# Synthesis, characterization, and crystal structures of two strained cyclic diacetylenes and their precursors

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The synthesis, characterization, and crystal structures of two novel strained cyclic diacetylenes are reported. A discussion is presented about the relative bond distances of the diacetylenes compared to a previously reported strained cyclic diacetylene to further determine the degree of aromaticity of that compound. 1,2:5,6:9,10:13,14-Tetrabenzo-3,7,11,15,17-pentadehydro[18] annulene (5) is triclinic,  $P^-1$ , with  $\alpha = 9.489(5)$ , b = 10.550(5), c = 12.155(6) Å,  $\alpha =$ 100.50(4),  $\beta = 106.50(4)$ ,  $\gamma = 100.85(4)^\circ$ . 1,2:5,6:9,10:13,14:17,18-Pentabenzo-3,7,11,15,19,23,25-heptadehydro[26]annulene (7) is triclinic,  $P^-1$ , with a = 9.611(2), b =10.388(3), c = 15.963(3) Å,  $\alpha = 88.67(2)$ ,  $\beta = 76.25(1)$ ,  $\gamma = 68.69(2)$ . In addition, two precursors of **5**, **3** and **4** which have a helical twist, are reported. [1,2-ethynediyl-bis(2,1phenylene-2,1-ethynediyl-2,1-phenylene-2,1-ethynediyl]bis[trimethyl-silane] (**3**) is monoclinic,  $P_{1/c}$ , with a = 13.682(4), b = 9.787(2), c = 13.448(4) Å,  $\beta = 112.37(2)^\circ$ . 1,1'-(1,2-ethynyldiyl)bis[2-[(2-ethynylphenyl)ethynyl]-benzene (**4**) is monoclinic,  $P_{2_1/n}$ , with a =15.951(3), b = 3.999(1), c = 18.168(4) Å,  $\beta = 99.05(3)^\circ$ .

KEY WORDS: Cyclyne; strained cyclic; diyne; diacetylene; benzo dehydro annulene.

# Introduction

Polydiacetylenes are a class of organic polymers with extended  $\pi$ -conjugation along their backbones. Possible applications are as photonic<sup>1</sup> and electronic<sup>2</sup> devices. Polymerization of diacetylenes occurs to form polydiacetylenes via a topochemical 1,4 addition<sup>3</sup> in the solid state (see Fig. 1).

Delocalizing substituents, such as an aromatic ring, bound directly to the diacetylene moiety would maximize conductivity and nonlinear optical properties.<sup>4</sup> Other strained cyclic monomers with aromatic substituents bound to the diacetylene moiety have appeared in the literature.<sup>5</sup> The X-ray structure and



Fig. 1. Example of a 1,4 addition polymerization of a diacetylene.

reactivity of  $1^6$  and related heterosubstituted<sup>7</sup> molecules encouraged us to investigate other cyclic diacetylenes. As part of our continuing investigation of cyclic diacetylenes, in this paper we report the syntheses, crystal structures, and preliminary reactivity data of compounds 5 and 7 and their precursors.



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# Experimental

#### General procedures

Copper (I) chloride (Aldrich) was stored in a glove box prior to use. Pyridine and methanol were used as received from Aldrich. Oxygen was bubbled through the pyridine-methanol solution prior to the addition of the terminal acetylenic compound. Column chromatography was carried out using silica gel (Baker: 40 µm). NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer. FT-IR spectra were recorded on a Nicolet 510P FT-IR and manipulated with OMNIC software. UV-Vis spectra were recorded on an IBM UV/Visible 9420 spectrometer. Elemental analyses were done by Midwest Microlabs. DSC plots were recorded with a Du Pont Instruments 910 DSC run to 500°C at 10°C/min. The pressure for the gas used in the DSC was 200 psi and 100 psi for nitrogen and air, respectively. TGA were recorded with a Perkin Elmer TGA TGS-2 run to 900°C at 10°C/ min. Nitrogen and air were purged at 60 cc/min for TGA. Both TGA and DSC used PL Thermal Sciences Version 4.30, and an OmniTherm CCI-II computer controlled interface.

Synthesis of [1,2-ethynediyl-bis(2,1-phenylene-2, 1-ethynediyl-2,1-phenylene-2, 1-ethynediyl]bis[trimethyl silane] (3)

Compound  $2^8$  (0.70 g: 2.1 mmol) was added to a flask with PdCl<sub>2</sub>(PhCN)<sub>2</sub> (0.041 g: 0.11 mmol), Cul (0.041 g: 0.21 mmol) and PPh<sub>3</sub> (0.056 g: 0.21 mmol). Triethylamine (50 mL) was added under vacuum and o-iodo-trimethylsilylethynyl benzene (1.3 g: 4.4 mmol) was added via syringe with a nitrogen purge. After stirring for 12 hr the mixture was filtered and the solvent was removed in vacuo leaving a dark oil. Column chromatography (5% acetone in hexanes) gave a pale yellow solid (1.1 g: 92%). 3 ( $C_{40}H_{34}$ ): FDMS = 570. Calc. C 84.18, H 6.01. Found C 84.08,H 5.99. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.619-7.574 (m:4H), 7.536-7.505 (m: 2H), 7.462-7.431 (m: 2H), 7.310-7.273 (m: 4H), 7.219-7.189 (m: 4H), 0.222 (s: 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 132.26, 132.10, 128.12, 128.06, 128.00, 127.88, 126.03, 125.78, 125.44, 103.46, 98.59, 92.40, 92.30, 92.13, -0.04. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>: nm [log  $\epsilon$ ]): 352.0 (4.06), 256.0 (4.68). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2218.0, 2158.7, 2014.2, 1953.9.

# Synthesis of 1,1'-(1,2-ethynyldiyl) bis [2-[(2-ethynylphenyl)ethynyl]-benzene (4)

Compound 3 (3.346 g: 5.87 mmol) was dissolved in DMF (80mL). KF (0.512 g: 8.81 mmol) and deionized water (0.4mL: 20 mmol) were added to the reaction flask. The reaction was monitored by TLC and after 4 hr it was stopped with the addition of crushed ice. The aqueous layer was washed with diethyl ether (400 mL). The combined organic layers were washed with deionized water (750 mL), dried over anhydrous MgSO<sub>4</sub>, filtered and the solvent was removed in vacuo resulting in a brown solid. Column chromatography (20% acetone in hexanes) yielded a white solid that later changed to a blue-green color when crystalline. (2.16 g: 86.4%). 4  $(C_{34}H_{18})$ : FDMS = 426. Calc. C 95.74, H 4.26. Found C 95.64, H 4.37. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.628-7.598 (m: 4H), 7.532-7.502 (m:2H), 7.321-7.288 (m:4H), 7.235-7.205 (m: 4H), 3.218 (s: 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 132.41, 132.34, 132.20, 128.36, 128.12, 128.07, 127.94, 126.24, 125.74, 125.65, 125.45, 92.29, 92.22, 91.96, 82.05, 81.34. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>: nm [log  $\epsilon$ ]): 341.6 (7.19), 331.2 (7.14), 306.4 (7.15), 276.8 (7.56), 251.2 (7.78). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2676.8, 2636.8, 2537.5, 2473.2, 2325.6, 2215.7, 2105.5, 1972.1, 1941.9, 1865.6.

# Synthesis of 1,2:5,6:9,10:13,14-tetrabenzo-3,7,11,15,17-pentadehydro [18] annulene (5)

Compound 4, (0.280 g: 0.660 mmol) dissolved in pyridine (50 mL), was added via addition funnel to a stirring mixture of copper (I) chloride (6.5 g; 65 mmol) in pyridine (200 mL) and methanol (200 mL) which had been saturated with oxygen. Addition proceeded for 30 min during which time oxygen was bubbled through the mixture. The aqueous layer was washed with chloroform and the combined organic layers were washed with 1N H<sub>2</sub>SO<sub>4</sub>, saturated sodium bicarbonate, dried over anhydrous magnesium sulfate and filtered. The solvent was removed in vacuo and then pumped on overnight to remove traces of pyridine yielding a yellow powder (0.249 g: 89.3%). 5 (C<sub>34</sub>H<sub>16</sub>): FDMS = 424.5, Calc. C 96.20, H 3.80. Found C 92.25, H 3.86, Ash formation was observed during analysis. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.549-7.503 (m:6H), 7.421-7.393 (m:2H), 7.341-7.216 (m:8H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 133.22, 132.42, 131.53, 131.21, 128.67, 128.16, 128.09, 127.94, 125.86, 125.40, 124.70, 92.81, 91.36, 91.14, 81.05, 78.45. IR (KBr): 2221.4, 1971.4, 1942.9,

1864.3, 1828.6, 1728.6, 1642.9, 1592.9, 1564.3, 1500.0, 1471.4, 1442.9, 1278.6, 1164.3, 1107.1, 1050.0, 878.6. DSC (nitrogen): sharp exotherm at 250°C. TGA (nitrogen): 12% weight loss at 250°C, gradual decrease in weight to a 15% total weight loss by 900°C.

Synthesis of 1,2:5,6:9,10:13,14:17, 18-pentabenzo-3,7,11,15,19,23,25-heptadehydro [26] annulene (7)

Compound 6 (2.07 g: 3.93 mmol) in pyridine (250 mL) was added dropwise over a period of 1 hr via an addition funnel to copper (I) chloride (21 g: 210 mmol) in pyridine (200 mL)/methanol (400 mL) solution saturated with oxygen. The aqueous layer was washed with chloroform. The combined organic layers were washed with 1N H<sub>2</sub>SO<sub>4</sub>, saturated sodium carbonate, dried over anhydrous magnesium sulfate, filtered and the solvent was removed yielding a pale yellow powder (1.67 g, 81%). 7 (C<sub>42</sub>H<sub>20</sub>) m/z: 524.13. Calc. C 96.15, H 3.85. Found C 94.20, H 4.25. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.545-7.448 (m: 8H), 7.402-7.371 (q: 2H), 7.306-7.221 (m: 8H), 7.188-7.157 (q: 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 134.87, 132.69, 131.34, 131.28, 128.52, 128.32, 128.18, 128.00, 127.83, 127.75, 126.67, 126.49, 125.99, 125.04, 124.33, 93.27, 92.53, 92.43, 91.96, 82.00, 78.07. IR (KBr): 2223.1, 1938.5, 1892.3, 1869.2, 1823.1, 1707.7, 1623.1, 1600.0, 1561.5, 1492.3, 1469.2, 1453.8, 1323.1, 1276.9, 1192.3, 1169.2, 1100.0, 1046.2, 969.2, 869.2. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>: nm  $[\log \epsilon]$ : 364.4 (0.342), 308.8 (1.320), 276.8 (1.319), 250.8 (1.557), 224.4 (2.427), 220.0 (2.441). DSC (nitrogen): exothermic peak at 265°C. TGA (nitrogen): 20% lost at 265°C and gradually lost 2% more up to 900°C.

#### Crystal data

A unique data set was collected for each compound using a Syntex P2<sub>1</sub> diffractometer with monochromated MoK $\alpha$  ( $\lambda = 0.71073$  Å) radiation. Calculations were performed using Siemens SHELXTL PLUS program set.<sup>9</sup> The positions of atoms were found by direct methods and all nonhydrogen atoms were refined anisotropically using full matrix least squares on F<sup>2</sup>. Further details, refinement parame-

#### **Discussion and results**

Compound 3 is synthesized by reacting *o*-bis(ethynyl)tolane<sup>10</sup> (2) with two equivalents of *o*-iodo-trimethylsilylethynylbenzene using a palladium-copper catalyst<sup>11</sup> in the presence of an amine solvent. It is then desilylated with potassium fluoride to form 4.<sup>12</sup> An intramolecular Hay coupling reaction<sup>13</sup> of 4 with copper(1) chloride in pyridine and oxygen bubbling through the mixture gives 5. Similarly 6, whose preparation we have previously described,<sup>14</sup> undergoes an intramolecular Hay coupling to yield 7.



The X-ray structure of 3 shows a helical twist in the molecule. The two inner benzo rings lie in the same plane, while the outer phenyl rings each twist in opposite directions. One of the hydrogen atoms of the

Compounds	(3)	(4)	(5)	(7)	
Formula	$C_{40}H_{34}Si_2$	C <sub>34</sub> H <sub>18</sub>	C <sub>34</sub> H <sub>16</sub>	$C_{42}H_{20}$	
Mw	570.85	426.48	424.47	524.58	
Temp., °K	141	293	132	141	
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	
Space group	$P2_1/c$	$P2_1/n$	<i>P</i> 1bar	Plbar	
Unit cell dimensions					
a, Å	13.682(4)	15.951(3)	9.489(5)	9.611(2)	
<i>b</i> , Å	9.787(2)	3.999(1)	10.550(5)	10.388(3)	
c, Å	13.448(4)	18.168(4)	12.155(6)	15.963(3)	
α, °			100.50(4)	88.67(2)	
в. °	112.37(2)	99.05(3)	106.50(4)	76.25(1)	
<b>v</b> . °			100.85(4)	68.69(2)	
Volume (Å <sup>3</sup> )	1665.2(7)	1144.5(4)	1109.4(10)	1438.5(5)	
Z	2	2	2	2	
Calc. density, $g \text{ cm}^{-3}$	1.139	1.238	1.271	1.211	
Diffractometer	Syntex P2 <sub>1</sub>	Syntex P2 <sub>1</sub>	Syntex P2	Syntex P2 <sub>1</sub>	
20 range	3.5-45	3.5-45	3.5-45	3.5-45	
Scan type	ω	ω	ω	ω	
Scan range (° in ω)	1.2	1.5	1.8	1.8	
F(000)	604	444	440	544	
Crystal size (mm)	$0.3 \times 0.4 \times 0.4$	0.08  imes 0.4  imes 0.4	0.2  imes 0.2  imes 0.3	$0.3 \times 0.3 \times 0.4$	
Reflections collected	2380	2207	3507	4531	
Independent reflections	2057	1502	2887	3730	
Data	2057	1502	2882	3727	
Parameters	190	154	307	379	
Goodness of fit on $F^2$	1.011	1.037	1.080	1.046	
$R(\%) F^2$	5.27	5.46	7.63	6.16	
$R_{\rm w}$ (%) $F^2$	12.40	12.08	19.32	15.20	
Larg. diff. peak/hole e Å <sup>3</sup>	0.248/-0.287	0.142/-0.228	0.526/-0.241	0.182/-0.264	

 Table 1. Data Collection and Processing Parameters

carbon bound to the silyl group (C20) points directly into the center of the neighboring phenyl ring (C12a, C15a) in an intramolecular association. The distance was calculated to be 3.239 Å. Numerous C-H- $\pi$  interactions have been previously reported.<sup>15</sup> C-H bonds adjacent to silicon show increased acidity when compared to C-H bonds in a hydrocarbon fragment,<sup>16</sup> therefore, the C-H bond in 3 would be a better acceptor of  $\pi$ -electron density (Fig 2).

Compound 4 also has a helical twist but the twist is not as pronounced as that in 3. The steric bulk provided by the trimethylsilyl groups in 3 and the hydrogen-aromatic ring intramolecular interaction observed in 3 can account for this difference. The stacking of 4 is such that one molecule eclipses the molecule in the next layer. The distance between layers is 3.999 Å. An interesting phenomenon of 4 is that in solution it is yellow, but changes to a blue-green color when a crystalline solid. This behavior appears to be completely reversible (Figs. 3 and 4).

Compound 5 (Fig. 5) lies in a boat configuration. The majority of the strain in the molecule lies not in the diacetylene moiety, but in two of the single acetylene units. The diacetylene unit is slightly bent outward  $(2.5^{\circ})$ , while the three other acetylene linkages are bent inward relative to the ring  $(3.5-7.7^{\circ})$ . It packs in an alternating fashion such that the diacetylene moiety is close to one neighbor, but on the wrong side to interact with the other neighbor. Thus, a 1,4 topochemical polymerization is unlikely, but a dimerization may occur. An organized cross linking of the individual molecules must be occurring because a high char yield is observed from the TGA analysis. The distances and angles of incidence between the diacetylene linkages are 3.952 Å/91.2° (Fig. 6: molecule B to molecule D) to the nearest neighbor and 10.180 Å/26.5° (Fig. 6: molecule A to molecule D) to the next closest neighbor.

The X-ray structure of 7 (Fig. 7) shows a phenyl ring is positioned directly over the strained diacetylene moiety. The distances from the center of the phenyl

Atom	X	у	z	U (eq)
Si	6585(1)	2238(1)	8556(1)	44(1)
C(1)	6788(3)	871(4)	7721(3)	39(1)
C(2)	6862(2)	-4(3)	7126(2)	33(1)
C(3)	6903(2)	-1055(3)	6392(2)	30(1)
C(4)	6332(3)	-902(4)	5291(2)	36(1)
C(5)	6317(3)	-1933(4)	4584(3)	44(1)
C(6)	6867(3)	-3125(4)	4955(3)	43(1)
C(7)	7446(3)	-3284(4)	6036(3)	38(1)
C(8)	7477(2)	-2267(3)	6769(2)	30(1)
C(9)	8092(3)	-2460(3)	7889(3)	31(1)
C(10)	8613(3)	-2635(3)	8823(3)	32(1)
C(11)	9224(2)	-2886(3)	9943(2)	31(1)
C(12)	9171(3)	-4156(4)	10381(3)	42(1)
C(13)	9750(3)	-4403(4)	11458(3)	54(1)
C(14)	10385(3)	-3429(5)	12104(3)	56(1)
C(15)	10474(3)	-2171(5)	11683(3)	49(1)
C(16)	9881(2)	-1864(4)	10598(2)	35(1)
C(17)	9960(3)	-556(3)	10171(3)	39(1)
C(18)	6541(5)	3847(5)	7831(3)	98(2)
C(19)	5336(3)	1872(6)	8741(4)	90(2)
C(20)	7665(3)	2252(4)	9898(3)	46(1)

 
 Table 2. Table of Positional Parameters and Their Estimated Standard Deviations for 3

ring to each carbon in the diacetylene linkage are 4.514 Å (C42), 4.107 Å (C41), 4.134 Å (C40) and 4.618 Å (C39). This type of binding pocket, in addition to two other sets of phenyl alkyne links, suggests this compound would be an excellent ligand for metals.

 Table 3. Table of Positional Parameters and Their Estimated

 Standard Deviations for 4

Atom x		y	z	U (eq)	
C(1)	8324(3)	2904(13)	2939(2)	72(1)	
C(2)	8277(2)	4027(11)	3519(2)	55(1)	
C(3)	8213(2)	5475(9)	4239(2)	45(1)	
C(4)	8929(2)	6789(10)	4690(2)	59(1)	
C(5)	8881(3)	8139(11)	5373(2)	64(1)	
C(6)	8107(3)	8287(10)	5622(2)	59(1)	
C(7)	7387(2)	7038(10)	5190(2)	52(1)	
C(8)	7430(2)	5596(9)	4498(2)	41(1)	
C(9)	6667(2)	4246(9)	4073(2)	44(1)	
C(10)	6009(2)	3141(9)	3772(2)	43(1)	
C(11)	5208(2)	1798(9)	3433(2)	41(1)	
C(12)	4944(2)	1962(10)	2661(2)	52(1)	
C(13)	4171(3)	741(10)	2340(2)	58(1)	
C(14)	3639(2)	-763(11)	2776(2)	60(1)	
C(15)	3882(2)	-968(10)	3531(2)	55(1)	
C(16)	4664(2)	296(9)	3875(2)	42(1)	
C(17)	4910(2)	64(10)	4670(2)	47(1)	

 Table 4. Table of Positional Parameters and Their Estimated

 Standard Deviations for 5

Atom	x	у	z	U (eq)
C(1)	846(6)	10337(5)	7433(4)	23(1)
C(2)	812(6)	11079(5)	6788(5)	26(1)
C(3)	782(6)	11936(5)	6064(5)	25(1)
C(4)	790(6)	12698(5)	5437(4)	26(1)
C(5)	846(6)	13571(5)	4681(4)	22(1)
C(6)	-418(6)	13446(5)	3694(4)	29(1)
C(7)	-335(7)	14258(5)	2927(5)	35(1)
C(8)	992(7)	15182(5)	3102(5)	34(1)
C(9)	2257(6)	15359(5)	4104(4)	29(1)
C(10)	2192(6)	14575(5)	4912(4)	28(1)
C(11)	3415(6)	14829(5)	5997(5)	29(1)
C(12)	4350(6)	15068(5)	6973(5)	26(1)
C(13)	5359(6)	15448(5)	8174(4)	24(1)
C(14)	5468(6)	16678(5)	8906(4)	27(1)
C(15)	6341(6)	17051(5)	10093(5)	29(1)
C(16)	7128(6)	16213(5)	10573(5)	33(1)
C(17)	7083(6)	15002(5)	9882(4)	27(1)
C(18)	6164(6)	14583(5)	8675(4)	23(1)
C(19)	6057(6)	13294(5)	7992(4)	23(1)
C(20)	6050(6)	12191(5)	7508(4)	23(1)
C(21)	6121(5)	10916(5)	6902(4)	22(1)
C(22)	6947(6)	10872(5)	6123(4)	27(1)
C(23)	7034(6)	9659(5)	5509(5)	31(1)
C(24)	6305(6)	8477(5)	5682(5)	31(1)
C(25)	5479(6)	8499(5)	6451(4)	28(1)
C(26)	5377(6)	9718(5)	7070(4)	23(1)
C(27)	4411(6)	9675(5)	7787(4)	26(1)
C(28)	3520(6)	9502(5)	8320(4)	25(1)
C(29)	2277(5)	9175(5)	8769(4)	22(1)
C(30)	2348(6)	8466(5)	9620(5)	29(1)
C(31)	1077(6)	8020(5)	9919(5)	32(1)
C(32)	-303(6)	8256(5)	9337(5)	34(1)
C(33)	-381(6)	9013(5)	8526(4)	28(1)
C(34)	912(6)	9509(5)	8230(4)	25(1)

As was observed in 5, the diacetylene moieties are not aligned correctly for a 1,4 topochemical polymerization. The distances and angles of incidence of the diacetylene linkages are 8.795 Å/64.4° (Fig. 8: molecule A to molecule C) to the nearest neighbor and 10.388 Å/34.1° (Fig. 8: molecule A to molecule B) to the next nearest neighbor. These distances are too long for a 1,4 topochemical interaction between either neighbor. However, as the char yield of 7 is also high, an organized cross linking of the molecule must be occurring.

Compared to 5, the diacetylene bond in 7 is quite distorted. It is bent inward  $(14.8^{\circ})$  relative to the ring, while the other acetylene linkages are bent outward. One acetylene linkage of 7 is significantly distorted (acetylene with C22:  $6.8^{\circ}$ ) while the other three acety-

Atom	x	у	7.	U (eq)
C(1)	208(4)	-2074(4)	6876(2)	55(1)
C(2)	-1088(5)	-2389(4)	7253(3)	69(1)
C(3)	-1250(5)	-3550(5)	6973(3)	81(1)
C(4)	-140(6)	-4413(5)	6311(4)	83(1)
C(5)	1138(5)	-4129(4)	5928(3)	76(1)
C(6)	1348(5)	-2958(4)	6193(3)	58(1)
C(7)	2690(5)	-2674(4)	5811(3)	58(1)
C(8)	3831(5)	-2441(4)	5520(2)	58(1)
C(9)	5184(4)	-2113(4)	5220(2)	53(1)
C(10)	5930(5)	-2277(4)	4352(3)	71(1)
C(11)	7175(6)	-1908(5)	4069(3)	82(1)
C(12)	7726(5)	-1368(5)	4632(3)	79(1)
C(13)	7003(5)	-1194(4)	5516(3)	69(1)
C(14)	5733(4)	-1580(4)	5811(2)	54(1)
C(15)	4989(5)	-1442(4)	6722(3)	57(1)
C(16)	4348(5)	-1365(4)	7465(3)	57(1)
C(17)	3606(4)	-1229(4)	8361(2)	55(1)
C(18)	2789(5)	-2066(4)	8716(3)	72(1)
C(19)	2096(6)	-1931(5)	9589(3)	85(2)
C(20)	2230(7)	-980(6)	10117(3)	104(2)
C(21)	3017(7)	-146(5)	9781(3)	95(2)
C(22)	3690(5)	-237(4)	8897(2)	61(1)
C(23)	4384(5)	714(4)	8519(3)	64(1)
C(24)	4852(5)	1521(4)	8133(3)	62(1)
C(25)	5315(5)	2535(4)	7637(2)	54(1)
C(26)	6802(5)	2206(4)	7127(3)	66(1)
C(27)	7233(5)	3157(5)	6633(3)	73(1)
C(28)	6155(5)	4481(5)	6628(3)	70(1)
C(29)	4681(5)	4825(4)	7112(3)	61(1)
C(30)	4216(4)	3869(4)	7622(2)	52(1)
C(31)	2637(5)	4192(4)	8070(2)	58(1)
C(32)	1302(5)	4444(4)	8398(3)	60(1)
C(33)	-314(4)	4811(4)	8756(2)	56(1)
C(34)	-1163(5)	6064(4)	9252(3)	74(1)
C(35)	-2738(6)	6475(5)	9559(3)	85(1)
C(36)	-3509(5)	5682(5)	9362(3)	81(1)
C(37)	-2689(5)	4445(4)	8888(3)	68(1)
C(38)	-1093(4)	3975(4)	8595(2)	54(1)
C(39)	-320(4)	2640(4)	8149(2)	56(1)
C(40)	83(4)	1488(4)	7827(2)	58(1)
C(41)	317(4)	211(4)	7465(2)	57(1)
C(42)	342(4)	-852(4)	7181(2)	58(1)

 
 Table 5. Table of Positional Parameters and Their Estimated Standard Deviations for 7

lene linkages are not  $(0.6-3.1^{\circ})$ . The total strain in 7 is minimal as it is quite thermally stable. No bond breaks until heated to  $265^{\circ}$ C in a nitrogen atmosphere.

A comparison among the bond distances of 1, 5, and 7, was done to evaluate the claimed aromaticity of 1.<sup>6</sup> Table 6 lists the bond distances between C's A–J which are shown in Fig. 9. As can be seen from the table, the bond distances of 1 show no significant delocalization when compared with those of 5 and 7.



Fig. 2. Thermal ellipsoid plot of 3 drawn at 50% probability.



Fig. 3. Thermal ellipsoid plot of 4 drawn at 50% probability.



Fig. 4. Stacking diagram of 4 drawn at 20% probability, hydrogen atoms omitted for clarity.



Fig. 5. Thermal ellipsoid plot of 5 drawn at 50% probability.



Fig. 6. Packing diagram of 5 drawn at 20% probability, hydrogen atoms omitted for clarity.



Fig. 7. Thermal ellipsoid plot of 7 drawn at 50% probability.



Fig. 8. Packing diagram of 7 shown at 50% probability, hydrogen atoms omitted for clarity.

However, the <sup>1</sup>H NMR chemical shifts of 1 are slightly more de-shielded than the hydrogen atoms of 5 and 7, which is consistent with some aromaticity in 1 (see Table 7).

#### Conclusions

While crystallographically compounds 5 and 7 do not appear to be good candidates for a topochemical polymerization, these compounds do exhibit extreme thermal stability with char yields greater than 78% in both cases. The arrangement of their atoms suggests they would be excellent ligands for transition metals. In particular, 7 has a pocket lying between an aromatic ring and a diacetylene bond. To our knowledge this is the first type of ligand to have a diacetylene linkage in close proximity to an aromatic ring within the same molecule. The reactivity of these compounds with transition metals is being investigated.

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**Supplementary material.** Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1003/5343 (for 3), CCDC-1003/5344 (for 4), CCDC-1003/5345 (for 5), and CCDC-1003/5346 (for 7). Copies of available material can be obtained, free of charge, on application to the director, CCDC, 12 Union Road,

			Ca-	Cb≡Cc−Cd≡	Ce-Cf=Cg-C	h≡Ci−Cj			
1	1.430	1.192	1.366	1.213	1.417	1.411	1.437	1.203	1.433
5	1.415	1.203	1.370	1.205	1.419	1.418	1.429	1.212	1.434
7	1.429	1.193	1.379	1.201	1.424	1.399	1.428	1.197	1.432

 Table 6. Comparison of Bond Distances (Å) Between 10 of the Carbons in the Annulene Ring, Shown in Fig. 9, of Compounds 1, 5, and 10"

" The ESD's are ca. 0.006Å on average for all bond distances.



Fig. 9. The diacetylene linkage and acetylene between the first two phenyl rings is shown for compounds 1, 5, and 7. The thermal ellipsoid plots are drawn at 50% probability.

Table 7. Comparison of <sup>1</sup>H NMR between 1, 5, 7<sup>a</sup>

Compound	<sup>1</sup> H NMR peak (ppm)		
1	7.908		
5	7.549		
7	7.545		

<sup>a</sup> The peak listed for each compound is the peak shifted farthest downfield.

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