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^{27}Al-^{13}C SPIN COUPLING CONSTANT IN LITHIUM TETRAMETHYLALUMINATE

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^{27}Al-^{13}C and ^{13}C-^{1}H spin coupling constants in LiAl(CH$_3$)$_4$ were obtained from the ^{13}C NMR spectra, and found to be 71.5 ± 0.5 Hz and 106.5 ± 1.0 Hz, respectively. A brief discussion was made on the coupling constants obtained.

While a number of spin coupling constants between ^{13}C and a nucleus other than proton or fluorine have been reported recently,$^{1)}$ the coupling constants between ^{13}C and ^{27}Al (J_{AlC}) have not yet been obtained because of a large quadrupole interaction of ^{27}Al ($I = 5/2$) with the electric field gradient surrounding the nucleus in the molecule. Even in the symmetrical species containing ^{27}Al such as LiAl(CH$_3$)$_4$ (I), the proton signal collapses into a single line in most of solvents, since the tetramethylaluminate anion exists as a contact ion pair with Li$^+$ in the solutions and the Al atom is still in an environment of the asymmetrical electric field gradient.$^{2,3,4)}$ Only in 1,2-dimethoxyethane (DME), the molecule exists as a separated ion pair, and indeed shows a well resolved signal split by the ^{27}Al-^{1}H spin coupling in the proton resonance (J_{AlCH} = 6.34 Hz).$^{2)}$

This suggests us the possibility to obtain the J_{AlC} of (I) in DME. With the expectation we have measured the ^{13}C spectrum of (I) in DME, and actually we were able to obtain a well resolved sextet signal of the methyl carbon in Al(CH$_3$)$_4^-$, which is shown in Figure 1. This is the first observation of J_{AlC} as far as the author's knowledge is concerned. J_{AlC} directly obtained from the chart (the average of the five spacings of the sextet) is 71.2 ± 0.5 Hz. The J_{CH} was also obtained from the proton-undecoupled ^{13}C spectrum of (I) in diethylether at about -40°C, and found to be 106.5 ± 1.0 Hz. The ^{13}C chemical shifts of (I) in DME and in ether are 4.2 and 5.2 ppm upfield from TMS, respectively. This trend is reverse to that observed in the proton resonance.$^{2)}$

Smith,$^{5)}$ and Roberts et al.$^{6)}$ have proposed the correlations of J_{XCH} with J_{HCH} and J_{XC} with J_{CC}, respectively, for the tetramethyl derivatives of group IV elements, on the basis of the Fermi contact interaction as follows:

$$J_{XC} = (\alpha_X^{2}/\ \alpha_C^{2})(\ \Delta E_C/\ \Delta E_X)(Z^*_X/Z^*_C)^3(n_C/n_X)^3(g_X/g_C)J_{CC} \qquad (1)^{\#}$$

$$J_{XCH} = \ \alpha_X^{2}(\ \Delta E_C/\ \Delta E_H)(Z^*_X/n_X)^3(g_X/g_H)J_{HCH} \qquad (2)$$

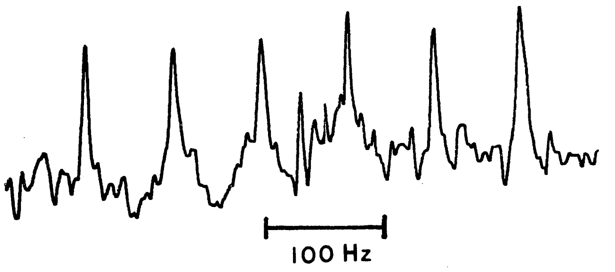

Fig. 1. The proton-decoupled ^{13}C spectrum of $LiAl(CH_3)_4$ at about 8 mole % in DME at room temperature.

where the notations are the same as those in the references. α_X^{2} can be calculated from J_{CH} according to Smith$^{5)}$ and found to be 0.361 for $Al(CH_3)_4^{-}$. Although these relations are based on rather crude and oversimplified model, both J_{AlC} and J_{AlCH} calculated from equations (1) and (2) are in good agreement with the observed one's, if Z* for Al in the anion is assumed to be 5.3 - 5.4 (for Z* = 5.3, J_{AlC} = 65.5 and J_{AlCH} = 6.43 Hz; for Z* = 5.4, J_{AlC} = 69.3 and J_{AlCH} = 6.80 Hz). This value of Z* for Al may be compared with Z^*_{NMR} for Si (= 6.02) given by Smith.$^{5)}$ The overall validity of equations (1) and (2) is conserved for $Al(CH_3)_4^{-}$, and thus the dominant mechanism is the Fermi contact interaction also in J_{AlC}.

(I) was prepared by a known method in the literature,[7] and was dissolved in DME or diethylether in a dry box, a small amount of C_6D_{12} being added to the solution, which served as a deuterium lock signal. ^{13}C spectra were obtained on a NEVA NV-14 spectrometer with a Varian 620/L computer in an FT mode. So-called long term averaging technique was employed to avoid the difficulty in the dynamic range arising from the presence of strong signals of the solvents.

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[#] The equation (1) originally described in reference 6 is probably misprinted. $(n_X/n_C)^3$ in reference 6 should be inverted as in (1).

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