# The PMR Study of the *cis-trans* Isomerization of the Dimethylaluminum Methylphenylamide Dimer, $[(CH_3)_2AlN(CH_3)(C_6H_5)]_2$

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The dimethylaluminum methylphenylamide dimer exists as an equilibrium mixture of *trans*- (I) and *cis*-isomers (II) with respect to the four-membered $Al_2N_2$ skeleton, and the latter involves the magnetic non-equivalence of the Al–$CH_3$ groups. Thermodynamic parameters for the *cis* to *trans* isomerization are obtained from the variable-temperature PMR spectra; $\Delta H=4.47\pm0.09$ kJ·mol$^{-1}$ and $\Delta S=1.74\pm0.48$ J·deg$^{-1}$·mol$^{-1}$. The isomerization is markedly accelerated by adding 4-methylpyridine or tetrahydrofuran. A possible mechanism of the isomerization is proposed.

Structural studies of organoaluminum compounds have been widely undertaken by means of X-ray analysis and the PMR spectra in connection with stereospecific catalysis and the bridge-bond character in dimeric or oligomeric aluminum derivatives.[1–12)]

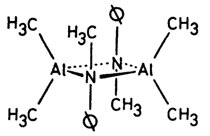
In the course of our studies of the reaction of aluminum amides with carbon disulfide,[13)] we have found that the dimethylaluminum methylphenylamide dimer $[(CH_3)_2AlN(CH_3)(C_6H_5)]_2$ exists as an equilibrium mixture of *trans*- (I) and *cis*-isomers (II) with respect to the four-membered $Al_2N_2$ skeleton. This paper will report the PMR study of the equilibrium between the two isomers, of which the *cis*-isomer involves a magnetic non-equivalence of the terminal Al–$CH_3$ groups. The isomerization between the *cis*- and *trans*-isomers upon the addition of Lewis bases will also be described.

## Experimental

The preparation of dimethylaluminum methylphenylamide has been described elsewhere.[13)] The PMR spectra were obtained at 100 MHz on a JEOL JNM-PS-100 spectrometer equipped with a variable-temperature probe. Toluene or cyclohexane was used as the internal reference. The sampling was carried out under dry nitrogen. The materials were dried over appropriate desiccants and were distilled under dry nitrogen.

## Results and Discussion

The molecular-weight determination indicates the association degree of 1.96 for $(CH_3)_2AlN(CH_3)(C_6H_5)$ (Found: 319 at the 1.96 wt% solution in benzene by the cryoscopic method. Calcd for $C_9H_{14}NAl$: 163). The PMR spectrum of this compound in benzene at room temperature shows two N–$CH_3$ proton signals ($\delta$ 2.68 (relative intensity 4.4) and 2.64 (1.0) ppm) and three Al–$CH_3$ proton signals ($\delta$ −0.21 (4.4), −0.36 (2.0), and −0.54 (4.4) ppm) (Fig. 1a). The relative intensities of these signals change reversibly with the temperature. These results confirm that dimethylaluminum methylphenylamide exists essentially as an equilibrium mixture of dimeric *trans*- (I) and *cis*-isomers (II), with the mole ratio of *ca.* 1.0: 4.4 in benzene at room temperature. The mole ratio is a little solvent-dependent, such as *ca.* 1.0: 5.0 in dichloromethane at room temperature. The existence of analogous isomers has been reported for $[(C_2H_5)XAlN(H)(tert\text{-}C_4H_9)]_2$ ($X=C_2H_5$, Cl, Br, I) in the course of preparing this paper.[14)]



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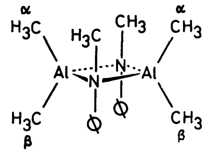


II

The *cis*-isomer involves two kinds of Al–$CH_3$ groups located in magnetically different environments: α and β, while the four Al–$CH_3$ groups of the *trans*-isomer are equivalent. The signals at $\delta$ 2.64 and −0.36 ppm are assigned to the *trans*-isomer, while the others are assigned to the *cis*-isomer on the basis of their relative intensities. A similar non-equivalence of terminal Al–$CH_3$ groups has only been reported in the low-temperature PMR spectra of the dimethylcyclopropylaluminum dimer in toluene, in which the two bridging cyclopropyl groups are both bent toward the same side of the four-membered ring.[5)]

TABLE 1. THE EQUILIBRIUM CONSTANTS BETWEEN *trans*- AND *cis*-$[(CH_3)_2AlN(CH_3)(C_6H_5)]_2$ AT VARIOUS TEMPERATURES IN DICHLOROMETHANE

| *T*(K) | 296 | 279 | 268 | 257 | 244 | 229 | 216 | 205 |
|---|---|---|---|---|---|---|---|---|
| *K*([*cis*-]/[*trans*-]) | 5.00 | 5.76 | 5.82 | 6.40 | 7.59 | 8.34 | 10.17 | 10.94 |

Equilibrium constants (*K*) measured in dichloromethane at various temperatures (*T*) are given in Table 1. A plot of log *K versus* 1/*T* gives $\Delta H=4.47\pm0.09$ kJ·mol$^{-1}$ and $\Delta S=1.74\pm0.48$ J·deg$^{-1}$·mol$^{-1}$ in the *cis*-to-*trans* isomerization. Both the enthalpy and entropy changes are fairly small compared with those in the interconversion of trimeric $[(CH_3)_2AlN(CH_2)_3]_3$ to the dimer ($\Delta H=57.8$ kJ·mol$^{-1}$, $\Delta S=168$ J·deg$^{-1}$·mol$^{-1}$).[10)] This may imply that the steric effects and valence-angle strains are not very different between the two isomers of the present compound.

Figure 1 displays the PMR spectra of dimethylaluminum methylphenylamide in benzene containing varying amounts of 4-methylpyridine. When a small amount of 4-methylpyridine ($4.32\times10^{-2}$ M) was added to a benzene solution of the aluminum amide ($3.93\times10^{-1}$ M as monomer), the Al–$CH_3$ signals of both the *trans*- and *cis*-isomers broadened and new Al–$CH_3$ and N–$CH_3$

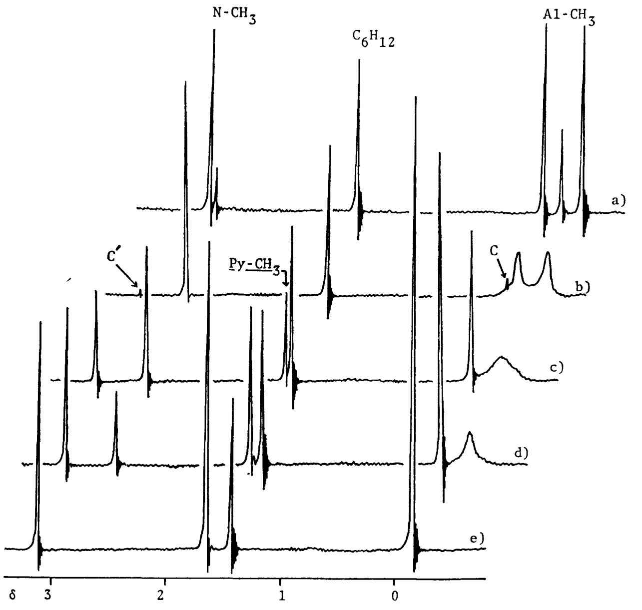


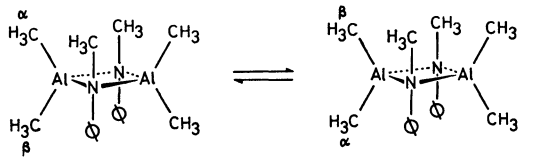
Fig. 1. The PMR spectra of $(CH_3)_2AlN(CH_3)(C_6H_5)$ ($3.93\times10^{-1}$ M) in benzene containing varying amounts of 4-methylpyridine; mole ratios of a) 1.00: 0.00, b) 1.00: 0.11, c) 1.00: 0.41, d) 1.00: 0.70, and e) 1.00: 1.37, measured at 100 MHz at 23 °C.

signals (denoted C and C′) occurred at $\delta$ −0.12 and 3.13 ppm respectively (Fig. 1b). The pyridine–$CH_3$ signal, however, was obscured by the proton signal of cyclohexane used as the internal reference in this case, probably because of their almost identical chemical shifts. This is supported by the fact that the pyridine–$CH_3$ signal gradually moves to a low field and is intensified as the amount of 4-methylpyridine added increases (Figs. 1c, d). The C and C′ signals were similarly strengthened when increasing amounts of 4-methylpyridine were added, and the intensity ratios of the C, C′ and pyridine–$CH_3$ signals were almost 2: 1: 1 up to the addition of an equimolar amount of 4-methylpyridine to the aluminum amide as a monomer. All the signals of the aluminum amide dimer disappeared in the presence of excess 4-methylpyridine (Fig. 1e). These observations suggest the formation of the 1: 1 adduct between the aluminum amide monomer and 4-methylpyridine; therefore, the C and C′ signals are assigned to the Al–$CH_3$ and N–$CH_3$ protons of the adduct respectively. In addition, the sharp and broad Al–$CH_3$ signals observed in Fig. 1c coalesced at about 50 °C, while the two N–$CH_3$ signals also merged at the same time. The spectrum was reversibly changed with the temperature. Thus, for the dimethylaluminum methylphenylamide–4-methylpyridine system the following equilibria are suggested:

$$\begin{tikzcd}
\mathit{cis}\text{-}[(CH_3)_2AlN(CH_3)(C_6H_5)]_2 \arrow[dd, shift right] \arrow[dr, shift left, "+2D"'] & \\
& 2(CH_3)_2AlN(CH_3)(C_6H_5)\cdot D \arrow[ul, shift left, "-2D"'] \arrow[dl, shift left, "-2D"'] \\
\mathit{trans}\text{-}[(CH_3)_2AlN(CH_3)(C_6H_5)]_2 \arrow[uu, shift right] \arrow[ur, shift left, "+2D"'] &
\end{tikzcd} \qquad (1)$$

D: 4-methylpyridine

The broadening of the Al–$CH_3$ signals of the *cis*- and *trans*-isomers (Figs. 1b—d) suggests that the *cis-trans* isomerization and the site-exchange between α- and β-$CH_3$ of the *cis*-isomer (shown as Eq. (2)) could be accelerated by the presence of 4-methylpyridine. It



(2)

is noted that the adduct invariably exhibits sharp Al–$CH_3$ and N–$CH_3$ signals at room temperature, irrespective of the amount of 4-methylpyridine added. This fact seems to indicate that neither the isomerization nor the site-exchange proceeds *via* the adduct formation at room temperature. At high temperatures, however, both the isomerization and site-exchange possibly occur *via* the adduct formation, since the signals of the 1: 1 adduct and the non-complexed aluminum amide coalesce at about 50 °C.

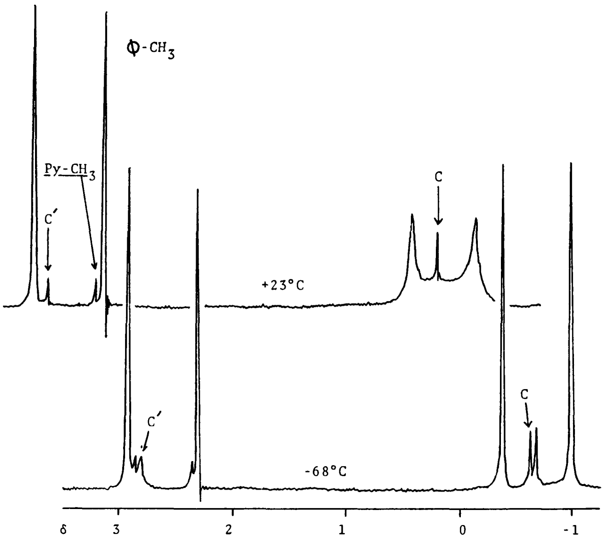


Fig. 2. The temperature-dependent PMR spectra of a mixture of $(CH_3)_2AlN(CH_3)(C_6H_5)$ ($5.80\times10^{-1}$ M) and 4-methylpyridine ($7.10\times10^{-2}$ M) measured at 100 MHz in dichloromethane.

Figure 2 shows the temperature-dependent PMR spectra of the aluminum amide ($5.80\times10^{-1}$ M as monomer) in dichloromethane containing a small amount of 4-methylpyridine ($7.0\times10^{-2}$ M). The spectral pattern observed at room temperature was similar to that in benzene, except that the Al–$CH_3$ and N–$CH_3$ signals (C, C′) of the adduct occurred very close to those of the respective *trans*-isomer. Each signal becomes sharp with a lowering of the temperature, and the spectrum at −65 °C indicates that the rates of the *cis-trans* isomerization and of the site-exchange are much slower than the NMR time scale. Tetrahydrofuran can also accelerate the *cis-trans* isomerization and the site-exchange. In the presence of less than one mol of tetrahydrofuran per mol of Al, the Al–$CH_3$ signals were seemingly coalesced into a broad one at room

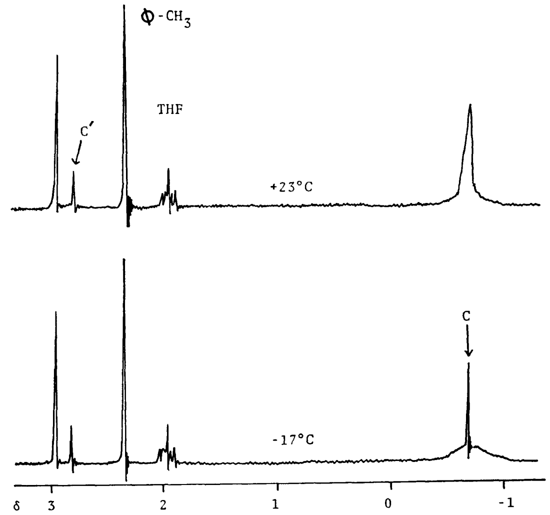
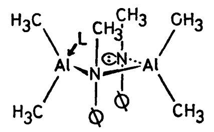


Fig. 3. The temperature-dependent PMR spectra of a mixture of $(CH_3)_2AlN(CH_3)(C_6H_5)$ ($6.20\times10^{-1}$ M) and tetrahydrofuran ($1.85\times10^{-1}$ M) measured at 100 MHz in dichloromethane.

temperature, while at −17 °C the Al–CH$_3$ protons of the 1:1 adduct occurred as a sharp signal, as is shown in Fig. 3. The appearance of the Al–CH$_3$ signal at room temperature is, rather, probably due to the overlap of a sharp signal of the 1:1 adduct and a broadened signal resulting from the isomerization and site-exchange, because the N–CH$_3$ signal of the 1:1 adduct was observed as a sharp signal even at room temperature. Thus, the isomerization and the site-exchange in the presence of tetrahydrofuran also do not proceed *via* the adduct formation.

There are two possible mechanisms for the *cis-trans* isomerization or the site-exchange; one involves the breaking of an Al–N bond in the (Al–N)$_2$ ring, followed by the rotation-inversion of the non-bridged nitrogen atom or by the rotation of the bridged Al–N bond. The other involves simply the dissociation of the dimeric unit, followed by recombination. The former mechanism is more probable, since the breaking of two Al–N bonds requires a high energy barrier. In the presence of less than one mol of Lewis base per mol of Al, the formation of an intermediate such as III, where L is either the 1:1 adduct of the aluminum amide with a base or the base itself, may be considered to lower the barrier of the isomerization and the site-exchange. The formation of such an intermediate is supported by a similar dimeric structure for $C_5H_5N\cdot Al_2(OC_3H_7\text{-}iso)_6$ tentatively proposed by Oliver and Worrall.[15]



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