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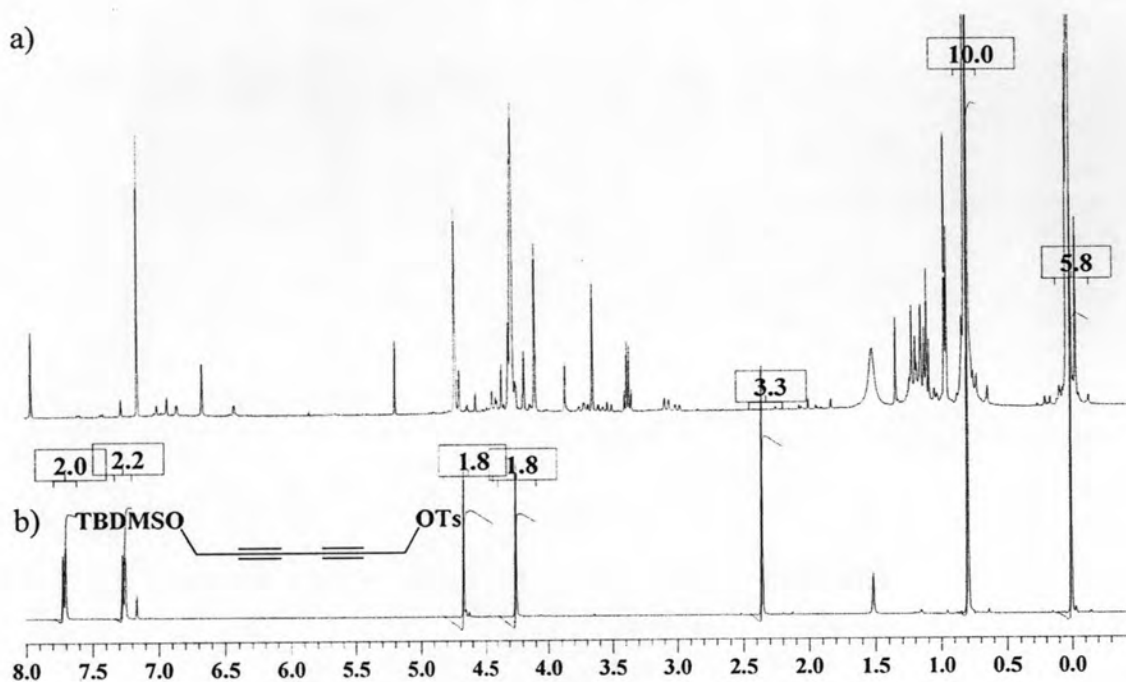
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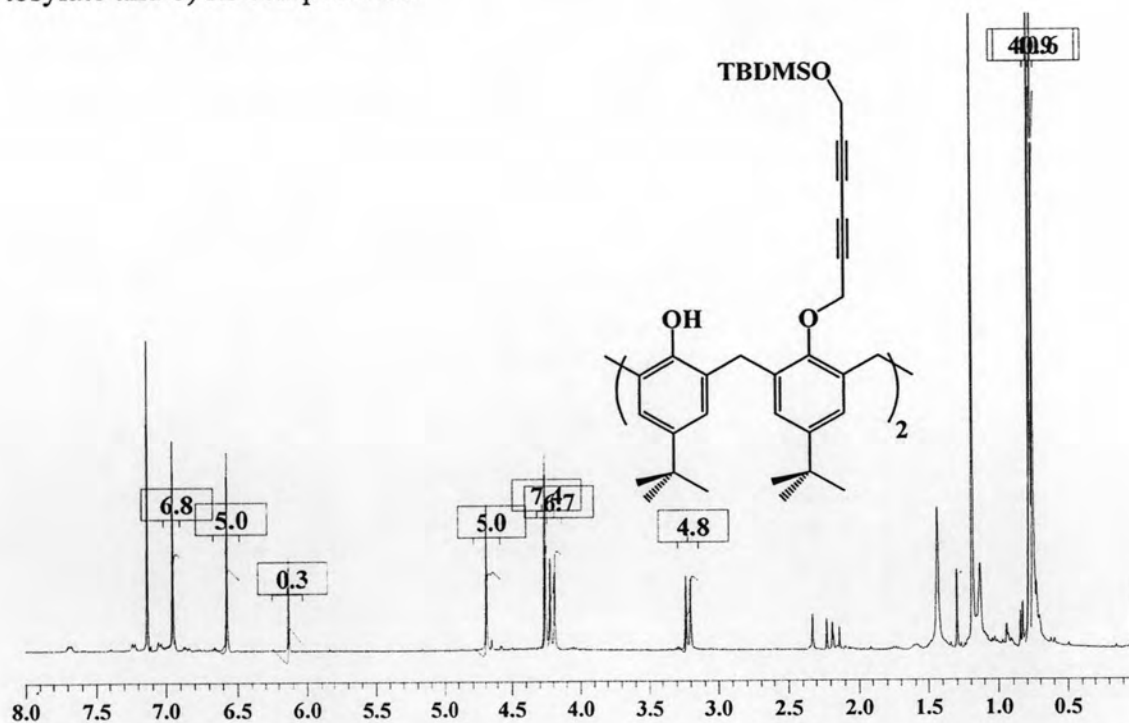
## APPENDICES

## APPENDIX A

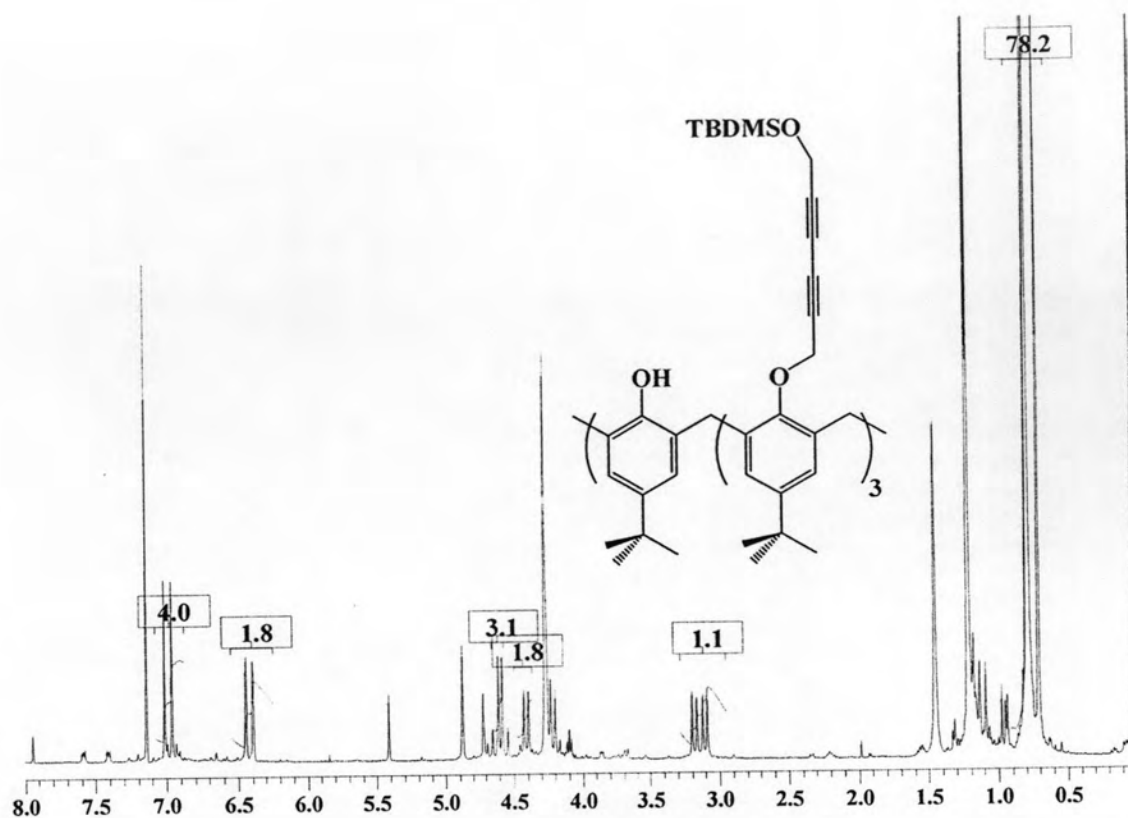
### NMR SPECTRA



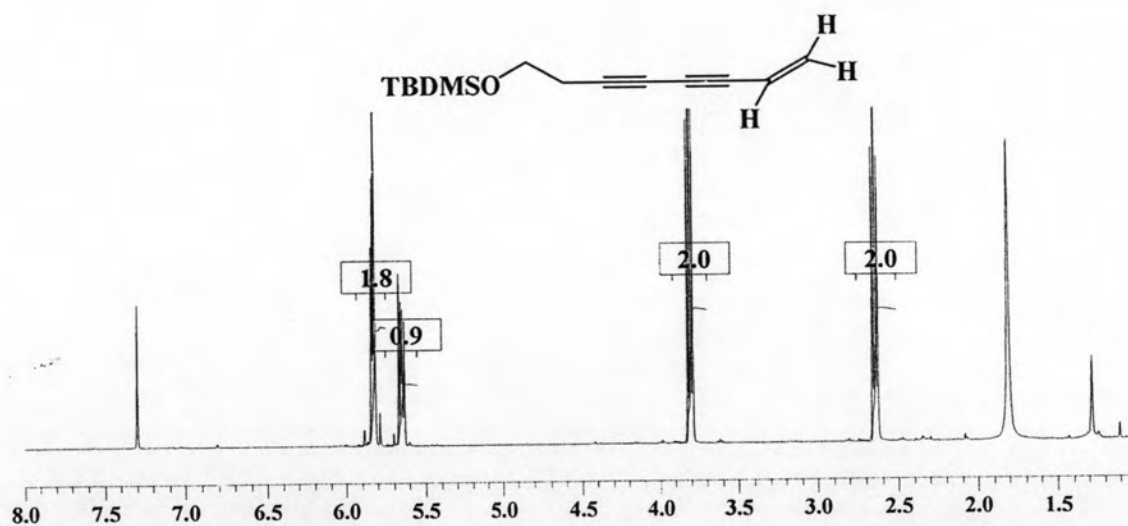
**Figure A1**  $^1\text{H}$  NMR spectrum of a) 6-*tert*-butyltrimethylsilyloxy-2,4-hexadiynyl tosylate and b) its composition.



**Figure A2**  $^1\text{H}$  NMR spectrum of di(6-*tert*-butyltrimethylsilyloxy-2,4-hexadiynyloxy) calix[4]arene.



**Figure A3**  $^1\text{H}$  NMR spectrum of tri(6-tert-butyl dimethylsilyloxy-2,4-hexadiynyloxy) calix[4]arene.



**Figure A4**  $^1\text{H}$  NMR spectrum of tert-butyl dimethyl(octa-7-en-3,5-diynyloxy)silane.

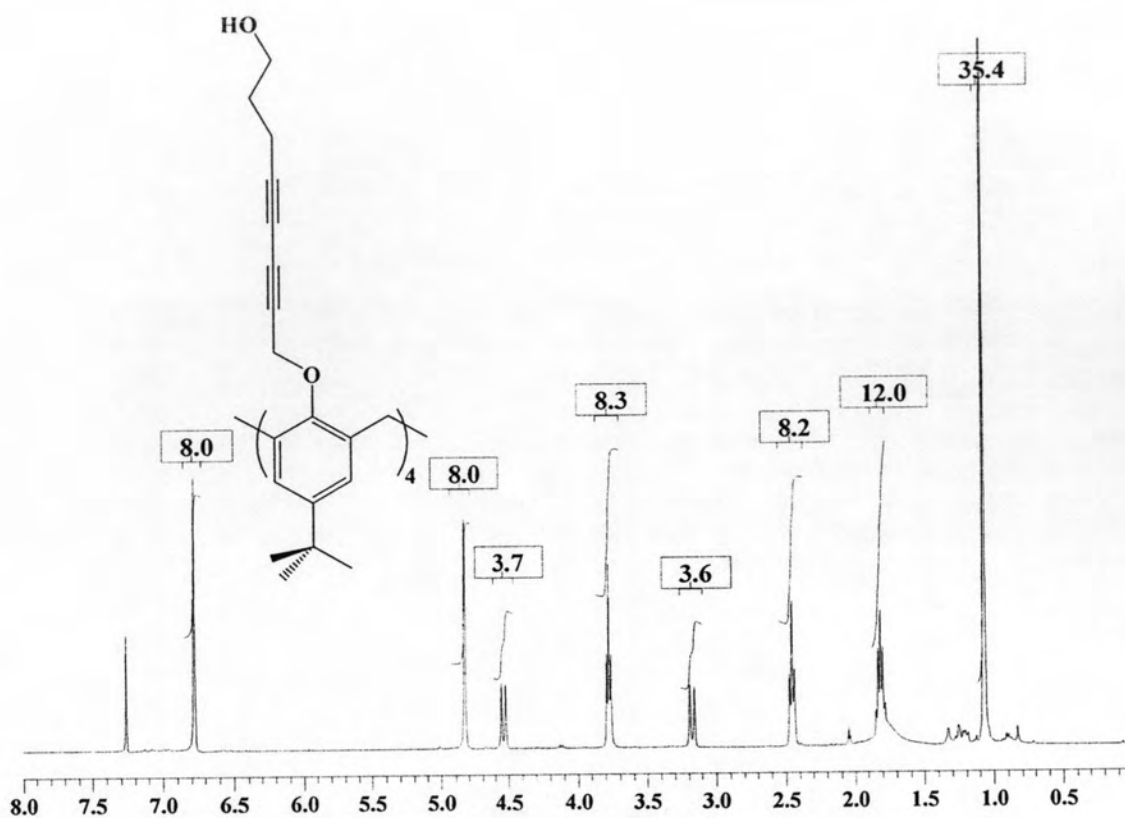


Figure A5  $^1\text{H-NMR}$  spectrum of C4A.

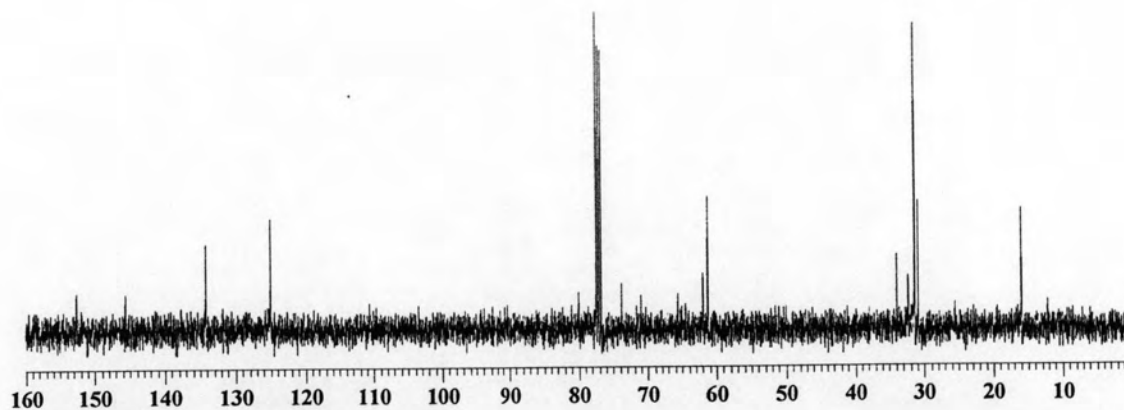


Figure A6  $^{13}\text{C-NMR}$  Spectrum of C4A.

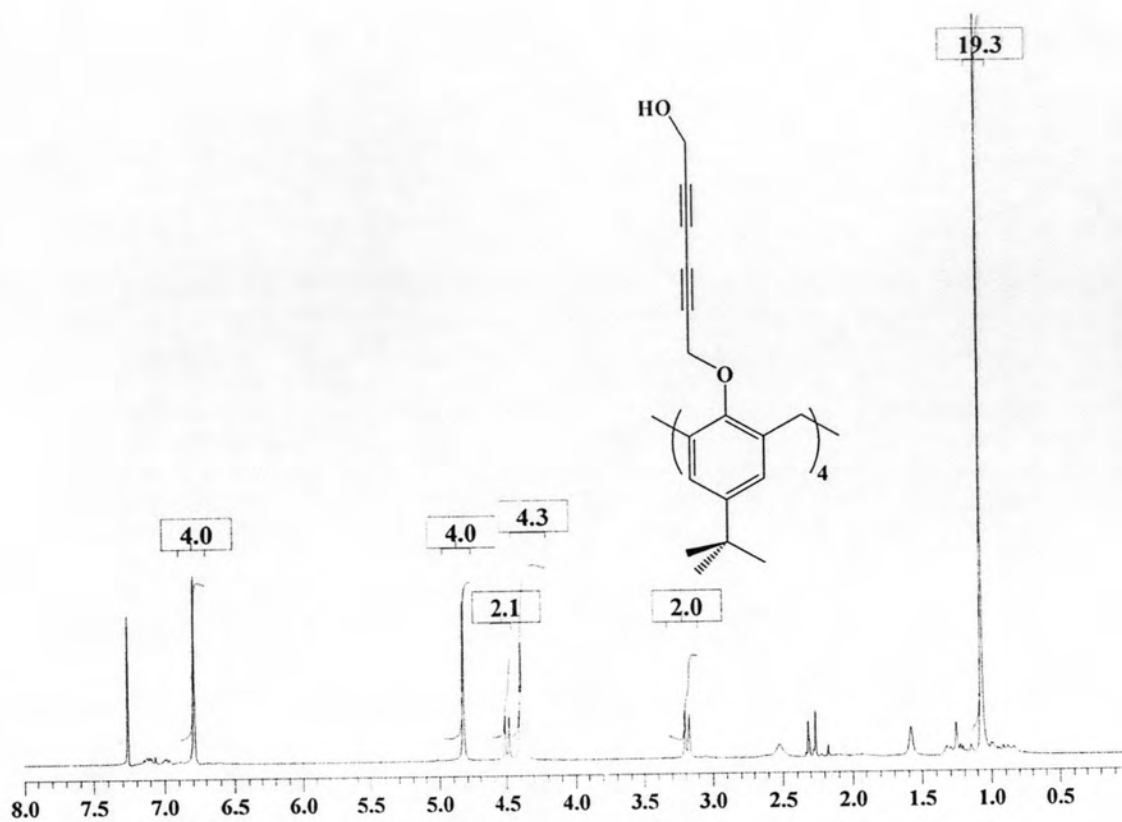


Figure A7  $^1\text{H-NMR}$  spectrum of C4A'.

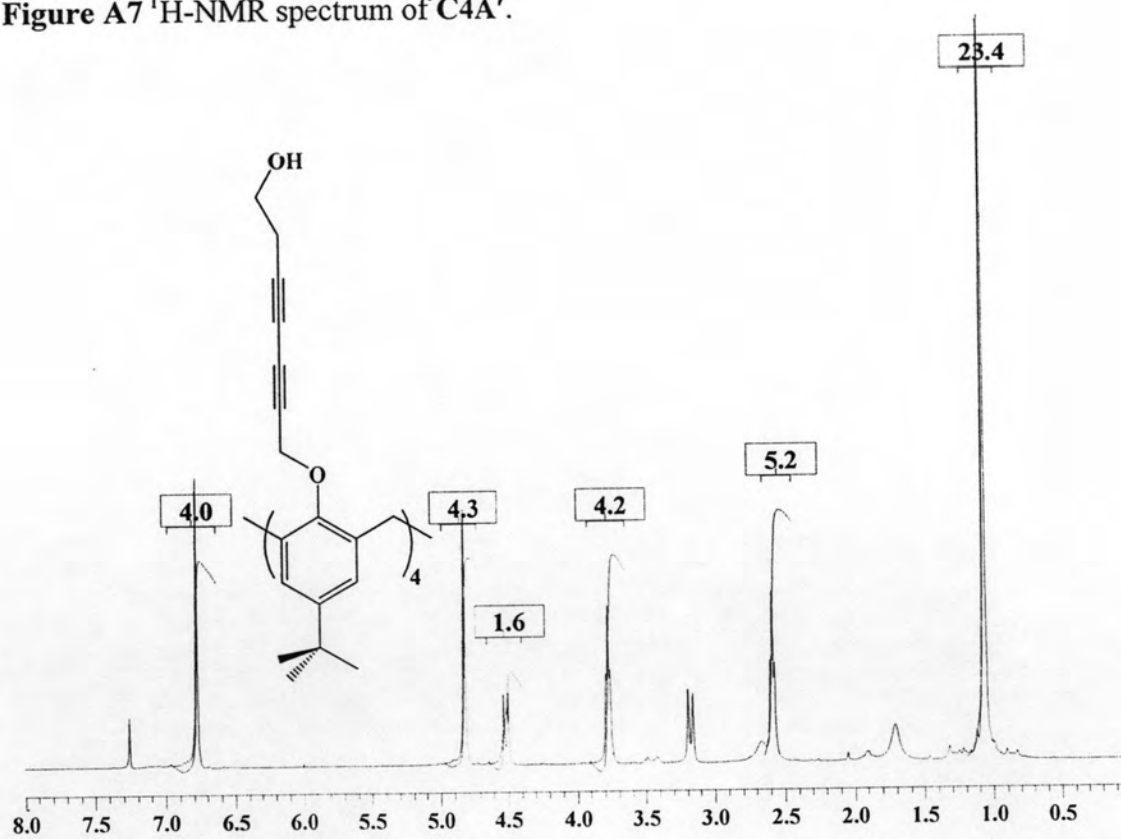


Figure A8  $^1\text{H-NMR}$  spectrum of C4A''.

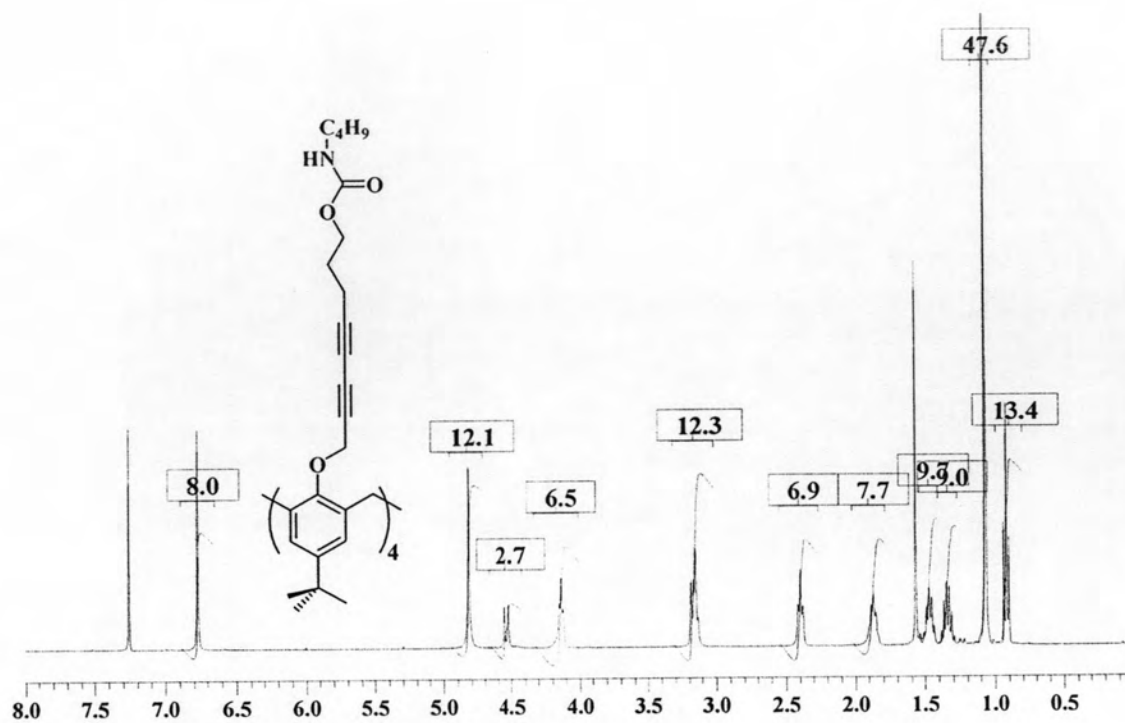


Figure A9  $^1\text{H-NMR}$  spectrum of C4BU.

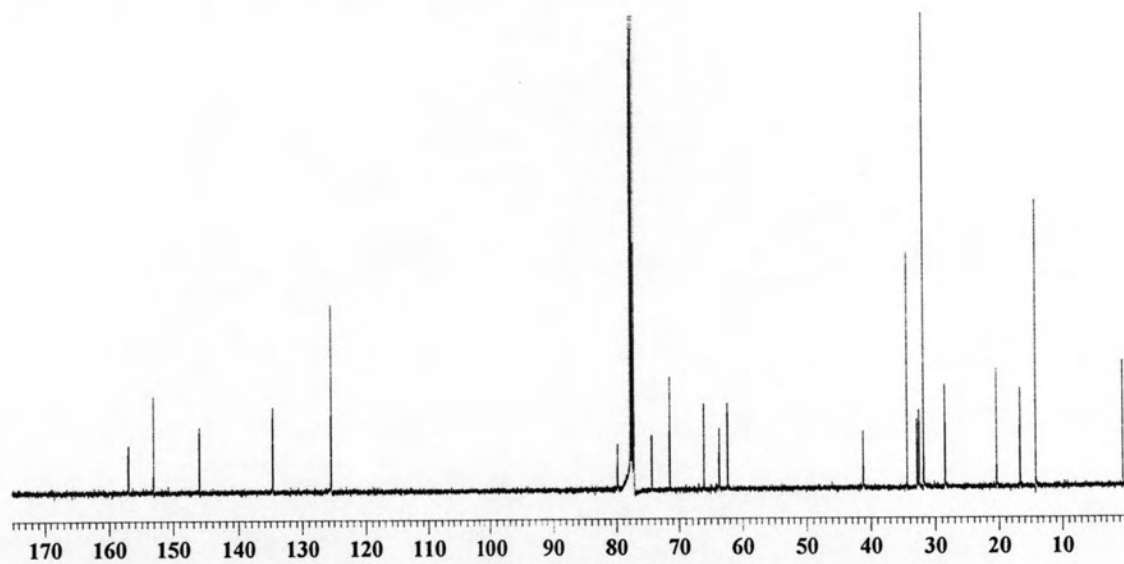


Figure A10  $^{13}\text{C-NMR}$  spectrum of C4BU.



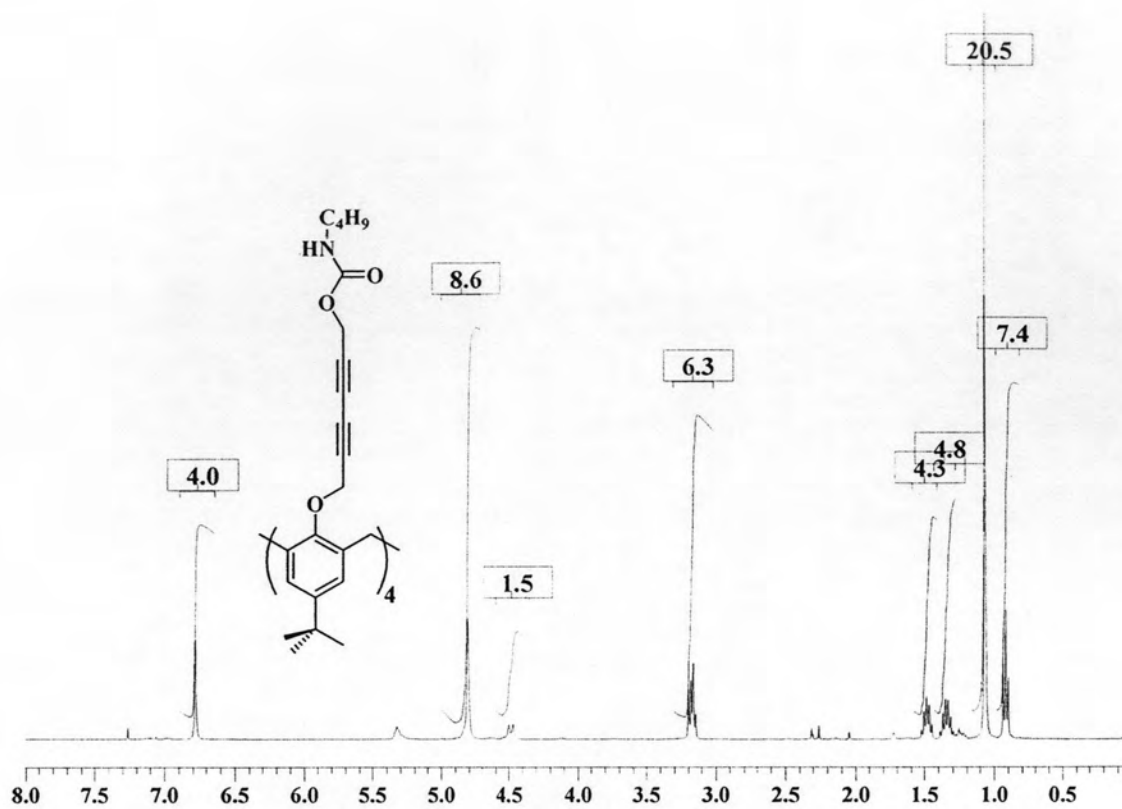


Figure A11  $^1\text{H-NMR}$  spectrum of C4BU'.

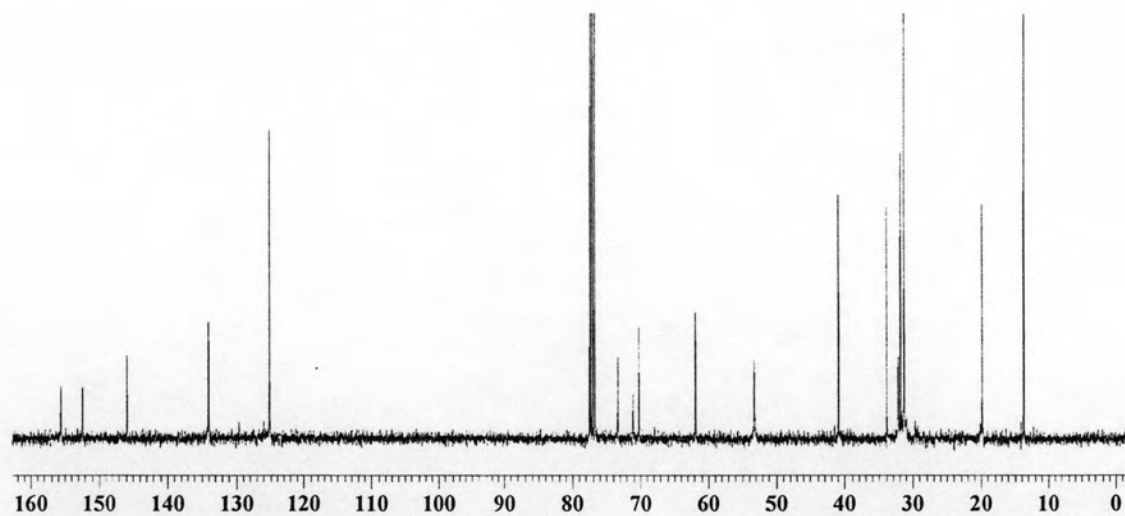


Figure A12  $^{13}\text{C-NMR}$  spectrum of C4BU'.

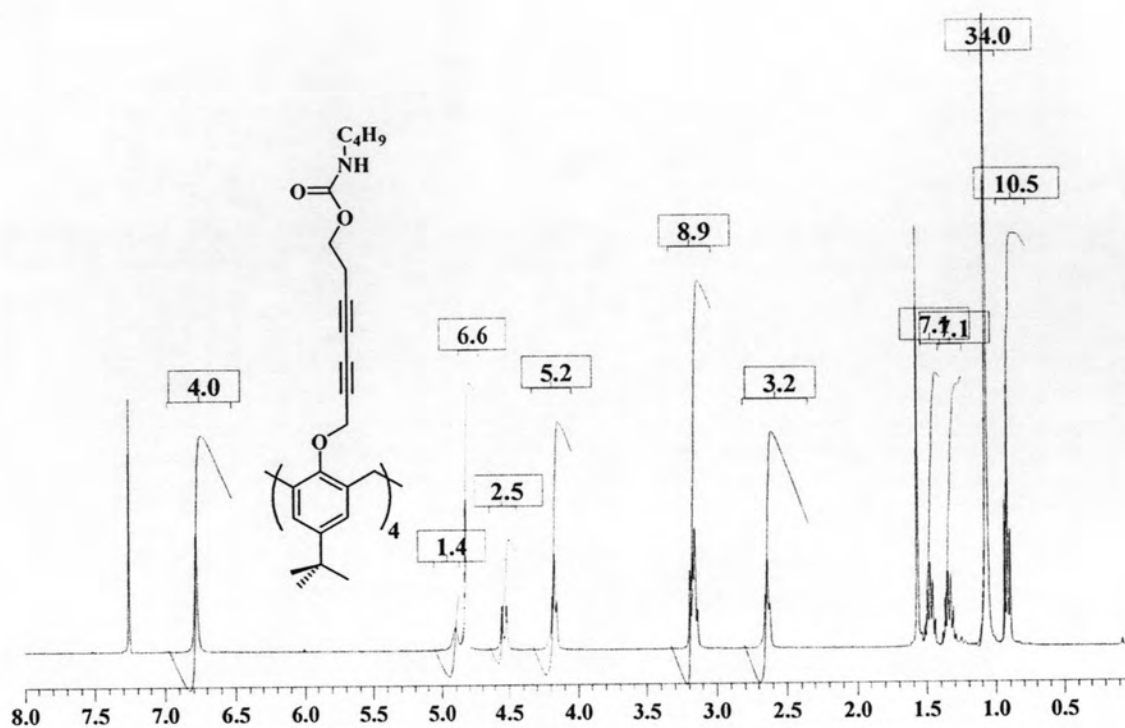


Figure A13  $^1\text{H-NMR}$  spectrum of C4BU''.

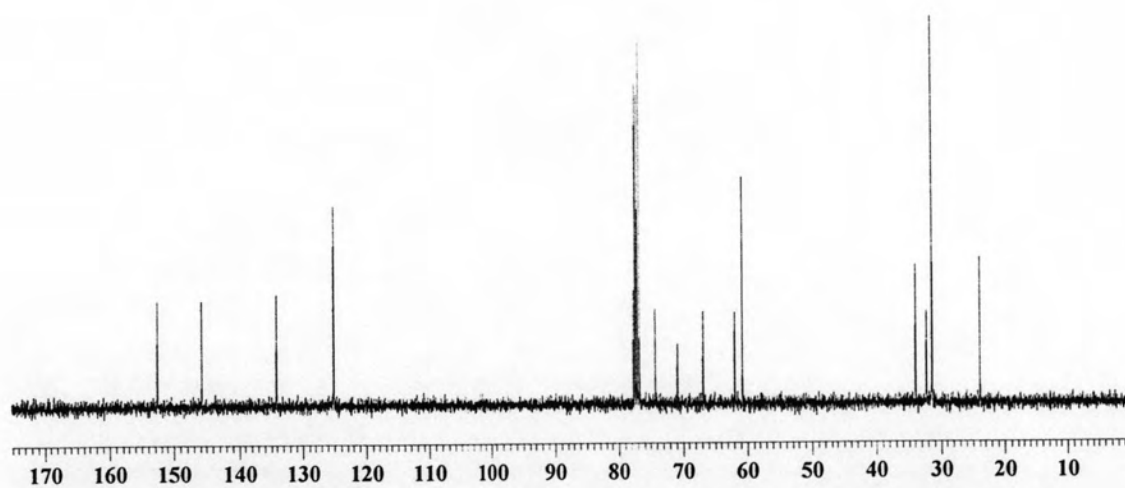


Figure A14  $^{13}\text{C-NMR}$  spectrum of C4BU''.

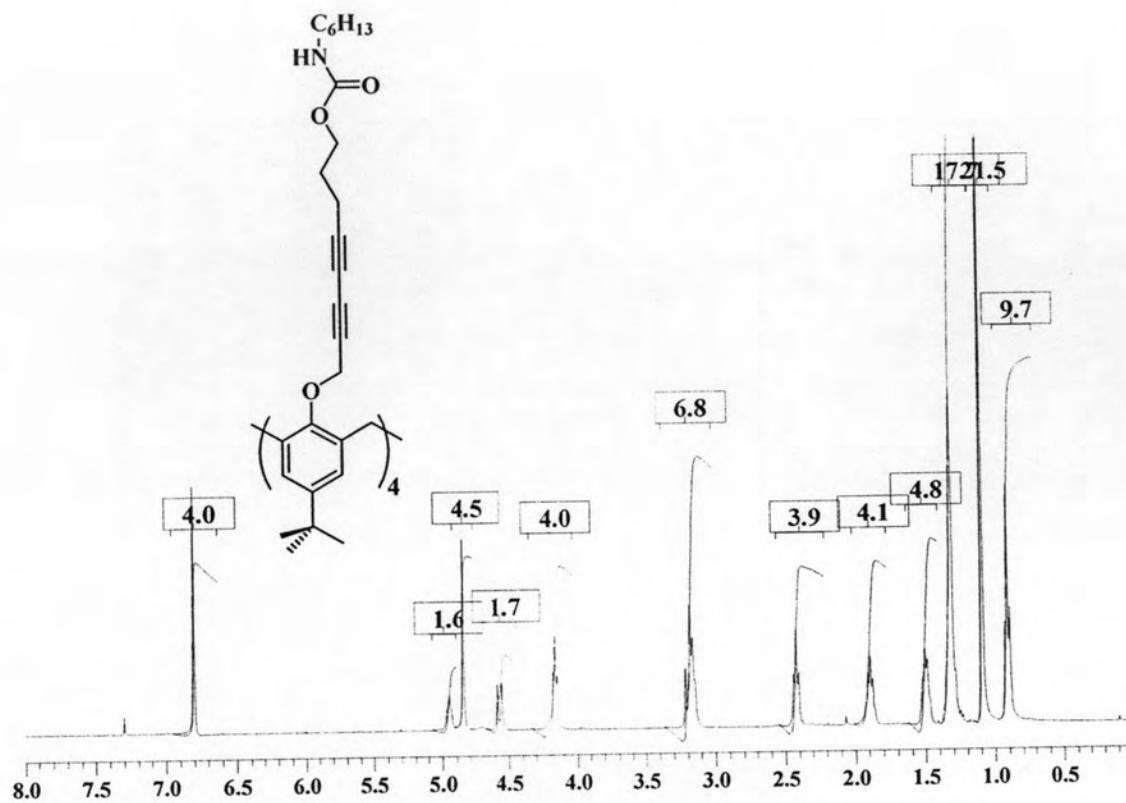


Figure A15  $^1\text{H-NMR}$  spectrum of C4HU.

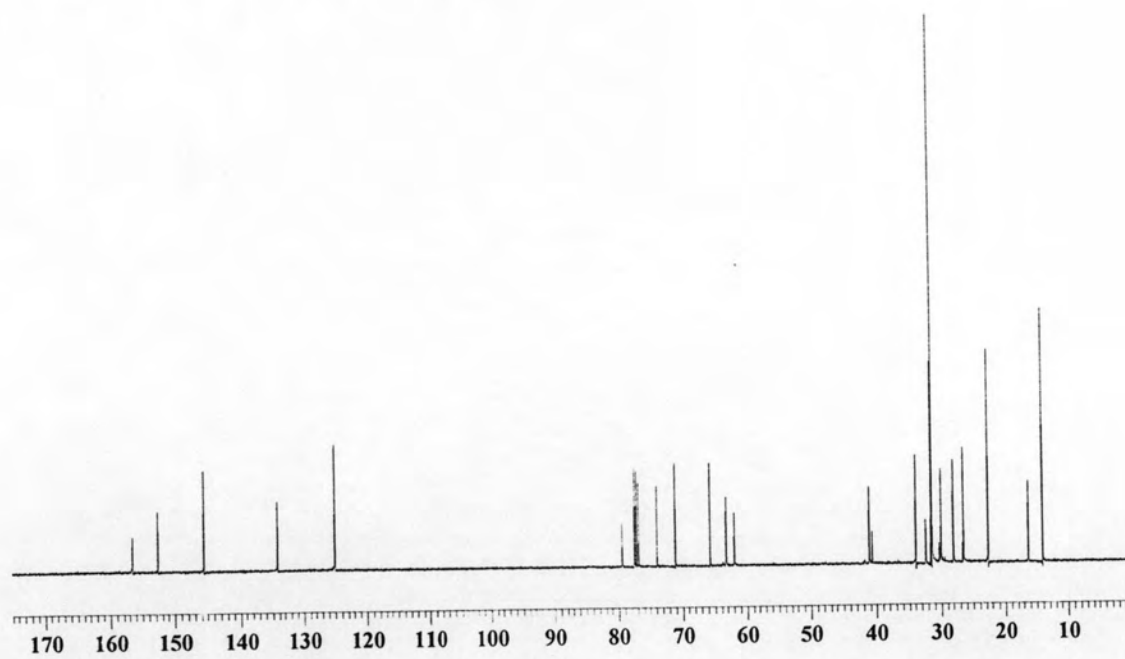


Figure A16  $^{13}\text{C-NMR}$  spectrum of C4HU.

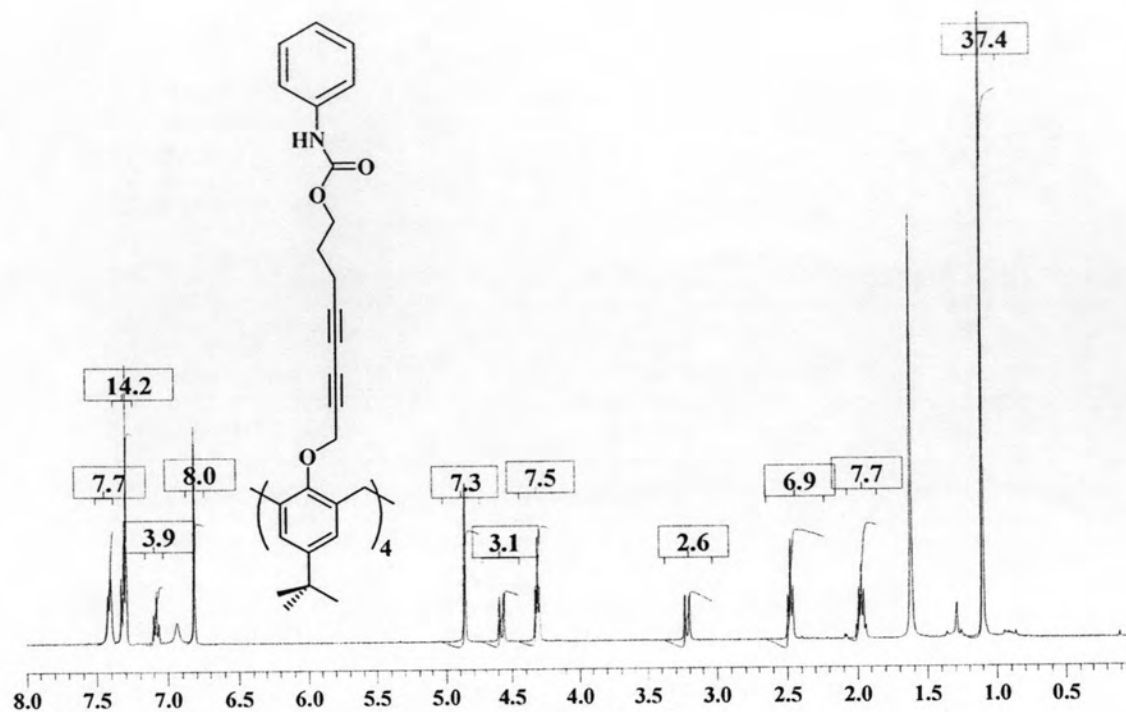


Figure A17  $^1\text{H-NMR}$  spectrum of C4PU.

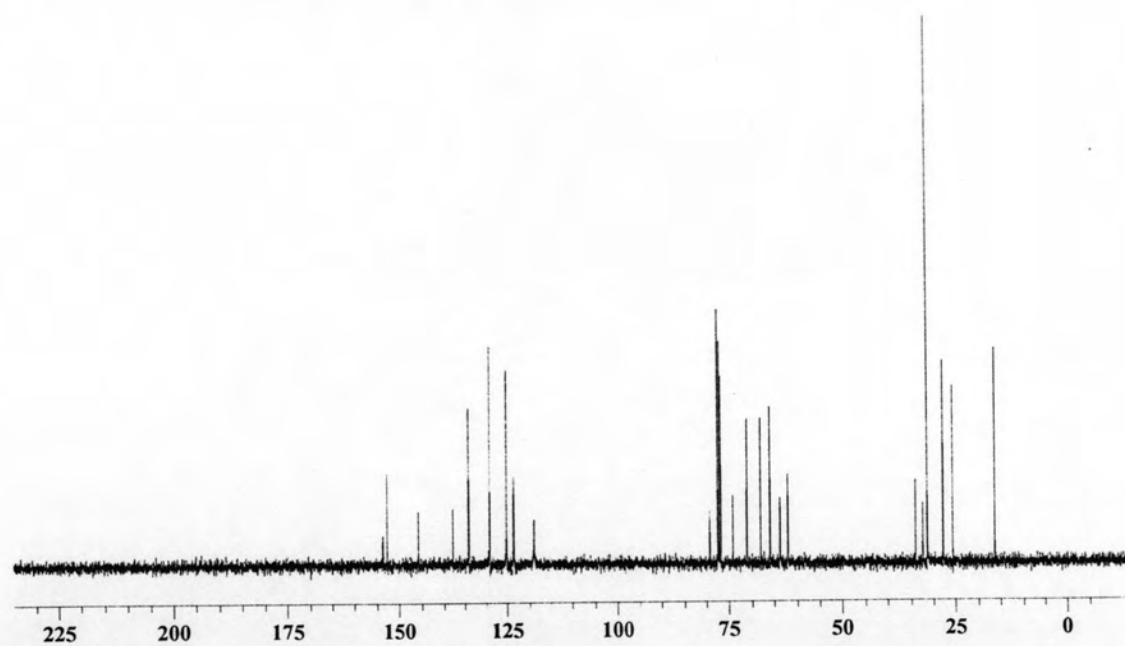


Figure A18  $^{13}\text{C-NMR}$  spectrum of C4PU.

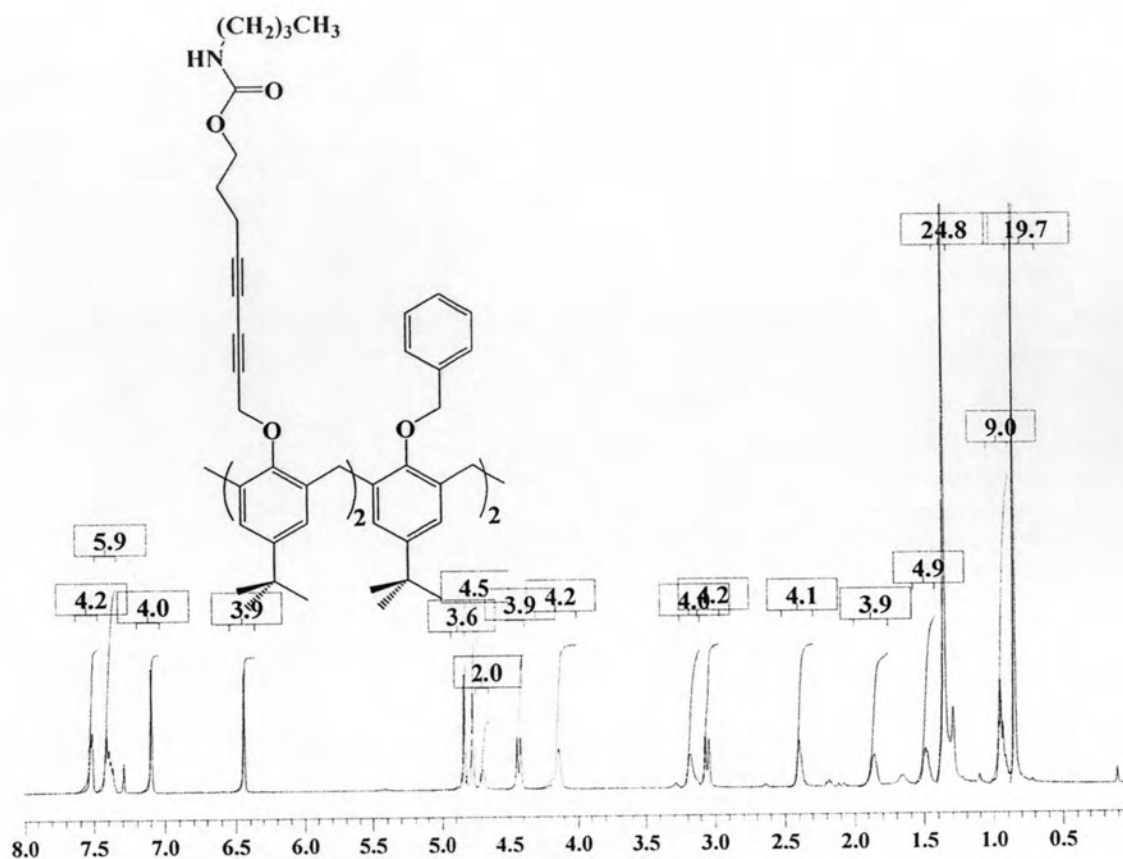


Figure A19  $^1\text{H-NMR}$  spectrum of BnC2BU.

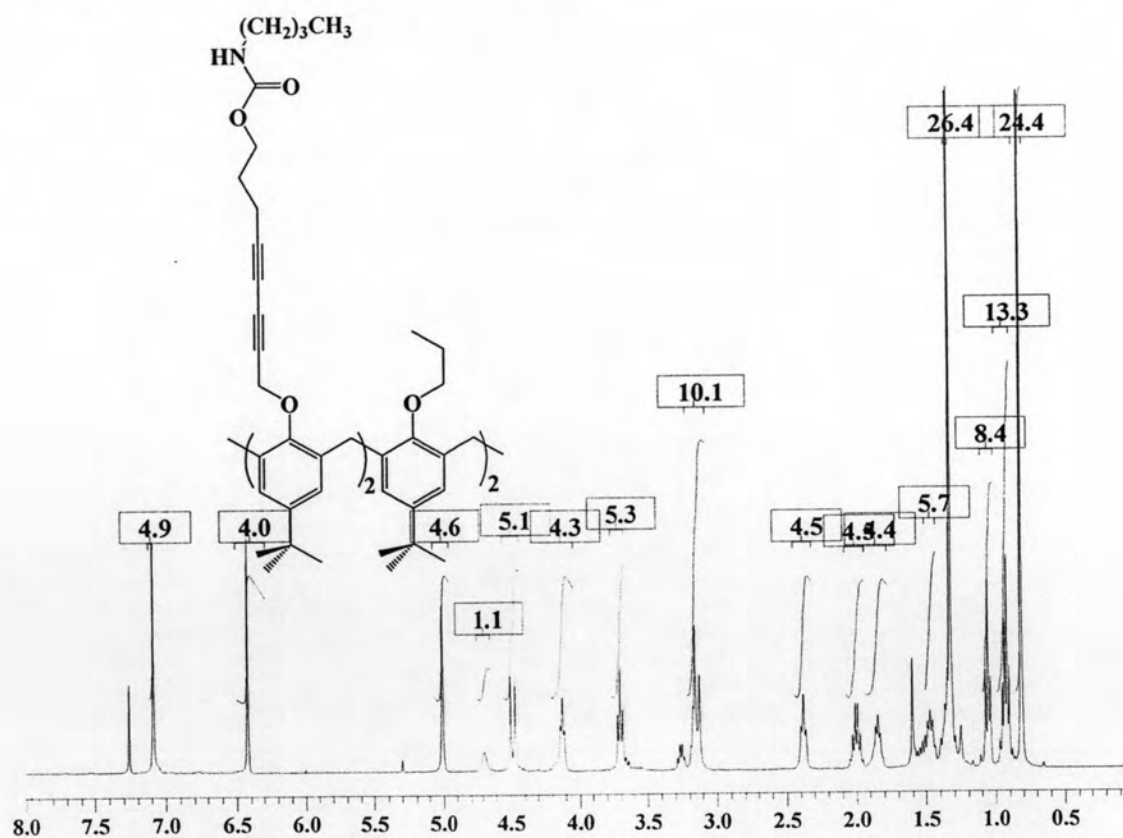


Figure A20  $^1\text{H-NMR}$  spectrum of PrC2BU.

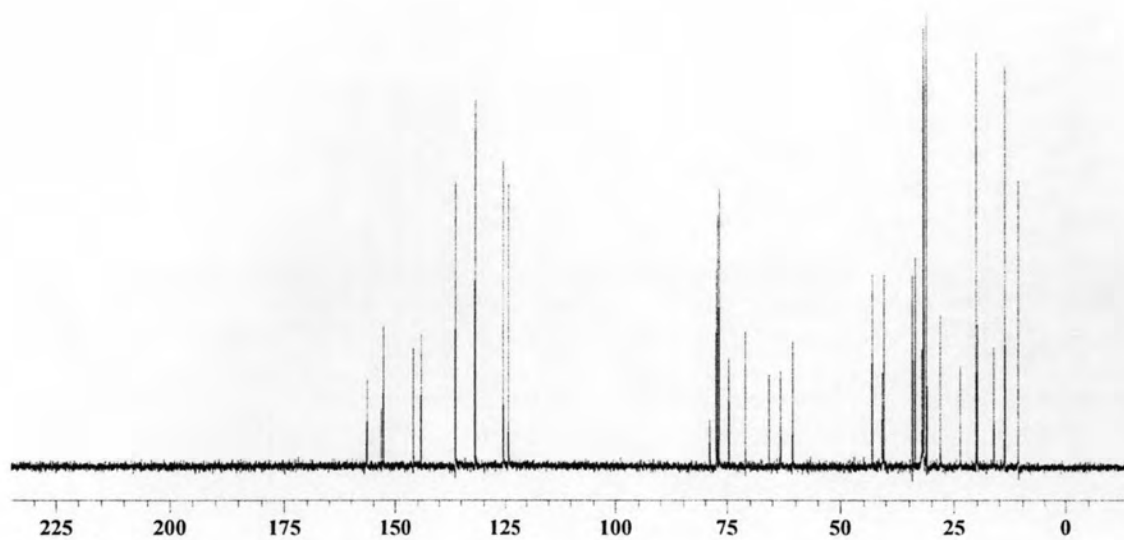


Figure A21  $^{13}\text{C}$ -NMR spectrum of PrC2BU.

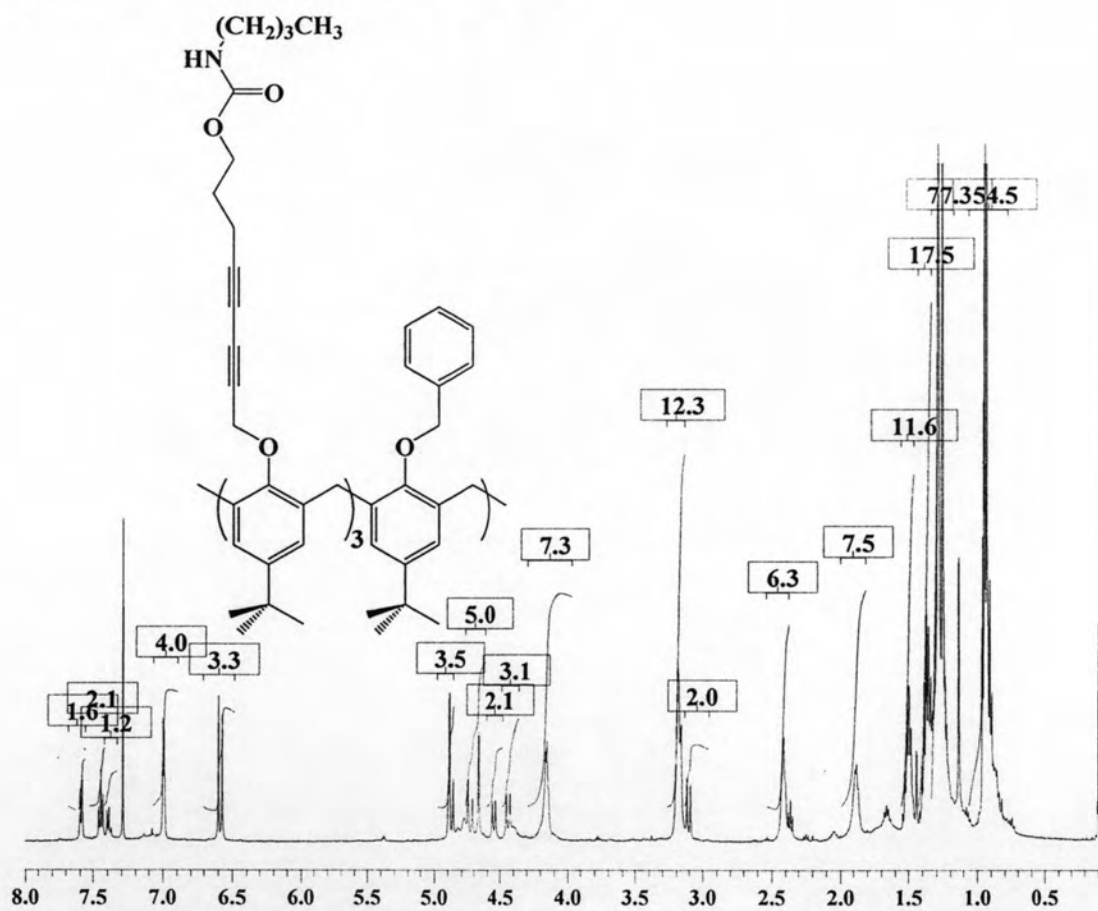


Figure A22  $^1\text{H}$ -NMR spectrum of BnC3BU.

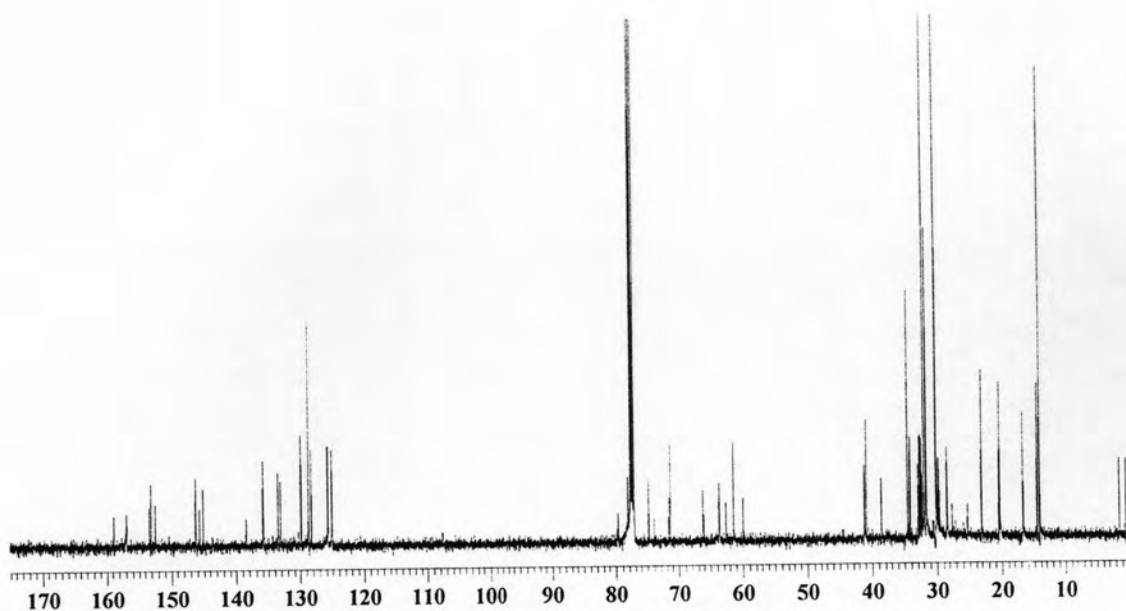


Figure A23  $^{13}\text{C}$ -NMR spectrum of BnC3BU.

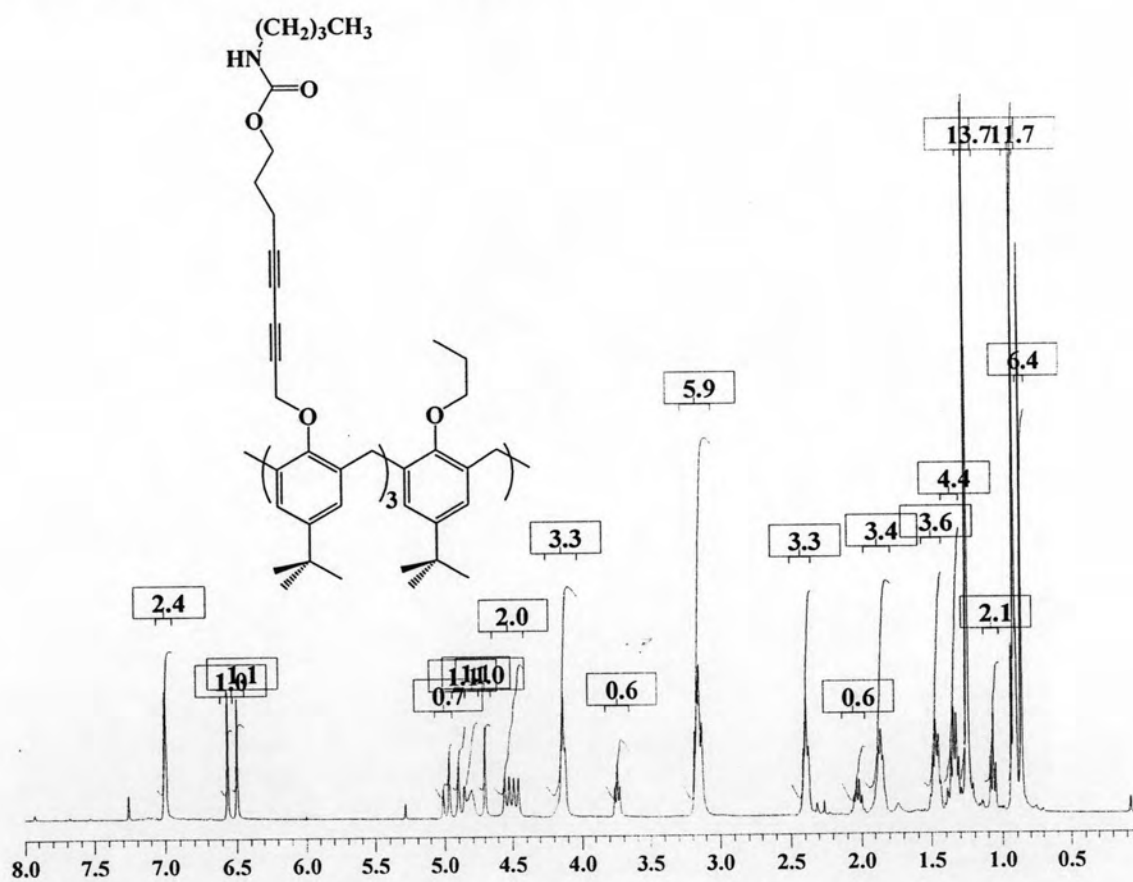


Figure A24  $^1\text{H}$ -NMR spectrum of PrC3BU.

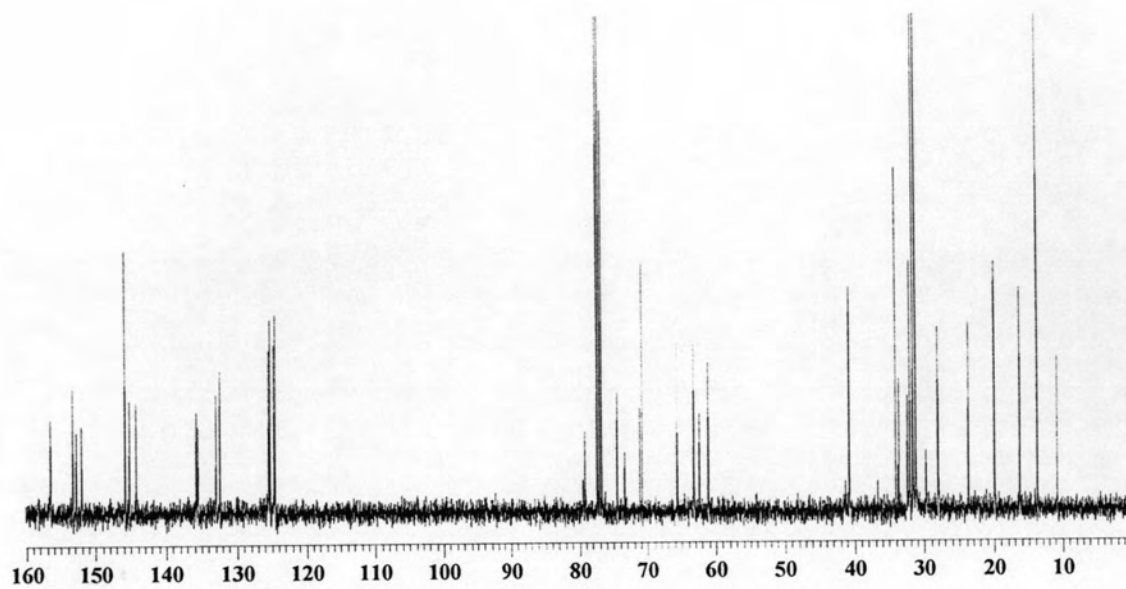
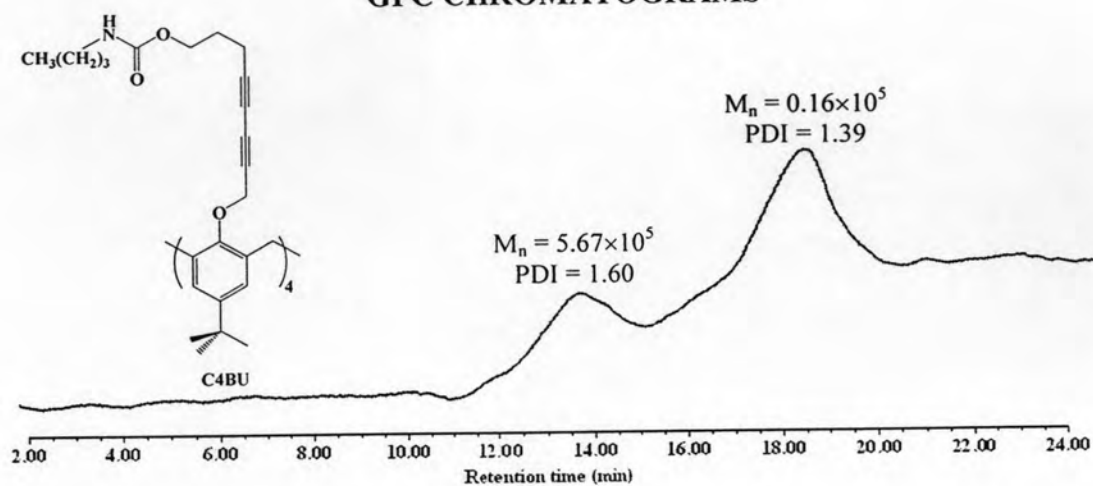


Figure A25  $^{13}\text{C}$ -NMR spectrum of PrC3BU.

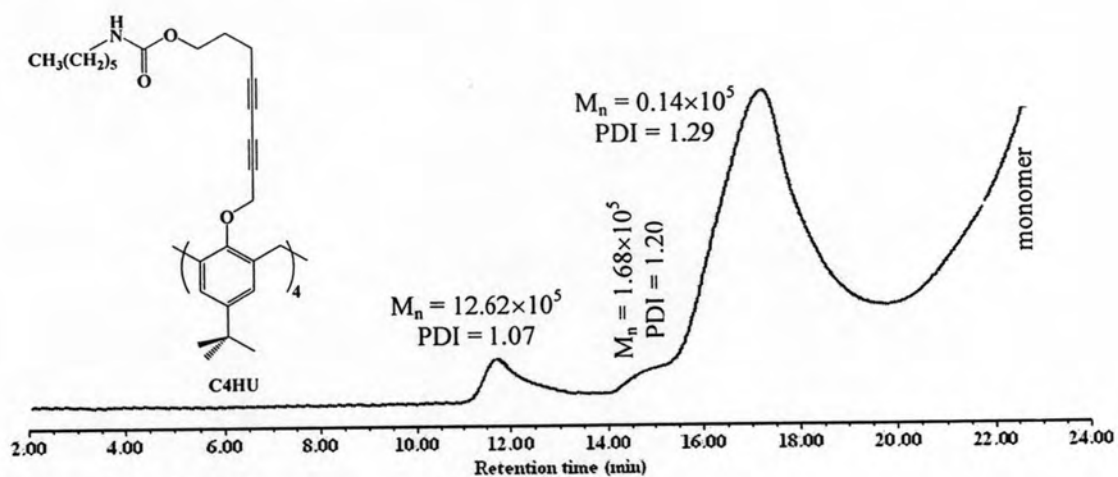


## APPENDIX B

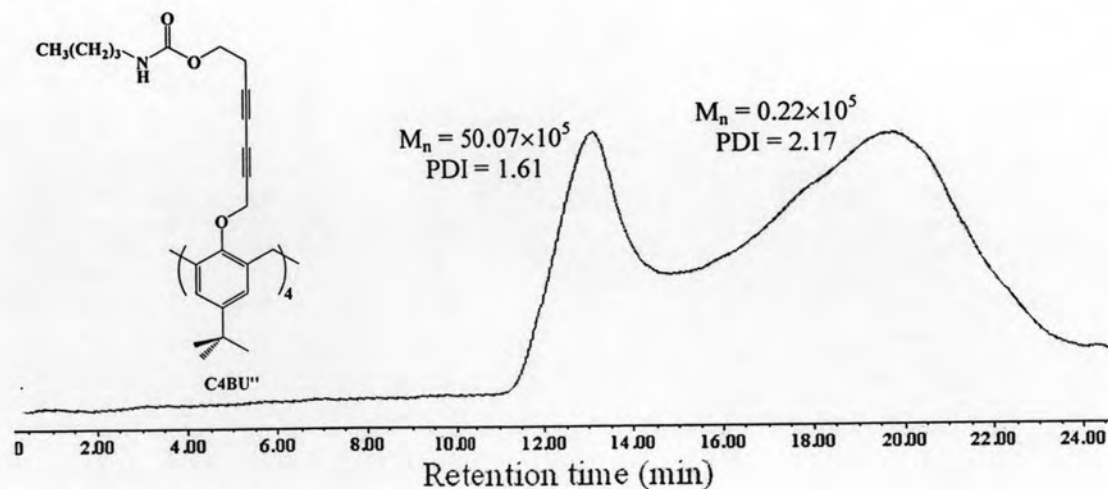
### GPC CHROMATOGRAMS



**Figure B1** GPC chromatogram of PC4BU.



**Figure B2** GPC chromatogram of crude PC4HU.



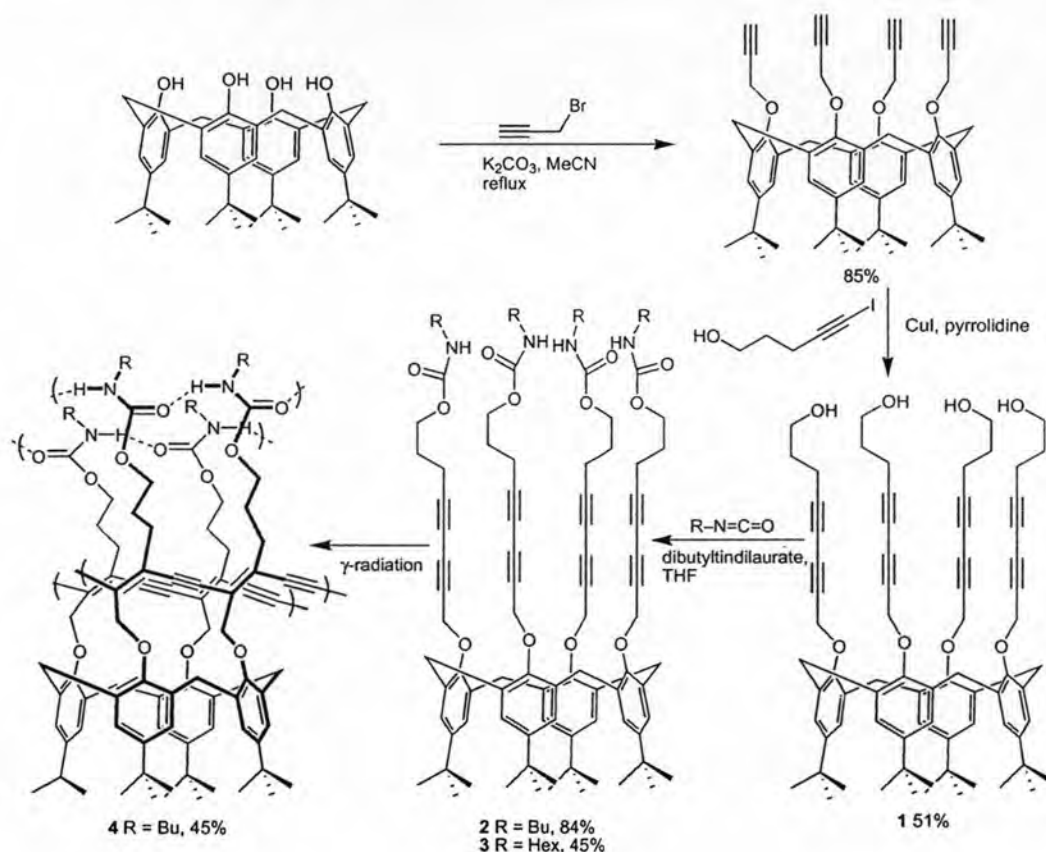
**Figure B3** GPC chromatogram of PC4BU''.

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Topological Polymerization of *tert*-Butylcalix[4]arenes Containing Diynes

*Macromolecules* 2008, 41, 675-681.

## Topological Polymerization on Calixarene Template



**Significance:** The authors report a synthesis of *tert*-butylcalix[4]arenes with pendant diynyl groups (**1**). When **1** was exposed to UV radiation, no significant transformation took place. When hydroxyl groups were converted into urethanes (**2** and **3**), the compound exhibited color change from white to intense red upon a five-minute exposure to UV radiation. The authors exposed **2** to  $\gamma$ -radiation in order to achieve a more thorough transformation of the solid material. The resulting solid material was shown to have spectroscopic properties which suggest the presence of eneyne conjugation of the expected product, **4**.

**SYNFACTS Contributors:** Timothy M. Swager, Jeewoo Lim  
*Synfacts* 2008, 4, 0369-0369 Published online: 19.03.2008  
DOI: 10.1055/s-2008-1042844; Reg-No.: S02008SF

**Comment:** The solid-state transformation from **2** to **4** involves a topological 1,4-addition polymerization of the diynyl moieties, which is possible when diacetylenes are closely packed and are arranged in proper angles. The fact that **1** did not undergo noticeable transformation under irradiation, while **2** and **3** did, suggests that not only the calixarene template, but also the hydrogen-bonding network of the urethane end groups helped lock the diynyl groups in the correct conformation for the topological polymerization.

Category

Synthesis of  
Materials and  
Unnatural Products

Key words

calixarenes

topological  
polymerization

solid-state photo-  
polymerization

## Topological Polymerization of *tert*-Butylcalix[4]arenes Containing Diynes

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**ABSTRACT:** The new 25,26,27,28-tetra(8-hydroxyocta-2,4-diynyl)-*tert*-butylcalix[4]arene was synthesized in good yield from copper-catalyzed coupling reaction of 25,26,27,28-tetra(2-propynyl)-*tert*-butylcalix[4]arene with 5-iodo-4-pentynol in pyrrolidine. The hydroxyl end groups were converted to urethane groups through addition to alkyl or phenyl isocyanate. Di- and trisubstituted *tert*-butylcalix[4]arene analogs were also synthesized through the same approach. The solid-state photopolymerization study revealed that only the calix[4]arene derivatives containing four diyne units with alkyl urethane groups were substantially polymerized upon exposure to UV or gamma irradiation to give polydiacetylenes containing calix[4]arene. The visible absorption band at 350–600 nm and the Raman signals around 1500 and 2100  $\text{cm}^{-1}$  characterized the ene–yne conjugation formed through the topological 1,4-addition polymerization of the diyne units.

### Introduction

Topological polymerization of preorganized monomers can be used to control the structures of polymers at both the molecular and the supramolecular levels, which is vital for the preparation of unique materials with interesting properties that cannot be achieved by conventional polymerization.<sup>1</sup> Along this line, the favorable packing of diacetylene compounds has attracted much attention because their noncovalently organized structures can be topologically polymerized to form the corresponding polydiacetylenes. Closely-packed suprastructures of properly designed diacetylenes undergo 1,4-addition polymerization upon UV or gamma irradiation.<sup>2</sup> Tremendous interest in polydiacetylenes (PDAs) arises from the extensive ene–yne conjugation in the polymer backbone, leading to unique optical and electronic properties that are promising in a variety of applications such as chemical sensors,<sup>3</sup> biosensors,<sup>4</sup> nonlinear optical materials,<sup>5</sup> photoresists,<sup>6</sup> thermal,<sup>7</sup> and mechanical sensors.<sup>8</sup>

To make a polydiacetylene via topochemical polymerization, it is required that the monomer diyne units be arranged with a repeat distance ( $r$ ) of  $\sim 5$  Å and an orientation angle ( $\theta$ ) of  $\sim 45^\circ$  relative to the translation axis, as shown in Figure 1.<sup>9</sup> These packing requirements limit the shape and size of the substituents (R) on diynes in that the sterically bulky substituents usually preclude the topopolymerization.<sup>10</sup> Due to this limitation, the design of molecules that can undergo intramolecular 1,4-addition reaction of diyne units is challenging and, to our knowledge, has not been reported.

Bisdiyne incorporated within an alkyl chain had been studied for topological polymerization in Langmuir–Blodgett films.<sup>11</sup> However, the mode of topological polymerization was purely intermolecular as the diyne units were not restricted to the parallel alignment. A molecule containing multiple diyne units aligned in an appropriate direction is required to demonstrate an intramolecular 1,4-addition reaction between the diyne groups.

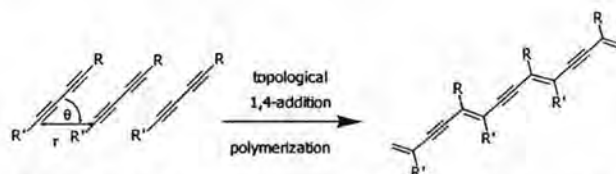


Figure 1. Packing parameters,  $r = \sim 5$  Å and  $\theta = \sim 45^\circ$ , required for the topological polymerization of a diacetylene monomer.

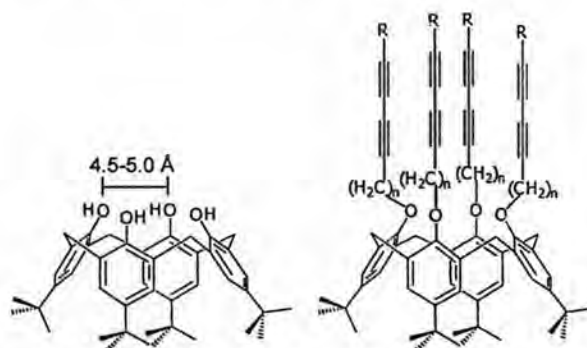


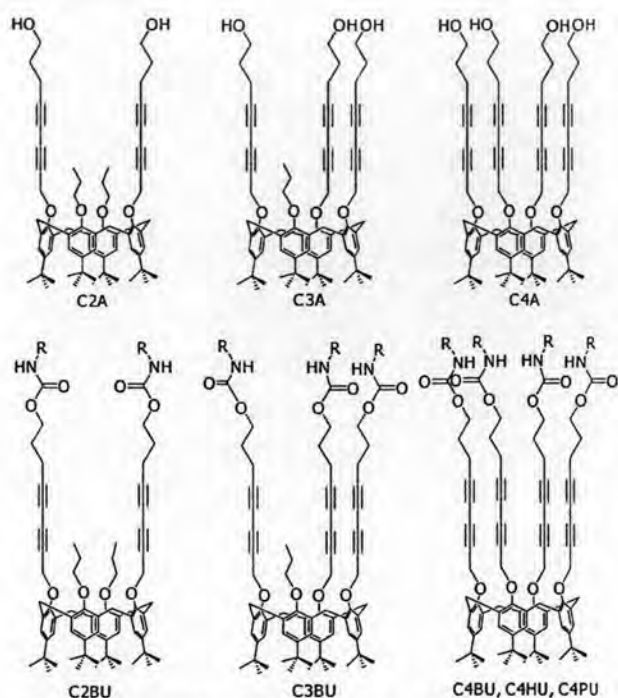
Figure 2. The structures of *tert*-butylcalix[4]arene and its tetra diyne derivative.

Calix[4]arene has a unique three-dimensional cavity-shaped architecture that its derivatives exhibit interesting supramolecular binding behaviors in solution,<sup>12</sup> and in the solid state.<sup>13</sup> The self-assembled PDA/*tert*-butylcalix[4]arene bilayer on gold surface acts as a chemically sensitive interface for surface acoustic wave mass balances in vapor-phase sensing applications.<sup>14</sup> With the knowledge that *tert*-butylcalix[4]arene having four squarely arranged hydroxyl groups has a preorganized basket like structure and the distance between the neighboring hydroxyl groups is 4.5–5.0 Å (Figure 2),<sup>15</sup> we contemplated that its derivatives containing multiple diyne units may undergo topological polymerization to form PDA-containing *tert*-butylcalix[4]arene. Study of topological polymerization of *tert*-butylcalix[4]arene mounted with multiple diyne chains will not

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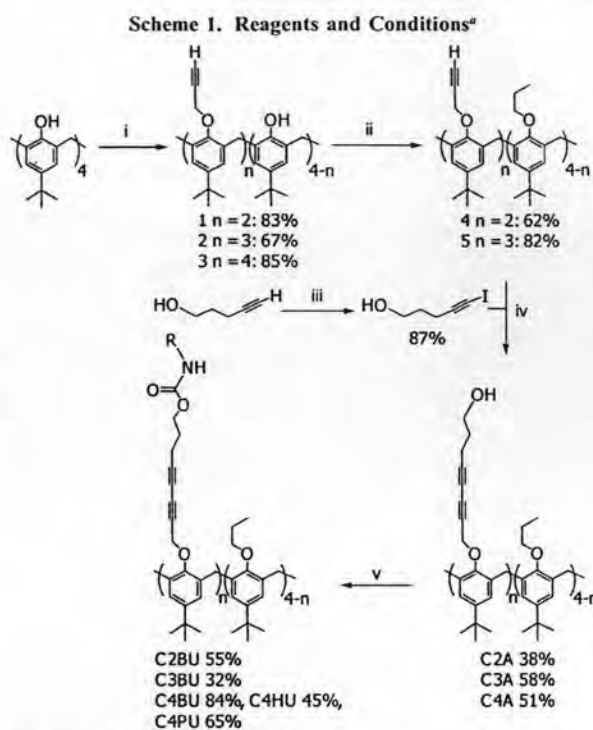
**Figure 3.** The structures of calix[4]arenes containing multiple diyne units synthesized in this work. The letters B, H, and P denote R = butyl, hexyl, and phenyl, respectively.

only be mechanistically interesting but may also give novel interesting sensing materials.

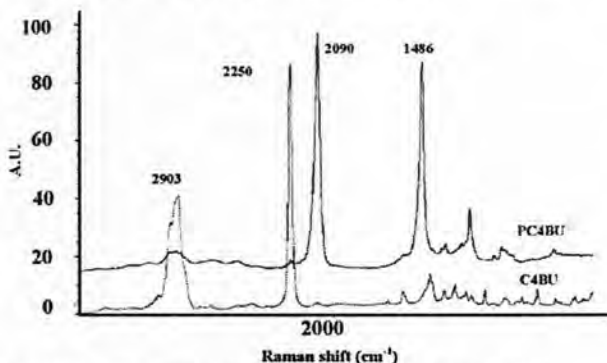
## Results and Discussion

**Synthesis of Calix[4]arenes Containing Multiple Diyne Units.** Calix[4]arenes mounted with two, three, and four diyne units (Figure 3) were synthesized and studied for their possibility to undergo topological 1,4-addition polymerization. The synthesis was started from multiple *O*-alkylation of *tert*-butylcalix[4]arene with appropriate equivalents of propargyl bromide in the presence of a suitable inorganic base at reflux temperature.<sup>16–18</sup> Di-, tri-, and tetrapropargyl-*tert*-butylcalix[4]arenes were obtained in 65–85% yields (Scheme 1). The remaining phenolic hydroxyl groups of di- and tripropargyl-*tert*-butylcalix[4]arene were protected with propyl group prior to the subsequent coupling to form the diynes. The Cadiot–Chodkiewicz coupling<sup>19</sup> of the propargyl substituted *tert*-butylcalix[4]arenes with 5-iodo-4-pentynol afforded the desired calix[4]arenes containing multiple diyne units in good yields. The iodine-terminated alkyne used in the coupling step was generated from the iodination of 4-pentyn-1-ol with iodine in the presence of morpholine base.<sup>20</sup> Further modification of the hydroxyl end of the diyne chains to carbamate (urethane) was accomplished by the addition of hydroxyl group to an isocyanate. Unless commercially available, the isocyanates were generated in situ from the corresponding amine by reacting with triphosgene using triethylamine as a base in dry chloroform in the presence of dibutyltindilaurate as a catalyst.<sup>21</sup> All diacetylene products were purified by column chromatography until their <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were clean. The elemental analysis was used to confirm their purity prior to the study of their photopolymerization.

**Solid-State Photopolymerization of *tert*-Butylcalix[4]arene Containing Four Diyne Units.** UV irradiation (TUV 15W/G15 T18 lamp, Philips, Holland) at a distance of 30 cm of C4A, C4BU, C4HU, and C4PU powders showed that the white color



<sup>a</sup> Key: (i) Propargyl bromide, K<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>CN, reflux for *n* = 2 and 4; Ba(OH)<sub>2</sub>·8H<sub>2</sub>O, BaO, THF, reflux for *n* = 3; (ii) NaH, propyl bromide, THF, Reflux; (iii) I<sub>2</sub>, morpholine, toluene; (iv) CuI, pyrrolidine; (v) R–N=C=O, dibutyltindilaurate, THF.



**Figure 4.** FT-Raman spectra of C4BU and PC4BU (in KBr).







of C4BU and C4HU rapidly turned into intense red color (within 5 min) while the white color of C4A and C4PU solids were virtually unchanged upon long exposure to UV irradiation (30 min) (Table 1). The intense color change of a diacetylene solid after UV irradiation typically signifies the formation of extensive ene–yne conjugation resulting from the topological 1,4-addition polymerization of the diyne units. Dissolution of the irradiated C4BU and C4HU in chloroform gave solutions of C4BU and C4HU (confirmed by TLC and NMR) and insoluble red powders. No significant insoluble solid was observed in the dissolution of irradiated C4A and C4PU in chloroform, and the soluble materials were identified as the starting C4A and C4PU. The red insoluble solids obtained from the irradiation of C4BU and C4HU are thus likely to be polydiacetylenes of the corresponding monomers which will be denoted as PC4BU and PC4HU, respectively, for later discussion.

Due to its low penetration power, UV irradiation is known to lead to only surface reaction on the solid. To obtain higher

**Table 1. Color Change of *tert*-Butylcalix[4]arene Derivatives Containing Four Diyne Units upon Exposure to UV Irradiation for 30 min**

| Compound | Color              |                   |
|----------|--------------------|-------------------|
|          | Before irradiation | After irradiation |
| C4A      | white              | white             |
| C4BU     | white              | red               |
| C4HU     | white              | red               |
| C4PU     | light yellow       | yellow            |

**Table 2. Dispersion of PC4BU in Tetrahydrofuran and *N,N*-Dimethylformamide under Sonication and the Storage Stability of the Dispersion**

| Solvent                       | Appearance  |   |   |
|-------------------------------|---|---|---|
|                               | Before sonication   | After sonication  | After 2 month in refrigerator   |
| Tetrahydrofuran               |  |  |  |
| <i>N,N</i> -Dimethylformamide |  |  |  |

yields of PC4BU and PC4HU for a more definitive characterization, the polymerization was conducted by exposing C4BU and C4HU to 50 Mrad of  $\gamma$  radiation from  $^{60}\text{Co}$ . The resulting deep red polymerized solid was dissolved in tetrahydrofuran with the assistance of ultrasonication. The red solution was filtered through a 0.45  $\mu\text{m}$  cellulose acetate filter and concentrated under reduced pressure. The concentrated crude was dropped into methanol at room temperature to give a red insoluble precipitate. The precipitate was collected by filtration and dried under vacuum to afford pure red polydiacetylene (45% yield for PC4BU).

Raman scattering spectroscopy has been one of the most effective techniques to unambiguously characterize the ene-yne conjugation of polydiacetylenes especially for the insoluble polymers. The FT-Raman spectra of C4BU and PC4BU powders are shown in Figure 4. The spectrum of C4BU has a single  $\text{C}\equiv\text{C}$  stretching peak at  $2250\text{ cm}^{-1}$  associated with the internal diyne groups. The  $\text{C}\equiv\text{C}$  stretching peak shifts to lower energy at  $2090\text{ cm}^{-1}$  in the spectrum of PC4BU and a new  $\text{C}=\text{C}$  stretching peak appears at  $1486\text{ cm}^{-1}$ , confirming the presence of ene-yne conjugation in the red PC4BU powder.

Initially, PC4BU appeared to be insoluble in all solvents tested. The polymer however formed clear red solution when sonicated in dimethylformamide or tetrahydrofuran for 5 min. The solution (5% w/w) was stable upon standing in refrigerator for months without noticeable precipitation as shown in Table 2. The electronic spectra of C4BU and PC4BU in tetrahydrofuran are shown in Figure 5 (For clarity sake, the similar spectra of C4HU and PC4HU are not included in the figure.) The spectrum of C4BU has no visible absorption, while that of PC4BU shows a broad absorption band in the range of 350–620 nm with maximum absorption peaks at 440 and 560 nm.

Due to the rigidity of the preorganized *tert*-butylcalix[4]arene platform, the topological 1,4-addition polymerization of the four diyne units of C4BU is most likely to proceed through a parallel intramolecular 1,4-addition (Scheme 2). The observation of polydiacetylene from C4BU thus provided us the first evidence

of the intramolecular 1,4-addition of diynes. The resulting polydiacetylene also possesses intriguing molecular architecture containing a parallel conjugated ene-yne backbone with *tert*-butylcalix[4]arene as hollow side chains.

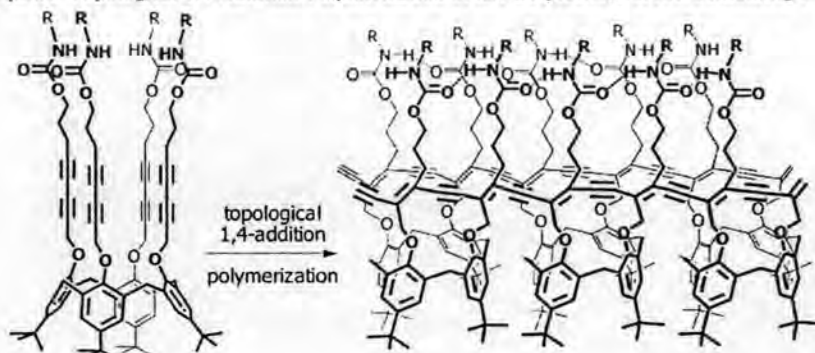
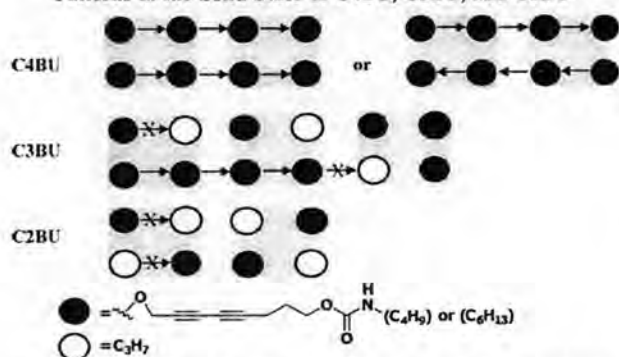
The good solubility of PC4BU and PC4HU in tetrahydrofuran indicated that the polymers were not crosslinked and allowed the molecular weight determination by gel permeation chromatography (GPC). The molecular weights of PC4BU and PC4HU were determined from the tetrahydrofuran eluted GPC chromatograms calculated against polystyrene standards using a universal calibration method. The GPC chromatograms of the purified PC4BU and the crude PC4HU have common bimodal features (Figure 6). The monomer peak appearing in the chromatogram of crude PC4HU but not in the chromatogram of purified PC4BU indicates that the purification of the polymers by precipitation is effective. The number average molecular weights of PC4BU are  $3.62 \times 10^5\text{ Da}$  ( $M_w/M_n = 1.08$ ) and  $5.31 \times 10^4\text{ Da}$  ( $M_w/M_n = 1.13$ ), and those of PC4HU are  $7.39 \times 10^5\text{ Da}$  ( $M_w/M_n = 1.03$ ),  $1.58 \times 10^5\text{ Da}$  ( $M_w/M_n = 1.03$ ), and  $1.01 \times 10^5\text{ Da}$  ( $M_w/M_n = 1.15$ ).

The inability to undergo topological polymerization of C4A indicated the importance of the carbamate group present at the movable end of the diyne chains. The strong hydrogen bonds among the carbamate groups in C4BU and C4HU are important for restraining the diyne units in an appropriate packing for topological polymerization. However, C4PU was also photoinactive despite having four carbamate groups probably due to the steric bulkiness of the phenyl end groups, preventing the intimate packing of the diyne chains.

**Solid-State Polymerization of *tert*-Butylcalix[4]arene Containing Two and Three Diyne Units.** The C2BU powder did not change its color while the color of C3BU powder changed to orange upon exposure to UV light. These results suggested that C2BU is photoinactive while C3BU can topologically polymerize somewhat but not as extensive as C4BU does. The difference in topological polymerizability of *tert*-butylcalix[4]arene containing different number of diyne units maybe explained by the molecular packing in the solid state of the monomers. For C4BU to be effectively polymerized topologically, the calix[4]arene cones must arrange themselves in the same direction that will allow the diyne units to align side by side. This arrangement can be continued for at least in each row of C4BU molecules and can be attributed to inter- and intramolecular hydrogen bonding among the carbamate groups (Scheme 3). For C3BU, the same molecular arrangement is subjected to the possibility of some defects because of one missing diyne unit per each monomeric molecule. The topological polymerization of C3BU thus cannot proceed very far. With two diyne units missing, C2BU will not have any continuous alignment of the diyne units beyond two consecutive units, and thus its topological polymerization is totally forbidden. This packing analysis confirms that the topological polymerization of C4BU operates through parallel or antiparallel 1,4-addition involving both inter- and intramolecular reactions.

## Conclusion

The derivatives of *tert*-butylcalix[4]arene containing two, three, and four diyne units were successfully synthesized. Only the derivatives that contain four diyne with *N*-alkyl carbamate moieties readily undergo solid-state topological photopolymerization to give ene-yne conjugated polydiacetylenes. The presence of carbamate groups is necessary for aligning the diynes through their continuous hydrogen bonding. The replacement one or two diyne units with a simple alkyl chain results

Scheme 2. Proposed Topological 1,4-Addition Polymerization of *tert*-Butylcalix[4]arene Containing Four Diyne UnitsScheme 3. Top View of the Proposed Molecular Packing Patterns in the Solid State of C4BU, C3BU, and C2BU<sup>a</sup>

<sup>a</sup> The arrow indicates the direction of the topological polymerization and X indicates the mismatched pair of the substituents to undergo the topological polymerization.

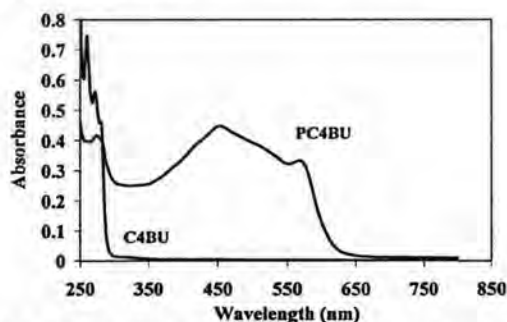


Figure 5. UV-vis spectra of 2.5 mM C4BU and 0.05 mM PC4BU in tetrahydrofuran.

in the reduction of the molecular symmetry and hence the topological polymerizability of the compound. The polymerizability of the tetra diyne derivatives provides not only the first evidence of the intramolecular 1,4-addition of diynes but also a route to synthesize some novel polydiacetylenes with interesting molecular architecture.

### Experimental Section

**Materials.** Propargyl bromide, iodine, morpholine, copper(I) iodide, pyrrolidine, propyl bromide, sodium hydride, potassium carbonate, barium oxide, barium hydroxide octahydrate, triethylamine, and butylamine were purchased from Fluka (Switzerland). Dibutyltindilaurate, 4-pentyn-1-ol, butylamine, hexyl isocyanate, phenyl isocyanate, and triphosgene were purchased from Aldrich (USA). Butyl isocyanate was purchased from Merck (Germany) and used without further purification. *tert*-butylcalix[4]arene was prepared according to the literature.<sup>22</sup> Tetrahydrofuran was distilled

over sodium and benzophenone, and acetonitrile was distilled over calcium hydride and stored over molecular sieves. Other analytical grade solvents were used as received without further distillation. Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. Column chromatography was performed using Merck silica gel 60 (70–230 mesh).

**Analytical Instruments.** <sup>1</sup>H spectra were recorded on Varian Mercury 400 MHz NMR spectrometer (Varian, USA) and AC Bruker 200, 250, and 500 MHz NMR spectrometer (Bruker, USA) using the residual solvent proton resonance of CDCl<sub>3</sub> at 7.26 ppm as the reference. <sup>13</sup>C NMR spectra were recorded on the same instruments as <sup>1</sup>H NMR and the data are provided in Supporting Information. Elemental analysis was performed on PE 2400 Series II (Perkin-Elmer, USA). Infrared spectra (data provided in Supporting Information) were measured from KBr pellets on a Nicolet Impact 410 FT-IR spectrophotometer (Thermo Nicolet, USA). UV-vis spectra were recorded on Varian Cary 100 Bio UV-vis spectrophotometer (Varian, USA). The melting points were recorded on a Mettler Toledo DSC 823c (Mettler Toledo, USA) instrument with an aluminum standard cell (40 μL) as a holder at a heating rate of 10 °C/min. The FT-Raman experiments were performed by exciting neat solid samples with a cw Nd:YAG laser at 1.064 μm, and the Raman spectra were recorded on the same IR spectrometer with Raman accessories using 180° optical collection geometry. GPC analysis was measured on a Water system (Waters, USA) with a Water 600 pump, a Water 2414 refractive index detector, and a set of Styragel columns (HR1, HR3, and HR4) at 35 °C using tetrahydrofuran as an eluent at a flow rate of 1.00 mL/min.

**Synthesis Procedures.** *25,27-Dipropargyloxy-26,28-dihydroxy-tert-butylcalix[4]arene (1)*. A mixture of potassium carbonate (1.71 g, 12.34 mmol) and *tert*-butylcalix[4]arene (4.01 g, 6.18 mmol) in acetonitrile (200 mL) was stirred at room temperature for 1 h. A solution of propargyl bromide (1.24 g, 12.98 mmol) in acetonitrile (50 mL) was added dropwise into the stirred mixture over 30 min. The reaction mixture was refluxed for 48 h and was then allowed to cool to room temperature. The reaction mixture was filtered to remove insoluble particles, and the filtrate was concentrated in a rotating evaporator. To the concentrated reaction mixture was added 2 M HCl (100 mL) and then extracted with dichloromethane (3 × 100 mL). The combined organic extracts were washed with brine (100 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated to dryness in vacuo. The crude mixture was crystallized from CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH to afford **1** as a white solid (3.72 g, 83% yield). Mp: 232 °C (decomposed). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 7.13 (s, 4H, Ar-H), 6.78 (s, 4H, Ar-H), 6.55 (s, 2H, OH), 4.80 (d, *J* = 4.0 Hz, 4H, OCH<sub>2</sub>), 4.42 (d, *J* = 14.0 Hz, 4H, ArCH<sub>2</sub>Ar), 3.38 (d, *J* = 14.0 Hz, 4H, ArCH<sub>2</sub>Ar), 2.58 (t, *J* = 4.0 Hz, 2H, C≡CH), 1.35 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>), 0.94 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>).

*25,26,27-Tripargyloxy-28-hydroxy-tert-butylcalix[4]arene (2)*. A mixture of Ba(OH)<sub>2</sub>·8H<sub>2</sub>O (3.66 g, 11.60 mmol), BaO (1.02 g, 6.63 mmol), and *tert*-butylcalix[4]arene (2.15 g, 3.31 mmol) were dissolved in tetrahydrofuran (50.0 mL), and the solution was stirred at room temperature for 1 h. A solution of propargyl bromide (4.93 g, 33.0 mmol) in tetrahydrofuran (30 mL) was added dropwise into

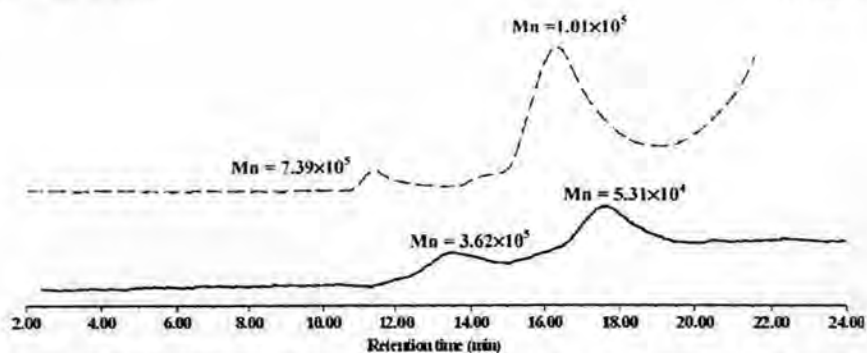


Figure 6. GPC traces of purified PC4BU (solid line) and crude PC4HU (dash line) using tetrahydrofuran as an eluent.

the stirred mixture over 30 min. The reaction mixture was refluxed for 48 h and was then allowed to cool to room temperature. The reaction mixture was filtered to remove insoluble particles, and the filtrate was concentrated in a rotating evaporator. To the concentrated reaction mixture was added 2 M HCl (50 mL) and then extracted with dichloromethane ( $3 \times 60$  mL). The combined organic extracts were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and filtered, and the solvent was removed to give a brown oily residue. The residue was purified by column chromatography with dichloromethane/hexane (15/85) to give **2** as a white solid (67% yield, 1.69 g). Mp: 157 °C.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.18 (s, 2H, Ar-H), 7.13 (s, 2H, Ar-H), 6.63 (s, 2H, Ar-H), 6.59 (s, 2H, Ar-H), 5.83 (s, 1H, OH), 5.08 (d,  $J = 2.5$  Hz, 2H,  $\text{OCH}_2$ ), 4.70 (d,  $J = 3.0$  Hz, 4H,  $\text{OCH}_2$ ), 4.66 (d,  $J = 14.0$  Hz, 2H,  $\text{ArCH}_2\text{Ar}$ ), 4.43 (d,  $J = 14.0$  Hz, 2H,  $\text{ArCH}_2\text{Ar}$ ), 3.36 (d,  $J = 14.0$  Hz, 2H,  $\text{ArCH}_2\text{Ar}$ ), 3.27 (d,  $J = 14.0$  Hz, 2H,  $\text{ArCH}_2\text{Ar}$ ), 2.56 (t,  $J = 3.0$  Hz, 2H,  $\text{C}\equiv\text{CH}$ ), 2.50 (t,  $J = 2.5$  Hz, 1H,  $\text{C}\equiv\text{CH}$ ), 1.37 (s, 18H,  $(\text{CH}_3)_3$ ), 0.90 (s, 9H,  $(\text{CH}_3)_3$ ), 0.89 (s, 9H,  $(\text{CH}_3)_3$ ).

**25,26,27,28-Tetra(propargyloxy)-tert-butylcalix[4]arene (3).** A mixture of potassium carbonate (43.37 g, 313.76 mmol) and tert-butylcalix[4]arene (10.18 g, 15.68 mmol) in acetonitrile (200 mL) was stirred at room temperature for 1 h. A solution of propargyl bromide (23.33 g, 156.88 mmol) in acetonitrile (50 mL) was added dropwise into the stirred mixture over 30 min. The reaction mixture was allowed to reflux for 48 h and then allowed to cool to room temperature. The reaction mixture was filtered to remove insoluble particles, and the filtrate was concentrated in a rotating evaporator. To the concentrated reaction mixture was added 2 M HCl (100 mL) and then extracted with dichloromethane ( $3 \times 100$  mL). The combined organic extracts were washed with brine (100 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and evaporated to dryness in vacuo. The crude mixture was crystallized from  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  to afford **3** as a white solid (10.68 g, 85% yield). Mp: 107 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.78 (s, 8H, Ar-H), 4.80 (d,  $J = 2.4$  Hz, 8H,  $\text{OCH}_2$ ), 4.60 (d,  $J = 13.2$  Hz, 4H,  $\text{ArCH}_2\text{Ar}$ ), 3.16 (d,  $J = 13.2$  Hz, 4H,  $\text{ArCH}_2\text{Ar}$ ), 2.48 (t,  $J = 2.4$  Hz, 3H,  $\text{C}\equiv\text{CH}$ ), 1.07 (s, 36H,  $(\text{CH}_3)_3$ ).

**25,27-Dipropargyloxy-26,28-dipropyl-tert-butylcalix[4]arene (4).** **1** (1.03 g, 1.42 mmol) and NaH (0.40 g, 14.16 mmol), which was washed with hexane ( $3 \times 10$  mL), were dissolved in tetrahydrofuran (20 mL), and the solution was stirred at room temperature for 1 h. Then a solution of propyl bromide (1.74 g, 14.16 mmol) in tetrahydrofuran (20 mL) was added dropwise to the above mixture. After the addition was complete, the reaction mixture was allowed to reflux for 24 h. The reaction mixture was then allowed to cool to room temperature and quenched with ethanol (20 mL). The solvent was removed in vacuo to obtain a yellow residue, and then the residue was extracted with dichloromethane ( $3 \times 30$  mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and filtered, and the solvent was removed in vacuo to give a brown oily residue. The residue was isolated by column chromatography with dichloromethane as an eluent to afford **4** as a white solid (0.35 g, 31% yield). Mp: 190 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.09 (s, 4H, Ar-H), 6.45 (s, 4H, Ar-H), 5.02 (s,  $J = 2.4$  Hz, 4H,  $\text{OCH}_2\text{Ar}$ ), 4.52 (d,  $J = 12.0$  Hz, 4H,  $\text{ArCH}_2\text{Ar}$ ),

3.71 (t,  $J = 6.0$  Hz, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 3.14 (d,  $J = 12.0$  Hz, 4H,  $\text{ArCH}_2\text{Ar}$ ), 2.39 (t,  $J = 2.4$  Hz, 3H,  $\text{C}\equiv\text{CH}$ ), 2.00 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.33 (s, 18H,  $(\text{CH}_3)_3$ ), 1.05 (t,  $J = 6.0$  Hz, 6H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.83 (s, 18H,  $(\text{CH}_3)_3$ ).

**25,26,27-Tripargyloxy-28-propyl-tert-butylcalix[4]arene (5).** **2** (0.93 g, 1.22 mmol) and NaH (0.15 g, 6.08 mmol), which was washed with hexane ( $3 \times 10$  mL), were dissolved in tetrahydrofuran (20 mL), and the solution was stirred at room temperature for 1 h. Then a solution of propyl bromide (0.75 g, 6.08 mmol) in tetrahydrofuran (20 mL) was added by dropwise to the above mixture. After the addition was complete, the reaction mixture was allowed to reflux for 24 h. The reaction mixture was then allowed to cool to room temperature and quenched with ethanol (20 mL). The solvent was removed in vacuo to obtain a yellow residue, and then the residue was extracted with dichloromethane ( $3 \times 30$  mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and filtered, and the solvent was removed in vacuo to give a brown oily residue. The residue was isolated by column chromatography with dichloromethane as an eluent to afford **5** as a white solid (0.80 g, 82% yield). Mp: 140 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.00 (s, 2H, Ar-H), 6.98 (s, 2H, Ar-H), 6.60 (s, 2H, Ar-H), 6.54 (s, 2H, Ar-H), 4.98 (d,  $J = 2.4$  Hz, 2H,  $\text{CH}_2\text{C}\equiv\text{C}$ ), 4.89 (d,  $J = 2.4$  Hz, 2H,  $\text{CH}_2\text{C}\equiv\text{C}$ ), 4.63 (d,  $J = 2.0$  Hz, 2H,  $\text{CH}_2\text{C}\equiv\text{C}$ ), 4.59 (d,  $J = 12.5$  Hz, 2H,  $\text{ArCH}_2\text{Ar}$ ), 4.51 (d,  $J = 12.5$  Hz, 2H,  $\text{ArCH}_2\text{Ar}$ ), 3.76 (t,  $J = 7.4$  Hz, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 3.17 (d,  $J = 5.6$  Hz, 2H,  $\text{ArCH}_2\text{Ar}$ ), 3.13 (d,  $J = 5.6$  Hz, 2H,  $\text{ArCH}_2\text{Ar}$ ), 2.4 (t,  $J = 2.0$  Hz, 1H,  $\text{C}\equiv\text{CH}$ ), 2.44 (t,  $J = 2.4$  Hz, 2H,  $\text{C}\equiv\text{CH}$ ), 2.00 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.28 (s, 18H,  $(\text{CH}_3)_3$ ), 1.07 (t,  $J = 7.4$  Hz, 3H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.96 (s, 9H,  $(\text{CH}_3)_3$ ), 0.94 (s, 9H,  $(\text{CH}_3)_3$ ).

**5-Iodo-4-pentynol.** A solution of morpholine (33.25 mL, 381.60 mmol) in toluene (350 mL) at 45 °C was treated with iodine (13.56 g, 53.42 mmol) shielded from light and stirred for 1 h. A solution of 4-pentyn-1-ol (3.21 g, 38.16 mmol) in toluene (30 mL) was added and the reaction mixture was stirred at 45 °C for 1 h. The reaction mixture was cooled to room temperature and filtered to remove the salt. The filtrate was poured over a mixture of diethylether (200 mL) and a saturated aqueous solution of  $\text{Na}_2\text{S}_2\text{O}_3$  (100 mL) and shaken vigorously until the organic layer was colorless. The organic layer was separated, washed with  $\text{Na}_2\text{S}_2\text{O}_3$  (100 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, concentrated, and purified by column chromatography (ethyl acetate/hexane = 7/93) to afford 5-iodo-4-pentynol as a light yellow oil (6.97 g, 87% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.78 (t,  $J = 6.0$  Hz, 2H,  $\text{CH}_2\text{OH}$ ), 2.53 (t,  $J = 6.0$  Hz, 2H,  $\text{C}\equiv\text{CCH}_2$ ), 1.80 (quintet,  $J = 6.0$  Hz, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ), 1.61 (br s, 1H, OH).

**25,27-Di(octa-4,6-diyne-1-ol)oxy-26,28-dipropyl-tert-butylcalix[4]arene (C2A).** To a stirred solution of **4** (0.22 g, 0.27 mmol) and 5-iodo-4-pentynol (0.28 g, 1.34 mmol) in pyrrolidine (1.0 mL) was added copper(I) iodide (0.01 g, 0.05 mmol). After the reaction mixture was stirred at room temperature for 2 h, it was hydrolyzed with a saturated aqueous solution of ammonium chloride (30 mL) and extracted with diethyl ether ( $3 \times 50$  mL). The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and filtered, and the solvent was removed in vacuo. The crude product was purified by

column chromatography (dichloromethane/ethyl acetate = 10/90) to obtain C2A as a light yellow solid (0.10 g, 38% yield). Mp: 168 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.09 (s, 4H, Ar-H), 6.43 (s, 4H, Ar-H), 5.01 (s, 4H, OCH<sub>2</sub>C≡C), 4.48 (d, *J* = 13.6 Hz, 4H, ArCH<sub>2</sub>Ar), 3.76 (t, *J* = 6.0 Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.71 (t, *J* = 7.5 Hz, 4H, CH<sub>2</sub>OH), 3.14 (d, *J* = 13.6 Hz, 4H, ArCH<sub>2</sub>Ar), 2.43 (t, *J* = 7.5 Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 2.00 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.81 (quintet, *J* = 7.5 Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>OH), 1.33 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>), 1.05 (t, *J* = 6.0 Hz, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.82 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>).

**25,26,27-Tri(octa-4,6-diyne-1-ol)oxy-28-propyl-tert-butylcalix[4]arene (C3A).** To a stirred solution of **5** (0.24 g, 0.30 mmol) and 5-iodo-4-pentynol (0.36 g, 1.79 mmol) in pyrrolidine (2.00 mL) was added copper(I) iodide (0.02 g, 0.08 mmol). After the reaction mixture was stirred at room temperature for 2 h, it was hydrolyzed with a saturated aqueous solution of ammonium chloride (30 mL) and extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered, and the solvent was removed in vacuo. The crude product was purified by column chromatography (dichloromethane/ethyl acetate = 50/50) to give C3A as a light yellow solid (0.18 g, 58% yield). Mp: 145 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.00 (s, 4H, Ar-H), 6.58 (s, 2H, Ar-H), 6.51 (s, 2H, Ar-H), 5.01 (s, 2H, CH<sub>2</sub>C≡C), 4.87 (s, 2H, CH<sub>2</sub>C≡C), 4.71 (s, 2H, CH<sub>2</sub>C≡C), 4.55 (d, *J* = 12.5 Hz, 2H, ArCH<sub>2</sub>Ar), 4.46 (d, *J* = 12.5 Hz, 2H, ArCH<sub>2</sub>Ar), 3.76 (m, 8H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> and CH<sub>2</sub>OH), 3.17 (d, *J* = 6.4 Hz, 2H, ArCH<sub>2</sub>Ar), 3.14 (d, *J* = 6.4 Hz, 2H, ArCH<sub>2</sub>Ar), 2.44 (t, *J* = 6.6 Hz, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 2.00 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.81 (m, 6H, CH<sub>2</sub>CH<sub>2</sub>OH), 1.25 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>), 1.08 (t, *J* = 7.4 Hz, 3H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.92 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>), 0.87 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>).

**25,26,27,28-Tetra(octa-4,6-diyne-1-ol)oxy-tert-butylcalix[4]arene (C4A).** To a stirred solution of **3** (4.18 g, 5.22 mmol), and 5-iodo-4-pentynol (10.96 g, 52.18 mmol) in pyrrolidine (40.00 mL) was added copper(I) iodide (0.40 g, 2.09 mmol). After the reaction mixture was stirred at room temperature for 2 h, it was hydrolyzed with a saturated aqueous solution of ammonium chloride (200 mL) and extracted with diethyl ether (3 × 150 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered, and the solvent was removed in vacuo. The crude product was purified by column chromatography (ethyl acetate) to afford C4A as a light yellow solid (2.73 g, 51% yield). Mp: 212 °C (decomposed). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.77 (s, 8H, Ar-H), 4.82 (s, 8H, OCH<sub>2</sub>), 4.53 (d, *J* = 13.2 Hz, 4H, ArCH<sub>2</sub>Ar), 3.77 (t, *J* = 7.0 Hz, 8H, CH<sub>2</sub>OH), 3.17 (d, *J* = 13.2 Hz, 4H, ArCH<sub>2</sub>Ar), 2.45 (t, *J* = 7.0 Hz, 8H, C≡CCH<sub>2</sub>), 1.90 (bs, 1H, OH), 1.81 (quintet, *J* = 7.0 Hz, 8H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.07 (s, 36H, (CH<sub>3</sub>)<sub>3</sub>).

#### Urethane Formation of C2BU and C3BU. General Procedure for Synthesis.

Butylamine was dissolved in chloroform. Triphosgene was gradually added to this solution with stirring. Triethylamine was added dropwise to this stirred mixture (a water bath may be needed to keep the temperature below 30 °C). The reaction mixture was refluxed for 2 h before diacetylenic alcohol-*tert*-butylcalix[4]arene derivatives [C2A or C3A] and dibutyltindilaurate were added. The stirring was continued for 10 h at room temperature. The solvent was evaporated, and the residue was redissolved in hexane. The resulting solution was filtered, and the solid was washed several times with hexane. The filtrate was collected, and the solvent was evaporated. The residue was eluted through a silica gel column.

**25,27-Di(octa-4,6-diyne-1-ol-(carboxy-butyl-urethane))oxy-26,28-dipropyl-tert-butylcalix[4]arene (C2BU).** C2BU was synthesized according to the above urethane formation procedure from C2A (0.07 g, 0.07 mmol), butylamine (0.32 g, 4.32 mmol), triphosgene (0.43 g, 1.44 mmol), triethylamine (1.20 mL, 8.63 mmol), and dibutyltindilaurate (0.18 g, 0.29 mmol) in chloroform (10 mL) and purified by column chromatography (ethyl acetate/dichloromethane = 1/99). A light yellow solid (0.05 g, 55% yield) was obtained. Mp: 100 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.09 (s, 4H, Ar-H), 6.42 (s, 4H, Ar-H), 5.01 (s, 4H, OCH<sub>2</sub>C≡C), 4.69 (br s, 2H, NH), 4.48 (d, *J* = 13.6 Hz, 4H, ArCH<sub>2</sub>Ar), 4.12 (t, *J* = 5.8 Hz, 4H, OCOCH<sub>2</sub>), 3.70 (t, *J* = 6.0 Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.14 (m, *J* = 13.6 Hz, 8H, ArCH<sub>2</sub>Ar and NCH<sub>2</sub>), 2.38 (t, *J* = 6.6 Hz, 4H, C≡

CCH<sub>2</sub>), 2.00 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.84 (quintet, *J* = 5.8 Hz, 4H, C≡CCH<sub>2</sub>CH<sub>2</sub>), 1.47 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.32 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>), 1.05 (t, *J* = 6.0 Hz, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.92 (m, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.81 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd for C<sub>76</sub>H<sub>102</sub>N<sub>2</sub>O<sub>8</sub>: C, 77.91; H, 8.77; N, 2.89. Found: C, 76.28; H, 8.43; N, 3.19.

**25,26,27-Tri(octa-4,6-diyne-1-ol-(carboxy-butyl-urethane))oxy-28-propyl-tert-butylcalix[4]arene (C3BU).** C3BU was synthesized according to the above urethane formation procedure from C3A (0.07 g, 0.07 mmol), butylamine (0.07 g, 1.00 mmol), triphosgene (0.10 g, 0.30 mmol), triethylamine (0.28 mL, 2.00 mmol), and dibutyltindilaurate (0.13 g, 0.21 mmol) in chloroform (10 mL) and purified by column chromatography (ethyl acetate/hexane = 15/85). A light yellow solid (0.03 g, 32% yield) was obtained. Mp: 117 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.00 (s, 4H, Ar-H), 6.56 (s, 2H, Ar-H), 6.50 (s, 2H, Ar-H), 4.99 (s, 2H, OCH<sub>2</sub>C≡C), 4.88 (s, 2H, OCH<sub>2</sub>C≡C), 4.80 (br s, 3H, NH), 4.70 (s, 2H, OCH<sub>2</sub>C≡C), 4.54 (d, *J* = 13.0 Hz, 2H, ArCH<sub>2</sub>Ar), 4.47 (d, *J* = 13.0 Hz, 2H, ArCH<sub>2</sub>Ar), 4.12 (t, *J* = 5.6 Hz, 6H, CH<sub>2</sub>OCO), 3.74 (t, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.15 (m, 10H, ArCH<sub>2</sub>Ar and NHCH<sub>2</sub>), 2.39 (t, *J* = 6.4 Hz, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCO), 2.03 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.86 (m, 6H, CH<sub>2</sub>CH<sub>2</sub>OCO), 1.47 (m, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.34 (m, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.25 (s, 18H, (CH<sub>3</sub>)<sub>3</sub>), 1.07 (m, 9H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.91 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>), 0.86 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd for C<sub>86</sub>H<sub>113</sub>N<sub>3</sub>O<sub>10</sub>: C, 76.58; H, 8.44; N, 3.12. Found: C, 74.40; H, 7.71; N, 3.21.

**Urethane Formation of C4BU, C4HU, and C4PU. General Procedure for Synthesis.** Diacetylenic alcohol-*tert*-butylcalix[4]arene derivatives and dibutyltindilaurate were dissolved in tetrahydrofuran, and R-N=C=O (commercially available) was added dropwise to this solution with stirring at 0 °C. The mixture was allowed to warm up to room temperature and the stirring was continued for another 2 h before ice/water was added. Tetrahydrofuran was evaporated, and the aqueous residue was extracted several times with CH<sub>2</sub>Cl<sub>2</sub> and brine. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered, and the solvent was removed in vacuo. The crude product was eluted through a silica gel column.

**25,26,27,28-Tetra(octa-4,6-diyne-1-ol-(carboxy-butyl-urethane))oxy-tert-butylcalix[4]arene (C4BU).** C4BU was synthesized according to the above urethane formation procedure from C4A (0.85 g, 0.75 mmol), butyl isocyanate (0.75 g, 7.53 mmol), and dibutyltindilaurate (1.90 g, 3.01 mmol) in tetrahydrofuran (20 mL) and purified by column chromatography (ethyl acetate/hexane = 45/55). A white solid (0.96 g, 84% yield) was obtained. Mp: 119 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.77 (s, 8H, Ar-H), 4.82 (s, 8H, OCH<sub>2</sub> and NH), 4.53 (d, *J* = 13.2 Hz, 4H, ArCH<sub>2</sub>Ar), 4.13 (t, *J* = 5.8 Hz, 8H, OCOCH<sub>2</sub>), 3.17 (m, 12H, ArCH<sub>2</sub>Ar and NCH<sub>2</sub>), 2.39 (t, *J* = 6.8 Hz, 8H, C≡CCH<sub>2</sub>CH<sub>2</sub>), 1.87 (quintet, *J* = 6.0 Hz, 8H, C≡CCH<sub>2</sub>CH<sub>2</sub>), 1.47 (quintet, *J* = 6.6 Hz, 8H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.33 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), 1.06 (s, 36H, (CH<sub>3</sub>)<sub>3</sub>), 0.95 (t, *J* = 7.4 Hz, 12H, CH<sub>3</sub>). Anal. Calcd for C<sub>96</sub>H<sub>124</sub>N<sub>4</sub>O<sub>12</sub>: C, 75.56; H, 8.19; N, 3.67. Found: C, 75.58; H, 8.39; N, 3.65. Raman: 2250 cm<sup>-1</sup> (—C≡C—C≡C—).

**25,26,27,28-Tetra(octa-4,6-diyne-1-ol-(carboxy-hexyl-urethane))oxy-tert-butylcalix[4]arene (C4HU).** C4HU was prepared as described above from C4A (0.54 g, 0.48 mmol), butyl isocyanate (0.61 g, 4.78 mmol), and dibutyltindilaurate (1.21 g, 1.91 mmol) in tetrahydrofuran (15 mL) and purified by column chromatography (ethyl acetate/hexane = 27/73). A white solid (0.35 g, 45% yield) was obtained. Mp: 103 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.76 (s, 8H, Ar-H), 4.91 (br s, NH), 4.80 (s, 8H, OCH<sub>2</sub>), 4.53 (d, *J* = 12.8 Hz, 4H, ArCH<sub>2</sub>Ar), 4.12 (t, *J* = 6.0 Hz, 8H, CH<sub>2</sub>OCO), 3.16 (d, *J* = 12.8 Hz, 4H, ArCH<sub>2</sub>Ar), 3.12 (t, *J* = 6.0 Hz, 8H, NHCH<sub>2</sub>), 2.38 (t, *J* = 6.4 Hz, 8H, C≡CCH<sub>2</sub>), 1.85 (quintet, *J* = 6.4 Hz, 8H, C≡CCH<sub>2</sub>CH<sub>2</sub>), 1.47 (m, 8H, NHCH<sub>2</sub>CH<sub>2</sub>), 1.27 (m, 24H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.05 (s, 36H, (CH<sub>3</sub>)<sub>3</sub>), 0.87 (t, *J* = 6.2 Hz, 12H, CH<sub>3</sub>). Anal. Calcd for C<sub>104</sub>H<sub>140</sub>N<sub>4</sub>O<sub>12</sub>: C, 76.25; H, 8.61; N, 3.42. Found: C, 76.24; H, 8.64; N, 3.76.

**25,26,27,28-Tetra(octa-4,6-diyne-1-ol-(carboxy-phenyl-urethane))oxy-tert-butylcalix[4]arene (C4PU).** C4PU was prepared as described above from C4A (0.36 g, 0.32 mmol), phenyl isocyanate



(0.38 g, 3.19 mmol), and dibutylindilaurate (0.81 g, 1.27 mmol) in tetrahydrofuran (15 mL) and purified by column chromatography (ethyl acetate/hexane = 22/78). A light yellow solid (0.33 g, 65% yield) was obtained. Mp: 107 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.37 (d, *J* = 8.0 Hz, 8H, *H*<sub>ortho-Ar</sub>), 7.28 (t, *J* = 8.0 Hz, 8H, *H*<sub>meta-Ar</sub>), 7.04 (t, *J* = 8.0 Hz, 4H, *H*<sub>para-Ar</sub>), 6.90 (br s, NH), 6.78 (s, 8H, *H*-Ar<sub>calix</sub>), 4.82 (s, 8H, OCH<sub>2</sub>), 4.54 (d, *J* = 12.8 Hz, 4H, ArCH<sub>2</sub>Ar), 4.27 (t, *J* = 6.0 Hz, 8H, OCOCH<sub>2</sub>), 3.18 (d, *J* = 12.8 Hz, 4H, ArCH<sub>2</sub>Ar), 2.44 (t, *J* = 7.0 Hz, 8H, C≡CCH<sub>2</sub>), 1.96 (m, 8H, CH<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>), 1.06 (s, 36H, (CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd for C<sub>104</sub>H<sub>108</sub>N<sub>4</sub>O<sub>12</sub>: C, 77.78; H, 6.78; N, 3.49. Found: C, 77.39; H, 6.78; N 3.24.

**Poly(25,26,27,28-Tetra[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]oxy-tert-butylcalix[4]arene) (PC4BU).** The monomer C4BU (50 mg) was exposed to 50 Mrad of  $\gamma$  radiation from <sup>60</sup>Co. The resulting deep red polymerized solid was dissolved in 20 mL tetrahydrofuran with the assistance of ultrasonication. The red solution was filtered through a 0.45  $\mu$ m cellulose acetate filter and concentrated to 2 mL under reduced pressure. The concentrated crude was dropped into methanol (100 mL) and stirred for 2 h at room temperature to give a red precipitate. The precipitate was collected by filtration and dried under vacuum to afford pure red polydiacetylene (23 mg, 45% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.05 (br, 8H), 6.77 (br, 8H), 4.97 (br, 8H), 4.82 (br, 8H), 4.54 (br, 8H), 4.15 (br), 4.00 (br), 3.12 (br), 2.39 (br, 8H). 1.66–0.90 (br). Raman: 2090 cm<sup>-1</sup> (—C≡C—), 1486 cm<sup>-1</sup> (—C=C—).

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**Supporting Information Available:** Preparation procedures and full spectroscopic data of all compounds synthesized. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Synthesis and Crystallographic Study of 1,6-bis-(*N*-phenothiazinyl)-2,4-hexadiyne

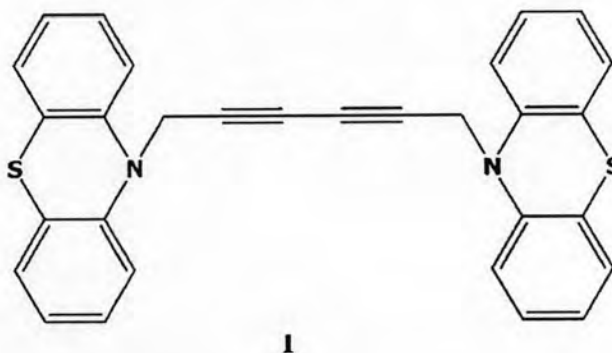
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*1,6-bis-(N-phenothiazinyl)-2,4-hexadiyne (I) was synthesized in high yield by oxidative coupling of N-propargyl phenothiazine. Grown from methylene chloride-hexane solution, I is a monoclinic crystal, space group C2/c  $a = 14.9500(18)$  Å;  $b = 13.5512(15)$  Å;  $c = 12.0116(10)$  Å;  $\beta = 102.628(9)^\circ$ ;  $V = 2374.6(4)$  Å<sup>3</sup>. The intermolecular distances and arrangement of I in the unit cell preclude the usual diacetylene reactivity.*



*Nevertheless, heating of I at 145°C results in decomposition of I to phenothiazine and a dark brown solid. In addition, cation-radicals of I were prepared by oxidation with nitrosonium tetrafluoroborate and iodine to give stable ion-radical salts.*

**Keywords** polydiacetylene, diacetylene monomer, X-ray crystal structure, thermal reactivity

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## Introduction

The initially synthesized polydiacetylene (PDA) single crystals did not exhibit electronic absorption at energies lower than the charge-transfer exciton (1). This situation changed with the report of electronic spectral features at energies lower than the exciton in the PDA of bis-*N*-ethyl-*p*-benzylidenemalononitrile of 2,4-hexadiyne (2). The new near infrared feature was associated with charge transfer from the electron-rich PDA backbone to the electron deficient cyano groups of the side chain (2). Such features were also observed in another PDA single crystal (3).

Interesting extensions of PDA crystals with a charge-transfer band would include PDA with a neutral-to-ionic transition (4). This might involve a material with an insulator-to-conductor transition leading to a single crystal specimen of a conducting polymer. Another approach to a single crystal conducting PDA would involve a monomer with a side group that would lead to a stable cation radical. Electron transfer from the electron-rich PDA backbone to an oxidized side group would result in a *p*-doped crystal. The list of potential side group precursors includes phenothiazines, dihydrophenazines, tetrathiafulvalenes, and *p*-phenylenediamines. In this paper we report the synthesis of **I**, the determination of its crystal and molecular structure, and an initial study of the solid-state reactivity of this monomer.

## Experimental

### Synthesis of 10-(prop-2-ynyl)-10*H*-phenothiazine (5)

In a flask with a reflux condenser, 5.0 g (25.0 mmol) of phenothiazine was dissolved in 50.0 mL anhydrous toluene under nitrogen. Sodium carbonate (3.98 g, 37.5 mmol) was added into the clear solution. After stirring for 1 h, 13.3 g (125.5 mmol) of propargyl bromide was added. The mixture was refluxed for 24 h and then mixed with 2M hydrochloric acid until the solution was acidic. The product was extracted with methylene chloride (100 mL  $\times$  2), and the organic layer was dried over anhydrous sodium sulfate. After purification by silica gel column chromatography with hexane as eluent, a pale yellow solid was obtained (4.4 g, 73% yield.), m.p. 91°C, IR (KBr,  $\text{cm}^{-1}$ )  $\nu_{\text{max}}$ : 3320, 1600  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  (ppm): 7.1 (m, 8H,  $\text{C}_6\text{H}_4$ ); 4.4 (d, 2H,  $\text{CH}_2$ ); 2.3 (t, 1H, CH).

### Synthesis of 1,6-bis-(*N*-phenothiazinyl)-2,4-hexadiyne (**I**, (6))

To a round-bottomed flask in a water bath at 28°C was added isopropanol (10.0 mL), copper (I) chloride (0.08 g, 0.8 mmol) and *N,N,N',N'*-tetramethylethylenediamine (0.1 g, 0.8 mmol).

Oxygen was bubbled into the solution as it was vigorously stirred. 2.0 g (8.4 mmol) of 10-(prop-2-ynyl)-10*H*-phenothiazine in isopropanol was added to the reaction mixture over a 15 min period in a dropwise manner. After the addition was complete, the reaction was continued for 5 h; then isopropanol was removed and 20 mL water containing 2 drops concentrated hydrochloric acid was added. The colorless solid was filtered, washed with a small amount of water, and dried under vacuum. A pale brown solid (3.2 g, 81%) that turned dark brown on heating at 200°C (decomposition) was obtained. IR (KBr,  $\text{cm}^{-1}$ )  $\nu_{\text{max}}$ : 1600  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  (ppm): 7.2 (m, 8H,  $\text{C}_6\text{H}_4$ ); 4.6 (s, 4H,  $\text{CH}_2$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , TMS)  $\delta$  (ppm): 144.3 ( $\text{C}_6\text{H}_4$ ); 128.0 ( $\text{C}_6\text{H}_4$ ); 127.5 ( $\text{C}_6\text{H}_4$ ); 123.8 ( $\text{C}_6\text{H}_4$ ); 123.5 ( $\text{C}_6\text{H}_4$ ); 115.1 ( $\text{C}_6\text{H}_4$ ); 75.0 (CC), 70.5 (CC); 39.5 ( $\text{CH}_2$ ).

#### *Preparation of Tetrafluoroborate Salt of I*

**I** (0.1 g, 0.2 mmol) was dissolved in methylene chloride; nitrosonium tetrafluoroborate (0.03 g, 0.2 mmol) was added at  $-40^{\circ}\text{C}$ , and the reaction mixture was stirred for 1 h. After removal of NO gas, hexane was added. The precipitate of the cation radical was filtered, washed with cold hexane, and dried under vacuum. It gave a turbid white solid (0.08 g, 82% yield) that turned dark on heating at  $155^{\circ}\text{C}$ .

#### *Preparation of Iodide Salt of I*

To a stirred solution of 0.1 g (0.2 mmol) of **I** in methylene chloride (10.0 ml) was added a solution of iodine (0.08 g, 0.6 mmol) in methylene chloride by a dropping funnel. The reaction mixture was stirred at  $0^{\circ}\text{C}$ . After 1 h, the solution was poured into aqueous sodium bicarbonate, the mixture was extracted with benzene, and the benzene was removed to give 0.08 g (80%) of **I** iodide salt as a pale red solid. The solid turned black on heating at  $180^{\circ}\text{C}$ .

#### *X-Ray Structure Determination*

Single crystals of **I** were obtained from a methylene chloride-hexane solution and mounted on a Pyrex fiber affixed to a brass pin. The crystal was optically centered and placed on an Enraf-Nonius CAD4-U diffractometer. X-ray data were collected using the Enraf-Nonius EXPRESS (7) program. The structure was solved by direct methods using SIR-92 (8) and refined using the Oxford CRYSTALS package (9,10). Non-hydrogen atoms were refined using anisotropic displacement parameters; hydrogen atoms were refined by using isotropic displacement parameters. Crystallographic data is presented in Table 1. CCDC 299079 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## Results and Discussion

### *Synthesis*

**I** was synthesized in high yield by oxidative coupling of *N*-propargyl phenothiazine according to Scheme 1.

The monomer became very dark after heating for 24 h at  $145^{\circ}\text{C}$  in a vacuum oven. After heating, phenothiazine itself was isolated as a colorless crystal and a dark brown solid as an unidentified product. Raman spectroscopy of the brown solid did not reveal the features expected for a PDA. From this result, it is indicated that **I** undergoes thermal decomposition at temperatures above  $145^{\circ}\text{C}$ . Note that bis-(3', 6'-dibromo-*N*-carbazolyl)-2,4-hexadiyne undergoes thermal reaction with a loss of 3,6-dibromocabazole and PDA formation (11).

The formation of cation-radical salts of **I** was studied. Salts of **I** were prepared by oxidation with nitrosonium tetrafluoroborate and iodine, respectively, to give stable ion-radical salts (Scheme 2).

### *Thermogravimetric Analysis of I and Iodide Salt*

TGA was carried out under nitrogen at a heating rate of  $10^{\circ}\text{C}/\text{min}$ . From Figure 1, **I** lost about 60% of its weight in the  $225\text{--}500^{\circ}\text{C}$  temperature range. Loss of one

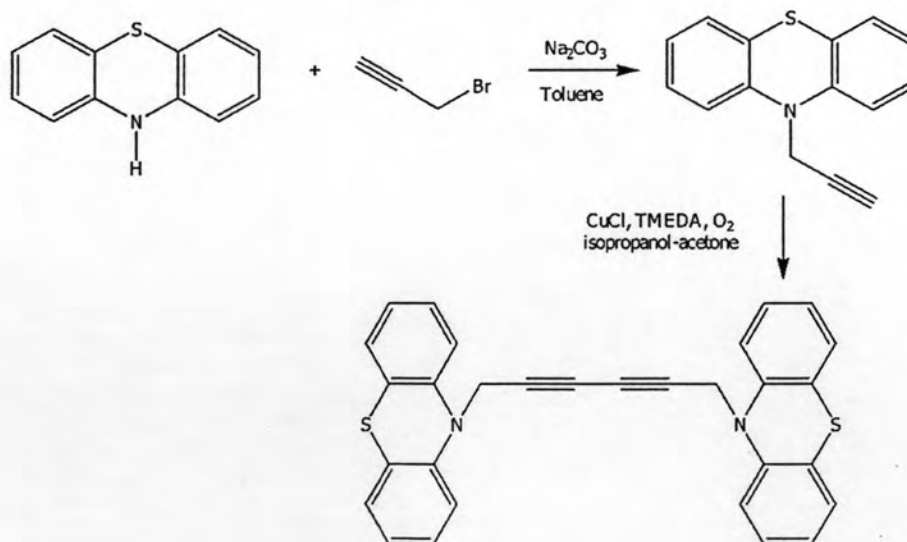
**Table 1**  
Crystallographic data of **I**

| Compound                               | <b>I</b>  |
|--|---|
| Chemical formula                       | C <sub>30</sub> H <sub>20</sub> N <sub>2</sub> S <sub>2</sub> |
| <i>a</i> , Å                           | 14.9500 (18)  |
| <i>b</i> , Å                           | 13.5512 (15)  |
| <i>c</i> , Å                           | 12.0116 (10)  |
| β, deg.                                | 102.628 (9)   |
| <i>V</i> , Å <sup>3</sup>              | 2374.6 (4)  |
| <i>Z</i> , <i>Z'</i>                   | 4, 0.5  |
| Formula Wt. g/mol                      | 472.62  |
| Space group                            | <i>C2/c</i>   |
| <i>T</i> , °C                          | 21 (1)  |
| λ, Å                                   | 1.54178   |
| ρ <sub>calc</sub> , g cm <sup>-3</sup> | 1.322   |
| μ, mm <sup>-1</sup>                    | 2.189   |
| Transmission factors                   | 0.53 – 0.58   |
| <i>R</i> <sub>av</sub>                 | 0.028   |
| <i>R</i> <sup>a</sup>                  | 0.0354  |
| <i>R</i> <sub>w</sub> <sup>b</sup>     | 0.0474  |
| <i>S</i> <sup>c</sup>                  | 0.95  |
| No. reflections                        | 2353  |
| No. parameters                         | 195   |
| Secondary extinction parameter         | 109 (6)   |

$$^a R = \frac{\sum \|F_o\| - |F_c|}{\sum \|F_o\|}$$

$$^b R_w = \left[ \frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2}$$

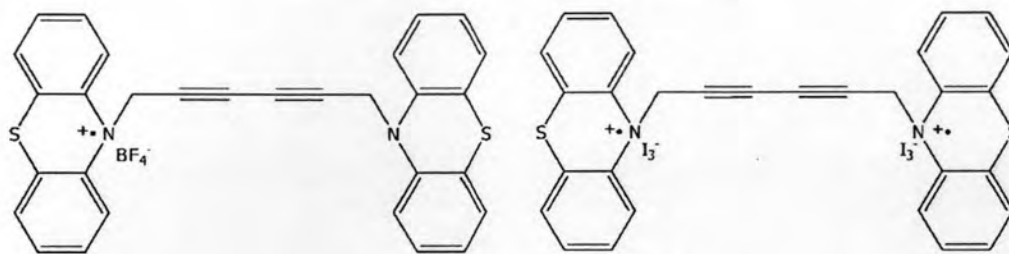
$$^c S = \left[ \frac{\sum w(|F_o| - |F_c|)^2}{(n - m)} \right]^{1/2}$$



**Scheme 1.** The synthesis of **I**.

1,6-bis-(*N*-phenothiazinyl)-2,4-hexadiyne

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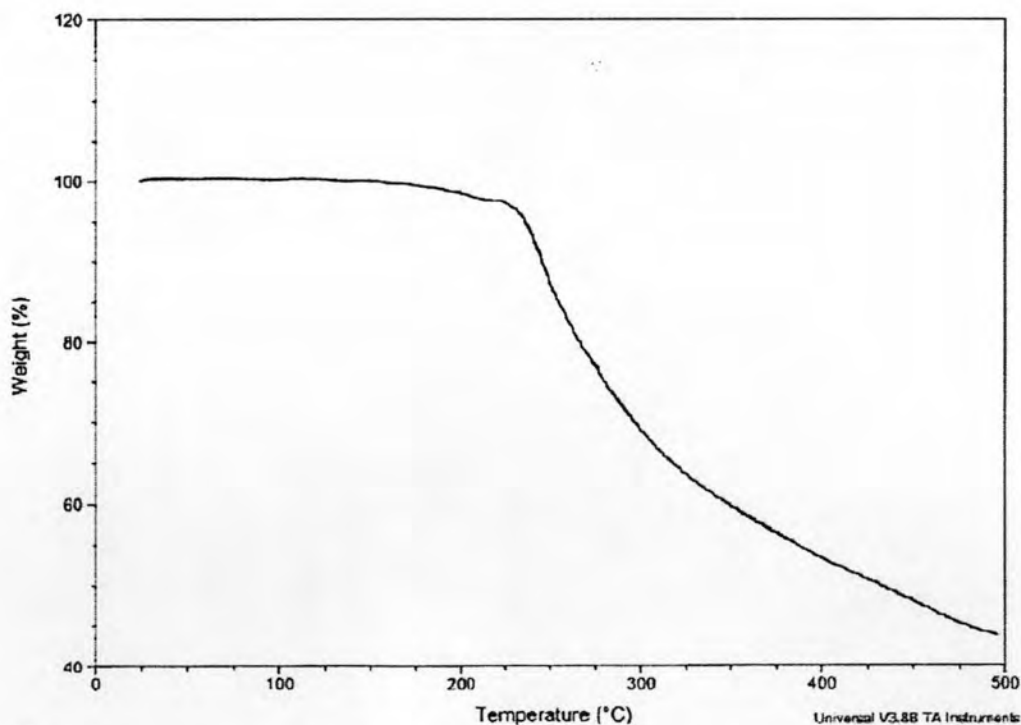


Scheme 2. The structure of I salts.

molecule of phenothiazine from **I** would involve a 42.2% wt loss. The iodide salt (Figure 2) seems to lose weight in three stages. In the narrow temperature range 130–155°C, it lost 7% of its weight. At about 400 °C, the material has lost about 40% of its weight. This might correspond to loss of 4 I atoms, but further work is needed to establish this suggestion.

*Crystal and Molecular Structure of I*

The molecular structure and numbering scheme for **I** is shown in Figure 3; bond lengths and angles lie in normal ranges. Compound **I** crystallizes in space group  $C2/c$ ; **I** resides on a crystallographic  $C_2$  axis. The phenothiazine side groups are arranged in a *syn*-fashion, with a pseudo-torsion angle, N1-C3 ... C3'-N1' of 30.7°.

Figure 1. Thermogravimetric analysis of **I**.

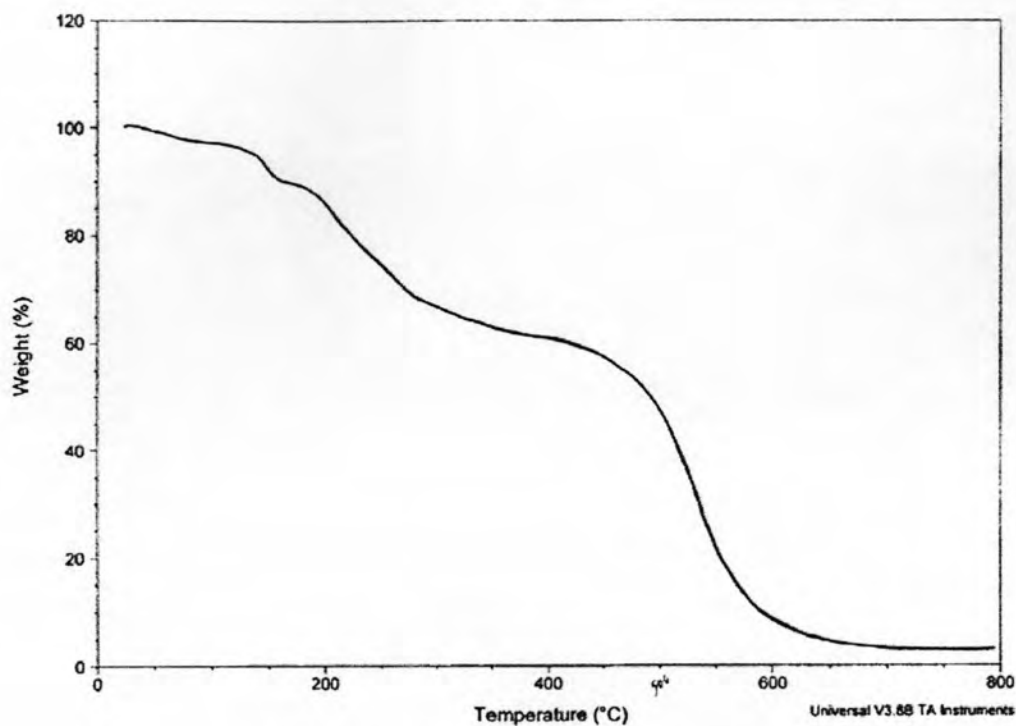


Figure 2. Thermogravimetric analysis of I iodide.

As shown in Figure 4, the molecular conformation influences the packing such that the often-encountered short  $\text{—C}\equiv\text{C—C}\equiv\text{C—}$  contacts observed for diacetylenes that are reactive in the solid state are not present in this structure (12). The shortest intermolecular contact between acetylenic carbon atoms is C1—C2 ( $1 - x, 1 - y, -z$ ); the 7.35 Å distance observed for this contact precludes the usual diacetylene solid-state reactivity (12).

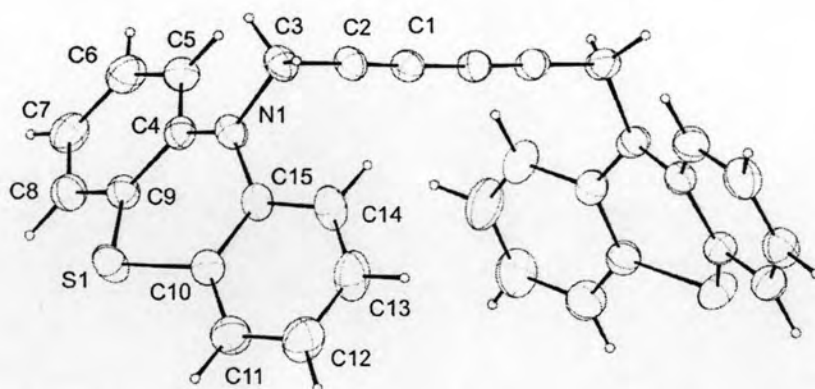


Figure 3. Molecular structure of I, showing 40% probability ellipsoids for atoms refined by using anisotropic displacement parameters; only the asymmetric unit is labeled.

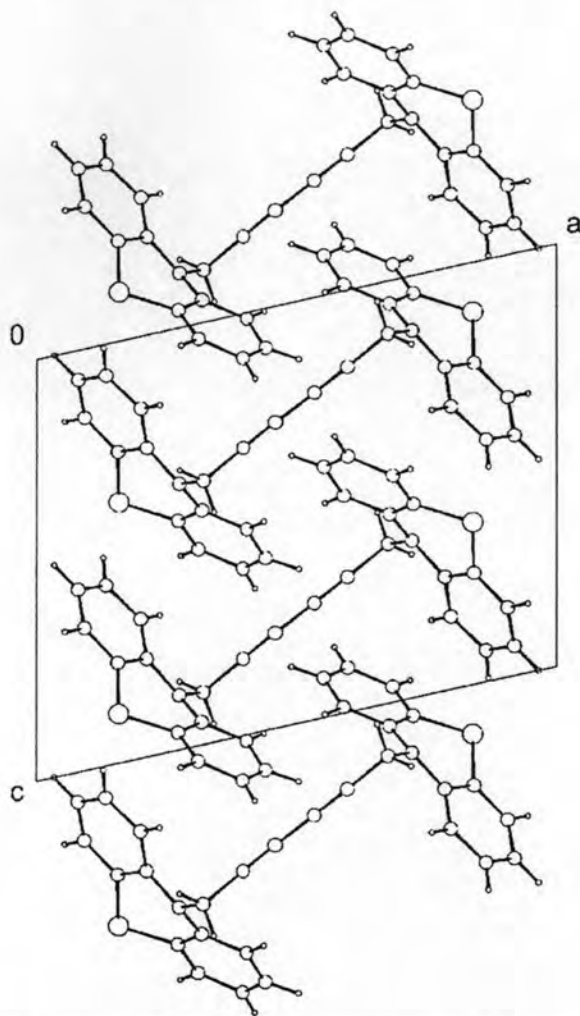


Figure 4. Packing of molecules viewed in projection down the b-axis.

### Conclusions

Diacetylene monomer **I** was synthesized by oxidative coupling of propargyl phenothiazine. The crystal structure of **I** precludes the usual 1,4-addition polymerization of the diacetylene. Nevertheless, **I** decomposes on heating to phenothiazine and an undefined solid.

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## The Interaction of Cinnamic Acids with $^{60}\text{Co}$ Gamma Radiation

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*In the interest of expanding our knowledge of the interaction of cinnamic acid and its derivatives with ionizing radiation, (E)-cinnamic acid and several of its chlorinated and brominated derivatives were exposed to  $^{60}\text{Co}$  gamma radiation. Dimer yields were estimated from integration of the proton NMR signals of the irradiated material. (E)-Cinnamic acid itself is relatively unreactive. The largest yield of dimer was obtained with p-bromocinnamic acid where exposure to a dose of 116 megarads led to a 24% yield.*

**Keywords:** cinnamic acid dimerization; gamma radiation; heavy atom effect

### INTRODUCTION

In the investigation of solid-state reactions, our current level of understanding behooves the researcher to study each reaction with all available probes: heat, ultraviolet light, ionizing radiation, and pressure. The structural basis of the photodimerization of cinnamic acids with ultraviolet light [1] is well known. Attempts to study the dimerization process thermally are made difficult by the sublimation that occurs

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on heating. Cinnamic acid has typically been regarded as relatively unreactive to ionizing radiation [2,3]. A relative lack of reactivity is not surprising because aromatic compounds are much more resistant to radiation than alkanes and alkenes [4]. Yet, ionizing radiation produces higher excited states as well as ionization. The higher excited states might rapidly decay to the lowest singlet state by Kasha's Rule and that state should lead to dimerization. Such was the situation when it was reported [5] that electron beam irradiation (1 MeV, 0.5 mA) of (*E*)-cinnamic acid with a 500 Mrad dose gave truxillic acid in 58% yield.

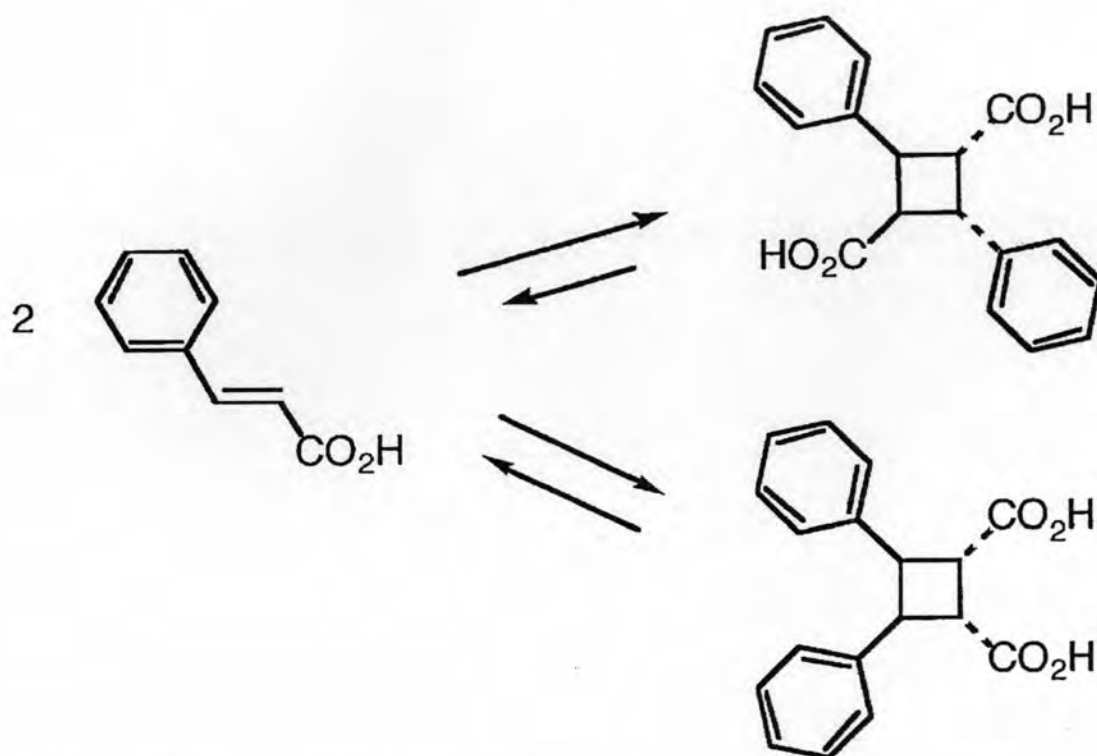
In the interest of learning more about the reactivity of (*E*)-cinnamic acids with ionizing radiation, we have exposed (*E*)-cinnamic acid and several of its chloro and bromo derivatives to  $^{60}\text{Co}$  gamma radiation. This line of inquiry uses a heavy atom strategy. In the interaction of  $\gamma$ -radiation with matter, the photoelectric effect and Compton scattering are major processes. Both of these processes are more probable for materials with high atomic numbers [6]. Hence, it would be expected that molecular structures containing heavy atoms that are involved in the electronic structure would be more reactive to  $\gamma$ -radiation than similar molecular structures lacking a heavy atom, other things (*e.g.*, crystal structure in the solid state) being equal. Earlier, the role of heavy metal atoms in the reaction of metal propynoates with  $^{60}\text{Co}$   $\gamma$ -radiation [7,8] was discussed.

## EXPERIMENTAL SECTION

Cinnamic acid and its derivatives were used as received from Aldrich Chemical Company. Their crystalline phase was established by X-ray powder diffraction in earlier studies. Truxillic and truxinic acids were prepared by uv irradiation [9] as previously described. Proton NMR spectra were recorded on Bruker 500 or 250 MHz spectrometers. The compounds were irradiated in screw cap vials in the presence of air at ambient temperature. The dose rate was 0.76 Mrad/hr. The irradiated solids were dissolved in an appropriate solvent and their NMR spectra were recorded. The product yield was obtained from the relative areas of the olefinic signals of the cinnamic acid and the aliphatic protons of the dimer. Obtaining the yields of the irradiation experiments by integration of the  $^1\text{H}$  NMR spectra is clearly a more accurate method than solvent extraction [3] of the irradiated solid.

## RESULTS AND DISCUSSION

The products of dimerization of the cinnamic acids are illustrated in Figure 1. The compounds that were exposed to  $\gamma$ -radiation are listed

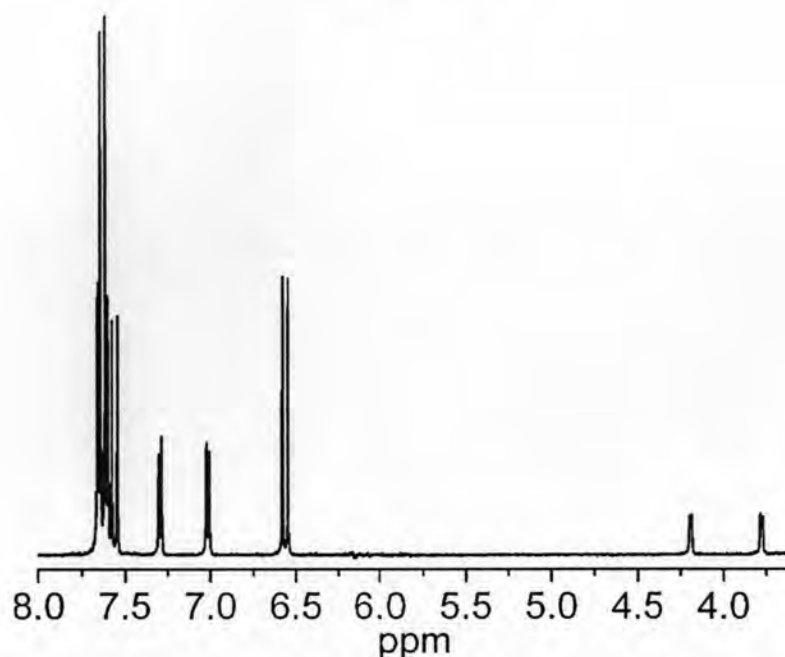


**FIGURE 1** Cinnamic acid, its dimerization to truxillic and truxinic acids and the reverse processes.

in Table 1 along with the radiation dose and the product yield. The radiation dose was a minimum of 50 Mrad as this is the dose used to polymerize diacetylene monomers to completion when possible. Integration of the proton resonances of the vinylic protons of the reactant and the aliphatic protons of the dimer was used to obtain the yields. With respect to Table 1, the largest yield of dimer was obtained with

**TABLE 1** Cinnamic Acids and their Dimers, the Dose of  $\gamma$ -Radiation they Received, and the Product Yield

| Starting compound                     | Dose of $^{60}\text{Co}$ , Mrad | Yield of product |
|---------------------------------------|---------------------------------|------------------|
| <i>E</i> -Cinnamic acid               | 50                              | 0.8–5.6%         |
| 4-Chlorocinnamic acid                 | 50                              | 8.1%             |
| 4-Bromocinnamic acid                  | 50                              | 7.1%             |
| 2,4-Dichlorocinnamic acid             | 50                              | 0.0%             |
| 2,4-Dichlorocinnamic acid             | 116                             | 20%              |
| 4-Bromocinnamic acid                  | 116                             | 24%              |
| Truxillic acid                        | 50                              | 0.03%            |
| 4,4'-Dichloro- $\beta$ -truxinic acid | 50                              | 0.4%             |
| 4,4'-Dibromo- $\beta$ -truxinic acid  | 50                              | 1.3%             |



**FIGURE 2** Expanded region of the proton NMR spectrum (DMSO- $d_6$  solution) of *p*-bromocinnamic acid irradiated with 116 Mrad  $^{60}\text{Co}$  gamma radiation. The two multiplets located in the 3.5–4.5 ppm range are the methine protons of the truxinic acid. The doublets near 6.6 and 7.6 ppm are alkene protons of *p*-bromocinnamic acid.

4-bromocinnamic acid with a dose of 116 Mrad, and the yields of dimers were typically higher with cinnamic acids with halogen substituents than without. The  $^1\text{H}$  NMR spectrum of the products of  $\gamma$ -radiation of 4-bromocinnamic acid is displayed in Figure 2.

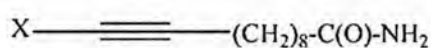
Since the yield of truxillic acid decreased [5] at electron beam doses greater than 500 Mrad, we chose to inquire if the dimer was reactive to radiation. As shown in Table 1, the largest amount of cinnamic acid was obtained with the Br-substituted truxinic acid, 1.3% yield. This invited the question as to whether the dimers were stable under UV irradiation. Under conditions (254-nm light) [9] where 4-bromocinnamic acid was converted to dimer in 90% yield, the Br-substituted truxinic acid converted to monomer in 1.5% yield.

While (*E*)-cinnamic acid has the  $\alpha$ -crystal structure and the halogenated cinnamic acids have the  $\beta$ -structure [1], it appears that the major reason for the results in Table 1 is the heavy atom effect. While it is also apparent that both electron beams [5] and  $^{60}\text{Co}$   $\gamma$ -radiation can convert cinnamic acid to its dimer, the doses involved are very large. Ultraviolet irradiation and sunlight remain the methods of choice to carry out this dimerization for synthetic purposes.

It was suggested [5] that the interaction of electron beams with cinnamic acid to give truxillic acid proceeds via the same lowest excited state as the photochemical dimerization. While this suggestion is plausible, as discussed above, it may well be oversimplified. The potential of ionizing radiation to produce excited states that are electric dipole forbidden is at the heart of this suggestion. In addition, it is appropriate to note that the excited state leading to dimerization may be more complex than the lowest singlet of monomeric (*E*)-cinnamic acid. The fluorescence of solid cinnamic acids [9,10] is clearly not molecular and may be excimeric.

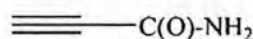
While the presence of halogens in the cinnamic acid molecular structure enhances reactivity toward  $\gamma$ -radiation, it is not the only example of this type. The molecular structures given in Figure 3 provide several additional examples. While N-propargylcarbazole is relatively unreactive to  $\gamma$ -radiation, N-(3-bromo-2-propynyl)carbazole [11] reacts. The term "relatively unreactive" means that, after exposure to radiation, the solid retained its original color and its melting point is not changed. Ultimately, everything is reactive to ionizing radiation. Again, 10-undecyanamide [12] is relatively unreactive to  $\gamma$ -radiation, 11-bromo-10-undecyanamide [13] reacts. Vacuum sublimed crystals of

## Cinnamic Acids and Gamma Radiation

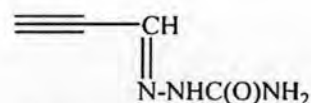


X = H, 10-undecyanamide

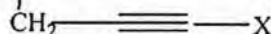
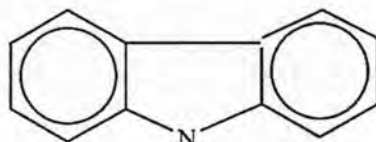
X = Br, 11-bromo-10-undecyanamide



Propiolamide

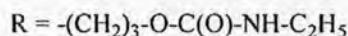
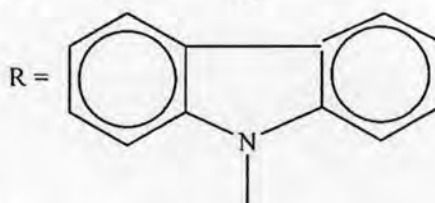
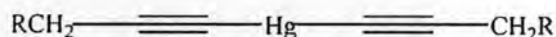


Propiolaldehyde semicarbazone



X = H, N-propargylcarbazole

X = Br, N-(3-bromo-2-propynyl)-carbazole



**FIGURE 3** Molecular structures and names of solid compounds that were exposed to  $^{60}\text{Co}$   $\gamma$ -radiation.

the semicarbazone of propiolaldehyde and propiolamide [14] are relatively unreactive, but crystals of these compounds obtained from chlorinated solvents show reactivity that was traced to the presence of solvent in crystalline defects. The presence of short intermolecular contacts between alkyne carbons in the crystal structures of 10-undecyanamide [12] and the semicarbazone of propiolaldehyde [14] is not sufficient to render these compounds reactive to  $\gamma$ -radiation. They are also melt-stable. Certain aromatic acetylenes, e.g., 1,4-diethynylbenzene [15], are reactive to  $\gamma$ -radiation, but p-ethynylbenzoic acid, with a linear chain crystal structure [16], is unreactive to both  $\gamma$ -radiation and UV light.

While the above examples show the effectiveness of halogen atoms in imparting solid state reactivity to otherwise unreactive molecular structures, the presence of a heavy atom in a molecular structure is not sufficient to impart significant reactivity. The mercury compounds [17] in Figure 3 are relatively unreactive to  $\gamma$ -radiation.

While (*E*)-cinnamic acid is relatively unreactive to radiation, its molecular structure contains an  $\alpha,\beta$  unsaturated aromatic acid that undergoes a 2 + 2 cycloaddition.  $\alpha,\beta$  Unsaturated acids such as sorbic and muconic give some dimer and also oligomer on exposure [18] to  $\gamma$ -radiation. Acenaphthene is an  $\alpha,\beta$  unsaturated aromatic compound that undergoes a 2 + 2 cycloaddition [19] under the influence of  $\gamma$ -radiation.

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- Njus, J. M.; **Lim, C.**; Sandman, D. J. The Interaction of Cinnamic Acids with <sup>60</sup>Co Gamma Radiation. *Mol. Cryst. Liq. Cryst.* 456(2006): 55.
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