Synthesis and X-ray Characterization of an Octaalkynyldibenzooctadehydro[12]-annulene

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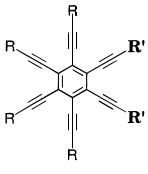
We have recently reported a straightforward synthesis of a variety of tetraalkynylcyclopentadienones (**1**).[1] In view of the inverse-demand Diels−Alder reactivity of cyclopentadienones,[2] we were interested in the use of these systems for the preparation of 1,2,3,4/5,6-differentially protected hexaalkynylbenzenes (HEBs, **2**), which are otherwise not accessible by known methods.[3,4] Differentially protected HEBs are precursors of well-defined molecular fragments (e.g., **3b**, **4**) representing novel planar carbon networks in which the graphitic texture is extended by acetylene or butadiyne units (graphynes).[5] Some of these networks are predicted to be semiconductors having large third-order nonlinear susceptibilities.[6,7] Their synthesis is out of the reach of current methodology;[8] however, their properties can be investigated on smaller—even though sizable—fragments such as compounds **3b** and **4**.[4]



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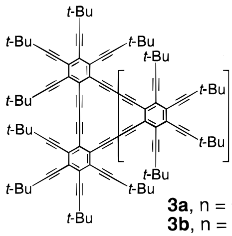
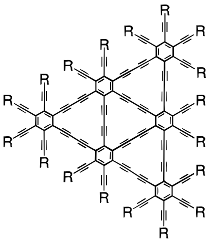
2a, R = *t*-Bu, **R'** = H



3a, n = 0
3b, n = 1
3c, n = 2



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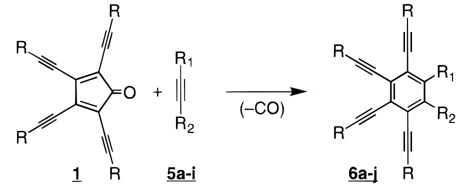
The synthesis and characterization of the cyclic dimer **3a**, obtained in pure form next to trimer **3b** and tetramer **3c** by Hay coupling of the 1,2-diacetylene **2a**, is described in this report. The Diels−Alder reactivity of the dienones **1a**−**c** was first investigated on several alkynes (**5a**−**i**, Table 1). Heating the dienones in the presence of a slight excess of alkyne afforded tetraalkynyl- and pentaalkynylbenzenes in good yields, except for alkynes with strong steric requirements (**6b**,**f**,**i**,**j**).

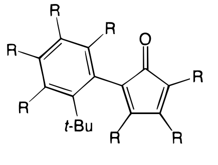
Since each alkyne moiety of **1a**−**c** can act as its own dienophile to give dimers or higher oligomers, it is remarkable that the adducts **6a**−**j** are formed with such fidelity. Indeed, in the lower yielding reactions of dienone **1b**, a single purple dimer (**7a** or **7b**) was formed competitively as a byproduct.[9] As judged by the larger size of the HOMO coefficients (PM3) and reduced steric hindrance at carbons **a**,**b**, compared to carbons **c**,**d** (Figure 1), it is most likely that the dimerization product is regioisomer **7a**, although a definitive structural proof will require X-ray characterization. Dimer formation was largely inhibited by running reactions in the melt of excess dienophile (**6f**,**j**).

Table 1. Diels−Alder Cycloaddition of Cyclopentadienones 1a−c with Alkynes 5a−i

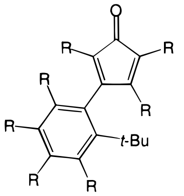


dienone 1	R	alkyne	R_1	R_2	product	yield (%)
1a	TIPS	**5a**	Et	Et	**6a**	84[a]
		5b	Ph	Ph	**6b**	30[a]
		5c	Ph	C≡CPh	**6c**	58[a]
		5d	CO_2Me	CO_2Me	**6d**	92[a]
		5e	H	CH_2OH	**6e**	74[a]
		5f	C≡C-TMS	C≡C-TMS	**6f**[c]	55[d] (12)[a]
1b	*t*-Bu	**5g**	Br	CO_2Et	**6g**	46[b]
		5h	CHO	$CH(OEt)_2$	**6h**	61[a]
		5i	TMS	C≡C-TMS	**6i**	20[a]
		5f	C≡C-TMS	C≡C-TMS	**6j**[c]	41[d] (9)[a]
1c	C≡C-TIPS	**5f**	C≡C-TMS	C≡C-TMS	**6k**	*a*,*e*

[a] Toluene, reflux, 1.3−2 equiv of alkyne. [b] Xylenes, reflux. [c] R_1 = TMS, R_2 = C≡CC≡C-TMS. [d] Neat $TMS(C{\equiv}C)_3TMS$ (20−40 equiv), 100 °C. [e] Complex mixture.



7a, R = C≡C-*t*-Bu



7b, R = C≡C-*t*-Bu

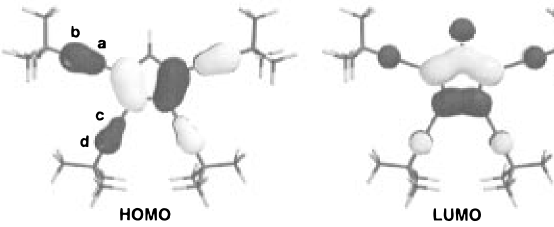


Figure 1. HOMO and LUMO frontier orbitals for **1b** (PM3).

Interestingly, bis(trimethylsilyl)hexatriyne (**5f**)[10] did not add to dienones **1a**,**b** across its central, least sterically hindered C≡C bond[11] to give the desired C_{2v}-symmetric HEBs, but rather at one of the two peripheral triple bonds to give **6f** and **6j**. This can be understood as a result of the large steric repulsion created between the TMS and *t*-Bu/TIPS groups at the transition state (T.S., Figure 2);[12] an unsymmetrical approach is more favorable. Since the more extended diynyl system of the green

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[8] See, for example: Feldman, K. S.; Mareska, D. A.; Weinreb, C. K.; Chasmawala, M. *J. Chem. Soc., Chem. Commun.* **1996**, 865−866.

[9] See the accompanying paper: Tobe, Y.; Kubota, K.; Naemura, K. *J. Org. Chem.* **1997**, *62*, 3430−3431.

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[11] Rubin, Y.; Knobler, C. B.; Diederich, F. *J. Am. Chem. Soc.* **1990**, *112*, 4966−4968.

[12] The PM3 calculated T.S. (Spartan 4.0) gave one imaginary frequency at 591.2 cm^{-1} by vibrational analysis.

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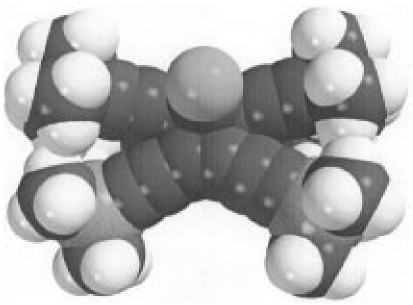
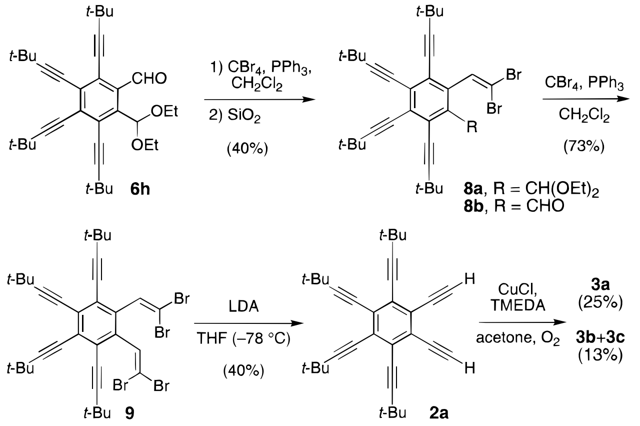


Figure 2. Space-filling view of the PM3-calculated T.S. in the symmetrical addition of **1b** and **5f**.

cyclopentadienone **1c** should not display this steric bias, its reaction with hexatriyne **5f** was attempted. Unfortunately, the expected symmetrical adduct **6k** was not observed among a complex mixture of highly colored compounds.

The preparation of the desired HEB **2a** was carried out from adduct **6h**. Attempts to deprotect acetal **6h** to the corresponding dialdehyde led to decomposition. Therefore, sequential dibromo-olefination (CBr_4, PPh_3) afforded **9** *via* **8b**.[13] Contrary to **6h**, acetal **8a** hydrolyzed cleanly



upon flash chromatography on silica gel (CH_2Cl_2/hexanes 2:1) to give aldehyde **8b**. Tetrabromide **9** was converted readily to the diethynyl system **2a** by treatment with LDA. Cyclization of **2a** under Hay coupling conditions[14] ($CuCl{\cdot}Me_2NCH_2CH_2NMe_2$, O_2, acetone, 25 °C) afforded a mixture of highly fluorescing oligomers **3a**–**c**. Separation by column chromatography on silica gel (hexanes/CH_2Cl_2 4:1) afforded pure dimer **3a** as a surprisingly stable yellow crystalline solid, together with an inseparable fraction containing trimer **3b** and tetramer **3c**.

Single crystals of [12]annulene **3a** were obtained from MeOH/$CHCl_3$. X-ray structural analysis[15] shows that the diyne units forming the [12]annulene portion of this molecule are bent to the same extent as for two other octadehydro[12]annulenes (Figure 3a).[16,17] However, there are some surprising bond elongations within the [12]-annulene and benzene rings along the C_2-axis passing through both six-membered rings. For example, the benzene π-bonds vary from 1.380(7) to 1.499(8) Å (1.40 Å expected value). Calculations (PM3 or *ab initio* 3-21G) do not reproduce these distortions, which must be attributed to packing effects. The unusual stability of this system, in strong contrast with literature precedence,[16] is explained by the steric shielding of the strained [12]-annulene moiety by bulky *t*-Bu groups and $CHCl_3$ molecules in the packing structure (Figure 3b).[17]

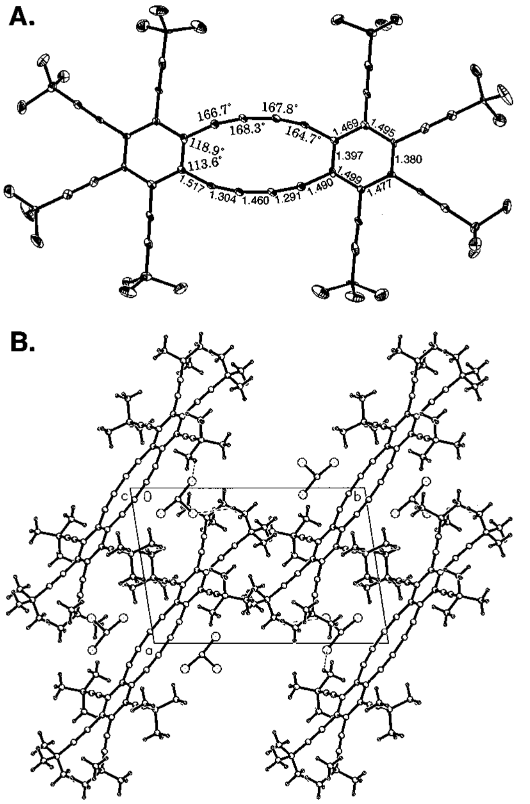


Figure 3. (a) X-ray structure of dimer **3a**. (b) Cell packing for **3a**·$(CHCl_3)_2$·MeOH where MeOH is omitted for clarity.

Dimer **3a** constitutes a piece of an extended network polymer incorporating this unit,[5b] and its properties will be reported elsewhere. We are now pursuing the synthesis of the interesting large graphyne fragment **4**.

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Supporting Information Available: Experimental section and $^1H/^{13}C$ NMR spectra for new compounds (37 pages).

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(15) Compound **3a** ($C_{68}H_{72}{\cdot}(CHCl_3)_2{\cdot}MeOH$; $M_r = 1160.11$) crystallized in the triclinic space group $P\bar{1}$ with cell dimensions of $a = 11.491(2)$ Å, $b = 16.457(3)$ Å, and $c = 9.982(2)$ Å; $\alpha = 102.37(2)°$, $\beta = 110.84(1)°$, $\gamma = 77.71(1)°$, $V = 1703.6(5)$ Å^3, and an occupation of $Z = 1$ in the unit cell. Data were collected at 100 K on a AFC5R Rigaku diffractometer (Cu Kα radiation), to a maximum $2\theta = 120°$, giving 3949 unique reflections; the structure was solved by direct methods (SHELX86) and refined within full matrix least squares, yielding $R = 0.066$, $R_w = 0.080$ for 2394 unique reflections with $I > 3\sigma(I)$. The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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