The Nuclear Magnetic Resonance Spectra of Triethylaluminum and Diethylaluminum Monohalides

By Osamu Yamamoto

(Received July 5, 1963)

The high resolution proton magnetic resonance spectra of a considerable number of metal alkyls have been studied in recent years; special attentions has been directed to ethyl compounds[1-4] in an attempt to correlate the electronegativity of the metal with the internal chemical shift of the ethyl group. An empirical linear relation between them was first proposed by Dailey and Shoolery[5] and later modified by Shoolery[6] for substituents of lower electronegativity through altering the empirical constants of the equation. The modified form of the equation is:

$$x=0.62\delta+2.07 \qquad (1)$$

where x is the electronegativity of the metal atom and δ is the internal chemical shift in p. p. m., i. e., the difference between the methyl and the methylene proton shifts.

It can easily be predicted from the equation that if x is equal to the constant term, the δ value is zero, and that if x is less than the constant term, δ is negative; that is, the methyl protons will be less shielded than the methylene protons. The spectrum shows the "inverted ethyl signals." These have clearly been demonstrated by Baker for tetraethyllead and diethylaluminum chloride respectively.[1]

Aluminum alkyls occupy an interesting position in structural chemistry because of their dimeric forms;[7,8] consequently, they have been studied extensively by means of X-ray[9] and electron diffraction[10] as well as by Raman[11-15] and infrared[12,14,16-18] spectroscopy. Some studies of the proton magnetic

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[1] E. B. Baker, *J. Chem. Phys.*, **26**, 960 (1957).
[2] P. T. Narasimhan and M. T. Rogers, *J. Am. Chem. Soc.*, **82**, 34 (1960).
[3] P. T. Narasimhan and M. T. Rogers, ibid., **82**, 5983 (1960).
[4] P. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, **34**, 1049 (1961).
[5] B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).
[6] J. N. Shoolery, Lecture Notes, *Varian Associates Conference* (1957); see also Ref. 3.
[7] A. W. Laubengayer and W. F. Gilliam, *J. Am. Chem. Soc.*, **63**, 477 (1941).
[8] K. S. Pitzer and H. S. Gutowsky, ibid., **68**, 2204 (1946).
[9] P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953).
[10] L. O. Brockway and N. R. Davison, *J. Am. Chem. Soc.*, **63**, 3287 (1941).
[11] K. W. F. Kohlrausch and J. Z. Wagner, *Z. phys. Chem.*, **B52**, 185 (1942).
[12] E. G. Hoffmann, *Z. Elektrochem.*, **64**, 616 (1960).
[13] C. P. Van der Kelen and M. A. Herman, *Bull. soc. chim. Belges*, **65**, 362 (1956).
[14] M. P. Growenewege, *Z. phys. Chem.*, (*N. F.*), **18**, 147 (1958).
[15] O. Yamamoto, This Bulletin, **35**, 619 (1962).
[16] K. S. Pitzer and R. K. Sheline, *J. Chem. Phys.*, **16**, 552 (1948).
[17] E. G. Hoffmann and G. Schomburg, *Z. Elektrochem.*, **61**, 1101 (1957).
[18] G. Schomburg and E. G. Hoffmann, ibid., **61**, 1110 (1957).

resonance spectra of these compounds have also been reported.[1,19,20] These compounds, however, except for methyl derivatives, give moderately complicated spectra, and the reported values of the chemical shifts, δ, and the coupling constant, J, are based on the firstorder approximation of the analysis.

In the present paper, the δ and the J values for triethylaluminum and diethylaluminum monohalides will be revised by a rigorous A_3B_2 analysis of the spectra; moreover, some consideration will be given for the internal chemial shifts and the coupling constants of the compounds. At the same time, the dilution effect on the δ values will be considered.

Experimental

The proton magnetic resonace spectra were obtained by means of a Varian Associate DP-60 spectrometer equipped with V-4311 R-F units of 40 and 60 Mc./sec., the usual sideband technique being employed. The spectra were obtained with pure liquid samples as well as solutions in benzene.

The solvent was dehydrated and purified by the conventional methods. All the materials used were prepared by Grosse and Mavity's methods.[21] Since aluminum alkyls are in general very reactive with air and moisture, the purified samples were transferred into cylindrical sample tubes (5 mm. o. d.) in a high vacuum apparatus; appropriate amounts of solvent, if employed, were directly distilled therein, and then the tubes were sealed off.

Results

The spectra obtained at 40 Mc./sec. using the pure liquid samples are reproduced in Figs. 1—4. The triplet-like signals on the lower field side are due to the methyl protons, and the higher field side signals, to the

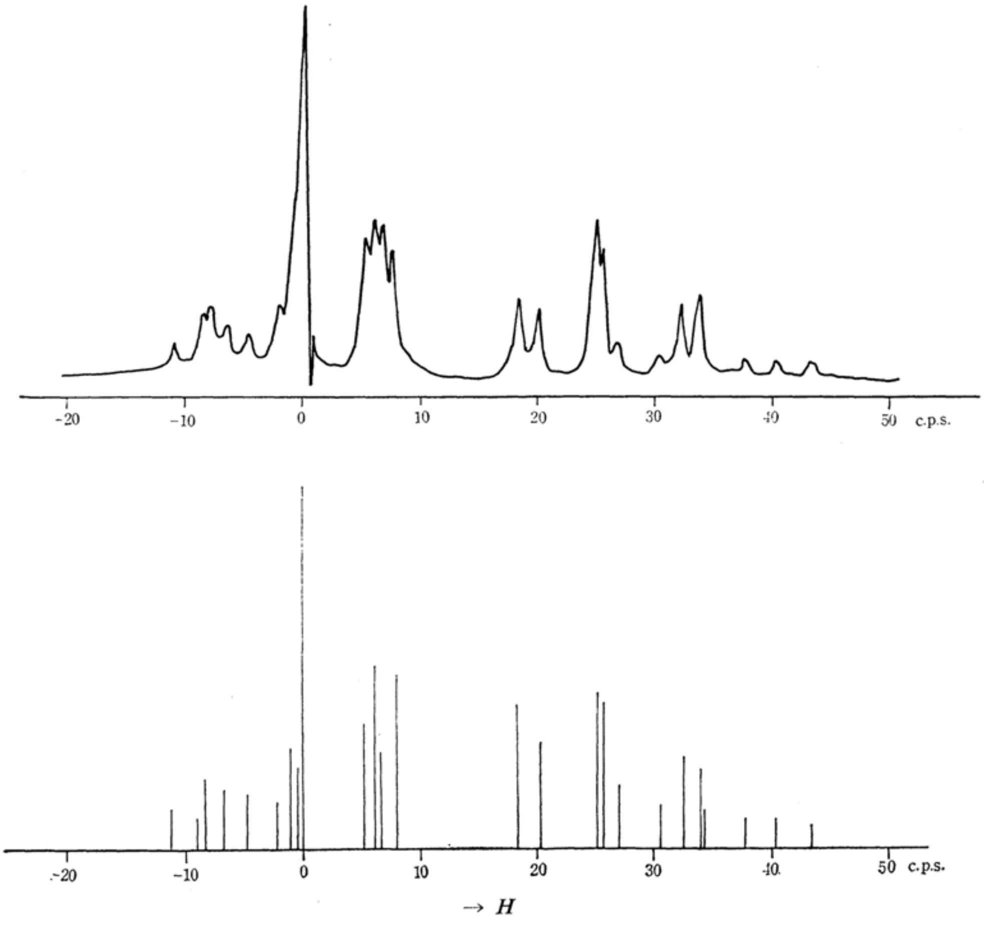

Fig. 1. Observed and calculated spectra of triethylaluminum in pure liquid state at 40 Mc./sec.

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19) E. G. Hoffmann, ibid., **64**, 144 (1960).

20) M. P. Growenewege, J. Smidt and H. de Vries, *J. Am. Chem. Soc.*, **82**, 4425 (1960).

21) A. von Grosse and J. M. Mavity, *J. Org. Chem.*, **5**, 106 (1940).

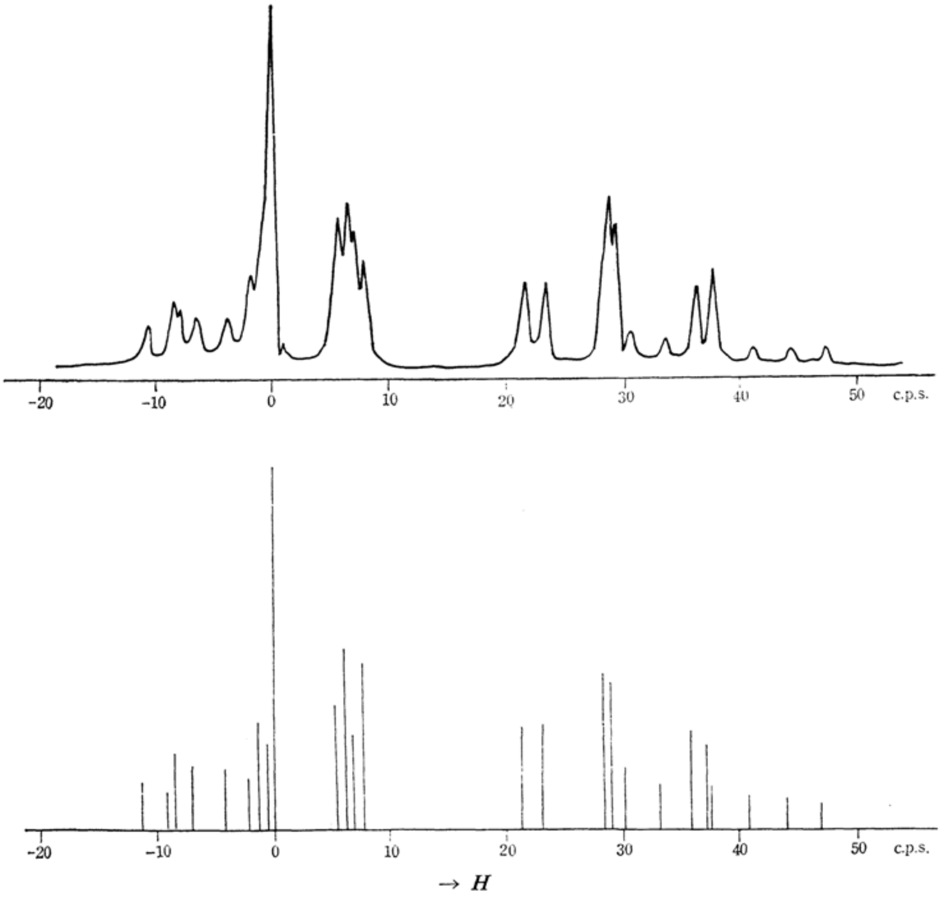

Fig. 2. Observed and calculated spectra of diethylaluminum chloride in pure liquid state at 40 Mc./sec.

TABLE I. OBSERVED AND CALCULATED SPECTRA OF TRIETHYLALUMINUM AT 40 Mc./sec. The designation for the transitions is according to Narasimhan and Rogers.[2]

Transition at the limit $J \rightarrow 0$	Frequency c.p.s.		Relative intensity	
	Calcd.	Obs.	Calcd.	Obs.
CH$_3$-transition				
$Q_3T_1 \rightarrow Q_1T_1$	−11.3	−11.4	1.4	1.7
$D_1T_1 \rightarrow D_{-1}T_1$	−8.9	−8.7	1.1	3.9
$Q_1T_1 \rightarrow Q_{-1}T_1$	−8.2	−8.1	2.4	
$Q_{-1}T_1 \rightarrow Q_{-3}T_1$	−6.6	−6.6	2.0	2.3
$Q_3T_0 \rightarrow Q_1T_0$	−4.6	−4.7	1.8	2.5
$D_1T_0 \rightarrow D_{-1}T_0$	−2.1	−2.2	1.6	20.0
$Q_1T_0 \rightarrow Q_{-1}T_0$	−1.0	−1.2	3.5	
$Q_{-1}T_0 \rightarrow Q_{-3}T_0$	−0.5	−0.7	2.8	
QS and DS transition	0.0	0.0	12.0	
$Q_{-1}T_{-1} \rightarrow Q_{-3}T_{-1}$	5.3	5.4	4.2	18.3
$Q_1T_{-1} \rightarrow Q_{-1}T_{-1}$	6.1	6.1	6.2	
$D_1T_{-1} \rightarrow D_{-1}T_{-1}$	6.7	6.7	3.2	
$Q_3T_{-1} \rightarrow Q_1T_{-1}$	7.6	7.5	5.8	
CH$_2$-transition				
$Q_3T_0 \rightarrow Q_3T_{-1}$	18.5	18.5	4.8	4.6
$Q_3T_1 \rightarrow Q_3T_0$	20.3	20.3	3.6	3.4
$D_1T_0 \rightarrow D_1T_{-1}$	25.2	25.3	5.2	11.8
$D_1T_1 \rightarrow D_1T_0$	25.8	25.8	4.9	
$Q_1T_1 \rightarrow Q_1T_0$	27.0	26.9	2.0	
$Q_1T_0 \rightarrow Q_1T_{-1}$	30.6	30.6	1.4	1.4
$D_{-1}T_1 \rightarrow D_{-1}T_0$	32.6	32.5	3.1	3.2
$D_{-1}T_0 \rightarrow D_{-1}T_{-1}$	34.1	34.1	2.8	3.9
$Q_{-1}T_0 \rightarrow Q_{-1}T_{-1}$	34.3		1.3	
$Q_{-1}T_1 \rightarrow Q_{-1}T_0$	37.7	37.6	1.0	1.2
$Q_{-3}T_1 \rightarrow Q_{-3}T_0$	40.0	40.4	1.0	1.0
$Q_{-3}T_0 \rightarrow Q_{-3}T_{-1}$	43.4	43.4	0.8	0.7

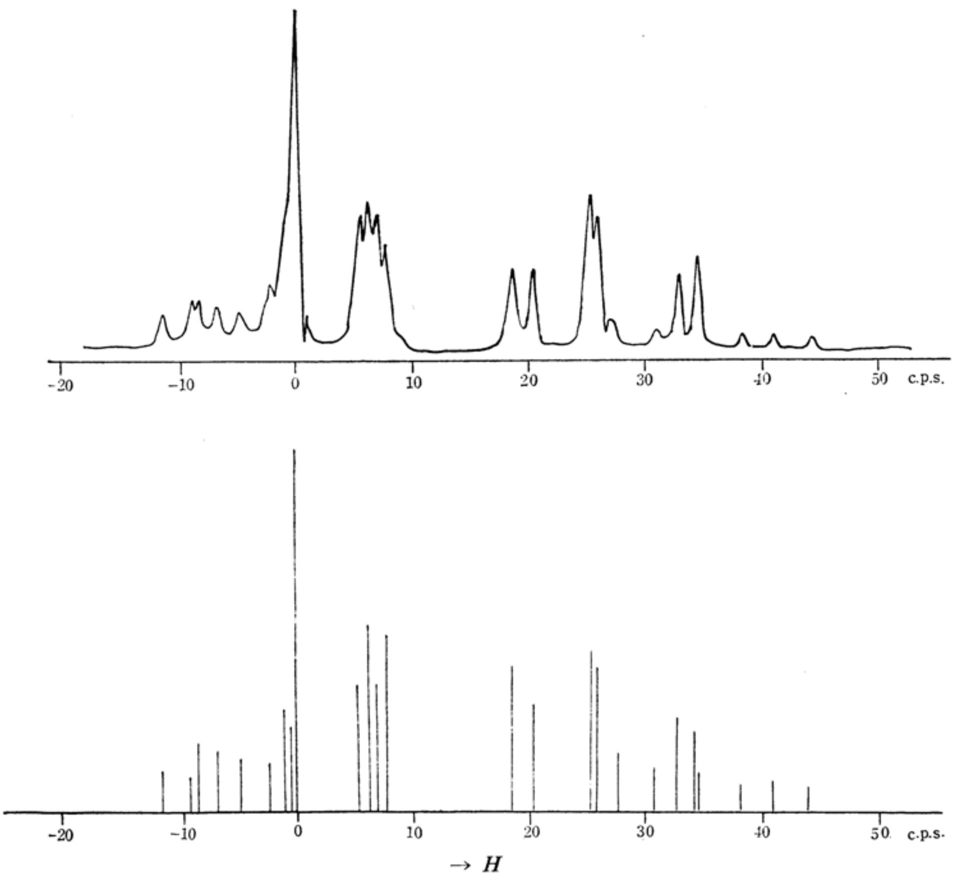

Fig. 3. Observed and calculated spectra of diethylaluminum bromide in pure liquid state at 40 Mc./sec.

methylene protons, so the spectra show "inverted ethyl signals." The individual spectral lines are somewhat broadened, probably because of the nuclear spin of aluminum ($I=5/2$).

The analysis of the spectra as an A_3B_2 system was accomplished using a NEAC-2101 digital computor. Three equivalent protons of the methyl group and two of the methylene group were treated as composite spin particles which have total spin angular momenta of 3/2 and 1 respectively. The initial assignment of the signals was determined by comparison with the theoretical spectra calculated for various J/δ values in advance. Since the observed spectra were not very muth deformed from the first-order triplet-quartet spectra (when J/δ is quite small), the assignments were rather easy. All the data from the observed lines according to the tentative assignment were fed into the input of the computor, and calculations were made to obtain the stationary state energies and the transition intensities. The program further proceeded to iteration, using the least-squares method for the difference between the observed and the calculated frequencies.

TABLE II. δ AND J_{CH_3, CH_2} VALUES OBTAINED FROM A_3B_2 ANALYSIS OF THE SPECTRA EOR TRIETHYLALUMINUM AND DIETHYLALUMINUM MONOHALOGENIDES IN THE PURE LIQUID STATE

Compound	δ, p.p.m.		J_{CH_2, CH_3} c.p.s.	
	40 Mc.	60 Mc.	40 Mc.	60 Mc.
$Al(C_2H_5)_3$	−0.72	−0.72	7.9_3	8.0_1
$Al(C_2H_5)_2Cl$	−0.81	−0.82	8.1_1	8.1_2
$Al(C_2H_5)_2Br$	−0.73	−0.73	8.0_8	8.0_7
$Al(C_2H_5)_2I$	−0.60	−0.60	8.0_5	8.1_1

The numerical details of the calculation are shown in Table I for only the 40 Mc. spectrum of triethylaluminum, while schematic illustrations of the theoretical spectra for each compound are given at the bottom in Figs. 1—4. The δ and the J values obtained both at 60 and 40 Mc./sec. for the pure liquid samples are summarized in Table II.

The spectra of benzene solutions were obtained only with 60 Mc./sec.; similar calculations were made to obtain the δ values,

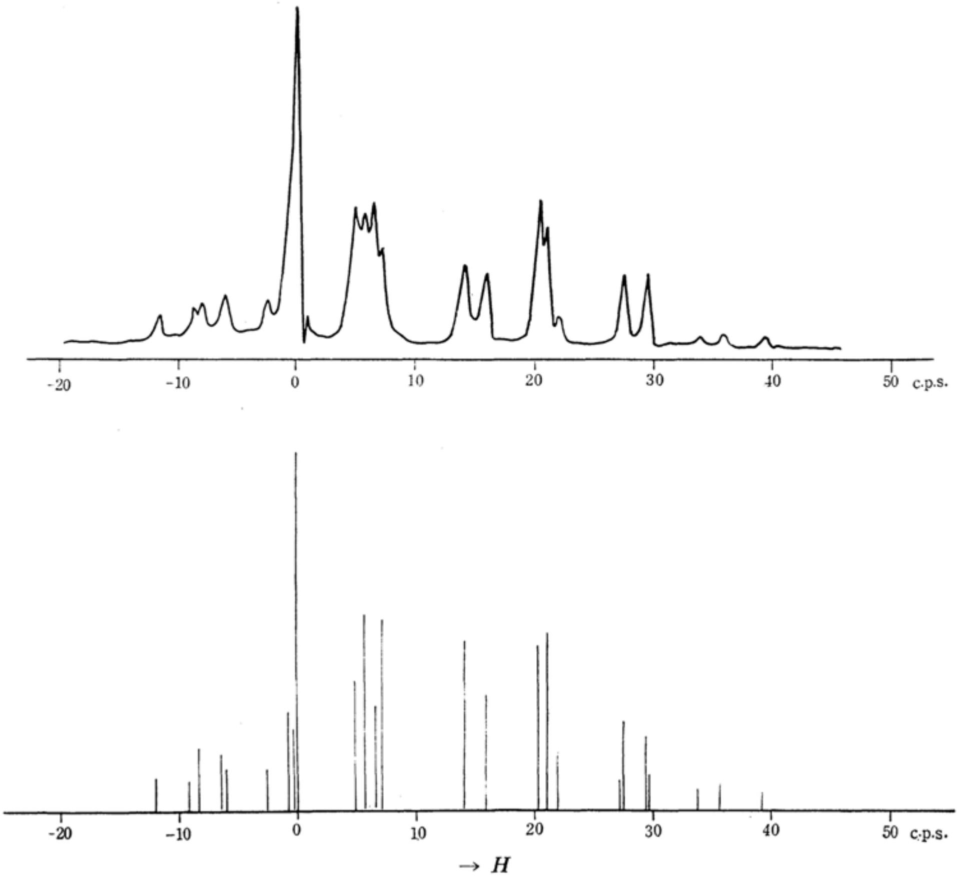

Fig. 4. Observed and calculated spectra of diethylaluminum iodide in pure liquid state at 40 Mc./sec.

which are shown in Fig. 5 plotted against the concentration.

TABLE III. J_{CH_2, CH_3} OF SOME METAL ETHYL COMPOUNDS

Compound	J_{CH_3, CH_2}, c. p. s.	Ref.
$P(C_2H_5)_3$	7.6	4
$Sn(C_2H_5)_4$	8.2	4
$Hg(C_2H_5)_3$	7.0	2
$Pb(C_2H_5)_4$	8.2	4
$Zn(C_2H_5)_2$	8.6	3
$Ge(C_2H_5)_4$	7.8	3
$Ga(C_2H_5)_3$	9.1	3
$Si(C_2H_5)Cl_3$	8.0	3
$Si(C_2H_5)_2Cl_2$	8.0	3

Discussion

Coupling Constants. — The agreement in the J values at 40 Mc./sec. and at 60 Mc./sec. assures the accuracy of the obtained spin-spin coupling constants between the methyl and the methylene protons, J_{CH_3, CH_2}. All of the values are found to be near 8.0 c. p. s. and to be approximately the same as those obtained with other metal compounds (See Table III). Hence, it seems that the coupling constants, J_{CH_3, CH_2}, in the ethyl groups of such metal compounds are independent of the nature of the metal atoms attached to the ethyl groups.

The Dilution Effect of Benzene on δ Values.— Narasimhan and Rogers[3] have suggested that it would be preferable to obtain the δ values at infinite dilution in an inert solvent. Originally Dailey and Shoolery[5] employed 50 volume % benzene solutions in correlating the δ values with the electronegativity of metals. Although benzene is not necessarily an adequate solvent because of its considerable solvent effect, other solvents commonly used in NMR measurements cannot be employed in the case of metal alkyls because of the overlap of the signals and/or the reaction between the solvent and the solutes.

Thus, it is necessary to obtain the δ values at infinite dilution using benzene as the solvent and to observe their differences from those obtained with pure liquid samples for each

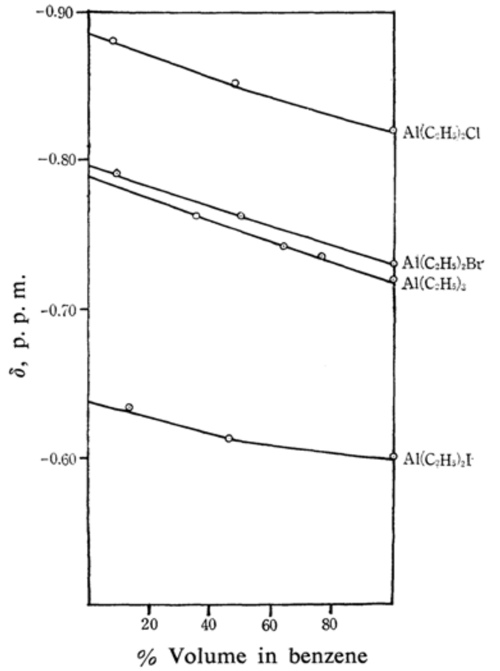

Fig. 5. Solvent effect benzene on δ values of $Al(C_2H_5)_3$ and $Al(C_2H_5)_2X$.

particular metal compound. Figure 5 shows the dilution effect on the δ values obtained in the present work. It may be seen from this figure that the maximum difference is about 0.1 p. p. m., the extent being quite large.

As far as the electronegativity of the metal itself is concerned, it is not so much affected by such a change in δ values as indicated by Narasimhan and Rogers.[3] However, when the effect of substituents attached to the metal atom on the δ values, as will be described below, is involved, the dilution effect plays more or less a significant role; in these instances, one must discuss the problem using δ values obtained under substantially the same conditions.

The Effects of Substituents Attached to the Metal Atom on the δ Values. — As is shown in Fig. 5 and Table II, the δ values of the diethylaluminum monohalides increase as the substituents change from chlorine through bromine to iodine. (Throughout the discussion below, the sign of δ is taken into account when the δ values are compared.) Figure 6 shows that the methyl protons, which are at the γ-position to the halogens, do not change in the resonance position throughout the compounds under the same conditions of dilution. Thus, the difference in δ values for these compounds is due to the methylene proton shifts. The methylene protons are at the β-position to the halogens and are, hence, influenced by the substituents.

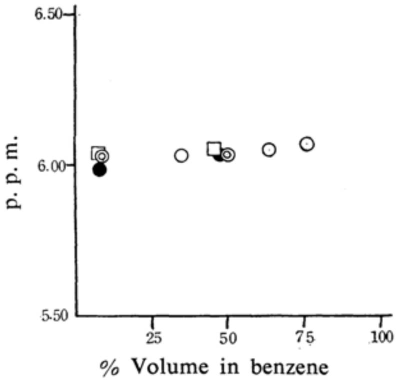

Fig. 6. Chemical shifts of the methyl signals in $Al(C_2H_5)_3$ and $Al(C_2H_5)_2X$ in benzene (referred to solvent benzene).

○ $Al(C_2H_5)_3$ ◎ $Al(C_2H_5)_2Br$
● $Al(C_2H_5)_2Cl$ □ $Al(C_2H_5)_2I$

In the CH_3-CH_2-X type compounds it has already been found that, for a simple atomic substituent, the shift to a lower field of the protons at the β-position, i. e., the methyl proton shift, increases in the order of the substituent from upper to lower down the periodic table.[22] The shielding by a β group to the methyl protons is largely controlled by the diamagnetic anisotropy of the substituent, with a smaller contribution from its inductive effect. Thus, the extents of the low field shifts increase in the descending order of chlorine, bromine and iodine. This order is contrary to that of the electronegativity but is consistent with that of the diamagnetic polarizability of the atom.

The same is true for the methylene protons of diethylaluminum monohalides. Thus, since the methylene protons in these compounds are shifted to lower fields in the order of chloride, bromine, and iodine by the diamagnetic anisotropy of the halogen atoms and since the methyl signals are substantially invariant, diethylaluminum monohalides have δ values increasing in the order of chlorine, bromine and iodine.

Triethylaluminum, which has a larger δ value than diethylaluminum monochloride, provides another problem. As was mentioned above, the substitution of the halogen atom at the β-position to a certain group of protons causes the proton signal or signals to shift to a lower field. This can be interpreted in terms of the electron-withdrawing power of the halogen atoms. For example, diethylsilane dichloride has a larger δ value (+0.01 p.p.m.)

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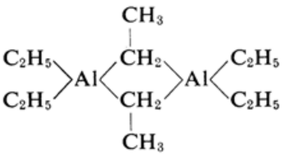
[22] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York (1959), p. 53.

than tetraethylsilane (−0.42 p. p. m.).[3,23] A similar consideration will lead to a larger expected value for δ in diethylaluminum monochloride than in triethylaluminum, but actually the reverse is true.

Growenewege, Smidt, and de Vries[20] reported that trimethylaluminum, which gives a sharp singlet signal at room temperature, shows two separate signals at −78°C, one of which appears at higher and the other at lower fields than that of the original one. They assigned the higher signal to the terminal methyl protons and the lower one to the bridged methyl protons of trimethylaluminum dimer. The fact that trimethylaluminum gives only one singlet signal at room temperature was attributed to the rapid exchange between the terminal and the bridged methyl groups.

Since triethylaluminum has also been reported to have a dimeric form in liquid or in solutions,[7,8] the fact that the obtained spectra can be interpreted by a simple A_3B_2 system rather than by the superposition of two different A_3B_2 spectra must be responsible for the rapid exchange between the terminal and the bridged ethyl groups, as in the trimethylaluminum. In these circumstances the observed signals will be a weighted mean of the two A_3B_2 signals. If it is assumed that in this case also both the methyl signals are at approximately the same position and that the ethyl bridge is formed through the methylene group, i. e.,



then the terminal methylene signals which are observed when the rapid exchange does not occur may be expected to appear at higher fields than the methylene signals observed at room temperature; therefore, the δ value of the terminal ethyl groups would be smaller than the δ value of diethyl aluminum monochloride. Then the apparent abnormality of the δ values of triethylaluminum may be eliminated. The confirmation of this assumption requires the low temperature spectra of triethylaluminum, work on which is now proceeding in this laboratory.

Baker in his early paper[1] suggested that the aluminum atom in triethylaluminum has a greater tendency to donate an electron to the methylene group than in diethylaluminum chloride, so that the former has a larger δ value. However, this conception seems to be improbable to judge the discussion of tetraethylsilane and diethylsilane dichloride mentioned above.[3]

The Electronegativity of Aluminum. — The electronegativity of the aluminum atom evaluated from Eq. 1 with the δ value of triethylaluminum at infinite dilution turns out to be 1.58. The electronegativity of metals can be obtained by various methods, including the method using the vibrational frequency of the methyl derivatives of the metals.[24-28] Several relationships between the electronegativity and the symmetric deformation frequency of the methyl group have been proposed. The following experimental formula, for instance, has been presented by Takenaka:[26]

$$\delta_{\mathrm{CH_3}} = 375 \log(x/r^2_{\mathrm{cx}}) + 1366 \qquad (2)$$

where $\delta_{\mathrm{CH_3}}$ is the symmetric deformation frequency of the methyl group in $\mathrm{cm^{-1}}$, x is the electronegativity of the metal atom, and r_{cx} is the distance between carbon and the metal atom in Å.

If the obtained values, 1.58 for the electronegativity of aluminum and 2.00 Å for the terminal Al–C distance,[9] are used, one obtains 1215 $\mathrm{cm^{-1}}$ for $\delta_{\mathrm{CH_3}}$, which agrees approximately with the observed value, 1200 $\mathrm{cm^{-1}}$, for the symmetric deformation of the methyl group in trimethylaluminum.[12] When the electronegativity which would be obtained for the terminal ethyl signal of triethylaluminum is substituted into formula 2 above, one can expect a smaller $\delta_{\mathrm{CH_3}}$ value and the agreement between the observed and the expected values will be much improved.

The author wishes to express his hearty thanks to Dr. Shinnosuke Saëki of the Government Chemical Industrial Research Institute, Tokyo, for his kind advice and discussions regarding computor calculation, and to Mr. Joseph Yamada of the same Institute for his experimental work.

Government Chemical Industrial
Research Institute, Tokyo
Shibuya-ku, Tokyo

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[23] Assuming the bridge structure in the aluminum compounds and comparing the substituents attached to the metal atom, diethylsilane dichloride rather than triethylsilane monochloride is appropriate, the δ value of the latter having not yet been reported but predicted to be −0.215 p. p. m. by Narasimhan and Rogers.[3]

[24] N. Sheppard, *Trans. Faraday Soc.*, **51**, 1465 (1955).

[25] J. K. Wilmshurst, *J. Chem. Phys.*, **26**, 426 (1957).

[26] T. Takenaka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 1309 (1961).

[27] T. Takenaka, ibid., **83**, 267 (1962).

[28] T. Takenaka and R. Gotoh, ibid., **83**, 997 (1962).