Convenient synthesis and reduction properties of [7]circulene

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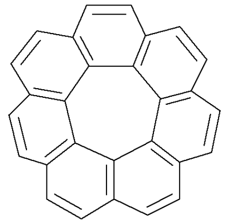
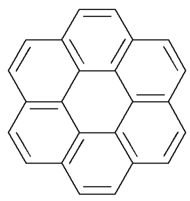
Saddle-shaped [7]circulene (1) is prepared by an extremely simple procedure that involves a 2,15-ethano-bridged hexahelicene intermediate. Reduction properties of the [7]circulene have been investigated by means of voltammetry and ESR spectroscopy and compared with those of planar [6]circulene (coronene) (2).

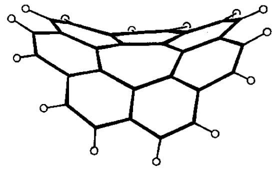
Introduction

The discovery of buckminsterfullerene (C_{60})[1] and related carbon cage systems[2] has led to a general interest in the properties and behavior of non-planar polycyclic aromatic hydrocarbons with curved carbon systems. We are interested in synthetic studies of twisted π-electron systems,[3] and have described the first successful syntheses of twisted saddle-shaped [7]circulene (**1**)[4] (pleiadannulene)[5] with a circular arrangement of seven benzene rings and saddle-shaped [7.7]circulene (**3**)[6] with a contiguous benzoannulated ring around a central bicyclo[5.5.0]-dodecane framework. Recent advances in large carbon cluster chemistry[7] such as higher fullerenes and nanotubes led us to investigate the convenient new synthesis of [7]circulene (**1**)[8] as a subunit of the inner surface of a helix-shaped nanotube.[9]

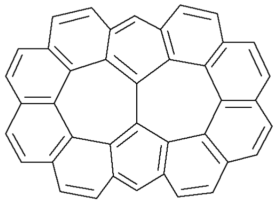




planar coronene **2**



saddle-shaped [7]circulene **1**



saddle-shaped [7.7]circulene **3**

We are also interested in the properties of twisted π-electron systems. Here, we focused on the reduction properties of the twisted saddle-shaped [7]circulene. When an electron was introduced electrochemically into [7]circulene, a new radical anion was formed. It was of interest how the radical anion differed from the coronene radical anion which was formed by a one-electron reduction of planar coronene.[10,11]

Results and discussion

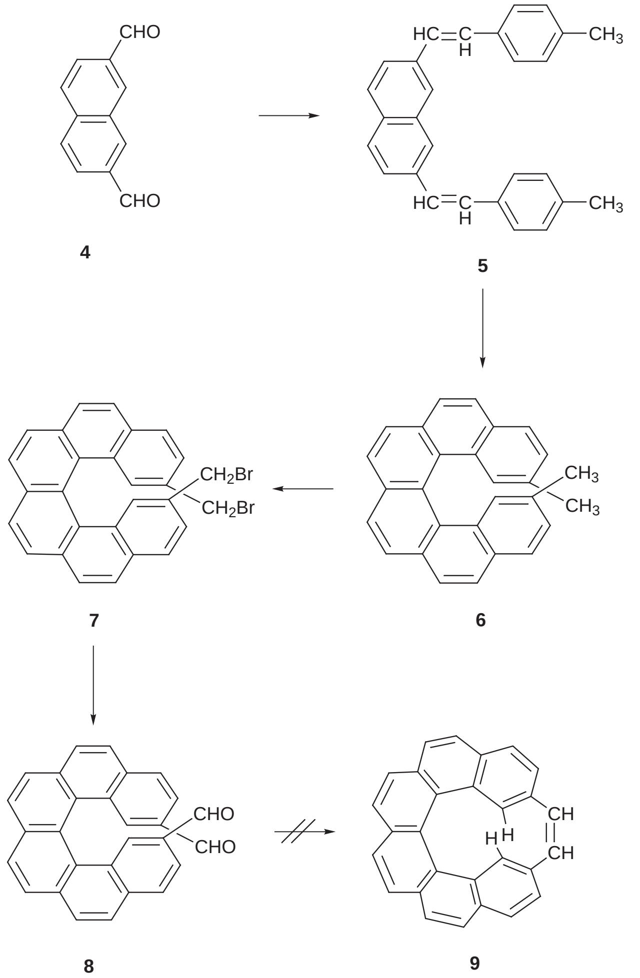
Our previous paper reported the preparation of [7]circulene **1** which involved a 1,16-dehydrohexahelicene intermediate with an internal framework of [7]circulene **1** in a stunning tour pathway.[4] In the extremely simple procedure,[8] we selected as the key intermediate 2,15-bridged hexahelicene which was easily convertible into dihydro[7]circulene **13** to complete the synthesis.[12]

Convenient synthesis of [7]circulene (1)

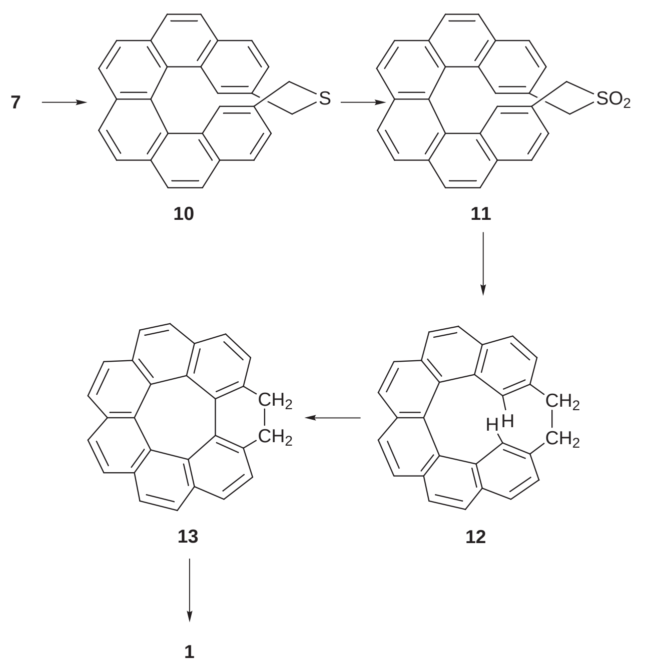
First, we attempted to carry out a convenient synthesis of [7]-circulene **1** from a 2,15-etheno-bridged hexahelicene precursor (see Scheme 1). The Wittig condensation of 2,7-naphthalenedicarbaldehyde **4**[13] with 4-methylbenzyltriphenylphosphonium bromide using NaOMe–DMF (DMF = *N*,*N*-dimethylformamide) gave a mixture of *cis–cis*, *cis–trans* and *trans–trans*-stereoisomeric products **5** (85% yield).

The mixture was dissolved in benzene and irradiated with a high-pressure mercury lamp for 2 h to give 2,15-dimethylhexahelicene **6** (mp 212–214 °C, 89% yield). Bromination of **6** with *N*-bromosuccinimide afforded the dibromide **7** (mp 196–198 °C, 45% yield) which was treated with the sodium salt of 2-nitropropane in ethanol to yield the dialdehyde **8**[13] (mp 287–289 °C, 75% yield). Reductive coupling of **8** to give the etheno-bridged hexahelicene **9** by using low-valent titanium[14] was unsuccessful, invariably giving a polymer as the product.

In the next approach, we selected 2,15-ethano-bridged hexahelicene **12** as a key intermediate (see Scheme 2). An advantage of this intermediate is that it can be easily converted to dihydro-[7]circulene **13**,[12] a precursor of **1**. Intramolecular cyclization of **7** with sodium sulfide nonahydrate in refluxing benzene–ethanol afforded the 2,15-bridged hexahelicene sulfide **10** (mp 252–254 °C, 48% yield) whose oxidation with hydrogen peroxide gave the sulfone **11** (mp > 300 °C) in quantitative yield. Flash vacuum pyrolysis (550 °C, 0.01 Torr) of **11** gave the dihydro[7]circulene **13** directly (yellow prisms, mp 225–227 °C, 42% yield). The mechanism for this striking transformation presumably involves the initial formation of the ethano-bridged hexahelicene **12** by pyrolysis followed by dehydrogenation at both ends of the hexahelicene framework.[12] An MM3 calculation[15] predicted a strain energy of about 32.2 kcal mol^{-1} for **13**, which should make it greater than 12 kcal mol^{-1} more stable than **12** (44.3 kcal mol^{-1}). The 500 MHz ^1H NMR spectrum of **13** in $CDCl_3$ shows a single peak at δ 2.70 for the two enantiotopic methylene groups at room temperature, but sets of peaks for aliphatic hydrogens centered at δ 2.98 and 3.75 at −50 °C ($\Delta\nu = 149.5$ Hz), characteristic of an AA′BB′ pattern and corresponding to the chiral saddle-shaped geometry of **13**. The coalescence temperature for those two signals was found to be



Scheme 1



Scheme 2

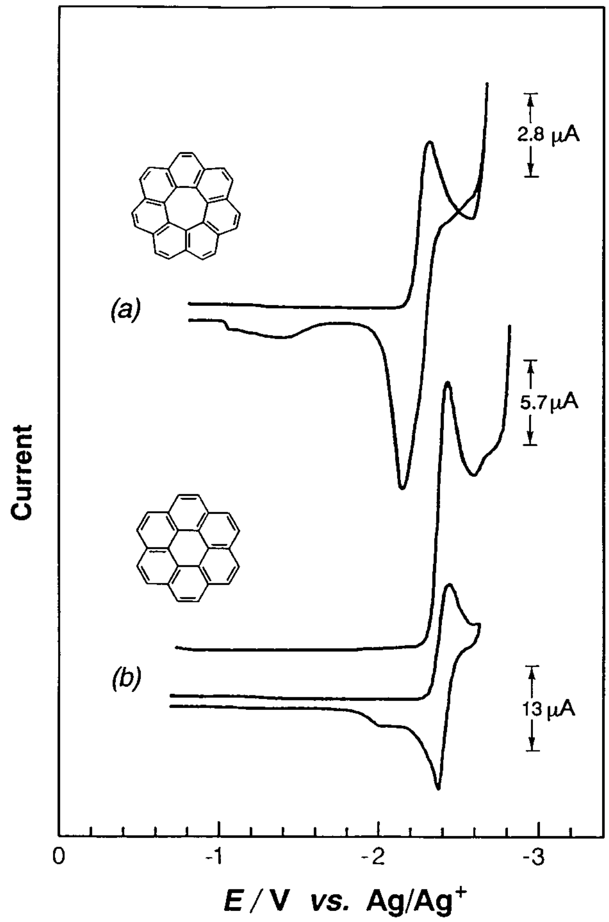


Fig. 1 Voltammograms for the redox of (*a*) [7]circulene and (*b*) coronene at a hanging mercury drop electrode in DMF–0.2 mol dm^{-3} NBu_4ClO_4 with a scan rate of 300 mV s^{-1}

−10 °C, from which we calculated the barrier for ring inversion in **13** to be $\Delta G^{\ddagger}$ 12.2 kcal mol^{-1} at this temperature. Finally, dehydrogenation of **13** with 5% Pd/C in 1-methylnaphthalene at 280 °C for 1 h led to [7]circulene **1** (mp 295–296 °C, 85% yield) with a twisted saddle-shaped geometry. The 500 MHz ^1H NMR spectrum of **1** in CD_2Cl_2 showed only a single signal for the fourteen protons of **1** even though the temperature was decreased from 25 °C (δ 7.52) down to −90 °C (δ 7.55). This single signal revealed that the twisted saddle-shaped geometry of **1** was not fixed even at the low temperature. This was in contrast with the fixed saddle-shaped geometry of **13** at temperatures lower than −10 °C.

Reduction properties

Although reduction properties of [5]circulene (corannulene)[16] have been examined, no electrochemical property of [7]circulene **1** has been reported. A successful shorter new synthetic route to [7]circulene prompted us to investigate the reduction properties of this prototypical saddle-shaped hydrocarbon.

A voltammogram of [7]circulene is shown in Fig. 1(*a*), where a quasi-reversible redox couple appeared at −2.1–−2.4 V *vs.* Ag/Ag^+ and an irreversible cathodic current at more negative potentials than −2.6 V *vs.* Ag/Ag^+. These reduction properties were similar to those of well-studied coronene,[10] shown in Fig. 1(*b*), except that the first and the second electron transfers took place at less negative potentials ($\Delta E = 0.1$–0.2 V).

Using a two-electrode cell, *in situ* ESR spectra were recorded. When the helical-gold-wire electrode[17] in the electrolytic cell containing the DMF solution of [7]circulene was negatively polarised, an ESR signal appeared as shown in Fig. 2(*a*). This signal indicated that a radical anion of [7]circulene was formed by the reduction. The *g*-value was 2.0025. A computer simulation[18] of the spectrum revealed that the radical anion had a hyperfine splitting constant (a_H) of 0.083 mT. Similar ESR signals were obtained when [7]circulene was reduced by lithium, sodium, potassium or caesium metals. Fifteen splitting lines arose from fourteen equivalent hydrogens at the outer-ring carbon atoms of [7]circulene. Fig. 3 shows the plot of ESR signal intensity of the centre peak *versus* applied voltage. On

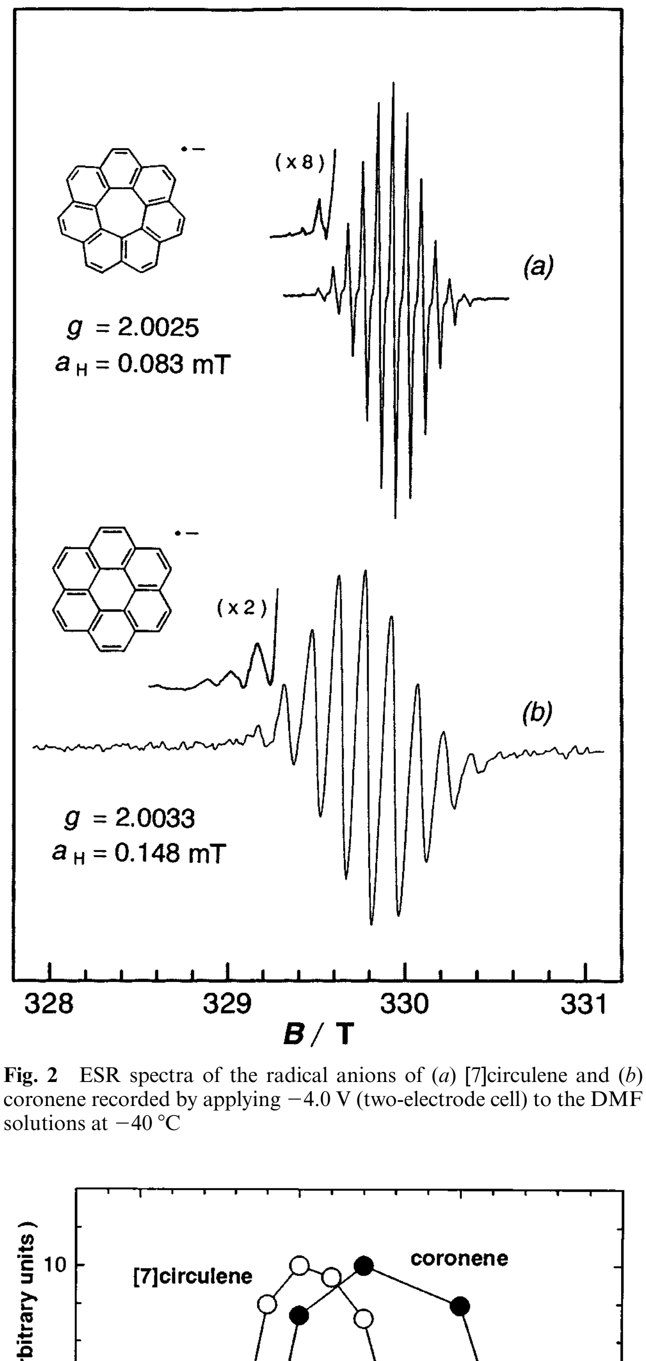


Fig. 2 ESR spectra of the radical anions of (*a*) [7]circulene and (*b*) coronene recorded by applying −4.0 V (two-electrode cell) to the DMF solutions at −40 °C

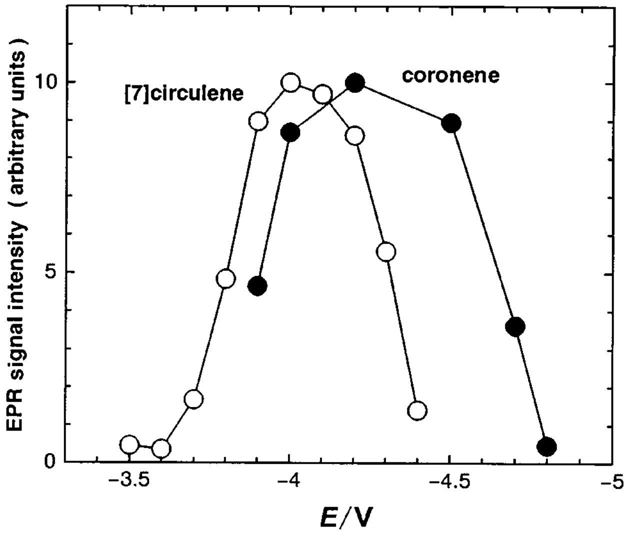
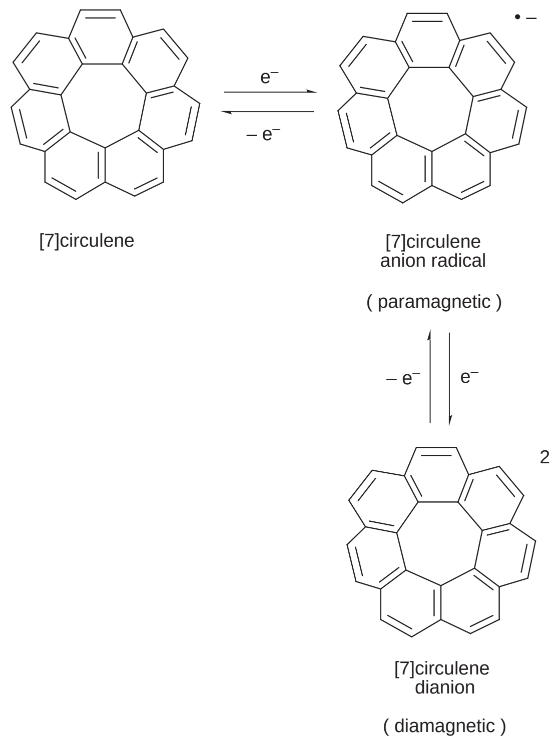


Fig. 3 Plot of ESR signal intensity *versus* applied voltage (two-electrode cell) in the DMF solution at −40 °C: (○) reduction of [7]-circulene, (●) reduction of coronene

increasing the applied voltage in the negative direction, this signal became larger until it reached a maximum intensity at −4.0 V. Then, it became smaller, and at −4.4 V it decreased to 13% of the maximum value. This decrease did not indicate that the radical anion decomposed at this negative voltage but rather that it was reduced further to a dianion of [7]circulene that was diamagnetic (see Scheme 3). By bringing the applied potential from −4.4 back to −4.0 V, the original maximum signal intensity was recovered.



Scheme 3

Fig. 2(*b*) shows an *in situ* ESR spectrum of the coronene radical anion, which was obtained by the electrochemical method. The *g*-value was 2.0033 and a_H was 0.148 mT. This spectrum was similar to that reported for the coronene radical anion which was prepared by a reduction with alkali metal.[11] Thirteen splitting lines arose from twelve equivalent hydrogens at the outer-ring carbon atoms of coronene. The intensity of the ESR signal first increased and then decreased as in the case of [7]circulene but the curve for coronene shifted to negative voltages. Similar shifts were observed in the voltammograms of [7]circulene and coronene shown in Fig. 1. These results indicate that the first and the second electron transfers to [7]circulene take place at less negative potentials than those to coronene.

Comparing the two ESR spectra of Fig. 2(*a*) and (*b*), a remarkable difference was found in the a_H values: 0.083 mT for [7]circulene and 0.148 mT for coronene. The smaller a_H value of the [7]circulene radical anion was thought to reflect a poor spin distribution at the outer-ring carbon atoms where hydrogen atoms are attached. Although structural differences in the two radical anions may have some role, unfortunately no structural analysis has yet been successfully carried out. *Ab initio* MO calculations for the [7]circulene radical anion revealed that the calculated geometry was saddle-shaped with C_2 symmetry similar to the structure of the neutral molecule.[8] In the case of bowl-shaped [5]circulene,[16] the radical anion was reported to have an a_H value of 0.157 mT, which is similar to the a_H value for planar coronene.

Theoretical calculations for the LUMO by the extended Hückel method suggested that the spin population of the [7]circulene radical anion was localised mainly at the inner-ring carbon atoms, while that of the coronene radical anion was localised at the outer-ring carbon atoms (see Fig. 4). This change in the location of the spin population explains well the reason for the small a_H value for the [7]circulene radical anion.

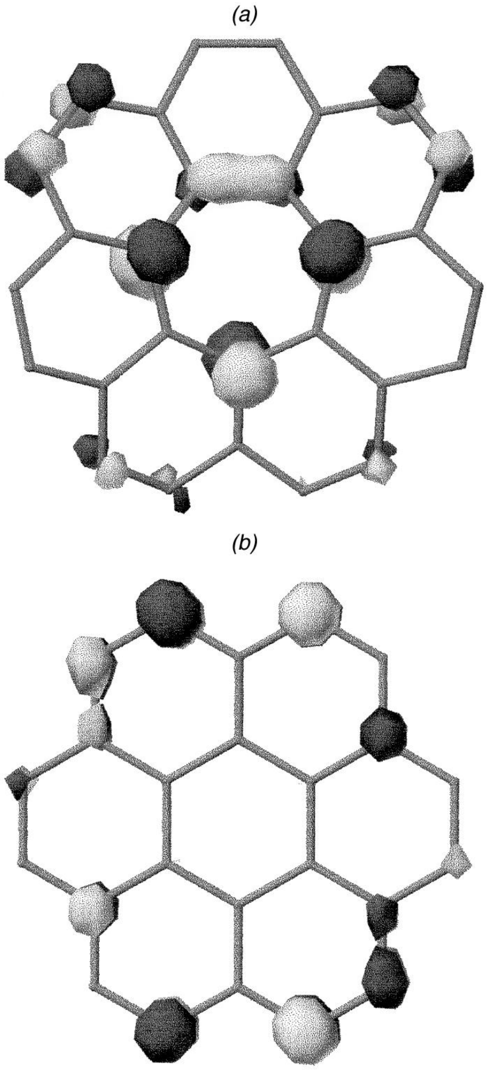


Fig. 4 Shapes of the LUMO of (*a*) [7]circulene and (*b*) coronene according to extended Hückel MO calculations

To clarify the non-planar structural effect, we are devoting our efforts to synthesising various types of non-planar circulenes and to revealing their characteristic properties.

Experimental

General

All melting points are uncorrected. IR data were obtained with a JASCO FT-5300 spectrophotometer. ^1H NMR spectra and ^{13}C NMR spectra were recorded for $CDCl_3$ or CD_2Cl_2 solutions with a JEOL JNM-A500 spectrometer, with tetramethylsilane as an internal standard. *J* values are given in Hz. Mass spectral data were measured on a JEOL JMS-AX500 spectrometer (EI, 70 eV). Elemental analyses were performed on a Yanagimoto CHN-Corder, Type II. Merck alumina or Merck silica gel was used for column chromatography. The progress of most reactions was followed by TLC with Merck precoated silica gel. A Halos ET-500 high-pressure mercury lamp (Eikosha Co., Osaka, Japan) was used for irradiations.

Voltammetric measurements

Voltammetric experiments were carried out using a Fuso 315A potentiostat/programmer. A hanging mercury drop electrode (PAR 9323) was used as a working electrode. Pt wire and Ag/Ag^+ were used as counter and reference electrodes, respectively. HPLC grade DMF solvent (Aldrich, 99.9+%) was purified by passing through an alumina (ICN Biomedicals, neutral alumina grade super I) column prior to the measurement. The sample (*ca.* 0.4 mg of [7]circulene or 0.8 mg of coronene) and tetrabutylammonium perchlorate (NBu_4ClO_4, 68 mg) were dissolved in the DMF solvent (1 ml) in the presence of suspended alumina (100 mg). Deaeration was done by bubbling with pure nitrogen (99.9999%) and the voltammetric measurement was performed under the nitrogen atmosphere at room temperature. Voltammograms were recorded by a Riken Denshi F-3DG XY recorder.

ESR measurements

ESR spectra were measured with a JEOL JES-RE1X spectrometer with 100 KHz field modulation. The electrolytic cell for the ESR measurement, that was fabricated as reported by Ohya-Nishiguchi,[17] was mounted in a cylindrical ESR cavity with a temperature control dewar. The electrolytic cell consists of a Pyrex tube (inner diameter of 3.5 mm), a helical-gold-wire working electrode at the cell-wall, and a straight-gold-wire counter electrode in the centre of the cell. Applied voltages between the two electrodes were controlled by a Takeda Riken TR-614 DC-Voltage/Current Generator without using a reference electrode. After the cell was pumped and flashed with dry nitrogen, the DMF solution (*ca.* 0.2 mg of sample, 34 mg of NBu_4ClO_4, and 0.7 ml of DMF) was taken into the cell under the nitrogen atmosphere.

2,7-Bis(*p*-methylstyryl)naphthalene (5)

To a stirred solution of 4-methylbenzyltriphenylphosphonium bromide (8.6 g, 19.2 mmol) and 2,7-naphthalenedicarbaldehyde (**4**) (1.75 g, 9.5 mmol) in dry DMF (45 ml) was added dropwise a solution of NaOMe (1.1 g, 20.3 mmol) in dry DMF (20 ml). After being stirred for 16 h at room temperature, the reaction mixture was poured into water and extracted with chloroform. The organic layer was washed with water and then dried. After evaporation of the solvent, the residual solid was chromatographed on silica gel. Elution with hexane–benzene (1 : 1) produced a mixture of the *cis–cis*, *cis–trans*, *trans–trans*-isomers of **5**, mp 160–169 °C (2.96 g, 85%); *m/z* (EI) 362 (M^+); δ (500 MHz; $CDCl_3$) 2.32 (6H, s, 2 × CH_3), 6.62–6.68 (4H, m, *cis* and *trans* CH=CH) and 7.02–7.62 (14H, m, ArH).

2,15-Dimethylhexahelicene (6)[19]

A solution of **5** (0.2 g, 0.55 mmol), in benzene (450 ml) containing iodine (0.28 g, 1.10 mmol) and propylene oxide (5 g), was irradiated with a 500 W high-pressure mercury lamp in an atmosphere of nitrogen for 2 h. Removal of the solvent followed by column chromatography on silica gel [hexane–chloroform (1 : 1) as eluent] afforded the hexahelicene **6** (0.17 g, 89%) which was recrystallised from benzene–hexane to give pale-yellow prisms; mp 212–214 °C; *m/z* (EI) 356 (M^+); δ (500 MHz; $CDCl_3$) 1.76 (6H, s, 2 × CH_3), 7.07 (2H, d, *J* 7.93, 3,14-H), 7.37 (2H, s, 1,16-H), 7.69 (2H, d, *J* 7.93, 4,13-H), 7.83–7.86 (4H, m, 5,6,11,12-H), 7.95 (2H, d, *J* 8.23, 7,10-H) and 7.99 (2H, d, *J* 8.23, 8,9-H).

2,15-Bis(bromomethyl)hexahelicene (7)[20]

A mixture of **6** (2.1 g, 5.89 mmol), *N*-bromosuccinimide (2.2 g, 12.36 mmol), benzoyl peroxide (30 mg), and carbon tetrachloride (65 ml) was heated to reflux for 4 h. Removal of the deposited succinimide followed by concentration of the filtrate *in vacuo* gave a solid, which was recrystallised from chloroform–hexane to give fine, pale-yellow crystals of **7** (1.36 g, 45%); mp 196–198 °C; *m/z* (EI) 514 (M^+); δ (500 MHz; $CDCl_3$) 3.83 (2H, d, J_{gem} 10.37, 2 × CH), 3.95 (2H, d, J_{gem} 10.37, 2 × CH), 7.26 (2H, d, *J* 8.23, 3,14-H), 7.56 (2H, s, 1,16-H), 7.82 (2H, d, *J* 8.23, 4,13-H), 7.92 (2H, d, *J* 8.54, 5,12-H), 7.97 (2H, d, *J* 8.54, 6,11-H), 7.99 (2H, d, *J* 8.24, 7,10-H) and 8.03 (2H, d, *J* 8.24, 8,9-H).

Hexahelicene-2,15-dicarbaldehyde (8)[13]

2-Nitropropane (0.12 g, 1.35 mmol) was added dropwise to a solution of sodium ethoxide, prepared from sodium (0.03 mol) and absolute ethanol (10 ml). The resulting nitronate salt was brought into solution by the addition of absolute ethanol (20 ml). To this ethanolic solution, the bromide **7** (0.25 g, 0.486 mmol) was added and the mixture was stirred for 10 h at room temperature. The reaction mixture was poured into water (150 ml) and then extracted with chloroform. The extract was washed with water and then dried. After evaporation of the solvent, the resulting solid was recrystallised from benzene to give **8** (0.14 g, 75%) as yellow plates [Found: C, 87.42; H, 4.21%; M^+ (EI) 384. $C_{28}H_{16}O_2$ requires C, 87.48; H, 4.20%; *M* 384]; mp 287–289 °C; ν_{max}(KBr)/cm^{-1} 1690 (C=O); δ (500 MHz; $CDCl_3$) 7.65 (2H, dd, *J* 8.24, 1.52, 3,14-H), 7.91 (2H, d, *J* 8.24, 4,13-H), 7.96 (2H, d, *J* 1.52, 1,16-H), 8.00 (2H, d, *J* 8.54, 5,12-H), 8.09 (2H, d, *J* 8.24, 7,10-H), 8.14 (2H, d, *J* 8.24, 8,9-H), 8.15 (2H, d, *J* 8.54, 6,11-H) and 9.15 (2H, s, 2 × CHO).

2,15-(2-Thiapropano)bridged hexahelicene (10)

To stirred and refluxed ethanol (500 ml) under nitrogen were simultaneously added, over a period of 24 h, a solution of sodium sulfide nonahydrate (0.48 g, 2.0 mmol) in ethanol (200 ml) and a solution of **7** (1.0 g, 1.94 mmol) in ethanol (200 ml). After being refluxed for 15 h, the reaction mixture was concentrated under vacuum and the resulting solid was extracted with chloroform. Removal of the solvent followed by recrystallisation from benzene–hexane gave **10** (0.36 g, 48%) as yellow needles [Found: C, 87.16; H, 4.63%; M^+ (EI) 386. $C_{28}H_{18}S$ requires C, 87.01; H, 4.69%; *M* 386]; mp 252–254 °C; δ (500 MHz; $CDCl_3$) 2.54 (2H, d, J_{gem} 12.80, 2 × CH), 3.75 (2H, d, J_{gem} 12.80, 2 × CH), 7.40 (2H, s, 1,16-H), 7.94 (2H, d, *J* 8.85, 3,14-H) and 8.02–8.13 (10H, m, ArH).

The sulfone of 2,15-(2-thiapropano)bridged hexahelicene (11)

To a stirred solution of **10** (0.2 g, 0.51 mmol) in benzene (30 ml) and acetic acid (15 ml) was added 30% hydrogen peroxide (0.24 g, 2.18 mmol). After the mixture was refluxed for 7 h, the resulting crystals were collected by filtration, washed with ether, and then dried (0.195 g, 90%); mp >300 °C; *m/z* (EI) 418 (M^+); ν_{max}(KBr)/cm^{-1} 1305, 1105 (SO_2).

Dihydro[7]circulene (13)

Following Staab's procedure,[21] the sulfone **11** (0.1 g, 0.24 mmol) was pyrolysed at 550 °C under vacuum (0.01 Torr) using a nitrogen bleed, and the pyrolysate was subjected to silica gel column chromatography. Elution with hexane–chloroform (4:1) gave **13** (35 mg, 42%), which when recrystallised from benzene–hexane gave: mp 225–227 °C [Found: C, 95.58; H, 4.42%; M^+ (EI) 352. $C_{28}H_{16}$ requires C, 95.42; H, 4.58%; *M* 352]; δ (500 MHz; $CDCl_3$) 2.62 (4H, s, 2 × CH_2), 7.43 (2H, d, *J* 7.93, 2,11-H), 7.50 (2H, d, *J* 8.55, 3,10-H), 7.54 (2H, d, *J* 7.93, 1,12-H), 7.60 (2H, d, *J* 8.24, 5,8-H), 7.61 (2H, d, *J* 8.55, 4,9-H) and 7.72 (2H, d, *J* 8.24, 6,7-H).

[7]Circulene (1)[4]

The hydrocarbon **13** (35 mg, 0.01 mmol) was mixed with 1-methylnaphthalene (0.2 ml) and 5% palladium on carbon (10 mg), and the mixture was heated at 240 °C in a salt bath for 1 h. The product was taken up in benzene, filtered free of catalyst. Removal of the solvent afforded a yellow solid which was chromatographed on neutral alumina. Elution of the column with hexane afforded 1-methylnaphthalene. Further elution with benzene–hexane (1:1) gave [7]circulene **1** (30 mg, 85%), which was recrystallised from benzene–hexane to give yellow plates [Found: C, 96.01; H, 3.98%; M^+ (EI) 350. $C_{28}H_{14}$ requires C, 95.97; H, 4.03%; *M* 350]; mp 295–296 °C; δ_H (500 MHz; $CDCl_3$) 7.45 (14H, s, 2 × ArH); δ_C (125 MHz; $CDCl_3$) 127.5, 132.1, 136.0.

References

1 H. W. Kroto, J. R. Heath, S. C. O'Breien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 162.
2 F. Diedrich, R. Ettl, Y. Rubin, R. L. Whitlen, R. Beck, M. Alvarez, S. Anz, D. Sensharma, F. Wudl, K. C. Khemani and A. Koch, *Science*, 1991, **252**, 548.
3 M. Nakazaki, K. Yamamoto and K. Naemura, *Top. Curr. Chem.*, 1984, **125**, 1.
4 K. Yamamoto, T. Harada, M. Nakazaki, Y. Kai, T. Nakao, M. Tanaka, S. Harada and N. Kasai, *J. Am. Chem. Soc.*, 1983, **105**, 7171; K. Yamamoto, T. Harada, Y. Okamoto, M. Nakazaki, Y. Kai, T. Nakao, M. Tanaka, S. Harada and N. Kasai, *J. Am. Chem. Soc.*, 1988, **110**, 3578.
5 J. S. Siegel and T. J. Seiders, *Chem. Ber.*, 1995, 313.
6 K. Yamamoto, Y. Saitho, D. Iwaki and T. Ooka, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1173; K. Yamamoto, *Pure Appl. Chem.*, 1993, **65**, 157.
7 S. Iijima, *Nature*, 1992, **56**, 354.
8 K. Yamamoto, H. Sonobe, H. Matsubara, M. Sato, S. Okamoto and K. Kitaura, *Angew. Chem., Int. Ed. Engl.*, 1996, **95**, 69.
9 S. Iijima, P. M. Ajayan and T. Ichihashi, *Phys. Rev. Lett.*, 1992, **69**, 3100; V. Ivanov, J. B. Nagy, P. Lambin, A. Cucas, X. B. Zhang, X. F. Zhang, D. Bernaerts, G. van Tendeloo, S. Amellinckx and J. van Landuyst, *Chem. Phys. Lett.*, 1994, **223**, 329.
10 P. H. Given, *J. Chem. Soc.*, 1958, 2684; B. S. Jensen and V. D. Parker, *J. Am. Chem. Soc.*, 1975, **97**, 5211; T. Kubota, K. Kano, B. Uno and T. Konse, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 3865.
11 M. G. Townsend and S. I. Weissman, *J. Chem. Phys.*, 1960, **32**, 309; J. R. Bolton and A. Carrington, *Mol. Phys.*, 1961, **4**, 271.
12 J. H. Dopper, D. Oudman and H. Wynberg, *J. Org. Chem.*, 1975, **40**, 3398.
13 K. Yamamoto, T. Ikeda, T. Kitsuki, Y. Okamoto, H. Chikamatsu and M. Nakazaki, *J. Chem. Soc., Perkin Trans. 1*, 1990, 271.
14 J. E. McMurry and K. L. Kess, *J. Org. Chem.*, 1977, **42**, 2655.
15 N. L. Allinger, Y. H. Yuh and J.-H. Lii, *J. Am. Chem. Soc.*, 1989, **111**, 8551; J. C. Tai, L. Yang and N. L. Allinger, *J. Am. Chem. Soc.*, 1993, **115**, 11 906.
16 M. Baumgarten, L. Gherghel, M. Wagner, A. Weitz, M. Rabinovitz, P.-C. Cheng and L. T. Scott, *J. Am. Chem. Soc.*, 1995, **117**, 6254.
17 H. Ohya-Nishiguchi, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 2064.
18 S. Nakajima, PhD Thesis, Kyoto University, 1987.
19 J. H. Borkent and W. H. Laarhoven, *Tetrahedron*, 1978, **34**, 2565.
20 H. J. Dauben and L. L. McCoy, *J. Am. Chem. Soc.*, 1959, **81**, 4863.
21 M. Haenel and H. A. Staab, *Chem. Ber.*, 1973, **106**, 2190.

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