

# Hexacyclo[8.7.0.0<sup>3,8</sup>.0<sup>5,15</sup>.0<sup>6,13</sup>.0<sup>12,16</sup>]heptadeca-1(10),5-diene-3,8-dicarboxylic anhydride, a tetrahydro[4]beltene with two $\sigma$ -conjugated double bonds

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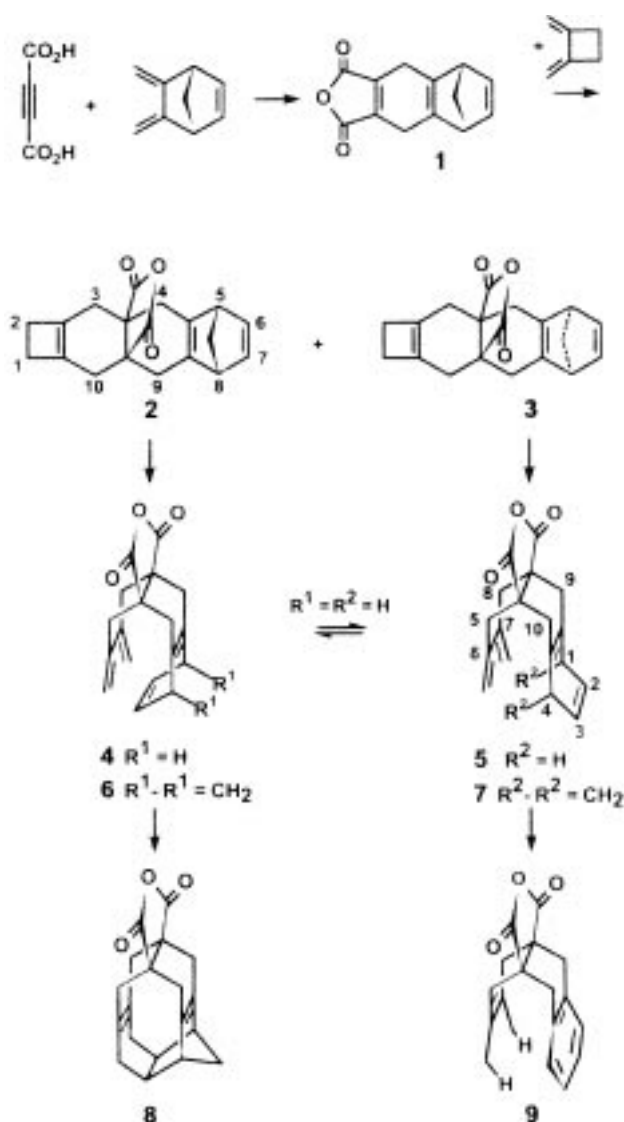
The tetrahydro[4]beltene **8** has been synthesized *via* a sequence of three Diels–Alder reactions. As shown in the crystal structure of **8**, the two double bonds in the cage diene are positioned face-to-face at a distance of 2.92 Å, which is smaller than the sum of their van der Waals radii. The resulting  $\sigma$ -conjugation in **8** is evident from the long wavelength UV adsorption and from the formation of a stable radical cation at low potential. Hydrogenation increases the strain of **8** such that only one double bond can be saturated under forcing conditions.

Molecular belts formed by ring closure of a ladder type array of  $n$  linear condensed cyclohexa-1,4-diene rings were visualized as interesting structures by Ermer<sup>1</sup> and Alder and Sessions<sup>2</sup> and classified by the latter as  $[n]$ beltene. Subsequently, several partially bridged and hydrogenated beltene with six to fourteen units have been prepared, with a view to investigating their host properties.<sup>3</sup> Our attention was attracted by a smaller member of this group, the tetrahydro[4]beltene (see core of anhydride **8**), because of its two double bonds that are rigidly fixed face-to-face at a close distance. A similar constraint is encountered by dienes in the pagodane framework<sup>4</sup> where  $\sigma$ -conjugation is observed.

A force field<sup>5</sup> calculation ascribes a total strain of 48 kcal mol<sup>-1</sup> to the tetrahydro[4]beltene, *i.e.* 3 kcal mol<sup>-1</sup> per C atom. In comparison with the strain of 1.4 kcal mol<sup>-1</sup> for each C atom of cyclohexene in the boat form, there does not seem to be much extra strain in this beltene, although the calculated distance of 2.81 Å between its double bonds is well below the sum of their van der Waals radii. Even taking this ambiguity into account it is surprising that the tetrahydro[4]beltene structure has only been proposed, to the best of our knowledge, for two intermediates in thermal reactions.<sup>6</sup>

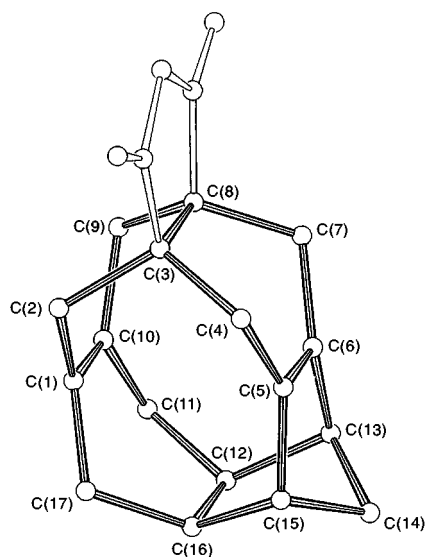
The method used for the synthesis of hydrobeltenes is a sequence of Diels–Alder reactions. In the intermolecular steps for building the ladder structure an activated dienophile is of advantage, whereas prior to the final ring closure a diene function has to be unmasked.<sup>7</sup> In our first approach according to this strategy we synthesized the 2,3-bis(methylene)decahydroanthracene-4a,9a-dicarboxylic anhydride **4**.<sup>8</sup> To our surprise, on heating to 150 °C it did not close to the beltene but aromatized *via* a (6 + 4)-dyotropic hydrogen transfer<sup>9</sup> to the isomer **9**. This competing reaction is due to the mobile equilibrium between its conformations **4** and **5**. In order to fix the desired conformation **4**, we decided to make it the configuration **6** by introducing a methano-bridge.

As in our first approach, the synthesis of **6** started with the cycloaddition of acetylene dicarboxylic acid to 5,6-bis(methylene)norbornene to give tetrahydro-5,8-methanonaphthalene-2,3-dicarboxylic anhydride **1**. In the second step 1,2-bis(methylene)cyclobutane was added to the activated double bond of **1**, resulting in a 1:1 mixture of the diastereomeric decahydromethanocyclobutananthracenedicarboxylic anhydrides **2** and **3**. Without separation, the diene function was unmasked in both diastereomers by thermal opening of the cyclobutene rings. At 150 °C the bis(methylene)decahydro-



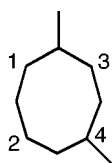
Scheme 1

methanoanthracene **6** resulting from **2** underwent the expected ring closure to the tetrahydro[4]beltene **8**, whereas the stereoisomer **7**, formed from **3**, did not react further.



**Fig. 1** Computer generated crystal structure diagram of tetrahydro[4]beltene **8**

Distance/Å	Angle between planes
C(1)–C(5) 2.923(3)	Planes 1 and 2 162.6°
C(6)–C(10) 2.922(3)	Planes 3 and 4 167.6°
	Planes 2 and 3 0.7°

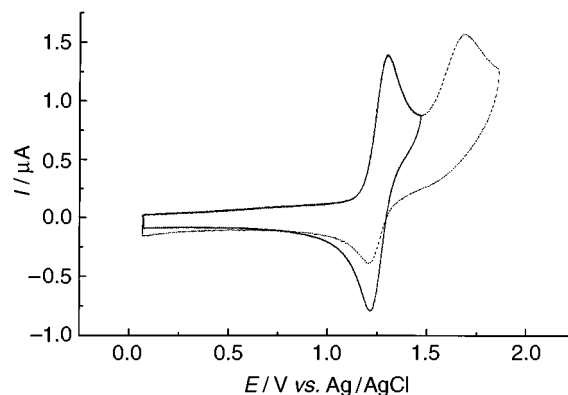


The interaction of the stacked double bonds in **8** is indicated in the UV spectrum by a broad shoulder at  $\lambda = 256$  nm ( $\epsilon = 1200$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) that overlaps the weak adsorption of the anhydride function.

The X-ray structure analysis of **8** gives the distance between the double bonds as  $d = 2.92$  Å. This is larger by 0.1 Å than the distance calculated by the MM2 force field but smaller than the sum of the van der Waals radii. This observed widening of the tetrahydro[4]beltene is achieved by out-of-plane deformations of both double bonds to angles of 162.6 and 167.6°.

A special feature of dienes stacked face-to-face in a very rigid  $\sigma$ -framework is that their radical cations, and sometimes their dications, are formed with low oxidation potentials and do not undergo rearrangement.<sup>10</sup> The cyclic voltammogram of **8** meets this expectation by displaying a reversible one-electron oxidation wave at 1.27 V and a further irreversible one at 1.69 V. A recent calculation<sup>11</sup> ascribes two configurations to the radical cation from two ethene units stacked face-to-face. One has a distance of 2.6 Å between the non-bonded centers, the other one is cyclobutanoid at a distance of 1.75 Å. As a model for the extended configuration we chose the transition state for the intramolecular (2 + 2)-cycloaddition of our tetrahydro[4]beltene and calculated<sup>5</sup> its strain energy at a bond length of 2.6 Å. It resulted in a strain release of 19 kcal mol<sup>-1</sup> in going to this transition state as the pyramidalization of the double bonds is lost. When the same calculation was performed for *syn*-sesquibicyclo[2.2.2]octene or for perdechloroisodrin a strain increase of 5 kcal mol<sup>-1</sup> was found for the transition state. Neither of these dienes form persistent radical cations on electrochemical oxidation. These calculations allow us to propose the cyclic delocalized structure **11** for the stable radical cation of **8**, while being aware that substantiation by an EPR spectral analysis is needed.

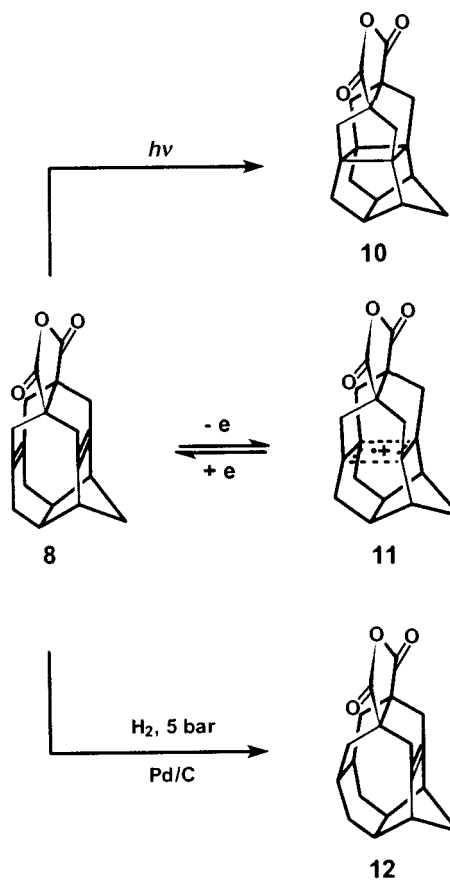
UV irradiation of the tetrahydro[4]beltene **8** in the presence of xanthone results in the (2 + 2)-cycloaddition of the double bonds under formation of the tris(demethano)pagodane **10**. Catalytic hydrogenation under ambient conditions does not



**Fig. 2** Cyclic voltammogram for the oxidation of tetrahydro[4]beltene **8** in methylene chloride–tetrabutylammonium hexafluorophosphate at 298 K; sweep rate = 0.5 V s<sup>-1</sup>;  $E_2^1 = 1.27$  V;  $E_{pa}^2 = 1.69$  V

affect **8** but under a pressure of 5 bar the more pyramidalized double bond is saturated and the hexahydro[4]beltene **12** is formed with the norbornene moiety intact. This reluctance to undergo hydrogenation exceeds that of normal tetrasubstituted double bonds. A force field calculation<sup>5</sup> reveals that both double bonds of **8** are hyperstable,<sup>12</sup> *i.e.* their hydrogenation is accompanied by a strain increase of 2.2 and 5.7 kcal mol<sup>-1</sup>, respectively. Under forcing conditions only the hydrogenation which leads to lower strain occurs. The UV spectrum of **12** no longer displays the absorption of the stacked double bonds and uncovers that of the anhydride function at  $\lambda = 281$  nm ( $\epsilon = 60$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>).

In summary, it is shown that a tetrahydro[4]beltene can be obtained by an intramolecular Diels–Alder reaction if measures are taken to avoid the aromatization of the ladder precursor *via* an intramolecular dyotropic hydrogen transfer. The X-ray structure analysis of **8** indicates that the MM2 force field



**Scheme 2**

underestimates the repulsion between the stacked double bonds in **8** by calculating too small a cavity and too little strain. The strained double bonds in the rigid tetrahydro[4]beltene **8** allow its electrochemical oxidation to a stable radical cation, for which structure **11** with a cyclic  $\sigma$ -conjugation is proposed.

## Experimental

NMR spectra were recorded on a Bruker AM 300 spectrometer at 300 MHz ( $^1\text{H}$ ) and 75.5 MHz ( $^{13}\text{C}$ ) in  $\text{CDCl}_3$ . Chemical shifts are in ppm relative to internal TMS. Signals were assigned by C–H COSY and NOE methods. Multiplicity and the position of protons are abbreviated as follows: AB (AB system centered at the position given);  $\Delta\nu$  (shift difference of the nuclei of the AB system in Hz);  $J$  (coupling constant between the nuclei of the AB system in Hz). UV spectra were obtained using a Perkin-Elmer Lambda 7 spectrometer, mass spectra were recorded on a Finnigan MAT INCOS 50 spectrometer. Reactions under high pressure were performed in a 10 ml steel autoclave (Nova Swiss, Neu-Isenburg) shielded by a heavy plastic case and heated with an electrical coil. The two stage pressure generator is a product of B. Dieckers GmbH, Krefeld. Melting points were determined in open capillaries with a Tottoli apparatus (Büchi, Flawil). Thin layer chromatography (TLC) was performed on Polygram SIL G/254 UV foils (Machery-Nagel, Düren), retention factors ( $R_f$ ) refer to TLC analyses. For flash chromatography Silitech 32-64 60A (ICN, Eschwege) was used in a column (50  $\times$  3 cm) filled to a third of its height.

### 5,8-Methano-1,4,5,8-tetrahydronaphthalene-2,3-dicarboxylic anhydride **1**

5,6-Bis(methylene)norbornene<sup>13</sup> (4.0 g, 33.8 mmol) and acetylenedicarboxylic acid (3.0 g, 26.3 mmol) in dioxane (10 ml) were refluxed for 5 h under argon. Acetyl chloride (3.0 g, 33.9 mmol) was added to the yellow solution and the heating continued for 0.5 h. The reaction mixture was evaporated to dryness and the residue was recrystallized from hexane to yield the yellow anhydride **1** (4.0 g, 71%), mp (hexane) 120 °C;  $\lambda_{\text{max}}$ (hexane)/nm 236 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  2600) and 315 (310);  $\delta_{\text{H}}$  2.06 (2 H, t), 3.00 (2 H, BB'), 3.36 (2 H, AA'), 3.43 (2 H, t), 6.79 (2 H, t);  $\delta_{\text{C}}$  24.00 (C-1, C-4), 52.00 (C-5, C-8), 72.24 (C-9), 142.48 (C-6, C-7), 143.75 (C-4a, C-8a), 144.8 (C-2, C-3), 164.38 (CO).

### 1,2-Bis(methylene)cyclobutane

*trans*-1,2-Dicyanocyclobutane was transformed into *trans*-1,2-bis(trimethylammoniomethyl)cyclobutane diiodide in two steps following known procedures.<sup>14</sup> Subsequently, the salt was converted into the base and thermolyzed as follows: a column with anion exchange resin Amberlite® IRA 420 (1 l, 1.2 meq ml<sup>-1</sup>) was loaded with hydroxide ion and percolated with a 0.6 M solution of the diiodide (27.3 g, 60 mmol). After washing the resin until neutral with water the eluates were concentrated at 15 Torr and 35 °C to a volume of 100 ml. The following thermolysis was conducted in an apparatus consisting of a two-necked 250 ml flask connected by ball joints to a series of three traps. The first was cooled with ice–water, the others with dry ice–propan-2-ol. After equipping the flask with a pressure equalizing dropping funnel (100 ml) filled with the aqueous base (50 ml, 30 mmol) a vacuum of 55 Torr was established and the flask was heated to 130 °C. Over a period of 0.5 h the base was added dropwise into the flask where it decomposed and distilled into the traps. The contents of the traps were extracted with pentane and the combined organic phases were washed with 1 M HCl, then with aq. sat. NaHCO<sub>3</sub> and dried (MgSO<sub>4</sub>). Fractionation of the pentane through a Vigreux column (15 cm  $\times$  1.5 cm) at 55 °C left a residue of 3 ml; the bis(methylene)cyclobutane content of this residue was determined by  $^1\text{H}$  NMR spectroscopy (1.32 g, 17 mmol, 55% yield).

### *syn*- and *anti*-1,2,3,3a,4,5,8,9,9a,10-Decahydro-5,8-methanocyclobut[*b*]anthracene-3a,9a-dicarboxylic anhydride **2** and **3**

PTFE tubing (10  $\times$  0.6 cm), sealed at one end, was charged with the anhydride **1** (1.1 g, 5.13 mmol), methylene chloride (1 ml) and a pentane solution of 1,2-bis(methylene)cyclobutane (0.42 g, 2.9 mmol). After sealing the other end, the tube was placed in an autoclave and heated at 80 °C for 20 h under a pressure of 7.7 kbar. The reaction mixture was washed from the tube with methylene chloride and evaporated. The oily residue was freed from excess starting anhydride **1** by sublimation (80 °C, 0.01 Torr) and flash chromatographed to yield a mixture of the product anhydrides **2** and **3** (0.20 g, 23%).  $R_f$  0.45 (toluene);  $\delta_{\text{H}}$  6.74 (2 H, t), 6.70 (2 H, t), 3.30 (2 H, q), 3.28 (2 H, q), 2.88 (2 H, d), 2.5 (18 H, m), 2.0 (8 H, m). The olefinic and the bridgehead protons of the norbornadiene subunits of **2** and **3** appear as separated signals at low field. Their equal intensities indicate the presence of a 1:1 mixture of diastereomers. In the  $^{13}\text{C}$  NMR spectrum all 10 signals are present as closely spaced pairs of equal intensities.  $\delta_{\text{C}}$  30.48 (41) (C-1, C-2), 31.09 (30.66) (C-4, C-9), 32.69 (62) (C-3, C-10), 48.11 (47.93) (C-3a, C-9a), 52.44 (33) (C-5, C-8), 71.33 (00) (C-11), 137.36 (05) (C-2a, C-10a), 142.55 (02) (C-6, C-7), 143.54 (46) (C-4a, C-8a), 174.73 (58) (CO);  $m/z$  294 ( $\text{M}^+$ , 42%), 266 (25, M – CO), 221 (M – CO, CO<sub>2</sub>, H), 141 (100).

### Thermolysis of the diastereomeric decahydromethanocyclobutanthracene dicarboxylic anhydrides **2** and **3**

The 1:1 mixture of **2** and **3** (400 mg, 1.36 mmol) in benzene (40 ml) was heated together with a few crystals of 4-*tert*-butylcatechol in a sealed ampoule to 120 °C for 120 h. The reaction mixture was evaporated to dryness and the residue flash chromatographed on silica gel with toluene as the eluent. The first fraction yielded *anti*-1,4,5,6,7,8,8a,9,10,10a-decahydro-1,4-methano-6,7-bis(methylene)anthracene-8a,10a-dicarboxylic anhydride **7** (60 mg, 15%), mp 135 °C;  $R_f$  0.38;  $\delta_{\text{H}}$  1.96 (2 H, t,  $J$  3, methano-CH<sub>2</sub>), 2.56 (4 H, AB,  $\Delta\nu$  116,  $J$  15.2), 2.58 (4 H, AB,  $\Delta\nu$  59,  $J$  14.5), 3.37 (2 H, q, 1-H, 4-H), 4.90 (2 H, s), 5.34 (2 H, s), 6.70 (2 H, t, 2-H, 3-H);  $\delta_{\text{C}}$  33.24 (C-9, C-10), 39.75 (C-5, C-8), 51.69 (C-8a, C-10a), 52.93 (C-1, C-4), 72.58 (C-11), 112.07 (=CH<sub>2</sub>), 139.46 (C-6, C-7), 143.29 (C-2, C-3), 147.77 (C-4a, C-9a), 175.82 (CO);  $m/z$  294 ( $\text{M}^+$ , 40%), 266 (24, M – CO), 221 (62, M – CO, CO<sub>2</sub>, H), 141 (100).

The second fraction of the flash chromatography contained the desired hexacyclo[8.7.0.0<sup>3,8</sup>.0<sup>5,15</sup>.0<sup>6,13</sup>.0<sup>12,16</sup>]heptadeca-1(10),5-diene-3,8-dicarboxylic anhydride **8** (60 mg, 15%), mp 221 °C;  $R_f$  0.26 (Found: C, 77.65; H, 6.24. Calc. for C<sub>19</sub>H<sub>18</sub>O<sub>3</sub>: C, 77.53; H, 6.16%);  $\lambda_{\text{max}}$ (dioxane)/nm 228 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  2100), 256sh (1200);  $\delta_{\text{H}}$  1.18 (2 H, AB,  $\Delta\nu$  25.4,  $J$  9, CH<sub>2</sub>-14), 2.22 (4 H, AB,  $\Delta\nu$  61.2,  $J$  15, CH<sub>2</sub>-11, CH<sub>2</sub>-17), 2.35 (2 H, s, 12-H, 16-H), 2.40 (4 H, AB,  $\Delta\nu$  33.9,  $J$  12, CH<sub>2</sub>-2, CH<sub>2</sub>-9), 2.53 (4 H, AB,  $\Delta\nu$  38.2,  $J$  13.5, CH<sub>2</sub>-4, CH<sub>2</sub>-7), 2.62 (2 H, m, 13-H, 15-H);  $\delta_{\text{C}}$  33.4 (C-11, C-17), 35.9 (C-4, C-7), 38.4 (C-12, C-16), 42.8 (C-2, C-9), 48.2 (C-14), 51.5 (C-13, C-15), 54.9 (C-3, C-8), 130.5 (C-1, C-10), 137.1 (C-5, C-6), 175.1 (CO);  $m/z$  294 ( $\text{M}^+$ , 22%), 266 (32, M – CO), 221 (100, M – CO, CO<sub>2</sub>, H), 129 (52), 104 (56), 91 (45).

### Crystal data

C<sub>19</sub>H<sub>18</sub>O<sub>3</sub>,  $M = 294.33$ . Monoclinic,  $a = 19.627(5)$ ,  $b = 7.360(1)$ ,  $c = 9.684(2)$  Å,  $\beta = 102.22(2)^\circ$ ,  $V = 1367.2$  Å<sup>3</sup> (by least-squares refinement on diffractometer angles for 25 automatically centered reflections,  $\lambda = 0.71069$  Å), space group  $P2_1/n$ ,  $Z = 4$ ,  $D_x = 1.430$  g cm<sup>-3</sup>. Crystal dimensions: 0.45  $\times$  0.35  $\times$  0.28 mm,  $\mu(\text{Mo-K}\alpha) = 0.96$  cm<sup>-1</sup>.

### Data collection

CAD4 diffractometer,  $\omega/2\theta$  mode with  $\omega$  scan width = 0.70 + 0.35 tan  $\theta$ ,  $\omega$  scan speed 2.2 deg min<sup>-1</sup>, graphite-monochromated Mo-K $\alpha$  radiation, 3313 reflections measured ( $2 < \theta < 27^\circ$ ), 2989 unique (merging  $R = 0.0189$ ), giving 2232 with

$I > 2\sigma(I)$ . Linear and approx. isotropic crystal decay, ca. 13% corrected during processing.

### Structure analysis and refinement

After data reduction, the structure was solved by direct methods using the MolEN<sup>15</sup> program package and refined against  $F_0^2$  for all unique reflections using SHELXL-93<sup>16</sup> (C, O atoms with anisotropic temperature factors and H atoms with isotropic ones). Final  $R_1$  and  $wR_2$  values for reflections  $I > 2\sigma(I)$  are  $R_1 = 0.062$  and  $wR_2 = 0.159$ . ( $R_1 = [\sum ||F_0| - |F_c|| / \sum |F_0|]$ ,  $wR_2 = \{[\sum w(F_0^2 - F_c^2)^2] / [\sum w(F_0^2)^2]\}^{1/2}$ ; weighting scheme  $w = 1/[\sigma^2(F_0^2) + (0.094 P)^2 + 0.737 P]$  where  $P = (F_0^2 + 2F_c^2)/3$ ). The calculations were performed at the Regional Computational Center at the University of Cologne. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/91.

### Irradiation of tetrahydro[4]beltene 8

**8** (10 mg, 0.03 mmol) in  $\text{CDCl}_3$  (0.5 ml) was irradiated together with a few crystals of xanthone in an NMR tube. The low pressure mercury burner Hanau NK25/7 was cooled in a quartz immersion well bearing the NMR tube attached to the outside. After 1.5 h the starting beltene could no longer be detected by NMR spectroscopy. The reaction mixture was separated by thick layer chromatography on silica gel with toluene as eluent yielding the photo product octacyclo[8.7.0.0<sup>1,5</sup>.0<sup>3,8</sup>.0<sup>5,15</sup>.0<sup>6,10</sup>.0<sup>6,13</sup>.0<sup>12,16</sup>]heptadecane-3,8-dicarboxylic anhydride **10** (4.5 mg, 45%), mp 223 °C;  $R_f$  0.26;  $\delta_{\text{H}}$  1.30 (4 H, AB,  $\Delta\nu$  126), 1.43 (2 H, AB,  $\Delta\nu$  87), 1.70 (4 H,  $\Delta\nu$  27), 1.77 (4 H, AB,  $\Delta\nu$  147), 2.21 (2 H, t, CH), 2.63 (2 H, t, CH);  $\delta_{\text{C}}$  27.67 (C-11, C-17), 30.74 (C-4, C-7), 33.20 (C-14), 34.55 (C-2, C-9), 45.28 (C-12, C-16), 48.91 (C-13, C-15), 49.86 (C-3, C-8), 56.77 (C-1, C-10), 57.61 (C-5, C-6), 172.92 (CO).

### Hydrogenation of tetrahydro[4]beltene 8

**8** (20 mg, 0.06 mmol) in ethyl acetate (5 ml) was placed in a heavy walled flask with a stem, fitting into a high pressure tubing. Pd/C (10 mg, 10%) was added and the flask was connected via a three-way valve to a hydrogen tank. After replacing the air in the system with hydrogen by two freeze-thaw cycles a hydrogen pressure of 5 bar was maintained over the magnetically stirred reaction mixture for 10 h. The reaction mixture was filtered through Celite<sup>®</sup> filter-aid and evaporated to dryness. Sublimation of the residue at 120 °C (0.01 Torr) yielded the hexahydro[4]beltene anhydride **12** (18 mg, 90%), mp 185 °C;  $\lambda_{\text{max}}/\text{nm}$  225 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  1400), 281 (60, anhydride);  $\delta_{\text{H}}$  1.26 (2 H, AB,  $\Delta\nu$  48.5,  $J$  8.1), 1.81 (4 H, AB,  $\Delta\nu$  103,  $J$  14.7), 1.90 (4 H, AX,  $\Delta\nu$  260,  $J$  15.6), 2.06 (4 H, br s, CH), 2.50 (4 H, AB,  $\Delta\nu$  39.2,  $J$  15), 2.68 (2 H, q, CH);  $\delta_{\text{C}}$  22.8 (CH), 29.6 (CH<sub>2</sub>), 34.6 (CH<sub>2</sub>), 34.9 (CH), 40.0 (CH<sub>2</sub>), 48.5 (CH<sub>2</sub>), 51.0 (CH), 138.4 (C=), 176.3 (CO).

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