

important spectral and other physical data for compounds **10**, **13**, **26**, and **29** are summarized in Table 1.

Table 1. Selected physical data of the compounds **10**, **13**, **26**, and **29**.

**10**:  $R_f=0.38$  (silica gel, petroleum ether:ether (95:5));  $[\alpha]_D^{25} = -8.1^\circ$  ( $c=1.17$ ,  $\text{CHCl}_3$ ); IR (film):  $\tilde{\nu}_{\text{max}}=3020$  (m), 2965 (vs), 2925 (vs), 2890 (s), 2860 (vs), 2180 (w), 1745 (s), 1425 (m), 1365 (m), 1255 (s), 1105 (s), 840 (vs), 775 (vs)  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta=6.55$  (dd,  $J(9,10)=15.4$  Hz,  $J(8,9)=10.8$  Hz, 1H, H-9), 6.16 (dd,  $J(7,8)=15.3$  Hz,  $J(8,9)=10.8$  Hz, 1H, H-8), 6.13 (dd,  $J(13,14)=15.7$  Hz,  $J(14,15)=5.3$  Hz, H-14), 5.80 (dt,  $J(13,14)=15.7$  Hz,  $J(13,15)=J(10,13)=1.9$  Hz, 1H, H-13), 5.72 (dd,  $J(7,8)=15.3$  Hz,  $J(6,7)=7.1$  Hz, 1H, H-7), 5.68 (dd,  $J(9,10)=15.6$  Hz,  $J(10,13)=2.1$  Hz, 1H, H-10), 5.46 (m, 1H, H-17), 5.32 (m, 1H, H-18), 4.19 (m, 1H, H-15), 3.97 (m, 1H, H-6), 3.66 (s, 3H,  $\text{COOCH}_3$ ), 3.56 (m, 1H, H-5), 2.28 (t,  $J(2,3)=7.4$  Hz, 2H, H-2), 2.24 (m, 2H, H-16), 2.02 (m, 2H, H-19), 1.68 (m, 2H, H-3), 1.50 (m, 2H, H-4), 0.95 (t,  $J(19,20)=7.5$  Hz, 3H, H-20), 0.89–0.86 (three singlets, total 27H, *SirBu*), 0.05–0.00 (six singlets, total 18H, *SiMe}\_2*); UV (qualitative, MeOH):  $\lambda_{\text{max}}=282, 296, 314$  nm

**13**:  $R_f=0.16$  (silica gel,  $\text{CH}_2\text{Cl}_2$ :MeOH (95:5));  $[\alpha]_D^{25} = +11.2^\circ$  ( $c=1.76$ ,  $\text{CHCl}_3$ ); IR ( $\text{CHCl}_3$ ):  $\tilde{\nu}_{\text{max}}=3610$  (m), 3020 (s), 2965 (m), 2935 (m), 2880 (m), 1735 (vs), 1440 (m), 1380 (m), 1220 (s), 1075 (m), 1000 (s), 980 (vs), 665 (m)  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta=6.58$  (m, 2H, H-10,13), 6.35 (dd,  $J(7,8)=15.0$  Hz,  $J(8,9)=10.8$  Hz, 1H, H-8), 6.21 (dd,  $J(9,10)=14.5$  Hz,  $J(8,9)=10.8$  Hz, 1H, H-9), 5.99 (m, 2H, H-11, 12), 5.76 (dd,  $J(13,14)=15.0$  Hz,  $J(14,15)=5.7$  Hz, 1H, H-14), 5.75 (dd,  $J(7,8)=15.0$  Hz,  $J(6,7)=7.8$  Hz, 1H, H-7), 5.56 (m, 1H, H-17), 5.33 (m, 1H, H-18), 4.24 (m, 1H, H-15), 4.11 (m, 1H, H-6), 3.66 (m, 1H, H-5), 3.63 (s, 3H,  $\text{COOCH}_3$ ), 2.32 (m, 5H, H-2,16, OH), 2.04 (m, 2H, H-19), 1.85 (br. s, 2H, OH), 1.81–1.66 (m, 2H, H-4), 1.40 (m, 2H, H-3), 0.94 (t,  $J(19,20)=7.5$  Hz, 3H, H-20); UV (qualitative, MeOH):  $\lambda_{\text{max}}=278, 288, 302, 316$  nm

**26**:  $R_f=0.29$  (silica gel,  $\text{CH}_2\text{Cl}_2$ :MeOH (95:5));  $[\alpha]_D^{25} = -89.9^\circ$  ( $c=0.525$ ,  $\text{CHCl}_3$ ); IR (film):  $\tilde{\nu}_{\text{max}}=3605$  (s), 3010 (s), 2980 (s), 2930 (vs), 2190 (w), 1735 (vs), 1440 (m), 1360 (m), 1255 (m), 1080 (m), 990 (s), 870 (m)  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta=7.63$  (m, 4H, aromatic), 7.40 (m, 6H, aromatic), 6.56 (dd,  $J(11,10)=15.4$  Hz,  $J(11,12)=10.9$  Hz, 1H, H-11), 6.34 (dd,  $J(12,13)=15.4$  Hz,  $J(12,11)=10.8$  Hz, 1H, H-12), 6.03 (dd,  $J(6,7)=15.7$  Hz,  $J(6,5)=5.95$  Hz, 1H, H-6), 5.82 (dd,  $J(12,13)=15.2$  Hz,  $J(13,14)=6.7$  Hz, 1H, H-13), 5.73 (d,  $J(10,11)=15.4$  Hz, 1H, H-10), 5.67 (d,  $J(7,6)=15.8$  Hz, 1H, H-7), 5.55 (m, 1H, H-17), 5.35 (m, 1H, H-18), 4.21 (m, 2H, H-5, 14), 5.70 (m, 1H, H-15), 3.59 (s, 3H,  $\text{COOCH}_3$ ), 2.26 (m, 2H, H-16), 2.11 (t,  $J(2,3)=7.2$  Hz, 2H, H-2), 2.03 (m, 2H, H-19), 1.54 (br. s, 2H, OH), 1.43 (m, 4H, H-3, 4), 1.04 (s, 9H, *SirBu*), 0.95 (t,  $J(20,19)=7.5$  Hz, 3H, H-20); UV (MeOH):  $\lambda_{\text{max}}=283, 297, 314$  nm

**29**:  $R_f=0.22$  (silica gel,  $\text{CH}_2\text{Cl}_2$ :MeOH (95:5));  $[\alpha]_D^{25} = +14^\circ$  ( $c=0.570$ , MeOH); IR (film):  $\tilde{\nu}_{\text{max}}=3610$  (s), 3020 (m), 2970 (m), 2940 (m), 2880 (m), 1730 (vs), 1445 (m), 1380 (m), 1250 (m), 1075 (m), 1000 (s), 980 (s), 870 (m)  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta=6.68$  (m, 2H, H-10, 12), 6.36 (dd,  $J(7,6)=14.9$  Hz,  $J(7,8)=10.5$  Hz, 1H, H-7), 6.23 (m, 2H, H-8, 9), 5.99 (m, 1H, H-11), 5.78 (dd,  $J(6,7)=15.2$  Hz,  $J(6,5)=6.9$  Hz, 1H, H-6), 5.72 (dd,  $J(13,12)=15.1$  Hz,  $J(13,14)=6.6$  Hz, 1H, H-13), 5.55 (m, 1H, H-17), 5.33 (m, 1H, H-18), 4.20 (m, 2H, H-5, 14), 3.69 (m, 1H, H-15), 3.64 (s, 3H,  $\text{COOCH}_3$ ), 2.33 (t,  $J(2,3)=7.2$  Hz, 2H, H-2), 2.24 (m, 2H, H-16), 2.15 (m, 2H, H-19), 2.02 (m, 2H, H-4), 1.73–1.61 (m, 2H, H-3), 1.57 (br. s, 3H, OH), 0.93 (t,  $J(20,19)=7.5$  Hz, 3H, H-20); UV (MeOH):  $\lambda_{\text{max}}=315, 301, 288$  nm

The described chemistry renders these two new metabolites of eicosapentaenoic acid (EPA), LXA<sub>5</sub> and LXB<sub>5</sub>, readily available and in optically active form. Comparisons of the synthetic compounds with naturally derived LXA<sub>5</sub> and LXB<sub>5</sub> and biological investigations with these compounds are currently in progress.<sup>[12]</sup>

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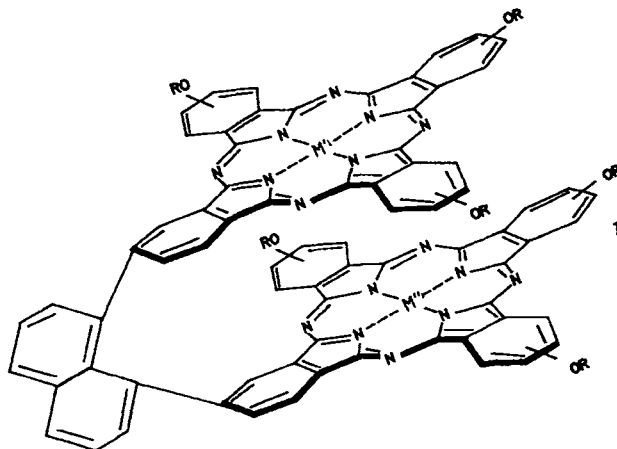
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[12] New compounds exhibited satisfactory spectral and analytical/exact mass data. Yields refer to spectroscopically and chromatographically homogeneous materials.

## 1,8-Naphthalene-Linked Cofacial Dimeric Phthalocyanines\*\*

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Binuclear phthalocyanines covalently linked by five,<sup>[1,2]</sup> four,<sup>[3]</sup> two,<sup>[3]</sup> one,<sup>[4]</sup> and “-1”<sup>[5]</sup> atom bridges have been recently described. We now report new cofacial binuclear phthalocyanines **1a–d** linked by a triatomic bridge on a rigid naphthalene framework. These compounds complement 1,8-anthracene bridged porphines,<sup>[6,7]</sup> and provide entry to a new class of pillared phthalocyanines. They



- a: R =  $\text{CH}_2\text{C}(\text{CH}_3)_3$ , M' = M'' =  $\text{H}_2$   
b: R =  $\text{CH}_2\text{C}(\text{CH}_3)_3$ , M' = M'' =  $\text{Co}^{\text{II}}$   
c: R =  $\text{CH}_2\text{C}(\text{CH}_3)_3$ , M' = M'' =  $\text{Cu}^{\text{II}}$   
d: R =  $\text{CH}_2\text{C}(\text{CH}_3)_3$ , M' = M'' =  $\text{Zn}^{\text{II}}$   
e: R =  $\text{CH}_2\text{C}(\text{CH}_3)_3$ , M' = M'' =  $\text{Co}^{\text{I}}$   
f: R =  $\text{CH}_2\text{C}(\text{CH}_3)_3$ , M' = M'' =  $\text{Co}^{\text{I}}$

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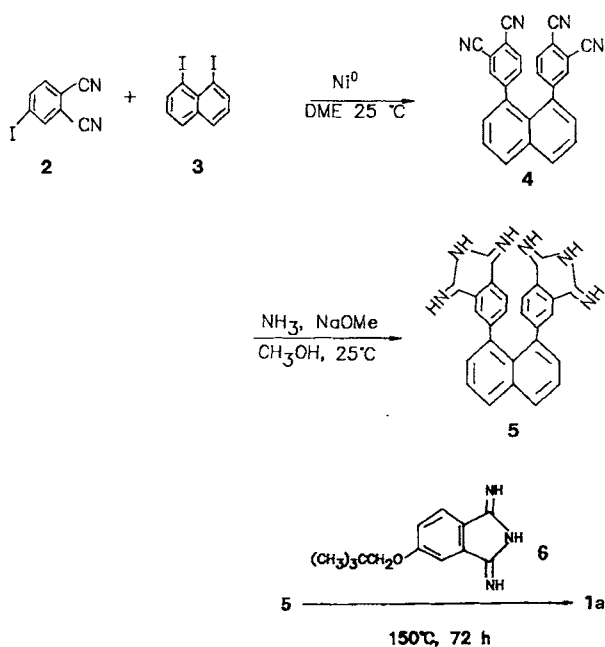
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should prove of value in the photo- or electroactivation of small molecules, such as dioxygen, carbon or sulfur dioxide.

Treatment of 4-iodophthalonitrile **2** (4.0 g, 16 mmol) with 1,8-diiodonaphthalene **3** (2.0 g, 5.3 mmol) in a mixed coupling reaction, in the presence of elementary nickel powder under conditions described for homocoupling reactions<sup>[8,9]</sup> led to 1,8-bis(3,4-dicyanophenyl)naphthalene **4** (310 mg, 15.5% yield) as a mixture of *syn* and *anti* isomers due to restricted rotation about the 1,8-positions of the naphthalene nucleus. Conversion of **4** (380 mg, 1 mmol) into its dihydroisoindole **5** and a mixed condensation of **5** with the dihydroisoindole **6** prepared from 4-neopentylphthalonitrile (6.0 g, 28 mmol) gave, following standard reaction conditions and chromatography,<sup>[11-5]</sup> the desired 1,8-bis-2'-(9',16',23'-trineopentylphthalocyaninyl)naphthalene **1a** in 15.5% yield. The dicobalt, dicopper, and dizinc derivatives (**1b-d**) of **1a** were prepared by refluxing **1a** with CoCl<sub>2</sub>, Cu(OAc)<sub>2</sub> and Zn(OAc)<sub>2</sub>, respectively, as previously described.<sup>[11-5]</sup>



**1a-d** and **4** have been fully characterized.<sup>[10]</sup> The fast atom bombardment<sup>[11]</sup> (FAB) mass spectra **1a-d** were most informative, exhibiting parent ions as the base peak. Furthermore, no evidence of partially or half-metalated derivatives of **1b-d** were detected in their mass spectra. The <sup>1</sup>H-NMR spectrum of **1a** exhibited the upfield shifted NH protons which were absent in the spectrum of the zinc derivative **1d**.

Electrochemical and spectroelectrochemical results show that the rigid geometry of the naphthalene bridge induces important changes in the cofacial dicobalt derivative **1b**, compared with previously studied mononuclear and "clamshell" binuclear cobalt phthalocyanines.<sup>[1-4,12]</sup> The halves of the molecule of **1b** do not oxidize and reduce at the same potential, resulting in clear splitting of the redox couples. Cyclic and differential pulse voltammetry of **1b** in *o*-dichlorobenzene (0.2 M *n*Bu<sub>4</sub>NClO<sub>4</sub>) revealed a series of three oxidation and four reduction waves with halfwave potentials of +0.53, +0.14, 0.00, -0.90, -1.29, -1.68,

and -2.08 V vs Fc<sup>⊖</sup>/Fc (Fc = ferrocene).<sup>[13,14]</sup> Comparison with the cyclic voltammogram of the mononuclear parent compound (2,9,16,23-tetrapentylphthalocyaninato)cobalt CoTNPc ( $E_{1/2} = +0.59, +0.03, -0.91, \text{ and } -2.07$  V in *o*-dichlorobenzene<sup>[12]</sup>) indicates splitting of the first oxidation (L<sup>⊖</sup>/L), and first reduction (Co<sup>II</sup>/Co<sup>I</sup>) couples by 140 and 390 mV, respectively. This is the first example of clearly observed splitting of the redox waves in a ring bridged binuclear metal-phthalocyanine and indicates a high degree of coupling between the halves of the molecule. Mixed valence L<sup>⊖</sup>/L and Co<sup>II</sup>/Co<sup>I</sup> species are thus potentially available.

In contrast to **1b**, the splitting of the corresponding redox couple in the case of a so-called (-1) binuclear derivative (two phthalocyanine rings sharing a common benzene ring)<sup>[5]</sup> was less than 100 mV (shoulder) in the mixed valence Co<sup>II</sup>-Co<sup>I</sup> species. The reduction couples at -0.90 and -1.29 V were investigated by controlled potential electrolysis in an optically transparent thin layer electrode (OTTLE) cell utilizing a gold minigrad or platinum mesh working electrode. Stepwise reduction across each of the couples in turn gives the spectroscopic changes shown in Figure 1. Reduction over the first wave gives a green solution, with isosbestic points occurring at 322, 348, 545, 642, 664, and 760 nm (Fig. 1a). The spectrum is unlike any seen previously for a reduced cobalt-phthalocyanine, having a Q band at 650 nm. It does however exhibit a new absorption band in the region of 450-470 nm associated with metal-to-ligand charge transfer (MLCT) [Co<sup>I</sup>Pc[d(xz,yz)] → π\*(1b<sub>10</sub>)Pc] of a Co<sup>I</sup>Pc species,<sup>[12,15,16]</sup> as well as a blue shift and increase in intensity of the Soret band.

The second reduction at -1.29 V (Fig. 1b) gives a yellow solution, with isosbestic points at 332, 395, 566, 678, and 758 nm. The final spectrum is very similar to that of the mononuclear Co<sup>I</sup>TNPc species,<sup>[12]</sup> indicating that both cobalt atoms have been reduced to Co<sup>I</sup>. The spectra are fully reversible by stepwise oxidation to the initial species.

Nernst plots of the spectroelectrochemical data over each of the reductions give slopes approaching 59 mV, showing that each step involves a one-electron transfer. Thus, the product of the reduction at -0.90 V must be a mixed valence species **1e**, of mainly [Co<sup>II</sup>-Co<sup>I</sup>] character. The intensity of the MLCT band is only 35% of that of the fully reduced Co<sup>I</sup>-Co<sup>I</sup> species **1f**, so that some delocalization of the added electron over the phthalocyanine ring system may be occurring. The presence of the well resolved Q band at 650 nm, rather than ca. 710 nm, may also indicate extensive delocalization throughout the molecule. A weak absorption occurs in **1e**, in the region of 800-900 nm (Fig. 1a), absent from the spectra of both **1b** and **1f** and which may be an intervalence band. The Q band region of the spectrum of **1e** mixed valence species is very different from that observed for the -1-bridged mixed valence Co<sup>II</sup>-Co<sup>I</sup> compound,<sup>[5]</sup> which has a split Q band at 700 and 760 nm.

Neither of the species **1b** or **1f** exhibit ESR absorption in *o*-dichlorobenzene. Species **1e**, however, exhibits typical low spin (dz<sup>2</sup>)<sup>1</sup>Co<sup>II</sup> ESR absorption when 2-methylimidazole is added to the solution. The spectrum ( $g = 2.25$ ) is very similar to that observed for the mixed valence Co<sup>II</sup>/Co<sup>III</sup> species of a cofacial dicobaltporphyrin<sup>[17]</sup> in the presence of *N*-methylimidazole.

In comparing these findings with those for the corresponding cofacial binuclear dicobalt porphyrins<sup>[17-20]</sup> note that the latter also show splitting of the Co<sup>II</sup>/Co<sup>I</sup> couple by up to 290 mV; however, unlike the phthalocyanines, no

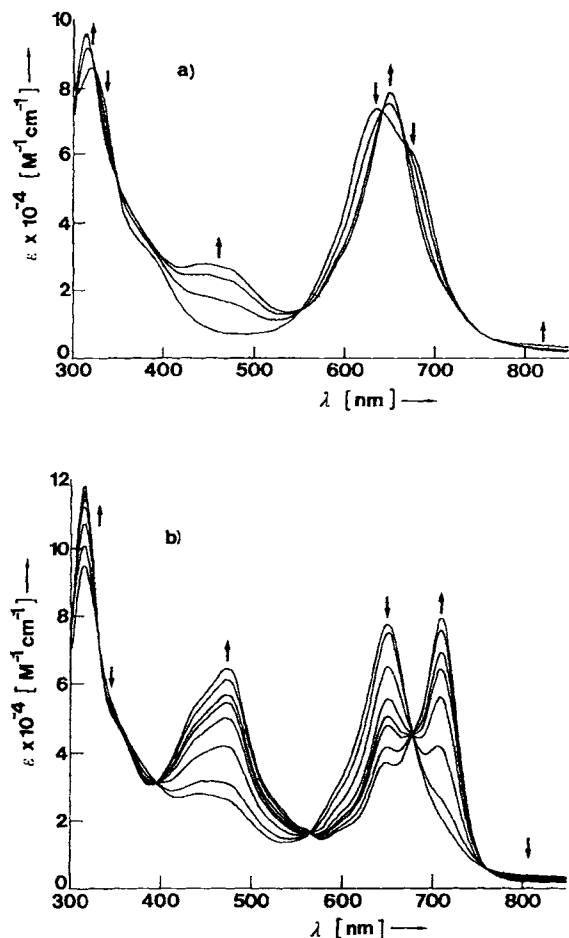


Fig. 1. Development of the electronic spectra with time (in *o*-dichlorobenzene), showing the formation of (a) the mixed valence  $\text{Co}^{\text{II}}\text{-Co}^{\text{I}}$  compound **1e**, and (b) the doubly reduced  $\text{Co}^{\text{I}}\text{-Co}^{\text{I}}$  species **1f** obtained by reduction of **1b** at potentials between  $-0.9$  and  $-1.2$  V, and  $-1.3$  and  $-1.6$  V, respectively, (vs  $\text{Fc}^{\oplus}/\text{Fc}$ ).  $[\mathbf{1b}] = 1 \times 10^{-4}$  M,  $[\text{TBAF}] = 0.3$  M.

distinct changes in the electronic spectra were observed for the mixed valence species.<sup>[19]</sup>

Electrocatalytic reduction of oxygen was examined at electrodes (glassy carbon and ordinary pyrolytic graphite) covered with adsorbed **1b**. Oxygen reduction occurred at  $-0.34$  V (vs SCE, cyclic voltammogram, pH 1 to pH 13), and the limiting current corresponding to two-electron reduction of oxygen to hydrogen peroxide was observed in rotating disc experiments. Logarithmic analysis of the wave yielded a Tafel plot of  $-120$  mV/decade, which corresponds to a charge-transfer coefficient of 0.5 and a one-electron transfer rate-determining step.

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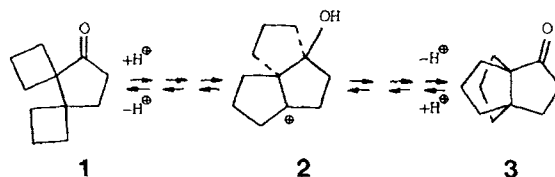
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- [10] The new compounds **4** and **1a-d** were completely characterized by the following physical and spectroscopic data. **4**: m.p.  $285^{\circ}\text{C}$ ; MS (EI):  $m/z$  380 (100%,  $M^{\oplus}$ , 253 ( $M^{\oplus} - \text{C}_6\text{H}_5\text{N}_2$ ));  $^1\text{H-NMR}$  (300 MHz,  $[\text{D}_6]\text{DMSO}$ ); complex absorptions from  $\delta = 7.3\text{-}8.5$  analyzed as a 1:1 mixture of *syn* and *anti* isomers; IR (KBr):  $\nu = 3060, 2240$  (CN), 1600, 1490, 835, 780  $\text{cm}^{-1}$ ; UV/VIS ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}} = 238$  ( $\epsilon = 21\,900$ ), 265 sh (17 000), 340 (11 000) nm; correct elemental analysis (C, H, N). — **1a**: MS (FAB):  $m/z$  1670 (100%,  $M^{\oplus}$ , molecular ion cluster);  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta = -6.9, -6.1, -5.5$  (br. weak NH), 1.0-1.6 (br., 36H,  $\text{CH}_3$ ), 3.3-3.8 (br., 8H,  $\text{OCH}_2$ ), 7.0-8.5 (br., aromatic); IR (KBr):  $\nu = 3300$  (NH), 1615, 1245, 1100, 1020 (NH), 750  $\text{cm}^{-1}$ ; UV/VIS (*o*-dichlorobenzene):  $\lambda_{\text{max}} = 340$  ( $\epsilon = 79\,500$ ), 648 (77 600) nm; correct elemental analysis (C, H, N). — **1b**: MS (FAB):  $m/z$  1784 (100%,  $M^{\oplus} + 1$ , molecular ion cluster); IR (KBr):  $\nu = 2950, 1610, 1100, 740$   $\text{cm}^{-1}$ ; UV/VIS (*o*-dichlorobenzene):  $\lambda_{\text{max}} = 306$  ( $\epsilon = 141\,000$ ), 638 (123 000), 674 (102 000) nm. — **1c**: MS (FAB):  $m/z$  1793.6 (100%,  $M^{\oplus} + 1$ , molecular ion cluster); IR (KBr):  $\nu = 2950, 1610, 1100, 740$   $\text{cm}^{-1}$ ; UV/VIS (*o*-dichlorobenzene):  $\lambda_{\text{max}} = 300$  ( $\epsilon = 63\,100$ ), 338 (102 000), 640 (95 500), 686 (93 300) nm. — **1d**: MS (FAB):  $m/z$  1797.6 (100%,  $M^{\oplus} + 1$ , molecular ion cluster);  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.0\text{-}1.6$  (br., 36H,  $\text{CH}_3$ ), 3.3-4.3 (br., 8H,  $\text{OCH}_2$ ), 7.5-8.5 (br., aromatic); IR (KBr):  $\nu = 2950, 1610, 1100, 740$   $\text{cm}^{-1}$ ; UV/VIS (*o*-dichlorobenzene):  $\lambda_{\text{max}} = 298$  ( $\epsilon = 72\,400$ ), 340 (112 000), 640 (107 000), 686 (93 300) nm.
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## Pentacyclo[11.3.0.0<sup>1,5</sup>.0<sup>5,9</sup>.0<sup>9,13</sup>]hexadecane ([4.5]Coronane)\*\*

By Lutz Fitjer\* and Ulrike Quabeck

Dedicated to Professor Ulrich Schöllkopf on the occasion of his 60th birthday

As has recently been reported,<sup>[1]</sup> reaction of the dispiroketone **1** with anhydrous *p*-toluenesulfonic acid in benzene leads via a fourfold 1,2-shift to formation of the propellanone **3**. The rearrangement proceeds via the  $\beta$ -hydroxy carbenium ion **2** and is quantitative.



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