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Quarterly Progress Report

# Molecular Catalytic Coal Liquid Conversion

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# Abstract

In this Quarter, the great bulk of our efforts were expended on investigating the organic base-activated reactions of dihydrogen. We have proven that the reagents can effect the hydrogenation of two ring and other polycondensed aromatic hydrocarbons(Task2). Various strong organic bases were employed as the catalysts for hydrogenation of naphthalene. Several effective catalyst systems have been found for this purpose. The dependence of the reaction rates on the various factors such as temperature, hydrogen pressure, reaction time, solvents etc. were thoroughly investigated. The substitution of dideuterium gas for dihydrogen gas in the catalytic reduction of naphthalene and anthracene has been found to provide important information concerning the simultaneous D-H exchange reactions that occur during the course of the reduction reactions. In addition, work on the development of molecular organometallic homogeneous catalysts (Task 1) was also done. We have prepared two organometallic compounds: naphthalenemolybdenum tricarbonyl and 1-methylnaphthalenemolebdenum tricarbonyl to extend the work that was begun on organometallic compounds in the last Quarter.

Our work is proceeding on schedule.

## Introduction

Research work has concentrated on the two general tasks that were described in the original proposal. The first task concerns the development of molecular organometallic homogeneous catalysts that can be used in the hydrogenation of coal liquids. The second task concerns non-metallic organic bases which can activate dihydrogen for arene hydrogenation, and that can be used in the conversion of coal liquids.

## Results and Discussion

### Task 1 Molecular Organometallic Catalytic Reactions

In the last Quarter's report (June 30, 1994), we described the synthesis of several organometallic compounds which were reported to exhibit good catalytic activities for the homogeneous hydrogenation of aromatic hydrocarbons. Another two organometallic compounds: naphthalenemolybdenum tricarbonyl ($C_{10}H_8Mo(CO)_3$) and 1-methylnaphthalenemolebdenum tricarbonyl($1\text{-}CH_3\text{-}C_{10}H_7Mo(CO)_3$) were synthesyzed in this Quarter. Their characterization is now underway. The catalytic properties of these organometallic compounds will be tested when the autoclave is available in the next quarter. We also have selected several other organometallic catalytic system for investigation.

## Task 2 Organic Base-catalyzed Arene Hydrogenation

This work is based on the concept that dihydrogen can be activated by molecular basic reagents. This elementary concept finds clear precedent in previous experimental work and in theoretical analyses of the chemistry. In essence, it has been postulated that the hydroxide ion, $OH^-$, converts dihydrogen, $H_2$, to a hydride-equivalent reagent, $[OH \cdot H_2]^-$, that is capable of transferring hydrogen to organic molecules under relatively mild conditions and in the absence of transition metal catalysts. Our current research was designed to investigate whether such basic reagents ranging from hydroxide to hydrosulfide ions and amide ions can accomplish the addition of dihydrogen to pure compounds and coal liquids and to simultaneously remove heteroatoms from them.

More specifically, after the discovery of the catalyst 1 in May which was described in last quarter's report, we have systematically studied other strong organic bases as the catalysts for the hydrogenation of naphthalene to tetralin (Table 1). Several excellent catalyst systems have been discovered. Lithium derivatives such as Catalyst 2 and Catalyst 3 are active. They easily hydrogenate naphthalene to tetralin in more than 95 % yield using hexane as solvent under relatively mild conditions(200 °C, 1000 psi of initial hydrogen pressure, 5 hrs). In contrast, the alkaline metal butoxides can not activate dihydrogen to reduce naphthalene under these conditions. Catalyst 4, the simplest substance in the series, can catalyze this reaction but only at relatively high temperature(>300°C). More work needs to be done on this relatively inexpensive reagent.

Table 2 shows the effect of the ligand on the catalytic activity of several catalysts for the hydrogenation of naphthalene to tetralin. It can be seen that the catalytic activity of the derivatives of Catalyst 4 are sensitive to the ligands in these molecules. It seems that the derivatives of Catalyst 4 with long aliphatic substituents such as diisopropyl and dicyclohexyl derivatives exhibit higher activities than the molecule with smaller substituents such as ethyl, methyl trimethylsilyl compounds. In addition, the complex of Catalyst 2 with THF exhibits only half the activity of Catalyst 2 itself.

Table 3 shows that effect of the cations of the catalysts on their catalytic activity. The catalytic activity of the trimethylsilyl derivatives is decreased in the order K+ > Na+ >Li+ in toluene solution. The potassium derivatives, like Catalyst 2 and Catalyst 3, is a very active catalyst which can catalyze the hydrogenation of naphthalene to tetralin in 100% of conversion without any byproduct detected using toluene as solvent under 1000 psi of hydrogen pressure at 200 °C, however the coversions of this reaction is 51.2 and 2.9% if the sodium and lithium derivatives were used as the catalysts, respectively, under the same conditions.

The influence of the molar ratio of substrate to catalyst on the conversion of naphthalene to tetralin is shown in Table 4. The yield of tetralin reached 93.4% and 58.0% when the catalyst concentrations are 12.5 mole% and 6.25 mol%, respectively.

Table 5 shows the dependence of the naphthalene conversion on the initial hydrogen pressure. The results indicate that the reaction proceeds very well even if the hydrogen pressure is as low as 300 psi( 20 atms). The lower yield(12.9%) under the lowest hydrogen pressure(150 psi) may be clearly attributed to the insufficiency of dihydrogen in the reaction system.

The reaction was also influenced by the temperature(Table 6). The yield of tetralin was decreased by lowing the temperature from 100% at 200 °C to about 0.5% at 100 °C. In addition, 4-5 hours was needed for the reaction to proceed completely(Table 7).

The substituention of deuterium gas for hydrogen gas in the catalytic reduction of naphthalene has been found to provide important information about the reaction pathway. The $^1$H and $^2$H NMR spectra of tetralin obtained by the hydrogenation of naphthalene with dihydrogen or dideuterium are shown in Fig.1. The ratios of proton1:proton 2 :proton 3 from the integration both in the $^1$H NMR and $^2$H NMR spectra are 1:1:1, indicating that one ring of the naphthalene molecule was saturated by adding dideuterium under the influence of organic base catalyst. The fact that the intensity of proton 1 in $^1$H NMR is decreased and the existance of the three resonances in $^2$H NMR , i.e. aromatic deuterium is present, clearly show that D-H exchange reactions occur at positions 1 and 2 when tetralin is treated with dideuterium under the same conditions as used in the hydrogenation of naphthalene. Under these conditions about 30% of the protons in position 1 and 10-15% in position 2 (benzyl protons) were exchanged by dideuterium, thereby indicating that the D-H exchange reactions occur simultaneously during the course of the hydrogenation. These results were confirmed by mass spectrometry(Fig. 2) which revealed the extent of the exchange reaction.

Fig. 3 is the $^1$H NMR of 9,10-dihydroanthracene(a) and of the compound (b) obtained by treating anthracene with dideuterium under 1000psi of dideuterium pressure at 200 °C. It can be seen that protons in position 1 almost disappear when dideuterium gas is used instead of hydrogen gas in the hydrogenation of anthracene Therefore, we reach the same conclusion as described above, that is, D-H exchange accompanies the hydrogenation.

## Plans for Next Quarter

The work in next quarter will be continued on the chemistry of base-catalyzed hydrogenation of aromatic compounds. And the coal liquids samples will be tested under the same catalystic conditions as the polycondensed aromatic hydrocarbons that we have already investigated.

Table 1 The organic bases attempted to activate hydrogen for the reduction of naphthalene

| Organic Bases | [Substrate]/ [Base] (mole/mole) | Solvent | Temperatur ( °C) | Conversion (%) |
|---|---|---|---|---|
| NaOR' | 4:1 | Hexane | 200 | 0.0 |
| LiOR' | 4:1 | Hexane | 200 | 0.0 |
| KOR' | 1:2 | Heptane | 200 | 0.95 |
|  | 1:2 | t-BuOH | 200 | 0.0 |
| NaR" | 4:1 | Hexane | 200 | 1.0 |
| LiR"(Catalyst 4) | 4:1 | Hexane | 200 | 7.7 |
|  | 2:1 | Hexane | 300 | 44.3 |
| Catalyst 2 | 4:1 | Hexane | 200 | 100 |
| Catalyst 3 | 4:1 | Hexane | 200 | 94.5 |

Conditions:

Substrate: naphthalene
Solvent: 50 ml
Initial $H_2$ pressure : 1000 psi
Reaction time : 18 hrs

Table 2 Influence of the ligand of catalysts on their catalytic activity for the hydrogenation of naphthalene to tetralin

| $LiL_2$ | [Substrate]/ [$LiL_2$] (mole/mole) | Conversion (%) |
|---|---|---|
| Catalyst 1 | 2:1<br>4:1 | 43.0<br>50.3 |
| Catalyst 2 | 4:1 | 100 |
| Catalyst 3 | 4:1 | 94.5 |
| Catalyst 5 | 4:1 | 3.2 |
| Catalyst 6 | 2:1 | 7.2 |
| Catalyst 7 | 2:1 | 15.5 |

Conditions:

Substrate: naphthalene
Solvent: hexane(50 ml)
Temperature: 200 °C
Initial $H_2$ pressure : 1000 psi
Reaction time : 18 hrs

Table 3 Effect of the cations of amides on its catalytic activity for the hydrogenation of naphthalene to tetralin

| $LiR_2$ | [Substrate]/ [$LiR_2$] (mole/mole) | Solvent | Conversion (%) |
|---|---|---|---|
| $LiR_2$ | 4:1 | Toluene | 2.9 |
| $NaR_2$ | 4:1 | Toluene | 51.2 |
| $KR_2$ | 4:1 | Toluene | 100 |

Conditions:
Substrate: naphthalene
Temperature: 200 °C
Initial $H_2$ pressure : 1000 psi
Reaction time : 18 hrs

Table 4 Influence of the molar ratio of substrate to catalyst on the conversion of naphthalene to tetralin

| No | [Substrate]/[catalyst] (mole/mole) | Conversion (%) |
|---|---|---|
| 1 | 2 : 1 | 100 |
| 2 | 4 : 1 | 100 |
| 3 | 8 : 1 | 93.4 |
| 4 | 12 : 1 | 66.6 |
| 5 | 16 : 1 | 58.0 |

Conditions:
Substrate: naphthalene
Catalyst: Catalyst 2
Solvent: hexane(50 ml)
Initial $H_2$ pressure: 1000 psi
Temperature: 200 °C
Reaction time: 18 hrs

Table 5 Dependence of the naphthalene conversion on the initial hydrogen pressure

| No | Initial $H_2$ pressure (psi) | Conversion (%) |
|---|---|---|
| 1 | 1500 | 100 |
| 2 | 1000 | 100 |
| 3 | 500 | 100 |
| 4 | 300 | 77.6 |
| 5 | 150 | 12.9 |
| 6 | 100($N_2$) | 0.0 |

Conditions:
Substrate: naphthalene
[Substrate]/[Catalyst] = 4 : 1
Catalyst: Catalyst 2
Solvent: hexane(50 ml)
Temperature: 200 °C
Reaction time: 18 hrs

Table 6 Effect of the temperature on the conversion of naphthalene to tetralin

| No | Temperature ( °C) | Conversion (%) |
|---|---|---|
| 1 | 200 | 100 |
| 2 | 180 | 55.4 |
| 3 | 150 | 29.2 |
|  | 150 | 24.5* |
| 4 | 100 | 0.5 |

Conditions:

Substrate: naphthalene
[Substrate]/[Catalyst] = 4 : 1
* [Substrate]/[Catalyst] = 8 : 1
Catalyst: Catalyst 2
Solvent: hexane(50 ml)
Reaction time: 18 hrs

Table 7 Effect of reaction time on the conversion of naphthalene to tetralin

| No | Reaction time ( Hrs) | Conversion (%) |
|---|---|---|
| 1 | 0.5 | 34.1 |
| 2 | 2.0 | 62.5 |
| 3 | 3.0 | 62.8 |
| 4 | 4.0 | 93.5 |
| 5 | 18 | 100 |

Conditions:
Substrate: naphthalene
[Substrate]/[Catalyst] = 4 : 1
Catalyst: Catalyst 2
Solvent: hexane(50 ml)
Temperature: 200 °C

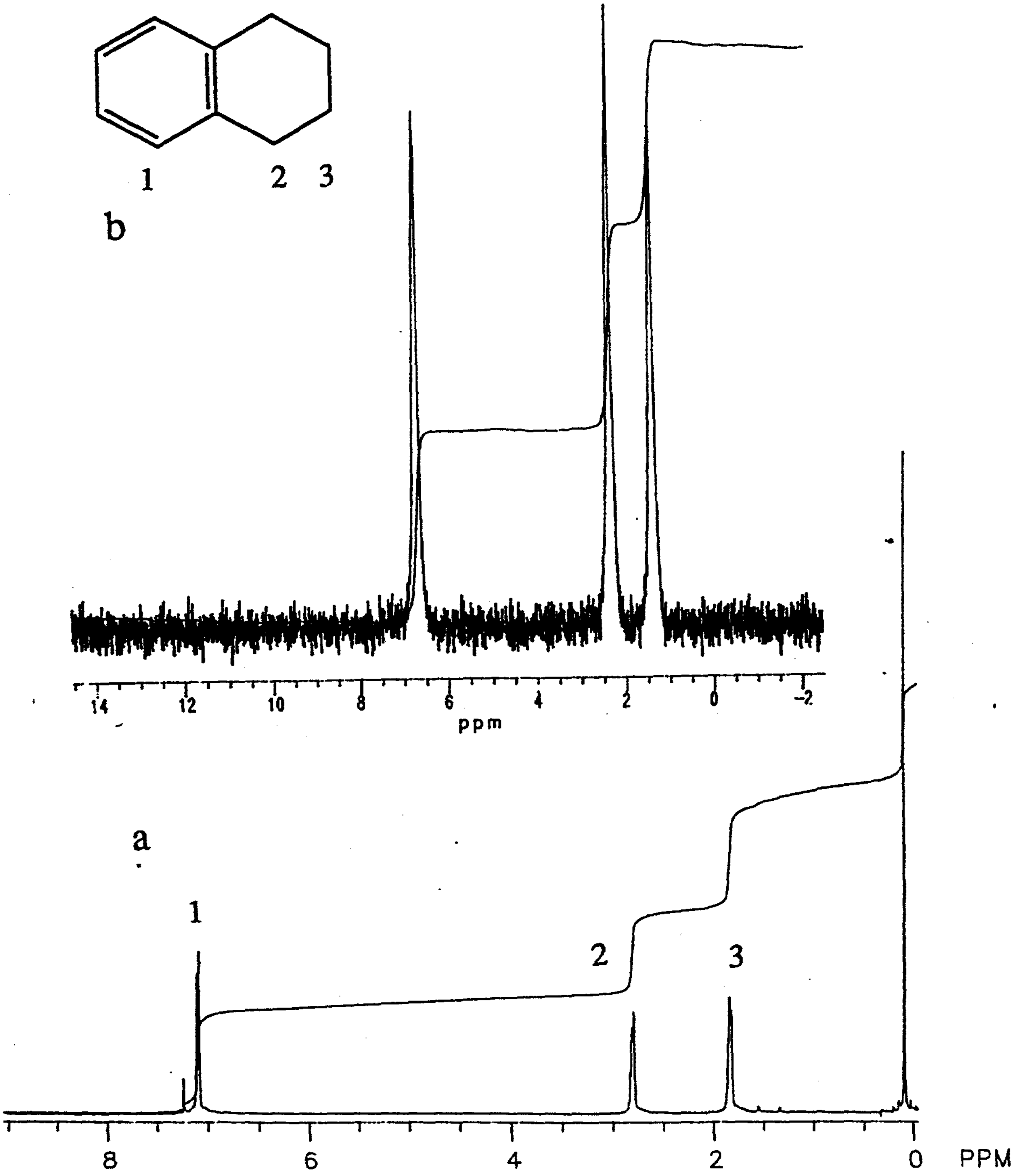

Fig. 1 $^1$H NMR(b) and $^2$H NMR(a) of Tetralin obtained by treating naphthalene with deuterium gas under 1000psi deuterium pressure at 200 °C

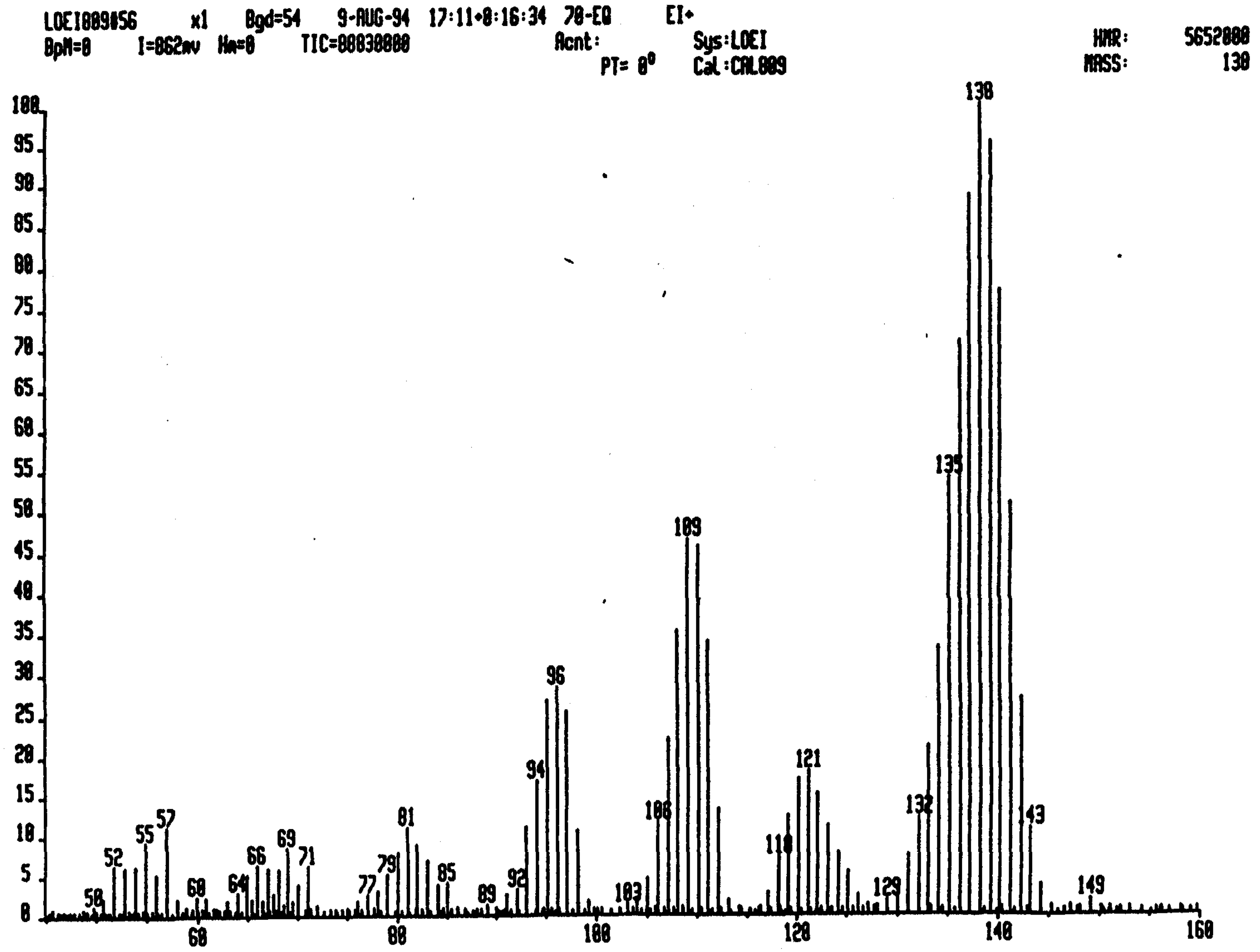

Fig. 2 Mass spectrometry of tetralin obtained by treating naphthalene with deuterium gas under 1000 psi deuterium pressure at 200 °C

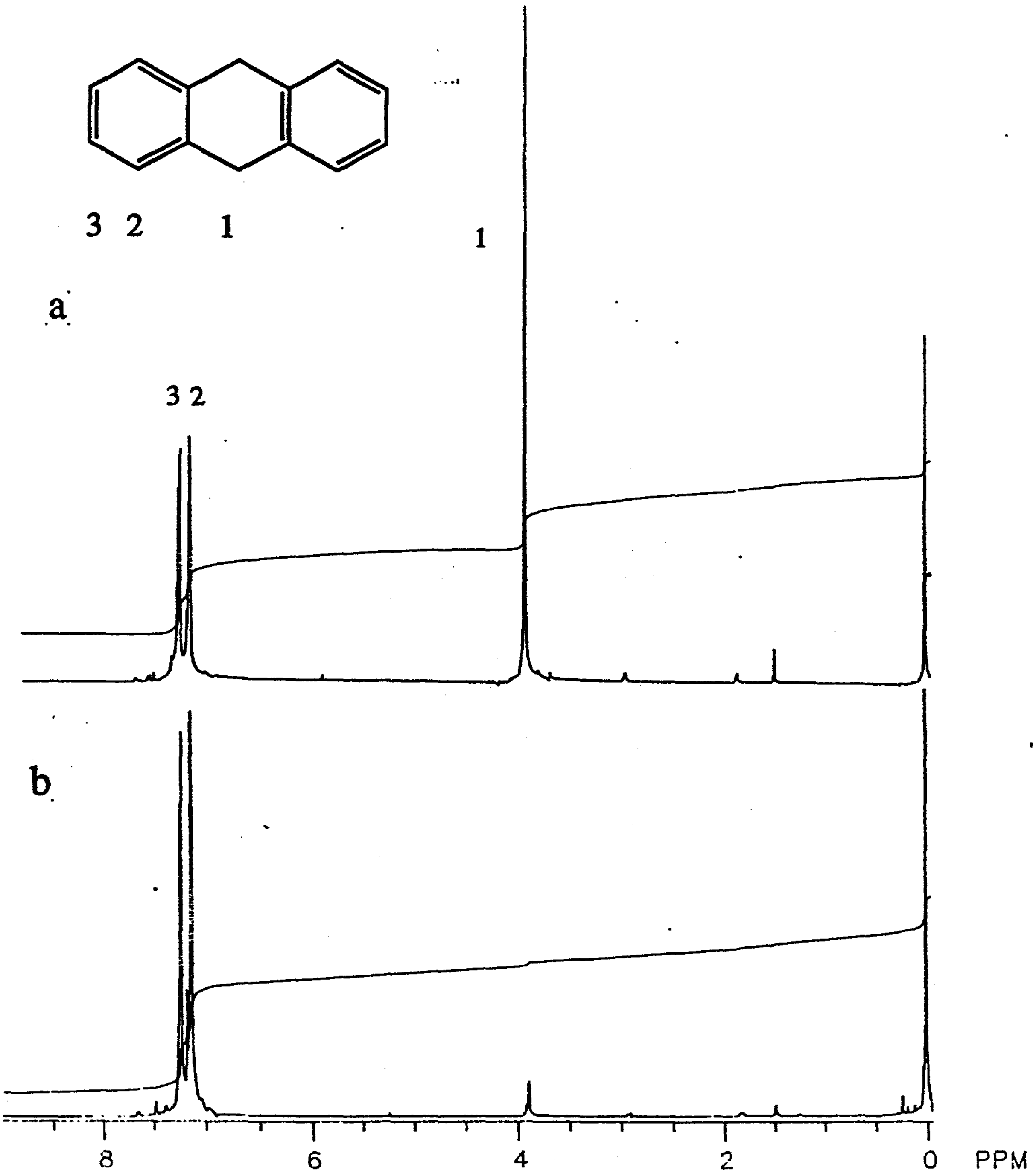

Fig. 3 $^1$H NMR of 9,10-dihydroanthracene(a) and of the compound (b) obtained by treating anthracene with deuterium under 1000 psi of deuterium pressure at 200 °C