

*Full Length Research Paper*

# Synthesis and characterization of dehydroannulene carbon allotrope apply for hydrogen fuel storage

Chaluy Souvakon<sup>1</sup>, Anusorn Vorasingha<sup>1\*</sup>, Sumrit Mopoung<sup>1</sup> and Akaraphan Vongkumhae<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Naresuan University, Maung, Phitsanulok, Thailand 65000.

<sup>2</sup>Department of Electrical and Computer Engineering, Faculty of Engineering, Naresuan University, Maung, Phitsanulok, Thailand 65000.

Accepted 18 February, 2011

Recent developments focusing on novel hydrogen storage media have helped to focus nano materials as one of the on going strategic research in science and technology. In particular, carbon nano materials and specifically dehydroannulene carbon stand to deliver unparalleled performance as the next generation of base materials for storing hydrogen. The very low boiling point of H<sub>2</sub> makes it necessary to apply temperatures of around 195 K to achieve sufficient amounts of adsorbed H<sub>2</sub>. Our experiment was carried out to study the hexa-dehydro-annulene carbon which synthesise by using a copper tube apparatus. In this research, the effects of conditions in the synthesis of hexadehydro[12]annulene were studied. The condition to give a moderate yield of di-phenyl-acetylene is discovered; Iodobenzene and Phenylacetylene were used for the concentration of starting materials. Di-metyl-formamide was used as solvent in reaction. Tri-phenyl-phosphine was used as ligand, copper (I) iodide was used as a catalyst under argon gas. This reaction was performed at 120°C for 16 h with copper tube reactor giving good yield of the coupling product. For the condition to give a moderate yield of Tri-naphthaleno-hexadehydro-annulene from 2-Iodo-3-ethynylnaphthalene; di-methyl-formamide and Tri-ethyl-amine were used as solvent, Tri-phenyl-phosphine was used as ligand and copper (I) iodide was used as the catalyst, the reaction was operated at 165 to 170°C for 24 h in a copper tube reactor. The corresponding arylated alkynes are produced in moderate yield. The hydrogen storage capacity of fishbone carbon nano fibers has been determined for several of intercalated compounds. The highest hydrogen storage capacity is 2.81% adsorption with 1.0 g of hexa- dehydro-anulene carbon.

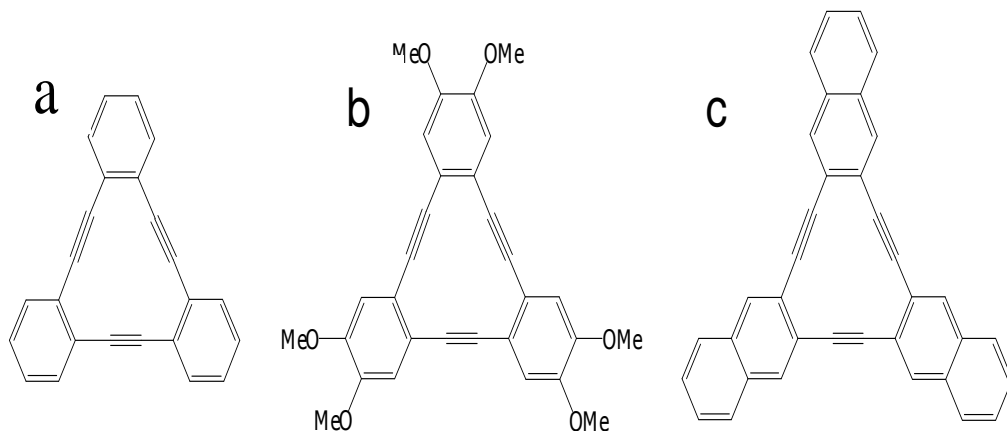
**Key words:** Triphenylphosphine, phenylacetylene, trimerization, adsorption capacities.

## INTRODUCTION

As supply of fossil fuels is limited and energy demand continues to rise, research is increasingly directed towards alternative renewable fuels. Biodiesel, as an alternative hydrogen fuel, is a promising non-toxic and clean renewable fuel comprised of hydrogen atoms of small molecules which are derived from water or hydrocarbon. Hydrogen can be made available on-board vehicles in containers of compressed or liquefied Hydrogen, in metal hydrides, or by gas-on-solid adsorption (Amankwah et al., 1989; Chambers et al., 1998). Hydrogen can also be generated on-board by

reaction or decomposition of hydrogen containing molecular species. Although each method possesses desirable characteristics, no approach satisfies all of the efficiency, size, weight, cost and safety requirements for transportation or utility use. Gas-on-solid adsorption is an inherently safe and potentially high energy density hydrogen storage method that should be more energy efficient than either chemical or metal hydrides, or compressed gas storage. Consequently, the hydrogen storage properties of high surface area "activated" carbons have been extensively studied. However, activated carbons are ineffective in hydrogen storage systems because only a small fraction of the pores in the typically wide pore-size distribution are small enough to interact strongly with gas phase hydrogen molecules (Fan et al., 1999; Hynek et al., 1997; Ahn et al., 1999).

\*Corresponding author. E-mail: [anusornv@nu.ac.th](mailto:anusornv@nu.ac.th). Tel: +66-55-963-461. Fax: +66-55-963-401.



**Figure 1.** Tribenzohexadehydro[12]annulene and its derivative applies to hydrogen storage.

Carbon nano filaments, either nano tubes or nano fibers and annulene carbon, have received increasing scientific and industrial interest during the last two decades owing to their exceptional physical and chemical properties. Small scale synthesis of dehydroannulene carbon structures are today mainly conducted through a catalytic route due to the high yield, high selectivity and low cost such as copper tube reactor. Annulene have attracted intense attention in the field of super molecular chemistry and materials science over the past decade due to their novel properties and potential applications.

In Figure 1, Tri-benzo-hexa-dehydro[12]annulene and its derivatives show structural units with isolated ethynyl free system. The annulenes can be prepared by several procedures including palladium catalyzed co-cyclization of 1,2-di-iodobenzene with acetylene gas, Stephens-Castro coupling of copper (2-iodo-phenyl) acetylide, a combination of a Wittig reaction and a bromination procedure and alkyne metathesis. Recently, the Iyoda group reported a novel synthetic procedure of Tri-benzo-hexa-dehydro[12]annulene and some derivatives employing a coupling reaction of acetylenes with iodoarenes in the presence of catalytic amounts of CuI and triphenylphosphine, together with 3 equivalents of potassium carbonate in dimethylformamide at 160°C in copper tube reactor. Despite the many considerable efforts to improve procedures, the synthesis of Tri-benzo-hexa-dehydro[12]annulene and its derivatives still remains troublesome.

Although, the Sonogashira reactions of phenylacetylene with iodobenzene produce diphenylacetylene in a quantitative yield, 9 cyclotrimerization by normal Sonogashira coupling of (2-iodophenyl)acetylene is still challenging. At present, few cyclotrimerization reactions under Sonogashira conditions are successful according to several reports. The problem is that cyclotrimerization under Sonogashira conditions affords tribenzocyclyne a very low yield due to

a preferential homocoupling between alkynes (Barton and Shepherd, 1984; Baughman et al., 1987).

The Sonogashira reaction of phenylacetylene with iodobenzene using Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and CuI in Et<sub>3</sub>N produces diphenylacetylene in a quantitative yield, cyclo-trimerization of (2-bromophenyl)acetylene under similar conditions affords Tri-benzo-hexa-dehydro[12]annulene a very low yield due to an undesired reaction of (2-bromophenyl) acetylene homocoupling. The cyclo-trimerization of (2-iodophenyl) acetylene under similar Sonogashira conditions also formed only a trace amount of Figure 1a. Thus, the homo-coupling of acetylene units takes place more easily than the normal Sonogashira coupling in the case of 2-iodophenyl acetylenes. In this research, to produce the target Tri-benzo-hexa-dehydro [12] annulene and its derivatives in Figure 1, the copper tube reactor equipment was used as shown in Figure 2 (Yamaguchi et al., 2000).

## EXPERIMENTAL

The copper catalyzed cross-coupling of phenylacetylene with iodobenzene in an aprotic solvent such as di-methyl-formamide and di-methyl-sulfoxide was reported to produce diphenylacetylene in a quantitative yield. Since this reaction proceeds smoothly to produce no homocoupling product, we tried to apply the cyclo-trimerization of (2-iodophenyl) acetylene (2a) and (2-iodoaryl) acetylene (2b) with catalytic amounts of Cu I and PPh<sub>3</sub> in the presence of K<sub>2</sub>CO<sub>3</sub> as a base in DMF on copper tube reactor as shown in Scheme 1. Although the reaction takes place at high temperatures (160 to 170°C), the desired 1a and related annulenes 1b can be prepared in moderate to good yields. Additionally, the trinaphthaleno hexadehydro [12]annulene derivative 1c can be synthesized in a short pathway.

For the construction of the Hexadehydro [12]annulene framework, the cyclotrimerization of 2a,b was first investigated under various conditions using CuI and PPh<sub>3</sub> (Scheme 2). The reaction of 2a with CuI (30 mol%) and PPh<sub>3</sub> (30 mol%) in DMF proceeded smoothly at 165 to 170°C using copper tube reactor (Figure 2) for 24 h to afford 1a in 62% yields.

The cyclotrimerization of 2a can be applied for the preparation of

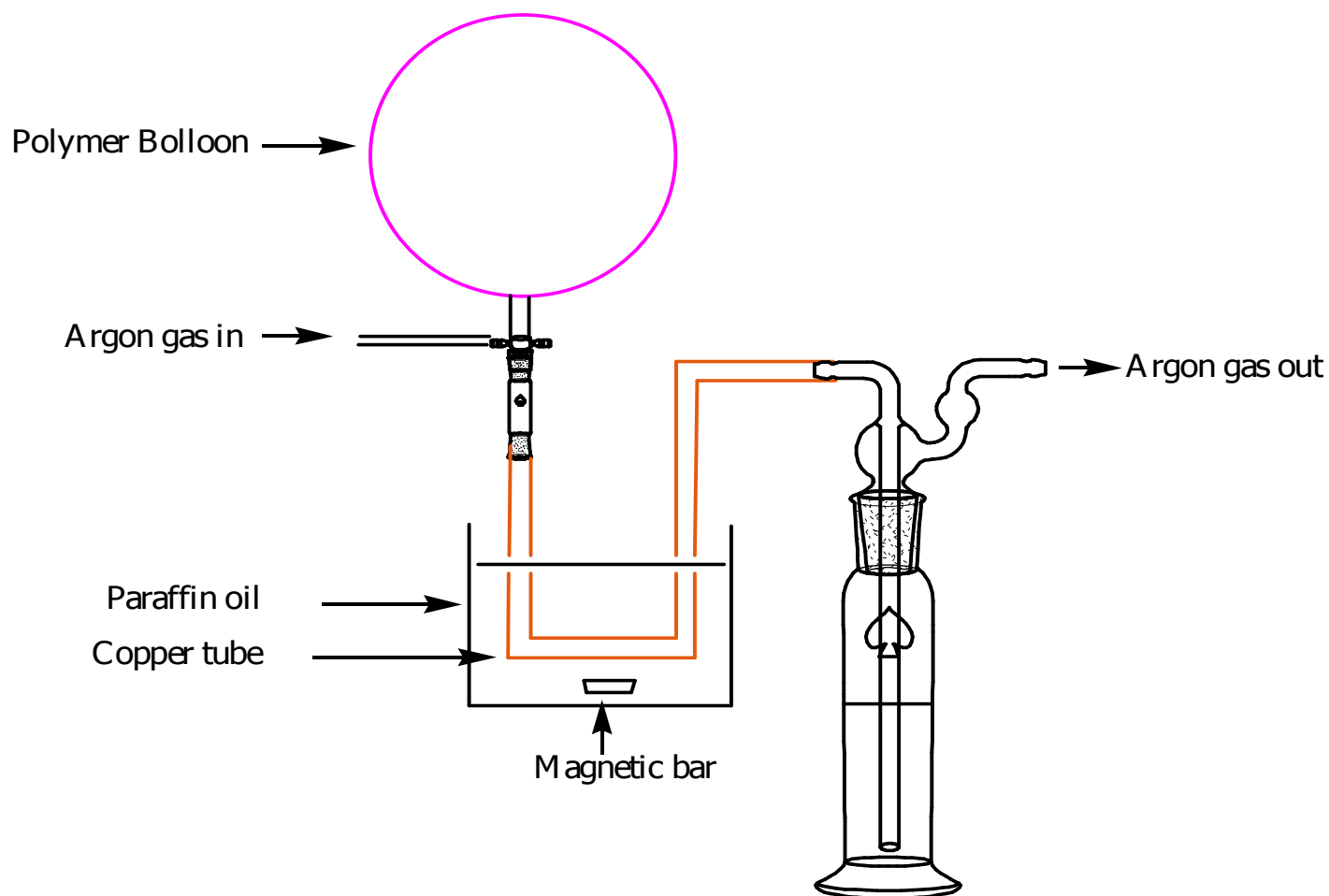
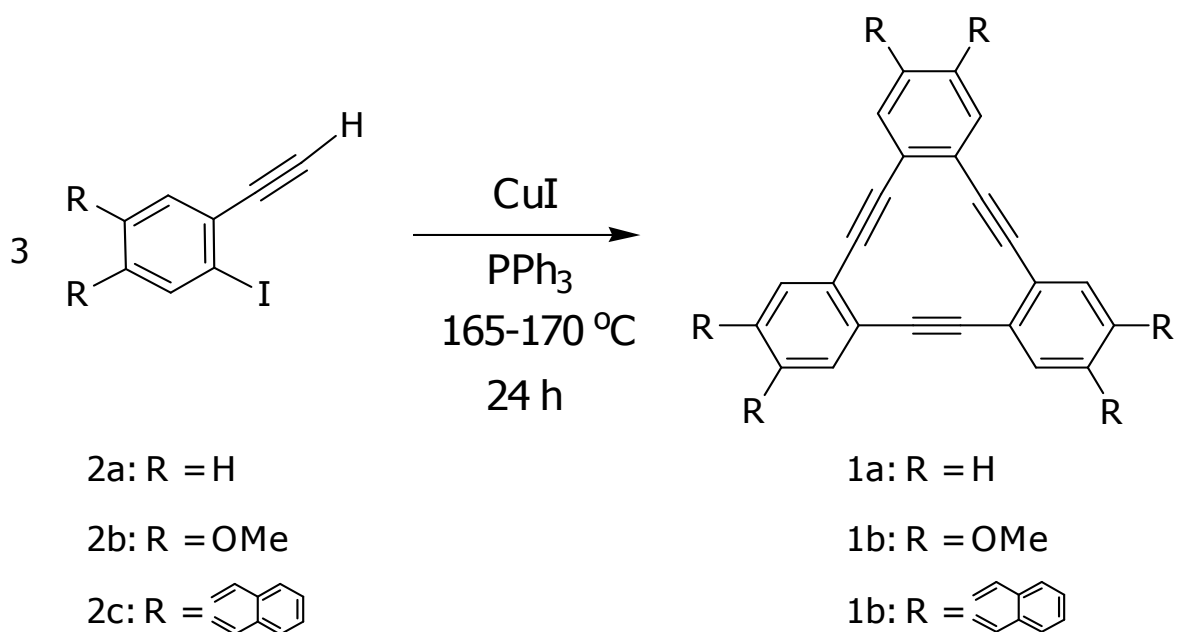
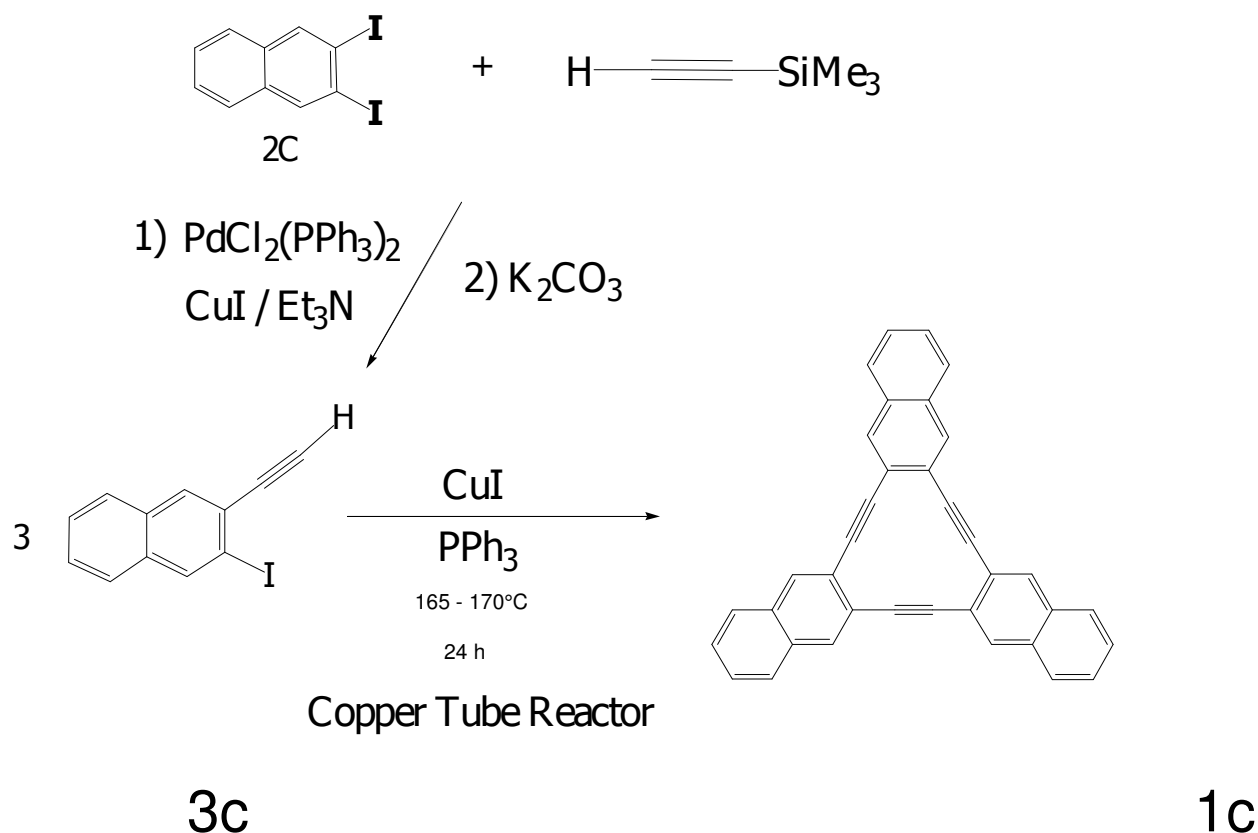


Figure 2. A copper tube reactor for hexadehydro- [12]annulene construction.



Scheme 1. Synthesis diagram for producing dehydroannulene compounds 1a, 1b and 1c.



**Scheme 2.** Synthesis method of producing Trinaphthalenohexadehydro[12]annulene.

substituted Tribenzohexadehydro[12]annulenes 1a. (2-Iodoaryl) acetylenes 2b were prepared by the Sonogashira reaction of the corresponding 1,2-diodoarenes, followed by deprotection with  $\text{K}_2\text{CO}_3$  in methanol. The reactions of 2b with  $\text{CuI}$  (30 mol%) and  $\text{PPh}_3$  (30 mol%) in DMF at  $165^\circ\text{C}$  for 24 h produced 1b in 47 % yields. In the case of 3c, the reaction with 30 mol% of  $\text{CuI}$  and  $\text{PPh}_3$  under similar condition can also proceed under copper tube reactor.

For the construction of the Hexadehydro [12]annulene framework, we tried the coupling cyclization using the copper mediated cross-coupling strategy. Since the Naphthalenohexadehydro[12] annulene 1c is an interesting target molecule, the synthesis of 1c was tried using our coupling reaction. Thus, the cross-coupling of 2b with 6.0 equiv of acetylene was carried out using  $\text{CuI}$  and  $\text{PPh}_3$  in DMF and gave 1c in 18 % yield.

For the construction of the trinaphthalenohexadehydro [12]annulene (1c), the precursor (3c) was prepared starting from 1,2-diodonaphthalene. The Sonogashira reaction of 3c with trimethylsilylacetylene, followed by deprotection yields 3c (two steps). The cross-coupling of 1,2-diodonaphthalene with trimethylsilylacetylene in the presence of  $\text{PdCl}_2(\text{PPh}_3)_2$  and  $\text{CuI}$  in  $\text{Et}_3\text{N}$  afforded 3c in 62% yield. The trinaphthalenohexadehydro[12]annulene (TNHA) 1c is a stable colourless crystalline compound and has a moderate solubility in dichloromethane, chloroform and tetrahydrofuran (Ebbesen and Ajayan, 1992; Takahashi et al., 1980; Youngs et al., 1999).

#### Spectroscopy data of TNHA

The new compound, tri-naphthalenohexadehydro[12]annulene (1c), was fully characterized by spectroscopic analyses. Selected data

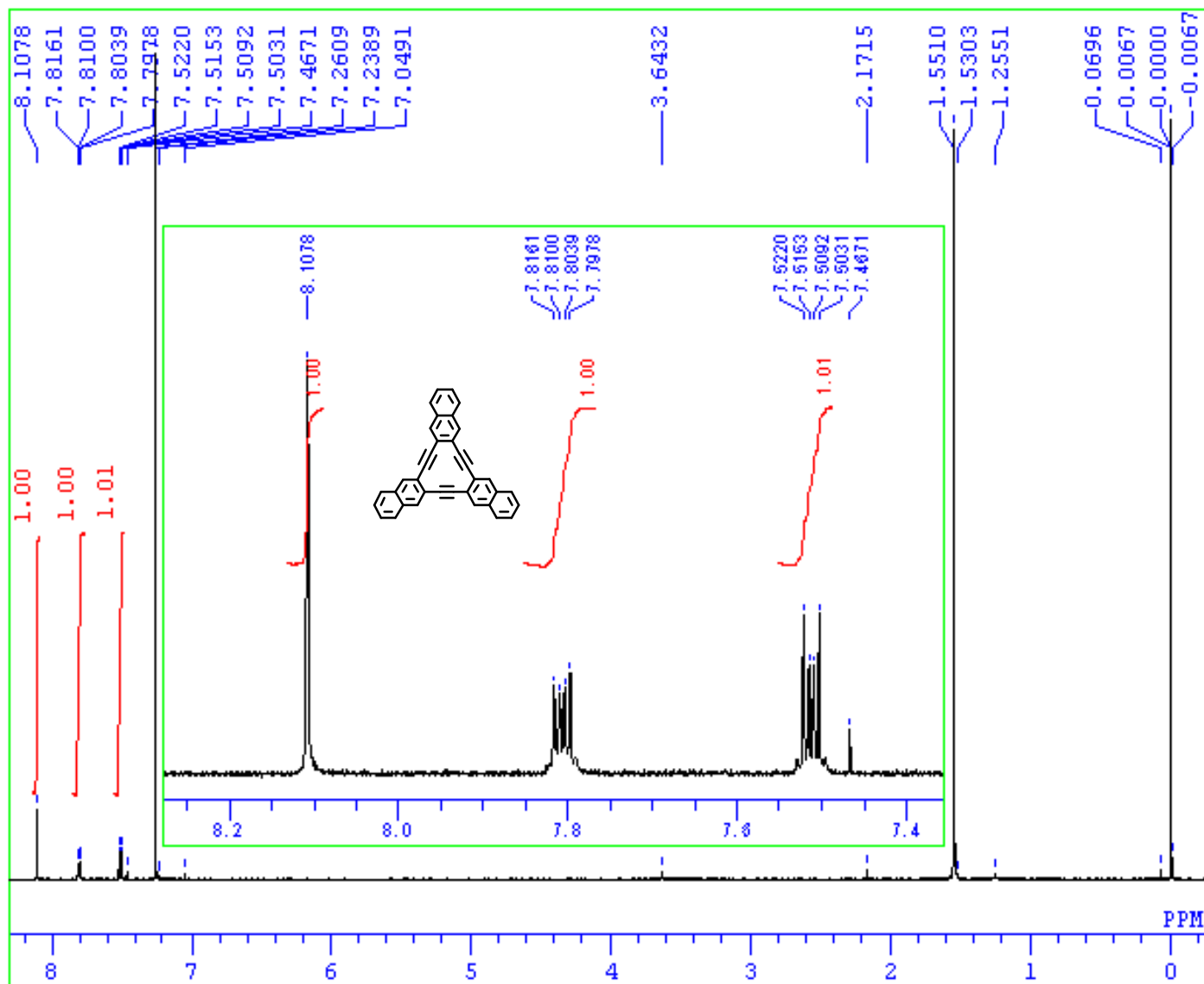
were; light colorless crystals, m.p.  $> 250^\circ\text{C}$ , electron impact mass spectroscopy, EI-MS ( $m/z$ ) = 450 ( $\text{M}^+$ , 100),  $^1\text{H}$  nuclear magnetic spectroscopy,  $^1\text{H-NMR}$  ( $\text{CDCl}_3/\text{TMS}$ , 500 MHz) = 8.13 (s, 6H,  $\text{H}^a$ ), 7.50-7.52 (m, 6H,  $\text{H}^c$ ), 7.79-7.81 (m, 6H,  $\text{H}^b$ ) ppm,  $^{13}\text{C}$  nuclear magnetic spectroscopy,  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3/\text{TMS}$ , 125 MHz) = 138.81, 132.74, 127.96, 127.84, 122.46, 91.08 ppm as shown in Figure 3, fourier transform infrared spectroscopy, FT-IR in Nujol shown = 3059 (Ar-H, st), 2217 ( $\text{C}\equiv\text{C}$ , st)  $\text{cm}^{-1}$ , ultraviolet and visible spectroscopy, UV-vis in cyclohexane, shown  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 260.5 (104,000), 265.5 (166,000), 273.5 (527,000), 281.0 (450,000), 290.5 (1,370,000) nm and high resolution mass spectroscopy, HRMS shown Calcd. for  $\text{C}_{36}\text{H}_{18}$ : 450.4389; Found: 450.4376.

#### Storage test

From the dry ice-acetone physisorption data, obtained with a Micromeritics apparatus at 195 K, the BET surface area, total pore volume and micro pore volume were derived. Prior to the physisorption measurements, the non-intercalated carbon fibers were evacuated at  $300^\circ\text{C}$ . When intercalated samples were studied with dry ice-acetone physisorption, they were evacuated at room temperature. Hydrogen adsorption experiments were performed in a conventional static volumetric adsorption apparatus, made of Pyrex glass, which could be operated at hydrogen pressures of up to 1.5 bar. The apparatus is displayed in Figure 4.

#### RESULT

As shown in Table 1, the hydrogen uptake capacity of all



**Figure 3.**  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectroscopic diagram of Trinaphthaleno-hexa-dehydro [12]annulene.

these intercalated samples was tested repeatedly, each after 30 min of evacuation at 195 K. All samples were tested in at least 3 cycles and still showed the same

## Conclusions

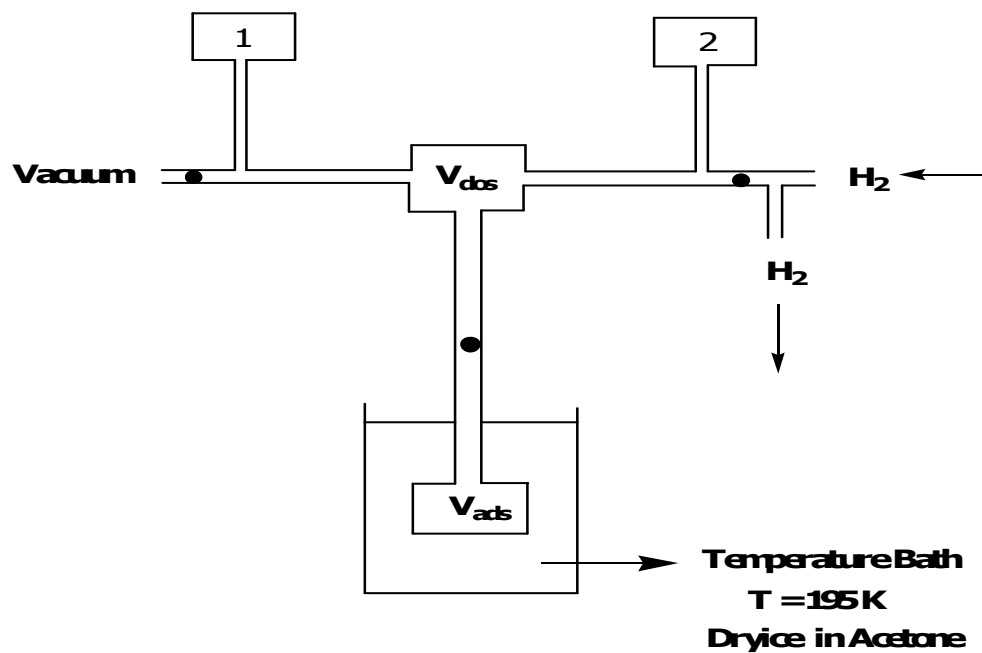
In this study, we intended to examine tri-merization reaction by a copper catalyst method in order to developed an effective catalytic conditions producing the tri-naphthaleno-hexa-dehydro [12]annulene 1c in 18% yield.

The hydrogen storage capacity of fishbone annulene carbon has been determined for several stages of intercalated compounds. The materials and their

adsorption capacities are summarized.

## ACKNOWLEDGEMENTS

We give thanks to Dr. Pornsawan Amornsakchai from Faculty of Science, Naresuan University, for her kind suggestion and discussions. Special thanks to Prof. Dr. Masahiko Iyoda from Tokyo Metropolitan University, Assistant Professor Dr. Sombat Thanawan from Mahidol University and Dr. Kittipong Chainok, for their kind discussions. This work was funded by the National Metal and Materials Technology Center and the Ministry of Energy Organization. Collaboration for this work was through the National Science and Technology



**Figure 4.** Hydrogen storage micromeritics apparatus with carbon fiber and Trinaphthalenohexahydro[12] annulene.

**Table 1.** Hydrogen storage capacities of several fishbone of hexadehydroannulene carbon at 195 K and 1.5 bar.

<b>Hydrogen storage capacity</b>		
<b>Sample</b>	<b>Weight (g)</b>	<b>Adsorption (%)</b>
Graphite	0.5	1.82
1a	0.5	2.47
1b	0.5	2.21
1c	0.5	2.62
1a	1.0	2.81

Development Agency with Faculty of Science, Naresuan University, uptake capacity. The samples did not show any uptake at 273 and 298 K.

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