

Enhancement of Through-Space and Through-Bond π -Orbital Interactions. Syntheses and Properties of Permethylated and Perspirocyclopropanated Cyclotetradeca-1,3,6,9,12-pentayne¹

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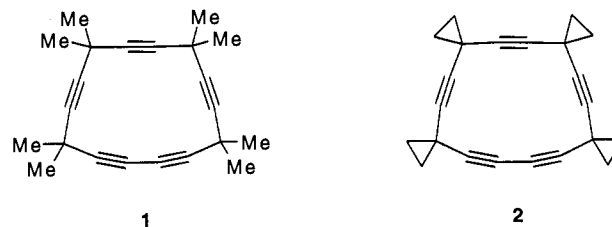
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Abstract: The permethylated and perspirocyclopropanated cyclotetradeca-1,3,6,9,12-pentaynes **1** and **2** have been synthesized and completely characterized by ¹H NMR, ¹³C NMR, UV, IR, and mass spectroscopy, as well as by X-ray crystal structure analysis. In the permethylated pentayne, compression of the internal C–C–C bond angles at the saturated carbon atoms flanking the diyne (103.8°) enhances the through-space π -orbital interactions and causes a bathochromic shift in the long wavelength UV absorption maximum (λ_{\max} 266 nm) relative to that of reference compounds (λ_{\max} 255–259 nm). In the perspirocyclopropanated pentayne, wider internal C–C–C bond angles at the corresponding carbon atoms (109.2°) reduce the through-space π -orbital interactions, but the through-bond π -orbital interactions are enhanced by spirocyclopropanation and cause a shift in the long wavelength UV absorption maximum to even longer wavelength (λ_{\max} 273 nm).

Introduction

The electronic interaction between two π systems that are formally insulated from one another by an intervening saturated carbon atom ("homoconjugation") can be divided conceptually into two components: a through-space interaction and a through-bond interaction. Cationic π systems have provided the most dramatic examples of homoconjugative effects in organic chemistry, e.g., homotropylium ion² and homocyclopropenylum ion;³ however, the properties of neutral molecules can likewise be affected by homoconjugation.⁴

Within the family of neutral hydrocarbons, octamethylcyclotetradeca-1,3,6,9,12-pentayne (**1**) represents an especially appealing new molecule to study, for it should exhibit constricted bond angles at its saturated vertices and a concomitant enhancement of through-space π -orbital interactions. The fully cyclopropanated counterpart **2**, on the other hand, offers a special opportunity for assessing the ability of cyclopropane rings to enhance the through-bond interactions (through cyclopropane Walsh orbitals) of formally insulated π systems. In both macrocycles, the 1,3-diyne provides a particularly convenient chromophore for examining the electronic properties of the compounds by UV spectroscopy. Accordingly, cyclic pentaynes



1 and **2** together constitute a unique pair of subjects for probing through-space and through-bond interactions in neutral hydrocarbon systems. In this paper, we describe the first syntheses, X-ray crystal structures, ¹H NMR, ¹³C NMR, UV, IR, and mass spectra of macrocycles **1** and **2**. A preliminary foray into the chemistry of **1** is also presented.

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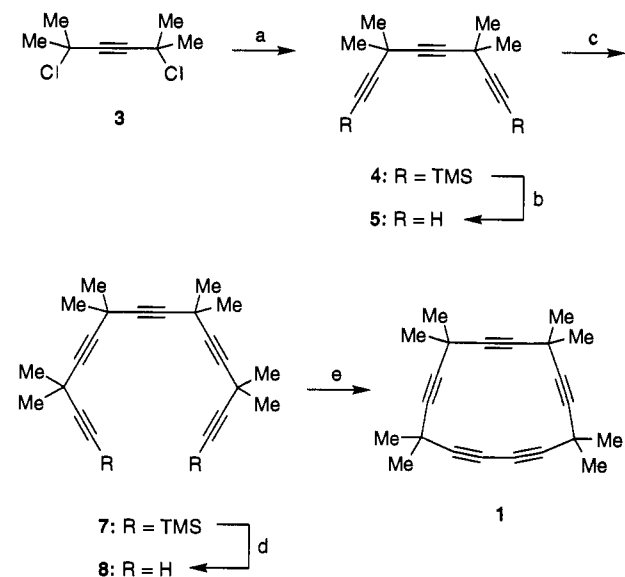
⊙ Abstract published in *Advance ACS Abstracts*, September 15, 1994.

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Scheme 1^a

^a (a) BrMgC≡TMS, CuCl (catalyst), THF, 53%; (b) KOH, MeOH, 60%; (c) EtMgBr, THF then CuCl (catalyst) then TMS-C≡C(Cl)Me₂ (6), 43%; (d) KOH, MeOH, C₆H₆, 90%; (e) CuCl, Cu(OAc)₂, pyridine, 67%.

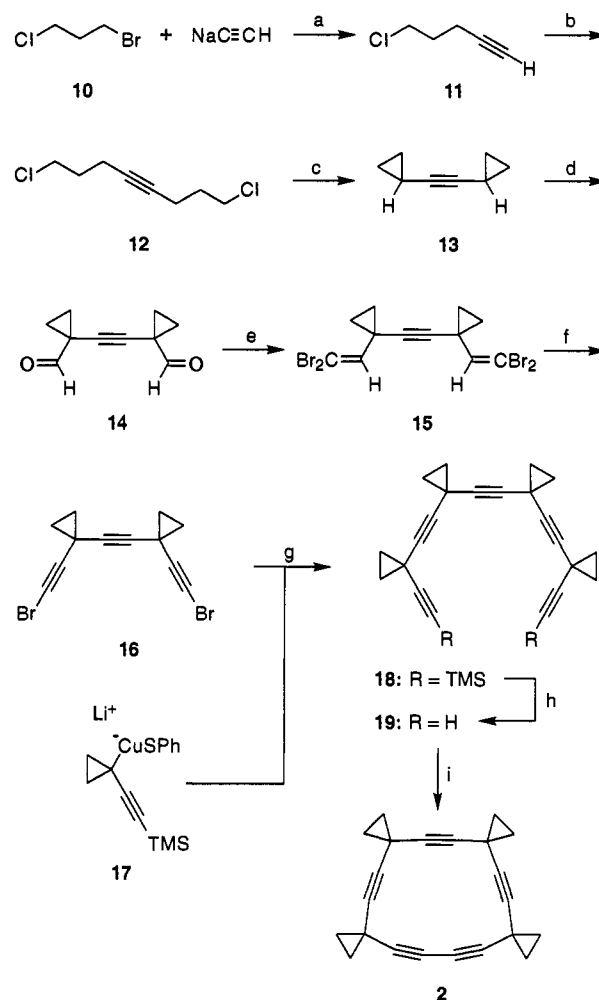
Results and Discussion

Syntheses. The octamethyl macrocycle (**1**) was prepared in five steps from dichloride **3**⁵ as outlined in Scheme 1. Thus, copper-catalyzed substitution of both chlorides in **3** by the anion of (trimethylsilyl)acetylene,⁶ followed by removal of the TMS protecting groups, gave triyne **5** as colorless crystals on a multigram scale. Double deprotonation of **5** then set the stage for a second copper-catalyzed coupling, this time with 3-chloro-3-methyl-1-(trimethylsilyl)-1-butyne (**6**),^{6a} to give pentayne **7**, which was cleanly desilylated to the corresponding hydrocarbon **8**.

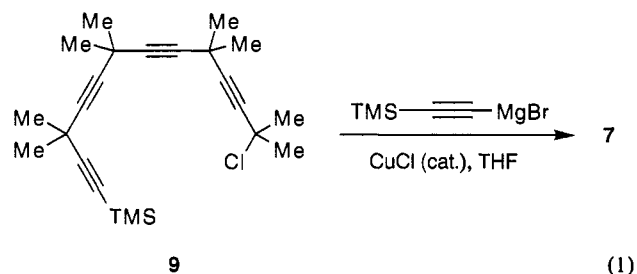
Cyclization of **8** to the 14-membered ring **1** was achieved in 67% yield by slow addition of the acyclic pentayne to a large excess of CuCl and Cu(OAc)₂ in pyridine. Slightly inferior, although still quite satisfactory, yields were obtained by use of the alternative oxidative coupling procedures of Breslow (64%) and Eglinton (54%).⁷ That the cyclization to make such an obviously strained diyne⁸ can be effected in better than 50% yield is particularly noteworthy.

A second route to the acyclic pentayne **7** was also developed (eq 1). This synthesis relies on the same copper-catalyzed coupling method employed above to join the components (*cf.* Scheme 1, first step) but makes use of the readily accessible tetrayne chloride **9**, an intermediate in our earlier synthesis of [*N*]pericyclines.^{6a}

The perspirocyclopropane derivative of cyclotetradeca-1,3,6,9,12-pentayne (**2**) was prepared according to the synthetic sequence summarized in Scheme 2. For the initial steps, alkylation of acetylene with 3-chloro-1-bromopropane (**10**) twice in succession was found to provide the most convenient and economical access to 1,8-dichloro-4-octyne (**12**) on a large scale. Then, in an extension of chemistry previously reported by de Meijere *et al.*,⁹

Scheme 2^a

^a (a) NH₃(liq) 34%; (b) NaNH₂ then **10** 32%; (c) LDA, THF 74%; (d) *t*-BuLi, TMEDA, pentane then DMF, 38%; (e) CBr₄, Ph₃P, Zn, CH₂Cl₂, 99%; (f) *t*-BuOK, THF, 90%; (g) Et₂O, THF, 63%; (h) NaOH, MeOH, 96%; (i) CuCl, Cu(OAc)₂, pyridine, 45%.



a 2-fold γ elimination of HCl was used to give dicyclopropyl acetylene (**13**) in 74% yield.

Onto this building block, aldehyde groups were introduced at the two propargylic positions by double lithiation of **13**¹⁰ and subsequent addition of *N,N*-dimethylformamide. Olefination to the tetrabromide **15** was then accomplished in essentially quantitative yield using the Corey-Fuchs procedure.¹¹

Treatment of **15** with potassium *tert*-butoxide in tetrahydrofuran (THF) at -78 °C cleanly afforded the triyne dibromide **16** as pale yellow crystals in 90% yield, and this product was coupled with an excess of the mixed cuprate **17** derived from lithiated [(trimethylsilyl)ethynyl]cyclopropane and (phenylthio)copper.¹²

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(11) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769-3772.

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(6) We have previously used this copper-catalyzed coupling reaction to prepare other *gem*-dimethyl "skipped diynes": (a) Scott, L. T.; DeCicco, G. J.; Hyun, J. L.; Reinhardt, G. *J. Am. Chem. Soc.* **1985**, 107, 6546. (b) See also refs 4b and 4l.

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(8) Strain energies calculated²⁰ for **1**, **2**, and cyclooctyne (for reference) are 29.1, 120.6, and 15.0 kcal/mol respectively.

(9) Millitzer, H.-C.; Schömenauer, S.; Otte, C.; Puls, C.; Hain, J.; Bräse, S.; de Meijere, A. *Synthesis* **1993**, 998-1012.

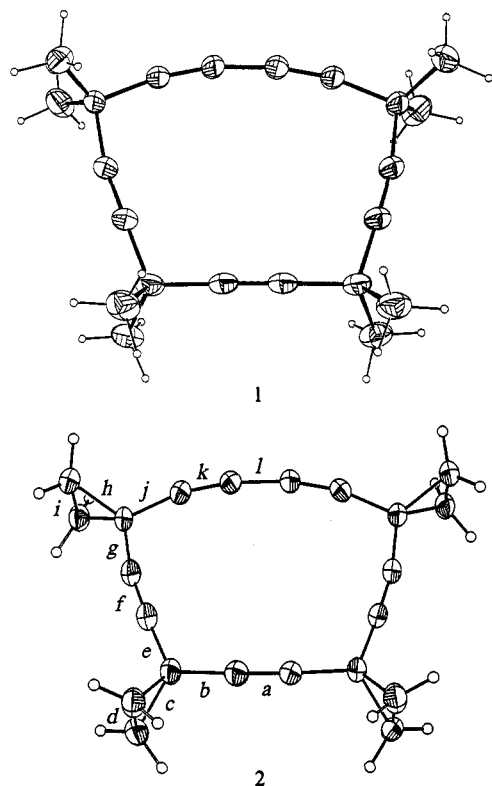


Figure 1. ORTEP plots from the X-ray crystal structures of the title compounds (1, top; 2, bottom).

Double desilylation of the resulting pentayne **18** with potassium hydroxide in methanol proceeded without complication to give **19**, the fully cyclopropanated analogue of **8**.

Cyclization of **19** to the perspirocyclopropanated 14-membered ring **2** was carried out using the recipe that worked best for **8**, *i.e.*, a large excess of CuCl and Cu(OAc)₂ in pyridine. In this case, the yield of the even more strained macrocycle **2** was still a respectable 45%.

Physical Properties and X-ray Crystal Structures. The two 14-membered ring pentaynes synthesized here are both stable, colorless, crystalline compounds. They survive heating to well over 100 °C and can both be recrystallized from hydrocarbon solvents. The octamethyl compound **1** melts cleanly without decomposition at 182–184 °C; however, the more strained perspirocyclopropane compound **2** turns brown at 155 °C and, in one instance, exploded¹³ when the bath of the melting point apparatus reached 192 °C.

Single-crystal X-ray diffraction studies gave the molecular structures of **1** and **2** shown in Figure 1 and the crystal packing pictures shown in Figures 2 and 3. Table 1 lists the internal C–C–C bond angles in the two macrocycles, which are especially relevant to the present discussion. Details of the X-ray structure analysis and complete tabulations of the data can be found in the Experimental Section and in the supplementary material.

The most conspicuous structural features of these cyclic pentaacetylenes are their bowed diyne moieties; the acetylenic carbon atoms of the diynes deviate from linearity by an average of 11.7° in the case of **1** and by an average of 13.4° in the case of **2**. The internal C–C–C angles at the saturated carbon atoms flanking the diyne in **1** are likewise smaller than normal (103.8°), and this draws the attached acetylenes closer to the diyne termini than one would find in an unconstrained system. The spirocyclopropane rings in **2**, on the other hand, force the corresponding internal angles to widen back to 109.2°.

A second unusual structural feature of the spirocyclopropane macrocycle **2** also deserves comment, *viz.*, the disparity of the

(13) Such thermal sensitivity has also been observed for the perspirocyclopropanated 30-membered ring dodecayne **24**, *cf.* ref 15.

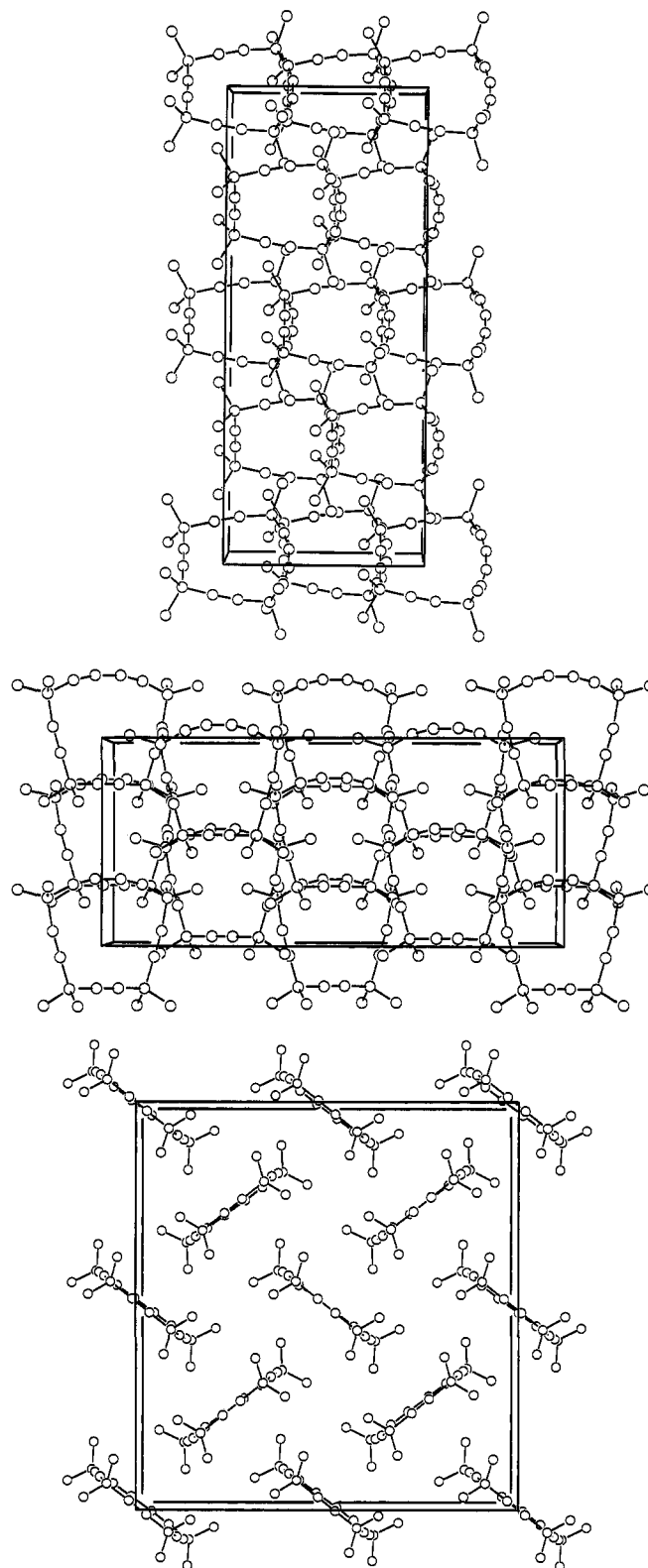


Figure 2. Crystal packing of title compound **1**.

C–C bond lengths in the cyclopropanes. In both pairs of cyclopropanes, the proximal bonds are longer than normal for a cyclopropane [$c = 1.525(4)$ Å, $h = 1.527(4)$ Å], while the distal bonds are shorter than normal [$d = 1.486(4)$ Å, $i = 1.481(4)$ Å]; the bond length disparity is slightly greater in the cyclopropanes adjacent to the diyne ($\Delta r = 0.046$ Å) than in those between two monoacetylenes ($\Delta r = 0.039$ Å). Figure 4 illustrates how the bond lengthening and bond shortening can be understood in terms of electronic interactions between the acetylene π systems and the cyclopropane Walsh orbitals.

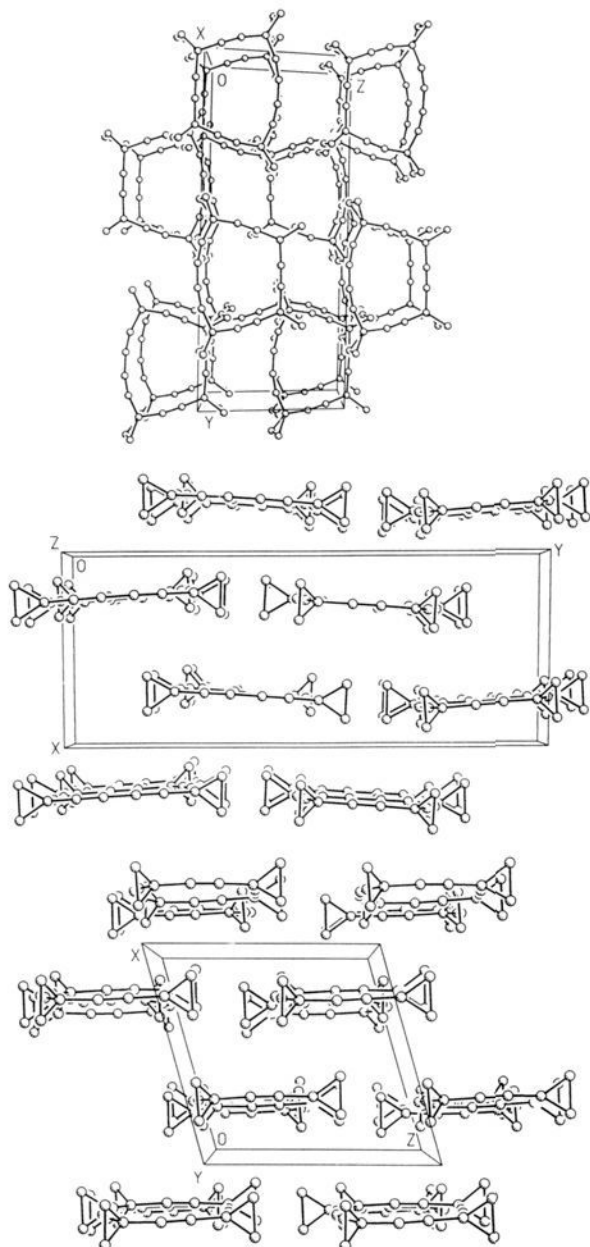


Figure 3. Crystal packing of title compound **2**.

Table 1. Internal C–C–C Bond Angles of the Title Compounds (**1** and **2**) from Their X-ray Crystal Structures^a

site	angle	
	permethyl macrocycle 1	perspirocyclopropane macrocycle 2
θ_{ab}	178.9(3)	177.7(4)
θ_{be}	109.2(2)	113.7(2)
θ_{ef}	177.6(3)	176.7(3)
θ_{fg}	170.7(3)	168.9(3)
θ_{gj}	103.8(2)	109.2(2)
θ_{jk}	168.1(3)	165.0(3)
θ_{kl}	168.5(2)	168.3(5)

^a Mean values reported in degrees with standard deviations in parentheses. See Figure 1 for site designations.

The acetylene out-of-plane π_+^* combination orbital has the proper symmetry to interact with the cyclopropane highest occupied molecular orbital (HOMO) and thereby withdraw electron density from it (Figure 4, bottom). Since the cyclopropane HOMO is bonding for the proximal bonds and antibonding for the distal bond, this loss of electron density should

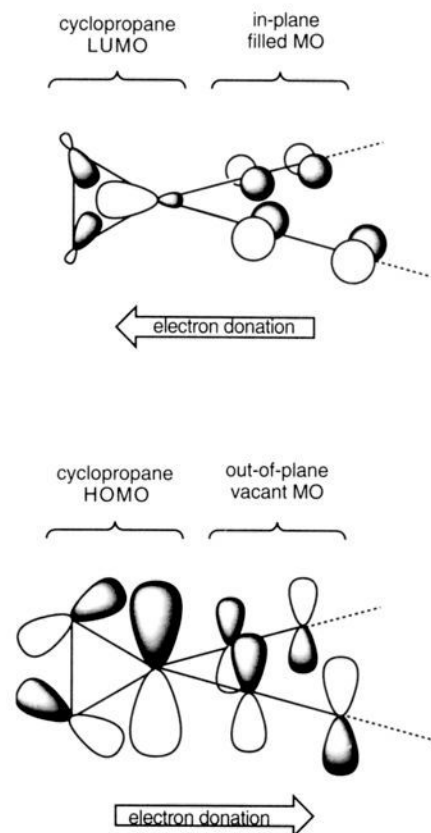


Figure 4. Dominant interactions between the cyclopropane Walsh orbitals and the acetylene π -combination orbitals.

weaken (lengthen) the proximal bonds and strengthen (shorten) the distal bonds, just as we observe.

The acetylene in-plane π_+ combination orbital, on the other hand, has the proper symmetry to interact with the cyclopropane lowest unoccupied molecular orbital (LUMO) and thereby donate electron density into it (Figure 4, top). Since the cyclopropane LUMO is antibonding for the proximal bonds and bonding for the distal bond, this gain of electron density should further weaken (lengthen) the proximal bonds and strengthen (shorten) the distal bonds, thus reinforcing the effects of the first interaction described above.

In 1,1-diethynylcyclopropane, a comparable bond length disparity in the same direction has been seen ($\Delta r = 0.043 \text{ \AA}$),¹⁴ presumably for the same reasons. An even greater disparity was recently found, however, in reference compound **24** (Figure 5), wherein spirocyclopropanes are flanked by diynes on *both* sides ($\Delta r = 0.059 \text{ \AA}$).¹⁵ Apparently, interactions between cyclopropanes and adjacent π systems of the sort depicted in Figure 4 are stronger with diynes than with unconjugated acetylenes. The lengthening of proximal bonds and shortening of distal bonds in cyclopropanes by electron withdrawing substituents has been known for many years¹⁶ and has generally been explained in terms similar to those in the bottom half of Figure 4.¹⁷ The remaining bond lengths in **1** and **2** all fall in the normal range.

Spectroscopic Properties. Table 2 lists the long wavelength UV absorption maxima and the NMR spectral properties of

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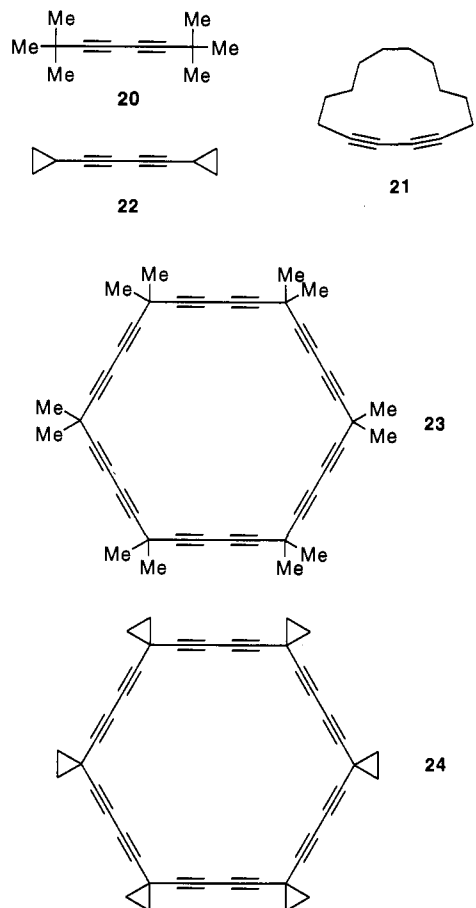


Figure 5. Reference compounds. See Table 2 for spectroscopic properties.

Table 2. Spectroscopic Properties of the Title Compounds (1 and 2) and Selected Reference Compounds (Pictured in Figure 5).

compound	UV ^a λ_{\max} (nm)	¹ H NMR ^b	¹³ C NMR ^b			
			diyne	alkyne	quat	CH ₃ or CH ₂
1	266	1.38	68.7	80.2	26.2	27.8
		1.41	88.8	81.7	28.7	31.1
20 ^c	255	1.24	63.7	82.3	28.0	30.6
			86.2			
21 ^d	256	134 ^f	67.5	27.0	29.9	
			82.8			
23 ^e	259	134 ^f	64.9	27.0	29.9	
			80.9			
2	273	1.03	69.2	76.0	3.4	17.2
		1.08	89.6	78.0	4.6	18.6
22 ^g	268	0.6–0.8	60.7	79.8	0.1	8.6
		1.2–1.3	79.7			
24 ^h	271	1.27	62.5	3.9	21.0	
			77.8			

^a Only the longest wavelength λ_{\max} 's are reported in this table; all UV spectra recorded in cyclohexane. ^b Parts per million (ppm) downfield from tetramethylsilane; NMR spectra recorded in CDCl₃ unless otherwise noted. ^c Reference 18. ^d References 8 and 19. ^e Reference 41. ^f Recorded in C₆D₆. ^g Reference 12. ^h Reference 15.

macrocycles **1** and **2** together with data for several cyclic and acyclic diyne reference compounds pictured in Figure 5.

Ordinary 1,3-diyne, such as di-*tert*-butyl-1,3-butadiyne (**20**),¹⁸ exhibit several absorption maxima in their UV absorption spectra, with the longest wavelength band typically appearing around 255 nm. In the spectrum of **1**, however, this absorption band is shifted to longer wavelength by 11 nm.

The 1,3-diyne chromophore in **1** differs from that in **20** in two important ways. Not only is it positioned so that it can interact

electronically at both ends with nearby π systems, it is also significantly bent. To assess how much of the bathochromic shift in the spectrum of **1** can be attributed to homoconjugation and how much is a consequence of steric distortion in the diyne chromophore from linearity, we draw a comparison with cyclohexadeca-1,3-diyne (**21**),^{8,19} a molecule that contains a bent diyne but has no opportunity for homoconjugation. Though no X-ray structure has been reported for **21**, molecular mechanics calculations²⁰ predict a distortion from linearity of 13.4° on average for the four acetylenic carbon atoms in this 14-membered ring diyne. Since the same molecular mechanics program²⁰ successfully reproduces the experimental values for the corresponding distortions in **1** and **2** to within ca. 1° (**1** calc 12.8°, X-ray 11.7°; **2** calc 14.2°, X-ray 13.4°), it seems safe to conclude that the steric distortion of the 1,3-diyne chromophore in **21** from linearity must closely match those in **1** and **2**. The absence of any significant bathochromic shift in the long wavelength UV absorption maximum of **21** (λ_{\max} 256 nm) with respect to that of the unstrained reference compound **20** (λ_{\max} 255 nm) implies that the substantial bathochromic shift in the long wavelength UV absorption maximum of **1** must be attributed almost entirely to factors other than strain, *e.g.*, to homoconjugation.

The "exploded" [6]pericyclicyne **23**⁴¹ shares with **1** the potential for cyclic homoconjugation and likewise exhibits a bathochromic shift in its long wavelength UV absorption maximum relative to those of **20** and **21**, albeit only 3–4 nm. Unlike **1**, however, macrocycle **23**, lacks constricted C–C–C bond angles at its saturated vertices. The "extra" bathochromic shift in the long wavelength UV absorption maximum of **1**, relative to that of **23**, can most reasonably be ascribed to an enhancement of homoconjugation by a stronger through-space π -orbital interaction in **1**. A stronger through-space π -orbital interaction is precisely what one would expect in a molecule where formally insulated π systems are drawn closer together by structural constraints.

From Table 2, it can be seen that the long wavelength UV absorption maximum of the perspirocyclopropane compound (**2**) is shifted even further to the red than is that of **1**. Since the internal C–C–C bond angles at the saturated vertices adjacent to the diyne in **2** (109.2°) are *larger* than those in **1** (103.8°), some factor(s) other than through-space π -orbital interactions must be exerting a significant effect in this molecule.

Reference compounds **22**¹² and **24**¹⁵ (Table 2) implicate the cyclopropane groups as the major cause of the bathochromic shift in the long wavelength UV absorption maximum of **2**, relative to that of a normal diyne, *e.g.*, **20**. Clearly, the presence of adjacent cyclopropanes strongly perturbs a diyne chromophore, presumably owing to strong σ - π interactions of the strained cyclopropane σ bonds with the diyne π system. For "isolated" diynes, flanking cyclopropanes cause a 13 nm bathochromic shift in the long wavelength UV absorption maximum, *cf.* **20** (λ_{\max} 255 nm) *vs* **22** (λ_{\max} 268 nm).

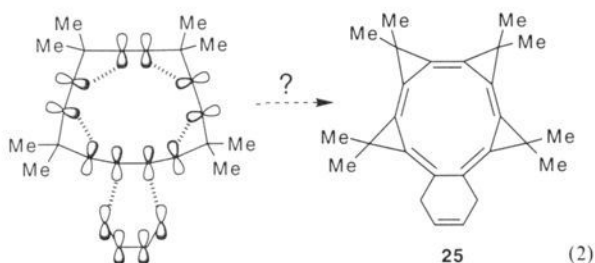
In macrocycle **24**, each cyclopropane must interact equally with two *geminally* attached diynes, and this interaction connects the diynes electronically *via* the cyclopropanes in a through-bond manner. Relative to macrocycle **23**, the perspirocyclopropanated macrocycles **24** and **2** both show strong bathochromic shifts in their long wavelength UV absorption maxima as a result of such through-bond π -orbital interactions. Squeezing the ring down in size from **24** to **2** has little effect on the magnitude of this through-bond interaction, nor should it, since it is only the out-of-plane π system that is properly aligned to overlap with the high-lying Walsh orbitals of the cyclopropanes, and the degree of this overlap should be relatively insensitive to in-plane angle deformations.

(19) (a) Matsuoka, T.; Negi, T.; Otsubo, T.; Sakata, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1825–1833. (b) We have also synthesized reference compound **21** by a somewhat different route than earlier workers in order to remeasure its UV spectrum.

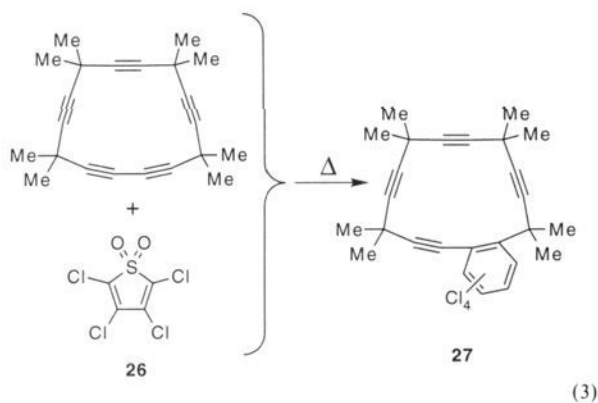
(20) Molecular mechanics calculations were performed using the program PCModel v 4.5, Serena Software, Bloomington, IN.

NMR spectroscopy has enjoyed widespread popularity as a tool for studying homoconjugation in ionic systems^{2,3} but is ill-suited for the evaluation of homoconjugation in neutral hydrocarbons. Accordingly, we abdicate discussion of the NMR data in Table 2 except to note that the diyne carbon atoms in the perspirocyclopropane compound **2** are slightly *deshielded* relative to those in **1**, whereas the carbon atoms of the three "isolated" alkynes are somewhat *shielded*. The magnitude of the shifts are small, however, so we hesitate to speculate on the origins of this effect.

Chemical Properties. Although we have not conducted a complete systematic investigation of the chemical properties of either **1** or **2**, we were intrigued by the possibility that this high-energy ring system might be transformed into a quintuply annulated [10]annulene by an unprecedented, but symmetry-allowed, [4 + 2 + 2 + 2 + 2 + 2] cycloaddition (eq 2). Unlike the parent *all-cis*-[10]annulene,²¹ which adopts a deep-tub conformation that effectively kills all cyclic conjugation, the smaller annulations in **25** ought to flatten the ring dramatically²² and restore the lost aromaticity of the [10]annulene.



Toward this objective, we exposed cyclic pentayne **1** to the electron-deficient diene tetrachlorothiophene 1,1-dioxide (**26**).²³ In refluxing chloroform, no reaction occurred; however, heating at 124 °C in tetrachloroethylene for 43 h gave a 1:1 adduct in 48% isolated yield. To our disappointment, however, the NMR and mass spectral properties of the adduct identify it as the product of a normal Diels-Alder reaction followed by SO₂ loss (**27**, eq 3) rather than as a derivative of the more symmetrical **25**.



Conclusions

Learning how to predict changes in the chemical and spectroscopic properties of molecules as a function of changes in

(21) (a) Masamune, S.; Darby, N. *Acc. Chem. Res.* **1972**, *5*, 272–281. (b) Masamune, S.; Hojo, K.; Bigam, G.; Rabenstein, D. L. *J. Am. Chem. Soc.* **1971**, *93*, 4966–4968. (c) Farnell, L.; Kao, J.; Radom, L.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1981**, *103*, 2147–2151.

(22) Compare with Paquette, L. A.; Wang, T. Z.; Cottrell, C. E. *J. Am. Chem. Soc.* **1987**, *109*, 3730–3734.

(23) For other recent uses of tetrachlorothiophene 1,1-dioxide as an "inverse electron demand" dienophile, see: (a) Gravett, E. C.; Howard, J. A. K.; Mackenzie, K.; Liu, S.; Karadakov, P. B. *Tetrahedron* **1993**, *49*, 4699–4710. (b) Tobe, Y.; Kawaguchi, M.; Kakiuchi, K.; Naemura, K. *J. Am. Chem. Soc.* **1993**, *115*, 1173–1174.

their structure has stood as one of the most fundamental goals of chemistry ever since the earliest concepts of molecular structure emerged more than a century ago. In the present study, structural changes designed to enhance homoconjugation in neutral hydrocarbons containing 1,3-diyne were predicted to cause bathochromic shifts in their long wavelength UV absorption maxima, and the experimental results conform to the predictions. For the permethylated compound, **1**, the bathochromic shift can be ascribed to a through-space π -orbital interaction that is enhanced by angle compression at the saturated carbon atoms in the macrocycle. For the perspirocyclopropane compound, **2**, the bathochromic shift can be ascribed to a through-bond π -orbital interaction that is enhanced by involvement of the cyclopropane bent-bond orbitals at the saturated carbon atoms in the macrocycle. The structure–property relationships exemplified by this pair of new compounds has deepened our understanding of the principles of homoconjugation.

Experimental Section

General Methods. All purchased reagents were used as received without further purification unless otherwise indicated. Tetrahydrofuran (THF) and diethyl ether were distilled from the potassium ketyl of benzophenone prior to use. All other solvents were purified as necessary using procedures in Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, 1980. *n*-Butyllithium was titrated with a THF solution of diphenylacetic acid (about 0.15 g/15 mL) until the yellow end point was visible for 30 s. Cupric chloride was dried in a 170 °C oven. Cuprous chloride was stored in a desiccator and protected from light. Baker silica gel 60–200 or Aldrich aluminum oxide (activated, neutral, Brockmann I, ca. 150 mesh, 0.58 Å) was used for standard column chromatography. Merck silica gel grade 60, 230–400 mesh, 60 Å was used for flash column chromatography. Either Whatman 250 mm Flexible plates (AL SIL G/UV) or Macherey & Nagel DC-Alufolien Kieselgel 60 F₂₅₄ (layer thickness 0.2 mm) were used for all TLC analyses. The plates were soaked for a few seconds in a 20–25% ethanolic solution of phosphomolybdic acid and developed with a heat gun. Analtech Uniplate Taper Plates, Silica Gel GF were used for preparative thin layer chromatography. Gas chromatographic analyses were performed with either a Varian Aerograph Model 1400 equipped with a wide bore capillary column (SPB-5, 30 meters \times 0.75 mm ID and 1.0 mm OD) or with a Hewlett-Packard 5890 GC equipped with a Supelco 30 m \times 0.32 mm \times 0.25 mm thick SPB-5 capillary column or a Supelco 30 m \times 0.32 mm \times 0.25 mm thick SE-54 capillary column. GC/MS analyses were carried out on a Hewlett-Packard 5890 GC/5970 series mass selective detector equipped with an HP 25 m \times 0.2 mm \times 0.11 mm thick HP-1 capillary column. ¹H NMR spectra were recorded on either an IBM AF 80 (80 MHz) or a GE QE 300 (300 MHz) and are referenced to chloroform or benzene. ¹³C NMR spectra were recorded on the same instruments at 20 or 75 MHz respectively and are referenced to chloroform or benzene. Infrared spectra were recorded on either a Perkin-Elmer 599 infrared spectrophotometer or a Perkin-Elmer 1600 series FT IR. UV spectra were recorded on either a Beckman Model 25 spectrophotometer or a Perkin-Elmer Lambda 4c UV/vis spectrophotometer driven by a Perkin-Elmer 7500 professional computer system. All melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. Boiling points at atmospheric pressure (about 650 torr in Reno, NV) are uncorrected to 760 Torr. Combustion analyses were performed by Spang, Eagle Harbor, MI. We are grateful to the Midwest Center for Mass spectrometry with partial support by the National Science Foundation, Biology Division (grant no. Dir9017262) for high-resolution mass spectral analyses.

3,3,6,6-Tetramethyl-1,8-bis(trimethylsilyl)-1,4,7-octatriyne (4). A solution of 21.3 g (217 mmol) of (trimethylsilyl)acetylene in 35 mL of dry THF was added dropwise over about 30 min to a mixture of 110 mL (220 mmol) of 2.0 M ethylmagnesium bromide in THF and 35 mL of THF at 0 °C. After the addition was completed, the mixture was warmed to 50–55 °C for 30 min to ensure complete deprotonation and was then cooled back to room temperature. Next, 2.15 g (21.7 mmol) of cuprous chloride was added, followed by the addition, over 5–10 min, of 16.9 g (94.3 mmol) of 2,5-dichloro-2,5-dimethyl-3-hexyne (**3**)⁵ in 70 mL of dry THF. The reaction mixture was stirred at 50–55 °C for 3 h and at room temperature overnight. The dark-colored reaction mixture was quenched

with 150 mL of 10% aqueous sulfuric acid, and the layers were separated. The aqueous phase was extracted with 200 mL of ether. The combined organic layers were washed with saturated sodium bicarbonate solution and with 10% ammonium chloride solution. The organic phase was dried over magnesium sulfate, concentrated under reduced pressure, and fractionally distilled. The fraction boiling between 65–75 °C at 0.2 Torr was collected to give 19.6 g of 77% pure silylated triyne (**4**) as a white solid which was used without further purification in the next reaction. An analytical sample was prepared by recrystallization from 95% ethanol: mp 54–55 °C; $^1\text{H NMR}$ (CDCl_3) δ 1.47 (s, 12), 0.15 (s, 18); $^{13}\text{C NMR}$ (C_6D_6) δ 110.7, 83.6, 83.2, 31.6, 26.9, 0.13; IR (CCl_4) ν (cm^{-1}) 3000, 2960, 2890, 2200, 1480, 1465, 1450, 1420, 1390, 1370, 1260, 1230, 1210, 1140, 970, 900, 790. Anal. Calcd for $\text{C}_{18}\text{H}_{30}\text{Si}_2$: C, 71.44; H, 9.99. Found: C, 71.57; H, 10.07.

3,3,6,6-Tetramethyl-1,4,7-octatriyne (5). To a mixture of 100 mL of ice-cold methanol and 11.3 g (176 mmol) of 85% potassium hydroxide was added the 19.6 g of crude bis(trimethylsilyl)triyne **4** prepared above (77% purity). The mixture was allowed to warm to room temperature and was stirred overnight. Then, 100 mL of water was added, and the mixture was extracted with 3 \times 100 mL of pentane. The combined extracts were washed with 100 mL of water, dried over magnesium sulfate, and concentrated under reduced pressure. Distillation followed by recrystallization from hexane or pentane gave 4.72 g [32% over two steps from 2,5-dichloro-2,5-dimethyl-3-hexyne, (**3**)] of triyne **5** as white crystals: bp 62–64 °C (15 torr); mp 38–41 °C; $^1\text{H NMR}$ (CDCl_3) δ 2.14 (s, 2), 1.47 (s, 12); $^{13}\text{C NMR}$ (C_6D_6) δ 88.0, 83.4, 66.1, 31.3, 25.7; IR (neat) ν (cm^{-1}) 3320, 3010, 2960, 2900, 2140, 1480, 1470, 1455, 1395, 1375, 1275, 1230 (sh), 1210, 1155, 1015 cm^{-1} ; MS, m/z (rel intensity) 158 (M^+ , 6), 143 (39), 128 (100), 91 (66), 77 (12), 67 (29), 65 (65), 41 (41). Anal. Calcd for $\text{C}_{12}\text{H}_{14}$: C, 91.08; H, 8.92. Found: C, 90.92; H, 8.81.

3,3,6,6,9,9,12,12-Octamethyl-1,14-bis(trimethylsilyl)-1,4,7,10,13-tetradecapentayne (7). Method A. Under a nitrogen atmosphere, a solution of 4.72 g (29.8 mmol) of triyne **5** in 20 mL of dry THF was added dropwise to 33 mL (66 mmol) of 2.0 *M* ethylmagnesium bromide in THF at 0 °C. The mixture was warmed to 50–55 °C for 30 min to ensure complete deprotonation and was then cooled back to room temperature. Next, 295 mg (2.98 mmol) of cuprous chloride was added, and this was followed by addition of a solution containing 11.5 g (66 mmol) of 3-chloro-3-methyl-1-(trimethylsilyl)-1-butynyl^{6a} in 20 mL of THF. The mixture was stirred at 50 °C for 3 h and at room temperature overnight. The reaction mixture was quenched with 75 mL of 10% aqueous sulfuric acid, and the layers were separated. The aqueous layer was extracted with 100 mL of ether. The combined organic layers were washed with 2 \times 150 mL each of saturated sodium bicarbonate solution and 10% aqueous ammonium chloride, dried over magnesium sulfate, and concentrated under reduced pressure. Column chromatography on silica gel using 20:1 hexane/ethyl acetate as eluant followed by two recrystallizations from hexane gave 4.73 g of pentayne **7** as a white solid that was 100% pure by GC. A second crop of the product was obtained from the mother liquor (0.78 g), for a total of 5.51 g (43%) of **7**: R_f = 0.78 (TLC, silica gel, 20:1 hexane/ethyl acetate); mp 86–87 °C; $^1\text{H NMR}$ (CDCl_3) δ 1.45 (s, 12), 1.43 (s, 12), 0.13 (s, 18); $^{13}\text{C NMR}$ (CDCl_3) δ 110.74, 84.13, 83.66, 83.12 (2 C's?), 31.61, 31.56, 26.95, 26.09, 0.11; GC/MS m/z (rel intensity) 434 (M^+ , 1), 419 (8), 361 (20), 331 (4), 121 (5), 97 (20), 83 (5), 74 (8), 73 (100), 59 (14), 45 (7). Anal. Calcd for $\text{C}_{28}\text{H}_{42}\text{Si}_2$: C, 77.34; H, 9.74. Found: C, 77.44; H, 9.71.

3,3,6,6,9,9,12,12-Octamethyl-1,14-bis(trimethylsilyl)-1,4,7,10,13-tetradecapentayne (7). Method B. Under a nitrogen atmosphere, a solution of 0.68 g (6.9 mmol) of (trimethylsilyl)acetylene in 3 mL of dry THF was added dropwise to 3.6 mL (7.2 mmol) of 2.0 *M* ethylmagnesium bromide in THF at 0 °C. The mixture was warmed to 50–55 °C for 30 min to ensure complete deprotonation and was then cooled back to room temperature. Next, 34 mg (0.35 mmol) of cuprous chloride was added, and this was followed by addition of a solution containing 2.45 g (6.6 mmol) of tetrayne chloride **9^{6a}** in 3 mL of THF. The mixture was stirred at 50 °C for 5 h and at room temperature overnight. The reaction mixture was quenched with 10 mL of 10% aqueous hydrochloric acid, and the layers were separated. The aqueous layer was extracted with 3 \times 50 mL of pentane. The combined organic layers were washed with 2 \times 50 mL each of saturated sodium bicarbonate solution and 10% aqueous ammonium chloride, dried over magnesium sulfate, and concentrated under reduced pressure. Column chromatography on silica gel using 20:1 hexane/ethyl acetate as eluant gave 1.16 g (40%) of pentayne (**7**) as a white solid with the same physical properties as the material obtained from method A above.

3,3,6,6,9,9,12,12-Octamethyl-1,4,7,10,13-tetradecapentayne (8). A mixture of 1.06 g (2.44 mmol) of bis(trimethylsilyl)pentayne **7**, 0.63 g (9.5 mmol) of 85% potassium hydroxide, 5 mL of methanol, and 2 mL of benzene was stirred at room temperature for 48 h. Then, 25 mL of water was added, and the mixture was extracted with 4 \times 50 mL of pentane. The combined extracts were washed with 100 mL of water, dried over magnesium sulfate, and concentrated under reduced pressure. Sublimation [70 °C (0.075 torr)] of the crude material gave 0.64 g (90%) of pentayne **8** as a white solid: mp 72–75 °C; $^1\text{H NMR}$ (CDCl_3) δ 2.15 (s, 2), 1.42 (s, 24); $^{13}\text{C NMR}$ (C_6D_6) δ 88.1, 84.1, 83.6, 82.9, 68.0, 31.6, 31.3, 26.1, 26.0; GC/MS m/z (rel intensity) 290 (M^+ , not observed), 275 (M^+ – CH_3 , 21), 260 (15), 245 (100), 230 (74), 229 (45), 217 (57), 215 (63), 203 (57), 193 (57), 189 (37), 178 (45), 165 (48), 152 (27), 141 (24), 128 (24), 115 (38), 91 (26), 77 (38), 65 (32), 51 (22), 41 (39). Anal. Calcd for $\text{C}_{22}\text{H}_{26}$: C, 90.98; H, 9.02. Found: C, 91.07; H, 9.13.

5,5,8,8,11,11,14,14-Octamethyl-1,3,6,9,12-cyclotetradecapentayne (1). A solution of 300 mg (1.03 mmol) of acyclic pentayne **8** in 35 mL of dry pyridine was added with a syringe pump over 5.5 h to a 60 °C mixture containing 7.5 g (41.2 mmol) of anhydrous cupric acetate and 2.0 g (20.6 mmol) of cuprous chloride in 500 mL of dry pyridine. Stirring was continued overnight at room temperature. The reaction mixture was slowly poured into 500 mL of ice-cold 25% aqueous hydrochloric acid. An additional 50 mL of concentrated hydrochloric acid was then added. The aqueous mixture, which was still blue at this point, was extracted with 3 \times 250 mL of pentane. The combined extracts were washed with 2 \times 300 mL of 10% aqueous hydrochloric acid and with 150 mL of saturated aqueous sodium bicarbonate, dried over magnesium sulfate, and concentrated under reduced pressure. Flash chromatography on silica gel using 10:1 hexane/ethyl acetate followed by recrystallization from hexane gave 200 mg (67%) of cyclic pentayne **1** as white crystals: mp 182–184 °C; $^1\text{H NMR}$ (CDCl_3) δ 1.41 (s, 12), 1.38 (s, 12); $^{13}\text{C NMR}$ (CDCl_3) δ 88.8, 82.3, 81.7, 80.2, 68.7, 31.1, 28.7, 27.8, 26.2; IR (KBr) ν (cm^{-1}) 2985, 2941, 2869, 2247, 1466, 1438, 1383, 1361, 1246, 1202, 1136, 1108, 998; UV (cyclohexane) λ_{max} (ϵ) 207 (8000), 230 (432), 240 (632), 252 (716), 266 (453) MS m/z (rel intensity) 288 (M^+ , 100), 273 (29), 257 (26), 243 (73), 228 (43), 215 (32), 202 (30), 189 (15), 165 (11); HRMS M^+ calcd for $\text{C}_{22}\text{H}_{24}$ 288.1872, found 288.1872.

5-Chloro-1-pentyne (11). A solution of sodium acetylide (2 mol) in 3 L of liquid ammonia was treated with 1-bromo-3-chloropropane (197 mL, 2 mol) at –70 °C. The mixture was warmed up to –35 °C and stirred for 4 h. Ammonia was allowed to evaporate overnight. To the dry residue was added very cautiously 1 L of water, and the aqueous phase was extracted with ether (4 \times 200 mL). The combined organic layers were washed with hydrochloric acid (1*N*, 2 \times 100 mL) followed by sodium bicarbonate (5%, 2 \times 100 mL) and brine (200 mL). The organic phase was dried over magnesium sulfate, and the solvent was removed by distillation at normal pressure. Vacuum distillation of the crude product gave 69.7 g (34%) of **11** as a colorless liquid: bp 62–65 °C (140 Torr); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 3.67, (t, 2, 3J = 6.3 Hz), 2.39 (dt, 2, 3J = 6.8 Hz, 4J = 2.7 Hz), 1.98 (m, 3); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 82.34, 69.17, 43.30, 30.97, 15.66; IR (film) ν (cm^{-1}) 3300, 2963, 2120, 1436, 1291, 988, 900, 848, 768, 726, 654, 538, 508.

1,8-Dichloro-4-octyne (12). A 102.5 g sample (1 mol) of 5-chloro-1-pentyne (**11**) was added to a solution of sodium amide (1 mol) in 1.5 L of liquid ammonia at –70 °C. After 1 h, 1-bromo-3-chloropropane (99 mL, 1 mol) was added, and the mixture was warmed up to –35 °C followed by stirring for 4 h. Ammonia was allowed to evaporate overnight. To the dry residue was added very cautiously 500 mL of water, and the aqueous phase was extracted with ether (4 \times 200 mL). The combined organic layers were washed with 1 *N* hydrochloric acid (2 \times 100 mL), 5% sodium bicarbonate solution (2 \times 100 mL), and brine (200 mL). The organic phase was dried over magnesium sulfate and concentrated under reduced pressure. Trap to trap distillation [110 °C (0.5 torr)] gave 58 g (32%) of **12** as a colorless liquid: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 3.65 (t, 4, 3J = 6.4 Hz), 2.34 (t, 4, 3J = 6.8 Hz), 1.93 (m, 4); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 83.4, 43.6, 31.5, 16.0; IR (film) ν (cm^{-1}) 2960, 2845, 1434, 1355, 1332, 1291, 972, 920, 859, 770, 725, 654, 534; MS m/z (rel intensity) 178 (M^+ , 2), 143 (M^+ – Cl, 21), 115 (16), 107 (21), 101 (15), 93 (15), 91 (41), 90 (18), 88 (60), 81 (34), 80 (18), 79 (100), 78 (17), 77 (99), 75 (15), 67 (44), 66 (10), 65 (44), 63 (21), 54 (17), 53 (44), 52 (34), 51 (52), 50 (19), 49 (15), 41 (30).

Dicyclopropylacetylene (13). A solution of diisopropylamine (85.5 mL, 0.6 mol) in 800 mL of anhydrous THF was treated with *n*-butyllithium (274 mL, 0.6 mol, 2.2 *N* in *n*-hexane) at 0 °C. After being stirred for 1 h, the mixture was slowly added to a –70 °C cold solution of 40 g (0.223 mol) of 1,8-dichloro-4-octyne (**12**) in 1.2 L of anhydrous THF. The

mixture was warmed up to 0 °C and stirred for 30 min. It was then poured into a saturated solution of ammonium chloride (500 mL) and extracted with pentane (4 × 300 mL). The combined organic layers were washed with water (300 mL) and brine (300 mL). After the layers were dried over magnesium sulfate, the solvent was removed by distillation at normal pressure, and the residue was purified by vacuum distillation to give 17.7 g (74%) of **13** as a colorless liquid: bp 61–64 °C (20 torr); ¹H NMR (300 MHz, CDCl₃) δ 1.23–1.12 (m, 2), 0.73–0.63 (m, 4), 0.62–0.56 (m, 4); ¹H NMR (300 MHz, C₆D₆) δ 1.08–0.98 (m, 2), 0.59–0.52 (m, 4), 0.38–0.30 (m, 4); ¹³C NMR (75 MHz, CDCl₃) δ 78.5, 7.8, –0.6; IR (film) ν (cm⁻¹) 3092, 3012, 1452, 1425, 1376, 1215, 1090, 1050, 1025, 1001, 902, 829, 810, 709; MS *m/z* (rel intensity) 106 (M⁺, 49), 105 (20), 103 (14), 91 (100), 79 (47), 78 (49), 77 (52), 66 (10), 65 (37), 63 (26), 62 (13), 53 (10), 52 (36), 51 (50), 50 (49).

1,1,4,4-Diethylene-1,4-diformyl-2-butyne (14). *tert*-Butyllithium (176.5 mL, 0.3 mol, 1.7 N in pentane) was added to a solution of *N,N,N',N'*-tetramethylethylenediamine (45.3 mL, 0.3 mol) and 10.6 g (0.1 mol) of dicyclopropylacetylene (**13**) in 1 L of anhydrous pentane at –78 °C. As the mixture was warmed up to room temperature, the dilithio derivative of **13** precipitated from the solution. The pale yellow suspension was stirred for 2 h at room temperature and then cooled again to –78 °C. *N,N*-Dimethylformamide (23 mL, 0.3 mol) was added, followed by stirring for 1 h. After being warmed up to room temperature, the mixture was poured into an ice cold saturated solution of ammonium chloride (300 mL), and the aqueous phase was extracted with ether (3 × 100 mL). The combined organic layers were washed with water (200 mL) and brine (200 mL) and dried over magnesium sulfate. Concentration in vacuo and chromatography on silica gel (100 g, pentane/ether 2:1) gave 6.1 g (38%) of crude **14** which was used without further purification: ¹H NMR (300 MHz, CDCl₃) δ 9.30 (s, 2), 1.58–1.51 (m, 8), 1.50–1.43; ¹³C NMR (75 MHz, CDCl₃) δ 197.9, 79.0, 23.7, 20.1; IR (KBr) ν (cm⁻¹) 3105, 3020, 2854, 2796, 2752, 1711, 1426, 1381, 1240, 1077, 1028, 906, 852, 778, 736, 536; MS *m/z* (rel intensity) 162 (M⁺, 59), 134 (12), 133 (75), 105 (40), 103 (28), 91 (53), 79 (56), 78 (28), 77 (100), 74 (13), 65 (26), 63 (20), 62 (11), 53 (15), 52 (18), 51 (51), 50 (30). Anal. Calcd for C₁₀H₁₀O₂: C, 74.06; H, 6.22. Found: C, 74.10; H, 6.26.

1,4-Bis(2,2-dibromovinyl)-1,1,4,4-bisethano-2-butyne (15). To a solution of carbon tetrabromide (37.2 g, 0.112 mol) in 600 mL of anhydrous dichloromethane was added triphenylphosphine (29.4 g, 0.112 mol) at room temperature with stirring. After a clear solution had been obtained, zinc (7.3 g, 0.112 mol) was added. The suspension was stirred for 45 h during which time the color changed from green to pink. Dialdehyde **14** (4.5 g, 28 mmol) was added, and after being stirred for 2 h, the mixture was poured into 1.2 L of hexane. The precipitate was filtered, dissolved in methylene chloride (300 mL), and precipitated with hexane (600 mL) again. This procedure was repeated two more times. The organic phases were combined and concentrated in vacuo. The crude product was purified by filtration over aluminum oxide (80 g, hexane/dichloromethane 10:1) to give 13.1 g (99%) of **15** as a pale yellow oil: ¹H NMR (300 MHz, CDCl₃) δ 6.37 (s, 2), 1.20–1.14 and 0.99–0.93 (m, 8); ¹³C NMR (75 MHz, CDCl₃) δ 138.6, 94.1, 78.2, 18.1, 14.2; MS *m/z* (rel intensity) 474 (M⁺, 4), 395 (10), 393 (11), 316 (22), 314 (44), 312 (24), 288 (13), 286 (26), 284 (14), 258 (13), 235 (45), 234 (14), 233 (45), 155 (14), 154 (M⁺ – 4 Br, 100), 153 (69), 152 (26), 128 (13), 126 (35), 98 (30), 86 (10), 77 (10), 76 (26), 75 (16), 74 (16), 63, (19), 51 (12).

1,8-Dibromo-3,3,6,6-diethylenocta-1,4,7-triyne (16). A solution of tetrabromide **15** (10 g, 21 mmol) in 400 mL of anhydrous THF was treated with potassium *tert*-butoxide (9.45 g, 84 mmol) at –78 °C. The mixture was stirred for 5 h at the same temperature followed by hydrolysis with 200 mL of water. The aqueous phase was extracted with hexane (3 × 150 mL). The combined organic layers were washed with hydrochloric acid (1 N, 100 mL) and 5% aqueous sodium bicarbonate (100 mL) and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residual crude product was used without further purification: yield: 5.9 g (90%) of **16** as pale yellow crystals; ¹H NMR (300 MHz, CDCl₃) δ 1.35–1.23 (m, 8); ¹³C NMR (75 MHz, CDCl₃) δ 80.8, 77.2, 35.7, 19.9, 3.6; IR (KBr) ν (cm⁻¹) 3101, 3015, 2241, 1447, 1420, 1357, 1260, 1070, 1064, 1040, 1010, 960, 893, 809, 785, 779, 668, 564, 538, 493; MS *m/z* (rel intensity) 314 (10), 313 (3), 312 (M⁺, 22), 310 (11), 258 (17), 256 (29), 254 (16), 233 (11), 231 (10), 205 (11), 203 (11), 178 (23), 175 (21), 153 (16), 152 (M⁺ – 2Br, 100), 151 (64), 150 (16), 126 (11), 124 (44), 98 (15), 97 (11), 96 (25), 76 (10), 75 (13), 74 (16), 63 (11), 62 (11), 61 (11).

1,14-Bis(trimethylsilyl)-3,3,6,6,9,9,12,12-tetraethylenetetradeca-1,4,7,10,13-pentayne (18). A solution of the (phenylthio)cuprate derived from [(trimethylsilyl)ethynyl]cyclopropane was prepared by a modification of

the procedure in ref 12. Thus, a solution of [(trimethylsilyl)ethynyl]cyclopropane⁹ (4.42 g, 32 mmol) in 150 mL of anhydrous ether was treated with *n*-butyllithium (12.7 mL, 30 mmol, 2.4 N in *n*-hexane) at 0 °C. After being stirred overnight at room temperature, the mixture was transferred into an addition funnel and added to a suspension of (phenylthio)copper (4.84 g, 28 mmol) in 440 mL of anhydrous THF at –25 °C. During a period of 20 min a clear orange solution was obtained, which then was cooled to –70 °C, followed by addition of dibromide **16** dissolved in 10 mL of THF. The reaction mixture was stirred for 30 min and directly poured into methanol (40 mL). A saturated solution of ammonium chloride (200 mL) was added, and filtration over Celite was performed immediately. The aqueous phase was extracted with ether (3 × 150 mL). The combined organic layers were washed with brine (100 mL) and dried over magnesium sulfate. The solvent was removed on a rotatory evaporator, and the residual crude product was flash chromatographed on silica gel (column 5 × 25 cm, petroleum ether/ether 200:1) and recrystallized from pentane to give 2.68 g (63%) of **18** as white crystals: mp 85 °C; ¹H NMR (300 MHz, CDCl₃) δ 1.17 (m, 8), 1.12 (m, 8), 0.13 (s, 9); ¹³C NMR (75 MHz, CDCl₃) δ 107.5, 80.2, 77.9, 77.5, 76.5, 20.8, 20.3, 3.4, 2.5, 0.0; IR (KBr) ν (cm⁻¹) 3104, 3054, 3020, 2960, 2165, 1420, 1374, 1265, 1061, 1033, 895, 843, 738, 703, 668, 643, 532; MS *m/z* (rel intensity) 353 (M⁺ – TMS, 3), 338 (3), 323 (8), 321 (3), 309 (7), 307 (6), 295 (7), 293 (7), 279 (10), 265 (7), 239 (4), 155 (3), 97 (4), 83 (3), 73 (100), 59 (7), 45 (7). Anal. Calcd for C₂₈H₃₄Si₂C, 78.81; H, 8.03. Found: C, 78.65; H, 8.23.

3,3,6,6,9,9,12,12-Tetraethylenetetradeca-1,4,7,10,13-pentayne (19). A suspension of compound **18** (2.44 g, 5.7 mmol) in 130 mL of methanol was treated with a solution of sodium hydroxide (10% in H₂O, 1 mL) and stirred at room temperature. After a clear solution had been obtained, the mixture was poured into a saturated solution of ammonium chloride (50 mL). The aqueous phase was extracted with ether (4 × 30 mL). The combined organic layers were washed with brine (30 mL), dried over magnesium sulfate, and concentrated in vacuo. The crude product was recrystallized from petroleum ether to give 1.56 g (96%) of **19** as white crystals: mp 69 °C; ¹H NMR (300 MHz, CDCl₃) δ 1.94 (s, 2), 1.19 (m, 8), 1.17 (m, 8); ¹³C NMR (75 MHz, CDCl₃) δ 85.6, 78.2, 77.4, 76.6, 64.3, 20.2, 20.1, 2.4, 2.3; IR (KBr) ν (cm⁻¹) 3286, 3013, 2115, 1423, 1374, 1248, 1063, 1029, 989, 941, 882, 818, 729, 674, 618, 568, 530; MS *m/z* (rel intensity) 280 (M⁺ – 2H, 3), 279 (13), 265 (100), 264 (45), 263 (48), 252 (88), 251 (70), 250 (98), 240 (21), 239 (88), 238 (23), 237 (52), 226 (74), 224 (60), 215 (26), 213 (24), 202 (31), 198 (20), 189 (23), 169 (40), 158 (10), 152 (11), 146 (14), 134 (13), 122 (16), 113 (10), 99 (11), 98 (11), 87 (11), 75 (9), 63 (10). Anal. Calcd for C₂₂H₁₈C, 93.57; H, 6.43. Found: C, 93.50; H, 6.26.

Tetraspiro[2.2.2.2.2.2.2.2]docosa-4,9,14,19,21-pentayne (2). To a solution containing cupric acetate (3.63 g, 20 mmol) and cuprous chloride (990 mg, 10 mmol) in 950 mL of anhydrous pyridine at 65 °C was added, by a syringe pump, a solution of pentayne **19** (564 mg, 2 mmol) in 50 mL of anhydrous pyridine over a period of 16 h. When the addition was completed the mixture was stirred for an additional hour and poured cautiously into 1 L of ice cold, vigorously stirred 25% aqueous hydrochloric acid. The aqueous phase was extracted with pentane thoroughly (5 × 200 mL), and the combined organic layers were washed with hydrochloric acid (1 N, 3 × 100 mL), sodium bicarbonate (200 mL), water (100 mL), and brine (100 mL), followed by drying over magnesium sulfate. The solvent was removed on a rotatory evaporator, and the crude product was purified by recrystallization from benzene/pentane to give 250 mg (45%) of **2**: mp 155 °C dec (CAUTION, one sample exploded when the oil bath temperature reached 192 °C); ¹H NMR (300 MHz, CDCl₃) δ 1.08 (m, 8), 1.03 (m, 8); ¹H NMR (300 MHz, C₆D₆) δ 0.87 (s, 8), 0.81–0.73 (m, 4), 0.73–0.66 (m, 4); ¹³C NMR (75 MHz, CDCl₃) δ 89.6, 79.8, 77.9, 76.0, 69.2, 18.6, 17.2, 4.6, 3.4; UV (cyclohexane), λ_{max} (ε) 208 (14 655), 243 (804), 256 (535), 273 (250), IR (KBr) ν (cm⁻¹) 3018, 1417, 1357, 1065, 1000, 989, 939, 819, 778, 668, 564, 538, 514, 482; MS *m/z* (rel intensity) 280 (M⁺, 20), 278 (17), 277 (30), 276 (43), 264 (30), 263 (100), 252 (32), 251 (27), 250 (94), 249 (26), 248 (27), 239 (20), 224 (24), 222 (27). Anal. Calcd for C₂₂H₁₆C, 94.25; H, 5.75. Found: C, 94.15; H, 5.80.

Cycloaddition of Tetrachlorothiophene Dioxide to 1. A solution of 25 mg (0.087 mmol) of **1** and 23 mg (0.09 mmol) of tetrachlorothiophene dioxide **26** in 1.5 mL of acid-free CDCl₃ was stirred at room temperature for 1 h. Thin layer chromatography on silica gel (30:1 hexane/ethyl acetate) indicated no reaction. The mixture was warmed to reflux for 1.5 h, but still no reaction was seen by TLC. The solvent was removed and replaced with 1,1,2,2-tetrachloroethane. The mixture was heated to 124 °C for 43 h. Then the solvent was removed under vacuum (0.2

Torr), and the crude material was dissolved in 3 mL of ether. This solution was adsorbed onto silica gel. The silica gel was dried under vacuum and then placed onto the top of a 4 in. column of dry silica gel. Elution with 50:1 hexane/ethyl acetate gave a yellow band which was further purified by preparative TLC on silica gel using 9:1 hexane/methylene chloride to give 20 mg (48%) of adduct (**27**) as white crystals: mp 187–190 °C dec (to yellow oil); $^1\text{H NMR}$ (CDCl_3) δ 1.97 (s, 6), 1.54 (s, 6), 1.37 (s, 6), 1.35 (s, 6); $^{13}\text{C NMR}$ (CDCl_3) δ 145.11, 136.29, 133.79, 131.34, 123.96, 110.52, 87.60, 85.81, 85.58, 84.59, 83.16 (2 C's?), 76.91, 38.70, 33.14, 30.15, 29.85, 29.51, 27.41, 26.35, 26.25; GC/MS m/z (rel intensity) 476 (M^+ , $\text{C}_{26}\text{H}_{24}^{35}\text{Cl}_4$, not observed), 465 ($\text{M}^+ - 15$, $\text{C}_{25}\text{H}_{21}^{37}\text{Cl}_2^{35}\text{Cl}_2$, 13), 463 ($\text{M}^+ - 15$, $\text{C}_{25}\text{H}_{21}^{37}\text{Cl}_1^{35}\text{Cl}_3$, 25), 461 ($\text{M}^+ - 15$, $\text{C}_{25}\text{H}_{24}^{35}\text{Cl}_4$, 20), 448 (26), 437 (13), 435 (49), 433 (100), 431 (72), 418 (51), 411 (47), 405 (53), 398 (46), 396 (49), 391 (40), 383 (47), 381 (46), 377 (30), 369 (47), 358 (30), 357 (41), 348 (30), 346 (43), 341 (29), 333 (37), 331 (37), 323 (25), 320 (39), 313 (16), 310 (45), 305 (19), 299 (20), 297 (31), 289 (29), 287 (31), 281 (15), 274 (34), 271 (19), 263 (29), 261 (26), 257 (13), 250 (26), 247 (19), 239 (14), 235 (17), 232 (10), 224 (16), 222 (12), 211 (13), 199 (16), 189 (10), 187 (11), 181 (13), 174 (11), 173 (12), 167 (15), 160 (11), 155 (22), 150 (12), 145 (27), 138 (26), 131 (22), 128 (16), 115 (16), 107 (12), 91 (20), 77 (27), 75 (11), 65 (20), 53 (18).

X-ray Crystal Structure of 1. Compound **1**, $\text{C}_{22}\text{H}_{24}$, crystallizes in the orthorhombic space group $Fdd2$ (systematic absences: $h0l$, $h + l = 4n + 1$, $2, 3$; $0kl$, $k + l = 4n + 1$, $2, 3$ and hkl , $h + k = 2n + 1$, $k + l = 2n + 1$, $h + l = 2n + 1$) with $a = 20.007(3)$, $b = 21.178(3)$, $c = 8.970(1)$ Å, $V = 3801(2)$ Å³, $Z = 8$, and $d_{\text{calcd}} = 1.008$ g/cm³. The cell constants were determined from a least-squares fit of the setting angles for 25 accurately centered reflections. X-ray intensity data were collected on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Cu K α radiation ($\lambda = 1.54184$ Å) and using the $\omega - 2\theta$ scan technique. X-ray data were processed, and the structure was solved and refined using the Enraf-Nonius MolEN²⁴ package on a DEC MicroVAX 3100 computer. A total of 1019 reflections were measured over the ranges: $4 \leq 2\theta \leq 140^\circ$, $0 \leq h \leq 24$, $0 \leq k \leq 25$, $0 \leq l \leq 10$. Three standard reflections measured every 3500 s of X-ray exposure showed no significant decay over the course of data collection.

The intensity data were corrected for Lorentz and polarization effects but not for absorption. Of the reflections measured a total of 922 unique reflections with $F_2 > 3\sigma(F_2)$ were used during subsequent structure refinement.

The structure was solved by direct methods (SIR88²⁵). Refinement was by full-matrix least-squares techniques based on F to minimize the quantity $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. Non-hydrogen atoms were

refined anisotropically and hydrogen atoms were included as constant contributions to the structure factors and were not refined. Refinement converged to $R_1 = 0.058$ and $R_2 = 0.073$.

X-ray Crystal Structure of 2. Compound **2**, $\text{C}_{22}\text{H}_{16}$, crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.653(3)$, $b = 20.980(9)$, $c = 9.092(3)$ Å, $\beta = 106.12(3)^\circ$, $V = 1585.7(1)$ Å³, $Z = 4$, and $d_{\text{calcd}} = 1.174$ g/cm³. The cell constants were determined from a least-squares fit of the setting angles for 25 accurately centered reflections (range $15 \leq 2\theta \leq 25$). X-ray intensity data were collected on a Nicolet R3m/V X-ray four cycle diffractometer employing graphite-monochromated Mo K α radiation ($\lambda = 1.71069$ Å) and using the Wyckoff scan technique (scan range 0.8°). The temperature of the data collection was 200 K. X-ray data were processed, and the structure was solved and refined using the SHELXTL-PLUS package on a SGI IRIS Indigo computer. A total of 2916 reflections were measured over the ranges: $3 \leq 2\theta \leq 50$, $0 \leq h \leq 9$, $0 \leq k \leq 24$, $-10 \leq l \leq 10$. Two standard reflections measured every 3600 s of X-ray exposure showed no significant decay over the course of data collection. The intensity data were corrected for Lorentz and polarization effects but not for absorption. Of the reflections measured, a total of 1573 unique reflections with $F_o > 4\sigma(F_o)$ were used during subsequent structure refinement. The structure was solved by direct methods. Refinement of 215 parameters was by full-matrix least-squares techniques based on F . All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included as constant contributions to the structure factors and were not refined. Refinement converged to $R = 0.0560$ ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) and $R_w = 0.0587$ ($R_w = [\sum (w||F_o| - |F_c||)^2 / \sum (|F_o|^2)]^{1/2}$ and $w^{-1} = (\sigma^2(F_o) + 0.0014F_o^2)$).

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Supplementary Material Available: Crystallographic data on macrocyclic pentaynes **1** and **2**, including cell information, data collection parameters, refinement data, final positional and equivalent isotropic thermal parameters, anisotropic thermal parameters, refined bond distances and bond angles (14 pages). This material is contained in many libraries on microfiche, immediately following this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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