Pleiadene Dimerization and Its Application to the Construction of Novel Carbon Networks

Ángela Sastre,[a][b] Gordana Srdanov,[a] and Fred Wudl*[a][b]

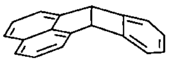
Abstract: The synthesis of the *anti*- and *syn*-pleiadene dimers **2** has been carried out in solution and in the solid state from (6b-10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene) (**3**). The structures of the *anti*- and *syn*-**2** dimers were determined by X-ray crystallography and by NMR spectroscopy and mass spectrometry. An exhaustive thermal analysis of the two dimers has been carried out, establishing that the equilibrium for their interconversion occurs via pleiadene as an intermediate species. Vinyl-6b-10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (**5**) has been synthesized and used as a pre-monomer for the preparation of poly(pleiadene) dimer through either thermal or photochemical polymerization.

Keywords: biradicals · carbon networks · pleiadene · polymerizations

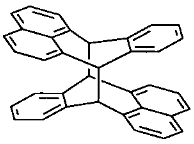
Introduction

Attempts in recent years to produce materials with properties approaching those of diamond have increasingly focused on the generation of cross-linked all-hydrocarbon polymers. The exceptional physical properties of diamond (hardness, high refractive index, and high thermal conductivity) can ultimately be ascribed to the compact, strong, directional carbon–carbon single covalent bonds that make up this three-dimensional extended solid.[1] Many approaches have been utilized to prepare high-strength organic materials by thermal cross-linking[2] and hypercross-linking.[3–6]

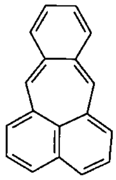
The elusive hydrocarbon pleiadene **1**[7] is of interest from a theoretical[8–12] and, more recently, from a practical viewpoint as a chain-extending end cap for flexible quinoline oligomers.[2] Attempts to isolate it at room temperature have always led to the formation of the *anti* dimer **2**,[9, 11, 12, 13] as characterized by ^{1}H NMR spectroscopy. Though the pleiadene dimer can be generated from either 7,12-dibromo- or 7,12-dihydropleiadene-7,12-sulfone,[13] the strained benzocyclobutene **3** (6b-10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene)[9, 11] is the most efficient precursor for the thermal or low-temperature photochemical generation of **1** as a short-lived intermediate.[10, 12]



3



***anti*-2**



1

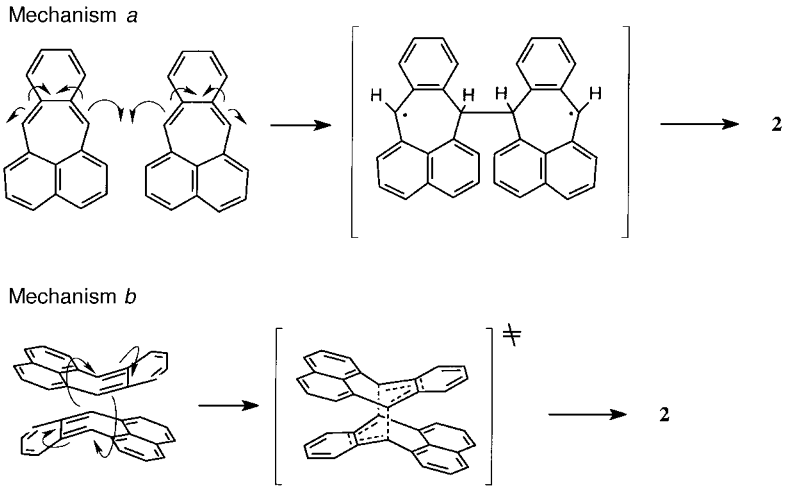
Though pleiadene dimerization has been briefly described for the chain extension of macromolecules,[2] there are no reports of its utilization as a polymerization functional group. This pleiadene polymerization/cross-linking process possesses the two distinct advantages usually associated with cycloadditive polymerizations such as the Diels–Alder polymerization: 1) it is achieved without the evolution of volatile by-products, allowing easier processing of the polymer into the final molded product in a single step and, 2) it does not introduce any weak links into the polymer in the form of heteroatoms or free radical-, anion-, or cation-stabilizing groups. With this type of monomer we are able to fill a mold of the desired shape and then heat it to obtain a finished product directly without the properties of the polymer being degraded by contamination with a catalyst or by-product fragment such as CO_2, H_2O or N_2.

In their studies of the dimerization of **1** Kolc and Michl[10] concluded that it is not possible to distinguish between a stepwise biradical pathway (mechanism a, Scheme 1) or a concerted, symmetry-controlled process (mechanism b, Scheme 1). The principal argument against a concerted thermal process is that a $[\pi 4s + \pi 4s]$ reaction is symmetry-

---

[a] Prof. Dr. F. Wudl, G. Srdanov, Dr. A. Sastre
Departments of Chemistry and Materials
Institute for Polymers and Organic Solids
University of California
Santa Barbara, CA 93106–5090 (USA)

[b] Prof. Dr. F. Wudl, Dr. A. Sastre
Exotic Materials Institute
Department of Chemistry and Biochemistry
University of California, Los Angeles
CA 90095–1569
Fax: (+1) 310-805-0767
E-mail: wudl@chem.ucla.edu



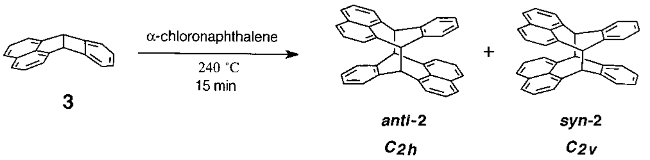
Scheme 1. Mechanisms for the dimerization of **1**.

forbidden. Conversely, the primary argument in favor of concertedness is the previously claimed selective *anti*-specific product formation. In other words, the observation of *anti*-specificity is a fundamental argument against a stepwise process. The same authors have proposed that regardless of whether mechanism a or mechanism b is operative, *anti*-specific dimerization is to be expected on the basis of secondary orbital interactions.[10]

In this work, we have studied the pleiadene dimerization reaction, and report herein the isolation, spectroscopic properties, structural analysis, thermal analysis, and crystal structures of the *anti* and the *syn* pleiadene dimers. We are able to show unequivocally, and contrary to previous findings, that the formation of **2** *is not anti-specific* and that the observed ratio of *syn* to *anti* product is not a reflection of relative thermodynamic stability. We also report the preparation of poly(pleiadene dimer) based on a self-initiated thermal or photochemical polymerization of dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene subunits.

Results and Discussion

Pleiadene dimerization: Compound **3** was synthesized according to the experimental procedure described by Kolc and Michl.[10] Heating the monomer **3** in a sealed tube at 240 °C, afforded a 4.9:1 mixture (83:17) of the *anti*- and *syn*-**2** isomers, respectively, in an overall yield of 84%. The same ratio was also obtained as described previously[10] by refluxing for 15 min in α-chloronaphthalene under an argon atmosphere (Scheme 2). The isomers differ in their physical and chemical properties, but no separation could be achieved by normal column chromatography, which could explain why the dimerization was previously thought to be *anti*-specific. Special semipreparative HPLC (see Experimental Section) was necessary to separate the isomers. The EI-MS analyses performed separately on both *anti*-**2** and *syn*-**2** showed the parent ion at *m/z* 456 (M^+) as well as an additional peak at half the molecular mass (*m/z* 228) corresponding to the aromatic pleiadene. Proton NMR spectra of the crude reaction mixture allowed a clear distinction to be made between the resonances of the two isomers. Two sharp singlets at $\delta = 5.07$ and 5.36 are assigned to the four benzhydryl protons of the *anti* isomer and the *syn* isomer respectively. Decoupling experiments in $CDCl_3$ for *anti*-**2**, and in CD_2Cl_2 for *syn*-**2**, allowed the assignment of all the aromatic protons, as shown in Figure 1. The ^{13}C NMR spectra of *anti*- and *syn*-**2** both show 10 signals, corresponding to C_{2h} and C_{2v} symmetry, respectively.



Scheme 2. Reaction of **3** with αchloronaphthalene to give *anti*-**2** and *syn*-**2**.

UV/Vis spectroscopy showed a slight hypsochromic shift and a broadening in the signals of the *syn*-pleiadene dimer relative to the *anti isomer*. The major difference was in the 270–330 nm region (Figure 2). The long-wavelength bathochromic shift in the *anti* isomer may be due to a transannular $\pi-\pi$ interaction between the phenylene and naphthylene units, the same interaction which may account for the crystal packing in the *syn* isomer (see below and Figure 4).

The *anti* dimer crystallizes (see Experimental Section) together with one molecule of disordered *o*-dichlorobenzene (ODCB). The two halves of the molecule either side of the inversion center are crystallographically different. The structure has no unusual bond lengths or angles. The longest single bond, the equatorial C(1A)–C(5B) bond (1.606(10), 1.575(11) Å) is different by about 3σ for the two independent parts of the asymmetric unit and is shorter than the corresponding bond (1.621(8) Å) in the *syn* conformer (Figure 3). The average length of the phenylene bonds is 1.390(11) Å for the *anti* dimer, these being slightly shorter (1.380(9) and 1.387(9) Å) for the *syn* isomer; the naphthylene bond lengths are comparable with previously reported data[14–16] and have average values of 1.393(11) and 1.401(11) Å (*anti*) and 1.393(11) and 1.396(11) Å (*syn*) (Table 1). A comparison of the dihedral angles about the two long bonds for the *anti* and *syn* isomers shows the isomers to have different angle strains, with the two independent halves of *anti*-**2** also having slightly different molecular strain (Table 1).

The packing of the two structures is significantly different owing to the presence of a disordered solvent molecule in the *anti* crystals. The *syn* molecules form stacks along the crystallographic *a* axis in such a way that an *o*-phenylene ring from one molecule and a naphthalene ring from a neighbor

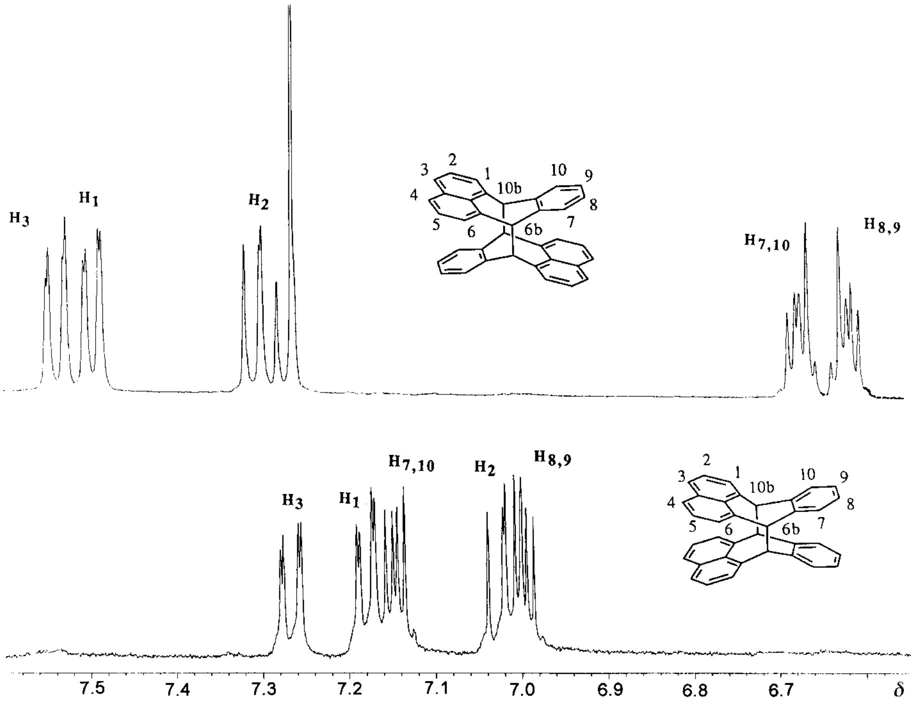


Figure 1. Top: ^1H NMR spectrum of the *anti*-**2** isomer in $CDCl_3$ solution; bottom: ^1H NMR spectrum of the *syn*-**2** isomer in CD_2Cl_2 solution. Controls revealed no change in chemical shift on changing from $CDCl_3$ to CD_2Cl_2. The latter was used for the *syn* isomer because one of its resonances overlapped with the $CDCl_3$ signal.

facing one other with a normal van der Waals separation (3.422 Å) (Figure 4).

A thermal analysis on the dimers was carried out to study the possibility of interconversion between the two isomers. Differential scanning calorimetry (DSC) of **3** between 40 and 400 °C at 5 °C min^{-1} under a nitrogen atmosphere showed a melting endotherm at 130 °C (m.p. 130–132 °C[10]) and a maximum exotherm for the dimerization at 216 °C. Integration of the area under the exotherm gave a value of 105.25 cal g^{-1}, which corresponds to an exothermicity of 31.58 kcal mol^{-1} for the dimerization process. The melting points of *anti*- and *syn*-**2** were 377.45 and 338.92 °C, respectively, and were followed very closely by broad exothermic peaks centered at 380.21 °C and 340.69 °C. Pyrolysis in the DSC apparatus of the less stable dimer, *syn*-**2**, with quenching at 340 °C before the exothermic reaction was complete, yielded a sublimed mixture of *anti*- and *syn*-**2** (60:40), which equates with a very low difference in energy (0.5 kcal mol^{-1})

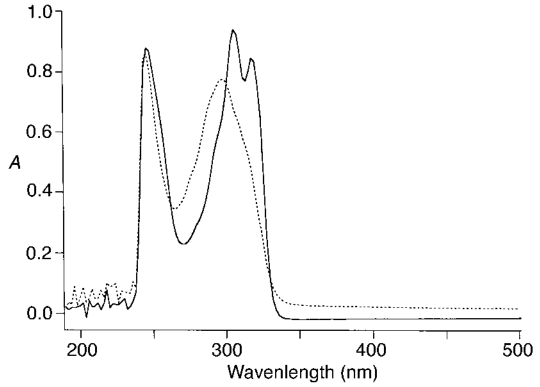


Figure 2. UV/Vis spectrum of *anti*-**2** (solid line) and *syn*-**2** (dotted line) in $CHCl_3$ as solvent. The region below about 240 nm is an instrumental artifact due to solvent absorption. A = absorbance.

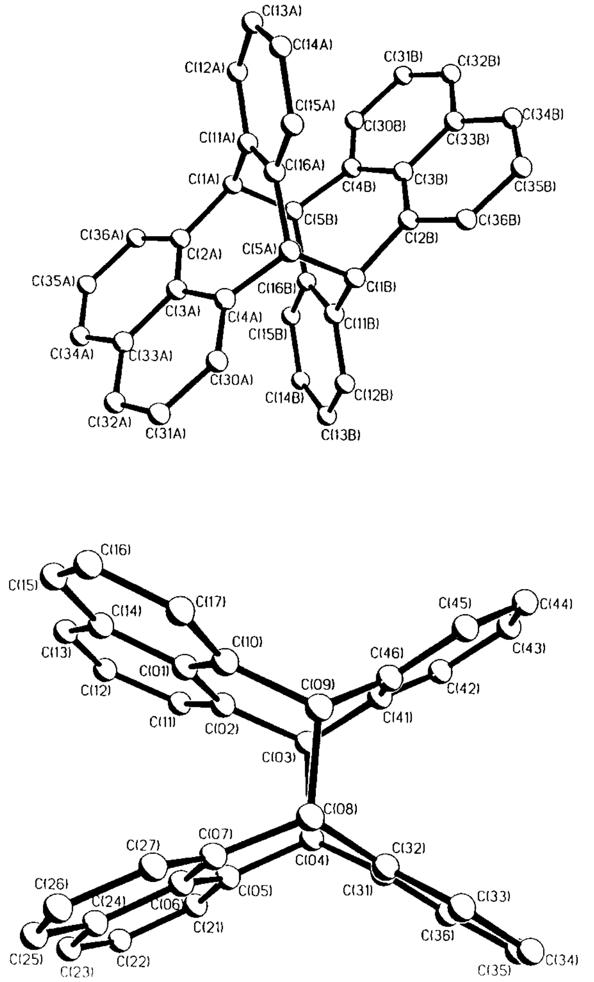


Figure 3. Labeling scheme for the *anti*-**2** (top) and *syn*-**2** (bottom) molecular units. The actual asymmetric unit for *anti* consists of two independent halves, denoted by the suffixes A and B, but drawn as a single unit. See Table 1 for bond lengths.

Table 1. Selected bond lengths [Å] and torsion angles [°].

anti-**2**	Molecule 1	Molecule 2	
C(1) – C(2)	1.538(11)	1.515(11)	
C(1) – C(5)[a,b]	1.606(10)	1.575(11)	
C(1) – C(11)	1.498(8)	1.546(8)	
C(5) – C(4)	1.521(11)	1.524(11)	
C(5) – C(16)	1.515(8)	1.512(8)	
C(2)-C(1)-C(5)-C(16)	27.90	– 26.26	
C(2)-C(1)-C(5)-C(4)	162.0	– 162.75	
C(11)-C(1)-C(5)-C(16)	– 106.89	109.47	
C(11)-C(1)-C(5)-C(4)	27.20	– 27.02	
syn-**2**			
C(03) – C(02)	1.505(8)	C(09) – C(10)	1.525(8)
C(03) – C(04)	1.621(8)	C(09) – C(46)	1.496(8)
C(03) – C(41)	1.496(8)	C(09) – C(08)	1.614(8)
C(04) – C(05)	1.504(9)	C(08) – C(07)	1.513(8)
C(04) – C(31)	1.521(8)	C(08) – C(32)	1.494(8)
C(07)-C(08)-C(09)-C(10)	4.49	C(02)-C(03)-C(04)-C(05)	4.14
C(07)-C(08)-C(09)-C(46)	– 128.03	C(02)-C(03)-C(04)-C(31)	– 129.8
C(32)-C(8)-C(9)-C(10)	141.09	C(41)-C(03)-C(04)-C(05)	141.69
C(32)-C(08)-C(09)-C(46)	8.56	C(41)-C(03)-C(04)-C(31)	7.75

Symmetry transformations: [a] Molecule 1: $-x, -y+2, -z-1$. [b] Molecule 2: $-x+1, -y+1, -z$.

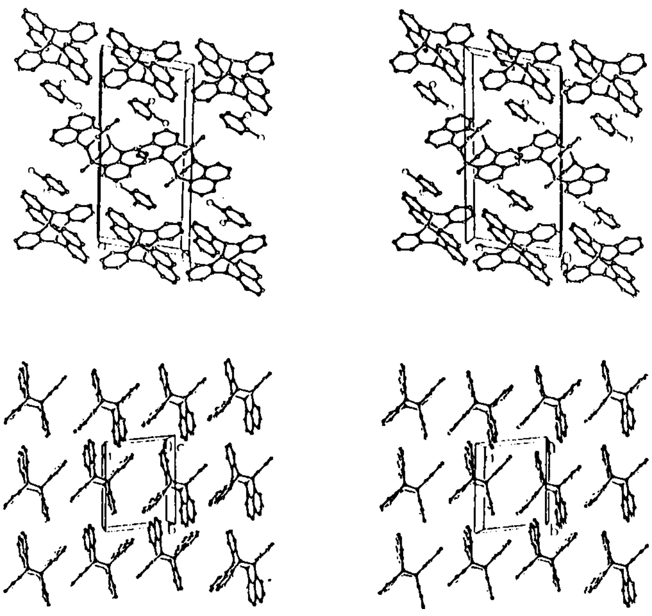
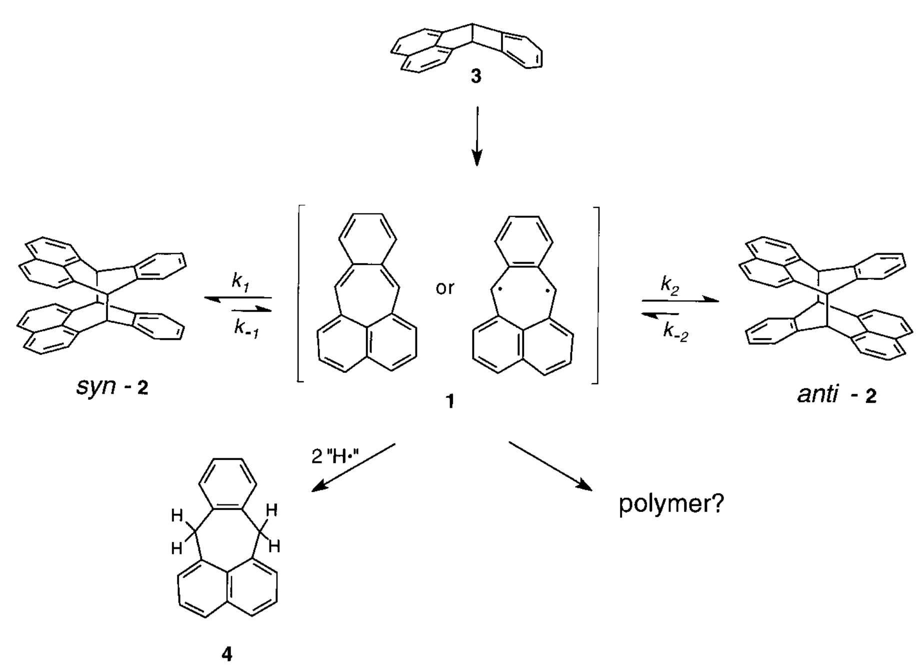


Figure 4. Stereodiagram of the packing for *anti*-**2** (top; viewed along the *b* axis) and *syn*-**2** (bottom; viewed along the *c* axis).

between the two isomers. Moreover, at this temperature a solid mixture of *anti*- and *syn*-**2** (75:25) was left in the DSC vessel, but no dihydropleiadene **4** was detected in either the sublimate or the residue. Similar studies performed at the lower temperatures of 280, 290, 300, 310, 320, and 330 °C afforded approximately the same mixture of sublimed product, with isomer ratios of between 55:45 and 60:40, as determined by HPLC. When the same experiment was performed with pure *anti*-**2** at 380 °C, *anti*- and *syn*-**2** were observed in the sublimate in a ratio of 96:4, together with dihydropleiadene, leaving a black powder as the DSC residue. This indicates, as shown in Scheme 3, that the interconversion between *anti*-**2** and **1** at 380 °C is quite different from the interconversion between *syn*-**2** and **1** at 280 – 340 °C. On this basis it would appear that under the usual reaction conditions for the conversion of **3** to **2** (neat at 240 °C or in refluxing α-chloronaphthalene at 259 °C), interconversion does not occur. The preference in this reaction for the *anti* product could be the consequence of slightly higher π – π electron repulsion in the *syn* isomer, with an energy difference of about 2 kcal mol^{-1} (calculated experimentally by calorimetry). The 5:1 ratio observed in the bulk reaction is therefore not a reflection of the relative stabilities of *syn* and *anti* dimers of **2**.

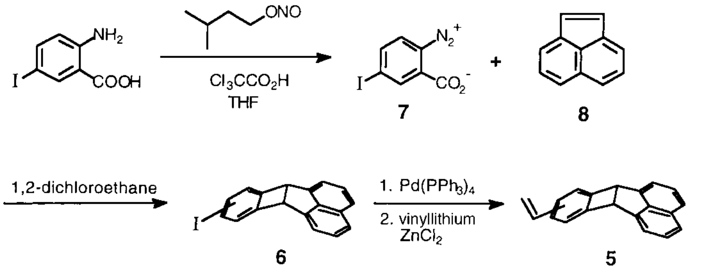
This allows the course of the dimerization reaction to be explained as represented in Scheme 3, in which the dimerization is rendered reversible through the pleiadene monomer as an intermediate. However, the pleiadene does not revert to the starting material **3**. The pleiadene monomer is a radicaloid (singlet ground state, ESR silent),[10] which dimerizes in an energetically downhill process. A further thermal study of the mixture of the two isomers at > 400 °C led to the isolation of a black powder and dihydropleiadene (**4**, 20 % yield). The source of H· is not known at the present time.

Pleiadene-based polymers: Armed with the above information, we set out to establish the applicability of pleiadene



Scheme 3. Interconversion between *syn*-**2** and **1** and between *anti*-**2** and **1**.

dimerization in an actual polymerization reaction. To this end, 8-vinyl-6b-10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (**5**) was prepared from 8-iodo-6b-10b-dihydrobenzo-[j]cyclobut[a]acenaphthylene (**6**) by a Negishi coupling.[17] The [2+2] cycloaddition of iodobenzyne, generated from 4-iodobenzenediazonium-2-carboxylate (**7**), to acenaphthylene (**8**) gave a 20% yield of the iodo derivative **6**. Reaction of a vinylzinc with **6** in the presence of a Pd^0 catalyst proceeded readily to give the vinyl pleiadene derivative in 98% yield (Scheme 4). Substitution of the bromo pleiadene derivative[2] for the iodo compound, reduced the yield substantially (10–30%). DSC analysis of the iodo derivative showed a melting endotherm at 162 °C, a dimerization exotherm peak at 218 °C, and the ring-opening exotherm at 306 °C.



Scheme 4. Synthesis of **5**.

The DSC analysis of vinylbenzocyclobutane **5** (Figure 5) exhibited a melting endotherm at 102 °C and an exotherm peak at 214 °C that could in principle, by analogy with the data for the parent compound **3** and the iodo derivative **6**, be attributable to the dimerization process. However, opening of the dimer, as evidenced by an exotherm peak in the DSC between 300 and 400 °C, was not observed, in contrast to the other examples already mentioned. Pyrolysis of **5** at 230 °C for 15 min in the DSC apparatus afforded an insoluble, thick monolith.

A photochemical polymerization with a 450 W mercury lamp, produced material with similar properties. These observations prompted to us to consider the possibility of a spontaneous polymerization having occurred during the pleiadene dimerization process. Thermal gravimetric analysis (TGA) of **5** demonstrated the high thermal stability of the compound generated after heating at 214 °C (Figure 6). In the first step of the curve, beyond the melting point, a 29% loss of mass can be attributed to sublimation. The sublimation was fortunately incomplete, and the residue polymerized to a polymer of exceptional thermal stability with an onset of decomposition of 480 °C (Figure 6).

Upon quenching the polymerization process by sudden cooling, the only isolated soluble product was the divinyl pleiadene dimer **9**. No evidence of a Diels–Alder adduct was found. The divinyl pleiadene dimer **9** can be easily prepared from the iodo benzocyclobutene **6**. Heating compound **6** for 15 min in refluxing *α*-chloronaphthalene gave the diiodopleiadene dimer **10** in 79% yield. In this case, a 98% yield of *anti*-iodo pleiadene dimer **10** was obtained as a an inseparable mixture of the three possible stereoisomers depicted in Scheme 5, as was established by HPLC analysis.[18] The divinyl pleiadene dimer **9** was then obtained in 70% yield, likewise as a mixture of stereoisomers, under the Negishi conditions described above (Scheme 5).

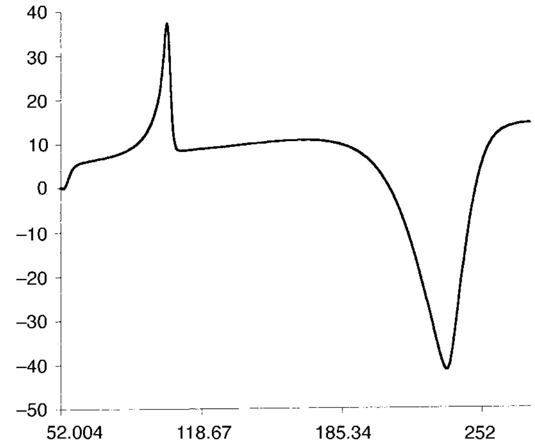


Figure 5. DSC of vinylbenzocyclobutane derivative **5**.

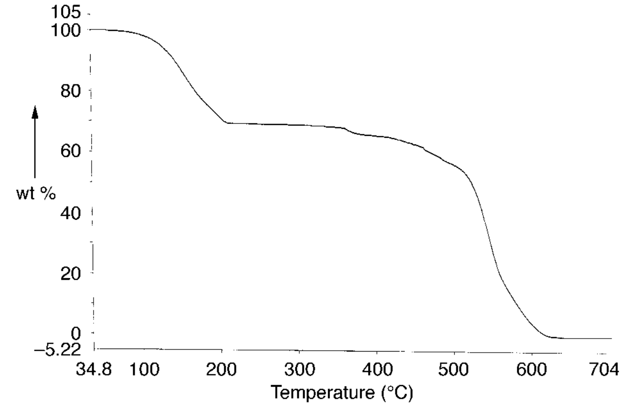
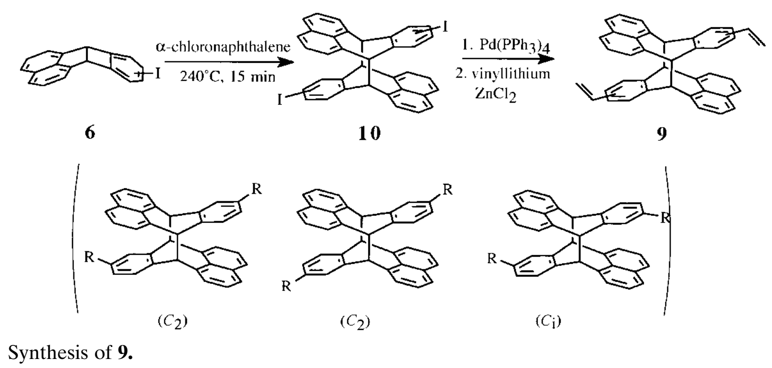


Figure 6. TGA of vinylbenzocyclobutane derivative **5**.



Scheme 5. Synthesis of **9**.

The DSC analysis of the dimer **9** showed only an exothermic peak at 298 °C, corresponding to the polymerization process. Heating **9** for 15 min at 300 °C in the DSC apparatus afforded an insoluble monolith with the same properties as the material generated from the vinyl monomer **5** described above. TGA analysis of compound **9** showed no loss of mass until 480 °C, at which point decomposition occurred.

Figure 7 shows the FTIR spectra of the divinyl pleiadene dimer **9** and the cross-linked polymer generated by pyrolysis of **5** or **9**. In the latter spectrum the -CH=CH$_2$ stretching vibration of dimer **9** at 989 cm^{-1} has clearly disappeared. The spectra of both the vinyl dimer **9** and the cross-linked polymer are otherwise similar, indicating that the *anti*-pleiadene skeleton is still present in the cross-linked polymer.

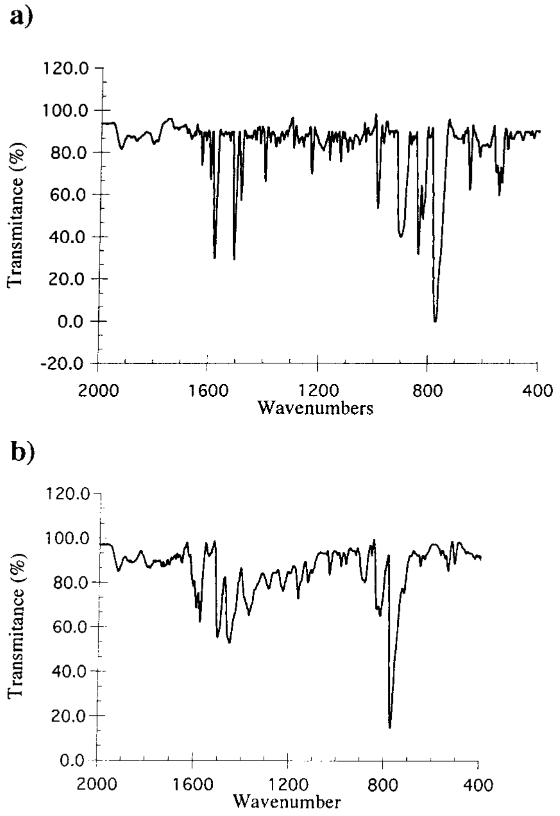
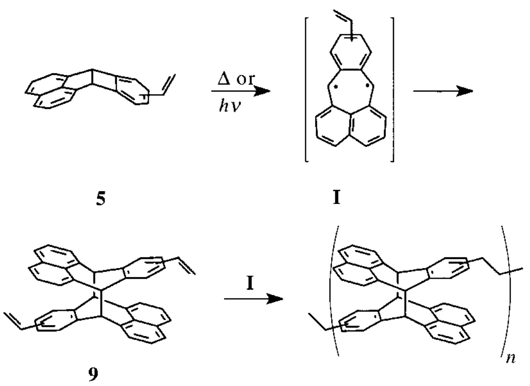


Figure 7. a) FTIR spectrum of divinyl pleiadene dimer **9**. b) FTIR spectrum of the cross-linked polymer generated by pyrolysis or photolysis of vinylbenzocyclobutene derivative **5** or divinyl pleiadene dimer **9**.

Taking into consideration all the experimental data shown above, we can postulate a spontaneous cross-linking polymerization of 8-vinyl-6b-10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (**5**), via the divinyl pleiadene dimer as an intermediate. An intriguing possibility here is that the pleiadene biradical (**I**) initiates the chain-polymerization of the vinyl groups (Scheme 6).

In conclusion, contrary to previous findings, we have proved that both the *syn* and *anti*-**2** dimers are produced in the pleiadene dimerization reaction and that the dimerization process is reversible through pleiadene as an intermediate. We have also established the thermolysis or photolysis of 8-vinyl-6b-10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (**5**) as a promising new approach to the generation of carbon networks. Further work will be directed at the preparation of polymers incorporating these units, the investigation of their post-processing cross-linking, and the examination of the mechanical properties of the materials obtained.



Scheme 6. Chain polymerization of the vinyl groups by **I**.

Experimental Section

NMR spectra were recorded with a Varian Inova 400 spectrometer operating at 400 MHz for ^{1}H and 125 MHz for ^{13}C, and were referenced to tetramethylsilane. UV/Vis spectra were obtained with a Hewlett Packard 8452A diode array spectrometer. TGA and DSC were carried out using a Perkin Elmer 7 Series thermogravimetric analyzer and differential scanning calorimeter, respectively. HPLC measurements were performed by using a Nacalai tesque, Cosmosil Buckyprep (4.6 × 250 mm) column with UV detection at 318 nm, 80:20 hexanes:toluene as eluent, and a flow rate of 1 mL min^{-1}. Retention times: 5.79 min (*anti*-**2**), 8.01 min (*syn*-**2**).

Dimerization of 6b-10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (3): In solution: A solution of **3** (190 mg, 0.84 mmol) in α-chloronaphthalene (5 mL) was refluxed under an argon atmosphere for 15 min. After cooling, MeOH (25 mL) was added, precipitating a white solid. The solid was separated and washed several times with MeOH to obtain 160 mg (84 %) of a mixture of *anti*- (83 %) and *syn*- (17 %) pleiadene dimers (determined by analytical HPLC). The isomers were separated by semipreparative HPLC (Nacalai tesque, Semi-preparative Cosmosil Buckyprep Waters instrument with a 10 × 250 mm column), with UV detection at 318 nm, 80:20 hexanes:toluene as eluent, and a flow rate of 5 mL min^{-1}. Retention times: 6.02 min (*anti*-**2**), 9.4 min (*syn*-**2**). Recrystallization from toluene resulted in the exclusive precipitation of the *anti* isomer.

Neat reaction:[10] Compound **3** (50 mg, 0.22 mmol) was sealed in an ampoule under high vacuum (10^{-6} mm Hg) after several repeated freeze-thaw cycles, and was then heated in a tube furnace at 230–240 °C. The crude reaction mixture consisted of a mixture of the *anti*- (84 %) and *syn*-pleiadene dimers (16 %) (determined by analytical HPLC). Recrystallization from toluene gave 26 mg of the *anti*-**2** isomer (52 %).

***anti*-2**: ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta = 7.53$ (dd, 4H, $J = 8.2$, 1.3 Hz, H$_3$), 7.49 (dd, $J = 7.2$, 1.3 Hz, H$_1$, 4H), 7.30 (dd, 4H, $J = 8.2$, 7.2 Hz, H$_2$), 6.64 (8H, AA′BB′ system, H$_{7\text{-}10}$), 5.07 (s, 4H, CH); ^{13}C NMR (125 MHz, CDCl$_3$): $\delta = 140.3$, 137.4, 135.8, 131.6, 130.7, 128,7, 128.4, 126.4, 125.2, 63.4; UV/Vis (CHCl$_3$): $\lambda_{\max}$ ($\log \varepsilon$) = 246 (4.17), 294 (sh), 306 (4.19), 318 (4.15) nm; MS (70 eV): m/z (%): 456 (3) [M^+], 228 (100), [$C_{18}H_{12}^+$].

***syn*-2**: ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C): $\delta = 7.26$ (dd, 4H, $J = 8.2$, 1.3 Hz, H$_3$), 7.18 (dd, $J = 7.0$, 1.3 Hz, H$_1$, 4H), 7.00 (dd, 4H, $J = 8.2$, 7.0 Hz, H$_1$), 7.07 (8H, AA′BB′ system, H$_{7\text{-}10}$), 5.36 (s, 4H, CH); ^{13}C NMR (125 MHz, CDCl$_3$): $\delta = 140.8$, 136.7, 134.8, 131.0, 130.2, 130.1, 128.2, 127.1, 124.5, 60.5; UV/Vis (CHCl$_3$): $\lambda_{\max}$ ($\log \varepsilon$) = 246 (4.15), 280 (sh), 298 (4.11), 312 (sh) nm; MS (70 eV): m/z (%): 456 (3) [M^+], 228 (100), [$C_{18}H_{12}^+$].

8-Iodo-6b-10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (6): The preparation was carried out according to a slight modification of the synthesis of 8-bromo-6b-10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene. A solution of iodoanthranilic acid (25 g, 95 mmol) and trichloroacetic acid (260 mg, 1.6 mmol) in dry THF (350 mL) was cooled to 0 °C. Isoamyl nitrite (16 mL, 120 mmol) was then added dropwise over a period of 30 min, keeping the temperature at 0 °C for 30 min at room temperature for a further 2 h to yield the diazonium salt as a tan solid. The precipitate was cooled at 0 °C, filtered off (**Caution!** *The filter paper must not be allowed to dry out, because when dry benzenediazonium-2-carboxylate can detonate violently on being scraped or heated, and it is strongly recommended to keep it wet with solvent at all times*), and washed with cold THF until the filtrate was colorless. This material was used directly and was assumed to have been formed in quantitatively yield. This solid was added to a solution of acenaphthylene (30.4 g, 200 mmol) in 1,2-dichloroethane (400 mL) and the yellow mixture was stirred overnight at room temperature. It was then heated for 2 d at 45 °C and finally overnight to 60 °C. The solvent was removed under vacuum to obtain a brownish paste which was triturated with hot pentane. The yellow precipitate obtained on evaporation of the solvent was washed several times with methanol to obtain 2.76 g of the pure iodobenzocyclobutene derivative. An additional 3.2 g of pure iodo compound was obtained by silica column purification of the mother liquor together with the brownish paste, using petroleum ether as eluent to give an overall yield of 6 g (18 %); m.p. 162 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.63 (m, 2 H, H$_{ar}$), 7.52(s, 1 H, H$_{ar}$), 7.47 (m, 5 H, H$_{ar}$), 6.94 (d, 1 H, J = 7.2 Hz, H$_{ar}$), 5.33 (d, 1 H, J = 3.6 Hz), 5.28 (d, 1 H, J = 3.6 Hz); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 149.0, 146.4, 142.3, 142.2, 136.8, 131.8, 128.1, 124.8, 124.2, 124.1, 54.2, and 53.9 ppm; MS (FAB): m/z (%): 354 (100); IR (KBr): $\tilde{\nu}$ = 3051, 3039, 3028, 2951, 1605, 1497, 1446, 1400, 1371, 1245, 881, 804, 784, 770 cm^{-1}; UV/Vis (toluene): λ_{max} = 280 (sh), 287 (sh), 295, 305 (sh), 308 (sh), 318 (sh), 322 (sh) nm; elemental analysis calcd for $C_{18}H_{11}I$: C 61.04, H 3.13, I 35.83; found C 60.97, H 3.17, I 35.74.

Differential scanning calorimetry was carried out under nitrogen on a sample of pure **6**, heating from 50 to 400 °C at a rate of 10 °C min^{-1}. The melting endotherm was observed at 162 °C, the dimerization exotherm at 218 °C, and the ring-opening exotherm at 306 °C. Integration of the area under the first exotherm gave a value of 63.91 cal g^{-1}, which corresponds to 22.62 kcal mol^{-1}, and of the second exotherm gave a value of 53.03 cal g^{-1}, which corresponds to an exothermicity of 18.77 kcal mol^{-1} for the process.

8-Vinyl-6b-10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (5): Into a three-necked round-bottom flask was added at −78 °C vinyllithium (5 mL of a 2 M THF solution, 10 mmol,), ZnCl$_2$ (10 mL of a 0.5 M THF solution, 5 mmol), and dry THF (10 mL), and the mixture was warmed up to 0 °C during 1 h. A solution of the iodo derivative **6** (3.2 g, 9 mmol) and palladium tetrakis(triphenylphosphane) (600 mg, 0.5 mmol) in freshly distilled THF was then added by cannula and the mixture was heated to 45 °C overnight. Water was added and the mixture was extracted with diethyl ether (3 × 200 mL). The combined organic layers were washed with brine, dried with MgSO$_4$, filtered through a plug of silica, and evaporated under reduced pressure to obtain a yellow product, which upon purification by column chromatography (silica gel, petroleum ether as eluent) afforded 1.9 g (83 %) of a white solid**;** m.p. 102 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 5.13 (d, 1 H, J = 10.8 Hz), 5.37 (s, 2 H, C*H*-Ar), 5.62 (d, 1 H, J = 17.6 Hz), 6.62 (dd, 1 H, J = 10.8, 17.6 Hz), 7.16 (m, 2 H, H$_{ar}$), 7.27 (s, 1 H, H$_{ar}$), 7.48 (m, 4 H, H$_{ar}$), 7.63(d, 2 H, J = 7.7 Hz, H$_{ar}$); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 140.3, 137.4, 135.8, 131.6, 130.7, 128,7, 128.4, 126.4, 125.2, 63.4; MS (FAB): m/z (%): 254 (100); IR (KBr): $\tilde{\nu}$ = 1623, 1600, 1492, 1469, 1419, 1364, 1167, 1154, 1116, 1104, 997, 903, 889, 869, 829, 807, 781, 771, 741, 666 cm^{-1}; UV/Vis (toluene): λ_{max} = 274 (sh), 286 (sh), 296, 304 (sh), 315 (sh), 320 (sh) nm; elemental analysis calcd for $C_{20}H_{14}$ (254.33): C 94.45, H 5.55; found C 94.20, H 5.28.

Differential scanning calorimetry was carried out under nitrogen on a sample of pure **5**, heating from 50 to 500 °C at a rate of 10 °C min^{-1}. The melting endotherm was observed at 102 °C and the dimerization–polymerization exotherm at 214 °C. Integration of the area under the exotherm gave a value of 109.45 cal g^{-1}, which corresponds to an exothermicity of 27.81 kcal mol^{-1} for the process. The sample appears to be stable up to about 400 °C.

***anti*-Diiodopleiadene dimer (10)**: A solution of 8-iodo-6b-10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (500 mg, 1.4 mmol) in α-chloronaphthalene (5 mL) was refluxed under an argon atmosphere for 15 min. After cooling to room temperature, MeOH (50 mL) was added, affording a yellowish-white precipitate which was centrifuged and washed several times with methanol to yield **10** (390 mg, 79 %: 96 % *anti* isomer, as determined by HPLC): m.p. > 300 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.59 (d, 4 H, J = 8.24 Hz, H$_{ar}$), 7.45 (m, 4 H, H$_{ar}$), 7.35 (m, 4 H, H$_{ar}$), 7.04 (dd, 2 H, J = 2.4, 1.3 Hz), 6.91 (d, 2 H, J = 7.9, 1.3 Hz), 6.38 (dd, 2 H, J = 7.9, 2.4 Hz), 4.95 (m, 4 H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 142.5, 142.34, 139.9, 139.8, 139.1, 136.2, 135.8, 135.4, 132.5, 131.8, 131.2, 129.4, 129.3, 128.8, 128.7, 128.5, 128.4, 125.4, 125.3, 62.7, 62.6, 62.5; MS (FAB): m/z (%): 708 ([M^+], 10), 354 (100); IR (KBr): $\tilde{\nu}$ = 3052, 3035, 2920, 1601, 1582, 1507, 838, 772 cm^{-1}; UV/Vis (toluene): λ_{max} = 236 (sh), 244 (sh), 250 (sh), 254 (sh), 306, 318 nm; elemental analysis calcd for $C_{36}H_{22}I_2$ (Mw = 708.38): C 61.04, H 3.13, I 35.83; found C 60.82, H 3.20, I 35.68.

***anti*-Divinyl pleiadene dimer (9)**: Into a three-necked round-bottom flask was added at −78 °C vinyllithium (0.3 mL of a 2 M THF solution, 0.6 mmol,), ZnCl$_2$ (0.6 mL of a 0.5 M THF solution, 0.3 mmol), and dry THF (2 mL), and the mixture was warmed up to 0 °C during 30 min. A solution of the *anti*-diiodopleiadene dimer **10** (200 mg, 0.28 mmol) and palladium tetrakis(triphenylphosphane) (600 mg, 0.02 mmol) in freshly distilled THF was then added by cannula, and the mixture was heated to 45 °C overnight. Water was added and the mixture was extracted with diethyl ether (3 × 200 mL). The combined organic layers were washed with brine, dried with MgSO$_4$, filtered through a plug of silica, and evaporated under reduced pressure to obtain a yellow product. After purification by column chromatography (silica gel, petroleum ether), 100 mg (70 %) of a white solid was obtained; m.p. > 300 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.95 (d, 2 H, J = 10.8 Hz), 5.06 (m, 4 H, C*H*-Ar), 5.38 (d, 2 H, J = 17.6 Hz), 6.30 (dd, 2 H, J = 10.8, 17.6 Hz), 6.63 (m, 4 H, H$_{ar}$), 6.72 (m, 2 H, H$_{ar}$), 7.28 (m, 4 H, H$_{ar}$), 7.48 (m, 4 H, H$_{ar}$); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 140.4, 140.3, 140.0, 139.9, 137.3, 137.2 (2C), 137.1, 136.5, 135.8 (2C), 131.5, 130.9 (2C), 130.0, 128.9, 128.8, 128.7 (2C), 128.3, 128.2, 125.2, 125.1, 124.2, 112.9, 63.4, 63.3, 63.1, 63.0; MS (FAB): m/z (%): 509 ([MH]$^+$, 3), 508 ([M]$^+$, 3), 254 (100); IR (KBr): $\tilde{\nu}$ = 1623, 1600, 1580, 1505, 1493, 997, 900, 841, 817, 775, 650, 550, 535 cm^{-1}; UV/Vis (toluene): λ_{max} = 286, 307, 319 nm; elemental analysis calcd for $C_{40}H_{28}$ (Mw = 508.66): C 94.5, H 5.55; found C 94.2, H 5.71.

Differential scanning calorimetry was carried out under nitrogen on a sample of pure **9**, heating from 50 to 500 °C at a rate of 10 °C min^{-1}. The polymerization reaction exotherm occurred at 298 °C. The sample is stable up to about 400 °C.

X-ray structure analysis: Data were collected at 298 K with a Siemens Smart diffractometer with CCD detector, using Mo$_{K\alpha}$ radiation, λ = 0.71073 Å and operating at 50 kV and 40 mA. The structure was solved and refined by using the Siemens SHELXTL program package. Data collection: ω scan; 2θ range(°): 3.3–40/2.8–40; h,k,l range: $-12 < h < 12$, $-13 < k < 12$, $-24 < l < 24$/ $-11 < h < 10$, $-13 < k < 13$, $-19 < l < 19$; a total of 7338/5751 and 2787/2169 independent reflections for *anti* and *syn*, respectively, were collected. Full matrix least square refinement was performed with 2787/2169 unique reflections with $I > 2\sigma(I)$. The final agreement factors were: $R(F) = 0.096/0.089$ (where $R(F) = \Sigma||F_o| - |F_c||/|F_o|$ with $F_o > 2.0\sigma(F)$), $R_w(F^2) = 0.231/0.202$ (where $R_w(F^2) = \Sigma(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ with $F_o > 2.0\sigma(F)$; $w = 1/[\sigma^2(F_o^2) + (0.0612P)^2]$ where $P = (F_o^2 + 2F_c^2)/3)$, and $S(F^2) = 1.328/1.163$ for 366/326 parameters. In the final stages of the refinement a secondary extinction correction was included (0.007(4)/0.001(2)). The final parameters shifts were smaller than 0.001σ; in the final difference map the largest peak and a hole were 0.238/0.260 and −0.290/0.233 e Å^{-3} . The benzo groups for the *anti* isomer were refined as idealized hexagons with individual anisotropic thermal parameters. All other non-hydrogen atoms in the two structures were refined anisotropically with the hydrogens in the riding mode.

***anti*-2**: $C_{42}H_{26}Cl_2$, rectangular colorless transparent plate from ODCB (0.28 × 0.22 × 0.04 mm), M_W = 601.53; triclinic, space group $P1$, ρ_{calcd} = 1.32 g cm^{-3} , $\mu(Mo_{K\alpha}) = 0.246$ mm^{-1}, $Z = 2$, $a = 9.499(3)$, $b = 9.8995(3)$, $c = 18.22470(10)$ Å, $\alpha = 78.190(2)$, $\beta = 77.092(2)$, $\gamma = 66.059(2)$°, $V = 1514.33(7)$ Å^3.

***syn*-2**: $C_{39}H_{22}$, irregular colorless opaque crystal (0.2 × 0.12 × 0.08 mm) from CHCl$_3$, M_W = 454.54; triclinic, space group $P1$, ρ_{calcd} = 1.283 g cm^{-3} , $\mu(Mo_{K\alpha}) = 0.073$ mm^{-1}, $Z = 2$, $a = 8.2711(7)$, $b = 10.0185(8)$, $c = 14.8885(12)$ Å, $\alpha = 83.038(2)$, $\beta = 75.245(2)$, $\gamma = 82.079(2)$°, $V = 1176.9(2)$ Å^3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-108046 (*anti*-**2**) and 108047 (*syn*-**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was supported through NSF grant No. DMR-9704143, the Materials Research Laboratory at UCSB, and by the Exotic Materials Institute (EMI) at UCLA. Ángela Sastre thanks the Ministerio de Educación y Cultura (Spain) for a postdoctoral fellowship.

---

[1] J. E. Field, *The properties of diamond*, New York, **1979**.
[2] T. A. Upshaw, J. K. Stille, J. P. Droske, *Macromolecules*, **1991**, *24*, 2144–2150.
[3] T. X. Neenan, M. R. Callstrom, L. M. Scarmoutzos, K. R. Stewart, G. M. Whitesides, *Macromolecules*, **1988**, *21*, 3525–3528.
[4] E. B. Stephens, J. M. Tour, *Macromolecules*, **1993**, *26*, 2420–2427.
[5] G. T. Vischer, D. C. Nesting, J. V. Badding, P. A. Bianconi, *Science*, **1993**, *260*, 1496–1499.
[6] G. T. Vischer, P. A. Bianconi, *J. Am. Chem. Soc.*, **1994**, *116*, 1805–1811.
[7] L. Fieser, M. Fieser, *J. Am. Chem. Soc.* **1933**, *55*, 3010–3018.
[8] G. Binsch, I. Tamir, *J. Am. Chem. Soc.* **1969**, *91*, 2450–2455.
[9] J. Kolc, J. Michl, *J. Am. Chem. Soc.* **1970**, *92*, 4147–4148.
[10] J. Kolc, J. Michl, *J. Am. Chem. Soc.* **1973**, *95*, 7391–7401.
[11] J. Kolc, J. Michl, *J. Am. Chem. Soc.* **1970**, *92*, 4148–4150.
[12] J. Kolc, J. Downing, W., A. Manzara, P., J. Michl, *J. Am. Chem. Soc.* **1976**, *98*, 930–937.
[13] M. P. Cava, R. H. Schlessinger, *Tetrahedron* **1965**, *21*, 3073–3081.
[14] G. S. Pawley, E. A. Yeates, *Acta Cryst. B* **1969**, *25*, 2009–2013.
[15] A. C. Hazell, *Acta Cryst. B* **1976**, *32*, 2010–2013.
[16] A. C. Hazell, R. G. Hazell, *Acta Cryst. B* **1977**, *33*, 360–365.
[17] E. Negishi, *Acc. Chem. Res.* **1982**, *15*, 340–348.
[18] Nacalai tesque, Cosmosil Buckyprep waters (4.6 × 250 mm) column; UV detection at 318 nm, 70:30 hexanes:chloroform as eluent, flow rate 1 mL min^{-1}, retention time: 5.33 min

Received: May 5, 1998 [F1137]