

Synthesis of *syn*-3a(12c),9a(9b)-dihomoperylene-3,10-dione, (*E*)-*syn*-2,2'-bi(7*H*-1,6-methano[10]annulenyldiene)-7,7'-dione and of its rearrangement product, *trans*-12a,12b-dihydro-3a(12c),9a(9b)-dihomoperylene-3,10-dione

Aderson de Farias Dias,^a Thomas Helwig,^b Johann Lex,^b Joseph Miller*^a and Hans Schmickler^b

^a Universidade Federal da Paraíba/Laboratório de Tecnologia Farmacêutica, Campus I, Caixa Postal 5009, 58051-970 João Pessoa PB, Brazil

^b Institut für Organische Chemie der Universität Köln, Greinstraße 4, 50939 Köln, Germany

Received (in Cambridge, UK) 6th March 2000, Accepted 4th April 2000

Published on the Web 13th June 2000

The main objective of the present work was to evaluate the synthesis of 1,6-methano[10]annulene derivatives of perylene and perylene-3,10-dione. The starting material for the synthetic sequence was 2,7-dibromo-1,6-methano[10]annulene (**I**), which was converted by methoxy- and ethoxy-debromination S_NAr-type reactions to 2-bromo-7-methoxy- and -7-ethoxy-1,6-methano[10]annulenes (**II**). The reactions were much more facile than those of the apparently similar halogenonaphthalenes. Compounds **II** were reductively coupled, using a Ni(0) complex, to give isomeric mixtures of *rac*- and *meso*-7,7'-dimethoxy- and -diethoxy-2,2'-bi(1,6-methano[10]annulenylyls) (**III**A and **III**B). Oxidative coupling of a mixture of compounds **III**A and **III**B with thallium(III) trifluoroacetate in acetonitrile gave (*E*)-*syn*-2,2'-bi(7*H*-1,6-methano[10]annulenyldiene)-7,7'-dione **IV** as the main reaction product, accompanied by a small amount of *syn*-3a(12c),9a(9b)-dihomoperylene-3,10-dione, **VI**. Subsequent experiments showed that the *meso*-form (**III**B) produced the *syn*-dihomoperylenedione (**VI**); while the *rac*-form (**III**A) gave (*E*)-*syn*-2,2'-bi(7*H*-1,6-methano[10]annulenyldiene)-7,7'-dione **IV**. The low yield of the dihomoperylenedione suggests decomposition reactions occur, with various by-products remaining undetected. A solution of the annulene-quinone (**IV**) in carbon tetrachloride, when refluxed and illuminated rearranged to give *trans*-12a,12b-dihydro-3a(12c),9a(9b)-dihomoperylene-3,10-dione (**V**).

Introduction

The present work describes the synthesis and structural determination of the title compounds and corresponding intermediates. They have not previously been reported in the literature, where there are but few references to bi(annulenylyl) derivatives.¹⁻⁴

Discussion

The synthetic sequence used to obtain the title compounds is shown in Scheme 1, in which RO = MeO and EtO. The starting material was 2,7-dibromo-1,6-methano[10]annulene (**I**). Methoxide and ethoxide ions were used in parallel reactions.

The first step in the synthetic sequence is an S_NAr type alkoxy-debromination reaction forming 2-bromo-7-alkoxy-1,6-methano[10]annulenes cleanly in good yields. It is noteworthy that the reactions proceed under very mild conditions. This is in marked contrast with alkoxy-dehalogenation reactions of simple halogenobenzenes and halogenonaphthalenes. For example, the methoxy-dechlorination (MeO⁻-MeOH) of chlorobenzene proceeds slowly even close to the critical temperature of the solvent (232 °C).⁵ The admixture in our reactions of a dipolar aprotic solvent can contribute only modestly to the difference. It is relevant that (a) halogenonaphthalenes are a little more reactive than corresponding halogenobenzenes, (b) a second halogen has only a weak activating effect and (c) the leaving group mobilities of chloride, bromide and

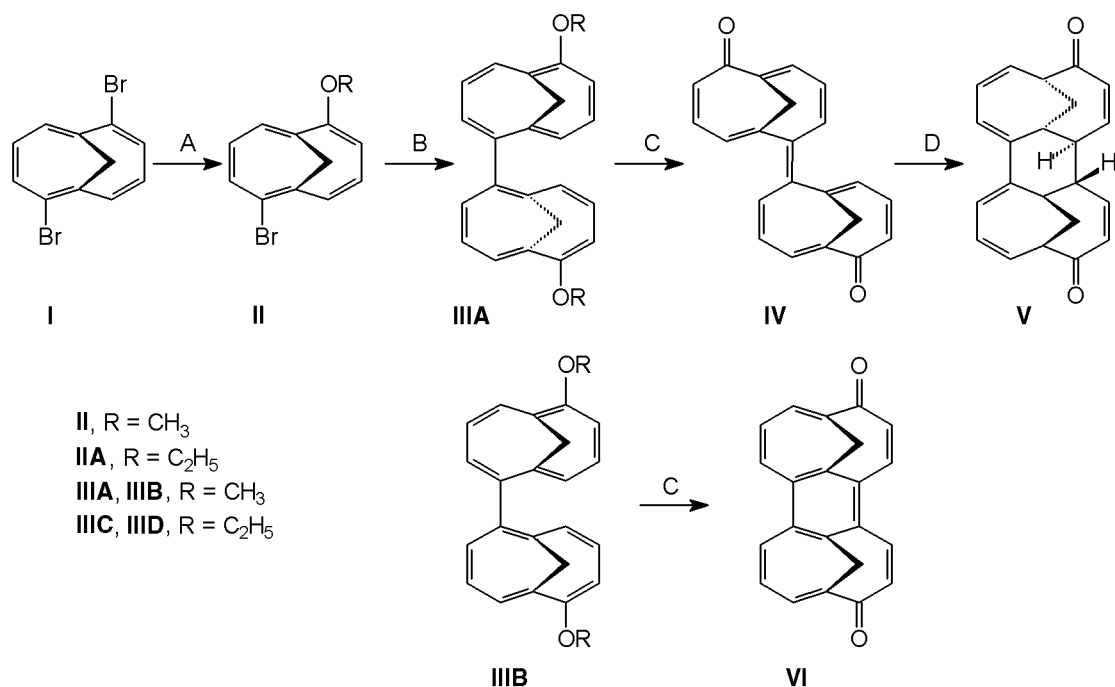
iodide are similar.⁶ We can therefore confidently ascribe the much greater facility of the reactions to the markedly greater stabilization of the intermediate (σ) complexes and their flanking transition states, resulting from full delocalization of π-electrons and negative charge over the 10-membered ring. This is supported by the formation of monoalkoxy bromo products cleanly in good yield. This is a consequence of the transmission of the deactivating effect of the entering alkoxy group *via* the π-system of the 10-membered ring from the 2- to the 7-position.

In the second step the bromoalkoxyannulenes were reductively coupled using tetrakis(triphenylphosphine)nickel(0). This reagent was prepared *in situ* (see Experimental section). This reaction led to a mixture of *rac*- and *meso*-7,7'-dialkoxy-2,2'-bi(1,6-methano[10]annulenylyls) (**III**A and **III**B).

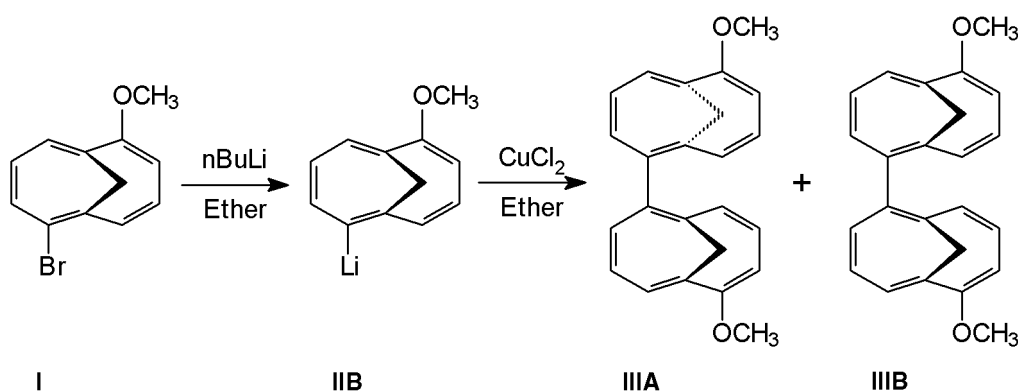
While the reaction with the bromoethoxy compound had the advantage of better solubility we could not separate the *rac*- and *meso*-forms. However this was possible with the bromomethoxy compound, as confirmed by X-ray diffraction (Fig. 1a,b), so that it was used for the next stage of the synthetic sequence (Scheme 1).

The *rac*-form of 7,7'-dimethoxy-2,2'-bi(1,6-methano[10]annulenylyl) (**III**A) was oxidized with thallium(III) trifluoroacetate (TTFA) in anhydrous acetonitrile forming (*E*)-*syn*-2,2'-bi(7*H*-1,6-methano[10]annulenyldiene)-7,7'-dione (**IV**) in 60% yield.

When dissolved in carbon tetrachloride and refluxed in daylight, it underwent a rearrangement, accompanied by a colour change from violet to yellow. It gave a 50% isolated yield



Scheme 1 Reagents and conditions: (A) RO⁻ in HMPT (2:1 v/v) at 40 °C; (B) Ni(0)(PPh₃)₄ prepared *in situ*, in THF; (C) Tl(III)(CF₃CO₂)₃ in anhydrous CH₃CN; (D) *hv* and Δ in CCl₄. The separate reaction of *rac*- and *meso*-forms (IIIA, IIIB) was possible only with OR = OMe.



Scheme 2 Preparation of *rac*- and *meso*-forms (IIIA and IIIB) by oxidative coupling of the lithium compound IIb.

of *trans*-12a,12b-dihydro-3a(12c),9a(9b)-dihomoperylene-3,10-dione (V), as confirmed by X-ray diffraction (Fig. 1d) and spectral data.

We also carried out oxidative, instead of reductive, coupling of the bromoalkoxy annulenes: oxidative coupling has been used by Rapson and by Wittig and their co-workers^{7,8} for some other syntheses.

In our oxidative reactions (Scheme 2) we obtained a 30% yield of a mixture of *rac*- and *meso*-7,7'-dimethoxy-2,2'-bi-(1,6-methano[10]annulenyloxy)s. This compared with 52% yield by the reductive coupling method.

When *meso*-7,7'-dimethoxy-2,2'-bi(1,6-methano[10]annulenyloxy) was oxidized by thallium(III) trifluoroacetate we obtained a 32% yield of *syn*-3a(12c),9a(9b)-dihomoperylene-3,10-dione (VI), confirmed by X-ray (Fig. 1c) and spectral data.

We also carried out the oxidation with vanadium(v) oxytrifluoride in anhydrous CH₂Cl₂. The same product was obtained but in only 18% yield.

In the temperature-dependent ¹H NMR spectrum of the racemic bi(annulenyloxy)s we observe at ambient temperature a singlet for the methyl group at 3.88 ppm, as well as two doublets at 7.67 ppm for H-5 and at -0.52 ppm for H-11b.

At 100 °C the protons H-3 and H-10 exhibit only broad absorptions. H-5 appears as a doublet with $\delta = 7.76$; H-4

absorbs as a triplet centred at 7.14 ppm. Signals at $\delta = 6.83$ and 6.51 can be assigned to H-9 and H-8. H-3 is responsible for the very broad signal at $\delta = 7.39$ –7.48. The protons of the methylene bridge absorb as an AB-system at $\delta = 0.07$ and -0.43 (H-11a, H-11b). The methyl protons produce a singlet at $\delta = 3.88$.

At -40 °C the two conformational isomers (R1 and R2) exist side by side. The assignment of the ¹H NMR signals is shown in Table 1. The protons H-3 in R1 and H-9 and H-10 in R2 are shifted to a higher field due to the shielding effect of the other annulenyloxy group. On the other hand, the protons H-3 of R2 and H-9/H-10 of R1 are shifted downfield due to the deshielding effect of the other annulenyloxy moiety. The difference in the chemical shifts for H-3 amounts to 1.18 ppm, for H-9, 0.41 ppm and for H-10, 1.52 ppm. R1 is probably the rotational isomer (IIIAa) or (IIIAc). NMR analysis does not serve to distinguish between them.

The twisting of the arene moieties in solution is greater than in the crystal, so that the torsion angle of approximately 36° determined by crystallography indicates the existence of (IIIAa).

The stereoisomers (IIIAb) and (IIIAc) are considered to be R2. As with R1 no decision can be made, on the basis of the ¹H NMR spectrum, in favour of (IIIAb) or (IIIAc). At 22 °C

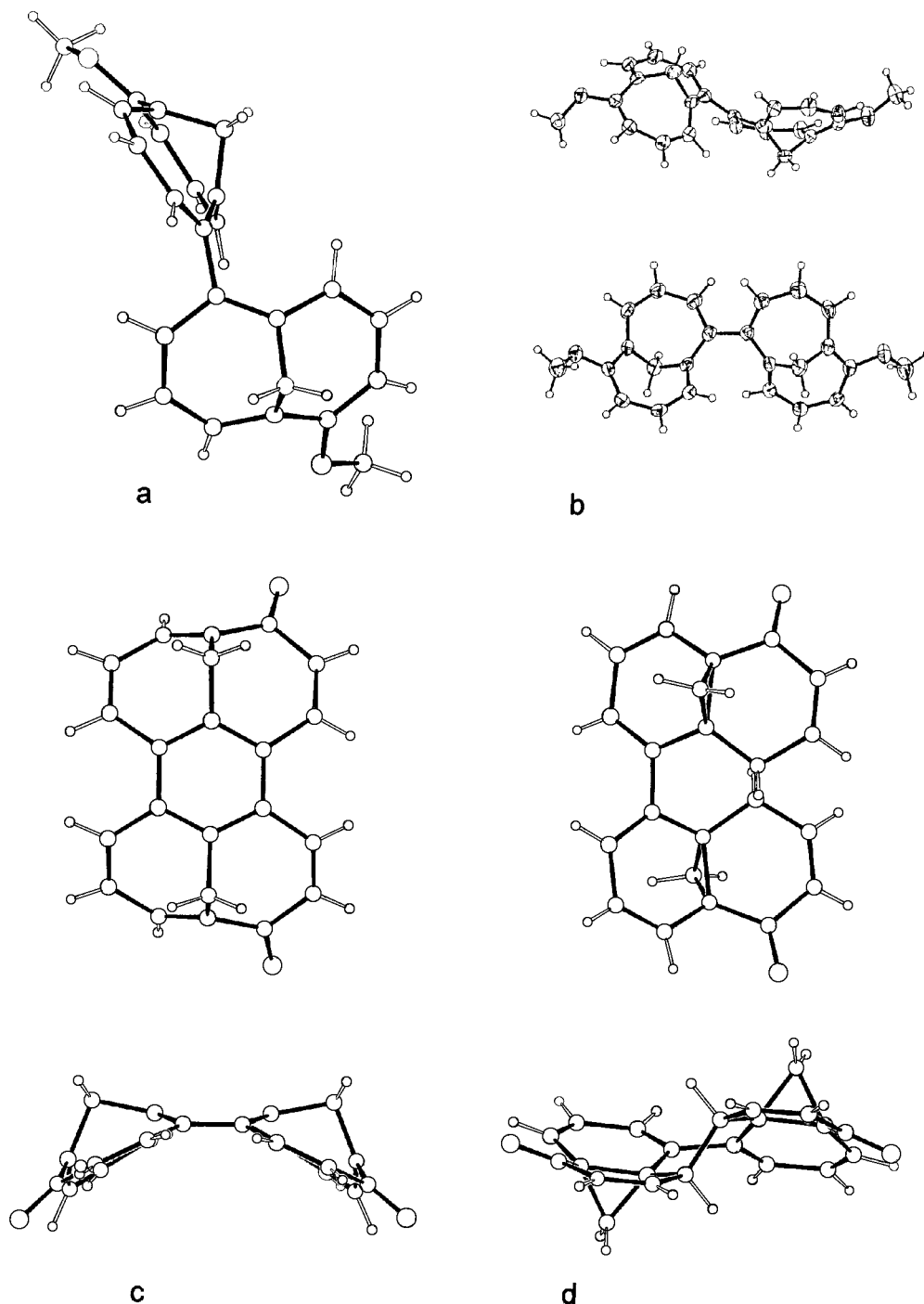


Fig. 1 X-Ray structures of (a) *rac*-7,7'-dimethoxy-2,2'-bi(1,6-methano[10]annuleny) (**IIIa**), (b) *meso*-7,7'-dimethoxy-2,2'-bi(1,6-methano[10]annuleny) (**IIIb**), (c) *syn*-3a(12c),9a(9b)-dihomoperylene-3,10-dione (**VI**), and (d) *trans*-12a,12b-dihydro-3a(12c),9a(9b)-dihomoperylene-3,10-dione (**V**).

the signals of H-11b coalesce, equivalent to a rotational barrier of 15 kcal mol^{-1} .

The ^1H NMR spectrum of the *meso*-form (**IIIb**) shows a broad absorption for H-10 at ambient temperature due to the lower activation enthalpy for the racemization. At 40°C the rapid interchange of the stereoisomers causes the signals of the protons of (**IIIb**) to exchange quickly. H-5 generates a doublet $\delta = 7.59$, H-3 absorbs at 7.14 ppm as a doublet. The protons H-8, H-9 and H-10 absorb at 6.46, 6.78 and 6.54 ppm. The methyl group appears at 3.89 ppm and the bridge-protons form an AB system with $\delta = 0.04$ and -0.52 (H-11a, H-11b). At -100°C the interchange of the stereoisomers of (**IIIb**) is very slow.

In the ^1H NMR spectrum, one can recognize 18 different

signals, corresponding to the existence of the pairs of enantiomers (**IIIb**a)/(**IIIb**b) and (**IIIb**c)/(**IIIb**d), respectively (Fig. 2). The resonance absorptions of the isomers are given in Table 1.

Despite our inability to separate the *rac*- and *meso*-forms of 7,7'-diethoxy-2,2'-bi(1,6-methano[10]annuleny)s we decided to repeat the second part of the synthetic sequence with the mixture. This proceeded well and we obtained the same product (*vide supra*).

Torsional isomerism involving planar chiral structures has been studied extensively.⁹ In addition to torsional isomerism, the compounds described in this paper are characterized by the so-called "annulene chirality".¹⁰ As a consequence, the coupling of **II** produces a diastereomeric mixture of *rac*-**IIIa** and *meso*-**IIIb**.

Table 1 ^1H NMR chemical shifts (ppm) and coupling constants (Hz) of **IIIA** and **IIIB** (300 MHz, THF-d_8 at $T = -100$ to -50 °C and $\text{THF-d}_8\text{-C}_2\text{D}_2\text{Cl}_4$ at $T = 50\text{--}100$ °C)

	H-3/H-3'	H-4/H-4'	H-5/H-5'	H-8/H-8'	H-9/H-9'	H-10/H-10'	O-CH ₃ /O-CH ₃ '	H-11a/H-11a'	H-11b/H-11b'
IIIB ^a	7.14	7.05	7.59	6.46	6.78	6.54	3.89	0.04	-0.52
		$J_{3,4} = 9.9; J_{4,5} = 8.0$			$J_{8,9} = 9.8; J_{9,10} = 9.5$			$J_{AB} = -9.7$	
M1	6.64/	6.99/	7.57/	6.64/	7.17/	7.70/	3.98/	0.11/	-0.62
M2 ^b	7.75	7.35	7.62	6.36	6.53	5.34	3.77	-0.05	-0.75
		$J_{3,4} = 9.9; J_{4,5} = 8.0$			$J_{8,9} = 9.8; J_{9,10} = 9.5$			$J_{AB} = -9.7$	
IIIA ^c	7.39–7.48	7.14	7.67	6.51	6.83	7.11–7.17	3.88	0.07	-0.43
		$J_{4,5} = 8.4$			$J_{8,9} = 9.8$			$J_{AB} = -9.7$	
R1 ^d	6.93	7.15	7.71	6.66	7.12	8.00	3.86	0.11	-0.61
		$J_{3,4} = 9.8; J_{4,5} = 8.2$			$J_{8,9} = 9.7; J_{9,10} = 9.3$			$J_{AB} = -9.7$	
R2 ^d	8.11	7.34	7.73	6.55	6.71	6.48	3.78	-0.02	-0.61
		$J_{3,4} = 9.98; J_{4,5} = 8.2$			$J_{8,9} = 9.4; J_{9,10} = 9.8$			$J_{AB} = -9.7$	

^a $T = 40$ °C. ^b $T = -100$ °C. ^c $T = 100$ °C. ^d $T = -40$ °C; M1, M2 = rotational isomers of **IIIB**; R1, R2 = rotational isomers of **IIIA**.

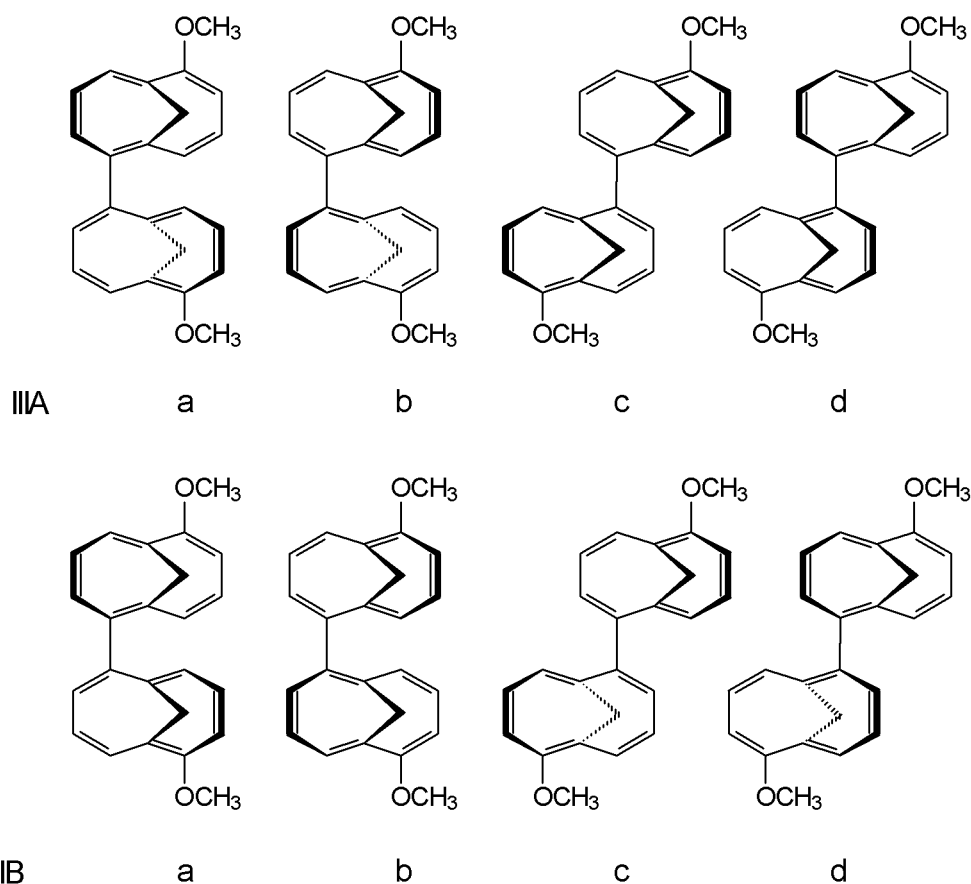


Fig. 2 *syn*- and *anti*-stereoisomers of *rac*-7,7'-dimethoxy-2,2'-bi(1,6-methano[10]annuleny) and *meso*-7,7'-dimethoxy-2,2'-bi(1,6-methano[10]annuleny) (**IIIA/IIIB**).

The rotational isomers **IIIBa** and **b**, **c** and **d** are pairs of enantiomers and in achiral solvents should exhibit identical NMR spectra, whereas **IIIAa** and **c**, and **b** and **d** are diastereoisomers and so may have different NMR spectra.

With a torsion angle of 0°, **IIIB** belongs to symmetry group C_s , while a rotation of 180° changes it to the C_i point group. As a consequence in both cases the protons of the corresponding positions in the annuleny moieties (that is, H-3 and H-3', H-4 and H-4', etc.) are magnetically equivalent and absorb at the same frequency in the NMR spectrum.

At any other torsion angle the symmetry decreases to C_1 and the structure becomes asymmetric. Consequently the protons at the corresponding positions are diastereotopic with differences in chemical shifts. With any torsion angle between 0° and 360° **IIIA** has a C_2 -axis. The protons at corresponding

positions are always equivalent. The atropisomers of the *rac*-form **IIIA** are diastereoisomers and should have different spectra.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker AM 300 or a VARIAN EM 390 spectrometer. Mass spectra were recorded using Finnigan 3000 Datensystem 6100, VARIAN MAT 212, Datensystem 6100 SS 200 and VARIAN MAT CH7A Datensystem SS 200 spectrometers. UV spectra were recorded on a Beckmann MUI spectrometer. IR spectra were recorded on a Perkin-Elmer 283 spectrometer. X-Ray diffraction studies were performed on an Enraf-Nonius CAD-4 diffractometer.

X-Ray analysis†

The configurations of *rac*- and *meso*-compounds (**IIIA** and **IIIB**), as well as of *syn*-3a(12c),9a(9b)-dihomoperylene-3,10-dione (**VI**) and the rearrangement product *trans*-12a,12b-dihydro-3a(12c),9a(9b)-dihomoperylene-3,10-dione (**V**) were established on the basis of their X-ray crystallographic analysis. The crystal structures were solved by direct methods and refined by full matrix least squares with anisotropic thermal parameters for C and O and isotropic thermal parameters for H.

1. meso-7,7'-Dimethoxy-2,2'-bi(1,6-methano[10]annuleny)l (IIIB). C₂₄H₂₂O₂, *M* 342.45, *d* (calcd.) = 1.268 g cm⁻³, μ = 0.73 cm⁻¹, number of independent reflections (*I* > 3 σ (*I*) 4039), space group *P* $\bar{1}$, *a* = 12.625(3), *b* = 12.775(3), *c* = 12.798(3) Å, *a* = 86.67(2), β = 79.32(2), γ = 62.29(2)°, *V* = 1794.7 Å³.

The compound crystallizes in the triclinic form with 4 molecules per unit cell in two independent isomeric conformations with different torsion angles (C-1-C-2-C-2'-C-1'). For *meso*-**IIIBa** the angle is 69.5° and for **IIIBb** it is 55.9°. The final *R* value was 0.039.

2. rac-7,7'-Dimethoxy-2,2'-bi(1,6-methano[10]annuleny)l (IIIA). The title compound crystallizes in the monoclinic form in the space group *P*₂₁/*c* with 4 molecules per unit cell, in a conformation similar to *rac*-structure **IIIAa**. The torsion angle of 36° is smaller than that of the *meso*-compound and the C-2-C-2' bond length is 0.01 Å shorter than in *meso*-**IIIB**. C₂₄H₂₂O₂, *M* 342.45, *d* (calcd.) = 1.284 g cm⁻³, *a* = 8.847, *b* = 12.812, *c* = 15.629 Å, β = 91.72°, torsion angles C-1-C-2-C-2'-C-1' 39.9°, C-1-C-2-C-2'-C-3' -143.2°, C-3-C-2-C-2'-C-3' 31.2°, C-3-C-2-C-2'-C-1' -145.7°. The final *R* value was 0.040. The number of independent reflections with *I* > 2 σ (*I*) was 1971.

Evidence for the predicted non-equivalence of protons H-3 and H-3', H-4 and H-4' of the *meso*-compound can be deduced from its X-ray crystal structure.

The smaller torsion angle of 26.7° for the *rac*-form than the average values for *meso*-forms **IIIBa** and **b** suggests that the conjugative interaction through the C-2-C-2' bond is more significant in *rac*- than in *meso*-compounds.

3. syn-3a(12c),9a(9b)-Dihomoperylene-3,10-dione (VI). Compound **VI** crystallizes in the monoclinic form in the space group *P*₂₁/*c* with 4 molecules per unit cell. The central 6-membered ring lies in the conformation of a flat tub and its benzenoid character is evident in the C-6a-C-6b bond length of 1.476 Å in *syn*-dihomoperylene¹¹ and of 1.429 Å in **VI**. C₂₂H₁₄O₂, *M* 310.36, *d* (calcd.) = 1.383 g cm⁻³, μ = 0.817 cm⁻¹, *a* = 15.389(4), *b* = 11.183(3), *c* = 8.838(2) Å, *a* = 90, β = 101.61(2), γ = 90°, *V* = 1489.9 Å³. The final *R* value was 0.048 and the number of independent reflections with *I* > 2 σ (*I*) was 3092.

4. trans-12a,12b-Dihydro-3a(12c),9a(9b)-dihomoperylene-3,10-dione (V). The *anti*-configuration of the methylene bridges, the norcaradiene structure and the *trans* cyclization at C-12a-C-12b are important stereochemical features shown in Fig. 1d. The average of the bond lengths C-3a-C-12c and C-9a-C-9b is equal to 1.586 Å and is coherent with the cyclopropane rings of the norcaradiene form. C₂₂H₁₆O₂, *M* 312.37, *a* = 9.226(2), *b* = 11.375(3), *c* = 15.582(4) Å, *a* = 109.90(2), β = 98.37(2), γ = 90.04(2)°, *V* = 1519 Å³, *Z* = 4, triclinic, space group *P* $\bar{1}$, *d* (calcd.) = 1.366 g cm⁻³, μ = 0.81 cm⁻¹, number of reflections *I* > 3 σ (*I*): 3665, *R* = 0.056.

2-Bromo-7-methoxy-1,6-methano[10]annulene

2,7-Dibromo-1,6-methano[10]annulene (15 g, 50 mmol) was dissolved in a mixture of anhydrous HMPT (20 ml) and meth-

anol (100 ml) and treated with methanolic sodium methoxide solution (prepared by reaction of metallic sodium (12 g, 0.52 mol) in 120 ml of anhydrous methanol). The reaction mixture was stirred at 30 °C for two days and was then quenched with a saturated solution of NiCl₂. Stirring was continued for a further half-hour and the reaction mixture was then extracted with diethyl ether (5 × 250 ml). The ether extract was washed with water (2 × 100 ml) and dried over anhydrous sodium sulfate. The yellow viscous residue was chromatographed over Al₂O₃ (Brockmann) and eluted with hexane. The first fraction consisted of unchanged starting material (3.1 g, 10%). Elution with hexane-dichloromethane (8:2 v/v) furnished the desired compound 2-bromo-7-methoxy-1,6-methano[10]annulene **II** as a yellow oil (19.4 g, 77.5%). Elution with hexane-dichloromethane (1:1) then yielded 2,7-dimethoxy-1,6-methano[10]annulene (2.4 g, 12%) as a crystalline compound with melting point 66–66.5 °C.

Elemental analysis: C₁₂H₁₁BrO [251.11], calculated: C = 57.39, H = 4.41. Found: C = 57.7, H = 4.4%. δ_{H} (90 MHz; CCl₄-TMS) -0.4, 0.16 (AB system, 2 H, methylene bridge), -0.46 (d, H-11a, *J*_{a,b} = 10 Hz), 0.1 (d, H-11b, *J*_{b,a} = 10.5 Hz), 3.94 (s, OCH₃), 6.5–7.76 (m, 6 H, peripheral protons, two superimposed ABC systems); δ_{H} (300 MHz; CD₃CN) 7.54 (*J*_{5,11b} = 0.9 Hz, H-5), 7.31 (*J*_{3,4} = 10.2 Hz, H-3), 7.25 (*J*_{10,11a} = 1.2 Hz, H-10), 7.00 (*J*_{9,10} = 9.8 Hz, H-9), 6.99 (*J*_{4,5} = 8.1 Hz, H-4), 6.48 (*J*_{8,9} = 9.8 Hz, H-8), 3.75 (OCH₃), 0.75 (H-11a), 0.05 (H-11b) (*J*_{11a,1b} = -10.5 Hz, *gem*); *m/z* (70 eV) 250, 252 (8.6, 8.9%) [M]⁺, 171 (36%) [M - Br]⁺, 140 (9%) [M - Br - OCH₃]⁺, 128 (100%) [M - Br - OCH₃ - CH₂]⁺. ν (KBr)/cm⁻¹ 3047, 3005 and 2952 (C-H stretching), 1576 (C=C stretching), 1251 (C-O stretching); λ (dichloromethane)/nm 265 (ϵ = 40289), 310 (5212), 330 (6622), 415 (1238).

Similarly 2,7-dibromo-1,6-methano[10]annulene (30 g, 0.1 mol) was dissolved in HMPT (200 ml) and treated at ambient temperature with an ethanolic sodium ethoxide solution (prepared by reacting metallic sodium (2.3 g, 0.1 mol) in 100 ml anhydrous ethanol). The deep brown mixture was stirred during 5 hours at 40 °C and then overnight at ambient temperature. The work-up was effected according to the procedure for the reaction with sodium methoxide. Very little unchanged starting material was isolated in the first fraction. The next main fraction was evaporated and the oily residue was distilled under vacuum and consisted of the desired product 2-bromo-7-methoxy-1,6-methano[10]annulene, **IIA**, in the form of a yellow oil (23.7 g, 90% yield). The third fraction (2.3 g, 6%) consisted of a highly viscous oil, which was identified as 2,7-diethoxy-1,6-methano[10]annulene. It solidified on standing at -25 °C.

rac- and *meso*-7,7'-dimethoxy-2,2'-bis(1,6-methano[10]annuleny)ls

(a) **Oxidative coupling of 2-bromo-7-methoxy-1,6-methano[10]annulenes (II) with CuCl₂.** Compound **IIA** (8.5 g, 33 mmol) was dissolved in anhydrous diethyl ether (100 ml) and treated at -50 °C with an ethereal solution of *n*-butyllithium (33 ml, 33 mmol). The mixture was stirred and transferred *via* cannula to a precooled suspension of copper(II) chloride (4.6 g, 34 mmol) in anhydrous diethyl ether (300 ml). The temperature of the reaction mixture was maintained at -78 °C while the reaction was stirred for 6 hours. It was then quenched with cold water (5 ml) and decanted over folded filter paper. The solid inorganic residue was washed with diethyl ether (2 × 50 ml) and the combined ethereal solutions were washed with water (4 × 50 ml) and dried over anhydrous sodium sulfate. After evaporation of the solvent the solid residue was chromatographed over Al₂O₃ (Woelm, activity III, *l* = 80 cm, *id* = 3 cm). Elution with hexane-dichloromethane (8:2) yielded a bright yellow fraction from which 1.73 g (30%) of a crystalline yellow substance (mixture of both *rac*- and *meso*-7,7'-dimethoxy-2,2'-bi(1,6-methano[10]annuleny)ls) was obtained.

† CCDC reference number 207/423.

(b) **Reductive coupling of 2-bromo-7-methoxy-1,6-methano[10]annulene (II) with $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]\text{-Zn-Et}_4\text{NI-THF}$.** Dichlorobis(triphenylphosphine)nickel(II) (13 g, 20 mmol), activated zinc (2.612 g, 40 mmol) and tetraethylammonium iodide (5.138 g, 20 mmol) were mixed together and dried by heating in an oil bath at 100 °C for four hours under vacuum (0.1 Torr). Anhydrous THF (100 ml) was added at ambient temperature and the suspension was sonicated to accelerate complex formation. Then a solution of **II** (5 g, 19 mmol) in anhydrous THF (50 ml) was added *via* cannula to the nickel complex suspension and the resultant reaction mixture was further sonicated for 6 hours. The mixture was passed through a sintered filter and the sediment was washed with ethyl ether (5 × 20 ml). The solution was dried over sodium sulfate, the solvent was evaporated and the residue was chromatographed over Al_2O_3 (Woelm, activity III, $l = 50$ cm, $id = 2.5$ cm). Elution with hexane gave triphenylphosphine and with hexane-dichloromethane (8:2) furnished the mixture of isomers (2.99 g, 52%) in an approximate ratio of 1:1.

Pure *rac*-**IIIa** (mp 195–196 °C) was obtained by recrystallization from anhydrous ethanol while the *meso*-form (mp 122–123 °C) was purified by column chromatography over silica gel of the **IIIb** enriched mother liquor from **IIIa**. Elution with pentane-*tert*-butyl methyl ether (97:3) produced firstly the *meso*-compound and further elution produced the *rac*-form (**IIIa**).

rac- and *meso*-7,7'-Diethoxy-2,2'-bi(1,6-methano[10]annuleny)s (**IIIc, D**)

The isomeric mixture of compounds **IIIc** and **IIId** was obtained through reductive coupling of 2-bromo-7-ethoxy-1,6-methano[10]annulene with the nickel(0) complex according to the procedure described for obtaining the *rac*- and *meso*-7,7'-dimethoxy-2,2'-bi(1,6-methano[10]annuleny)s (**IIIa, B**). The isomeric mixture was purified by column chromatography on Al_2O_3 (Woelm, activity III, $l = 40$ cm, diam. = 4.0 cm) with hexane as the mobile phase. The title compounds were obtained as a hard yellow wax of melting point 55–57 °C, yield 1.92 g (69%), which could not be separated into the pure isomers through conventional methods.

meso-Form. Found: 342.16. Calc. for $\text{C}_{24}\text{H}_{22}\text{O}_2$: 342.43; $\lambda(\text{CH}_2\text{Cl}_2)/\text{nm}$ 252.5 ($\epsilon/\text{dm}^3 \text{cm}^{-1} \text{mol}^{-1} = 61613$), 277 ($\epsilon = 4648$), 370 ($\epsilon = 16002$); $\nu(\text{C}=\text{C})/\text{cm}^{-1}$ 3047 and 3010 (=C–H stretching), 1532 and 1500 (C=C stretching), 1252 (C–O stretching); m/z (70 eV) 342 (<1%) $[\text{M}]^+$, 327 (<1%) $[\text{M} - \text{CH}_3]^+$, 311 (<1%) $[\text{M} - \text{OCH}_3]^+$, 296 (<1%) $[\text{M} - \text{OCH}_3 - \text{CH}_3]^+$, 280 (<1%) $[\text{M} - 2\text{OCH}_3]^+$, 266 (5%) $[\text{M} - 2\text{OCH}_3 - \text{CH}_2]^+$, 252 (8%) $[\text{M} - 2\text{OCH}_3 - 2\text{CH}_2]^+$, 239 (17%), 113 (26%), 45 (100%); δ_{H} (300 MHz; THF- d_6) 7.14 (H-3/H-3'), 7.05 (H-4/H-4'), 7.59 (H-5/H-5'), 6.46 (H-8/H-8'), 6.78 (H-9/H-9'), 6.54 (H-10/H-10'), 3.89 (O–CH₃/O–CH₃), 0.04 (H-11a/H-11a'), –0.52 (H-11b/H-11b') ($J_{3,4} = 9.9$; $J_{4,5} = 8.0$; $J_{8,9} = 9.8$; $J_{9,10} = 9.5$; $J_{\text{AB}} = 9.75$ Hz).

rac-Form. (Found: C, 84.1; H, 6.6. Calc. for $\text{C}_{24}\text{H}_{22}\text{O}_2$: C, 84.18; H, 6.48%); $\lambda(\text{CH}_2\text{Cl}_2)/\text{nm}$ 371 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1} = 16100$), 275 ($\epsilon = 42300$), 253 ($\epsilon = 56800$); $\nu(\text{KBr})/\text{cm}^{-1}$ 3051 and 3010 (=C–H stretching), 2967, 2945 and 2839 (–C–H stretching), 1532 and 1502 (C=C stretching), 1253 (C–O stretching); m/z (70 eV) 342 (<1%) $[\text{M}]^+$, 327 (<1%) $[\text{M} - \text{CH}_3]^+$, 280 (<1%) $[\text{M} - 2\text{OCH}_3]^+$, 252 (20%) $[\text{M} - 2\text{OCH}_3 - 2\text{CH}_2]^+$, 239 (34%), 113 (100%); δ_{H} (300 MHz; THF- d_6) (**IIIb**) 7.67 (H-5), 7.39–7.48 (H-3), 7.14 (H-4), 7.11–7.17 (H-10), 6.83 (H-9), 6.51 (H-8), 3.88 (O–CH₃), 0.07 (H-11a), –0.43 (H-11b) ($J_{4,5} = 8.4$; $J_{8,9} = 9.8$; $J_{\text{AB}} = 9.7$).

In the *meso*-form the proton H-5 appears as a doublet at 7.65 ppm while H-3 and H-4 absorb as a multiplet at δ 7.05–7.25. H-9 absorbs as a triplet at δ 6.81 and H-8 appears at δ 6.47 as a doublet. At δ 6.5–6.6 H-10 absorbs as a broad doublet and H-11a, H-11b appear at 0.03 and –0.52 ppm, respectively.

Because of hindrance to rotation, the *rac*-form exhibits a rather broad absorption pattern for the peripheral protons. H-3 and H-10 from two of the four rotational isomers appear at δ 8.05–8.15 and 7.9–8.0, respectively. H-11a and H-11b absorb at δ 0.08 and –0.2.

(Found: 370.1935. Calc. for $\text{C}_{26}\text{H}_{26}\text{O}_2$: 370.1933); δ_{H} (300 MHz; CDCl_3) of the mixture of *rac*- and *meso*-7,7'-diethoxy-2,2'-bi(1,6-methano[10]annuleny)s (**IIIc, D**): 8.15–8.05 (H-3 of R1*), 8.00–7.90 (H-10 of R2*), 7.76 (d, H-5, *rac*-form), 7.65 (d, H-5, *meso*-form), 7.25–7.05 (m, H-3, H-4, *meso*-form), 6.81 (t, H-9, *meso*-form), 6.60–6.50 (br d, H-10, *meso*-form), 6.47 (d, H-8, *meso*-form), 4.40–3.80 (m, methylene protons), 1.40 (m, methyl protons), 0.08–0.20 (H-11a, *rac*-form), 0.03 (dd, H-11a, *meso*-form), –0.47 (d, H-11b, *rac*-form); $\lambda(\text{CH}_2\text{Cl}_2)/\text{nm}$ 384 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1} = 11800$), 275 ($\epsilon = 52000$), 260 ($\epsilon = 62400$); $\nu(\text{film})/\text{cm}^{-1}$ 3044 (=C–H stretching), 2984 and 2949 (–C–H stretching), 1568, 1531 and 1499 (C=C stretching), 1252 (C–O stretching); m/z (70 eV) 370 (7%) $[\text{M}]^+$, 356 (1%) $[\text{M} - \text{CH}_2]^+$, 355 (1%) $[\text{M} - \text{CH}_3]^+$, 341 (5%) $[\text{M} - \text{C}_2\text{H}_5]^+$, 325 (2%), 313 (6%) $[\text{M} - \text{C}_2\text{H}_5 - \text{CO}]^+$, 297 (14%) $[\text{M} - \text{OC}_2\text{H}_5 - \text{C}_2\text{H}_4]^+$, 280 (5%) $[\text{M} - 2\text{OC}_2\text{H}_5]^+$, 252 (36%) $[\text{M} - 2\text{OC}_2\text{H}_5 - 2\text{CH}_2]^+$, 239 (58%), 226 (30%), 215 (34%), 202 (26%), 185 (25%), 55 (100%); * rotational isomers.

syn-3a(12c),9a(9b)-Dihomoperylene-3,10-dione (**VI**)

Oxidation of *meso*-7,7'-dimethoxy-2,2'-bi(1,6-methano[10]annuleny)s (IIIb**) with $\text{Ti}(\text{OCOCF}_3)_3$.** Thallium trifluoroacetate (Aldrich, 560 mg, 1.0 mmol) was dissolved in anhydrous acetonitrile (50 ml) and maintained at –40 °C under inert gas. A solution of the *meso*-compound (**IIIb**) (140 mg, 0.4 mmol) in carbon tetrachloride was then added and stirring was maintained for 1 hour at the same temperature. The solvent was evaporated at 0 °C under vacuum and the residue was filtered through a short path column ($l = 25$ cm, $id = 3$ cm). Recrystallization from diethyl ether afforded the title compound (**VI**) (40 mg, 32%) as orange coloured needles which decomposed at 250 °C without melting.

Oxidation of *meso*-7,7'-dimethoxy-2,2'-bi(1,6-methano[10]annuleny)s (IIIb**) with VOF_3 .** Vanadium(v) oxytrifluoride, VOF_3 (150 mg, 1.2 mmol) suspended in anhydrous dichloromethane was treated dropwise with a solution of the *meso*-compound (**IIIb**) (140 mg, 0.4 mmol) in dichloromethane under inert gas. The reaction mixture was stirred for 1 hour at ambient temperature and quenched with a 5% solution of sodium hydrogen carbonate (25 ml). The organic phase was washed with 5% sodium hydrogen carbonate (2 × 25 ml), then with water (3 × 50 ml) and dried over magnesium sulfate. After evaporation of the solvent the residue was chromatographed over silica gel ($l = 25$ cm, $id = 3$ cm) with diethyl ether. It yielded 22 mg (18%) of *syn*-3a(12c),9a(9b)-dihomoperylene-3,10-dione (**VI**).

(Found: C, 84.95; H, 4.5. Calc. for $\text{C}_{22}\text{H}_{12}\text{O}_2$: C, 85.14; H, 4.55%); δ_{H} (300 MHz; CD_2Cl_2) 6.35 (H-4,9), 7.13 (H-5,8), 8.10 (H-6,7) (parts A, M and X of an AMX-system), 6.28 (H-2,11), 7.60 (H-1,12) (parts A and X of an AX-system), 1.48 (H-13b,14b), 3.97 (H-13a,14a) (parts A and X of an AX-system); ($J_{1,2} = J_{11,12} = 11.84$; $J_{4,5} = J_{8,9} = 5.23$; $J_{4,6} = J_{7,9} = 0.12$; $J_{5,6} = J_{7,8} = 11.23$; $J_{13a,13b} = J_{14a,14b} = -10.89$; $J_{4,13a} = J_{9,14a} = 0.08$; $J_{4,13b} = J_{9,14b} = 0.66$; RMS-error = 0.03 Hz); δ_{C} (75.5 MHz; CD_2Cl_2) 189.52 (C-3,10), 133.94 (C-1,12), $^1J_{\text{C-H}} = 162.4$, 132.88 (C-6,7), $^1J_{\text{C-H}} = 158.5$, $^2J_{\text{C-H}} = 7.6$, 130.73 (C-2,11), $^1J_{\text{C-H}} = 162.4$, 129.13 (C-5,8), $^1J_{\text{C-H}} = 159.9$, 121.74 (C-4,9), $^1J_{\text{C-H}} = 162.1$, 117.81 (C-3a,9a), 33.16 (C-13,14), $^1J_{\text{C-H}} = 139.1$, $^2J_{\text{C-H}} = 6.9$, 134.54, 129.18 and 128.85 (C-6a,6b,9b,12a,12b,12c); $\lambda(\text{dioxane})/\text{nm}$ 467w ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1} = 1500$), 393 ($\epsilon = 20300$), 343 ($\epsilon = 16000$), 239 ($\epsilon = 25600$); $\nu(\text{CsI})/\text{cm}^{-1}$ 3144 (=C–H stretching), 2931 (–C–H stretching), 1644 (C=O stretching), 1587, 1577, 1543 and 1300 (C=C stretching), 836, 827 and 820 (=C–H def.);

m/z (70 eV) 310 (12%) $[M]^+$, 309 (3%) $[M - H]^+$, 281 (17%) $[M - H - CO]^+$, 252 (39%) $[M - 2H - 2CO]^+$, 239 (49%) $[M - H - 2CO - CH_2]^+$, 226 (38%) $[M - 2CO - 2CH_2]^+$, 125 (51%), 44 (100%).

(E)-syn-2,2'-Bi(7H-1,6-methano[10]annulenyliene)-7,7'-dione (IV)

Oxidation of rac-7,7'-dimethoxy-2,2'-bi(1,6-methano[10]-annulenyliene) (IIIA) with thallium trifluoroacetate, $Tl(OCOCF_3)_3$. The procedure used for the oxidation of the *meso*-form **IIIB** was also used in this case. Compound **IV** was obtained in 60% yield (95 mg) in the form of deep violet crystals of mp 119–120 °C.

(Found: 312.1148. Calc. for $C_{22}H_{16}O_2$: 312.1150); δ_H (300 MHz; CD_2Cl_2) 6.45 (H-4), 6.51 (H-5), 7.11 (H-3) (parts A, B and X of an ABX-system), 5.71 (H-10), 6.21 (H-8), 6.83 (H-9) (parts A, M and X of an AMX-system), 2.46 (H-11b), 3.32 (H-11a); ($J_{3,4} = 11.0$ Hz; $J_{4,5} = 5.5$; $J_{8,9} = 11.8$; $J_{9,10} = 5.7$; $J_{11a,11b} = -11.3$); NOE observed between H-3 and H-10; δ_C (75.5 MHz; CD_2Cl_2) 191.05 (C-7), 141.82, 141.70 (C-1,2,6), 140.74, 138.01 (C-9, $^1J_{C-H} = 156.8$), 134.63 (C-3, $^1J_{C-H} = 158.6$, $^2J_{C-H} = 7.2$), 131.14 (C-3, $^1J_{C-H} = 162.5$, $^2J_{C-H} = 7.2$), 129.76 (C-5, $^1J_{C-H} = 159.2$), 128.24 (C-4, $^1J_{C-H} = 158.3$), 127.72 (C-10, $^1J_{C-H} = 164.5$), 33.71 (C-11, $^1J_{C-H} = 136.2$); $\nu(CsI)/cm^{-1}$ 3023, 3012 (=C–H stretching), 2936 (–C–H stretching), 1631 (C=O stretching), 1592, 1536 (C=C stretching); m/z (70 eV) 312 (66%) $[M]^+$, 311 (16%) $[M - H]^+$, 297 (10%) $[M - H - CH_2]^+$, 295 (9%), 283 (14%) $[M - H - CO]^+$, 269 (17%) $[M - H - CO - CH_2]^+$, 252 (23%), 239 (57%) $[M - 3H - 2CO - CH_2]^+$, 43 (100%); $\lambda(CH_2Cl_2)/nm$ 515 ($\epsilon/dm^3 mol^{-1} cm^{-1} = 21600$), 405 ($\epsilon = 5400$), 337 ($\epsilon = 4700$), 286 ($\epsilon = 7900$), 228 ($\epsilon = 25500$).

Rearrangement to trans-12a,12b-dihydro-3a(12c),9a(9b)-dihomoperylene-3,10-dione (V). (E)-syn-2,2'-Bi(7H-1,6-methano[10]annulenyliene)-7,7'-dione (**IV**) (160 mg, 0.5 mmol) was dissolved in carbon tetrachloride (100 ml) and heated under reflux for 2 hours, while exposed to daylight. After evaporation of the carbon tetrachloride at ambient temperature, the residue was recrystallized from diethyl ether. The title compound was obtained in 50% yield as yellow crystals which decomposed at around 230 °C without melting.

(Found: 312.1151. Calc. for $C_{22}H_{16}O_2$: 312.1150); δ_H (300 MHz; CD_2Cl_2) 6.08 (H-6,7), 6.12 (H-5,8), 6.79 (H-4,9) (parts A, M and X of an AMX-system), 6.00 (H-2,11), 6.43 (H-1,12), 2.91 (H-12a,12b), 2.22 (H-13a,14a), 0.49 (H-13b,14b) ($J_{1,2} =$

$J_{11,12} = 10.8$; $J_{4,5} = J_{8,9} = 9.2$; $J_{5,7} = J_{7,8} = 6.4$; $J_{13a,13b} = J_{14a,14b} = 4$); δ_C (75.5 MHz; CD_2Cl_2) 193.07 (C-3,10), 142.37 (C-1,12, $^1J_{C-H} = 164.0$), 139.25 (C-6a,6b), 127.50 (C-2,11, $^1J_{C-H} = 165.4$), 122.18 (C-4,9, $^1J_{C-H} = 167.0$), 121.02 (C-5,8, $^1J_{C-H} = 161.7$), 117.69 (C-6,7, $^1J_{C-H} = 161.7$, $^2J_{C-H} = 9.9$), 43.51 (C-9b,12c), 43.29 (C-12a,12b, $^1J_{C-H} = 134.0$), 41.18 (C-3a,9a), 22.74 (C-13,14, $^1J_{C-H} = 166.1$ and 168.8); m/z (70 eV) 312 (8%) $[M]^+$, 311 (3%) $[M - H]^+$, 297 (5%) $[M - H - CH_2]^+$, 283 (12%) $[M - H - CO]^+$, 269 (24%) $[M - H - CO - CH_2]^+$, 255 (36%) $[M - H - 2CO]^+$, 252 (48%), 239 (100%) $[M - 3H - 2CO - CH_2]^+$, 226 (66%) $[M - 2H - 2CO - 2CH_2]^+$, 215 (52%), 202 (51%), 119 (78%), 113 (82%); $\nu(CsI)/cm^{-1}$ 2932 (=C–H stretching), 1682 (C=O stretching); $\lambda(dioxane)/nm$ 322 ($\epsilon/dm^3 mol^{-1} cm^{-1} = 8300$), 233 ($\epsilon = 16800$).

Acknowledgements

The authors thank Professor Dr Emanuel Vogel for suggesting the project and Dr W. Klug for supplying a quantity of 1,6-methano[10]annulene.

References

- 1 I. T. Stone and F. Sondheimer, *Tetrahedron Lett.*, 1978, **19**, 4567.
- 2 R. H. Mitchell, M. Chandry, T. W. Dingle and R. V. Williams, *J. Am. Chem. Soc.*, 1984, **106**, 7776.
- 3 M. Iyoda, K. Sato and M. Oda, *Tetrahedron Lett.*, 1985, **14**, 3829.
- 4 R. H. Mitchell and J. Zang, *Tetrahedron Lett.*, 1997, **38**, 6517.
- 5 J. Miller and K. Y. Wan, *J. Chem. Soc.*, 1963, 3492.
- 6 J. Miller, *Aromatic Nucleophilic Substitution*, Elsevier, Amsterdam, London and New York, 1968, ch. 1, 4–6.
- 7 W. S. Rapson, R. G. Shuttleworth and J. N. van Niekerk, *J. Chem. Soc.*, 1943, 326.
- 8 (a) G. Wittig and G. Lehmann, *Chem. Ber.*, 1957, **90**, 875; (b) G. Wittig, *Q. Rev. Chem. Soc.*, 1960, **20**, 205; (c) G. Wittig and E. Klar, *Liebigs Ann. Chem.*, 1967, **704**, 91; (d) G. Wittig and K.-D. Rümpler, *Liebigs Ann. Chem.*, 1971, **751**, 1; (e) G. Wittig, S. Fischer and G. Reiff, *Liebigs Ann. Chem.*, 1973, **767**, 495.
- 9 (a) R. B. Kress, E. N. Duesler, M. C. Etter, I. C. Paul and D. Y. Curtin, *J. Am. Chem. Soc.*, 1980, **102**, 7709; (b) K. A. Ken and J. M. Robertson, *J. Chem. Soc. B*, 1969, 1146; (c) W. A. C. Brown, J. Trotter and J. M. Robertson, *Proc. Chem. Soc. London*, 1961, 115.
- 10 (a) A. Meyer, K. Schlögl, U. Lerch and E. Vogel, *Chem. Ber.*, 1988, **121**, 917; (b) K. R. Wilson and R. E. Pincock, *J. Am. Chem. Soc.*, 1975, **97**, 1474; (c) A. K. Colter and L. M. Clemens, *J. Am. Chem. Soc.*, 1965, **87**, 846; (d) T. Hattori, N. Koike, Y. Oklaishi and S. Miyano, *Tetrahedron Lett.*, 1966, **37**, 2057.
- 11 E. Vogel, K. D. Sturm, A. de F. Dias, J. Lex, H. Schmickler and F. Wudl, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 590.