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HETEROCYCLES BASED ON GROUP III, IV AND V ELEMENTS
PRECURSORS FOR NOVEL GLASSES AND CERAMICS

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1. ABSTRACT

It has been established that the interaction of tris[bis-(trimethylsilyl)amino]aluminum with one mole of ammonia affords two isomers. The proposed structures are $[(\text{Me}_3\text{Si})_2\text{N})_2\text{AlNH}_2]_2$ for the higher and $[(\text{Me}_3\text{Si})_2\text{NAl}(\text{NHSiMe}_3)_2]_2$ for the lower melting compound. A scale-up process was developed for the lower melting isomer. This material, at 183°C , was transformed into $[(\text{Me}_3\text{Si})_2\text{NAlNH}]_4$; pyrolysis up to 1000°C failed to give aluminum nitride. At 183°C the higher melting isomer afforded a liquid of an unknown composition. Interaction of tris[bis(trimethylsilyl)-amino]aluminum with two moles of ammonia formed an aluminum nitride precursor, $[(\text{Me}_3\text{Si})_2\text{NAlNH}]_x$; the structural assignment has not been validated because there are discrepancies in the analytical data. Ammonia treatment of $[(\text{Me}_3\text{Si})_2\text{NAlNSiMe}_3]_2$ gave $\text{Me}_3\text{SiNAl}(\text{NH}_2)\text{N}(\text{SiMe}_3)\text{AlNHSiMe}_3$. This material when reacted with bis(trimethylsilyl)aminotrimethylsilylaminochloroborane yielded $\text{Et}_3\text{N}.\text{Cl}_2\text{Al}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$, a precursor of AlN.BN ceramic. Attempts to synthesize other well characterized precursors of AlN.BN ceramics were largely unsuccessful.

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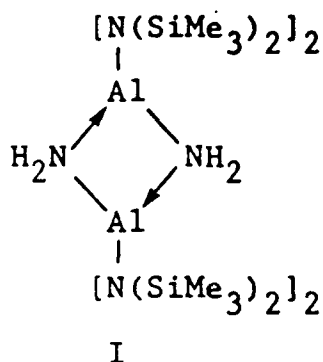
2. INTRODUCTION

The objective of this program is to explore the feasibility of synthesizing novel heterocyclics from the group of elements consisting of B, C, N, Al, Si, and P, the ultimate goal being the production of processible precursors leading to novel ceramics of unusual properties. The initial efforts under the program were devoted to development of processible preceramic systems leading to aluminum nitride ceramics. This involved the synthesis of novel trimethylsilylamino-substituted aluminum compounds and the study of their reactions. During the current reporting period the investigations of processible precursors of aluminum nitride were further pursued. Work was also directed at identification of processes leading to the formation of processible Al-N-B systems amenable to transformation into AlN.BN ceramics. (Continued)

3. RESULTS AND DISCUSSION

The objective of the program is to prepare processible precursors for aluminum nitride, as well as materials containing other group III, IV, or V elements, the latter to be utilized as precursors for novel classes of ceramics. The investigations performed during the past twelve months were centered on the exploration of processible chlorine-free aluminum nitride precursors and aluminum-boron-nitrogen systems. A part of the effort was devoted to scale-up synthesis of intermediates which in the past were obtained by processes not amenable to formation of more than a couple of grams of the compounds.

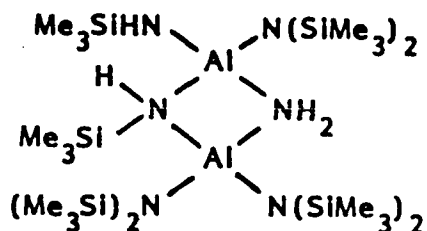
In the last Annual Report [Ref 1], the preparation of the amino-substituted aluminum compound I was reported:



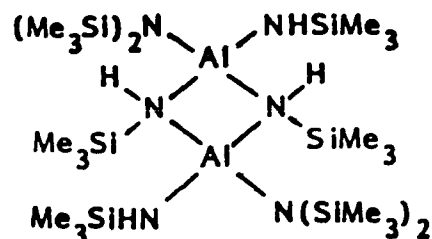
The above structure appeared consistent with the mass spectral and infrared data. Inasmuch as the material is air insensitive, the molecular weight was determined by osmometry and it was confirmed

that it is a dimer. To prepare larger quantities of this compound, it was necessary to scale up the synthesis of the precursor, namely tris[bis(trimethylsilyl)amino]aluminum. The experiments performed are listed in Table I. As evident from the data, to assure the best yields required slow addition of the solid aluminum chloride with external cooling, followed by stirring at room temperature. In one large batch, 50 g (50% yield) of the desired product was thus prepared. The next step involving the interaction of tris[bis(trimethylsilyl)amino]aluminum with ammonia was originally performed in a sealed tube. This operation did not lend itself to scale up. A number of different reaction conditions had to be evaluated. These are summarized in Table II. Apparently, the reaction proceeds only slowly at 0°C. At room temperature, the desired process is accompanied by side reactions. This is evident from the quantity of hexamethyldisilazane evolved, ammonia consumed, and starting material recovered. In spite of the difficulties, the pure product was obtained in a 30% yield. In some of the tests two products were isolated. Both materials had the same molecular weight, as determined by osmometry. The ¹H NMR spectra, Figures 1 and 2 were essentially identical with the ratio of the protons on nitrogen to the protons on carbon of 1:17.5 for the lower melting material and 1:16.5 for the higher melting isomer. The calculated value was 1:18. The NMR spectrum of the higher melting material looks cleaner; whether this appearance is due to traces of impurities in the lower melting compound or whether this is caused by

the presence of different structures, i.e.:



II



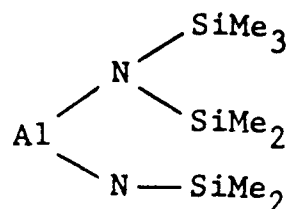
III

is unknown.

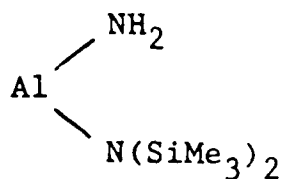
Both isomers showed a pair of doublets in the NH stretching region, but in the case of the higher melting isomer (215-217°C), the two bands in each pair were of an equal intensity [Figure 5, Ref 1], whereas in the case of the lower melting isomer (184-185°C), the bands at 3400 and 3320 cm^{-1} were of a higher intensity than those at 3380 and 3350 cm^{-1} [Figure 1, Ref 1]. As reported previously [Ref 1], the higher melting isomer was isolated initially from the reaction of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlCl}$ with ammonia. In the process involving $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Al}$ and ammonia, this isomer is formed but not in a reproducible fashion, i.e. none was observed in Tests 7A and 7B.

Based on the infrared data and melting characteristics, one is tempted to postulate that the higher melting isomer has the arrangement I, whereas the lower melting material has either the arrangement II or III. This assumption is partially based on the behavior of the anilino versus B-amino-N-phenyl borazines [Ref 2,

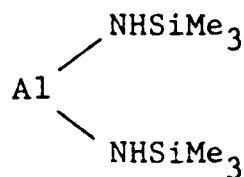
3]. The mass spectral breakdown patterns of the two compounds although essentially identical, Tables III and IV, do exhibit some differences, such as the 244^+ and 203^+ ions which are present in the higher melting isomer in a much higher intensity. The 244^+ ion:



could be derived from both isomers, however the 203^+ ion is much more likely to have the arrangement IV:



IV



V

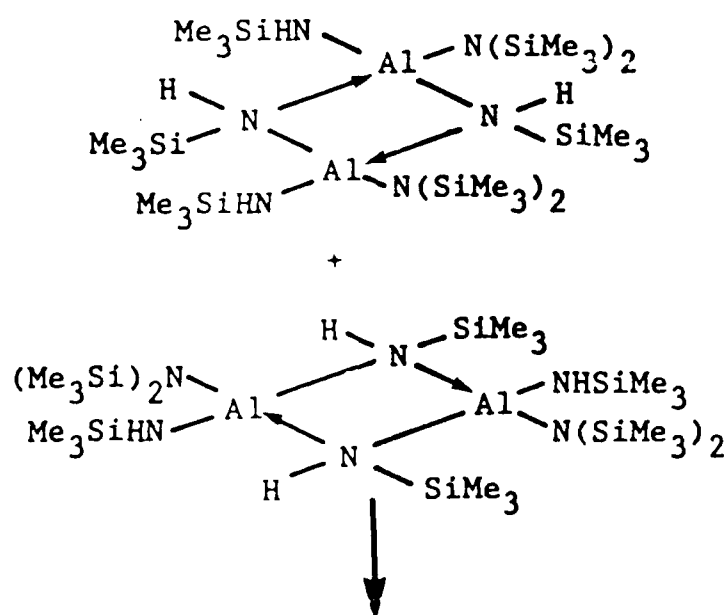
than V and thus its production from the isomer I is much more plausible.

There is no facile interchange of I and II or vice-versa since the pyrolyses of the two isomers yield different type of products. Thus, as reported previously [Ref 1], the pyrolysis of II or III gave essentially a quantitative yield of 2 moles of hexamethyldisilazane per mole of the dimer employed and a solid

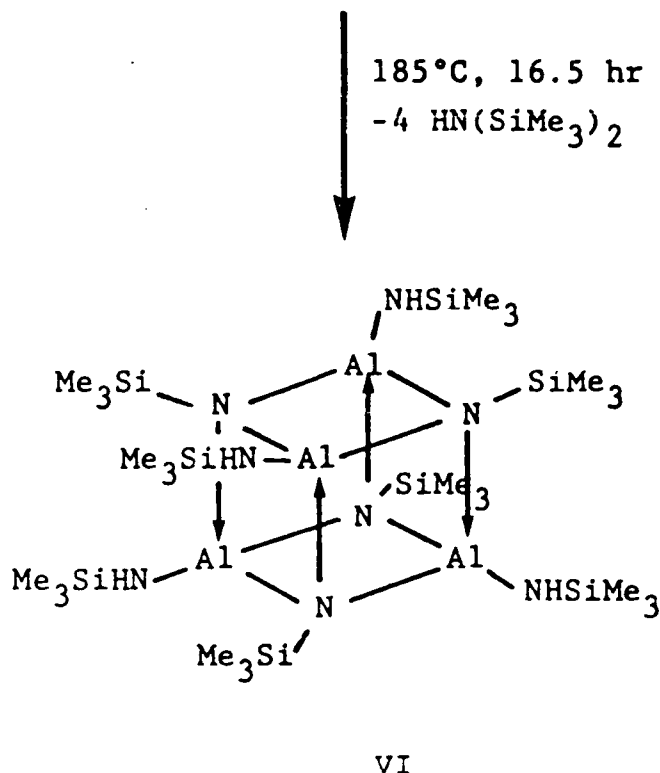
product which failed to melt up to 220°C. A parallel treatment performed on the higher melting isomer gave a viscous liquid, and only a 76% yield of the expected hexamethyldisilazane.

During the current reporting period, a considerable effort was expended to put in place the apparatus shown in Figure 3 for determining molecular weight by vapor pressure lowering. This is mandatory in the case of the moisture-sensitive materials. This technique has been now successfully employed in obtaining the molecular weight of the pyrolysis product, $[(\text{Me}_3\text{Si})_2\text{NAlNH}]$, which is formed upon heating of the lower melting dimer, structure II or III at 185°C for 16.5 hr. The molecular weight found was 790 which would imply that the product is a tetramer (theory 809), not a trimer. Based on the dimer arrangement of the starting material and an intermolecular elimination, this would be the expected configuration as illustrated by Scheme I below.

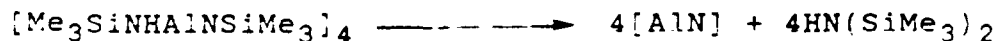
SCHEME 1:



SCHEME 1:



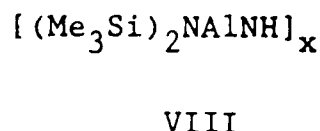
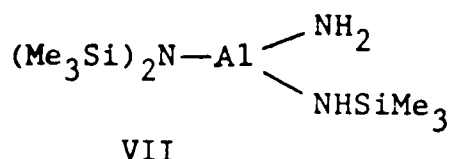
It was expected that the tetramer VI on pyrolysis would give aluminum nitride i.e.:



However, both under TGA conditions and utilizing a bulk pyrolysis procedure up to 980°C, carbon remained as evident from the residue's appearance and its weight which was more than twice the calculated weight for AlN. Based on these results it is obvious that this arrangement does not provide an aluminum nitride precursor.

It was of interest to determine whether treatment of tris[bis(trimethylsilyl)amino]aluminum with two moles of ammonia

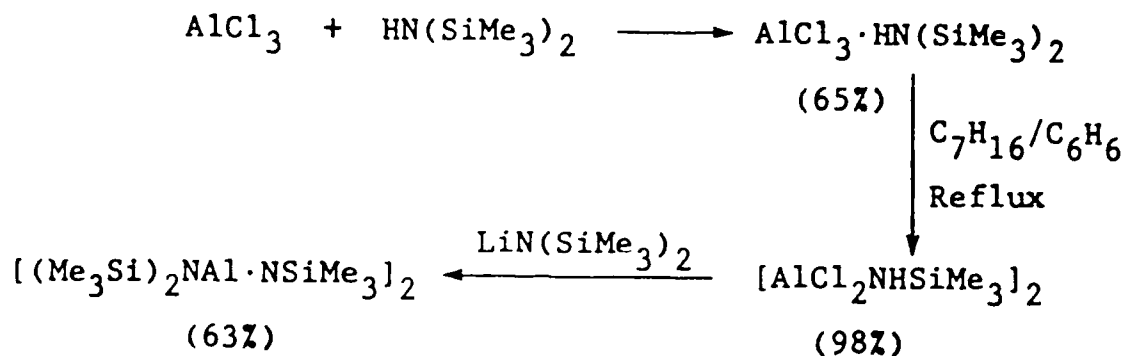
would afford a different product from that obtained using one mole of ammonia. Based on hexamethyldisilazane liberated, 1.5 moles per mole of tris[bis(trimethylsilyl)amino]aluminum, a structure represented by VII would be expected.



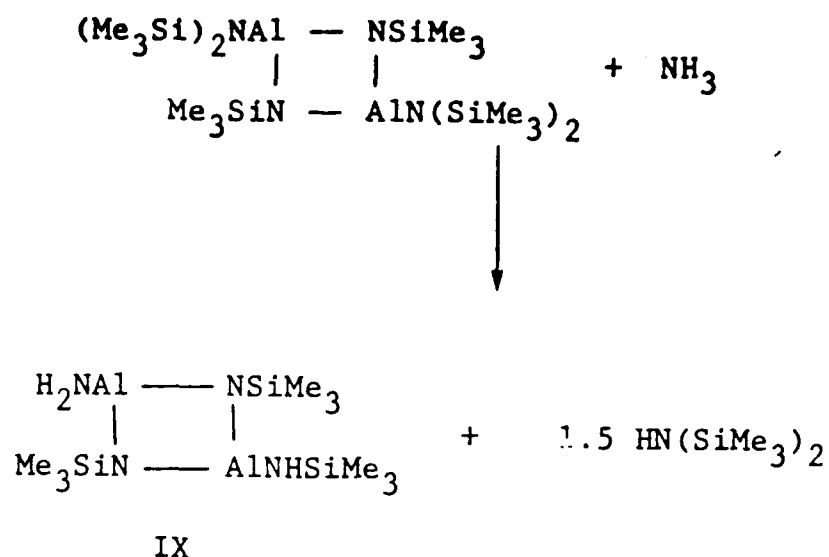
The nitrogen analysis, 14.5%, is in good agreement with the theoretical value of 14.4%. Also, the infrared spectrum, Figure 4, exhibits very strong NH bands at 3410 cm^{-1} and 3330 cm^{-1} . The DSC, Figure 5, shows a strong endotherm at 200°C which corresponds to the melting point and decomposition. This material on pyrolysis at 194°C exhibited 72.9% weight loss and the residue showed only a very weak C-H absorptions. The TGA of this material resulted in a further weight loss of 20.0% bringing the total weight loss to 78.3% which agrees with 79.6 weight loss for the arrangement VIII on pyrolysis to aluminum nitride. The residue was a white hard solid which exhibited an infrared spectrum comparable to that of the commercial aluminum nitride. The found nitrogen value of 14.5% is higher than the 13.84% calculated for VIII; also the infrared spectrum, as noted above, does not support VIII. The molecular weight of 1150 cannot be explained by either one of the compounds. It can be expressed as $[(\text{Me}_3\text{Si)}_2\text{NAlNH}]_6$ but the actual structural arrangement is hard to visualize. The

molecular weight was determined at two different times and the values obtained were within experimental error thus the effect of hydrolysis is not very likely. In view of these discrepancies further investigations of this material will be carried out, in particular since it appears to provide a soluble aluminum nitride precursor.

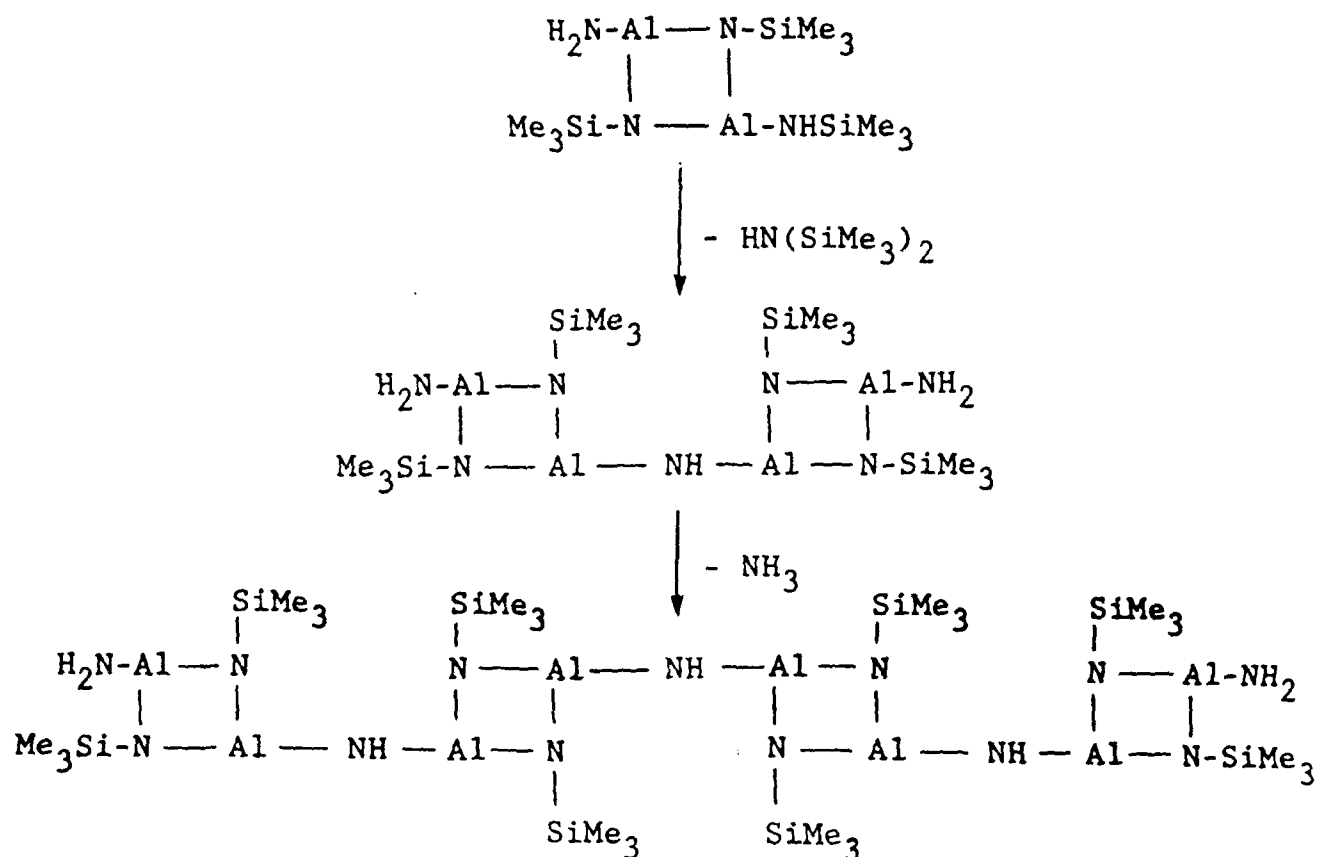
Another potential route to H₂N-substituted aluminum compounds was the reaction of the four-membered ring compound [(Me₃Si)₂Al₂NSiMe₃]₂ described earlier [Ref 1], with ammonia. The overall synthesis of the starting material from aluminum trichloride according to the sequence given below:



was successfully scaled up. The subsequent reaction with ammonia proceeded essentially in a quantitative yield. The postulated process is shown below, i.e.



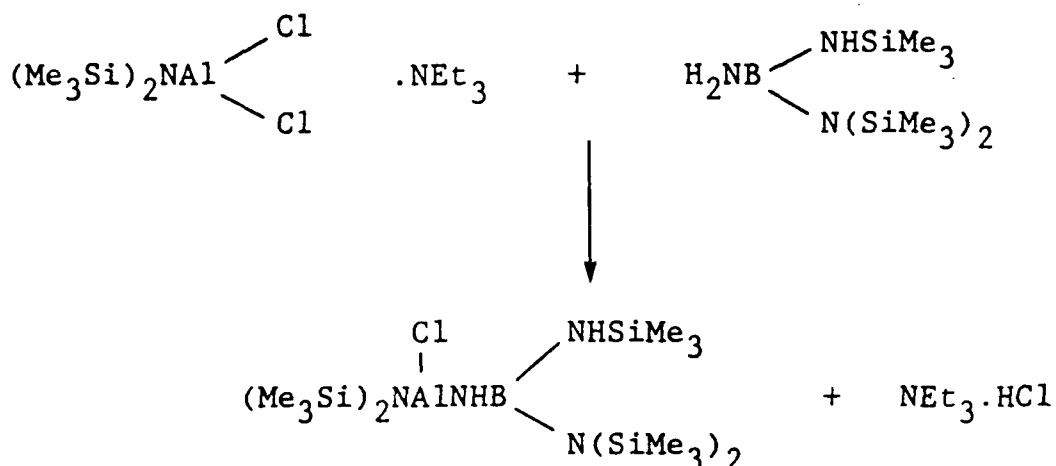
The product was very difficult to separate from hexane; this behavior was attributed to solvent association. This assumption was further supported by molecular weight determination in pentane, using vapor pressure depression which gave a value of 2300, versus the 332 calculated for the dimer. Thus, it would appear that the compound exists in solution in a polymeric, highly solvated form. The infrared spectrum, Figure 6, showed two types of N-H absorptions and the presence of NHSiMe₃ group (band at 1110 cm⁻¹) which supports the postulated structure. In the DSC, Figure 7, only a single endotherm was observed at ~ 275°C. Heating the material at 280°C for 21 hr resulted in the liberation of hexamethyldisilazane and ammonia. The mole ratio of the 4-membered ring compound to hexamethyldisilazane to ammonia was found to be 1:0.57:0.11. Based on these data one is tempted to speculate that a condensation process took place giving predominantly a two ring system together with a low extent of a further reaction to



The proposed mechanism is based on the quantity of hexamethyl-disilazane produced, the relative ratio of hexamethyldisilazane to ammonia and the infrared spectrum, Figure 8, of the residue; in particular the almost complete disappearance of the absorption at 1110 cm^{-1} (NHSiMe_3 entity) and the retention of the doublet at 3380 and 3290 cm^{-1} . Had the ammonia to hexamethyldisilazane ratio been 1:1 an elimination of trimethylsilylamine followed by disproportionation would have been indicated. This specific arrangement apparently does not lead to aluminum nitride formation on thermolysis since neither the TGA of the starting material, compound IX, nor its pyrolysis residue gave AlN on heating up to 1000°C as determined by the weight loss and product's appearance.

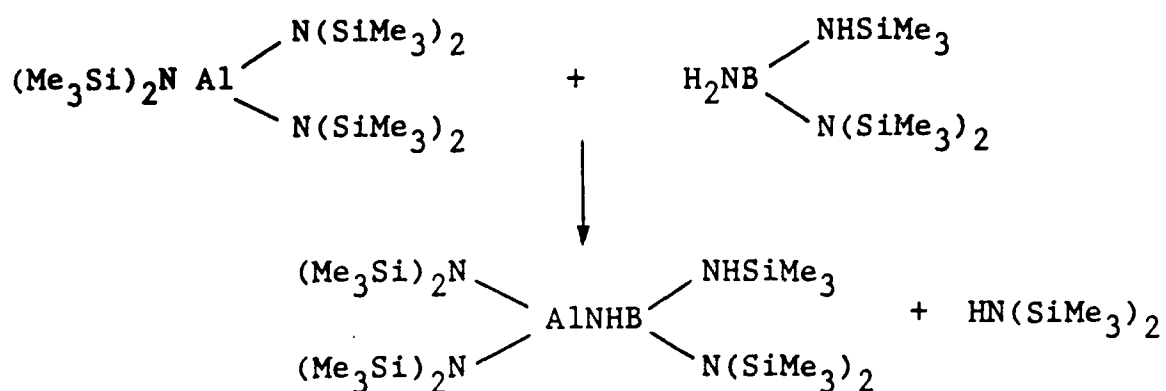
This does not mean that conducting the thermolysis in an ammonia atmosphere would not have afforded aluminum nitride. The latter environment was found to be necessary to transform boron pre-ceramic polymers to boron nitride [Ref 2, 4].

As discussed earlier in this section a part of the effort was directed at the synthesis of AlN.BN precursor compositions. One of the approaches involved the interaction of bis(trimethylsilyl)aminodichloroaluminum triethylamine complex with aminobis(trimethylsilyl)aminotrimethylsilylaminoborane. It was visualized that this reaction would lead to triethylamine hydrochloride elimination and establishment of an Al-N-B linkage, i.e.:



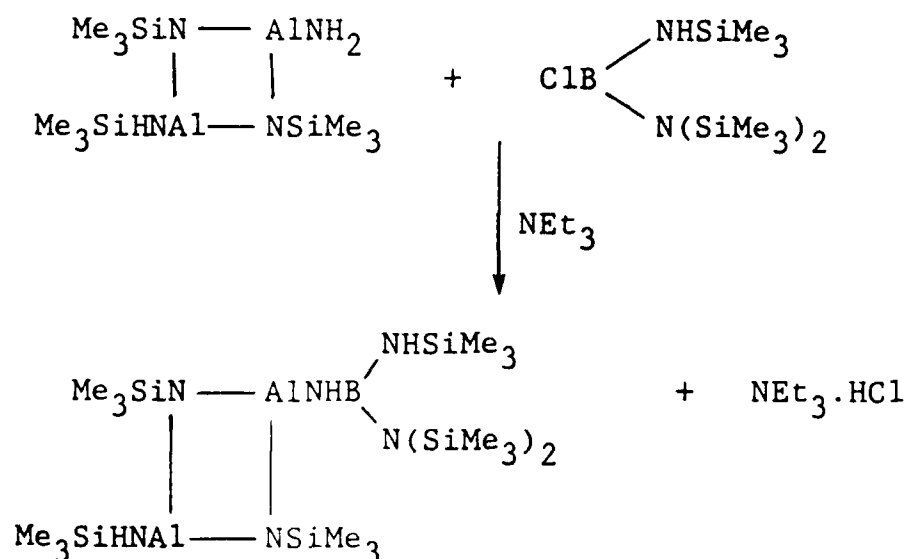
The desired reaction did not occur; no triethylamine hydrochloride was formed. However, a reaction did take place inasmuch as a by-product $(\text{Me}_3\text{Si})_2\text{NB}(\text{NHSiMe}_3)_2$ was found in a 50% yield; and the aluminum-containing portion of the product mix was insoluble in pentane. Unfortunately, attempts at purification were unsuccessful.

Inasmuch as tris[bis(trimethylsilyl)amino]aluminum undergoes readily stepwise aminolysis, discussed in the earlier portions of this report, it was considered feasible that a similar replacement might occur with aminobis(trimethylsilyl)aminotrimethylsilylaminoborane, i.e.:



No reaction was observed at 100°C. Higher temperatures or longer reaction periods might lead to the desired product.

Having been unsuccessful in a linkage establishment via a reaction of aluminumdichloride with an aminoboron compound the next avenue utilized the reaction of an aminoaluminum with a boronchloride. The visualized process is depicted below:

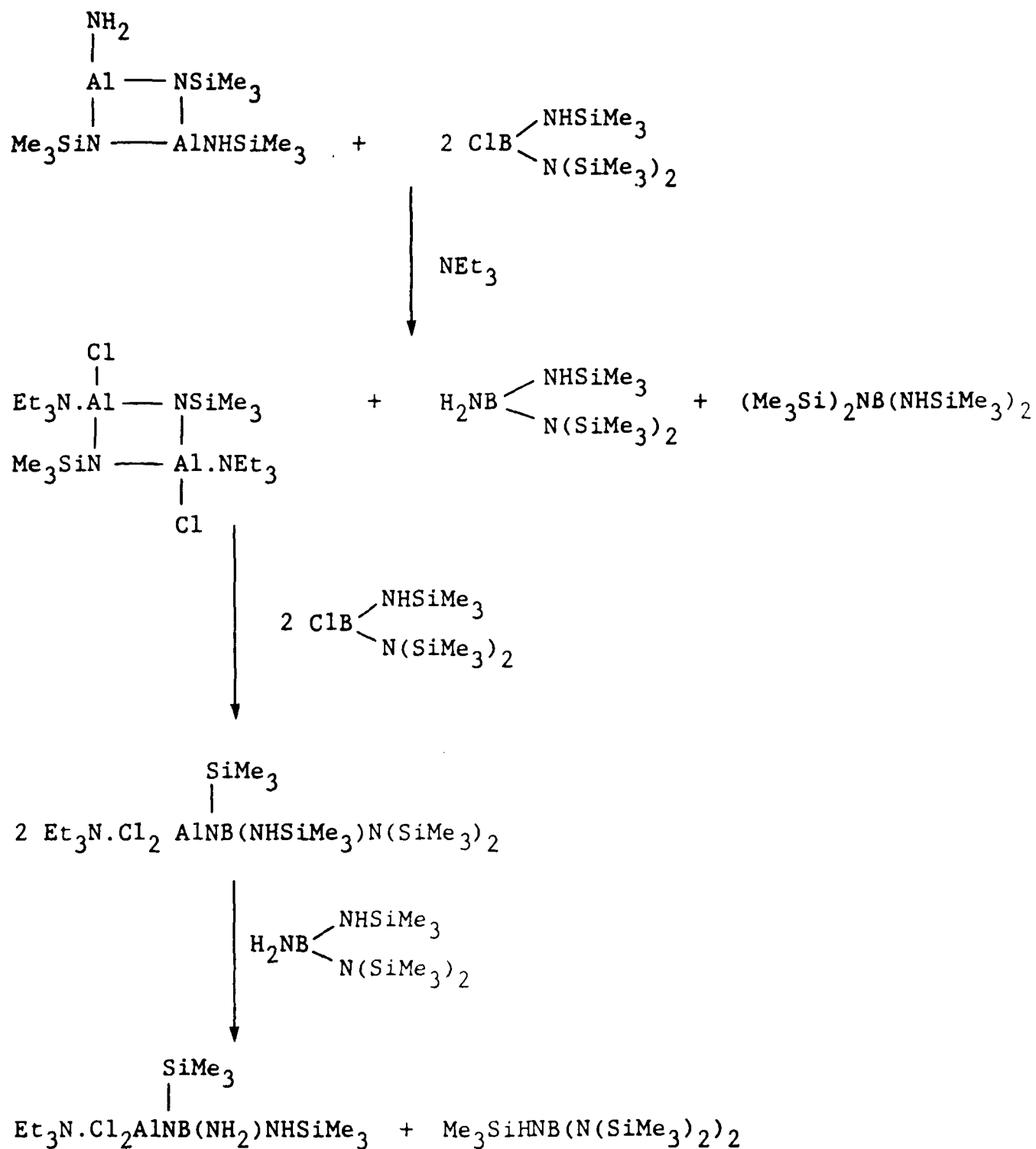


No triethylamine hydrochloride was obtained. In the 1:1 mole ratio reaction all the bis(trimethylsilyl)aminotrimethylsilyl-aminochloroborane was consumed; and bis(trimethylsilyl)aminobis-

(trimethylsilylamino)borane was produced. The product was a crystalline solid. From the elemental analysis and material balance data the structure $\text{Et}_3\text{N} \cdot \text{Cl}_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$ was derived. The infrared spectrum given in Figure 9 supports fully this arrangement i.e. the presence of triethylamine is indicated by the band at 3055 cm^{-1} (?), the NH by the band at 3420 cm^{-1} , the NHSiMe_3 arrangement by the absorptions in the $1120\text{--}1165\text{ cm}^{-1}$ region and the AlCl_2 group by the bands at 495 and 407 cm^{-1} [Ref 5]. The postulated mechanism given in Scheme 2 is based partially on the by-products found in the reaction mixture and confirms the validity of the proposed structure. There is no evidence at which stage the triethylamine complex is formed. It is also unknown whether the ring opening or exchange of the amino groups for chlorine groups occurs first. Unexpectedly, this material under TGA conditions gave $\text{AlN} \cdot \text{BN}$ as determined by the weight loss.

As noted the product was in a form of triethylamine complex. To avoid the complex formation the reaction was performed in the absence of triethylamine. From the bis(trimethylsilyl)aminotrimethylsilylaminochloroborane recovered the reaction does not proceed as readily as in the presence of triethylamine, furthermore the product formed must be of a different nature since a subsequent treatment with triethylamine failed to give the adduct. Employing bis(trimethylsilyl)aminodichloroborane instead of the monochloro-compound both in the presence and absence of triethylamine did not result in an easy to isolate product. Further studies are in progress.

SCHEME 4



4. EXPERIMENTAL DETAILS AND PROCEDURES

All solvents used were reagent grade and were dried and distilled prior to use. All the operations were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B), under nitrogen by-pass, or in vacuo. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means.

Infrared spectra were recorded either neat (on liquids) or as double mulls (Kel-F oil No. 10 and Nujol) using a Perkin-Elmer Corporation infrared spectrophotometer Model 1330. The mass spectrometric analyses were obtained employing a DuPont 21-491B double focusing mass spectrometer attached to a Varian Aerograph Model 2700 gas chromatograph (GC), equipped with a flame ionization detector, and a DuPont 21-094 data acquisition and processing system. Most of the mass spectra were obtained by direct insertion probe with rigid exclusion of air and moisture during loading. Gas chromatography was performed employing a 10' x 1/8" stainless steel column packed with 4% OV-101 on 80/100 mesh Chromosorb G using a programming rate of 8°C/min from 50-300°C. All thermal analyses were carried out on a DuPont 990 system with 951 TGA and DSC modules. The TGA determinations were conducted at 10°C/min from room temperature to 1000°C. Vapor pressure depression molecular weights were determined using the apparatus depicted in Figure 3, in conjunction with a cathetometer.

Elemental analyses were conducted by subjecting the sample to acid hydrolysis. Chloride and boron analyses were performed by titration; hydrolyzable nitrogen (NH_2 , NSiMe_3) was determined as ammonia by ion chromatography. Under these conditions nitrogen in e.g. triethylamine would not be detected.

Pyrolysis of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2$; isomer mp 219-221°C

A sample of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2$ (442.2 mg, 0.608 mmol) was heated in a sealed evacuated ampoule at 183°C for 15.5 hr. Opening to a vacuum system gave hexamethyldisilazane (150 mg, 0.929 mmol, 76.5% for a loss of one hexamethyldisilazane per aluminum) as the room temperature condensable volatile; the involatile product was a viscous fluid.

Pyrolysis of $[(\text{Me}_3\text{Si})_2\text{NAlNH}]_4$

A sample of $[(\text{Me}_3\text{Si})_2\text{NAlNH}]_4$ (260.9 mg, 0.322 mmol) was heated in an evacuated, sealed ampoule at 240-285°C for 17 hr, this was followed by a gradual temperature increase from 280-980°C over 4 hr and a 1 hr residence at 980°C. A black residue (132.9 mg, 50.9%) was collected; Calcd. for AlN : 20.23%; TGA of $[(\text{Me}_3\text{Si})_2\text{NAlNH}]_4$, residue 53.75%.

Treatment of tris[bis(trimethylsilyl)]aluminum with 2 moles of ammonia

In an inert atmosphere enclosure tris[bis(trimethylsilyl)]aluminum (9.73g, 19.15 mmol) was dissolved in hexane

(76.77g). Subsequently, the solution was degassed and it was then treated in vacuo at room temperature with ammonia (660 mg, 38.52 mmol). The reaction mixture was left stirring in an ammonia atmosphere for ~ 16 hr. The unreacted ammonia (0.93 mmol) was distilled at -78°C ; the solvent and the liberated hexamethyldisilazane (81.16 g) were removed at room temperature. The hexamethyldisilazane amounted to 4.39 g (27.27 mmol). The involatile solid (5.94 g) was boiled with hexane (40 ml); 3.60 g of the product failed to dissolve. Crystallization from benzene gave a solid (3.31 g, 85.5%) mp 197°C (dec), TGA weight loss 75.9%, IR, Figure 4. Anal. Calcd for $\text{C}_6\text{H}_{19}\text{N}_2\text{AlSi}_2$: N, 13.84%; MW, 202.38. Found: N, 14.5%; MW, 1150.

Pyrolysis of $[(\text{Me}_3\text{Si})_2\text{NAlNH}]_x$ (Product from reaction of $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$ with 2 NH_3)

A sample of $[(\text{Me}_3\text{Si})_2\text{NAlNH}]_x$ (760.7 mg, 3.76 mmol) was heated in a sealed, evacuated ampoule at 194°C for 20 hr. Opening to the vacuum system gave hexamethyldisilazane (554.5 mg, 3.44 mmol, 91.4% yield) corresponding to 72.9% weight loss. The residue, when subjected to TGA, exhibited 20.0% weight loss; a white hard residue was afforded. The total weight loss (pyrolysis plus TGA) 78.3%; Calcd for AlN : 79.8%.

Interaction of $(\text{Me}_3\text{Si})_2\text{NAlCl}_2\cdot\text{NEt}_3$ with aminobis(trimethylsilyl)aminotrimethylsilylaminoborane

In an inert atmosphere enclosure $(\text{Me}_3\text{Si})_2\text{NAlCl}_2\cdot\text{NEt}_3$

(350.5 mg, 0.975 mmol) and aminobis(trimethylsilyl)aminotrimethylsilylaminoborane (420.6 mg, 1.527 mmol) were placed in an ampoule and allowed to stir at room temperature for 72 hr. A small amount of solid was deposited; it was not triethylamine hydrochloride. The ampoule was sealed in vacuo and then was heated at 67°C for 15.5 hr. During that time a white solid admixed with a brown oil was formed. On opening to the vacuum system 0.135 mmol of a 1:1 mixture of triethylamine and hexamethyldisilazane was observed. The product was separated into a pentane soluble fraction, 400 mg, which based on GC/MS consisted of 1:1 mixture of $(\text{Me}_3\text{Si})_2\text{NB}(\text{NH}_2)\text{NHSiMe}_3$ and $(\text{Me}_3\text{Si})_2\text{NB}(\text{NHSiMe}_3)_2$. The pentane insoluble solid (60 mg) did not contain triethylamine hydrochloride; it exhibited a spectrum different from $(\text{Me}_3\text{Si})_2\text{NAlCl}_2 \cdot \text{NEt}_3$.

Interaction of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Al}$ with aminobis(trimethylsilyl)aminotrimethylsilylaminoborane

A mixture of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Al}$ (500 mg, 0.98 mmol) and $(\text{Me}_3\text{Si})_2\text{NB}(\text{NH}_2)\text{NHSiMe}_3$ (300 mg, 1.09 mmol) was heated in a nitrogen atmosphere at 100°C for 4 hr. The infrared spectrum of the product showed the presence of both starting materials; no additional bands were observed, indicating an absence of reaction.

Interaction of $(\text{Me}_3\text{Si})_2\text{NAlN}(\text{SiMe}_3)_2$ with ammonia

In an inert atmosphere enclosure into a 200 ml round bottom flask equipped with a stirring bar was introduced (10.10 g,

18.39 mmol) of $[\text{Me}_3\text{SiAlN}(\text{SiMe}_3)_2]_2$ followed by hexane (48.68 g). The apparatus was then attached to a vacuum system, cooled to -78°C and the nitrogen removed. Subsequently, the contents were warmed to 0°C and allowed to react with ammonia (0.67 g, 39.64 mmol). For the first hr the reaction was conducted at 0°C then it was allowed to warm up to room temperature for a total reaction time of 16 hr. The excess ammonia was removed in vacuo at -78°C ; the solvent was distilled at room temperature. The residue at this stage was still a liquid. It was then heated in vacuo at 85°C for 16 hr; 6.56 g of solid remained. This material was treated with Freon-113 (45 ml) in an inert atmosphere enclosure; an insoluble solid (0.87 g) remained. The filtrate on evaporation gave 5.76 g (93.5%) of the product, $\text{Me}_3\text{SiAl}(\text{NH}_2)\text{N}(\text{SiMe}_3)\text{AlNHSiMe}_3$ mp $195\text{--}218^\circ\text{C}$ (dec). Anal. Calcd. for $\text{C}_9\text{H}_{30}\text{N}_4\text{Al}_2\text{Si}_3$: N, 16.85; MW 332.59. Found: N, 16.90; MW 2300 (by vapor pressure depression), IR, Figure 6; DSC, Figure 7; weight loss, TGA 56.8%; Calcd. for AlN , 75.35%.

The analysis of the volatile condensibles collected showed the presence of ammonia (3.07 mmol, 7.7 % recovery) and hexamethyldisilazane (3.66 g, 22.73 mmol; 82.3% yield).

Pyrolysis of $\text{Me}_3\text{SiAl}(\text{NH}_2)\text{N}(\text{SiMe}_3)\text{AlNHSiMe}_3$

The above material (1.841 g, 5.54 mmol) was heated at 200°C for 24 hr; the volatiles evolved (175.1 mg, 9.5%) were composed of ammonia and hexamethyldisilazane. Heating at $278\text{--}280^\circ\text{C}$ for 21 hr gave an additional 280 mg of condensible volatiles

for a total weight loss of 24.7%. The condensible volatiles were composed of hexamethyldisilazane, 3.18 mmol, and ammonia, 0.63 mmol. Pyrolysis product weight loss, TGA 32.5%; total weight loss 51.7%; Calcd. for AlN 75.35%.

Interaction of $\text{Me}_3\text{SiAl}(\text{NH}_2)\text{N}(\text{SiMe}_3)\text{AlNHSiMe}_3$ with bis-(trimethylsilyl)aminotrimethylsilylaminochloroborane

a) In the presence of triethylamine. A mixture of $\text{Me}_3\text{SiAl}(\text{NH}_2)\text{N}(\text{SiMe}_3)\text{AlNHSiMe}_3$ (2.09 g, 6.29 mmol), triethylamine (1.31 g, 12.94 mmol), and $(\text{Me}_3\text{Si})_2\text{NBClNHSiMe}_3$ (7.33 g, 24.87 mmol) was heated in an evacuated, sealed ampoule at 63-67°C for 24 hr. During that period deposition of a solid was observed. Subsequently the ampoule was opened to the vacuum system; 1.081 g of volatiles were obtained. These consisted of triethylamine (4.51 mmol), trimethylchlorosilane (2.52 mmol), and hexamethyldisilazane (2.17 mmol). The residue was treated with pentane, in an inert atmosphere enclosure, yielding 3.85 g (76.4% yield) of white solid. The filtrate after removal of solvent gave a liquid (5.42 g) which consisted of $\text{HN}(\text{SiMe}_3)_2$, $(\text{Me}_3\text{Si})_2\text{NB}(\text{NH}_2)\text{NHSiMe}_3$, $(\text{Me}_3\text{Si})_2\text{NB}(\text{Cl})\text{NHSiMe}_3$ and $(\text{Me}_3\text{Si})_2\text{NB}(\text{NHSiMe}_3)_2$ in the ratio of 1:1:2.5:3.5 (these ratios are based on GC responses). Analysis of the residue Calcd. for $\text{C}_{12}\text{H}_{36}\text{N}_4\text{Cl}_2\text{BAI}$: N (NH_3), 10.47; Cl, 17.70; B, 2.74. Found: N (NH_3), 10.7; Cl, 17.8, B 2.65; IR, Figure 9. TGA 85.9% weight loss; Calcd for AlN.BN: 16.16%.

b) Neat. A mixture of $\text{Me}_3\text{SiAl}(\text{NH}_2)\text{N}(\text{SiMe}_3)\text{AlNHSiMe}_3$ (348.2 mg, 1.05 mmol) and bis(trimethylsilyl)aminotrimethyl-

silylaminochloroborane (1.28 g, 4.33 mmol) was heated in an evacuated, sealed ampoule at 56-60°C for 42 hr. No solid was deposited. GC/MS of the reaction mixture showed the presence of Me_3SiCl , $(\text{Me}_3\text{Si})_2\text{NH}$, $(\text{Me}_3\text{Si})_2\text{NB}(\text{NH}_2)\text{NHSiMe}_3$, $(\text{Me}_3\text{Si})_2\text{NBClNHSiMe}_3$ and $(\text{Me}_3\text{Si})_2\text{NB}(\text{NHSiMe}_3)_2$ in a ratio of 1:1.8:1:1.5:3.5. A portion of the reaction mixture (200 mg) was heated at 56-60°C with triethylamine (60 mg); no solid precipitate was observed.

Interaction of $\text{Me}_3\text{SiAl}(\text{NH}_2)\text{N}(\text{SiMe}_3)\text{AlNHSiMe}_3$ with bis(trimethylsilyl)aminodichloroborane

a) Neat. A mixture of $\text{Me}_3\text{SiAl}(\text{NH}_2)\text{N}(\text{SiMe}_3)\text{AlNHSiMe}_3$ (334.5 mg, 1.006 mmol) and bis(trimethylsilyl)aminodichloroborane (635.0 mg, 2.663 mmol) was heated in an inert atmosphere enclosure at 50-55°C for 24 hr. No solid formation was observed, the reaction mixture exhibited an infrared spectrum identical to that of its components.

b) In the presence of triethylamine. A mixture of $\text{Me}_3\text{SiAl}(\text{NH}_2)\text{N}(\text{SiMe}_3)\text{AlNHSiMe}_3$ (305.1 mg, 0.917 mmol), bis(trimethylsilyl)aminodichloroborane (547.8 mg, 2.263 mmol) and triethylamine (480.5 mg, 4.748 mmol) was heated in an evacuated, sealed ampoule at 59°C for 89 hr. On opening to the vacuum system condensible volatiles (460.9 mg) were collected; these consisted of triethylamine. The involatile residue consisted of a solid and a liquid portion. The liquid portion (0.41 g) was soluble in pentane; the solid was not crystalline and the attempts at purification were unsuccessful.

5. REFERENCES

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- 4) K.J.L. Paciorek, R.H. Kratzer, D.H. Harris, M.E. Smythe, and P.F. Kimble, Boron Nitride Preceramic Polymers, U.S. Patent 4,581,468, April 1986.
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TABLE 1
SUMMARY OF PREPARATIONS OF TRIS(BIS(TRIMETHYLSILYL)AMINO)ALUMINUM VIA
INTERACTION OF ALUMINUM TRICHLORIDE WITH THE LITHIUM SALT OF HEXAMETHYLDISILAZANE^a

Test No.	Reagents		(Me ₃ Si) ₂ NLi		Solvent		Addn time hr	React. Time hr	Cond. Temp °C	Yield %	Product mp °C
	g	mmol	g	mmol	type	ml					
1	1.33	9.97	5.02	30.0	B	25	0.5	23	RT	35.5 (27.4) ^c	182-202 (198.5-202)
3	1.37	10.27	5.18	30.96	B HE	25 25	0.8	26	RT	43.1 (34)	n.d. (189-194)
4	4.00	30.00	15.01	89.70	B HE	75 75	0.25	96	RT	39.0 (21)	182-205 (182-189)
5	4.00	30.00	15.01	89.70	B HE	75 75	0.25	24	90	35 ^d (22.2)	n.d. n.d.
6	25.0	187.5	94.12	562.5	B HE	200 100	0.58	15	60	25 ^d (16.7)	n.d. n.d.
7	30.5	229.0	116.2	697.7	B HE	250 150	0.33 ^e	64	RT	51.6 ^f (45.4)	n.d. n.d.
8	25.0	187.5	94.1	562.5	B HE	300 200	0.33 ^e	64	RT		

a) The general procedure was described previously. To summarize, to a solution of the lithium salt in the denoted solvent was added solid aluminum trichloride.

b) B = benzene; HE = heptane.

c) The values in parentheses correspond to the first crop obtained on crystallization.

d) First crops from Tests 5 and 6 were combined and recrystallized from Freon-113; 13.2 g, m.p. 210-211°C.

e) In these reactions, the addition of aluminum chloride was conducted outside the dry box under nitrogen by-pass with 0°C external cooling. After addition was completed, the reaction mixtures were allowed to warm up to room temperature and then were transferred to the inert atmosphere enclosure.

f) This material was recrystallized again from Freon-113 giving 74.26 g (35%), m.p. 215-217°C.

TABLE II
SUMMARY OF INTERACTIONS OF TRIS(BIS(TRIMETHYLSILYL)AMINO)ALUMINUM WITH AMMONIA^a

Test No.	Al(N(SiMe ₃) ₂) ₃		NH ₃ mmol	Solvent ^b		Reaction Conditions		HMD mmol	Product ^c		NH ₃ recov %
	g	mmol		Type	ml (g)	Period hr	Temp °C		Yield %	mp °C	
1	0.231	0.455	0.493	T	(1.77)	96	RT	0.495	n.d.	n.d.	
2	1.046	2.059	2.076	T	(3.57)	120	RT	1.75	33.3	n.d.	5.0
3	1.881	3.702	3.843	HE	(4.03)	72	RT	4.965	36.4	184-185	<4.6
4	3.27	6.435	7.844	HX	35	47	-78 to RT		24.4 (9.4)	(215-217)	
5	2.00	3.936	4.362	HE	25	2	0	2.83	54.5 (20.3)	n.d. n.d.	
6	2.08	4.093	4.462	HE	25	4.5 16.5	0 RT	2.61	43.6 (13.4)	n.d. n.d.	<2.6
7A	17.10	33.651	36.857	HE	(133.68)	1.25	0	n.d.	<19.2	n.d.	
7B	13.48	26.527	30.178	HE	(76.97)	16.5	RT	n.d.	30.8	n.d.	

a) Reactions 1-3 were carried out in sealed ampoules, wherein ammonia was condensed at -196°C and then the reaction was allowed to warm up to room temperature, RT. In all the other experiments, the aluminum compound was exposed in solution to the denoted quantity of ammonia for the specified period of time at the given temperature.

b) T - toluene; HE - heptane; HX - hexane.

c) The value in parentheses corresponds to the quantity of product obtained as the first crop on crystallization from hexane.

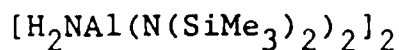
TABLE III
ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $[(\text{Me}_3\text{Si})_2\text{NAl}(\text{NHSiMe}_3)_2]_2$

m/e	%	m/e	%	m/e	%	m/e	%
73	14.0	331	14.3	445	4.9	550	<u>100.0</u>
74	5.6	332	18.5	447	3.2	551	60.9
130	13.4	333	11.5	461	8.0	552	46.7
146	54.9	334	4.6	462	6.5	553	16.1
147	13.7	346	6.0	463	3.5	554	6.1
148	3.9	347	11.6	478	3.5	565	14.3
187	4.3	348	47.3	479	18.5	566	39.5
202	10.7	349	21.2	480	7.5	567	21.8
203	6.3	350	10.0	481	3.0	568	14.1
243	3.3	362	3.3	492	14.6	569	7.4
259	25.7	373	6.8	493	17.0	570	5.4
260	11.6	374	4.4	494	12.0	640	4.1
261	5.6	388	7.5	495	10.8	641	3.6
275	30.4	389	23.0	496	4.8	711	18.3
276	10.3	390	10.6	533	8.2	712	13.9
277	6.1	391	8.1	534	10.3	713	8.7
315	3.3	404	6.5	535	8.9	714	3.8
316	8.6	405	15.4	537	3.6	726	4.1
317	3.2	406	4.6				

Peaks having intensities lower than 3% of the base peak and lower than m/e 73 are not reported.

TABLE IV

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF



m/e	%	m/e	%	m/e	%	m/e	%
73	53.4	205	3.5	332	24.7	517	4.2
74	22.3	207	3.1	333	16.0	518	5.8
75	7.1	219	3.2	334	8.2	519	3.4
77	7.7	227	3.8	335	3.2	533	10.6
86	7.1	228	3.4	346	4.4	534	12.5
100	15.0	229	3.2	347	7.7	535	8.4
101	3.8	243	9.9	348	53.3	536	8.4
102	3.4	244	10.5	349	23.5	537	4.5
113	3.9	245	9.1	350	12.7	538	3.1
114	6.6	246	4.0	351	5.1	550	100.0
115	8.1	259	60.9	362	5.8	551	68.1
116	7.9	260	38.1	372	3.3	552	44.0
130	44.4	261	20.7	373	5.4	553	19.2
131	39.3	262	6.6	374	4.6	554	9.3
132	11.6	273	5.2	375	3.8	565	19.8
146	66.6	274	4.9	388	7.3	566	48.7
147	22.7	275	50.8	389	22.3	567	29.5
148	11.6	276	24.6	390	9.3	568	19.4
150	4.5	277	16.6	391	7.7	569	7.3
161	7.5	278	4.0	404	3.1	570	4.4
171	5.5	291	7.6	405	15.1	711	28.0
172	3.9	292	4.1	406	7.5	712	22.0
173	3.8	300	6.7	407	4.1	713	17.8
186	6.5	301	5.5	445	5.2	714	8.9
187	21.4	302	4.6	446	3.6	715	4.7
188	9.0	315	3.9	461	6.0	726	9.0
189	6.3	316	15.2	462	7.2	727	6.3
202	5.9	317	9.4	463	3.8	728	4.7
203	30.4	318	6.4	493	9.0		
204	8.9	331	7.9	494	4.7		

Peaks having intensities lower than 3% of the base peak and lower than m/e 73 are not reported.

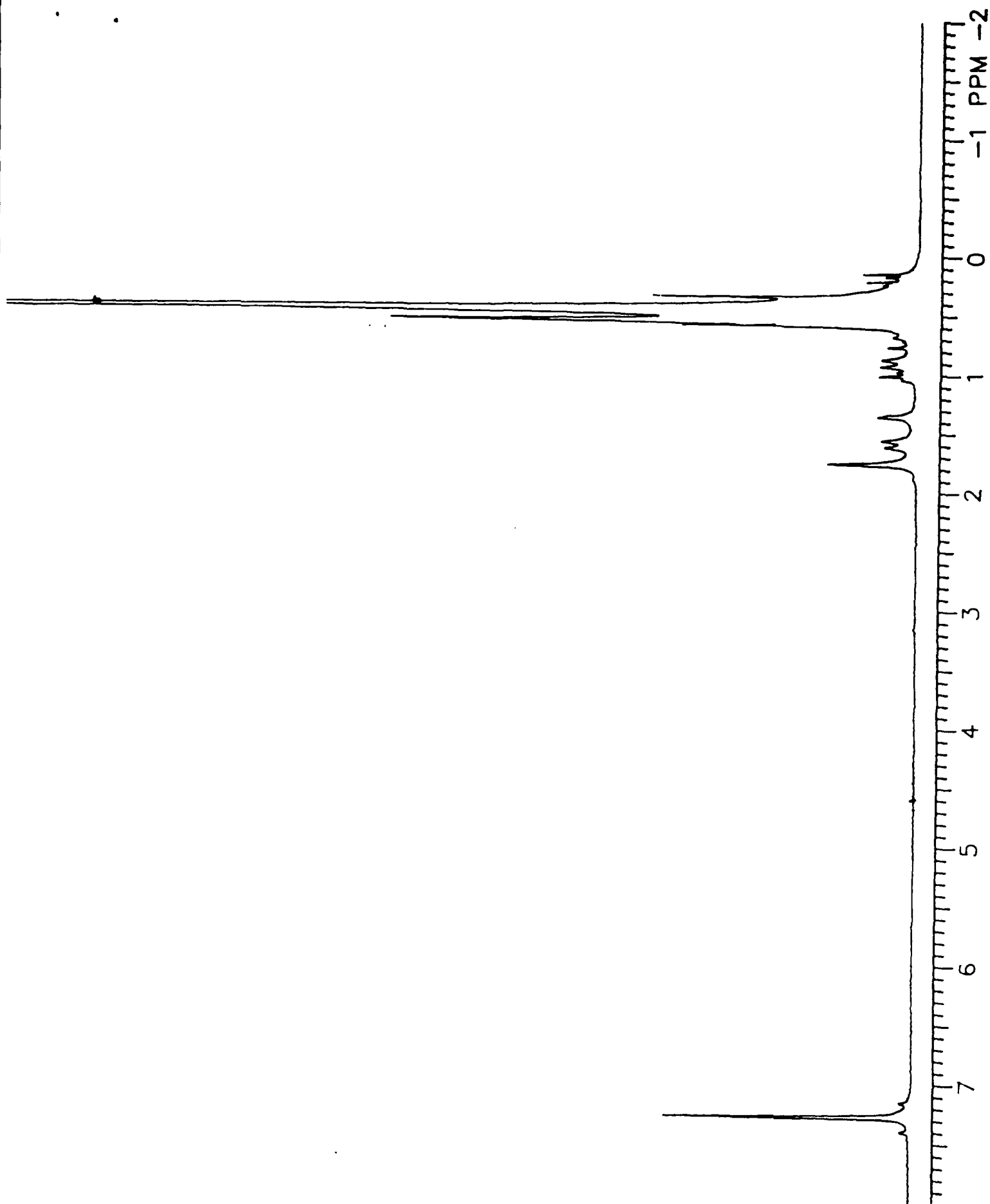


Fig. 1 NMR Spectrum of $[(\text{Me}_3\text{Si})_3\text{N}]_3\text{Al}(\text{NHSiMe}_2)_3$, mp 184 - 185°C

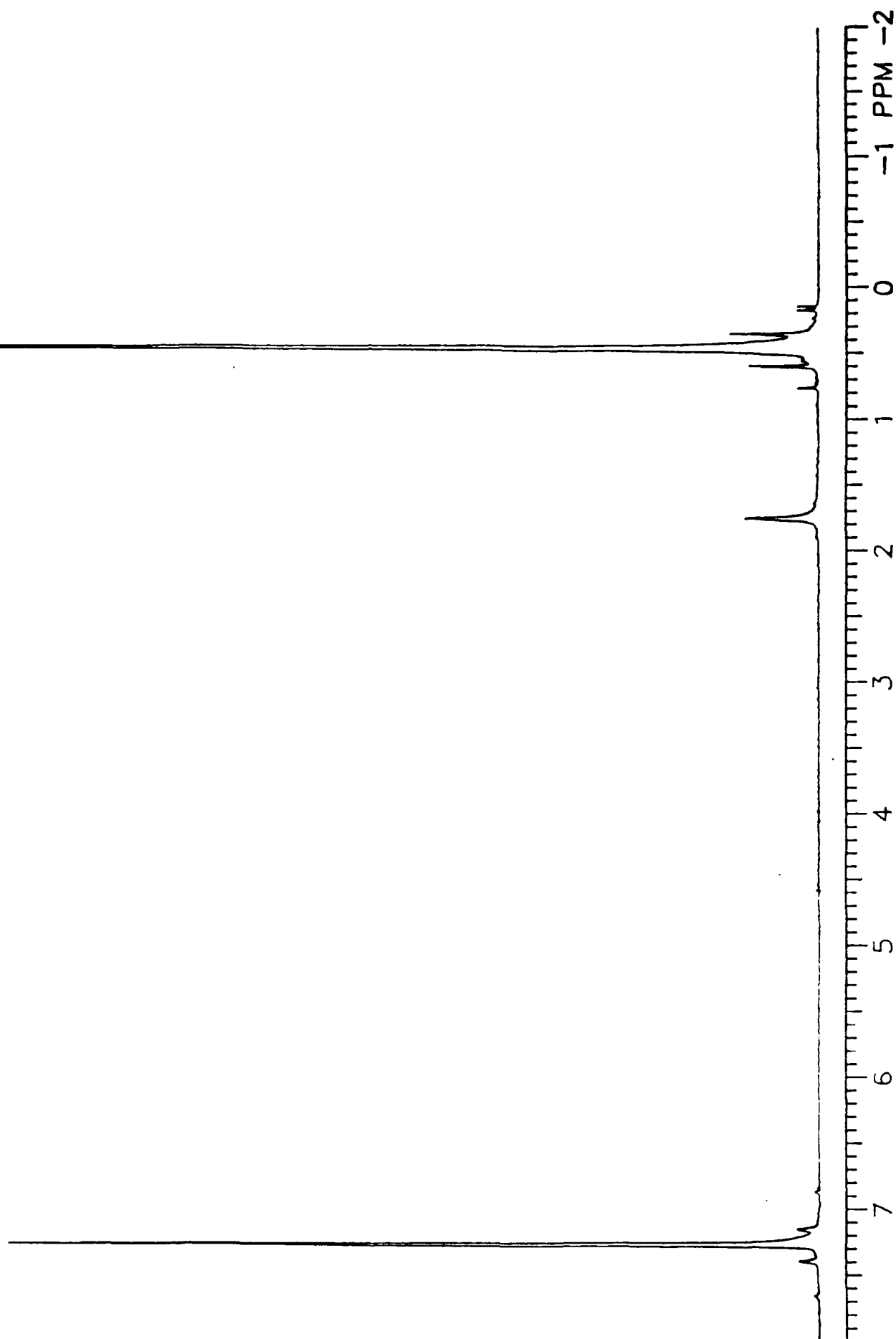


Fig. 2 NMR Spectrum of $[(\text{Me}_2\text{Si})_2\text{N})_2\text{AlNH}_2]_2$, mp 219 - 221°C.

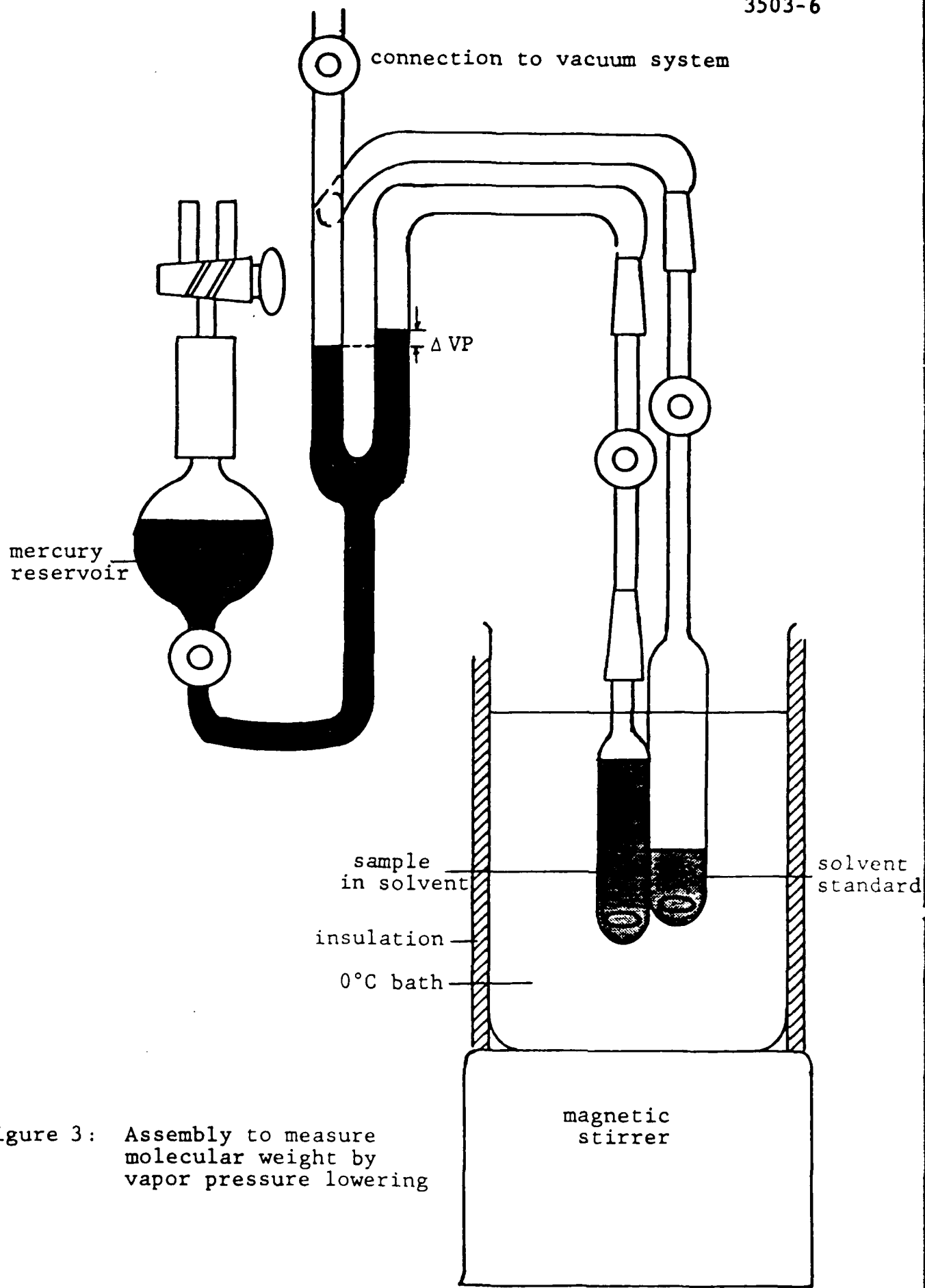


Figure 3: Assembly to measure molecular weight by vapor pressure lowering

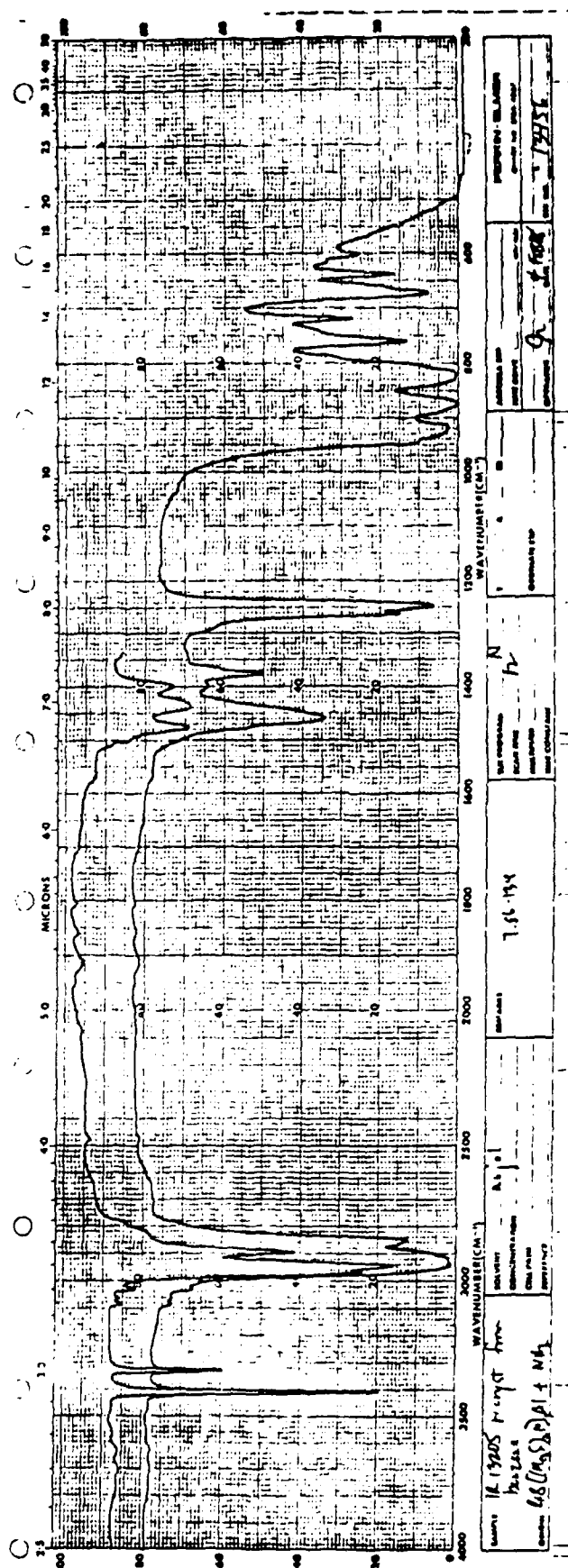
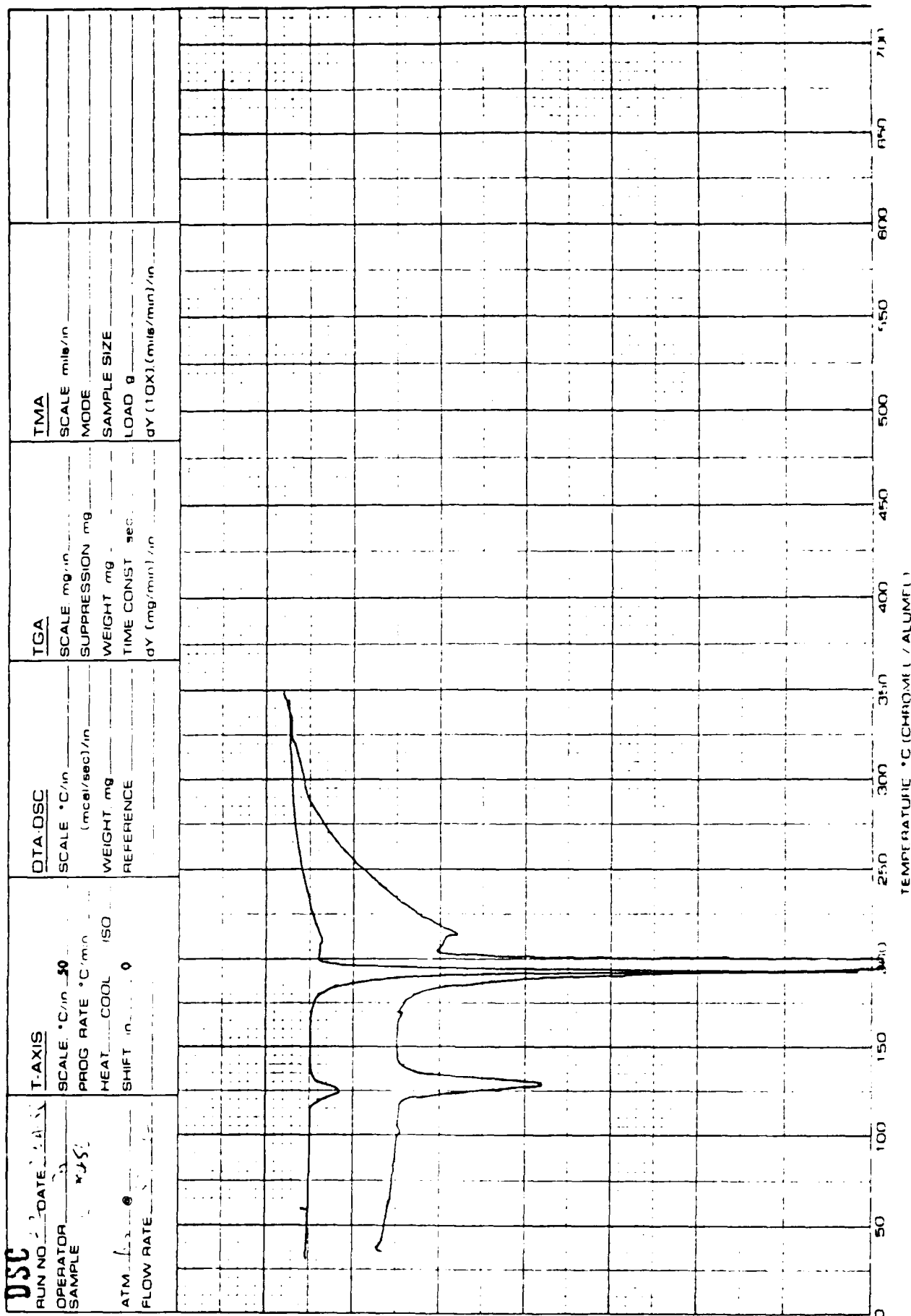


Figure 4: Infrared Spectrum of $[(\text{Me}_3\text{Si})_2\text{NAlNH}]_x$ (Kel-F/Nujol mull)

PART NO. 990088

Figure 5: DSC Scan of $[(\text{Me}_3\text{Si})_2\text{NALNH}]_x$

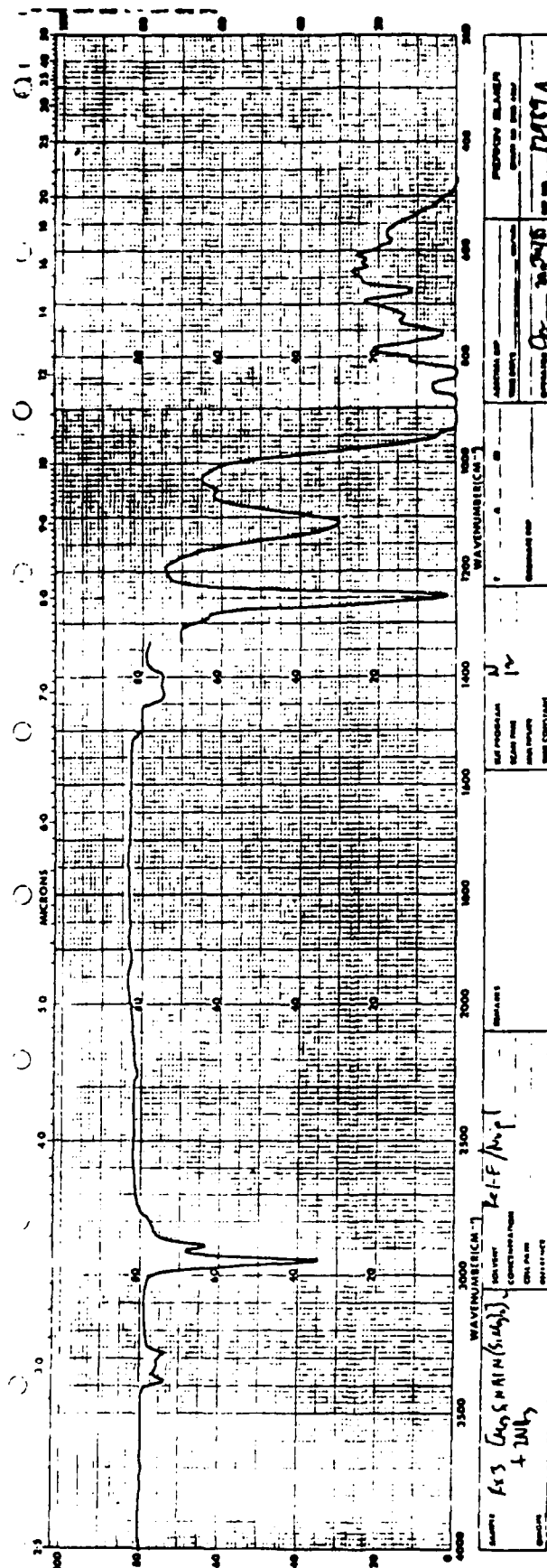
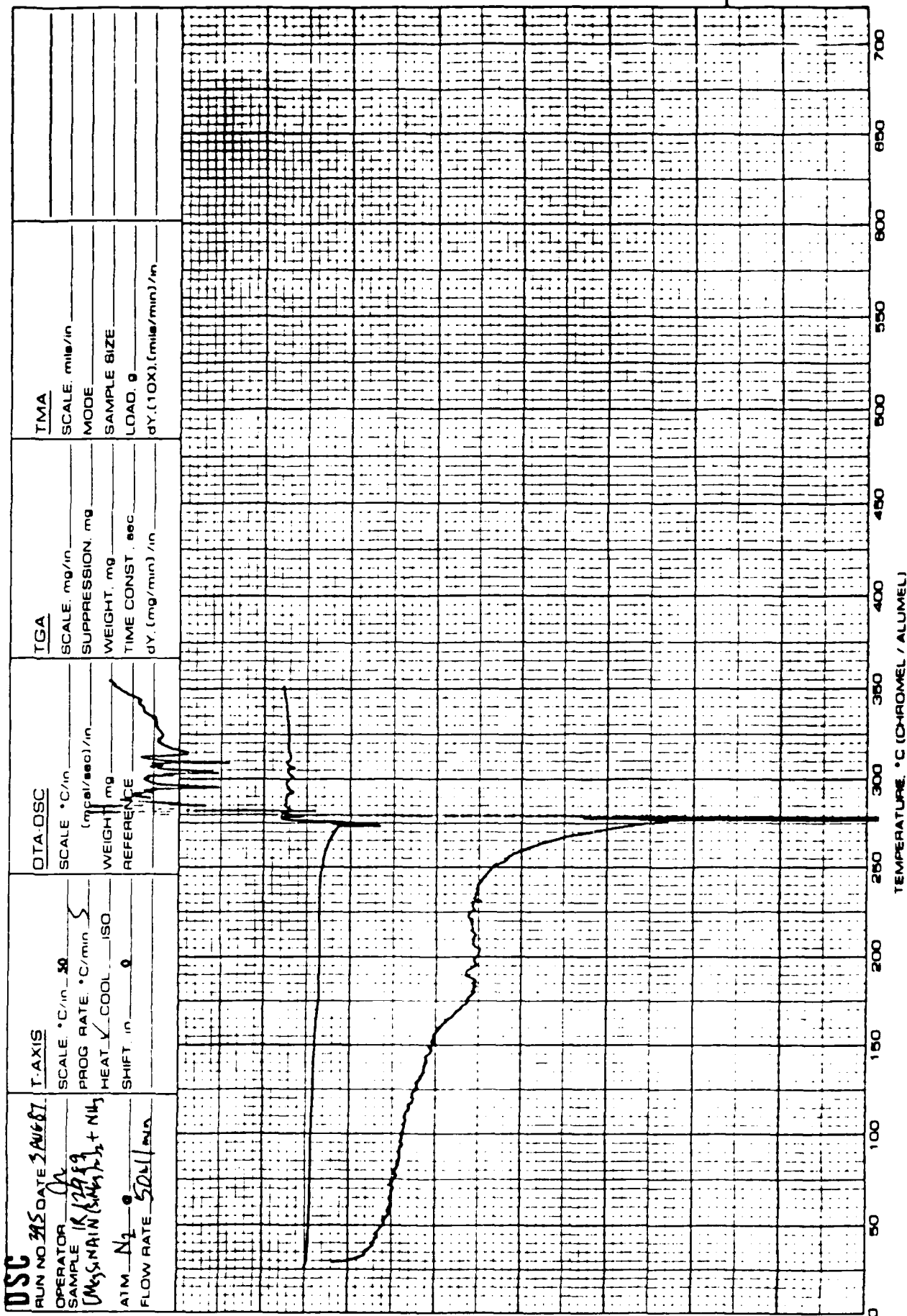


Figure 6: Infrared Spectrum of $\text{Me}_3\text{SiAl}(\text{NH}_2)\text{N}(\text{SiMe}_3)\text{AlNH}_2\text{SiMe}_3$ (Kel-F/Nujol mull)

PART NO. 990088

Figure 7: DSC Scan of Me₃SiAl(NH₂)N(SiMe₃)AlNH₂SiMe₃

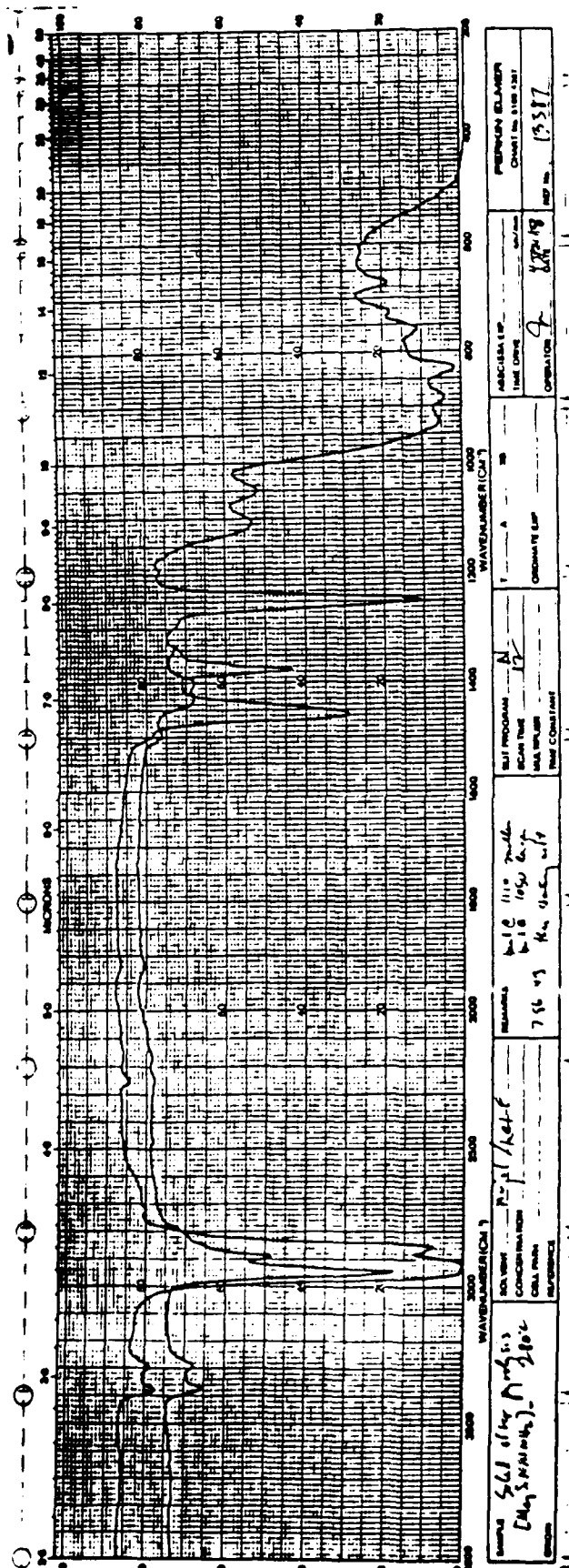


Figure 8: Infrared Spectrum of the pyrolysis product of $\text{Me}_3\text{SiAl}(\text{NH}_2)\text{NSiMe}_3\text{AlNH}_2\text{SiMe}_3$
 (Kel-F/Nujol mull)

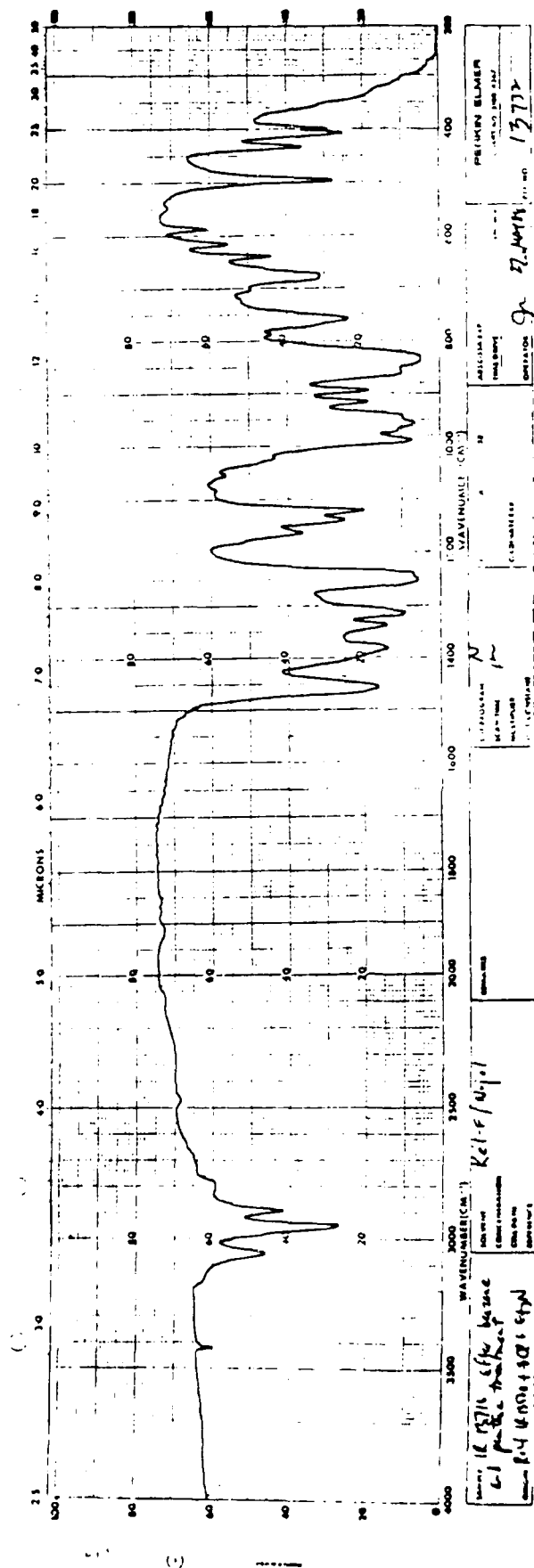
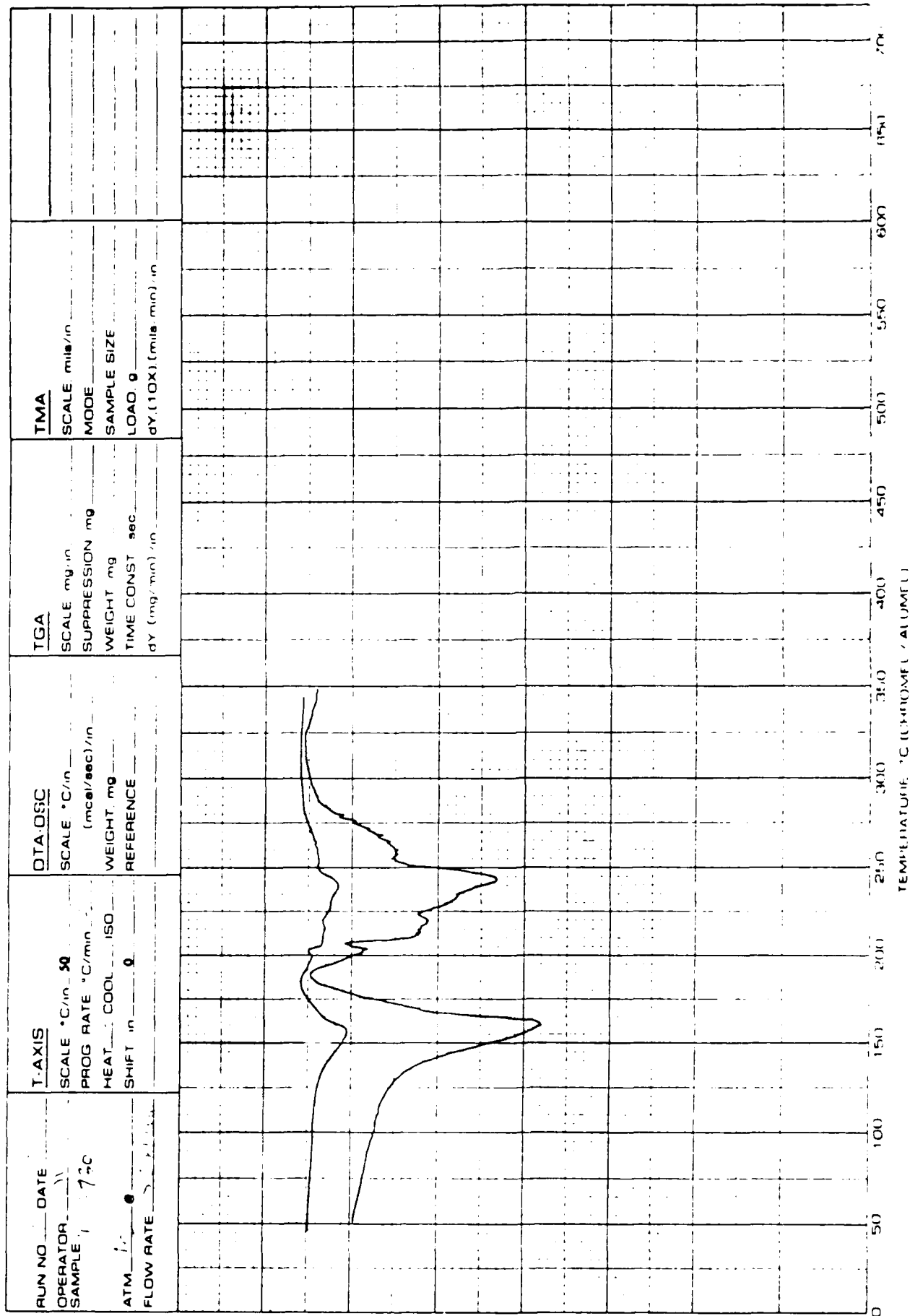


Figure 9: Infrared Spectrum of $\text{Et}_3\text{N} \cdot \text{Cl}_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$ (Kel-F/Nujol mull)

Figure 10: DSC Scan of $\text{Et}_3\text{N} \cdot \text{Cl}_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$