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X-ray Structure Determination and Mechanism of Formation of Two Unique Cumulene Cyclodimers

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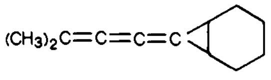
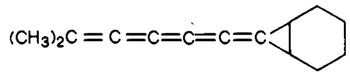
Abstract: Single-crystal X-ray determination established that the spontaneous cyclodimer of butatriene



is a syn-head-to-head bis(allenyl)cyclobutane (**5**) and the cyclodimer of the hexapentaene



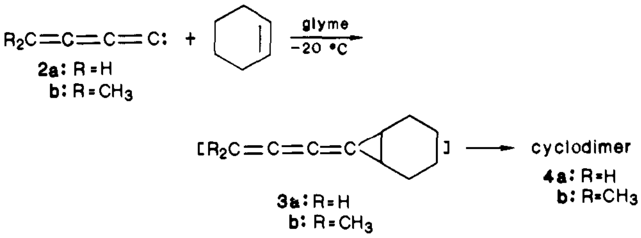
is a unique syn-head-to-head cyclyne, 1,3,7,9-cyclododecatetrayne (**18**). In both dimers **5** and **18** the cyclohexane positions of the [4.1.0]bicycloheptane groups are found to be disordered between two half-chair conformations. The central diacetylenic units in cyclyne **18** are part of a twelve-membered ring with a noncrystallographic twofold symmetry. These results, along with a plausible mechanism of formation, are discussed.

Strained organic molecules[2] have fascinated chemists for nearly a century. Because of their high energy and associated strain, these molecules generally have unusual chemical, spectral, and physical attributes that are of theoretical interest[2] and hence are a synthetic challenge.

Among the intriguing, strained, class of molecules are the cumulenes, **1**, a family of hydrocarbons with cumulated double bonds, with known members from the simple three carbon allenes (**1**: $n = 1$) through the 12-carbon dodecaudecaene (**1**: $n = 10$).[3]

$$>C{=}({=}C{=})_n{=}C< \quad \mathbf{1}:\ n = 1, 2...10$$

Recently one of us reported[4] the cyclodimerization of butatrienes **3**, derived[5] from unsaturated carbene(s) **2**. Cyclodimerization occurred spontaneously under the reaction conditions at −20 °C. Considering the unsymmetrical nature of the precursor butatienes **3**, a priori, there are 15 possible isomeric cyclodimers, **4**, consisting of three pairs of head-to-head **5**, **7**, **9** and head-to-tail **6**, **8**, **10** dimers, about the three different double bonds, each with syn and anti pairs, respectively, as shown in Chart I (isomers **5′**, **7′**, and **9′** can exist as enantiomeric pairs).



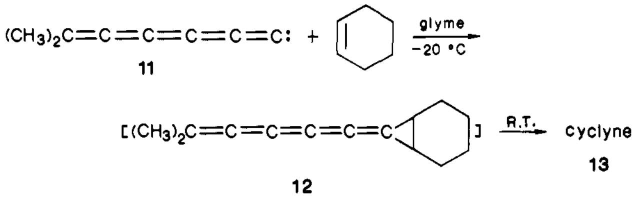
2a: R=H
b: R=CH3

3a: R=H
b: R=CH3

4a: R=H
b: R=CH3

Interestingly, despite the large number of possible cyclodimers, only a *single* compound was isolated from both the parent system **3a** and the dimethyl butatriene **3b**.[4,6] On the basis of spectral data and literature analogies we assigned the cyclodimers as the head-to-tail [4]radialene isomers **8**.[4] However, on the basis of the spectral data alone we could not, of course, be sure of this assignment, nor could we say anything about the *syn*-**8** or *anti*-**8′** forms.

Likewise, we subsequently reported[7] the unsaturated carbene, **11**, derived spontaneous cyclodimerization of hexapentaene **12** to a novel unsymmetrical cyclyne, **13**, a 1,3,7,9-cyclododecatetrayne.



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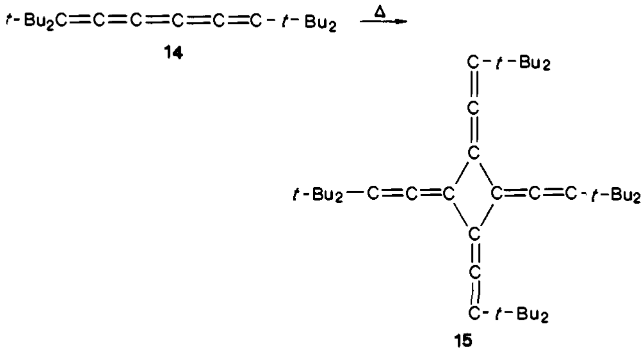
12

13

Once again a large number of cyclodimers are possible, including perhaps 2 + 2 dimers, such as the [4]radialene, **15**, reported by Hartzler[8] as the sole product in the thermal cyclodimerization of tetra-*tert*-butylhexapentaene **14**: Although the product cyclyne



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(2) Greenberg, A.; Liebman, I. F. *Strained Organic Molecules*; Academic: New York, 1978.

(3) For reviews and references on cumulenes see: Fischer, H. *The Chemistry of Alkenes*; Patai, S., Ed.; Wiley-Interscience: London, 1964; Chapter 13, pp 1025–1160. Murray, M. *Methoden Org. Chem. Houben-Weyl* **1977**, *V/2a*, 963–1076. Hopf, H. *The Chemistry of Ketenes, allenes and Related Compounds*; Patai, S., Ed.; Wiley-Interscience: Chichester, 1980; Part 2, Chapter, 20, pp 779–901.

(4) Stang, P. J.; Fisk, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 6813.

(5) For review see: Stang, P. J. *Acc. Chem. Res.* **1982**, *15*, 348. Stang, P. J. *Chem. Rev.* **1978**, *78*, 383.

(6) In the case of **3a** the dimer was isolated in 65% yield and with **3b** in 86% yield. No other products were isolated or observed by GC or TLC, although, in the absence of authentic samples, small amounts of the other possible dimers could, of course, have escaped detection. The simplicity[4] of both the ^1H and in particular the ^{13}C NMR spectra also argued against mixtures of isomers.

(7) Stang, P. J.; Ladika, M. *J. Am. Chem. Soc.* **1981**, *103*, 6437.

(8) Hartzler, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 4527.

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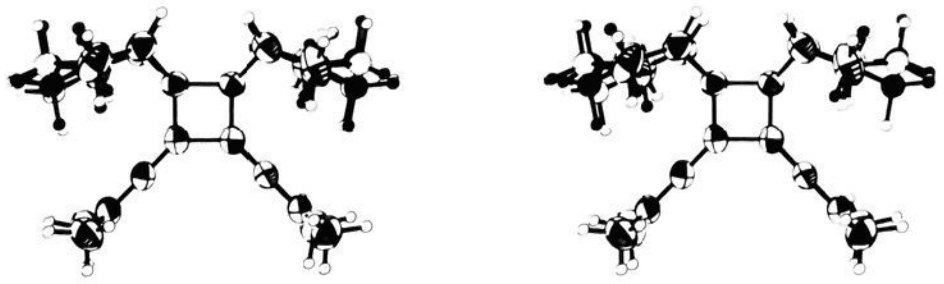
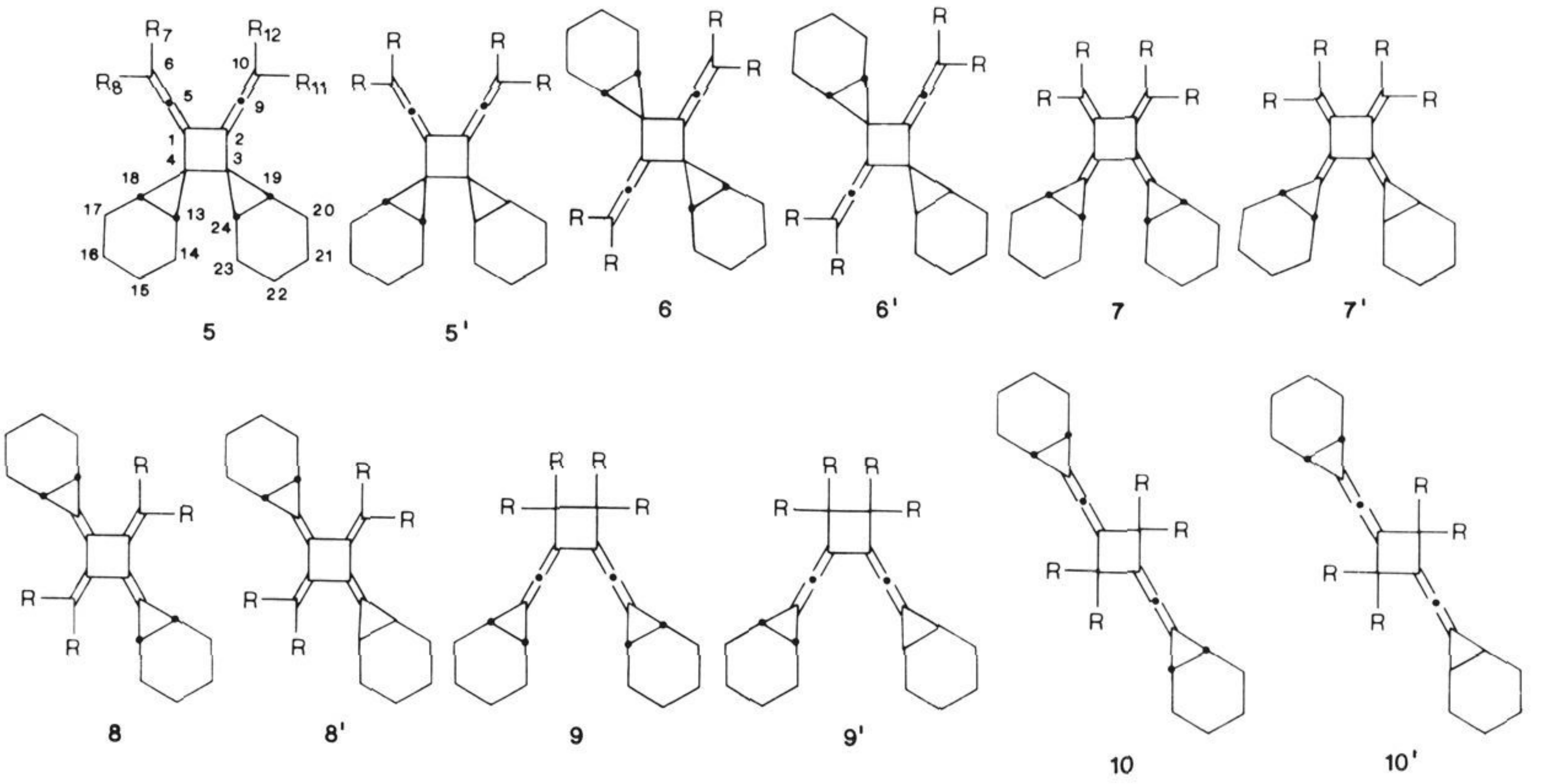


Figure 1.

Chart I



was isolated in only 31% yield, analytical data[7,9] once again indicated but a single isomer. On the basis of spectral data and the observation, by Scott and co-workers,[10] of a similar cyclyne, **17**, in the Cu^+ catalyzed cyclodimerization of tetramethylhexapentaene, **16**, we assigned[7] a cyclyne structure to our product.

$$(CH_3)_2C{=}C{=}C{=}C{=}C{=}C(CH_3)_2 \xrightarrow{Cu^+}$$

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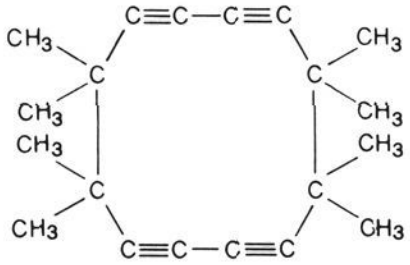

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However, one again, we could not *definitively* distinguish between the head-to-head *syn-anti* pairs **18** and/or the head-to-tail *syn-anti* pairs **19** as shown in Chart II. Hence, in order to firmly establish the exact identity, as well as the structural features and geometry, of these unique cumulene cyclodimers, we undertook a single-crystal X-ray analysis of dimers **4b** and **13**.

Results and Discussion

Final positional parameters of the non-hydrogen atoms for **4b** and **13** are listed in Tables I and II, respectively. Bond lengths and bond angles are given in Tables III and IV, respectively. The atomic numbering is indicated in Charts I and II, respectively. Stereoscopic drawings of the molecules are given in Figures 1 and 2 for **4b** and **13**, respectively. The data given clearly establish

Table I. Atomic Coordinates for Non-Hydrogen Atoms ($\times 10^4$) of **5**

atom	x	y	z	U_{eq}[a]
C(1)	2316 (3)	−839 (3)	6830 (4)	48 (2)
C(2)	3030 (3)	448 (3)	7479 (3)	48 (2)
C(3)	2346 (3)	999 (3)	8660 (3)	52 (2)
C(4)	1591 (3)	−305 (3)	7961 (4)	50 (2)
C(5)	2356 (3)	−1971 (3)	5723 (4)	53 (2)
C(6)	2362 (3)	−3091 (3)	4613 (4)	54 (2)
C(7)	3143 (3)	−4319 (4)	4945 (4)	77 (2)
C(8)	1547 (4)	−3239 (4)	2968 (4)	78 (2)
C(9)	3882 (3)	893 (3)	7105 (4)	53 (2)
C(10)	4740 (3)	1363 (3)	6769 (4)	59 (2)
C(11)	4449 (4)	2204 (4)	5631 (5)	88 (3)
C(12)	6074 (3)	1146 (4)	7586 (5)	89 (2)
C(13)	1888 (3)	2430 (3)	9273 (4)	66 (2)
C(14)	2227 (4)	3657 (4)	8908 (5)	89 (3)
C(17)	4147 (4)	2286 (4)	11099 (4)	82 (3)
C(18)	2859 (3)	1757 (4)	10376 (4)	67 (2)
C(19)	1136 (3)	−1043 (3)	8830 (4)	64 (2)
C(20)	1182 (3)	−2587 (4)	8474 (4)	79 (3)
C(23)	−610 (3)	−1241 (4)	6153 (5)	87 (2)
C(24)	235 (3)	−362 (3)	7665 (4)	68 (2)
				U_{iso}[b]
C(151)	3443 (9)	4330 (10)	10192 (14)	88 (3)
C(152)	3454 (10)	4098 (12)	9495 (14)	96 (4)
C(161)	4545 (8)	3332 (9)	10595 (10)	78 (2)
C(162)	4105 (9)	3792 (9)	11009 (10)	78 (2)
C(211)	−28 (8)	−3194 (8)	7341 (9)	70 (2)
C(212)	400 (8)	−3412 (8)	6867 (11)	79 (3)
C(221)	−434 (9)	−2765 (9)	5819 (0)	75 (3)
C(222)	−758 (8)	−2645 (9)	6279 (12)	81 (3)

[a] U_{eq} (Å$^2 \times 10^3$) = $^1/_3$ trace U. [b] U_{iso} (Å$^2 \times 10^3$).

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(9) No other viable products were isolated or observed by TLC, besides some highly polar oligomers or polymers with strong IR absorption at 2150 cm^{-1}. TLC as well as ^{13}C NMR indicated the product to be a single isomer.

(10) Scott, L. T.; DeCicco, G. J. *Tetrahedron Lett.* **1976**, 2663. Santiago, C.; Houk, K. N.; DeCicco, G. J.; Scott, L. T. *J. Am. Chem. Soc.* **1978**, *100*, 692.

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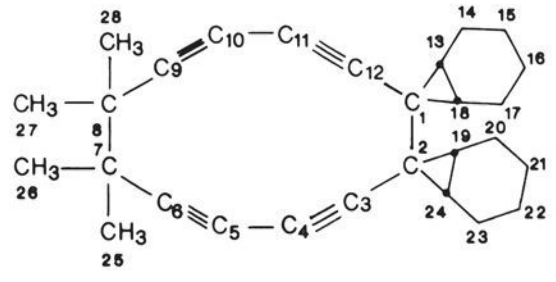
Chart II



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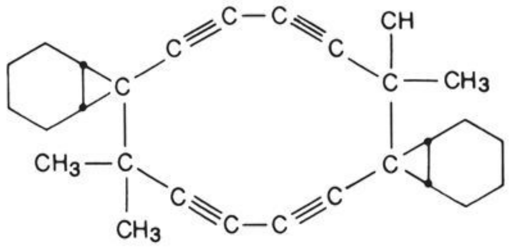

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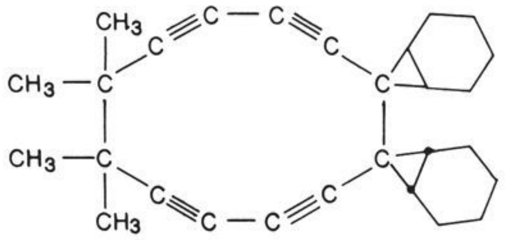

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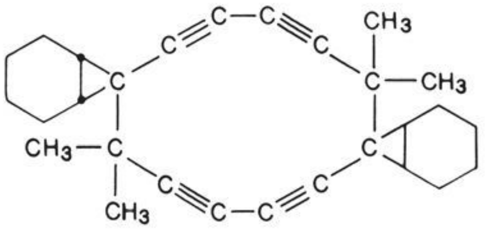

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Table II. Atomic Coordinates for Non-Hydrogen Atoms (×10⁴) of **18**

atom	x	y	z	U_{eq}[a]	atom	x	y	z	U_{eq}[a]
		A					B		
C(1)	11443 (4)	2064 (3)	6435	41 (2)	C(1)	2552 (4)	743 (3)	1310 (6)	39 (2)
C(2)	10762 (3)	2307 (3)	5829 (7)	41 (2)	C(2)	2550 (3)	76 (3)	659 (6)	36 (2)
C(3)	10158 (4)	2235 (4)	6589 (8)	49 (2)	C(3)	3097 (4)	−336 (3)	1011 (7)	43 (2)
C(4)	9743 (4)	2060 (4)	7282 (8)	50 (2)	C(4)	3544 (4)	−624 (3)	1580 (7)	46 (2)
C(5)	9375 (4)	1736 (4)	8133 (8)	56 (2)	C(5)	3999 (4)	−868 (4)	2391 (7)	48 (2)
C(6)	9166 (4)	1378 (4)	8901 (8)	62 (2)	C(6)	4337 (4)	−979 (4)	3235 (8)	57 (2)
C(7)	9083 (5)	905 (5)	9836 (9)	71 (3)	C(7)	4715 (4)	−974 (5)	4371 (8)	69 (3)
C(8)	9460 (4)	265 (4)	9448 (8)	64 (2)	C(8)	4199 (5)	−710 (4)	5289 (8)	69 (2)
C(9)	10161 (4)	463 (4)	8999 (7)	53 (2)	C(9)	3793 (4)	−145 (4)	4794 (7)	57 (2)
C(10)	10636 (4)	717 (4)	8487 (7)	48 (2)	C(10)	3444 (4)	198 (4)	4225 (7)	54 (2)
C(11)	11049 (4)	1104 (4)	7805 (7)	42 (2)	C(11)	3055 (4)	500 (3)	3351 (8)	48 (2)
C(12)	11300 (3)	1513 (3)	7179 (6)	39 (2)	C(12)	2770 (4)	672 (3)	2479 (6)	38 (2)
C(13)	11996 (4)	2550 (4)	6788 (6)	48 (2)	C(13)	2795 (4)	1349 (3)	631 (7)	45 (2)
C(14)	12438 (4)	2455 (4)	7893 (7)	69 (2)	C(14)	3210 (4)	1889 (3)	1198 (7)	50 (2)
C(15)	13118 (5)	2080 (5)	7632 (10)	87 (3)	C(17)	1684 (4)	1716 (3)	1814 (8)	59 (2)
C(16)	12978 (5)	1436 (6)	7012 (10)	94 (4)	C(18)	2032 (4)	1264 (3)	925 (7)	48 (2)
C(17)	12666 (4)	1568 (4)	5837 (8)	63 (2)	C(19)	2264 (4)	54 (3)	−574 (6)	44 (2)
C(18)	12123 (4)	2118 (4)	5773 (7)	47 (2)	C(20)	2596 (4)	−379 (4)	−1499 (7)	57 (2)
C(19)	10668 (4)	2172 (3)	4559 (6)	45 (2)	C(23)	1734 (4)	−976 (4)	438 (7)	64 (2)
C(20)	9960 (4)	2002 (4)	4009 (9)	66 (2)	C(24)	1836 (4)	−237 (3)	383 (6)	45 (2)
C(23)	10250 (4)	3370 (4)	4835 (9)	75 (3)	C(25)	5346 (5)	−480 (6)	4236 (10)	101 (4)
C(24)	10821 (4)	2845 (4)	4938 (7)	56 (2)	C(26)	5000 (5)	−1657 (5)	4654 (9)	87 (3)
C(25)	9419 (7)	1178 (6)	10948 (9)	102 (4)	C(27)	3651 (5)	−1249 (5)	5610 (11)	101 (3)
C(26)	8284 (5)	780 (5)	10079 (10)	96 (3)	C(28)	4566 (6)	−490 (5)	6428 (8)	86 (3)
C(27)	9074 (6)	−62 (5)	8437 (10)	91 (3)					
C(28)	9560 (6)	−225 (5)	10454 (11)	103 (3)					U_{iso}[b]
					C(15A)	2754 (5)	2454 (4)	1597 (11)	52 (4)
				U_{iso}[b]	C(16A)	2190 (5)	2189 (5)	2410 (9)	43 (4)
C(21A)	9621 (10)	2594 (6)	3444 (13)	79 (6)	C(15B)	2830 (10)	2231 (12)	2203 (16)	52 (8)
C(22A)	9547 (6)	3102 (8)	4410 (15)	69 (5)	C(16B)	2064 (10)	2364 (7)	1913 (30)	67 (9)
C(21B)	9437 (9)	2575 (7)	4083 (23)	67 (8)	C(21A)	2598 (7)	−1107 (4)	−1223 (14)	66 (5)
C(22B)	9709 (11)	3265 (8)	3889 (18)	65 (7)	C(22A)	1880 (8)	−1283 (8)	−750 (12)	79 (6)
					C(21B)	2209 (14)	−1030 (8)	−1600 (17)	67 (8)
					C(22B)	2138 (14)	−1380 (8)	−441 (16)	55 (8)

[a] U_{eq} (Å^2 × 10^3) = $^1/_3$ trace U. [b] U_{iso} (Å^2 × 10^3).

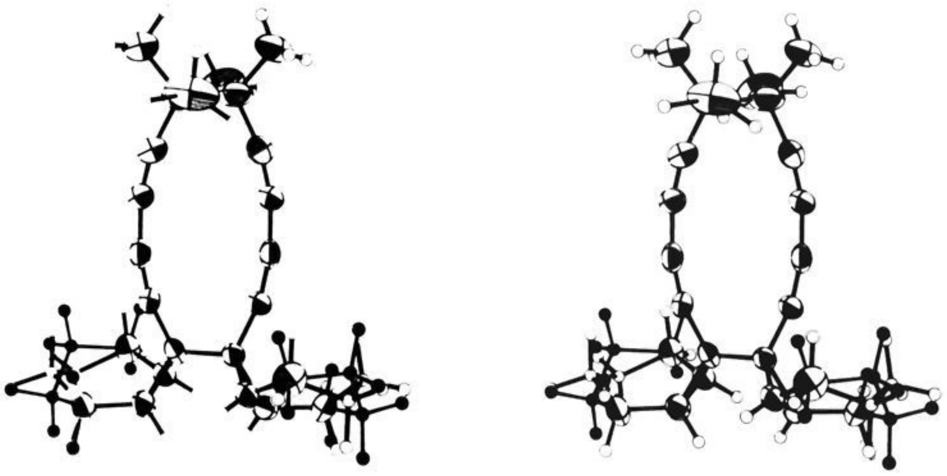


Figure 2.

Table III. Bond Lengths (Å) and Angles (deg) for **5**

	Bond Lengths		
C(1)–C(2)	1.497 (4)	C(17)–C(18)	1.508 (5)
C(1)–C(4)	1.503 (4)	C(19)–C(20)	1.515 (4)
C(1)–C(5)	1.315 (4)	C(19)–C(24)	1.518 (4)
C(2)–C(3)	1.507 (4)	C(23)–C(24)	1.523 (4)
C(2)–C(9)	1.314 (5)	C(14)–C(151)	1.589 (9)
C(3)–C(4)	1.534 (4)	C(14)–C(152)	1.42 (11)
C(3)–C(13)	1.509 (4)	C(17)–C(161)	1.47 (1)
C(3)–C(18)	1.514 (3)	C(17)–C(162)	1.57 (1)
C(4)–C(19)	1.503 (5)	C(20)–C(211)	1.519 (8)
C(4)–C(24)	1.502 (4)	C(20)–C(212)	1.528 (8)
C(5)–C(8)	1.302 (4)	C(23)–C(221)	1.501 (9)
C(6)–C(7)	1.510 (4)	C(23)–C(222)	1.51 (1)
C(6)–C(8)	1.496 (4)	C(151)–C(161)	1.55 (1)
C(9)–C(10)	1.311 (5)	C(152)–C(162)	1.48 (1)
C(10)–C(11)	1.498 (8)	C(211)–C(221)	1.53 (1)
C(10)–C(12)	1.502 (4)	C(212)–C(221)	1.40 (1)
C(13)–C(14)	1.521 (6)	C(212)–C(222)	1.49 (1)
C(13)–C(18)	1.514 (4)		
	Angles		
C(2)–C(1–)C(4)	90.8 (2)	C(3)–C(13)–C(14)	122.4 (3)
C(2)–C(1)–C(5)	133.0 (2)	C(3)–C(13)–C(18)	60.1 (2)
C(4)–C(1)–C(5)	136.2 (2)	C(14)–C(13)–C(18)	119.0 (3)
C(1)–C(2)–C(3)	60.6 (2)	C(3)–C(18)–C(13)	59.8 (2)
C(1)–C(2)–C(9)	133.3 (3)	C(3)–C(18)–C(17)	122.8 (3)
C(3)–C(2)–C(9)	136.1 (3)	C(13)–C(18)–C(17)	120.7 (2)
C(2)–C(3)–C(4)	89.2 (2)	C(4)–C(19)–C(20)	122.6 (3)
C(2)–C(3)–C(13)	130.4 (2)	C(4)–C(19)–C(24)	59.7 (2)
C(2)–C(3)–C(18)	127.9 (3)	C(20)–C(19)–C(24)	119.6 (3)
C(4)–C(3)–C(13)	126.6 (2)	C(4)–C(24)–C(19)	59.7 (2)
C(4)–C(3)–C(18)	127.2 (2)	C(4)–C(24)–C(23)	122.5 (3)
C(13)–C(3)–C(18)	60.1 (2)	C(19)–C(24)–C(23)	119.5 (3)
C(1)–C(4)–C(3)	89.3 (2)	C(13)–C(14)–C(151)	111.0 (5)
C(1)–C(4)–C(19)	129.9 (2)	C(13)–C(14)–C(152)	120.5 (6)
C(1)–C(4)–C(24)	129.0 (3)	C(151)–C(14)–C(152)	23.3 (7)
C(3)–C(4)–C(19)	127.0 (3)	C(18)–C(17)–C(161)	121.3 (5)
C(3)–C(4)–C(24)	125.5 (2)	C(18)–C(17)–C(162)	108.0 (5)
C(19)–C(4)–C(24)	60.7 (2)	C(161)–C(17)–C(162)	29.2 (5)
C(1)–Cn(5)–C(6)	178.4 (3)	C(19)–C(20)–C(211)	111.0 (4)
C(5)–C(6)–C(7)	121.4 (3)	C(19)–C(20)–C(212)	118.1 (4)
C(5)–C(6)–C(8)	121.4 (3)	C(211)–C(20)–C(212)	28.2 (4)
C(7)–C(6)–C(8)	117.1 (3)	C(24)–C(23)–C(221)	117.7 (5)
C(2)–C(9)–C(10)	178.4 (4)	C(24)—C(23)–C(222)	111.9 (6)
C(9)–C(10)–C(11)	122.3 (3)	C(221)–C(23)–C(222)	24.4 (5)
C(9)–C(10)–C(12)	121.0 (3)	C(221)–C(212)–C(222)	25.1 (5)
C(11)–C(10)–C(12)	116.6 (2)	C(211)–C(221)–C(212)	28.9 (5)

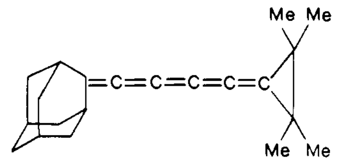
4b as the syn-head-to-head cyclodimer **5** and **13** as the syn-head-to-head dimer **18**.

One can rationalize the formation of these products as follows. Both the 2 + 2 cycloaddition of **4b** to give **5** and the cycloaddition of **12** to give dimer **18** are symmetry forbidden. Hence, these products are most likely the result of radical reactions, a process well known for cumulenes.[2] Bond formation can occur at either termini as shown in Chart III.

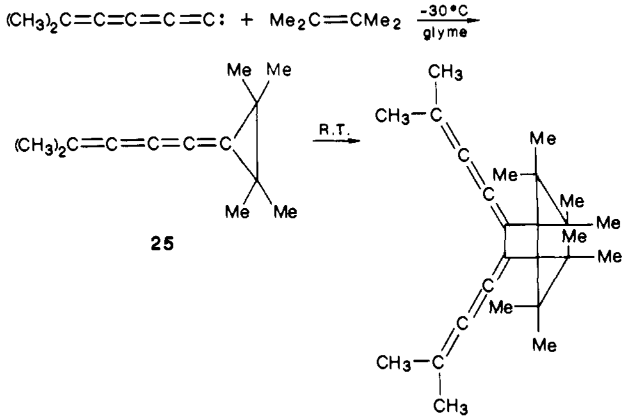
The exclusive head-to-head syn dimerization in *both* cases strongly suggests that *initial* bond formation occurs via the cyclopropyl carabons as in **20** and **22** rather than **21** and **23**. This is due to at least two favorable factors. Bond formation as indicated results in a radical that is both "allylic" and cyclopropyl carbinyl **20** (or **22**), whereas either **21** or **23**, although delocalized by allylic type resonance, does not gain cyclopropyl carbinyl type stabilization. In fact, even the allylic forms **21** and **23** are less stable because their resonance forms (as in **23a**) have an unfavorable cyclopropyl character. Second, bond formation as in **20** and **22**, but not in **21** and **23**, has the added benefit of relieving the approximately 12 kcal/mol strain energy of *each* methylenecyclopropane moiety. *Both* of these factors are *maximized* in the head-to-head approach as compared to the head-to-tail approach.

Syn adduct formation, in both cases, in turn, is a natural *consequence* of such a head-to-head approach via the initial cyclopropyl bond formation. Such a *syn* orientation allows the two sets of smaller hydrogen substituents to face each other and keeps the bulkier cyclohexane rings away from each other; the alternative anti orientation with the bulky cyclohexane rings in closer proximity is disfavored on steric grounds. Hence, the observed head-to-head approach with initial bond formation on the cyclopropyl ends of the molecules, as in **20** and **22**, is favored by electronic factors and relief of strain energy, whereas the syn orientation is favored on steric grounds.

Because of the symmetry of cumulene **16** no such factors were of course involved in its cyclodimerization to the symmetrical octamethyl cyclyne **17**. The fact that a [4]radialene, **15**, rather than a cyclyne is observed in the cyclodimerization of **14** is a consequence of the fact that no relief of strain (of the methylenecyclopropane type) is of course possible in **14**. Moreover, analogous cyclyne formation from **14** would place four bulky *tert*-butyl groups on two *adjacent* saturated carbons, a sterically highly unfavorable situation. Likewise, steric hindrance presumably prevents both cumulene[7] **24** and the known stable tetraphenylhexapentaene[3] from cyclodimerization, at least at room temperature. Analogous arguments can be used to rationalize the formation of cyclodimer **26**, rather than any of the other three possible formal head-to-head 2 + 2 cyclodimers, from unsaturated carbene derived cumulene **25**, as reported by le Noble and coworkers.[12]



24



25

26

What is not exactly clear is why butatrienes such as **3** and pentatetraenes, like **25**, prefer to give "2 + 2" cyclodimers rather than cyclynes and hexapentaenes like **12** and **16** give cyclynes rather than 2 + 2 dimers or vice versa.

The usual structural features of cyclodimers **5** and **18** deserve further comment. Molecule **5** possesses approximately C_{2v} symmetry with all chemically equivalent bond lengths and angles in good agreement. The four-membered ring is practically planar (the deviations of the atoms from the mean plane are smaller than 0.01 Å) and the allene moieties deviate by less than 0.1 Å from that plane. As expected, the dimethyl substituents are perpendicular to the four-membered ring (the angles between the planes described by atoms C(6), C(7), C(8), and C(10), C(11), C(12) and the four-membered ring are 90.0 and 90.4°, respectively). The angles at the central atom of the allene moieties are nearly linear at 178.4° as also found in 2,7-diphenyl-2,3,5,6-octatetraene (179.1°)[13] but not in allenecarboxamide (175.6°).[14]

It is of interest to compare the molecular structure of **18** with the related octamethylcyclododeca-1,3,7,9-tetrayne,[15] **17**. The

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[12] le Noble, W. J.; Basak, S.; Srivastava, S. *J. Am. Chem. Soc.* **1981**, *103*, 4638.

[13] Groth, P. *Acta Chem. Scand.* **1973**, *27*, 3302.

[14] Henn, L.; Himbert, G.; Diehl, K.; Kaftory, M. *Chem. Ber.*, in press.

Table IV. Bond Lengths (Å) and Angles (deg) for the Two Independent Molecules of **18**

A (Bond Lengths)

C(1)–C(2)	1.558 (9)	C(5)–C(6)	1.22 (1)	C(10)–C(11)	1.37 (1)	C(19)–C(24)	1.48 (1)
C(1)–C(12)	1.444 (8)	C(6)–C(7)	1.46 (1)	C(11)–C(12)	1.20 (1)	C(20)–C(21A)	1.52 (1)
C(1)–C(13)	1.509 (9)	C(7)–C(8)	1.56 (1)	C(13)–C(14)	1.54 (1)	C(23)–C(24)	1.54 (1)
C(1)–C(18)	1.511 (9)	C(7)–C(25)	1.54 (1)	C(13)–C(18)	1.49 (1)	C(23)–C(22A)	1.53 (1)
C(2)–C(3)	1.46 (1)	C(7)–C(26)	1.57 (1)	C(14)–C(15)	1.54 (1)	C(21A)–C(22A)	1.53 (2)
C(2)–C(19)	1.50 (1)	C(8)–C(9)	1.49 (1)	C(15)–C(16)	1.53 (1)	C(20)–C(21B)	1.55 (1)
C(2)–C(24)	1.51 (1)	C(8)–C(27)	1.53 (1)	C(16)–C(17)	1.50 (1)	C(23)–C(22B)	1.52 (2)
C(3)–C(4)	1.18 (1)	C(8)–C(28)	1.54 (1)	C(17)–C(18)	1.53 (1)	C(21B)–C(22B)	1.52 (2)
C(4)–C(5)	1.38 (1)	C(9)–C(10)	1.20 (1)	C(19)–C(20)	1.53 (1)		

A (Angles)

C(2)–C(1)–C(12)	111.0 (5)	C(8)–C(7)–C(25)	110.5 (8)	C(1)–C(18)–C(13)	60.4 (4)
C(2)–C(1)–C(13)	119.6 (5)	C(8)–C(7)–C(26)	111.3 (7)	C(1)–C(18)–C(17)	120.2 (6)
C(2)–C(1)–C(18)	117.9 (4)	C(25)–C(7)–C(26)	108.4 (8)	C(13)–C(18)–C(17)	120.7 (6)
C(12–C(1)–C(13)	119.3 (4)	C(7)–C(8)–C(9)	106.6 (6)	C(2)–C(19)–C(20)	123.4 (6)
C(12)–C(1)–C(18)	121.4 (5)	C(7)–C(8)–C(27)	111.2 (7)	C(2)–C(19)–C(24)	61.0 (4)
C(13)–C(1)–C(18)	59.0 (4)	C(7)–C(8)–C(28)	112.8 (8)	C(20)–C(19)–C(24)	120.7 (6)
C(1)–C(2)–C(3)	111.1 (5)	C(9)–C(8)–C(27)	106.7 (7)	C(19)–C(20)–C(21A)	111.7 (8)
C(1)–C(2)–C(19)	118.6 (5)	C(9)–C(8)–C(28)	109.0 (7)	C(24)–C(23)–C(22A)	113.3 (8)
C(1)–C(2)–C(24)	118.4 (5)	C(27)–C(8)–C(28)	110.2 (7)	C(2)–C(24)–C(19)	60.3 (4)
C(3)–C(2)–C(19)	118.2 (5)	C(8)–C(9)–C(10)	165.1 (8)	C(2)–C(24)–C(23)	120.8 (6)
C(3)–C(2)–C(24)	112.7 (5)	C(9)–C(10)–C(11)	165.9 (8)	C(19)–C(24)–C(23)	119.4 (6)
C(19)–C(2)–C(24)	58.7 (4)	C(10)–C(11)–C(12)	167.7 (7)	C(20)–C(21A)–C(22A)	106 (1)
C(2)–C(3)–C(4)	165.8 (7)	C(1)–C(12)–C(11)	167.0 (7)	C(23)–C(22A)–C(21A)	113 (1)
C(3)–C(4)–C(5)	166.0 (8)	C(1)–C(13)–C(14)	121.5 (5)	C(21B)–C(20)–C(19)	112.0 (8)
C(4)–C(5)–C(6)	167.4 (8)	C(1)–C(13)–C(18)	60.6 (4)	C(20)–C(21E)–C(22B)	118 (1)
C(5)–C(6)–C(7)	166.9 (8)	C(14)–C(13)–C(18)	119.0 (6)	C(21B)–C(22B)–C(23)	105 (1)
C(6)–C(7)–C(8)	107.3 (7)	C(13)–C(14)–C(15)	111.4 (7)	C(22B)–C(23)–C(24)	116.1 (9)
C(6)–C(7)–C(25)	109.2 (8)	C(14)–C(15)–C(16)	112.0 (7)	C(20)–C(9)–C(24)	120.7 (6)
C(6)–C(7)–C(26)	110.2 (7)	C(15)–C(16)–C(17)	109.6 (8)	C(23)–C(24)–C(19)	119.4 (6)
		C(16)–C(17)–C(18)	116.3 (7)		

B (Bond Lengths)

C(1)–C(2)	1.560 (9)	C(6)–C(7)	1.49 (1)	C(11)–C(12)	1.20 (1)	C(15A)–C(16A)	1.53 (1)
C(1)–C(12)	1.42 (1)	C(7)–C(8)	1.55 (1)	C(13)–C(14)	1.511 (9)	C(14)–C(15B)	1.54 (2)
C(1)–C(13)	1.539 (9)	C(7)–C(25)	1.58 (1)	C(13)–C(18)	1.51 (1)	C(17)–C(16B)	1.52 (1)
C(1)–C(18)	1.525 (9)	C(7)–C(26)	1.54 (1)	C(14)–C(15A)	1.52 (1)	C(15B)–C(16B)	1.53 (2)
C(2)–C(3)	1.404 (9)	C(8)–C(9)	1.51 (1)	C(17)–C(18)	1.53 (1)	C(20)–C(21A)	1.52 (1)
C(2)–C(19)	1.52 (1)	C(8)–C(27)	1.57 (1)	C(17)–C(16A)	1.53 (1)	C(20)–C(21B)	1.53 (2)
C(2)–C(24)	1.539 (9)	C(8)–C(28)	1.56 (1)	C(19)–C(20)	1.53 (1)	C(23)–C(22A)	1.53 (1)
C(3)–C(4)	1.23 (1)	C(9)–C(10)	1.17 (1)	C(19)–C(24)	1.496 (9)	C(23)–C(22B)	1.52 (2)
C(4)–C(5)	1.37 (1)	C(10)–C(11)	1.40 (1)	C(23)–C(24)	1.531 (9)	C(21A)–C(22A)	1.52 (2)
C(5)–C(6)	1.19 (1)					C(21B)–C(22B)	1.52 (2)

B (Angles)

C(2)–C(1)–C(12)	111.6 (5)	C(7)–C(8)–C(9)	109.8 (7)	C(2)–C(24)–C(23)	121.1 (5)
C(2)–C(1)–C(13)	117.6 (5)	C(7)–C(8)–C(27)	110.0 (7)	C(19)–C(24)–C(23)	119.7 (6)
C(2)–C(1)–C(18)	118.2 (5)	C(7)–C(8)–C(28)	113.0 (7)	C(14)–C(15A)–C(16A)	108.7 (7)
C(12)–C(1)–C(13)	118.5 (5)	C(9)–C(8)–C(27)	106.7 (7)	C(17)–C(16A)–C(15A)	113.3 (8)
C(12)–C(1)–C(18)	122.7 (6)	C(9)–C(8)–C(28)	109.2 (7)	C(14)–C(13)–C(18)	119.6 (6)
C(13)–C(1)–C(18)	58.9 (4)	C(27)–C(8)–C(28)	107.9 (8)	C(13)–C(14)–C(15B)	114.3 (9)
C(1)–C(2)–C(13)	112.7 (5)	C(8)–C(9)–C(10)	165.4 (8)	C(14)–C(15B)–C(16B)	112 (1)
C(1)–C(2)–C(19)	118.4 (5)	C(9)–C(10)–C(11)	166.9 (8)	C(15B)–C(16B)–C(17)	109 (1)
C(1)–C(2)–C(24)	117.8 (5)	C(10)–C(11)–C(12)	168.2 (8)	C(16B)–C(17)–C(18)	112 (1)
C(3)–C(2)–C(19)	121.3 (6)	C(1)–C(12)–C(11)	164.3 (7)	C(13)–C(18)–C(17)	120.1 (5)
C(3)–C(2)–C(24)	117.9 (5)	C(1)–C(13)–C(14)	122.0 (6)	C(20)–C(19)–C(24)	120.7 (5)
C(19)–C(2)–C(24)	58.5 (4)	C(1)–C(13)–C(18)	60.1 (4)	C(19)–C(20)–C(21A)	115.2 (7)
C(2)–C(3)–C(4)	164.0 (8)	C(14)–C(13)–C(18)	119.6 (6)	C(20)–C(21A)–C(22A)	108 (1)
C(3)–C(4)–C(5)	168.7 (8)	C(13)–C(14)–C(15A)	112.8 (6)	C(21A)–C(22A)–C(23)	113 (1)
C(4)–C(5)–C(6)	166.2 (8)	C(18)–C(17)–C(16A)	114.0 (6)	C(22A)–C(23)–C(24)	110.3 (8)
C(5)–C(6)–C(7)	167.8 (8)	C(1)–C(18)–C(16)	61.0 (4)	C(19–C(24)–C(23)	119.7 (6)
C(6)–C(7)–C(8)	107.0 (6)	C(1)–C(18)–C(17)	120.8 (6)	C(20)–C(19)–C(24)	120.7 (5)
C(6)–C(7)–C(25)	106.6 (7)	C(13)–C(18)–C(17)	120.1 (5)	C(19)–C(20)–C(21B)	111 (1)
C(6)–C(7)–C(26)	110.6 (7)	C(2)–C(19)–C(20)	121.3 (5)	C(20)–C(21B)–C(22B)	113 (1)
C(8)–C(7)–C(25)	109.2 (7)	C(2)–C(19)–C(24)	61.3 (4)	C(21B)–C(22B)–C(23)	112 (1)
C(8)–C(7)–C(26)	113.6 (7)	C(20)–C(19)–C(24)	120.7 (5)	C(22B)–C(23)–C(24)	116.6 (9)
C(25)–C(7)–C(26)	109.5 (7)	C(2)–C(24)–C(19)	60.2 (4)	C(19)–C(24)–C(23)	119.7 (6)

only chemical differences between the two compounds are that four methyl groups (in the latter compound) are replaced by two [4.1.0]bicycloheptanes. No significant differences were encountered in the bond lengths and angles, within the chemically equivalent portion of the two molecules: the average triple bond length is 1.199 (11) Å in **18** and 1.200 (4) Å in **17**, the sp–sp single bond is 1.382 (8) Å in **18** and 1.387 Å in **17**, the sp–sp^3 single bond to the $C(CH_3)_2$ group is 1.487 (14) Å in **18** and 1.482 Å in **17**, while the same type of bond to the [4.1.0]bicycloheptane is shorter [1.432 (12) Å]. All eight acetylenic carbons deviate substantially from linearity, in both structures, with bond angles ranging between 165.1° and 168.7° in **18** and 165.1° to 167.1° in **17**. The internal bond angles at the saturated carbons (bonded

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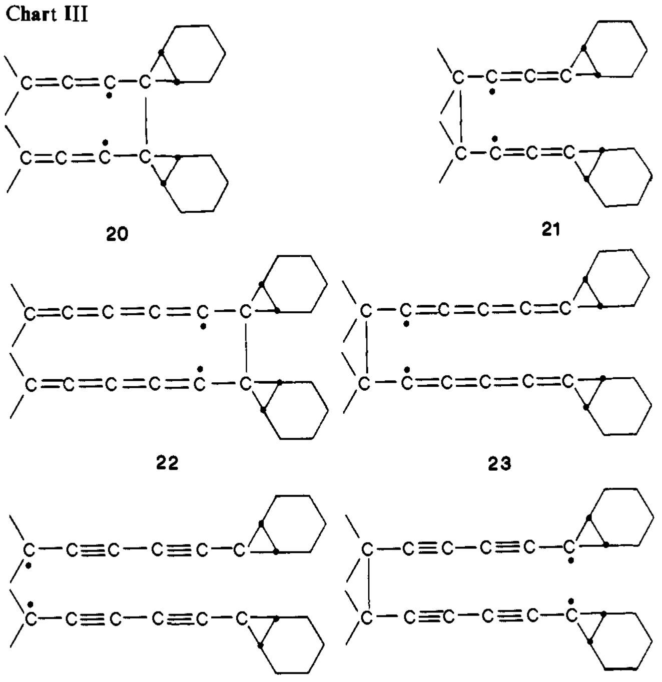
(15) Houk, K. N.; Scott, L. T.; Rondan, N. G.; Spellmeyer, D. C.; Reinhardt, G.; Hyun, J. L.; DeCicco, G. J.; Weiss, R.; Chen, M. H. M.; Bass, L. S.; Clardy, J.; Jorgensen, F. S.; Eaton, T. A.; Sarkozi, V.; Petit, C. M.; Ng, L.; Jordan, K. D. *J. Am. Chem. Soc.* **1985**, *107*, 6556.

Chart III



to the methyl groups), on the other hand, appear more nearly normal, ranging from 106.6° to 109.8° in **18** and 107.7° to 108.2° in **17**. The bond angles at the carbon atoms bonded to the [4.1.0]bicyclheptane portion are larger and range from 111.0° to 112.7°. Each diacetylenic unit forms an essentially planar arch; however, while these two arches are bonded to form a twelve-membered ring having the C_{2h} symmetry in **17** it has only C_2 symmetry in **18**. The differences between the two conformations are shown schematically in Figures 1 and 2.

Disordered [4.1.0]Bicycloheptane Moiety. In all three compounds (**5**, **18**, and **17**) a disorder was detected. However, while the disorder found in **17** (at room temperature) suggests that it arises from the possible inversion of four methyl groups, the disorder found in **5** and **18** arises from inversion within the cyclohexane portion of the bicycloheptane moiety. In both **5** and **18** the external atoms of the cyclohexane moiety [C(15), C(16), C(21), C(22)] occupy, to a different degree, the two inverted conformations (two possible half-chairs): in **5** the disordered cyclohexane moieties adopting the two conformations in equal proportion while in **18** one cyclohexane is not disordered and the remaining three adopting the two conformations in various ratios (61/39; 65/35; 57/43).

Experimental Section

Cyclodimers **5**[4] and **18**[7] were prepared via the cyclohexene trapping of the respective unsaturated carbenes as previously described. Slow recrystallization from hot saturated benzene solution gave appropriate single crystals.

Intensities from single prismatic crystals of **5** and **18** sealed into a glass capillary were measured with a Philips PW1100/20 four-circle computer-controlled diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The crystal structure of **5** was solved by MULTAN80[16] and that of **18** by SHELX,[17] and refined by SHELX,[17] using anisotropic atomic displacement parameters for the non-disordered carbon atoms, isotropic for hydrogen and disordered carbon atoms. Occupation factors for the disordered atoms were refined during the initial stages and were fixed at the last stages of the refinement. Hydrogen atoms positions were either located from difference Fourier maps or calculated. The positions of the H atoms in **5** were refined with fixed isotropic atomic displacement parameters, while in **18** the bond distances involving hydrogen atoms were fixed at 1.08 Å. Bond distance constrains were also applied to the disordered non-hydrogen atoms in **18**.

5 ($C_{24}H_{32}$): triclinic, space group $P\bar{1}$, a = 11.541 (6) Å, b = 10.248 (5) Å, c = 9.400 (5) Å, α = 107.32 (4)°, β = 109.13 (4)°, γ = 83.23 (4)°, $Z = 2$, D_x = 1.062 g·cm^{-3}, R = 0.074, R_w = 0.074 for 2233 observed reflections [$F_o > 1.5\sigma(F_o)$]. $w = 1.4894/[\sigma^2(F_o) + 0.0007F_o^2]$.

18 ($C_{28}H_{32}$): orthorhombic, space group $Pna2_1$, a = 19.114 (9) Å, b = 20.499 (11) Å, c = 11.523 (6) Å, Z = 8, D_x = 1.085 g·cm^{-3}, R = 0.085, R_w = 0.085 for 2569 observed reflections [$F_o > 1.5\sigma(F_o)$]. $w = 1.0653/[\sigma^2(F_o) + 0.0027F_o^2]$.

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Registry No. 3b, 105991-69-3; **5**, 105991-70-6; **12**, 74707-06-5; **18**, 106036-15-1.

Supplementary Material Available: A listing of atomic coordinates of the H atoms and isotropic and anisotropic atomic displacement parameters (9 pages); tables of structure factors (29 pages). Ordering information is given on any current masthead page.

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