Conclusions.—(1) For "light" elements containing four electron pairs in their valency shells the angles between bonds formed to hydrogen or to other "light" elements will be approximately tetrahedral and will generally differ only by a few degrees from this value.

(2) For "heavy" elements containing only four electron pairs in their valency shells the angles between bonds formed to hydrogen or to other "heavy" elements will be smaller than tetrahedral and will often approach 90°.

(3) For "light" elements forming bonds to "heavy" elements with vacant orbitals in their valency shells the angles between these bonds will in general be larger and often considerably larger than the tetrahedral angle.

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Proton Magnetic Resonance Spectra of Some Ethyl Compounds

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The proton magnetic resonance spectra of zinc diethyl, germanium tetraethyl, dichlorodiethylsilane and trichloroethylsilane have been studied at both 40 and 60 Mcs. Except for $SiCl_2(C_2H_5)_2$, the values of the internal chemical shift δ and the spin–spin coupling constant J between the methyl and methylene group protons in these compounds have been obtained from a complete analysis of the spectra as A_3B_2 systems. A simple method of obtaining the value of δ from complex A_3B_2 type spectra is outlined. The δ values in the series $Si(C_2H_5)_4$–$SiCl_3(C_2H_5)$ appear to vary linearly with the number of chlorine atoms attached to silicon. The problem of correlating δ values with electronegativity, x, of the substituents is discussed in the light of presently available data on several ethyl compounds of the type $X(C_2H_5)_n$.

Introduction

The proton magnetic resonance spectra of several ethyl compounds have been studied,[2–14] and attempts have been made to correlate the internal chemical shift δ between the methyl and methylene protons in the ethyl group with the electro-negativity, x, of the group or atom attached to this ethyl group.[2,3,7–9,11,14–16] An empirical linear relationship between δ and x was suggested by Dailey and Shoolery[3] which fit the data for the ethyl halides, but it was later noted by Shoolery[15] that for substituents of lower electronegativity one of the empirical constants of the equation had to be adjusted.

A linear correlation of electronegativity x with chemical shift δ might be expected if the inductive effect of the substituent were the predominant mechanism for altering the charge about the methylene protons and if the methyl group were relatively unaffected. However, chemical shielding effects arising from the magnetic anisotropy of the C–X bond, or from mesomerism, would cause deviations from this simple relationship.[4,9]

In the present investigation we have obtained δ values for two ethyl compounds with substituents of low electronegativity, $Zn(C_2H_5)_2$ and $Ge(C_2H_5)_4$, as well as for the pair $SiCl_2(C_2H_5)_2$ and $SiCl_3(C_2H_5)$ in which the effect of increasing chlorine substitution could be noted. A revised interpretation of the spectrum observed[14] for $Ga(C_2H_5)_3$ is included since the method developed for this purpose provides a precise general technique for extracting δ from the complex A_3B_2 (ethyl) spectra arising when the ratio J/δ is not small. Finally, we have used all available data from $X(C_2H_5)_n$ spectra to discuss the problem of correlating δ with electronegativity.

Experimental

The proton magnetic resonance spectra of $Zn(C_2H_5)_2$, $Ge(C_2H_5)_4$, $SiCl_2(C_2H_5)_2$ and $SiCl_3(C_2H_5)$ were obtained using liquid samples in sealed tubes (5 mm. o.d.). The samples were degassed before sealing and the spectra were recorded with a Varian V-4300 spectrometer (40 Mcs.) and at 60 Mcs. with a V-4311 r.f. unit. The usual spinning and sideband modulation techniques were employed.

Results

The experimental spectra along with the theoretically calculated spectra are given in Figs. 1–4 for the compounds studied. Although the spectra were obtained at both 40 and 60 mcs. for all the compounds studied, we have given here the experimental and theoretical spectra for only one of these two frequencies for each compound. The theoretical spectra were calculated in the manner outlined elsewhere.[11] The results are summarized in Table I. The proton magnetic resonance spectrum of $SiCl_2(C_2H_5)_2$ at 40 mcs. is a single line (slightly broadened) while at 60 mcs. some structure is seen. The δ value given in Table I for this compound is obtained from an approximate fit of the theoretical spectrum to the experimental spectrum at 60 mcs. assuming the value J = 8.0 c.p.s., a value found for

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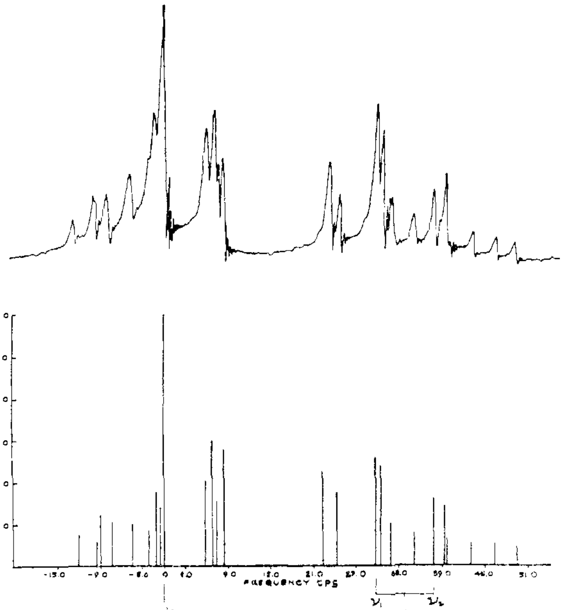

Fig. 1.—Experimental (top) and theoretical (bottom) proton magnetic resonance spectrum of zinc diethyl at 40 mcs.; the theoretical spectrum is calculated for $\delta = -33.9$ c.p.s. and $J = 8.6$ c.p.s.

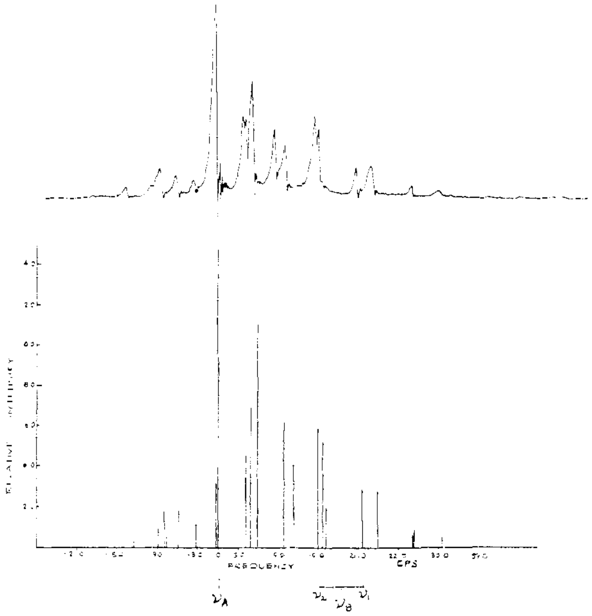

Fig. 2.—Experimental (top) and theoretical (bottom) proton magnetic resonance spectrum of germanium tetraethyl at 60 mcs.; the theoretical spectrum is calculated for $\delta = -18.4$ c.p.s. and $J = 7.8$ c.p.s.

$SiCl_3(C_2H_5)$. For this reason the δ value given here for this substance must be considered as only approximate.

In Table I the positive value of δ refers to the CH_3 group protons being more shielded than those of the CH_2 group. In the case of $Zn(C_2H_5)_2$ the proton magnetic resonance spectrum recorded at 60 Mcs. yielded a fairly simple 'ethyl' spectrum from which δ and J could be obtained. The values of δ for $Ge(C_2H_5)_4$ and $SiCl_3(C_2H_5)$ were obtained from the

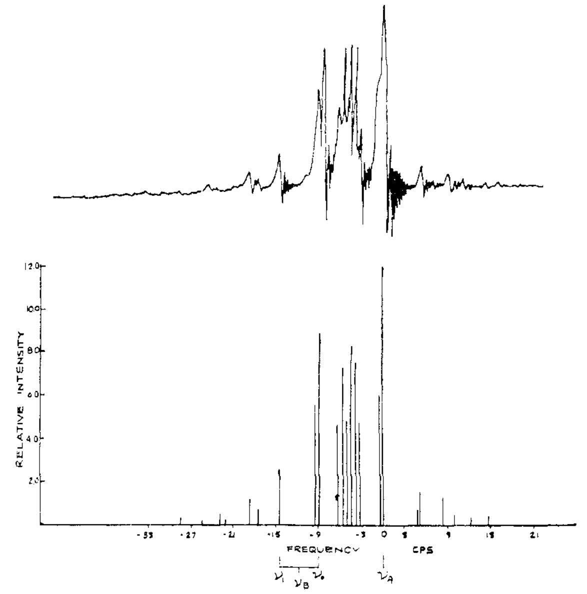

Fig. 3.—Experimental (top) and theoretical (bottom) proton magnetic resonance spectrum of $SiCl_3(C_2H_5)$ at 60 mcs.; the theoretical spectrum is calculated for $\delta = 11.7$ c.p.s. and $J = 8.0$ c.p.s.

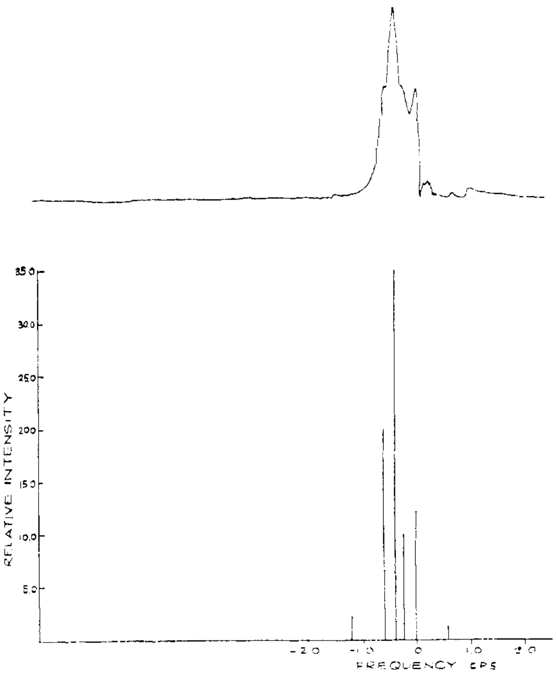

Fig. 4.—Experimental (top) and theoretical (bottom) proton magnetic resonance spectrum of $SiCl_2(C_2H_5)_2$ at 60 mcs.; the theoretical spectrum is calculated for $\delta = 0.9$ c.p.s. and $J = 8.0$ c.p.s.

complex spectra (see Figs. 2 and 3) by a fairly simple method. This method is based on the theoretical analysis of A_3B_2 type spectra outlined elsewhere.[11] The details are given in the following section.

Determination of δ from Complex A_3B_2 Spectra.—Using the notation of our earlier paper[11] we shall now consider the DT spin functions. In particular, we shall deal with the four allowed transitions, namely those from the two levels with $\Sigma I_Z = -{}^1/_2$

TABLE I

INTERNAL CHEMICAL SHIFT (δ) AND SPIN-SPIN COUPLING CONSTANT (J) FOR ETHYL GROUP PROTONS IN SOME ORGANOMETALLIC COMPOUNDS

Compound	δ (p.p.m.)	J (c.p.s.)
$Zn(C_2H_5)_2$	−0.848	8.6
$Ge(C_2H_5)_4$	− .307	7.8
$SiCl_3(C_2H_5)$	+ .195	8.0
$SiCl_2(C_2H_5)_2$	+ .015	(8.0)

to the two levels with $\Sigma I_Z = +\,{}^1/_2$. For $\Sigma I_Z = -{}^1/_2$ we have the secular equation

$$\text{(DT states)}\quad \begin{vmatrix} {}^1/_2\nu_A - W & \dfrac{\sqrt{2}\,J}{2} \\ \dfrac{\sqrt{2}\,J}{2} & {}^1/_2\nu_A - \delta - {}^1/_2J - W \end{vmatrix} = 0$$

(ν_A refers to the common frequency of the CH_3 group protons in our present case and $\delta = \nu_A - \nu_B$). The roots of the above equation are

$$W_1^{-1/2} = ({}^1/_2\nu_A - {}^1/_2\delta - {}^1/_4J) + {}^1/_2\,[(\delta + {}^1/_2J)^2 + 2J^2]^{1/2} \qquad (1)$$

and

$$W_2^{-1/2} = ({}^1/_2\nu_A - {}^1/_2\delta - {}^1/_4J) - {}^1/_2\,[(\delta + {}^1/_2J)^2 + 2J^2]^{1/2} \qquad (2)$$

For $\Sigma I_Z = +{}^1/_2$ we have the secular equation

$$\text{(DT states)}\quad \begin{vmatrix} -{}^1/_2\nu_A + \delta - {}^1/_2J - W & \dfrac{\sqrt{2}\,J}{2} \\ \dfrac{\sqrt{2}\,J}{2} & -{}^1/_2\nu_A - W \end{vmatrix} = 0$$

The roots are

$$W_1^{1/2} = (-{}^1/_2\nu_A + {}^1/_2\delta - {}^1/_4J) + {}^1/_2\,[(\delta - {}^1/_2J)^2 + 2J^2]^{1/2} \qquad (3)$$

and

$$W_2^{1/2} = (-{}^1/_2\nu_A + {}^1/_2\delta - {}^1/_4J) - {}^1/_2\,[(\delta - {}^1/_2J)^2 + 2J^2]^{1/2} \qquad (4)$$

Equations 1–4 may be re-written in the form

$$W_1^{-1/2} = ({}^1/_2\nu_A - {}^1/_2\delta - {}^1/_4J) + {}^1/_2A \qquad (5)$$

$$W_2^{-1/2} = ({}^1/_2\nu_A - {}^1/_2\delta - {}^1/_4J) - {}^1/_2A \qquad (6)$$

$$W_1^{1/2} = (-\,{}^1/_2\nu_A + {}^1/_2\delta - {}^1/_4J) + {}^1/_2B \qquad (7)$$

$$W_2^{1/2} = (-\,{}^1/_2\nu_A + {}^1/_2\delta - {}^1/_4J) - {}^1/_2B \qquad (8)$$

where

$$A = [(\delta + {}^1/_2J)^2 + 2J^2]^{1/2} \qquad (9)$$

and

$$B = [(\delta - {}^1/_2J)^2 + 2J^2]^{1/2} \qquad (10)$$

Let us consider the transition $W_1^{-1/2} \rightarrow W_1^{1/2} = \nu_1$. The frequency of this transition is seen to be

$$\nu_1 = \nu_A - \delta + {}^1/_2(A - B) \qquad (11)$$

Similarly, consider the transition $W_2^{-1/2} \rightarrow W_2^{1/2} = \nu_2$. The frequency of this transition is given by

$$\nu_2 = \nu_A - \delta - {}^1/_2(A - B) \qquad (12)$$

The average of ν_1 and ν_2 is thus $\nu_A - \delta = \nu_B$. Therefore, if one can identify these two transitions, ν_1 and ν_2, in an A_3B_2 spectrum and measure their positions with respect to ν_A, one can determine δ. Generally speaking, ν_A is easily identified by its intensity and narrow width. In order to locate ν_1 and ν_2, it may be necessary in practice to make at least one trial calculation. The values of J and δ obtained from approximate methods like the moment method may be used for such a trial calculation. However, if one has a set of theoretical spectra calculated for various J/δ values,[12] it is then a relatively simple matter to locate these transitions by comparison and thus determine δ. The relative intensities of ν_1 and ν_2 also can be calculated[11] and compared. Further check may be obtained by considering the other two transitions, namely $W_1^{-1/2} \rightarrow W_2^{1/2}$ and $W_2^{-1/2} \rightarrow W_1^{1/2}$.

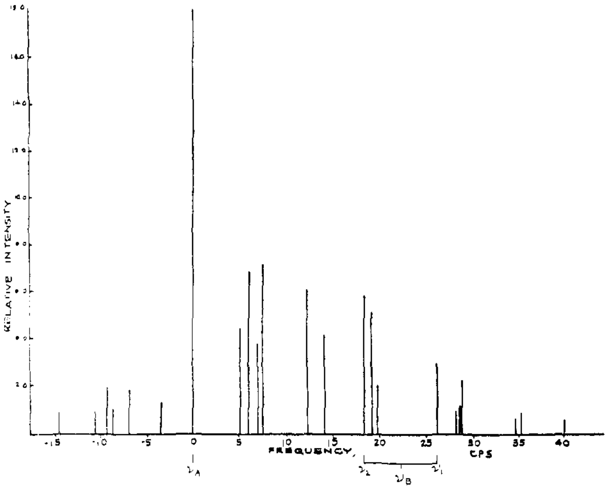

Fig. 5.—Theoretical proton magnetic resonance spectrum for gallium triethyl at 40 mcs. calculated with $\delta = -224.$ c.p.s. and $J = 9.1$ c.p.s.

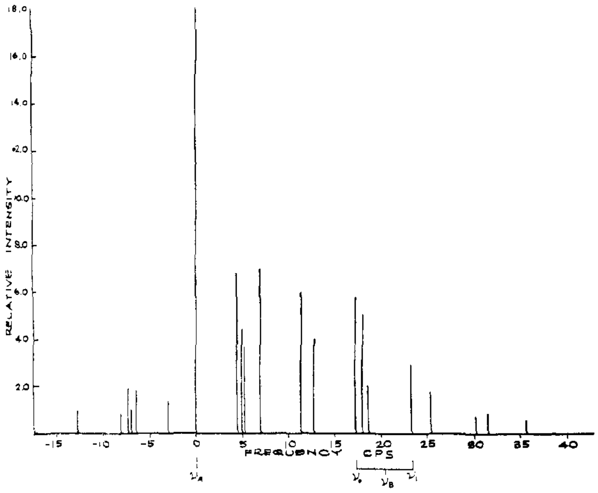

Fig. 6.—Theoretical proton magnetic resonance spectrum for gallium triethyl at 40 mcs. calculated with $\delta = -20.2$ c.p.s. and $J = 7.9$ c.p.s. (see ref. 41).

To illustrate the above method we have marked in Figs. 1–3, 5 and 6 the positions of ν_1 and ν_2; ν_B is seen to be just the average of these two. We wish to point out here that one can get accurate values of δ directly from some of the already published complex A_3B_2 spectra for which approximate methods have been used earlier. As an example, we may cite here the case of the 40 Mcs. spectrum of $Ga(C_2H_5)_3$ analyzed by Brownstein, *et al.*,[14] using the moment method. From the data given by these authors we have been able to determine by the present approach the value of δ to be −22.4 c.p.s. at 40 mcs. This value compares reasonably well with the value of −20.2 c.p.s. obtained by Brownstein, *et al.*, by the moment method. Incidentally, we find that the spectrum of $Ga(C_2H_5)_3$ obtained by them at 40 Mcs. fits better with a calculated theoretical spectrum using a J/δ value of 0.406 (see Figs. 5 and 6). (These are to be compared with the experimental spectrum given in ref. 14.) On this basis the value of J in $Ga(C_2H_5)_3$ is found to be 9.1 c.p.s. instead of the reported 7.9 c.p.s. Perhaps the value of J = 9.1 c.p.s. may be considered somewhat high and if so the 60 mcs. spectrum could be used to confirm this point. Since we are interested, however, only in δ values here, we have made use of the value of $\delta = -0.560$ p.p.m. for this compound in our later discussion. The value of $\delta = -0.420$ p.p.m. for $Si(C_2H_5)_4$ given by McGarvey and Slomp[13] has been confirmed by the present method.

Discussion

The δ values of the ethyl group in the series $Si(C_2H_5)_4$–$SiCl_3(C_2H_5)$ appear to vary linearly with the number of chlorine atoms attached to silicon. Thus the δ values of $SiCl_3(C_2H_5)$, $SiCl_2(C_2H_5)_2$ and $Si(C_2H_5)_4$ can be represented approximately by the equation

$$SiCl_n(C_2H_5)_{4-n} = -0.420 + 0.205n \text{ (in p.p.m.)} \quad (13)$$

On this basis the δ value of $SiCl(C_2H_5)_3$ is predicted to be -0.215 p.p.m. It would be interesting to compare the experimental value of δ for this compound with the above predicted value when measurements are forthcoming. It should be pointed out here that the δ values are for pure liquids and with this point in mind the observed linearity must be judged. An interesting feature of the chlorine substitution in the above series is the tendency of the δ values to change their sign from negative to positive. On the basis of the inductive mechanism one can interpret the effect of chlorine substitution as contributing to the electron withdrawal power of silicon.

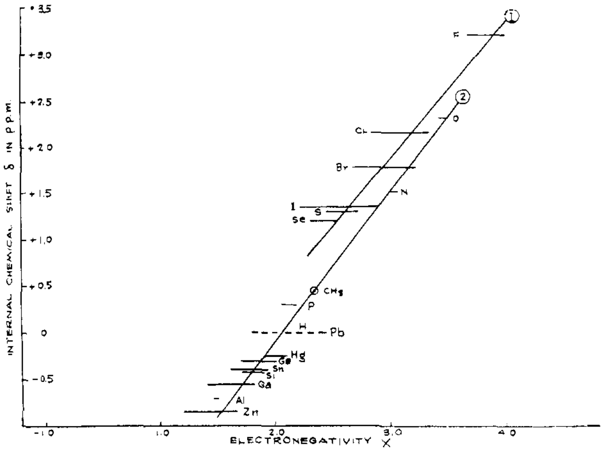

Fig. 7.—Internal chemical shift $\delta_{CH_2-CH_3}$ for protons in the ethyl group of compounds of the type $X(C_2H_5)_n$ plotted against the electronegativity x of the substituent X.

Turning now to the internal chemical shift of protons in an ethyl group, we have plotted in Fig. 7 the δ values for compounds of the type $X(C_2H_5)_n$ against the electronegativity x of the substituent atom or group X. The horizontal bar in the plot shows the range of electronegativity values given by various authors using different approaches. It is rather unfortunate that this range is quite large in most of the cases. The sources for the x values are Huggins,[17] Pritchard and Skinner,[18] Allred and Rochow[19] and references given in these articles. The value for CH_3 group has been taken from Gordy.[20] The δ values, with the exception of ethyl fluoride, are for the liquids. The δ value for ethyl fluoride is for a solution in benzene.[3] The δ values for $P(C_2H_5)_3$ and $Sn(C_2H_5)_4$ are from complete analyses of the proton resonance spectra.[5] Other δ values have been taken from references cited earlier in the introduction. From Fig. 7 it is seen that δ *vs.* electronegativity for the series F, Cl, Br, I, S and Se yields a fairly linear plot (line 1 in Fig. 7) while the other substituents fall in a different category (line 2 in Fig. 7). The latter by themselves seem to yield another linear plot, although it must be stressed that this is only approximately so. The surprising result is, of course, the fact that there is a fairly linear relationship between δ and x in the two classes of compounds. Considering the complex nature of the shielding mechanism,[4] the observed linearity is unexpected. While the δ *vs.* x plot for the first class of substituents yields the Dailey–Shoolery equation,[3] the second class yields the expression

$$x = \text{electronegativity} = 0.62\delta + 2.07 \quad (14)$$

Equation 14 differs only slightly from the modified Dailey–Shoolery[15] equation. We may mention here that the electronegativity value obtained by the use of equation 14 will be, in general, an average 'best value' rather than that from a particular scale.

It may be of interest to note here that the proton shielding studies in methyl compounds[19] also yielded two different relationships between δ and x, namely, one for the series F, Cl, Br, I and another for C, N, O, Si, Ge and Sn. A similar feature has been noted in the case of C^{13} chemical shift studies[21] on methyl compounds. It may be noted that the C–X bonds for the elements on curve 1 of Fig. 7 are those with the largest p-character in the bond orbitals. Also curves 1 and 2 are approaching one another for the most electronegative atoms where ionic character of the C–X bond is large and the paramagnetic contribution to the bond anisotropy is becoming small.[9]

These conclusions then may be reached on the basis of the present discussion: from the experimental δ values the order of electronegativity that is obtained here, Pb > Ge > Sn > Si, is exactly the same as that given by Allred and Rochow[19] from a study of the proton shielding values in the corresponding methyl compounds and from various other considerations. Using equation 14 we find that the x values of phosphorus and aluminum are 2.26 and 1.63, respectively. These values are somewhat higher than those given in the literature. Also, the value of 2.45 for the electronegativity of lead given by Allred and Rochow[19] seems to be rather high. The electronegativity of hydrogen and lead are probably nearly the same. The above conclusions, it must be remembered, are based on the approximate linearity between x and δ for the liquid compounds. It would be preferable to obtain the δ values at infinite dilution in inert solvents in much the same way as that adopted by Allred and Rochow for the methyl compounds. However, the internal chemical shift values for the ethyl protons are not very sensitive to solvent effects and hence the conclusions arrived at here may not be seriously affected.

Acknowledgments.—This work was supported in part by the Atomic Energy Commission through contract AT(11-1)-151. We are indebted to the Research Corporation for a grant which made possible the purchase of equipment necessary for this research.

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