spacing between the two highest peaks on each side of the central peak approximates to twice the coupling constant to a high degree of precision*. Thus, Fig. 1 shows a spacing between the two peaks in question of 13.58 Hz which is very close to  $2J=13.60$  Hz.

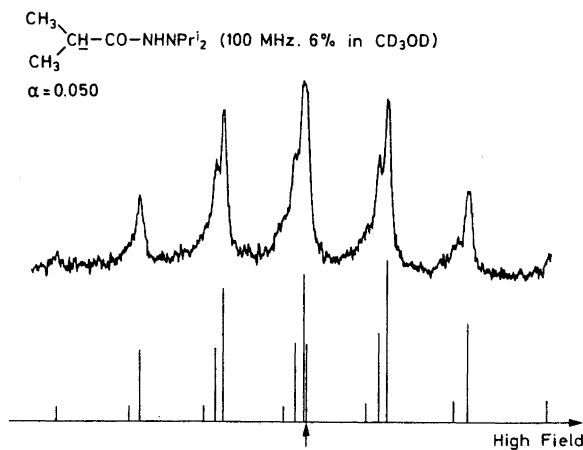


Fig. 2.

This method for obtaining  $J$  has proved valuable in practical work since the two peaks needed for the calculation are strong and almost always well resolved. In cases when very small  $\alpha$ -values are encountered this is no longer true as can be seen from Fig. 3, which gives the 100 MHz spectrum of the

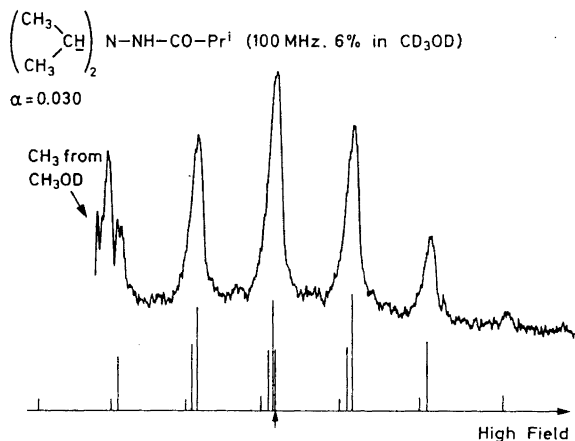


Fig. 3.

methine septuplet of one of the other isopropyl groups of isobutyryl *N,N*-diisopropylhydrazine than that shown in Figs. 1 and 2. However, it is seen from the calculated spectrum that the "tails" of the two peaks needed for estimation of  $2J$  both degrade uniformly towards lower field. Accordingly, it is expected that the spacing between the maxima of the two signals is still a reliable measure for  $2J$ .

It remains to be decided which value should be taken as the true center of the septuplet, *i.e.* the chemical shift of the *CH* proton. The calculations show that one of the four lines comprising the central peak of the septuplet is not affected by the second order splitting. It appears on Fig. 1 as a shoulder located on the high-field side of the central peak and is marked on the bottom of the calculated spectra with an arrow, pointing upwards. From Figs. 2 and 3 it is seen that this shoulder has disappeared from the main signal. This feature emphasized the need for an analytically simple expression for the chemical shift which can be used in connection with the position of the two peaks discussed above. Such an expression will be derived below.

In outlining the pattern expected for the  $\text{CH}_3$  groups of the isobutyryl group, we will consider the example of isobutyryl-*N,N*-dimethylhydrazine shown in Fig. 4. It can be seen from the calculated spectrum shown at the bottom part of the figure that the perturbed doublet consists of two areas of absorption, each composed by twelve lines. Some of these lines are very closely situated and drawn together two by two, indicated on the figure by heavy lines. At the top of Fig. 4 is superimposed the chemical shift of the methyl groups and the "unperturbed" doublet in the  $A_6X$  approximation.

It has been predicted by Anet<sup>4</sup> that the spacing in doublets arising from methyl groups attached to a *CH* group is not equal to the coupling constant between the methyl protons and the adjacent proton. Usually the separation will be less because most of the intensity of the extra lines arising from the second order splitting lies inside the positions of the "unperturbed" doublet

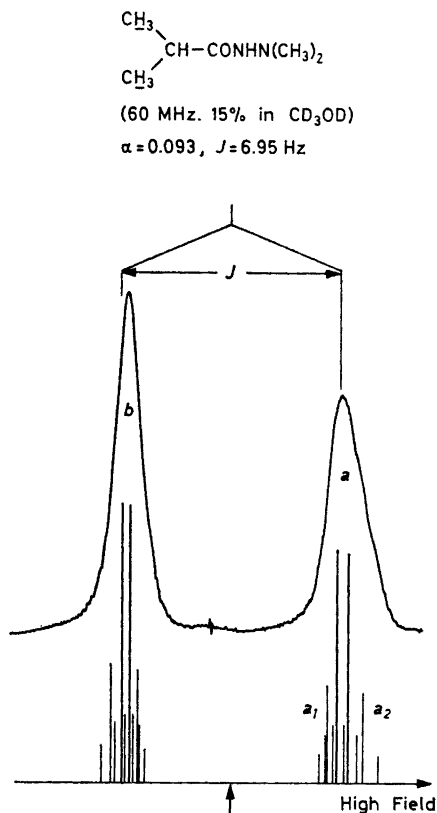


Fig. 4.

defined by the first order approximation. However, these conclusions were reached mainly on the basis of calculations on systems with only one methyl group attached to a methine group, and cannot, *mutatis mutandis*, be expected to apply to the isopropyl group as well.

The separation between the signals of the doublet was measured to be 6.75 Hz on Fig. 4 which, indeed, is less than the coupling constant  $J = 6.95$  Hz calculated on the basis of the septuplet. But in contrast to the argument forwarded by Anet it can be seen that the signal at high field (*a* at Fig. 4) has the maximum intensity at *higher* field than the "unperturbed" line position. The reason for this can readily be found from the calculated pattern showing that the added intensity to the line group  $a_1$  is more than outweighed by the increased separation of the line group  $a_2$  towards higher field. Nevertheless, the splitting of the doublet is less than  $J$  in accordance with Anet's prediction. It is apparent that this is a consequence of the change in position of the signal at low field (*b* at Fig. 4). The calculated spectrum again reveals the reason: The major number of lines arising from the second order splitting is situated

at higher field than the "unperturbed" line. In short, both components of the doublet are displaced towards higher field, but signal *b* more than signal *a*.

The true center of the doublet cannot readily be found from the experimental spectrum, especially since a one-to-one correspondence with the calculated spectrum cannot be established. The most reasonable approximation appears to be the chemical shift value of the high-field part *a* of the doublet plus  $J/2$ , *i.e.* one quarter of the value  $2J$  measured out on the septuplet.

#### SUBSPECTRA ANALYSIS

Since the six equivalent methyl protons can individually have a spin quantum number of  $\pm\frac{1}{2}$ , they can collectively have the quantum numbers 3, 2, 1, 0, -1, -2, -3. These situations arise in 1, 6, 15, 20, 15, 6, 1 number of ways. Accordingly, when the methine proton couples with the six protons a septuplet is produced with the individual lines in the same intensity proportions. This familiar way of describing the  $A_6X$  system can for the present purpose advantageously be replaced by a description which takes the magnetic equivalence implicitly into consideration.

Following this so-called magnetic equivalence factoring method, the group of methyl protons is instead treated as four *composite particles* of spins (resulting spin vectors) of 3, 2, 1, and 0. The composite particle with spin 3 can have each of the spin quantum numbers 3, 2, 1, 0, -1, -2, -3 with weights<sup>3</sup> 1, 1, 1, 1, 1, 1, 1, the particle with spin 2 the quantum numbers 2, 1, 0, -1, -2 with weights 5, 5, 5, 5, 5, the particle with spin 1 the quantum numbers 1, 0, -1 with weights 9, 9, 9, and that with spin 0 only the quantum number 0 with weight 5. The weights are seen to be uniquely determined by the condition, that they add up to give the binomial coefficients of the former description.

The methine spectrum can now be interpreted as a superposition of four *subspectra* arising from coupling of the methine proton with each of the four composite particles. The result of such an analysis is shown at the bottom part of Fig. 1 for this special case. When the methine proton couples with the composite particle with spin 0 the "unperturbed" singlet subspectrum (*s*) is obtained with weight 5. When the methine proton couples with the composite particle with spin 1 a triplet subspectrum ( $t_1, t_2, t_3$ ) is produced. It can be shown<sup>5</sup> that the total intensity of the subspectrum always represents a fixed fraction of the total intensity of the methine septuplet. Since the weights of the triplet subspectrum in the first order approach is 9, 9, 9 it follows that the total weight of the spectrum is 27 also when second order effects are included. However, it is seen from Fig. 1 that there is a distortion of the first order intensity pattern such that the line nearest the methyl doublet ( $t_3$ ) increases in intensity at the expense mainly of the line  $t_1$  furthest away from the methyl doublet, but also to a small extent at the expense of the intensity of  $t_2$ . These results have qualitative usefulness in that the subspectrum can readily be picked out from the total pattern. In the same way the quintuplet subspectrum ( $q_1-q_5$ ) and the septuplet subspectrum ( $s_1-s_7$ ) are produced by coupling of the methine proton with the composite particles with spin 2 and 3, and with total relative weights of  $5 \times 5 = 25$ , and  $7 \times 1 = 7$ , respectively.

Corio<sup>5</sup> has given closed form expressions for the line frequencies and intensities in the general A<sub>n</sub>B system. For the common situation  $\alpha < 0.1$  it is possible to apply Corio's formulas in a simplified form where terms of higher order have been neglected. In Table 1 the results are given for the four sub-

Table 1. Line positions in the B part of the A<sub>n</sub>B system classified according to the total spin of the methyl protons and approximated using  $\alpha \ll 1$ . The line positions are given in Hz relative to the chemical shift of the B proton. The B proton is assumed to be at lower field than the A protons as is the case for the protons of an isopropyl group.

| Singlet | Triplet                                    | Quintuplet   | Septuplet   |
|---------|--|--|---|
| s: 0    |  |  | $s_1: 3J + \frac{3J\alpha}{2+5\alpha}$                                |
|         |  | $q_1: 2J + \frac{J\alpha}{1+1.5\alpha}$                              | $s_2: 2J + \frac{5J\alpha}{2+3\alpha} + \frac{3J\alpha}{2+5\alpha}$   |
|         | $t_1: J + \frac{0.5J\alpha}{1+0.5\alpha}$  | $q_2: J + \frac{3J\alpha}{2+\alpha} + \frac{J\alpha}{1+1.5\alpha}$   | $s_3: J + \frac{5J\alpha}{2+3\alpha} + \frac{3J\alpha}{1+0.5\alpha}$  |
|         | $t_2: 0 + \frac{J\alpha}{1-0.25\alpha^2}$  | $q_3: 0 + \frac{3J\alpha}{1-0.25\alpha^2}$                           | $s_4: 0 + \frac{6J\alpha}{1-0.25\alpha^2}$                            |
|         | $t_3: -J + \frac{0.5J\alpha}{1-0.5\alpha}$ | $q_4: -J + \frac{3J\alpha}{2-\alpha} + \frac{J\alpha}{1-1.5\alpha}$  | $s_5: -J + \frac{5J\alpha}{2-3\alpha} + \frac{3J\alpha}{1-0.5\alpha}$ |
|         | $q_5: -2J + \frac{J\alpha}{1-1.5\alpha}$   | $s_6: -2J + \frac{5J\alpha}{2-3\alpha} + \frac{3J\alpha}{2-5\alpha}$ |   |
|         |  |  | $s_7: -3J + \frac{3J\alpha}{2-5\alpha}$                               |

spectra. It can be seen that all lines except the singlet will be displaced towards lower field, *i.e.* away from the methyl signal. The strong lines recommended above as a reliable measure for  $2J$  can now be identified as the two outermost lines of the triplet subspectrum,  $t_1$  and  $t_3$ . The line separation  $\kappa = t_1 - t_3$  can be calculated from Table 1 to be

$$\kappa = J \frac{2-\alpha^2}{1-0.25\alpha^2} \cong 2J$$

correct to the second order in  $\alpha$ . The fact that only quadratic terms in  $\alpha$  occurs explains why  $2J$  can be found accurately by this procedure as long as  $\alpha$  is

small. For larger values of  $\alpha$  an iterative determination based on this equation will be necessary. From the measured line separation  $\kappa$ ,  $J$  is found to a first approximation as

$$J = \frac{1 - 0.25 \alpha^2 [\kappa/\Delta\nu]^2}{2 - [\kappa/\Delta\nu]^2}$$

By substituting twice this value for  $\kappa$  an improved value for  $J$  can be obtained, and this procedure is repeated until convergence is realized. Another interesting value can be obtained from Table 1. It is readily shown that the midpoint between  $t_1$  and  $t_3$  is at

$$\frac{t_1 + t_3}{2} = \frac{0.5J\alpha}{1 + 0.25 \alpha^2}$$

which is just one-half of the distance between  $t_2$  and the true center of the septuplet at  $s$ . Since  $t_1$ ,  $t_2$  and  $t_3$  can always be located with certainty it is therefore easy to find the chemical shift of the methine proton even though  $s$  is only a poorly resolved shoulder in the spectrum.

In Table 2 a comparison is made of calculations performed with the approximate formulas of Table 1 and by electronic computer. The overall agreement is seen to be satisfactory.

Table 2. Line positions relative to the first order pattern ( $-3J$ ,  $-2J$ ,  $-J$ ,  $0$ ,  $J$ ,  $2J$ ,  $3J$ ) in the B part of an  $A_2B$  system with  $\alpha=0.1$  and  $J=7$  Hz calculated a) from the approximated formulas given in Table 1, and b) exact by electronic computer. The line positions are given in Hz relative to the chemical shift of the B proton.

| Singlet            | Triplet                      | Quintuplet                   | Septuplet                    |
|--------------------|------------------------------|------------------------------|------------------------------|
|                    |                              |                              | $s_1$ : a) 0.840<br>b) 0.832 |
|                    |                              | $q_1$ : a) 0.609<br>b) 0.614 | $s_2$ : a) 2.362<br>b) 2.326 |
|                    | $t_1$ : a) 0.333<br>b) 0.332 | $q_2$ : a) 1.609<br>b) 1.591 | $s_3$ : a) 3.522<br>b) 3.442 |
| $s$ : a) 0<br>b) 0 | $t_2$ : a) 0.702<br>b) 0.698 | $q_3$ : a) 2.116<br>b) 2.074 | $s_4$ : a) 4.211<br>b) 4.090 |
|                    | $t_3$ : a) 0.368<br>b) 0.366 | $q_4$ : a) 1.929<br>b) 1.900 | $s_5$ : a) 4.270<br>b) 4.134 |
|                    |                              | $q_5$ : a) 0.824<br>b) 0.812 | $s_6$ : a) 3.459<br>b) 3.357 |
|                    |                              |                              | $s_7$ : a) 1.400<br>b) 1.365 |



## EXPERIMENTAL

The preparation of isobutyryl *N,N*-diisopropylhydrazine used for the  $^1\text{H}$  NMR measurements will be published shortly <sup>2</sup> in connection with a general investigation of the  $^1\text{H}$  NMR spectra of acyl- and thioacylhydrazines.

*Isobutyryl N,N-dimethylhydrazine.* 1,1-Dimethylhydrazine (1.5 g) in dry ether (50 ml) was added to a solution of isobutyrylchloride (1.1 g) in ether (100 ml). The reaction mixture was left at room temperature for 24 h, and the 1,1-dimethylhydrazinium chloride was filtered off. After removal of the solvent *in vacuo*, the residue (70 % yield) was re-crystallized from pentane to give a colourless crystalline product. M.p. 98–99°C. (Found: C 55.22; H 11.00; N 21.40. Calc. for  $\text{C}_6\text{H}_{14}\text{N}_2\text{O}$ : C 55.35; H 10.84; N 21.52).

The 60 MHz spectra were obtained on a Varian A-60 instrument operating at 40°C. The 100 MHz spectra were recorded with a Varian HR-100 NMR spectrometer at 30°C. The spectra reproduced in this paper were selected amongst several scans, but show no features which could not be observed repeatedly.

The calculations were performed with a computer program NMRIT described by Ferguson and Marquardt.<sup>3</sup> The program (IBM Share Library, Distribution No. 3165) has been changed in a few less important points to operate under 7094 IBSYS and to utilize the overlay feature of the loader. We wish to thank members of the staff of Northern Europe University Computing Center (N.E.U.C.C.), The Technical University of Denmark, for technical advice with the computation work.

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Received April 23, 1969.