Professors Dale Margerum and Dave McMillin for helpful suggestions regarding this work.

Supplementary Material Available: Plots of transient absorbance vs time and k_e^{obsd} vs [ferrocene] for all ferrocenes studied and description of data reduction (7 pages). Ordering information is given on any current masthead page.

Homoconjugated Cyclic Polydiacetylenes[1]

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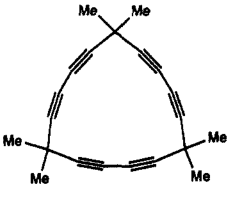
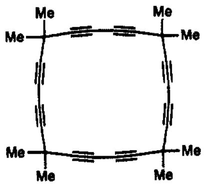
We have prepared and characterized the first cyclic homoconjugated polydiynes (**1**–**4**) and herein report our synthetic routes to these novel compounds, together with some of the properties they exhibit; their UV spectra show a distinct dependence on ring size.



1



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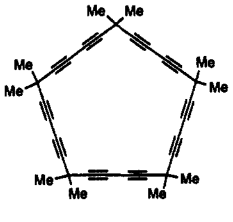

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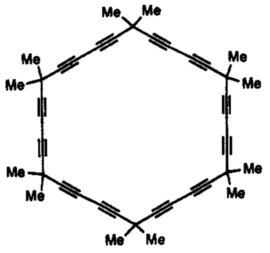


4

Earlier work in these laboratories[2-5] has focused on homoconjugated cyclic polyacetylenes bearing a single alkyne unit along each side of the ring ("[*N*]pericyclynes" with *N* = 5–8). Unfortunately, the first two members of that family (*N* = 3 and 4, the lower homologues of compounds **1** and **2** above) have so far escaped synthesis. Even in the larger pericyclynes, however, spectroscopic and thermochemical evidence indicates a strong electronic interaction among the cyclically juxtaposed alkyne units, and a similar degree of cyclic homoconjugation can be expected for the corresponding polydiynes. In compound **1**, bond-angle compression at the saturated carbon atoms should magnify the effect.

Scheme I

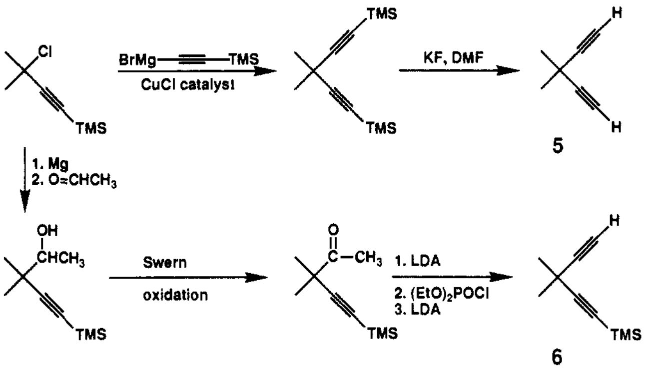


Table I. UV Spectra of Homoconjugated Cyclic Polydiacetylenes in Cyclohexane

compd	λ_{max} (ϵ)
1	219 (5170), 237 (2210), 253 (2060), 265 (1050, sh), 277 (760, sh)
2	212 (4900), 220 (4160), 232 (3880), 246 (4190), 260 (2150)
3	213 (6400), 220 (5840), 232 (5510), 245 (6210), 259 (4660)
4[a]	213, 220, 231, 245, 259

[a] Compound **4** does not dissolve completely in cyclohexane, so ϵ values are not reliable; however, the spectrum is virtually superimposable on that of compound **3**.

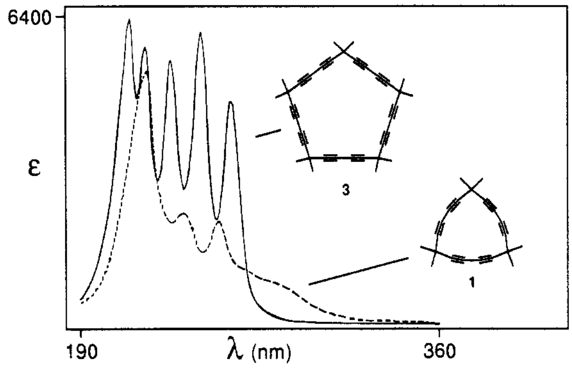
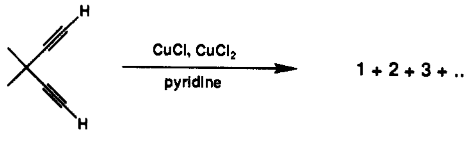


Figure 1. UV spectra of compounds **1** and **3** in cyclohexane.

We first prepared these homoconjugated cyclic polydiynes in a one-step "shotgun" synthesis by cyclooligomerization of 3,3-dimethyl-1,4-pentadiyne[6] under conditions known to effect oxidative coupling of terminal acetylenes (eq 1).[7] GC–mass spectral analysis revealed that compounds **1**–**3** were all produced in this reaction, albeit in low yield. Compound **4** (vide infra) does not pass through the gas chromatograph, so higher cyclic oligomers may also be present in this product mixture. The great abundance of easily bent acetylenic carbon atoms presumably accounts for the readiness with which the strained compounds **1** and **2** are formed.



(1)

Following this encouraging preliminary result, we set out to devise more efficient, stepwise syntheses of macrocycles **1**–**4**. Scheme I outlines practical routes we developed to the requisite

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(1) Part 7 in the series "Cyclynes". For part 6, see ref 5. This work was first presented at the 193rd National Meeting of the American Chemical Society, Denver, CO, April 1987.

(2) Scott, L. T.; DeCicco, G. J.; Hyun, J. L.; Reinhardt, G. *J. Am. Chem. Soc.* **1983**, *105*, 7760.

(3) Scott, L. T.; DeCicco, G. J.; Hyun, J. L.; Reinhardt, G. *J. Am. Chem. Soc.* **1985**, *107*, 6546.

(4) Houk, K. N.; Scott, L. T.; Rondan, N. G.; Spellmeyer, D. C.; Reinhardt, G.; Hyun, J. L.; DeCicco, G. J.; Weiss, R.; Chen, M. H. M.; Bass, L. S.; Clardy, J.; Jørgensen, F. S.; Sarkozi, V.; Petit, C.; Ng, L.; Jordan, K. D. *J. Am. Chem. Soc.* **1985**, *107*, 6556.

(5) Scott, L. T.; Cooney, M. J.; Rogers, D. W.; Dejroongruang, K. *J. Am. Chem. Soc.* **1988**, *110*, 7244.

(6) Diyne **5** has previously been prepared (Herberich, G. E.; Bauer, E.; Hengelsbach, J.; Kolle, U.; Huttner, G.; Lorenz, H. *Chem. Ber.* **1977**, *110*, 760), but we find the synthesis in Scheme I more convenient. All new compounds reported herein have been fully characterized by the usual spectroscopic methods plus elemental analysis and/or high-resolution mass spectrometry. ^{13}C NMR (CDCl$_3$): (**1**) 94.9, 66.1, 29.2, 27.5; (**2**) 81.3, 66.1, 29.9, 27.3; (**3**) 80.9, 64.9, 29.9, 27.0; (**4**) 80.7, 64.9, 30.3, 26.9.

(7) O'Krongly, D.; Denmeade, S. R.; Chiang, M. Y.; Breslow, R. *J. Am. Chem. Soc.* **1985**, *107*, 5544–5545.

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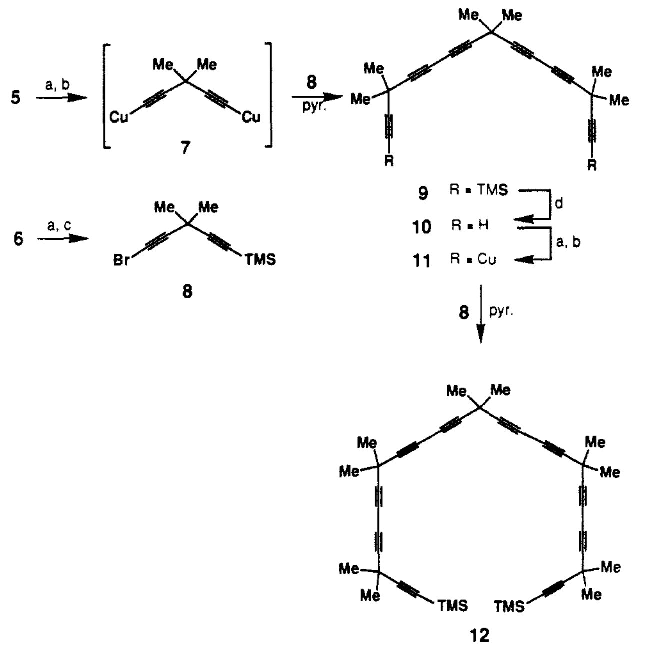
Scheme II[a]



[a](a) n-BuLi, THF, 0 °C. (b) CuCl, 0 °C. (c) TsBr, −78 to 25 °C. (d) KOH, MeOH.

monomer (**5**) and to a hemi-protected derivative thereof (**6**).

Conversion of **5** to the bis(copper acetylide) **7** and of **6** to the bromoacetylide **8**, as shown in Scheme II, followed by Cadiot–Chodkiewicz coupling gave the protected acyclic trimer **9** in 42% yield.[8] Cleavage of the trimethylsilyl groups from **9** released **10** (76%), which could then be cyclized to the closed trimer **1** in 30% yield under high-dilution conditions similar to those used in eq 1.[9] Alternatively, homologation of **10** at both ends, again with bromoacetylide **8**, as shown in Scheme II, gave the protected acyclic pentamer **12** in 45% yield. After cleavage of the trimethylsilyl groups from **12** (63%), cyclization as in eq 1 gave the 25-membered-ring pentamer in 89% yield.[10] Completely analogous chemistry, starting from the symmetrically coupled dimer of **6**, afforded the cyclic tetramer (**2**) and the cyclic hexamer (**4**).

The longest wavelength maximum in the UV absorption spectrum of the cyclic pentamer (**3**) appears at 259 nm, whereas the corresponding absorption in the spectrum of the cyclic trimer (**1**) appears as a shoulder at 277 nm (Table I and Figure 1). We believe this bathochromic shift to be a manifestation of significantly enhanced homoconjugation in **1** relative to that in **3**, as discussed above, and not of geometric distortion of the diyne chromophore. Other 1,3-diynes which, according to molecular mechanics calculations, are bent out of linearity to about the same extent as those in **1** but lack homoconjugation have long wavelength absorption maxima at only 256 nm.[11] The cyclic tetramer (**2**) and the cyclic hexamer (**4**) exhibit UV spectra very similar to that of the cyclic pentamer (**3**, Table I).

In conclusion, we have found that cyclic homoconjugated polydiynes **1**–**4** are easy to construct, simple to handle in the laboratory, and convenient to study by UV absorption spectroscopy. The smallest member of the series (**1**) appears to be significantly more strongly homoconjugated than its larger homologues. We are continuing to study these compounds as well as a variety of mixed acetylene–diyne macrocycles.

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.

Registry No. **1**, 126191-37-5; **2**, 126191-38-6; **3**, 126191-39-7; **4**, 126191-40-0; **5**, 62496-43-9; **6**, 4246-40-6; **6** (dimer), 126191-45-5; **8**, 126191-41-1; **9**, 126191-42-2; **10**, 126216-28-2; **12**, 126191-43-3; $ClC(CH_3)_2C\equiv CTMS$, 18387-63-8; $BrMgC\equiv CTMS$, 61210-52-4; $HC\equiv C[C(CH_3)_2C\equiv CC\equiv C]_4C(CH_3)_2C\equiv CH$, 126191-44-4.

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[8] CAUTION! Copper acetylides and some bromoacetylenes are potentially explosive when dry; it is safest never to remove solvent completely.

[9] A 30% yield of **1** was obtained by employing a mixture of $Cu(OAc)_2$ and CuCl at 60 °C for 3.5 h. The Breslow cyclization conditions[7] gave **1** in only 12% yield.

[10] The Breslow cyclization conditions[7] were employed for this cyclization.

[11] Matsuoka, T.; Negi, T.; Otsubo, T.; Sakata, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1825. Matsuoka, T.; Negi, T.; Misumi, S. *Synth. Commun.* **1972**, *2*, 87.

Automerization of Homocubylidene: Proof of a Reversible Olefin/Carbene Rearrangement

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Eaton and Hoffmann found that decomposition of cubylphenyldiazomethane gives 9-phenylhomocub-1(9)-ene (**1**) and discovered that this extremely twisted, anti-Bredt olefin rearranges to 1-phenylhomocubylidene (**2**), a singlet carbene.[1] Jones and Chen reported thereafter similar behavior for the desphenyl compound.[2] Herein we demonstrate that such extraordinary olefin-to-carbene rearrangements are reversible.[3]

We now know that the thermal decompositions of cubyl phenyl ketone tosylhydrazone (**3**) and of 1-phenylhomocubanone tosylhydrazone (**4**) in refluxing ethanolic sodium ethoxide give the *identical* distribution of ethyl ethers (Scheme I). As entry into the reaction from the "olefin side" (i.e., from **3**) gives the same product distribution as entry from the "carbene side" (i.e., from **4**), the reaction manifold would seem to allow for homocubene **1** and homocubylidene **2** to come into equilibrium. However, **2** might not be formed *directly* from the salt of **4**.[2,3] Carbon migration could proceed concomitantly with loss of dinitrogen (Scheme II); this would give **1** without the intervention of **2**, which would arise only subsequently from **1**. Under this less-than-simple circumstance, the observation of an identical product ratio from the decompositions of **3** and **4** does not require that equilibrium be reached between the olefin and the carbene, nor even that these be interconvertible. We demonstrate now that at least the latter does in fact pertain.

For unambiguous proof of the interconversion, an unequivocal source of homocubylidene is needed.[4] We use here 1(9)-homocubene itself (Scheme III: the atom numbering is of independent structures and is not meant to correlate atoms).

Eaton and White have shown that the rearrangement of olefin **1** to carbene **2** proceeds by a shift of C_2 (or C_8) from C_1 to C_9 rather than by phenyl migration (see Scheme I).[5,6] If 1(9)-homocubene (**5**) were to rearrange to homocubylidene (**6**) in the same way (as will be demonstrated), then *in the reverse reaction*, homocubylidene *to* 1(9)-homocubene, if it does occur, any one of four identical cage carbons (C_2, C_5, C_7, C_8) could shift to C_9 (homocubylidene numbering). Were the original precursor labeled

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[1] Eaton, P. E.; Hoffmann, K.-L. *J. Am. Chem. Soc.* **1987**, *109*, 5285. See also footnotes 13, 14, and 15 therein as well as the following: (a) Barton, T. J.; Yeh, M.-H. *Tetrahedron Lett.* **1987**, *51*, 6421. (b) Conlin, R. T.; Huffaker, H. B.; Kwak, Y.-W. *J. Am. Chem. Soc.* **1985**, *107*, 731. (c) Halton, B.; Bridle, J. H.; Lovett, E. G. *Tetrahedron Lett.* **1990**, *31*, 1313.

[2] Jones, M., Jr.; Chen, N. *J. Phys. Org. Chem.* **1988**, *1*, 305.

[3] Chen, N.; Jones, M., Jr. *Tetrahedron Lett.* **1989**, *50*, 6969.

[4] Cf. with refs 2 and 3.

[5] Eaton, P. E.; White, A. *J. Org. Chem.* **1990**, *55*, 1321.

[6] Scrambling of carbon-bearing-phenyl about the cage does not occur significantly. Presumably the phenyl group biases the rearrangement of carbene **2** such that **1** is always formed. This is sensible as **1** is stabilized by conjugation.