Journal of Organometallic Chemistry, 97 (1975) 145—150
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE ^{1}H NMR SPECTRA OF TRIVINYLBORANE AND ITS LEWIS ACID—BASE ADDUCTS WITH NH_3, $N(CH_3)_3$ AND $P(CH_3)_3$

LAURENCE W. HALL*, JEROME D. ODOM**, and PAUL D. ELLIS**

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208 (U.S.A.)

(Received March 25th, 1975)

Summary

The ^{1}H NMR spectra, with ^{11}B noise decoupling, of $B(C_2H_3)_3$ and its Lewis acid—base adducts with NH_3, $N(CH_3)_3$ and $P(CH_3)_3$ are reported. The broadening of the vinyl regions of the coupled spectra arises predominantly as the result of isotropic $J(^{11}B—^1H)$ coupling and is not a manifestation of quadrupolar effects.

Introduction

A nucleus with a spin greater than 1/2 can often exert a dominant influence on the line shape of the NMR absorption of the other magnetic nuclei in the same molecule. This influence can arise as a result of isotropic J coupling, nuclear quadrupole effects on the T_1 and/or T_2 of the observed spin system, or a combination of these two effects. The nuclear quadrupole effects can be manifested at the observed nucleus if there is a non-zero value of the electric field gradient at the quadrupolar nucleus and there is a non-zero value of the isotropic coupling constant. A primary effect of a quadrupolar nucleus is to provide an efficient T_2 relaxation mechanism for a spin 1/2 system. This is the so-called scalar coupling of the second kind [2]. The phenomenon is analogous (mathematically) to the problem of chemical exchange and can be analyzed in this fashion. A combination of several factors must be operational for scalar coupling to be an efficient T_1 relaxation mechanism. This mechanism can be efficient if either: (a) the Larmor frequencies of the spin 1/2 nucleus and the quadrupolar nucleus are nearly degenerate (e.g. ^{13}C and ^{79}Br) [3] or (b) the

---

* Taken in part from the thesis of L.W. Hall [1]; Tennessee Eastman Fellow 1974-1975.

** Authors to whom correspondence should be addressed.

absolute value of the isotropic coupling constant is large (>100 Hz) and the T_2 relaxation time for the quadrupolar nucleus is very short ($\sim 10^{-6}$ to 10^{-7} s). An example of such a system has been discussed by Sharp [4] in the analysis of the ^{119}Sn relaxation time (T_1) in SnI_4.

In the case of trivinylborane, if scalar coupling of ^{11}B with ^{13}C or the vinyl protons occurs it would be expected to involve a T_2 mechanism, since the effect of scalar coupling on T_1 decreases as the difference in resonance frequencies between the coupled nuclei increases. In a 23.5 kG field the difference between the resonance frequencies of ^{11}B and ^{13}C is 6.9 MHz while for protons the difference is 68.0 MHz. The ^{13}C NMR spectrum of $B(C_2H_3)_3$, with ^{1}H noise decoupling, consists of a broad resonance for the α-carbons, showing poorly resolved B—C spin—spin coupling, and a sharp singlet for the terminal carbons [5,6]. Boron-11 noise decoupling does not cause any significant line narrowing of the α-carbon resonance even though other experiments in our laboratories have demonstrated that sufficient decoupling power was employed to remove boron—carbon spin couplings. Apparently, the resonance due to $^{13}C_\alpha$ in $B(C_2H_3)_3$ is broadened by scalar coupling to the ^{11}B quadrupolar nucleus, which provides an effective T_2 relaxation mechanism for the directly bonded ^{13}C nuclei. In this example the apparent transverse relaxation rate (as indicated by the ^{13}C linewidth) is such that $T_2^{-1} \gg J(\mathrm{BC})$. When this condition exists the linewidth is controlled by the square of the coupling constant and the T_2 of the boron nucleus. Therefore, normal decoupling power (<20 watts) will have little or no effect on the ^{13}C linewidth, i.e. the decoupling cannot remove the relaxation mechanism. Spin decoupling can only remove the effects of spin—spin splitting.

We have investigated the proton NMR spectra of trivinylborane and three of its Lewis acid—base adducts. The analysis of these spectra is presented and the effect of the ^{11}B nucleus on these spectra is assessed.

Experimental

All preparative work was carried out in a conventional high-vacuum system equipped with greaseless stopcocks. Trivinylborane was obtained either by the thermal decomposition of $FB(C_2H_3)_2$ [7,8] or from the reaction of BBr_3 with $Sn(C_2H_3)_4$ [5]. Adducts of trivinylborane were prepared by condensing equimolar amounts of $B(C_2H_3)_3$ and the respective base into a reaction tube at —196°C and allowing the tube to gradually warm to room temperature. The thermally stable, white, solid adducts were characterized by their ^{13}C, ^{11}B, and ^{1}H (with ^{11}B noise decoupling) NMR spectra [6].

Proton (100.1 MHz) NMR parameters were obtained on a Varian Associates XL-100-15 NMR spectrometer. Field/frequency lock was employed by locking to either ^{1}H or ^{2}H. All chemical shifts are reported relative to tetramethylsilane. The spectra were analyzed using the LAOCN3 method*. By this method an iterative calculation, based on the least squares criterion, is used to bring the calculated frequencies of assigned lines as close as possible to the corresponding observed lines. Chemical shifts and coupling constants are then obtained from this best fit.

---

* This program was kindly provided by Dr. Bothner-By [9].

Results and discussion

The proton NMR spectrum of trivinylborane was first reported by Good and Ritter [10] who, at 60 MHz, observed an eight line multiplet, centered at τ 3.4. More recently the proton spectra of various Group IIB and IIIA vinyl derivatives have been investigated [11]. The vinyl ^{1}H resonance lines observed in the spectrum of $(C_2H_3)_3Al \cdot N(CH_3)_3$ were found to be very broad, presumably due to both aluminium-27 quadrupolar and spin—spin coupling effects. Due to this broadening an unequivocal analysis of the spectrum could not be obtained. We have observed a similar broadening of the ^{1}H NMR spectrum of $B(C_2H_3)_3$ obtained at 100.1 MHz. The ^{11}B coupled ^{1}H spectrum of $B(C_2H_3)_3$, shown in Fig. 1, consists of two distinct regions. The more deshielded region contains four resolved resonances while the other region is very broad and poorly resolved. The ratio of the integrated intensities of the two regions is 1/2 respectively. An initial assumption, later confirmed by complete analysis, was that the four most deshielded resonance lines represent H(1) (see Table 1). In a monosubstituted vinyl compound the geminal proton, relative to the substituent, generally gives the most deshielded vinyl ^{1}H resonance [11,12]. Furthermore, a general characteristic of J(HH) in monosubstituted vinyl compounds is that $J_{trans} > J_{cis} > J_{gem}$ [13]. Therefore, if it is assumed that Fermi contact interaction is still dominant ^{11}B would be expected to spin—spin couple more weakly with the geminal protons than with either of the vicinal protons. Also, the large splittings exhibited by the deshielded multiplet are consistent with the argument that vicinal proton—proton coupling constants are larger than geminal couplings in monosubstituted vinyl compounds.

Boron-11 noise decoupling in the case of the proton spectrum of $B(C_2H_3)_3$ causes significant line narrowing, as seen in Fig. 2, and allows an accurate spectral analysis to be made. In this way, the ^{1}H NMR spectra of trivinylborane and its 1/1 adducts with $(CH_3)_3N$, H_3N and $(CH_3)_3P$ have been assigned. The parameters obtained are listed in Table 1. The accuracy of the spectral analysis of $(CH_3)_3P \cdot B(C_2H_3)_3$ is limited due to the overlapping of several of the resonance lines of both H(2) and H(3). Because of this, unambiguous first-order approximations for J_{23}, J_{24} and J_{34} (see Table 1) cannot be made. Upper and lower limits for

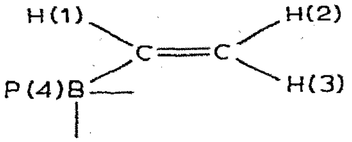
Fig. 1. 100.1 MHz ^{1}H NMR spectrum of $B(C_2H_3)_2$.

TABLE 1

PROTON NMR SPECTRAL PARAMETERS [a]

Compound	δ_1	δ_2	δ_3	J_{12} [d]	J_{13}	J_{23}	J_{14}	J_{24}	J_{34}
$B(C_2H_3)_3$ [b]	6.7	6.1	6.2	13.3	19.4	4.1			
$H_3NB(C_2H_3)_3$ [c]	6.3	5.6	5.1	13.3	19.6	3.9			
$(CH_3)_3NB(C_2H_3)_3$ [c]	6.2	5.6	5.3	13.3	19.4	4.9			
$(CH_3)_3PB(C_2H_3)_3$ [c,e]	6.5	5.8	5.6	13.2	19.5	4.7	6.9	5.2 ± 0.2	5.2 ± 0.2

[a] Protons are labelled as indicated:



[b] 10% solution in TMS. [c] ~50% solution in C_6D_6. [d] Signs of J(H—H) were not experimentally determined. J_{12} and J_{13} were assumed to be positive, based on sign determinations for the monosubstituted ethylene derivatives [13]. Best fits were then obtained when J_{23} was assumed to be positive. [e] $J(^{31}P—^{1}H(CH_3))$ 10.0 Hz.

these parameters can be obtained, however, by a comparison of the linewidth at half-height of the signals due to the overlap of two resonance lines with the linewidth at half-height of a signal representing a single resonance line. A series of values for these parameters ranging from the upper to lower limits can then be utilized by the LAOCN3 method [9] to obtain the best values for these coupling constants.

It has been observed that addition compounds generally have larger internal ^{1}H chemical shifts than the uncoordinated Lewis acid [11] and this observa-

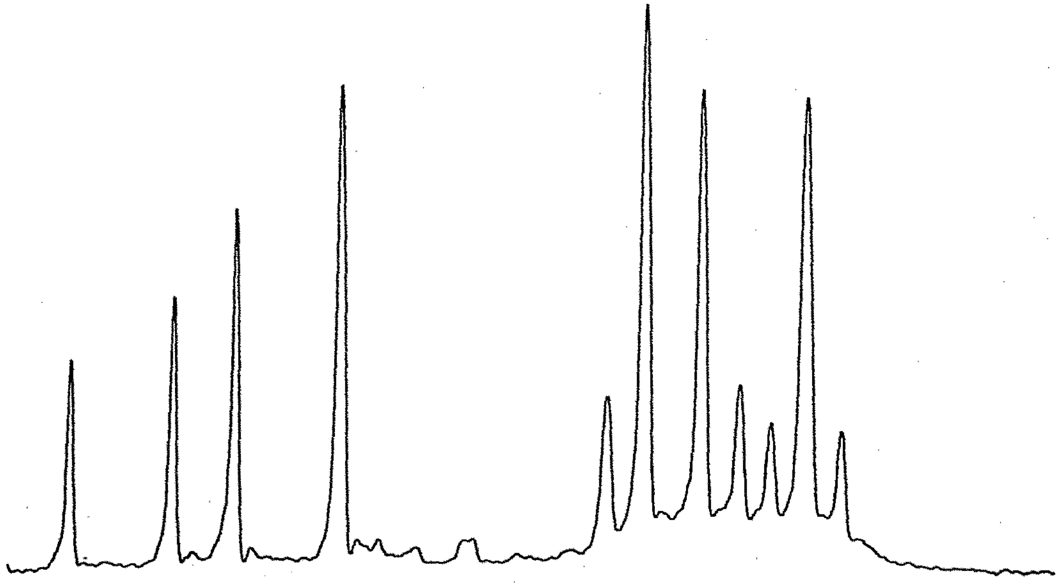


Fig. 2. ^{11}B decoupled 100.1 MHz ^{1}H NMR spectrum of $B(C_2H_3)_3$.

tion can be seen to be valid for $B(C_2H_3)_3$ and the three addition compounds studied. For $B(C_2H_3)_3$ the order of shielding of the vicinal protons is reversed upon adduct formation. In $B(C_2H_3)_3$ the most shielded resonance is that of the proton *trans* to boron, while the *cis* proton gives the most shielded vinyl resonance in the adducts studied.

Considerable attention has been given to the problem of obtaining a better understanding of the nature of the B—C bond in vinylboranes [14]. Carbon-13 NMR spectroscopy has been found to be a sensitive probe for detecting mesomeric interactions between the vinyl π-systems and the vacant p_π orbital of boron in these systems [6]. We were interested in determining whether small changes in the vinyl π-systems of $B(C_2H_3)_3$ that would occur with the removal of boron's vacant p_π orbital upon adduct formation, might be reflected by the ^1H NMR parameters of these compounds. As can be seen in Table 1, adduct formation causes little change in the values of the proton—proton coupling constants in $B(C_2H_3)_3$. This is in accord with previous work on ethylene in which the π-contribution to vicinal proton—proton coupling constants, ^3J, has been calculated to be only 1.5 Hz [15]. The proton chemical shifts appear to be sensitive to adduct formation. However, the interpretation of these chemical shifts and any relationship with the occurrence of B—C π-conjugation in $B(C_2H_3)_3$ is unclear.

In summary, the proton NMR spectra of $B(C_2H_3)_3$ and its adducts illustrate that broading of the ^1H NMR spectra of compounds containing organic groups directly bonded to a quadrupolar nucleus can, in many cases, be the result of unresolved spin—spin coupling, and not the result of quadrupolar relaxation effects. Such broadening can be removed by noise decoupling. Hence, the analysis of the ^1H NMR spectrum of $(C_2H_3)_3Al \cdot N(CH_3)_3$, previously alluded to, also may be facilitated by the inclusion ^{27}Al spin decoupling.

Acknowledgement

The authors gratefully acknowledge the financial support of the work by the National Science Foundation through GP 42454X.

References

1 L.W. Hall, Thesis Ph.D. Univ. South Carolina, submitted.
2 A. Abragam, The Principles of Nuclear Magnetism, Oxford, 1961, p. 306.
3 R. Freeman and H.D.W. Hill, Molecular Spectroscopy 1971, Institute of Petroleum, London, 1971, p. 105; R. Freeman and H.D.W. Hill, J. Chem. Phys., 54 (1971) 3367; G.C. Levy, J.D. Cargioli and F.A.L. Anet, J. Amer. Chem. Soc., 95 (1973) 1527 and refs. cited therein.
4 R.R. Sharp, J. Chem. Phys., 57 (1972) 5321.
5 L.W. Hall, D.W. Lowman, P.D. Ellis and J.D. Odom, Inorg. Chem., 14 (1975) 580.
6 L.W. Hall, J.D. Odom and P.D. Ellis, J. Amer. Chem. Soc., in press.
7 J.D. Odom, L.W. Hall, S. Riethmiller and J.R. Durig, Inorg. Chem., 13 (1974) 170.
8 F.E. Brinckman and F.G.A. Stone, J. Amer. Chem. Soc., 82 (1960) 6218.
9 A.A. Bothner-By and S. Castellano, J. Chem. Phys., 41 (1964) 2863.
10 C.D. Good and D.M. Ritter, J. Amer. Chem. Soc., 84 (1962) 1162.
11 H.D. Visser and J.P. Oliver, J. Organometal. Chem., 40 (1972) 7.
12 J.A. Pople, W.G. Schneider and H.J. Bernstein, High Resolution Nuclear Magnetic Resonance, McGraw-Hill Book Co., Inc., New York, 1959, Chapt. 11; S. Cowley and S.S. Danyluk, Can. J. Chem., 46 (1968) 2373.

13 A.A. Bothner-By, Advances in Magnetic Resonance, Vol. 1, Academic Press, New York, 1965.
14 T.D. Coyle, S.L. Stafford and F.G.A. Stone, J. Chem. Soc., (1961) 3103; J.R. Durig, R.O. Carter and J.D. Odom, Inorg. Chem., 13 (1974) 701; A.K. Holliday and W. Reade, Chem. Commun., (1971) 51; A.K. Holliday, W. Reade, K.R. Seddon and I.A. Steer, J. Organometal. Chem., 67 (1974) 1 and refs. cited therein.
15 M. Karplus, J. Chem. Phys., 33 (1960) 1842.