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Synthesis, Structure and Pyrolysis of Organoaluminum Amides Derived from the Reaction of Trialkylaluminum Compounds with Ethylenediamine in a 3:2 Ration

by

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Synthesis, Structure and Pyrolysis of Organoaluminum Amides Derived from the Reaction of Trialkylaluminum Compounds with Ethylenediamine in a 3:2 Ratio

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ABSTRACT

The reactions of triethylaluminum and trimethylaluminum with ethylenediamine (en) in a 3:2 ratio have been studied. Heating of the initially formed $2R_3Al{:}en$ and $R_3Al{:}en$ adduct mixture results in the formation of $RAl[(HN(CH_2)_2NH)AlR_2]_2$ (R= CH_3 [3] and C_2H_5 [4]). The structures and formation mechanisms of these two compounds, as well as their pyrolysis reactions, have been studied with ^1H, ^{13}C, ^{27}Al NMR, FTIR, MS, GC, DSC, and TGA. The methyl derivative (3) was characterized by a single crystal X-ray diffraction analysis: space group P2/c; a = 15.523(3)A, b = 8.419(1)A, c = 13.464(3); V = 1663.8(5)A^3; β = 109.00(2); Z = 4. Full-matrix least square refinement converges at R = 0.051 and Rw = 0.076 based on 2280 reflections with F > $4\sigma(F)$. Both 4- and 5-coordinated Al atoms were observed in which the en-2H groups

serve as both chelating and bridging ligands.

Introduction

The syntheses, structures and reactions of organoaluminum amides and imides have been the subject of investigation for many years.[1-2] Recently, there has been renewed interest in these compounds owing to their potential application as precursors to aluminum nitride or AlN-containing ceramics[3-7]. In order to obtain precursors with the appropriate physical and chemical properties for use in the generation of aluminum nitride in particular final forms (e.g. powder, monolith, fiber, thin film,), as well as control the purity and microstructure of these products, a better basic understanding of the dependence of the physical properties and pyrolysis reactions of organoaluminum nitrogen compounds on molecular structure is needed.

Prior studies have shown that the organoaluminum amides of the general formula, $R_2AlNR'R''$, where NR'R" is a simple, monofunctional amide group, occur as cyclic, oligomeric species with either 4- or 6-membered $(AlN)_n$ rings[1]. Both N and Al in these structures are typically in 4-coordinate, distorted tetrahedral environments analogous to that found in crystalline AlN. On the other hand, with bi- or multi-dentate amines, more complex structures involving chelating and/or bridging ligands and Al coordination numbers of 4, 5 and 6 have been observed[8-12].

Beachley and Racette[9] studied the factors affecting the formation of chelated monomeric or unchelated dimeric organoaluminum-nitrogen compounds derived from 1:1 reactions between R_3Al and various substituted ethylenediamine derivatives (i.e. $HR'NCH_2CH_2NRR"$; R=H, Me, Et, Ph; R', R"=Me, Et). These studies showed that factors such as steric effects of R, R' and R", ligand base strength, and chelate ring size, controlled the position of the monomer-dimer equilibrium.

Perego and coworkers[13] reported a single-crystal diffraction study of $HAl[(EtN(CH_2)_2NEt)AlH_2]_2$ (1). This compound has a chelated structure in which both four and five-coordinated Al atoms were observed. However, neither the formation mechanism of this compound nor its pyrolysis chemistry was investigated.

Our recent work[14] on the 1,4-bis(triethylaluminum)-ethylenediamine system (2:1 Et_3Al:en) suggested that a five-membered ring intermediate (2) was formed during the conversion of the adduct to the polymeric amide. The polymeric amide was soluble in hydrocarbon solvents and gave thin films of AlN on Si and other substrates by solution deposition followed by pyrolysis under NH_3. As an extension of this work, we report here detailed studies of the reactions of ethylenediamine with triethylaluminum or trimethylaluminum in a 2:3 ratio. These reactions have resulted in the formation of two new compounds, $MeAl[(HN(CH_2)_2NH)AlMe_2]_2$ (3) and $EtAl[(HN(CH_2)_2NH)AlEt_2]_2$ (4). The crystal and molecular structure of the former compound has been determined by single-crystal x-ray diffraction methods. In addition, the formation mechanism as well as the pyrolysis chemistry of these two compounds have been investigated.

Experimental

General

All reactions and manipulations were performed by using Schlenk techniques under N_2, or in a N_2-filled drybox. Ethylenediamine was refluxed and distilled from KOH under N_2; benzene was refluxed overnight over sodium under N_2 and distilled before use. Triethylaluminum was purified by vacuum distillation. Trimethylaluminum (98% purity) and deuterated benzene (C_6D_6) were used as received.

NMR spectra were obtained at ambient temperature on a Varian XL200 NMR spectrometer. Chemical shift values were determined relative to C_6H_6 as internal reference (δ 7.15 ppm (^{1}H-NMR) and δ 128.0 ppm (^{13}C-NMR)). ^{27}Al-NMR spctra were obtained on the same spectrometer with a delay time of 2 sec. $AlCl_3$ aqueous solution was used as an external standard (δ=0). IR spectra were recorded on a Perkin-Elmer FT-1800 Infrared spectrometer as KBr-pellet samples or as neat films between NaCl single crystal plates. DSC and TGA measurements of the compounds were carried out with a Perkin-Elmer TAS-7 DSC/TGA Thermal Analysis System with a heating rate of 10 °C/min. Both the TGA and DSC samples were loaded under inert atmosphere. The purging gas in the TGA experiments was either nitrogen which had been passed through a BTS catalyst (BASF CO.) and a molecular sieve column to remove O_2 and H_2O respectively, or electronic grade ammonia. Gas evolution studies were performed by heating the compounds at a rate of 10 °C/min under N_2 atmosphere and analyzing the volatile fractions using a Shimadzu GC-9A Gas Chromatograph with a 6 ft. VZ-10 column (ALLTECH ASSOCIATES, Inc.). Mass spectral data were obtained with a Hewlett-Packard 5987A GC/MS spectrometer (the chemical ionization mode was used with isobutane as the ionization gas). Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories and Galbraith Laboratories, Inc.

Preparation of $MeAl[(HN(CH_2)_2NH)AlMe_2]_2$ (3)

A solution of 6.01 g of ethylenediamine (0.1 mol) in 30 mL of toluene was added dropwise to 40 ml of a toluene solution containing 10.8 g of trimethylaluminum (0.15 mol) cooled in a dry ice-isopropanol bath (-40 °C). The resultant suspension was heated at 80 °C for 2 h, leaving a light yellow solution. During this period, the evolution of methane was observed by GC analysis. This mixture, after removal of toluene by evacuation at 40 °C, yielded an off-white solid. Upon sublimation (0.04 torr, 60 °C), a colorless crystalline material (3) was obtained. Yield: 89%, mp: 74-75 C. ^1H NMR (C_6D_6): δ -0.566 (singlet, 12H, $Al(C\underline{H}_3)_2$, -0.740 (singlet, 3H, $AlC\underline{H}_3$), -0.001 (broad triplet, 4H, $\underline{H}NCH_2CH_2N\underline{H}$), 1.912 (multiplet, 4H, $HNC\underline{H}_2C\underline{H}_2NH$), 2.385 (multiplet, 4H, $HNC\underline{H}_2C\underline{H}_2NH$). ^{13}C NMR (C_6D_6): δ 43.68 (singlet, $-N\underline{C}H_2\underline{C}H_2N-$), -9.03 (broad, $Al\underline{C}H_3$), -13.04 (broad, $Al(\underline{C}H_3)_2$. ^{27}Al (C_6D_6): NMR δ 104.2 (broad, $\underline{Al}CH_3$), 156.0 (broad, $\underline{Al}(CH_3)_2$). IR (KBr pellet, cm^{-1}) 3330 s, 3280 s, 2920 vs, 2870 s, 2810 m, 1590 w, 1460 w, 1470 w, 1365 m, 1290 m, 1185 s, 1055 vs, 905 s, 890 s, 845 m, 835 m, 765 s, 700 vs, 575 w, 490 m, 395 s. Anal. Calcd. for $\mathrm{C_9H_{27}Al_3N_4}$: C, 39.66; H, 9.92; Al, 29.74; N, 20.56. Found: C, 35.93; H, 8.01; Al, 27.77; N, 22.31. (note:the analysis reports from both Schwarzkopf and Galbraith Labs. indicated that reliable analyses (C, H, N, Al) were not obtained due to incomplete combustion of the sample during analyses.

Preparation of $\mathrm{EtAl[HN(CH_2)_2NH)AlEt_2]_2}$ (4)

To a solution of 17.1 g of triethylaluminum (0.15 mol) in 40 mL of benzene at ca. -10 °C was added 30 ml of a benzene solution containing 6.01 g (0.1 mol) of ethylenediamine. The resultant colorless solution was refluxed at 80 °C for 2 h, leaving a light brown solution. The mixture was then evacuated at 60 °C to remove the solvent. Upon distillation (0.3 torr, 160-165 °C), a colorless oil (4) was obtained. Yield: 81%, ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.339 (triplet, $\mathrm{Al(CH_2C\underline{H}_3)_2}$, 6H, J= 8.2 Hz), 1.257 (triplet, $\mathrm{Al(CH_2C\underline{H}_3}$, 6H, J=8.2 Hz), 1.062 (triplet, $\mathrm{AlCH_2C\underline{H}_3}$, 3H, J=8.0 Hz), 0.105 (quartet, $\mathrm{Al(C\underline{H}_2CH_3)_2}$, 4H, J=8.2 Hz), 0.023 (quartet, $\mathrm{Al(C\underline{H}_2CH_3)_2}$, 4H, J=8.2Hz), -0.130 (quartet, $\mathrm{AlC\underline{H}_2CH_3}$, 2H, J=8.0 Hz), 0.173 (broad triplet, $\mathrm{\underline{H}NCH_2CH_2N\underline{H}}$), 2.403 (multiplet, $\mathrm{HNC\underline{H}_2C\underline{H}_2NH}$, 4H), 1.956 (multiplet, $\mathrm{HNC\underline{H}_2C\underline{H}_2NH}$, 4H). ^{13}C-NMR ($\mathrm{C_6D_6}$): δ 9.801 (singlet, $\mathrm{Al(CH_2\underline{C}H_3)_2}$), 9.460 (singlet, $\mathrm{Al(CH_2\underline{C}H_3)_2}$), 10.601 (singlet, $\mathrm{AlCH_2\underline{C}H_3}$), -0.291 (broad,

$Al(\underline{C}H_2CH_3)_2$, -0.215 (broad, $Al\underline{C}H_2CH_3$), 43.851 (singlet, $HN\underline{C}H_2\underline{C}H_2NH$). ^{27}Al NMR (C_6D_6): δ 104.1 (broad, $\underline{Al}CH_2CH_3$), 150 - 170 (broad, $\underline{Al}(CH_2CH_3)_2$). MS (CI) m/e (relative intensity, ion) 341 (12%, M - 1), 313 (100%, M - 29), 113 (40%, M - 229), 85 (52%, M - 257). IR (neat liquid, NaCl plate, cm^{-1}) 3320 m, 3300 m, 3280 m, 2940 vs, 2900 vs, 2860 vs, 2790 s, 1460 s, 1410 m, 1360 s, 1330 s, 1290 s, 1230 w, 1190 m, 1150 s, 1065 vs, 980 s, 950 m, 900 vs, 830 s, 800 s, 770 s, 750 s, 675 s. Anal. Calcd. for $C_{14}H_{37}N_4Al_3$: C, 49.10; H, 10.82; N, 16.37; Al, 23.68. Found: C, 45.06; H, 8.36; N, 17.05, Al, 23.51. No reliable elemental data were obtained due to the same reason mentioned before.

NMR Study of the Conversion of An Ethylenediamine-triethylaluminum Adduct Mixture to (4)

10 mL of the as-mixed ethylenediamine-triethylaluminum (2:3) adduct solution (concentrations: en, 1.43 M. $AlEt_3$, 2.14 M) in benzene was kept at room temperature for 24 h. An oil bubbler allowed the gaseous product to escape. During this period, ^1H and ^{13}C-NMR spectra of this solution were taken at various times. The spectra observed in this manner were used to analyze the formation mechanism of (4).

Preparation of a Polymeric Glassy Solid (5) from Pyrolysis of (3)

A 25 mL flask containing 2 g of (3) was put into an oil bath which was pre-heated at 180 °C. The evolution of a gas was observed from the initially formed melt, which was found to be methane by gas chromotography. After 15 min, gas evolution ceased and a colorless glassy solid (5) remained. This solid was slightly soluble in hydrocarbon solvents. Further heating up to 430 °C under N_2 gave an insoluble, dark-brown solid.

Preparation of Polymeric Glassy Solid (6) from Pyrolysis of (4)

In a similar manner described for the preparation of (5), 4 g of (4) was heated at 240 °C under nitrogen for 10 min. During this period, ethane was evolved from the system. The increasingly viscous liquid finally became a light-yellow glassy solid (6), which was partially soluble in hydrocarbon solvents.

In order to study the pyrolytic chemistry of this compound, it was heated from 250 to 430 °C under nitrogen; the intermediate solid and the evolved gaseous products were analyzed with FT-IR and GC measurements, respectively.

Crystallographic analysis

Crystal data are summarized in Table 1. The X-ray study was carried out using a Siemens-Nicolet R3m diffractometer equiped with Cu-Kα radiation (graphite monochromator; λ = 1.54178 A). A Wyckoff scan mode was used for data collection (ω range = 1.20° + [$2\theta(K_{\alpha 1}) - 2\theta(K_{\alpha 2})$]; 2θ range = 3 to 130°). 2584 reflections were collected of which 2280 reflections were uniquely observed ($F > 4\sigma F$). The attenuation coefficient of the crystal is $\mu = 1.97$ mm^{-1}. An attempt was made to improve the R-value by applying an empirical absorption correction to the data set. This did not succeed because the ψ-scan reflections with high 2θ values were not collected due to the collision limit of the diffractometer. Therefore, the final results are reported with no absorption correction applied. SHELXTL PLUS (Release 3.4) computer programs were used for data reduction and all other calculations.

White crystals of (3) for X-ray diffraction were grown by slow cooling of a hexane solution under an atmosphere of nitrogen. A suitable crystal was sealed in a thin-walled capillary in a N_2-filled glove box and mounted on a diffractometer. The positions of the Al atoms were identified in a Patterson vector map. Three Fourier cycles allowed all 16 non-hydrogen atoms of the asymmetric unit to be recognized. Atomic coordinates and anisotropic temperature factors of all non-hydrogen atoms were refined by means of a full-matrix least squares and refinement procedure. All isotropic hydrogen atoms were included in calculated positions. The refinement converged at R = 5.1%, Rw = 7.6 %.

Results and Discussion

In the course of our prior studies of the R_3Al/ethylenediamine system[14], evidence was obtained for the formation of an amide-adduct intermediate when the ratio of R_3Al:en was 2:1. The chelated ring structure 2 (Scheme 1) was assigned to this intermediate on the basis of ^1H and ^{13}C NMR studies. Subsequent investigation of the 1:1 R_3Al:en system indicated a much more complex sequence of reactions on heating of the initially formed 1:1 Lewis acid base adduct, involving at least two parallel thermolysis pathways connected by different molecular intermediates. The isolation of one of these intermediates by crystallization from solution and subsequent sublimation revealed a 3:2 $R_{3-x}Al$:(en-xH) stoichiometry, suggesting the investigation of this particular proportion of R_3Al:en in the original starting mixture. In the case of Me_3Al, mixing with en in this proportion in toluene followed by heating to 80 C for 2 h and evaporation of the solvent led to a single-component, white solid which was purified by sublimation. Slow cooling of a hexane solution of this material produced large, colorless crystals of $MeAl[(HN(CH_2)_2NH)AlMe_2]_2$ 3 from which a sample suitable for single-crystal X-ray diffraction studies was selected.

Final parameters for all non-hydrogen atoms and selected bond distances and angles are reported in Table 2 and Table 3 respectively. As shown in Figure 1, the molecule contains two four-membered Al_2N_2 and two five-membered AlC_2N_2 rings and can be described as a distorted trigonal bipyramid. The axial coordination sites are occupied by nitrogen atoms (N2 and N4) and the equatorial sites by the C1, N1, and N3. The sum of the angles around Al1 with the equatorial atoms (N1, N3, and C1) is 360°.

demonstrating coplanarity of Al1 with N1, N3, and C1. The Al1-N2 (2.058(2)A) and Al1-N4 (2.073(2)A) bond distances are longer than the equatorial Al1-N1 (1.994(2)A) and Al1-N3 distances (1.988(2)A). In comparison with this five-coordinated Al, the Al-N bond distances of the four-coordinated Al atoms (Al2 and Al3) are significantly shorter (1.912(2)A - 1.938(2)A). on the other hand, the central Al1-C1(1.958(2)A) bond distance is not very much different from the mean (1.954(2)A) of the rest of the Al-C bond distances (Al2-C2a, Al2-C2b, Al3-C3a, and Al3-C3b). The nonbonding Al1-Al2 (2.897(2)) and Al1-Al3 (2.909(2)) distances are similar to those observed in a previously reported Al amide involving a multi-dentate amine ligand.[15] The nitrogen atoms in thefive-membered rings are bent out of the plane containing the C2, C3, N2 and Al1 atoms (36.3°, envelope form) although the four-membered $(AlN)_2$ rings show no significant deviation from planarity. A similar structure has been observed for $HAl[(EtN(CH_2)_2NEt)AlH_2]_2$.[13] The reported distances of the axial and equatorial Al-N bonds are same as those found in 3 within the experimental error, although the axial nitrogen atoms are less displaced from the axial sites of the undistorted bipyramid compared to the compound 3 (the N2-Al1-N4 bond angle is 149.2(1)°).

Figure 2a shows the ^1H NMR spectrum of 3. Based on the observed integration ratio, the peaks at -0.566 (labled as ϕ) and -0.740 (φ) ppm are attributed to $Al(C\underline{H}_3)_2$ and $AlC\underline{H}_3$ respectively. The finding that the peak of $AlCH_3$ appears at higher field compared with that of $Al(CH_3)_2$, is consistent with the expected greater shielding of H on the $AlCH_3$ group as the 4 N and 1 C atoms provide a more electron-rich environment to Al1 than that of Al3 (or Al2) which is bonded to 2 C and 2 N atoms. The two broad multiplets (labled τ and τ') at 1.9 and 2.4 ppm are assigned to the H atoms of the $-CH_2CH_2-$ groups which are split both by mutual CH_2/CH_2 coupling (the environment of C5 or C3 is different from that of C4 or C2.) as well as by the H atoms of the NH groups. The broad triplet labled σ is attributed to the N-H groups which are split by coupling with the H atoms of the adjacent CH_2 groups. In the ^{13}C spectrum of 3 (Figure 2b), the sharp peak near 44 ppm is assigned to the $-\underline{C}H_2-$ groups of the ethylene bridges. whereas the broad doublet centered at around 11 ppm is associated with the $Al\underline{C}H_3$ groups broadened by interaction with the quadruplar ^{27}Al nuclei. The ^{27}Al NMR spectrum of 3 (Figure 2c) shows two distinct peaks (centered at 156 and 104 ppm) corresponding to the four-coordinate Al3 and Al2 and five-coordinate Al1, respectively. The chemical shifts of these two kinds of Al atoms are consistent with prior observations on four- and five-coordinate Al atoms in the compounds of the type R_2AlR' (R= Me, Et; R'= NEt_2, OMe_2, OEt_2; etc.).[16] The peak attributed to the four-coordinate Al3 and Al2 is broader than that of the five-coordinated Al1; a similar situation has been observed in the case of the relative ^{27}Al NMR line widths of the four- or five-coordinated Al atoms of trimeric $(i\text{-}C_3H_7O)_3Al$ and tetrameric $(C_2H_5O)_3Al$.[17]

Compound 3 is relatively thermally stable. When heating this compound from 25 to 430 °C under a flow of N_2, no gaseous products are formed below 140 °C. Figure 3a shows the results of DSC studies of 3 from 30 to 460 °C, which indicate that compound 3 undergoes three thermal processes. The endotherm at 75 - 90 °C, is attributed to the observed melting. Since a substantial amount of methane was found at 180 °C from an independent pyrolysis experiment, the exotherm at 175 - 210 °C is attributed to a thermal decomposition to form methane (presumably from the reaction of $Al(CH_3)_x$ and N-H) with extension of the Al-N network bonding. Figure 4a shows the TGA curve for 3 under a flow of N_2. The weight loss below 140 °C is attributed to sublimation of the sample, which was observed visually during an independent pyrolysis in this temperature region. The actual thermal decomposition appears to begin above 140 °C; theweight loss is completed by 420 °C.

An insoluble, presumably polymeric solid 5 was prepared by heating 3 at 180 °C for 15 min. Its IR spectrum (Figure 5a) shows broad bands, suggestive of a complex, polymeric structure. The appearance of a broad band at around 3300 cm^{-1} suggests that some N-H groups are still left in this structure.

Figure 3b shows the DSC curve for compound 5. Compared that of 3 (Figure 3a), a similar exothermic peak above 400 °C is observed, but the peaks at lower temperature are now absent. The TGA curve for 5 (Figure 4b) shows that it begins to decompose above 220 °C and that no further weight loss is observed above 430 °C. It is notable that the DSC curves of both 3 and 5 show an exothermic process above 400 °C even though no substantial weight loss is found in that temperature range from the corresponding TGA studies. In addition, when heating colorless 5 up to 430 °C, it becomes a dark-brown solid, which indicates some carbon remains in the product. The above facts suggest that the exothermic process above 400 °C is not a simple methane-formation reaction; it could be related to the formation of carbon from the decomposition of methyl or ethylene groups.

The TGA curve of 5 under a flow of ammonia (Figure 4c) shows more weight loss above 200 °C than the corresponding TGA trace under nitrogen, indicating that different pyrolysis reactions are occurring in these two atmospheres. The residue from the TGA experiment carried out under a flow of ammonia is a off-white solid (which is identified as AlN by XRD), rather than the black amorphous solid (no diffraction peaks are observed by XRD) formed under a nitrogen atmosphere, indicating that the organic groups are effectively removed when ammonia is used as a purging gas. Our previous study[14] showed that ammonia can displace ethylenediamine from the polymeric imide $[EtAlNCH_2CH_2NAlEt]_x$ at ambient temperature. A similar process would be expected to occur for the present system, leading to amine exchange and elimination the ethylene groups as free en.

The mass spectrum (CI) of $EtAl[(HN(CH_2)_2NH)AlEt_2]_2$ 4 shows a weak peak at m/e 341 (12%), corresponding to M - 1, and the most abundant peak in the spectrum is at m/e 313 (100%), which is attributed to the loss of one ethyl fragment. Figure 6a and 6b show the ^{1}H and ^{13}C-NMR spectra of $EtAl[(HN(CH_2)_2NH)AlEt_2]_2$ 4 respectively. When compared with the corresponding spectra of compound 3 in Figure 2, it is apparent that compound 4 has a structure similar to that of its methyl analog, 3. Both ^{1}H and ^{13}C-NMR spectra show that the two ethyl groups on $Al(CH_2CH_3)_2$ can be resolved, which is expected from the corresponding structure. However, no difference is observed for the two methyl groups on $Al(CH_3)_3$ in 3 (Figure 2a), suggesting that a fast exchange process may be operative in this case.

Figure 6c shows the ^{27}Al-NMR spectrum of 4. The chemical shift values of both four-coordinated and five-coordinated Al peaks are similar to those of the corresponding methyl compound 3. However, the peaks attributed to both the four- and five-coordinated Al in the case of the ethyl compound show a larger linewidth than those of the corresponding methyl compound, which is consistent with the general trend in ^{27}Al-NMR studies[16], i.e. the larger the alkyl groups attached to Al, the broader the ^{27}Al peaks. In addition, a small peak at 40 ppm in Fig 6c is observed, which is attributed to a six-coordinated Al atom in an impurity[18].

In an attempt to obtain information regarding the formation mechanism of 4, as well as the structure of any intermediates formed during the conversion of the 2:3 adduct to 4, ^{1}H and ^{13}C-NMR spectra of solutions of the 2:3 adduct kept at room temperature for various amounts of time were determined. Figure 7 shows the ^{1}H-NMR spectra of the as-synthesized adduct solution and the corresponding thermolysis products. These spectra show a decrease in the relative intensity of peaks attributed to the starting adduct mixture (1.374 ppm, triplet; 0.058 ppm, quartet, labled as α and α' respectively) with increasing time. Concurrently, new peaks at 1.595 ppm (triplet, β), 1.036 ppm (triplet, π), 0.260 ppm (quartet, β') and -0.129 ppm (quartet, π') grow in (Figure 7b). On further standing, these peaks are eventually replaced with those characteristic of 4 (Scheme 1) (labled as ϕ, ϕ', μ, μ', τ, φ).

It is necessary to analyse the nature of the 2:3 en:AlR_3 system before discussing the formation mechanism of 4. The 2:3 system can be considered as a combination of one 1:2 en:AlR_3 adduct and one 1:1 adduct. Our previous studies on the 1:2 system[14] indicated that the 1:2 en-triethylaluminum adduct easily loses ethane forming a five-membered ring molecule 2 (Scheme 1) at room temperature. If we assume that this molecule reacts immediately on formation with the remaining 1:1 en:$AlEt_3$ adduct so as to couple the η N atom of the adduct with the Al_f of 2 and eliminate ethane, the proposed intermediate 7 would be formed. Subsequently, this intermediate could convert to 4 by ring closure accompanied by further ethane elimination.

Based on the above analysis, the new peaks (labled as β, β', π and π')observed in the ^1H-NMR spectrum of the 2:3 en:$AlEt_3$ adduct mixture (Figure 7b) after standing for three hours at room temperature are attributed to the intermediate 7. The structural assignment for 7 is based on the consideration of the chemical shift values, the splitting pattern and the relative intensities.

In the spectrum shown in Figure 7b, the peaks labeled β and β' are attributed to the CH_3 and CH_2 H-atoms of the ethyl groups attached to the Al_f atom of 7 respectively, and similarly, the peaks π and π' are assigned to the CH_3 and CH_2 H-atoms of the ethyl groups on the ring. The appearance of the β and β' peaks at lower field than the corresponding peaks of the ethyl groups of the adducts is attributed to the bonding of the Al_f atom to a four-coordinated N atom which is also shared by the Al_g atom on the ring; this should result in more deshielding from the Al_f relative to the Al atoms of the adduct.

In contrast, Al_g is connected to two four-coordinated nitrogen atoms, which should provide a more electron-rich environment to the π and π' H atoms as compared with that of the α and α' H atoms and subsequently make them more shielding. The chemical shifts for the H-atoms of the ethyl groups attached to Al_h would be unchanged from those of the adduct, since these ethyl groups are in a similar structural environment. Furthermore, the intensity of the β and π peaks are close to the expected 1:1 ratio for structure 7. The above assignment is also consistent with the ^{13}C-NMR spectrum. The ^{13}C-NMR spectrum of the adduct solution kept at room temperature for 1h (Figure 8a) shows a new set of peaks (assigned to the σ, σ', β and π C atoms of (7) respectively) in addition to the peaks attributed to the adduct (α, α' and γ). The chemical shift and relative intensities (β to π, σ to σ') of these peaks are consistent with what would be expected from structure 7.

It is notable that the five-membered intermediate 2 is not observed during the conversion of the 2:3 adduct mixture to 4, suggesting that it reacts immediately with the 1:1 adduct on formation of 7. The conversion process of 7 to 4 is clear from Figure 7c and Figure 7d. The quartet at ca. 1.045 ppm is believed to arise from the overlap of two triplets which are attributed to the π H of 7 and the methyl H-atoms of $AlCH_2CH_3$ of 4 (labled as φ) respectively. This conversion process is also observed in the ^{13}C-NMR spectrum (Figure 8b).

Further decomposition of compound 4 by heating it up to 240 °C for 10 min resulted in the formation of a polymeric glassy solid 6. The IR spectrum of 6 (Figure 5b), shows relatively broad absorption bands, indicating a crosslinked polymeric structure.

The DSC studies of compound 4 and 6 (Figure 3c and Figure 3d) show similar features compared with those of their trimethylaluminum counterparts, 3 and 5, (Figure 3a and 3b). Two exothermal processes are observed in the range 190 - 290 °C and above 400 °C respectively. The TGA curve of 4 under a flow of nitrogen (Figure 9a) is very similar to that of 3. The weight loss below 200 °C is attributed to evaporation; the actual decomposition begins above that temperature, which is consistent with the DSC studies. The TGA studies of 6 under a flow of nitrogen or ammonia (Figure 9c and 9b) show an yield of 58.5% and 30.5% respectively. In addition, GC measurements indicate that methane begins to appear in the gaseus decomposition products on heating 6 up to 400 °C (5%), in addition to the dominant ethane and some ethylene, and accounts for 22% of the total gaseous products by 430 C, suggesting that a complicated decomposition process ccuring in this temperature region.

Acknowledgement

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Supplementary Material Available: All calculated atomic coordinates, anisotropic displacement coefficients, bond lengths and angles (6 pages) and a listing of h, k, l, F_o and F_c (9 pages). Ordering information is given on any current masthead page.

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Captions

Figure 1 ORTEP plot (50% probability thermal ellipsoids) of the molecular structure of $MeAl[(HN(CH_2)_2NH)AlMe_2]_2$ (3) with the atom numbering scheme.

Figure 2 NMR spectra of $MeAl[(HN(CH_2)_2NH)AlMe_2]_2$ (3) (a) ^1H-NMR (b) ^{13}C-NMR (b) ^{27}Al-NMR.

Figure 3 DSC curves for: (a) $MeAl[(HN(CH_2)_2NH)AlMe_2]_2$ (3), (b) polymeric solid 5, (c) $EtAl[(HN(CH_2)_2NH)AlEt_2]_2$ (4), (d) polymeric solid 6.

Figure 4 TGA results of (a) $MeAl[(HN(CH_2)_2NH)AlMe_2]_2$ (3) under N_2, (b) polymeric solid 5 under N_2, (c) polymeric solid 5 under NH_3.

Figure 5 FT-IR spetra of (a) polymeric solid 5, (b) polymeric solid 6.

Figure 6 NMR spectra of $EtAl[(HN(CH_2)_2NH)AlEt_2]_2$ (4) (a) ^1H-NMR, (b) ^{13}C-NMR, (c) ^{27}Al-NMR. (Refer to the experimental section for peak assignments)

Figure 7 ^1H-NMR spectra of 2:3 en-triethylaluminum adduct solution, (a) as-synthesized, (b) kept at 25 C for 3 h, (c) kept at 25 C for 7 h, (d) kept at 25 C for 20 h. (see the text and Scheme 1 for peak assignments)

Figure 8 ^{13}C-NMR spectra of a 2:3 en-triethylaluminum adduct solution, (a) kept at 25 C for 1 h, (b) kept at 25 C for 7 h, (c) inset of (b).

Figure 9 TGA curve for (a) $EtAl[(HN(CH_2)_2NH)AlEt_2]_2$ **4** under nitrogen, (b) polymeric solid **6** under ammonia, (c) polymeric solid **6** under nitrogen.

Scheme 1

2:3 system

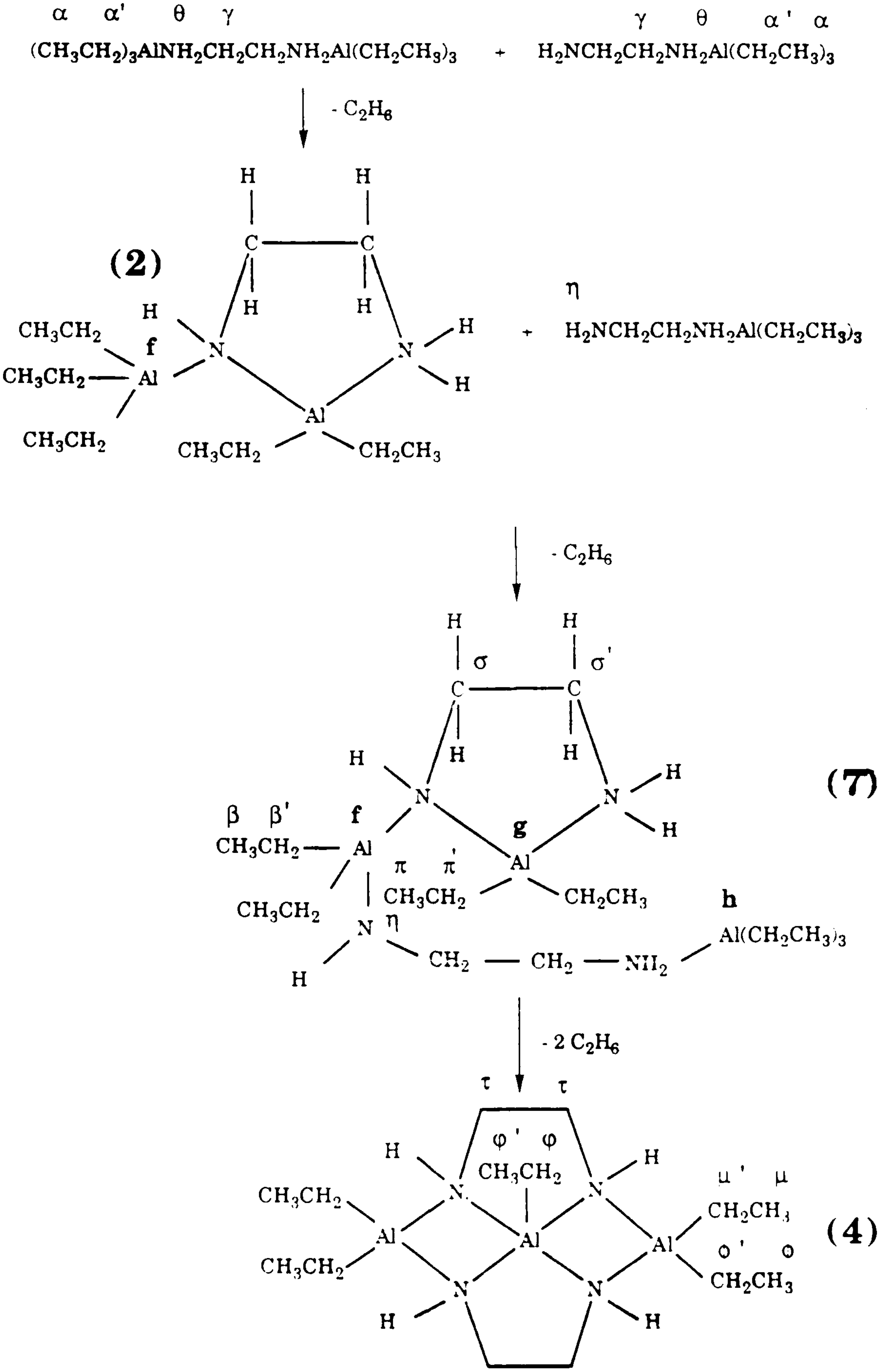


Table 1. Crystallographic Data for $MeAl[(HN(CH_2)_2NH)AlMe_2]_2$(3)

formula	$C_9H_{27}Al_3N_4$
mol. wt.	272.3
color	white
space group	P2/c (No. 13)
a,b,c (Å)	15.523(3), 8.419(1), 13.464(3)
β (°)	109.00(2)
cell volume (Å^3)	1663.8(5)
Z	4
density,calc. (g/cm^3)	1.087
crystal dimensions (mm)	0.36 x 0.40 x 0.56
scan speed (/min)	Variable; 3.0 to 29.30 in ω
scan range (ω)	1.20°
2θ range (°)	3.0 to 130.0°
absorption coefficient (mm^{-1})	1.967
F(000) (e)	592
index ranges	$-16 < h < 16$
	$-9 < k < 0$
	$0 < l < 14$
unique data	2584
observed data (F>4σ(F))	2280
R	0.051
R_w	0.076
goodness of fit	1.31
largest difference peak (eÅ^{-3})	0.21

Table 2. Atomic Coordinates (x 10^4) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for **$\mathrm{MeAl[(HN(CH_2)_2NH)AlMe_2]_2}$(3).**

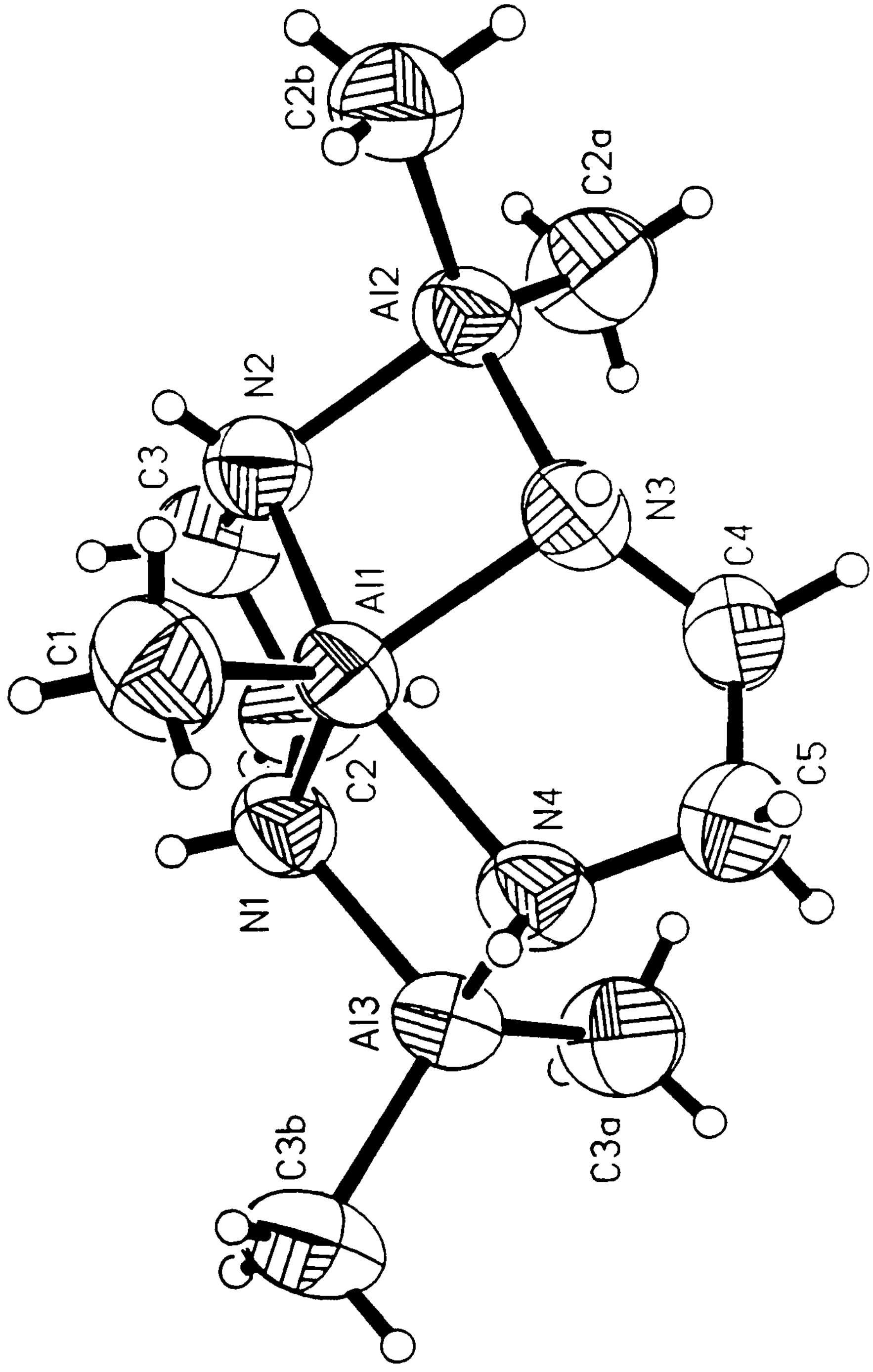
Atoms	x	y	z	U(eq)
Al1	2150(1)	2380(1)	-465(1)	56(1)
C1	1351(2)	2236(2)	-1926(1)	87(1)
N1	1912(1)	922(2)	583(1)	65(1)
C2	2793(2)	152(3)	1157(2)	80(1)
C3	3248(2)	-426(3)	399(2)	86(1)
N2	3189(1)	812(2)	-379(1)	65(1)
N3	3147(1)	3975(2)	-157(1)	62(1)
C4	3141(1)	4851(3)	782(2)	71(1)
C5	2181(2)	5389(2)	649(2)	79(1)
N4	1560(1)	4018(2)	267(1)	67(1)
Al2	4071(1)	2477(1)	-235(1)	61(1)
C2A	5131(1)	2325(2)	1023(2)	96(1)
C2B	4242(2)	2780(3)	-1597(2)	85(1)
Al3	1335(1)	2479(1)	1197(1)	64(1)
C3A	2008(2)	2882(2)	2682(1)	93(1)
C3B	26(2)	2042(3)	792(2)	98(1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized Uij tensor

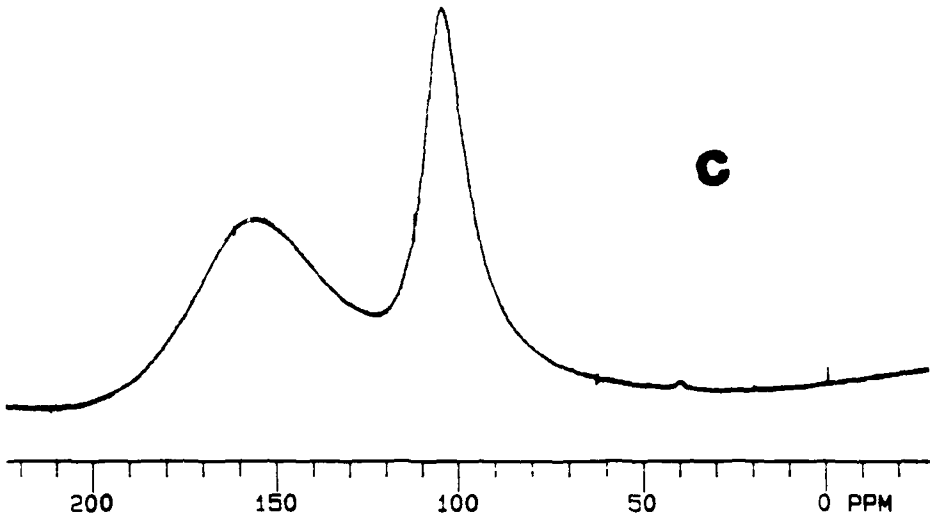
Table 3. Bond Distances in Angstroms and Selected Bond Angles in degrees for $MeAl[(HN(CH_2)_2NH)AlMe_2]_2(3)$.

Bond		Distance	Bond		Distance
Al1	C1	1.958(2)	Al1	N1	1.994(2)
Al1	N2	2.058(2)	Al1	N3	1.988(2)
Al1	N4	2.073(2)	N1	C2	1.483(3)
N1	Al3	1.921(2)	C2	C3	1.498(4)
C3	N2	1.459(3)	N2	Al2	1.925(2)
N3	C4	1,467(3)	N3	Al2	1.938(2)
C4	C5	1.511(3)	C5	N4	1.484(3)
N4	Al3	1.912(2)	Al2	C2A	1.944(2)
Al2	C2B	1.953(3)	Al3	C3A	1.960(2)
Al3	C3B	1.959(3)			

Atoms			Angles	Atoms			Angles
C1	Al1	N1	118.0(1)	C1	Al1	N2	104.2(1)
N1	Al1	N2	83.5(1)	C1	Al1	N3	116.5(1)
N1	Al1	N3	125.4(1)	N2	Al1	N3	83.1(1)
C1	Al1	N4	106.6(1)	N1	Al1	N4	82.0(1)
N2	Al1	N4	149.2(1)	N3	Al1	N4	83.5(1)
Al1	N1	C2	106.6(2)	Al1	N1	Al3	96.0(1)
C2	N1	Al3	123.7(1)	N1	C2	C3	110.3(2)
C2	C3	N2	108.9(2)	Al1	N2	C3	111.4(2)
Al1	N2	Al2	93.3(1)	C3	N2	Al2	124.9(1)
Al1	N3	C4	107.1(1)	Al1	N3	Al2	95.1(1)
C4	N3	Al2	125.9(1)	N3	C4	C5	109.4(2)
C4	C5	N4	108.1(2)	Al1	N4	C5	110.2(2)
Al1	N4	Al3	93.7(1)	C5	N4	Al3	122.4(1)
N2	Al2	N3	88.0(1)				



C2b
C2a
Al2
N2
C3
N3
C4
C1
Al1
C2
C5
N4
N1
Al3
C3b
C3a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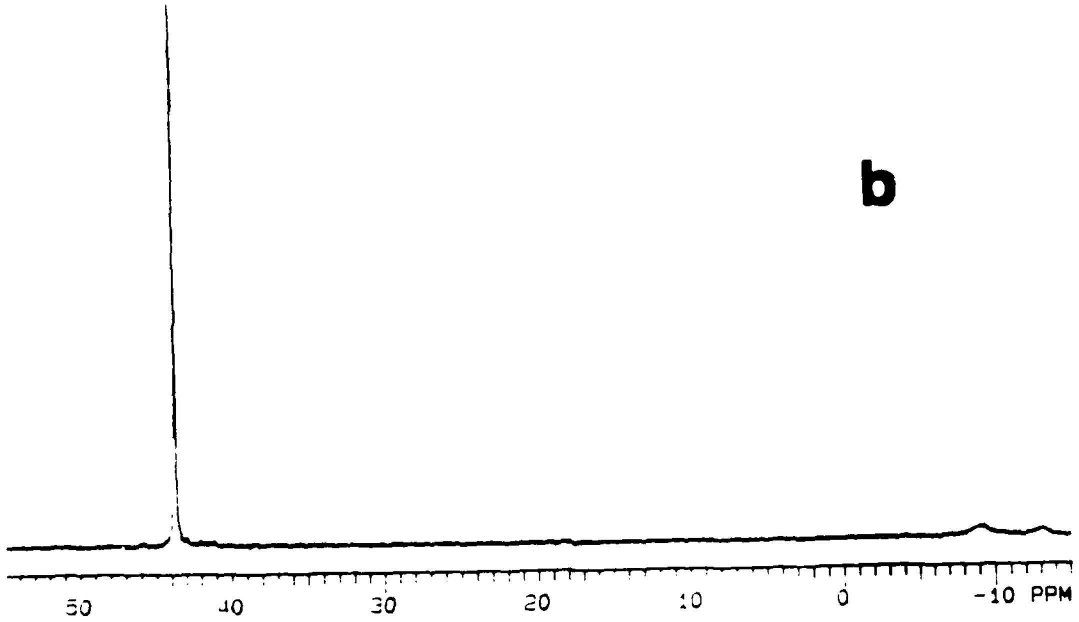
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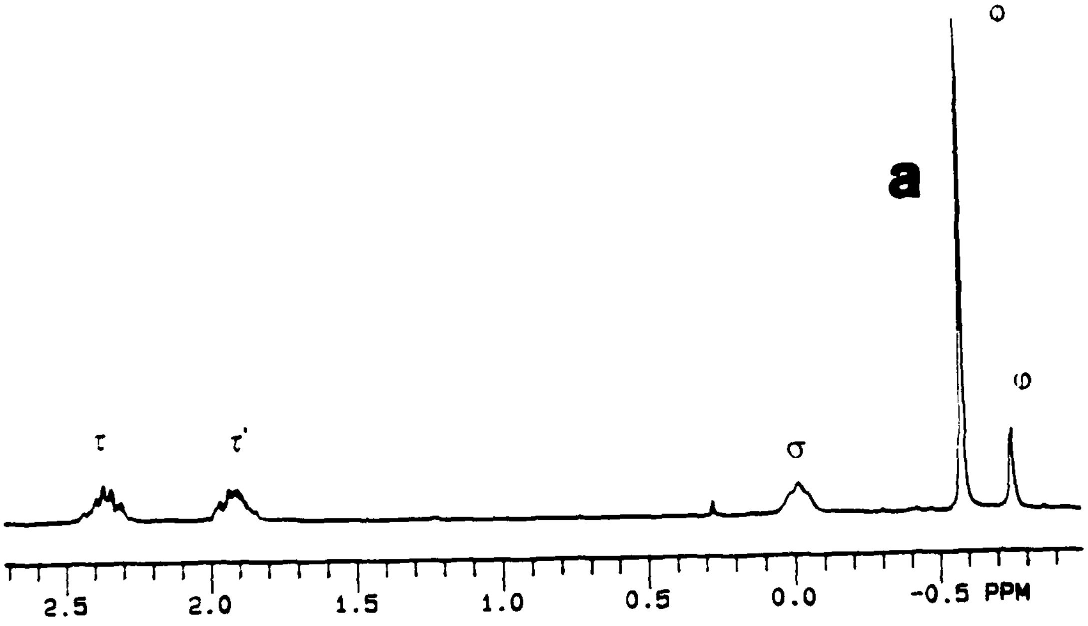
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a
ω
τ
τ'
σ
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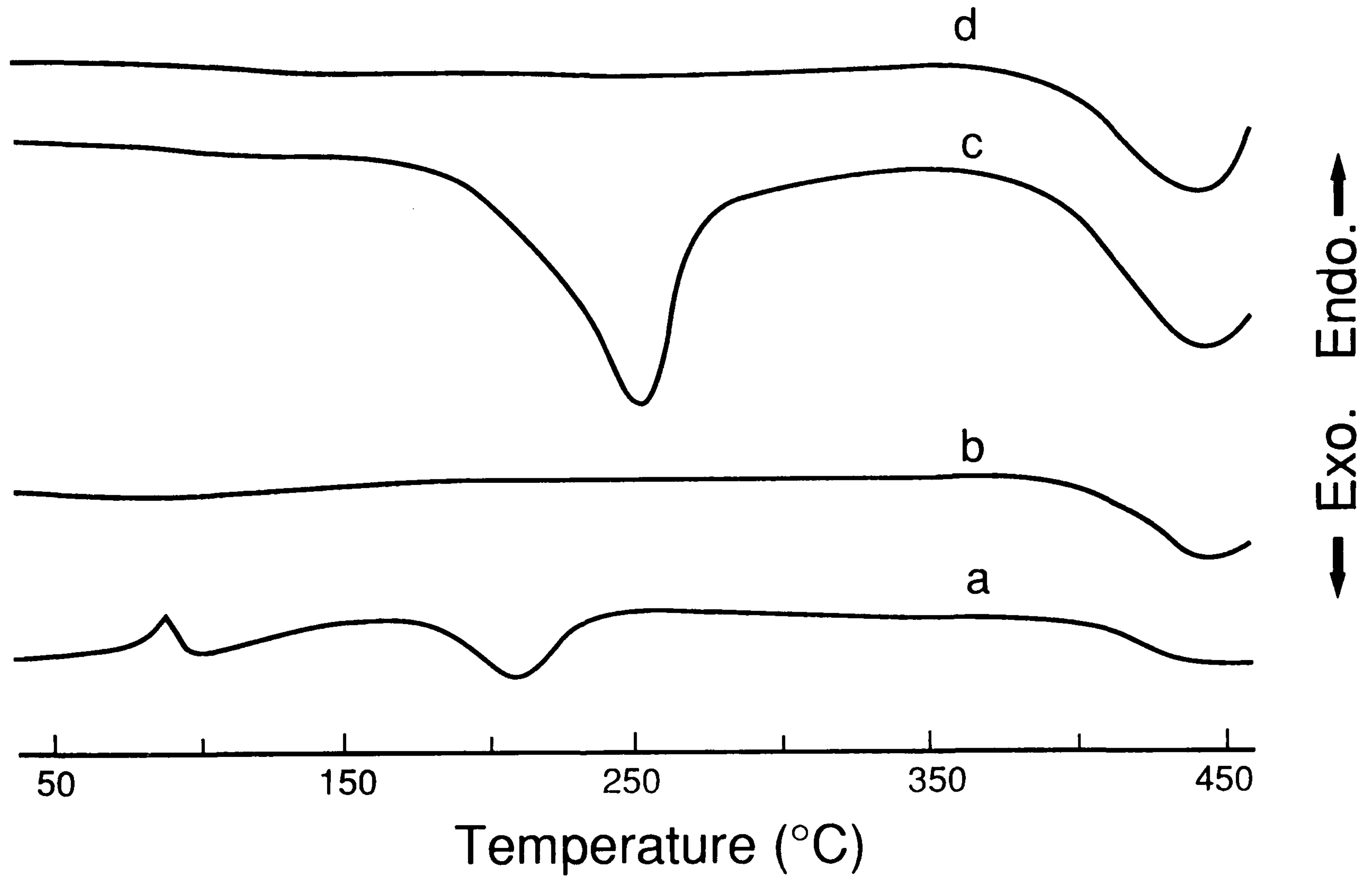
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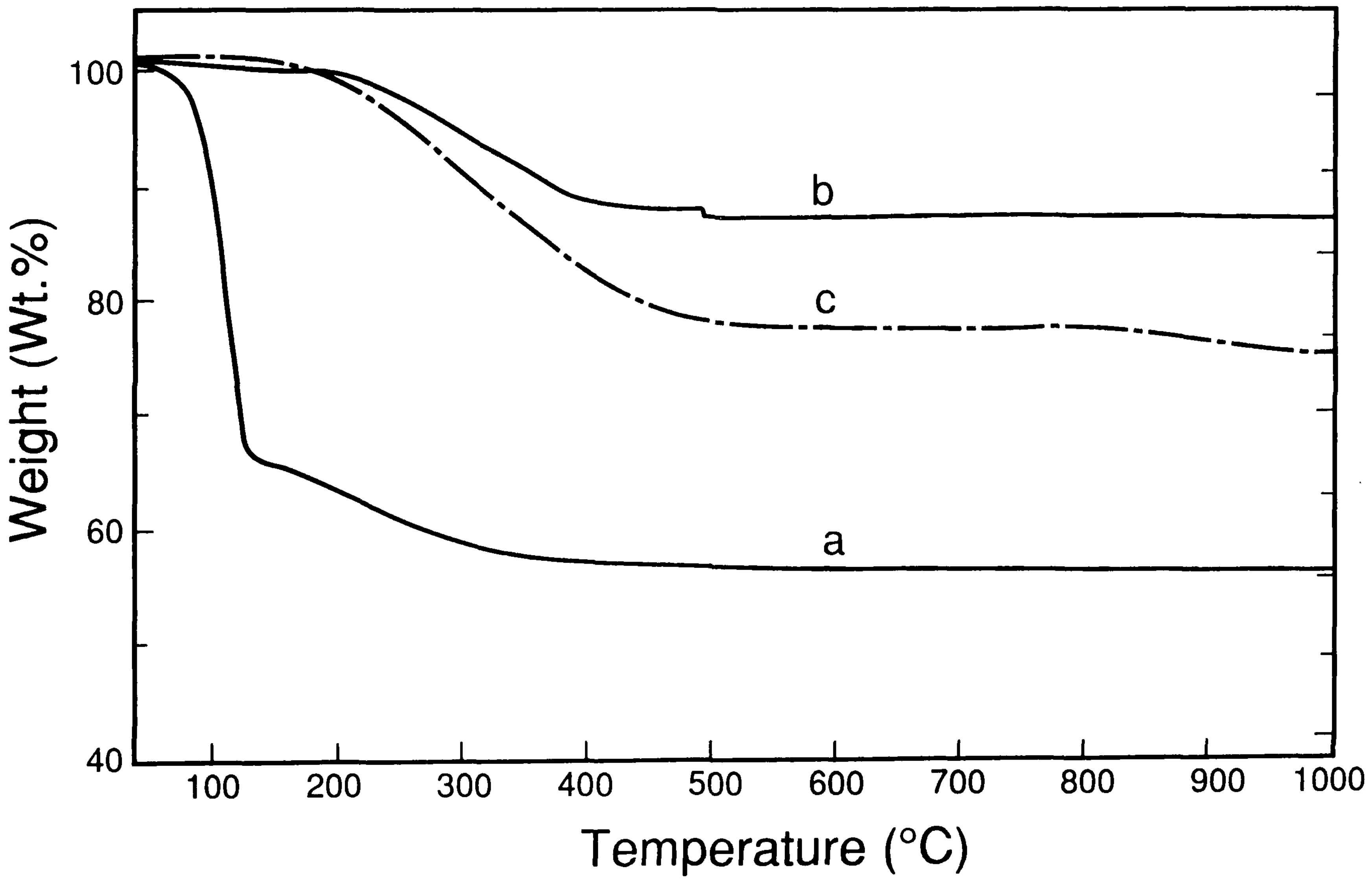
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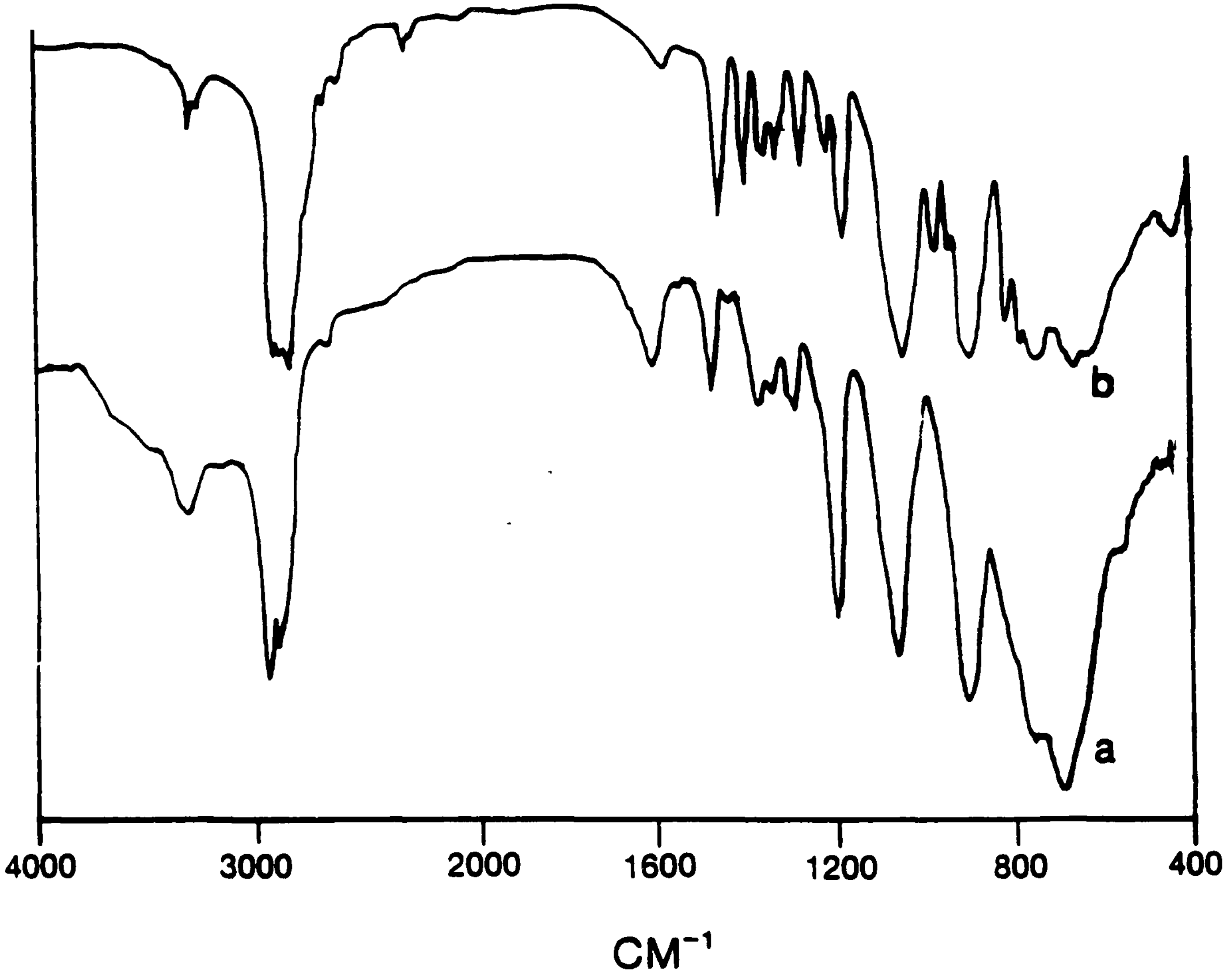
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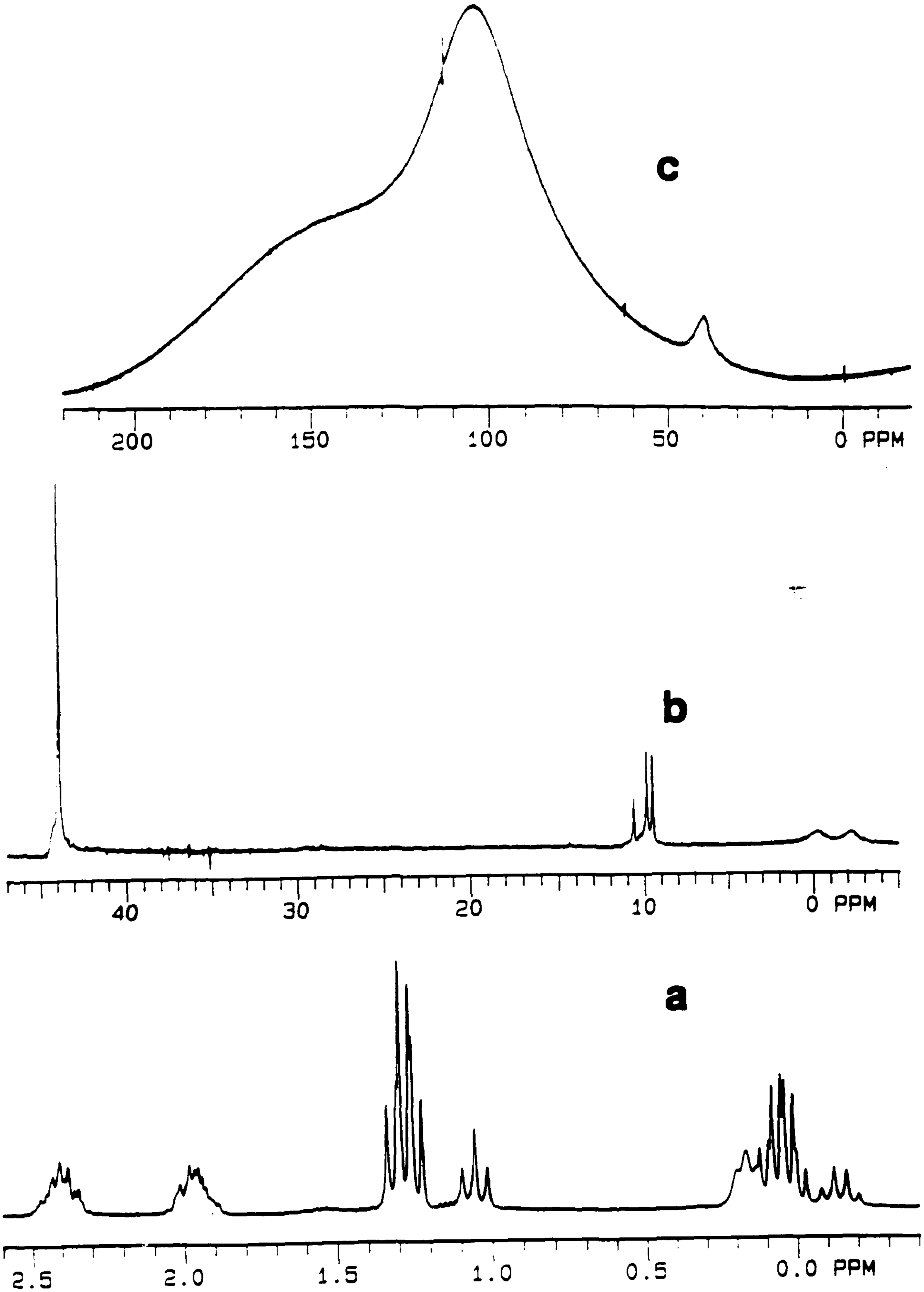

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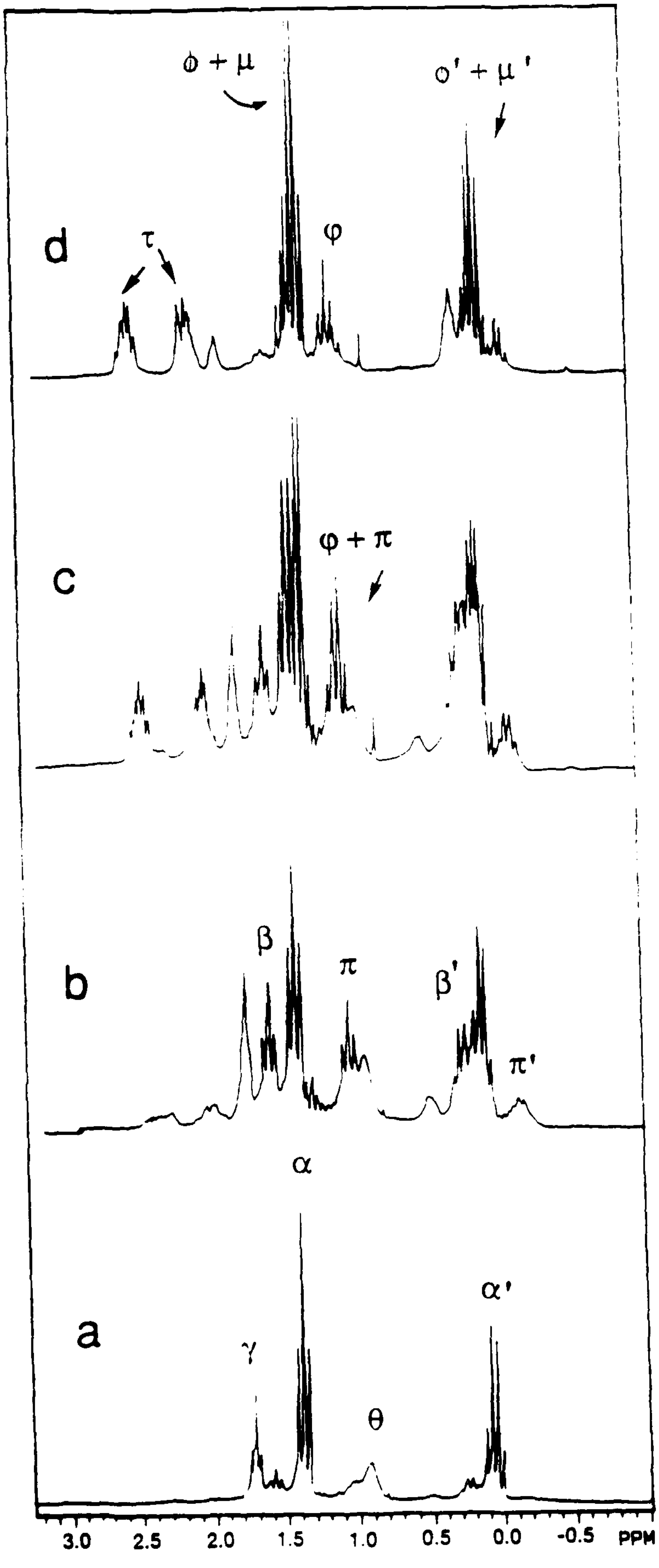
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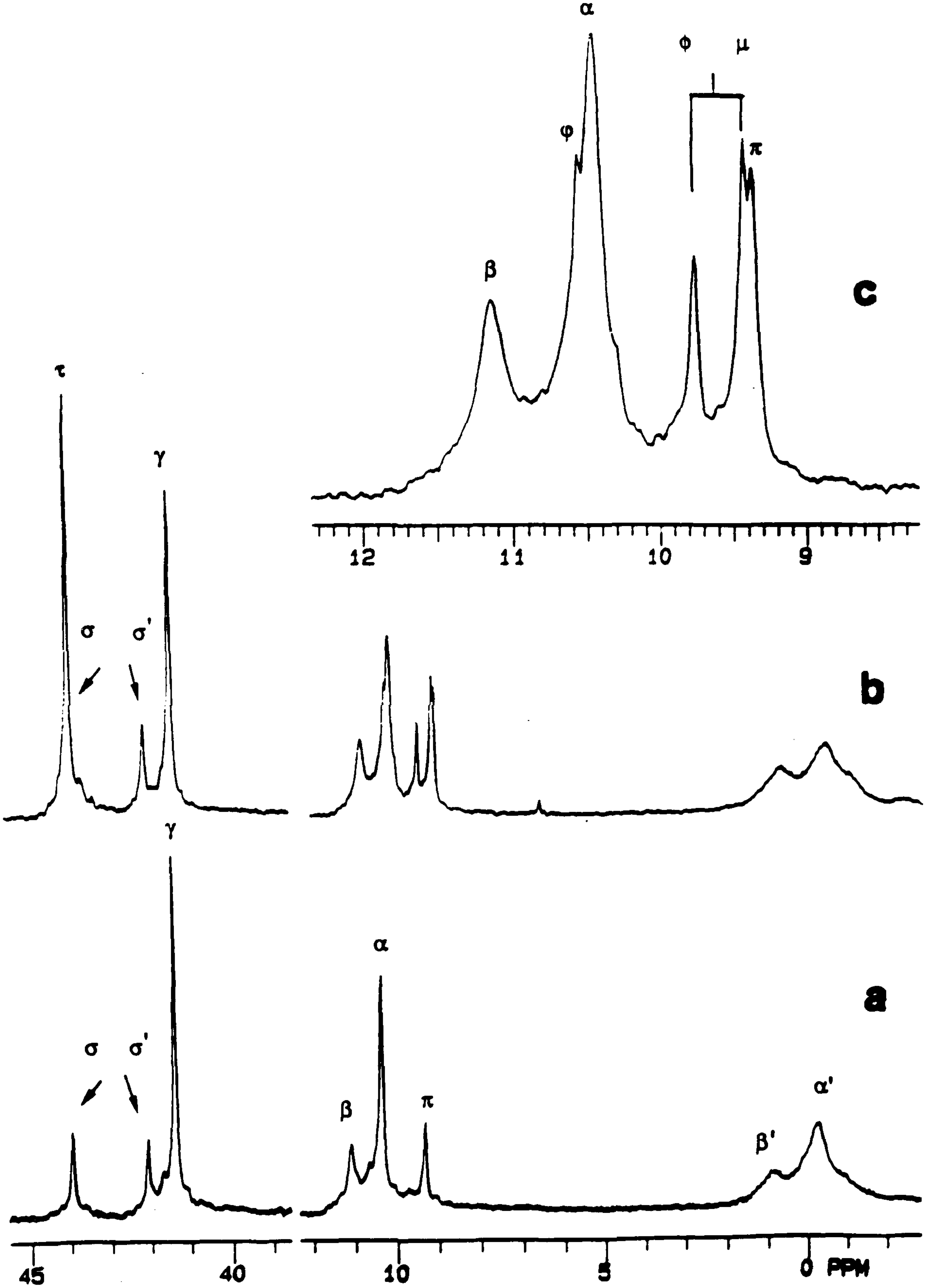
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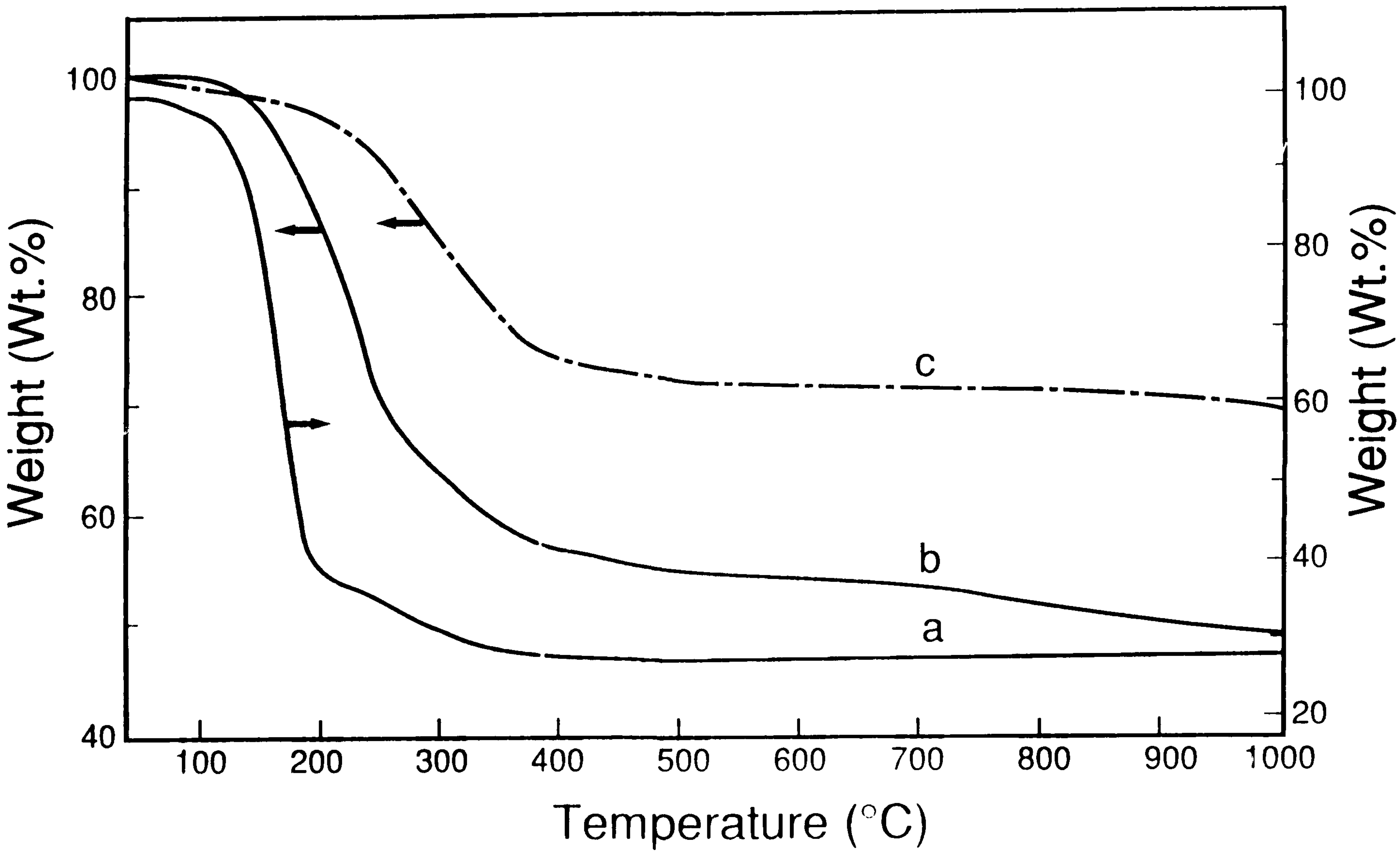
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a
Weight (Wt.%)
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80
60
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