CCA-335

538.24:547.361:456.11.02
Original Scientific Paper

The NMR Spectra of Allyl Alcohol-d_2 and Allyl Alcohol

G. T. Jones, M. Randić, and J. J. Turner***

Department of Chemistry, The University, Sheffield, England

Received August 7, 1964

The high resolution NMR spectrum of specifically deuterated allyl alcohol has been analysed as an ABC type. The following spin-spin coupling constants of vinyl hydrogens are obtained:

$J_{trans} = 17.3_3$ c/s $J_{cis} = 10.5_3$ c/s and $J_{gem} = 1.8_5$ c/s.

The relative signs have been established by calculating the line intensities for various possibilities. A close agreement with experiment is obtained only when they are all positive. An explanation of the large effect of the sign of J_{AB} (J_{gem}) on calculated intensities is given. The spectrum of undeuterated allyl alcohol has been interpreted on the basis of $ABCX_2$ and the following approximate coupling constants of methylene to vinyl hydrogens are obtained:

$J_{XA} = J_{XB} \approx 1.5$ c/s and $J_{XC} \approx 5$ c/s.

INTRODUCTION

High resolution NMR spectra of a large number of molecules containing three non-equivalent hydrogens have been analyzed and molecular parameters (screening and spin-spin coupling constants) obtained. For olefins it was found experimentally[1,2] and estimated theoretically[3] that *trans* spin-spin coupling constants are greater than *cis*. Particularly extensive studies of vinyl compounds by Brügel, Ankel, Krückeberg[4] and Banwell and Sheppard[5] have accumulated sufficient data to formulate an empirical rule concerning the magnitudes of spin-spin coupling constants.

They tend to be fairly characteristic:

$$J_{trans} = 10\text{—}20 \text{ c/s}, \quad J_{cis} = 4\text{—}15 \text{ c/s and } J_{gem} = \text{less than } 4 \text{ c/s}.$$

As is well known one way of establishing the relative signs of the coupling constants is by calculating the intensities of the transitions. It seems well established that both J_{trans} and J_{cis} have the same sign, taken as positive. The sign of J_{gem}, which is smaller in magnitude, is in some cases positive, others negative. The spectrum of allyl alcohol has been analysed (Brügel *et al.*[4]) as an ABC type, neglecting the presence of the CH_2 protons, which will couple with the protons H_A, H_B and H_C (for notation see Fig. 1). These couplings are shown here to be approximately 5 c/s for CH_2—H_C and 1.5 c/s for CH_2—H_A and CH_2—H_B, and as they are of the order of J_{gem}, they may have a considerable effect on the ABC spectrum. In this work we have analysed the spectrum of specifically deuterated allyl alcohol $CH_2 = CHCD_2OH$ and

---

* Visiting from Institute »Ruđer Bošković«, Zagreb, Yugoslavia.
** University Chemical Laboratories, Cambridge, England.

have determined the magnitudes and signs of all the spin-spin coupling constants. The substitution of deuterium for hydrogen at the CH_2 position reduces the CH_2—H couplings by a factor of 6.51 (the quotient of the magnetogyric ratio of D and H), so that coupling to H_A and H_B will be negligible, and that to the H_C may only cause some broadening of the H_C lines. The spectrum of allyl alcohol is discussed using the above analysis as a guide.

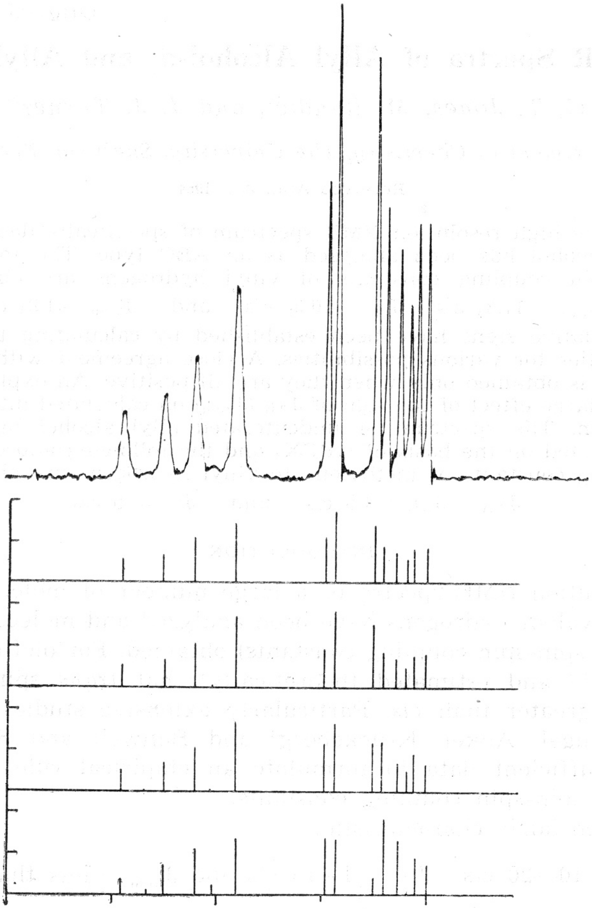

Fig. 1. Spectrum of allyl alcohol-d_2 with its schematic spectrum immediately below. The following diagrams represent the calculated spectra for a) J_{AB}, J_{AC}, J_{BC} all positive, b) J_{BC} negative and c) J_{AC} negative.

THE ANALYSIS OF AN ABC SYSTEM

An ABC spectrum consists of 15 lines characterised by three spin-spin coupling constants J_{AB}, J_{AC}, J_{BC} and three chemical shifts σ_A , σ_B, σ_C. There are generally 40 possibilities for the assignment of these lines to individual nuclei. However, if the resonance frequency of one nucleus is considerably shifted from the other two, the system is approaching the limiting ABX case, and a unique assignment can be made. This is frequently the case in vinyl compounds (*e. g.* vinylethylether, and vinylphenylether[4]) and is the case in $CH_2 = CHCD_2OH$. Therefore the combinations to be examined are reduced to only the uncertainties of the signs of the coupling constants. The Hamiltonian matrix for an ABC system is listed in the book of Pople, Schneider, Bernstein[6]. The only non-zero off-diagonal elements are H_{23}, H_{24}, H_{34} and H_{56}, H_{57}, H_{67}, with the result that the original 8 × 8 matrix is split into two 1 × 1 determinants associated with wavefunctions $\psi_1 = \alpha\alpha\alpha$ and $\psi_8 = \beta\beta\beta$, and two 3 × 3 blocks defining linear combinations of the three spin functions belonging to the total spin projection $F_z = \frac{1}{2}$ and $-\frac{1}{2}$ respectively:

$$\psi_i = c_{i2}(\alpha\alpha\beta) + c_{i3}(\alpha\beta\alpha) + c_{i4}(\beta\alpha\alpha) \qquad i = 2,\ 3,\ 4$$
$$\psi_j = c_{j5}(\alpha\beta\beta) + c_{j6}(\beta\alpha\beta) + c_{j7}(\beta\beta\alpha) \qquad j = 5,\ 6,\ 7.$$

By solving the secular determinant $|H_{ik} - E_{ik}| = 0$ a set of eight energy levels E_i are obtained. The selection rule $F_z = \pm 1$ allows fifteen transitions, the relative intensities of which are simply expressed by coefficients c_{ik} characterizing the eigenfunctions ψ_i (Tables of allowed transitions and their intensities are listed for example in ref. 4 and 5).

Detailed expressions for solving an ABC system are given by Brügel, Ankel, Krückeberg[4] and Castellano and Waugh[7], who describe a systematic approach, starting from observed line positions and calculating the spectral parameters σ's and J's. Final choice of the parameters is based on the agreement between calculated and experimental intensities. Another approach, useful for cases when one of the resonance group is shifted from the other two, is to apply perturbation theory. The spectrum is first analysed as an ABX approximation, from which initial values of the coupling and screening constants are obtained. These are then used to calculate better parameters, and if this is repeated several times a convergent solution of the ABC system is obtained[8]. A third approach, applicable in a general case when all σ's and J's are of the same order, is to make an estimate of σ's and J's, (based on repeated spacing in the spectrum), and then calculate better values by iteration until a desired consistency is reached. With the availability of an ABC computer programme[9] we have adopted the latter method. Before discussing the actual calculation it may be pointed out that a number of rules concerning the spacings and intensities of an ABC system are known[5,7]:

1. There are three splittings which are repeated four times throughout the spectrum.
2. The sum of the observed separations equals the sum of the J's.
3. The sum of the separations between the centres of the four lines corresponding to transitions of each nuclei add together to the sum of the chemical shifts, though individual separations will differ from corresponding σ.
4. Intensity sum rule:

$$\sum_{i=2}^{4} I_{1i} = \frac{3}{4}, \qquad \sum_{i=2}^{4}\sum_{j=5}^{7} I_{ij} = \frac{3}{2}, \qquad \sum_{j=5}^{7} I_{j8} = \frac{3}{4}$$

In addition there are some other regularities concerning combination lines. All these rules prove very useful for interpretation of the spectra and to check successive steps in the analysis.

SPECTRUM OF $CH_2 = CHCD_2OH$

The spectrum of specifically deuterated allyl alcohol is shown in Fig. 1. It was taken with a Varian high resolution spectrometer at 60 Mc/s. The list of the frequencies and intensities is given in Table I, the origin being taken at the position of the line assigned as A_1. The intensities are determined by simply reading the integrator. Finally all the intensities are normalized to 12, in order to reduce them to the same scale as that adopted in the computer programme.

The assignment of lines is based on repeated spacings, as shown

$A_1 - A_2 = 2.4$
$B_1 - B_2 = 2.4$
$A_3 - A_4 = 2.4$
$B_3 - B_4 = 2.4$
J^1_{AB} approx. $= 2.4$

$A_1 - A_3 = 9.9$
$A_2 - A_4 = 9.9$
$C_1 - C_4 = 9.8$
$C_3 - C_4 = 9.8$
J^1_{AC} approx. $= 9.9$

$B_1 - B_3 = 17.5$
$B_2 - B_4 = 17.5$
$C_1 - C_3 = 17.3$
$C_2 - C_4 = 17.3$
J^1_{BC} approx. $= 17.4$

where the primes indicate spectral splittings; these are only approximately equal to the actual coupling constants. The computer programme used, written by Banwell[9], employs an iterative method, as mentioned, and approaches by successive approximations the experimental spectrum to within specified limits. The initial chemical shifts (relative to σ_A) and spin-spin coupling constants J^1 used in calculations are

$\sigma_A{}^1 = 0$ (definition)
$\sigma_B{}^1 = {}^1\!/_2\,(B_2 + B_3) - {}^1\!/_2\,(A_2 + A_3) = 8.0$
$\sigma_C{}^1 = {}^1\!/_2\,(C_2 + C_3) - {}^1\!/_2\,(A_2 + A_3) = 53.2$

$J^1_{AB} = 2.4$
$J^1_{BC} = 17.4$
$J^1_{AC} = 9.9$

The final parameters, after the iteration procedure are

$\sigma_A = 0$
$\sigma_B = 8.92$
$\sigma_C = 50.23$

$J_{AB} = 1.85$
$J_{BC} = 17.33$
$J_{AC} = 10.53$

The line positions and their intensities calculated using the final parameters are listed alongside the experimental values in Table I. The agreement with experiment is very good, the maximum deviation of the frequencies being 0.1 c/s. The theoretical spectrum is shown in Fig. 1 under the actual tracing of the experimental spectrum. It will be noted that the C resonance lines are broadened somewhat, because of coupling with the deuterium (each line should really be a 1 : 2 : 3 : 2 : 1 quintet) but that the perturbation of the CD_2 group on the A and B resonance is negligible.

To eliminate alternative possibilities for the signs of the J's calculations were performed when J^1_{AB}, J^1_{BC} and J^1_{AC} in succession, have been assumed negative. The calculated intensities for cases $J_{BC} < 0$, $J_{AB} < 0$, are included in Fig. 1, and it can be seen that only in the case when all J's are positive is there a close agreement with the experimental spectrum. When initial parameters with $J^1_{AB} = -2.4$ are fed into the computer no solution is obtained. It was noted by Cavanaugh[10] that such situations, which correspond to imaginary solutions, should not be discarded without examination. By a slight change in the input parameters, justified by experimental errors in measuring line positions, complex solutions may become real. Mereover in some cases the actually accepted solution, giving correct intensities, is arrived at from an initially discarded set. Though J_{AB} has generally a small magnitude, a change of its sign may cause very violent changes of calculated transition intensities[11]. Such a situation arises for vinyl protons in allyl amine where zero intensities were predicted for some of the lines observed, while some weak transitions become very strong if reversed sign of J_{AB} is employed.[11] The reason for the large influence of the sign of J_{AB} was not understood, and the explanation is given here: The intensities of lines are obtained through a second order perturbation, and

TABLE I

Assignment	Observed		Calculated	
	Position	Intensity	Position	Intensity
A_1	0	0.84	0	0.80
A_2	2.4	0.83	2.40	0.78
B_1	4.2	0.56	4.25	0.50
B_2	6.6	0.75	6.65	0.73
A_3	9.9	0.89	9.90	0.85
A_4	12.3	1.39	12.30	1.53
B_3	21.7	1.74	21.65	1.84
B_4	24.1	1.09	24.05	0.95
C_1	45.8	1.54	45.70	1.70
C_2	55.6	1.08	55.60	1.05
C_3	63.1	0.69	63.10	0.67
C_4	72.9	0.58	73.00	0.52
X_1	—	—	—39.05	0.00
X_2	—	—	51.35	0.05
X_3	—	—	67.35	0.02

The positions are measured to within 0.2 c/s.

$$H_{AB} / (H_{AA} - H_{BB}) = {}^1/_2\, J_{AB} / \ [(\sigma_A - \sigma_B) \pm {}^1/_2\, (J_{AC} - J_{BC})]$$

is the responsible term. This expression depends critically on the relative magnitudes of $(\sigma_A - \sigma_B)$ and $(J_{AC} - J_{BC})$. Therefore whenever a situation arises that the relative shift $(\sigma_A - \sigma_B)$ is of the order of ${}^1/_2(J_{AC} - J_{BC})$, which is frequently the case, a change of the signs of both J_{AC} and J_{BC} will profoundly affect $H_{AB} / (H_{AA} - H_{BB})$. It is therefore not the change of sign of J_{AB}, but rather that of $(J_{AC} - J_{BC})$ which is responsible for such a sudden changes of intensities of calculated spectra. A change of sign J_{AB} is of course, equivalent to changes of signs of both J_{AC} and J_{BC} simultaneously.

In deuterated allyl alcohol $CH_2 = CH\,CD_2OH$ one can expect, because of structural similarities with allyl amine, that spectra obtained using $J_{AB} < 0$ would again be so different that this possibility can be rejected offhand.

SPECTRUM OF $CH_2 = CHCH_2OH$

A replacement of CD_2 by CH_2 will result in the appearance of additional lines due to methylene hydrogens, and in a further splitting of the original 12-line spectrum. Each line should according to simplified theory split into three, corresponding to possible values $+1$, 0, -1 of the components of an $S = {}^1/_2 + {}^1/_2$ spin system. This causes a more complex spectrum, which may be further complicated by mixing of spin functions with the same F_z, and by an insufficient resolution of resonance lines. The spectrum (Fig. 2) is only partially resolved, with the resonance lines due to H_C only being sufficiently resolved. This does not allow a detailed analysis (which in itself presents rather a difficult task), but conveniently, the perturbation of the ABC spectrum of vinyl protons by the methylene group is small, and the simplified approach is justified. We will therefore only indicate how the more complicated spectrum is related to that of $CH_2 = CH\,CD_2OH$, and we will derive from a qualitative analysis approximate spin-spin constants between CH_2 and vinyl hydrogens. By treating the actual $ABCD_2$ system as $ABCX_2$, coupling constants J_{XA}, J_{XB} and J_{XC} could be readily obtained from repeated spacings. This approximation introduces quite small errors in view of the large chemical shifts of the CH_2 protons *versus* the ABC protons. J_{XC} which appears in H_C and CH_2 resonance, both of which are quite well resolved, may be estimated at $|\sim 5\ c/s|$. The other two constants J_{XA} and J_{XB} produce a group of less resolved lines in H_A, H_B resonance, and act as two almost identical nuclei. Therefore approximately $J_{XA} = J_{XB}$, and a value $|\sim 1.5\ c/s|$ can be derived from line spacing of CH_2 resonance. This value gives a good agreement with the experimentally observed splitting of the AB resonance. The limitations of this simple approach are

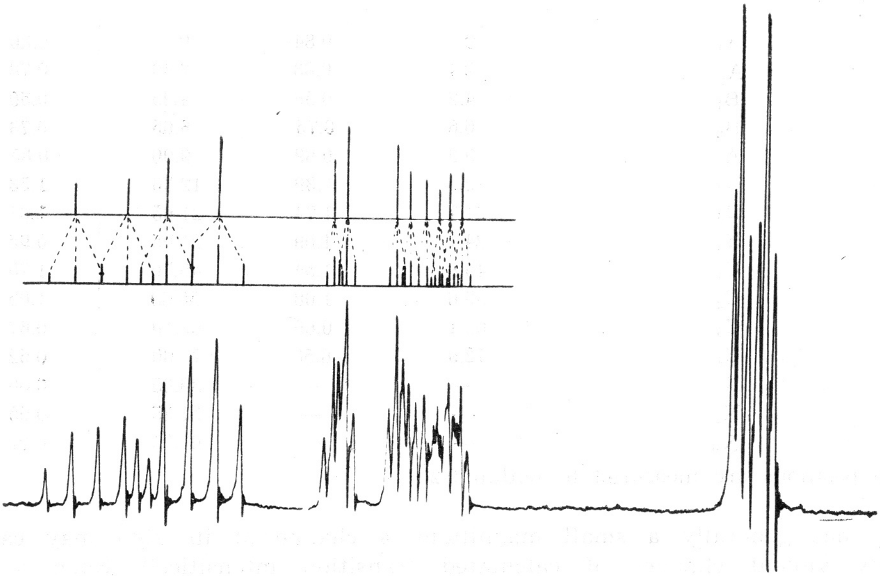

Fig. 2. Spectrum of allyl alcohol with the schematic spectrum of allyl alcohol-d_2, indicating the splittings due to the methylene hydrogens, of the original ABC spectrum.

to be noted in a small variation in the intensities of the four weaker lines in CH_2 resonance, as well as in a slight asymmetry within the spacings of the two triplets. However, there seems to be no doubt that this asymmetry would be resolved in a more accurate treatment.

Acknowledgements. We wish to thank Dr. Belanić-Lipovac, who prepared the samples and made the spectra available (recorded through the courtesy of Professor V. Prelog). We also thank Dr. C. N. Banwell for the computer programme, and Dr. J. N. Murrell for useful discussions. M. R. is indebted to The Royal Society for a research grant, and G. T. J. to the D. S. I. R. for a maintenance grant.

REFERENCES

1. H. M. McConnell, C. A. Reilly, and A. D. McLean, *J. Chem. Phys.* **24** (1956) 479
2. S. Alexander, *J. Chem. Phys.* **28** (1958) 358.
3. M. Karplus, *J. Chem. Phys.* **30** (1959) 6, 11.
4. W. Brügel, Th. Ankel, and F. Krückeberg, *Z. Elektrochem.* **64** (1960) 1121.
5. C. N. Banwell and N. Sheppard, *Mol. Phys.* **3** (1960) 351.
6. J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance,* McGraw Hill, 1959.
7. S. Castellano and J. S. Waugh, *J. Chem. Phys.* **34** (1961) 295, errata: *ibid,* **35** (1961) 1900; see also: J. R. Cavanaugh, *J. Chem. Phys* **39** (1963) 2378.
8. C. A. Reilly and J. D. Swallen, *J. Chem. Phys.* **32** (1960) 1378.
9. C. N. Banwell, *Ph. D. Thesis,* University of Cambridge, England 1960.
10. J. R. Cavanaugh, *J. Chem. Phys.* **40** (1964) 249.
11. S. Alexander, *J. Chem. Phys.* **32** (1960) 1700.

IZVOD

NMR spektri alil alkohola-d_2 i alil alkohola

G. T. Jones, M. Randić i J. J. Turner

NMR spektar specifično deuteriranog alil alkohola, analiziran je kao ABC tip. Dobivene su slijedeće vrijednosti za spin-spin konstante vodika u vinil grupi:

$$J_{trans} = 17.33 \text{ c/s} \qquad J_{cis} = 10.53 \text{ c/s} \quad \text{i} \quad J_{gem} = 1.85 \text{ c/s}$$

Izračunani su intenziteti linija za različite kombinacije predznaka. Dobro slaganje između eksperimentalnih i izračunanih intenziteta je postignuto kada su svi J istog predznaka. Dano je objašnjenje zašto J_{gem} ima veliki utjecaj na izračunane intenzitete. Spektar nedeuteriranog alil alkohola je interpretiran na osnovi ABC X_2 tipa, i slijedeće približne vrijednosti za spin-spin konstante metilena i vinil vodika su dobivene:

$$J_{XA} = J_{XB} \approx 1.5 \text{ c/s} \qquad \text{i} \qquad J_{XC} \approx 5 \text{ c/s.}$$

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY
SHEFFIELD, ENGLAND

Primljeno 7. kolovoza 1964.