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Bis[indanyl]- and Bis[indenyl]arylmethanes: New Molecular Three-Bladed Propellers

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Summary. Proton-catalyzed arylmethylation of indan and indene derivatives with 4-methoxybenzaldehyde yield novel triarylmethanes bearing indan or indene substituents. According to Mislow's definition, these molecules belong to the class of molecular three-bladed propellers and exhibit an interesting stereochemistry.

Keywords. Arylmethylation of indans and indenes; Molecular three-bladed propellers; Bis[indanyl]- and bis[indenyl]arylmethanes.

Bis[indanyl]- und Bis[indenyl]-aryl-methane: Neue molekulare Dreiblatt-Propeller

Zusammenfassung. Die proton-katalysierte Arylmethylierung von Indan- und Inden-Derivaten mit 4-Methoxybenzaldehyd liefert neue Triarylmethane mit Indan- und Inden-Resten. Nach dem Mislowschen Prinzip gehören diese Verbindungen zur Klasse der molekularen Dreiblatt-Propeller.

Introduction

Syntheses and structural investigations of triarylmethanes and their heteroaryl analogues are of general importance in dye chemistry as so-called leukobases [1–3]. Furthermore, the conformations of these compounds are also of major interest for theoretical stereochemistry. Numerous investigations by Mislow and coworkers [4, 5] as well as those by our group with particular emphasis on the heteroarylmethane series [6–9] have revealed that these molecules adopt the energetically favoured three-bladed propeller conformations in the solid state and in solution. The stereochemistry of these systems is based on planar and axial chirality [4, 5] and is further complicated by the existence of stereocenters in the propeller blades resulting from the additional central chirality [7, 8].

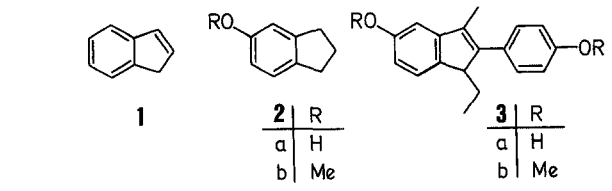
In the present paper, we report on the first synthesis of triarylmethanes bearing two indan or indene moieties which generally constitute new, three-bladed propellers.

Results and Discussion

In analogy to the classical arylalkylation methodology for arenes using aldehydes, compounds **1**–**4** were subjected to electrophilic substitution by 4-methoxybenzal-

dehyde under proton catalysis. Racemic mixtures of the chiral starting materials **3** and **4** were employed in these reactions.

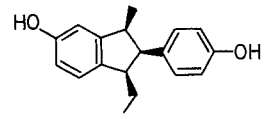
Whereas the reaction of **1** give rise to an inseparable mixture of bis[indenyl]arylmethanes **5**, the oxygen functionalized derivatives **2–4** reacted exclusively to furnish the bis[indanyl]- or bis[indenyl]arylmethanes **6–8**.



1

2	R
a	H
b	Me

3	R
a	H
b	Me



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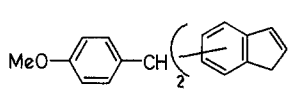

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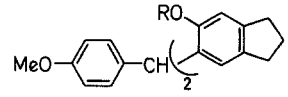
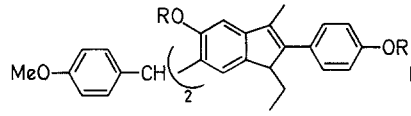
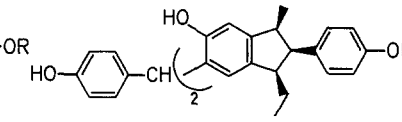


6	R
a	H
b	Me



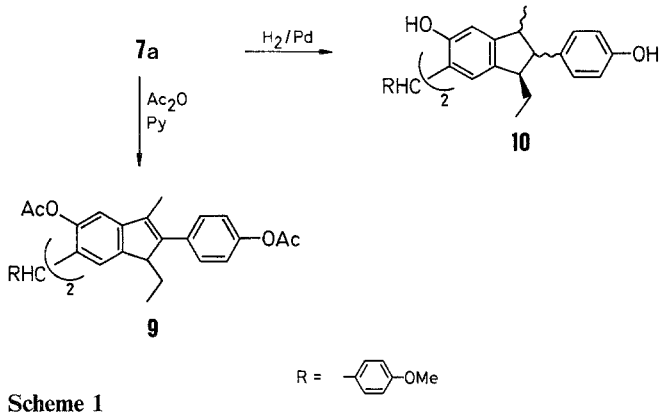


7	R
a	H
b	Me

8

The pronounced regioselectivity of the repetitive arylmethylation of the aldehyde cation, generated in situ by protonation, on treatment with compounds **2–4** can be predicted on the basis of charge and/or frontier orbital control [10]. π-MO calculations using the π-VESCF method [11] for the establishment of the charge and topology of the π-MO's reveal a significant π-charge and a significant HOMO coefficient at the given reaction center in the electron-rich starting materials (see, for example, MO data for **3a** in Fig. 1). According to the FMO concept, a HOMO(indene or indane)-LUMO(aldehyde cation) interaction should control the regiochemistry in the first step; for aldehyde cation: E(LUMO)= −9.03 eV, *E*-configuration [11]. In addition, steric effects are also in accord with the experimental results of the "symmetrical" electrophilic tandem-substitution.

6,6'-Bis[indenyl]arylmethane **7a** was submitted to further transformations during which decomposition of the methane framework did not take place (Scheme 1). Thus, acetylation gave rise to the tetraacetate **9** while palladium-catalyzed hydrogeneration (10% Pd on carbon) furnished the indan derivative **10** as a complex mixture of stereoisomers having C_1 and C_s symmetry.



Scheme 1

The structures of the reported triarylmethanes were elucidated with the aid of several ^{1}H and ^{13}C NMR techniques (e.g., 400 MHz ^{1}H NOE experiments, ^{13}C, ^{1}H single frequency off-resonance decoupling, ^{13}C APT, DEPT experiments, and, especially for **7a**, inverse H, C-COSY measurements at 500 MHz).

According to Mislow's principle [4, 5], compounds **5–10** should adopt the energetically favoured triarylmethane propeller conformations as a consequence of the planar and axial chirality. Moreover, MMX molecular mechanics calculations [12] using the Monte Carlo Metropolis algorithms did indeed reveal propeller conformations for all compounds **5–10** in the minima of the energy hyperface (Fig. 2).

In the case of compounds **7–10**, the existence of at least one stereocenter in the indene or indan ring appreciably increases the "theoretical" number of stereoisomers. Thus, for example, compounds **7** and **9** each give rise to 4 stereoisomers **A–D** (two C_1 symmetrical diasteromers and two C_s symmetrical *meso*-forms, Fig. 3) when only the central chirality of the indene ring is taken into consideration. When the planar and axial chiralities are additionally brought into account, a maximum

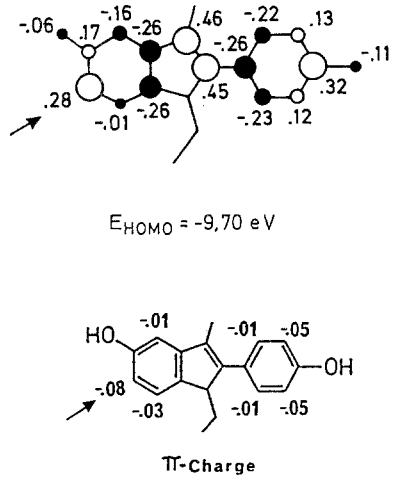


Fig. 1. HOMO and π-charge of **3a** on the basis of π-VESCF calculations [11]; a fully geometry optimized coplanar structure was calculated throughout

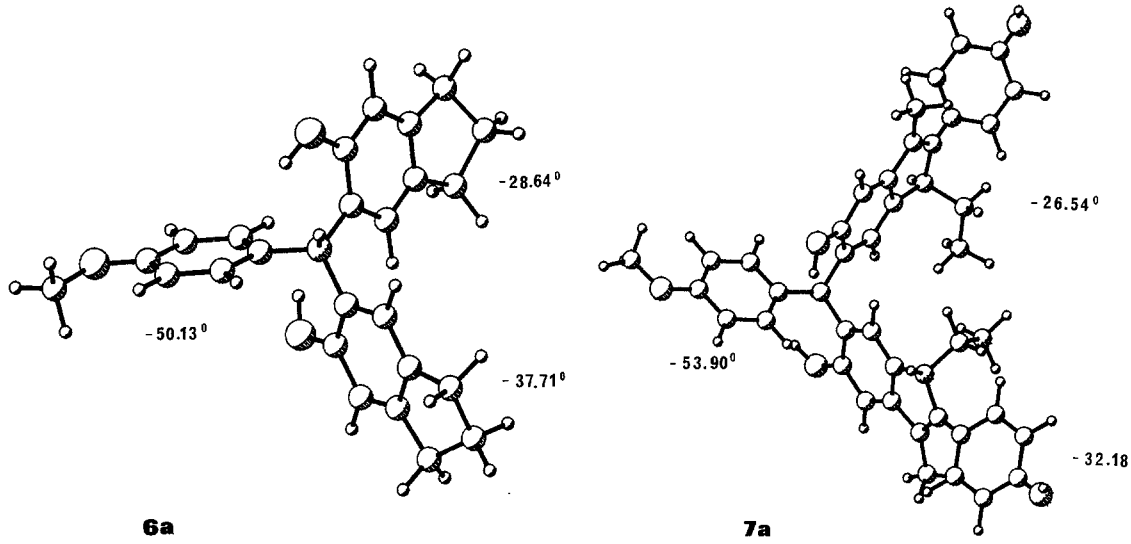


Fig. 2. Global minimum conformers of **6a** and **7a** (PLUTO plots) according to MMX molecular mechanics calculations (Monte Carlo Metropolis approach) [12] (viewed along the helix axis). Both compounds adopt an M-helix in the minimum conformer given. Compound **7a** has the *RR*-configuration in the two indene frameworks. The torsional angles of the unsymmetrical propellers are given according to Mislow's definition [4, 5]. In the *SS*-configurated isomer and in the two *meso*-forms **7a** also adopts the M-forms in the global minimum

of 32 propeller stereoisomers is possible (including enantiomeric and diastereomeric forms). Of these, the global minimum conformer of **7a** with the *RR*-configuration in the two indene units is depicted in Fig. 2. As a result of the above phenomena, complicated NMR spectra are to be expected from this class of comounds. For example, the 400 MHz ^{1}H NMR spectrum of the constitutionally 100% pure compound **7a** at 20°C reveals, first of all, three sets of signals for the protons of the indene moiety. Accordingly, the resonances of the three central methine protons are observed at 6.32, 6.33, and 6.34 ppm and the three sets of signals for the protons of the CH_3CH_2 group at 0.36, 0.38, and 0.39 ppm (acetone-d_6, 20°C). This should be the result of a combination of axial and central chirality. At 100°C in *DMSO*-

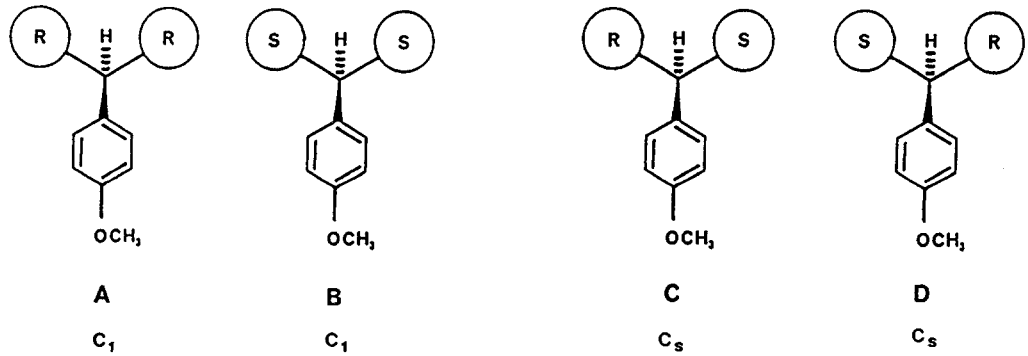


Fig. 3. Maximum number of configurational isomers of compounds **7** and **9** considering solely the central chirality of the indene rings

d_6, the signals begin to broaden, indicating the start of a coalescence process probably due to enhanced propeller stereoisomerization[1].

Experimental Part

Melting points (not corrected): Linström apparatus. Mass spectra: Varian MAT (70 eV) spectrometer; field desorption mass spectra: Varian MAT 711 spectrometer. ^{1}H NMR (400 MHz) and ^{13}C NMR spectra (100.6 MHz): Bruker WM 400 spectrometer. Elemental analyses: Carlo Erba Strumentazione Model 1064 apparatus. Flash chromatography: silica gel 60 (Merck, grain size 0.040–0.063 mm); MPLC: Büchi 681 apparatus, LiChroprep® Si 60 (Merck, grain size 25–40 μm). All reactions were performed under an argon atmosphere in highly pure solvents. The indan and indene derivatives **2**–**4** were prepared according to Ref. [13].

Mixture of Constitutional Isomers of 4-Methoxybenzylidene-bis[indene] (**5**)

Indene (**1**; 1.0 g, 8.61 mmol) was dissolved in 10 ml of ethanol, 10 ml of hydrochloric acid (25%, 2.5 g, 68.57 mmol) and 0.55 ml of 4-methoxybenzaldehyde (0.61 g, 4.48 mmol) were added to the solution, and the resultant mixture was heated for 5 h on a water bath at 100°C. The mother liquor was extracted with a total of 70 ml of dichloromethane, the extract was neutralized with $NaHCO_3$ ($pH = 6$), and dried with Na_2SO_4. The organic phase was filtered and concentrated. The concentrated dichloromethane solution was then absorbed on to 10 g of silica gel. The silica gel mixture was then put on to the top of the prepared column for flash chromatography. The first flash chromatography was performed on silica gel 60 with petroleum ether (40–60°C)/ethyl acetate (80/20) using an Aldrich column and the second with the changed eluent combination petroleum ether/ethyl acetate (90/10). The solvent was then removed using a rotary evaporator and the residue recrystallized from petroleum ether to furnish a yellowish crystalline powder. The mixture of isomers could not be separate analytically. Yield: 40 mg (2.6%), m.p. decomposition at 50–60°C.

EI-MS (70 eV): *m/z* (%) = 350 (M^+, 46), 121 ($C_8H_9O^+$, 100). ^{1}H NMR ($CDCl_3$): δ (ppm) = 3.42 (s, 2 H, 2 × C 1-H), 3.79 (s, 3 H, OCH_3), 6.48 (s, 1 H, methine H), 6.80–7.36 (m, 14 H, aromatic H and vinyl H). ^{13}C NMR ($CDCl_3$): δ (ppm) = 37.56 (2 × C 1), 40.91, 49.22 (methine C), 54.86 (OCH_3), 113.87 (C 3′, C 5′), 120.53 (2 × C 4), 123.53 (2 × C 7), 124.16 (2 × C 6), 126.35 (2 × C 5), 127.18 (2 × C 3), 128.89 (C 2′, C 6′), 129.60 (2 × C 2), 130.55, 134.54 (C 1′), 141.72, 142.70, 143.33 (2 × C 7 a), 144.95 (2 × C 3 a), 151.66 (C 4′). $C_{26}H_{22}O$ (350.46); calcd. C 89.11, H 6.33; found C 88.87, H 6.11.

6,6′-(4-Methoxybenzylidene)-bis(indan-5-ol) (**6 a**)

5-Hydroxyindan (**2 a**; 1.0 g, 7.45 mmol) was dissolved in 20 ml of ethanol. After addition of 10 ml of hydrochloric acid (25%; 2.5 g, 68.57 mmol) and 0.45 ml of 4-methoxybenzaldehyde (0.5 g, 3.70 mmol), the mixture was heated at 100°C for 1 h whereupon a red colouration was formed. The red organic phase was extracted with 80 ml of dichloromethane, the extract was neutralized with $NaHCO_3$, dried with Na_2SO_4, filtered, and the filtrate was concentrated for a subsequent MPLC separation. After 3 h preconditioning of a Büchi column filled with silica gel LiChroprep® Si 60 (Merck) and fitted with a pre-column, a column chromatographic separation was performed under the following conditions: eluent: petroleum ether (40–60°C)/ethyl acetate (70/30); pressure: 2 bar; drop rate 10 ml/70 sec; duration: 90 min. Yield: 69 mg (4.8%), m.p. 214°C.

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[1] In all cases for compounds **7**–**10**, the coalescence points for fast propeller stereoisomerization could not be determined since the compounds began to decompose at about 105–120°C. However, in the region of fast propeller stereoisomerization, solely the central chirality of the indene (indan) moieties would still give rise to some sets of signals as a result of the C_1 and C_s symmetry in the triarylmethanes [7, 8] (see Fig. 3)

EI-MS (70 eV): *m/z* (%) = 386 (M^+, 31), 221 ($M^+ - C_9H_9O, -OH, -CH_3$, 100). ^{1}H NMR (acetone-d_6): δ (ppm) = 1.96 (quint., $^3J_{2,1}$ = 7.31 Hz, 4 H, 4 × C 2-H), 2.66 (t, $^3J_{3,2}$ = 7.28 Hz, 4 H, 4 × C 3-H), 2.76 (t, $^3J_{1,2}$ = 7.34 Hz, 4 H, 4 × C 1-H), 3.73 (s, 3 H, OCH_3), 6.11 (s, 1 H, methine H), 6.66 (s, 2 H, 2 × C 4-H), 6.70 (s, 2 H, 2 × C 7-H), 6.79 (d, **J** = 8.70 Hz, 2 H, C 3′-H, C 5′-H), 6.98 (d, *J* = 8.75 Hz, 2 H, C 2′-H, C 6′-H), 7.78 (s, 2 H, 2 × OH). ^{13}C NMR (acetone-d_6): δ (ppm) = 26.40 (2 × C 2), 32.78 (2 × C 3), 33.35 (2 × C 1), 43.38 (methine C), 55.36 (OCH_3), 111.93 (2 × C 4), 114.02 (C 3′C 5′), 126.29 (2 × C 7), 129.85 (2 × C 6), 131.04 (C 2′, C 6′), 134.79 (2 × C 7 a), 137.47 (C 1′), 143.36 (2 × C 3 a), 154.26 (2 × C 5), 158.69 (C 4′). $C_{26}H_{26}O_3$ (386.49), calcd. C 80.80, H 6.78; found: C 80.86, H 6.86.

6,6′-(4-Methoxybenzylidene)-bis[5-methoxyindan] (**6 b**)

5-Methoxyindan (**2 b**; 1.0 g, 6.75 mmol) was dissolved in 20 ml of ethanol. After addition of 10 ml of hydrochloric acid (25%; 2.5 g, 68.57 mmol) and 0.40 ml of 4-methoxybenzaldehyde (0.45 g, 3.30 mmol), the mixture was heated at 100°C for 4 h whereupon a red colouration was formed. The red mixture was extracted with 80 ml of dichloromethane, the red extract was neutralized with $NaHCO_3$, dried with Na_2SO_4, filtered, and the filtrate was concentrated for a subsequent MPLC separation. After 5 h preconditioning of a Büchi column filled with silica gel LiChroprep® Si 60 and fitted with a pre-column, a column chromatographic separation was performed under the following conditions: eluent: petroleum ether (40–60°C)/ethyl acetate (80/20); pressure: 2 bar; drop rate 10 ml/60sec; duration: 120 min. Yield: 38 mg (2.7%), m.p. 142°C.

EI-MS (60 eV). *m/z* (%) = 414 (M^+, 100). ^{1}H NMR ($CDCl_3$): δ (ppm) = 2.04 (quint., $^3J_{2,1+2,3}$ = 7.38 Hz, 4 H, 4 × C 2-H), 2.75 (t, $^3J_{3,2}$ = 7.30 Hz, 4 H, 4 × C 3-H), 2.88 (t, $^3J_{1,2}$ = 7.38 Hz, 4 H, 4 × C 1-H), 3.66 (s, 6 H, 2 × OCH_3 at C 5), 3.77 (s, 3 H, OCH_3 at C 4′), 6.08 (s, 1 H, methine H), 6.66 (s, 2 H, 2 × C 4-H), 6.76 (s, 2 × C 7-H), 6.77 (d, *J* = 9.13 Hz, 2 H, C 3′-H, C 5′-H), 6.98 (d, *J* = 8.58 Hz, 2 H, C 2′-H, C 6′-H). ^{13}C NMR ($CDCl_3$): δ (ppm) = 25.60 (2 × C 2), 32.33 (2 × C 3), 33.17 (2 × C 1), 42.42 (methine C), 55.09 (OCH_3 at C 4′), 56.17 (2 × OCH_3 at C 5), 107.58 (2 × C 4), 113.22 (C 3′, C 5′), 125.63 (2 × C 7), 130.16 (C 2′, C 6′), 131.33 (2 × C 6), 135.23 (2 × C 7 a), 137.03 (C 1′), 142.68 (2 × C 3 a), 156.18 (2 × C 5), 157.44 (C 4′). $C_{28}H_{30}O_3$ (414.55); calcd. C 81.13, H 7.29; found: C 81.34, H 7.25.

6,6′-(4-Methoxybenzylidene)-bis[1-ethyl-2-(4-hydroxyphenyl)-3-methyl-inden-5-ol] (**7 a**)

1-Ethyl-2-(4-hydroxyphenyl)-3-methylinden-5-ol (**3 a**; 0.50 g, 1.88 mmol) was dissolved in 10 ml of ethanol. After addition of 10 ml of hydrochloric acid (25%; 2.5 g, 68.57 mmol) and 0.10 ml of 4-methoxybenzaldehyde (0.11 g, 0.81 mmol), the resultant mixture was heated at 100°C for 5 min on an oil bath. The reaction mixture was then successively extracted with 80 ml dichloromethane, the organic phase was neutralized with $NaHCO_3$, dried with Na_2SO_4 and filtered. The blue-coloured filtrate was then concentrated in preparation for the subsequent MPLC separation. A preconditioned Büchi column filled with silica gel LiChroprep® Si 60 and fitted with a pre-column was used, the eluent was petroleum ether (40–60°C)/ethyl acetate (50/50), the pressure was 2 bar, and the drop rate was 10 ml per 55 sec (duration: 90 min). Subsequent recrystallization from petroleum ether/acetone of the concentrated and precipitated fractions gave rise to a colourless crystalline powder. Yield: 20 mg (3.3%), m.p. decomposition at about 160°C.

FS-MS: *m/z* (%) = 650 (M^+, 100). ^{1}H NMR (*DMSO-d*$_6$, 100°C): δ (ppm) = 0.40 (t, ^3J = 7.27 Hz, 6 H, 2 × **CH**$_3$ − CH$_2$), 1.40 (m, 2 H, CH$_3$ − **CH**$_2$), 1.66 (m, 2 H, CH$_3$ − **CH**$_2$), 2.14 (d, ^5J = 1.93 Hz, 6 H, 2 × CH$_3$ − C =), 3.73 (m, 2 H, 2 × C 1-H), 3.74 (s, 3 H, CH_3O), 6.18 (s, ^{1}H, methine H), 6.82 (d, $^3J_{3,5}$ = 8.88 Hz, 6 H, 2 × C 3′-H, 2 × C 5′-H, C 3″-H, C 5″-H), 6.85 (2 × s, 2 H, 2 × C 4-H), 6.97 (s, 2 H, 2 × C 7-H), 7.17 (d, $^3J_{2,6}$ = 8.26 Hz, 6 H, 2 × C 2′-H, 2 × C 6′H, C 2″-H, C 6″-H), 8.64 (s, 2 H, 2 × OH), 9.19 (s, 2 H, 2 × OH). ^{13}C NMR (acetone-d_6): δ (ppm) = 8.69 (2 × **CH**$_3$ − CH$_2$), 11.78 (2 × **CH**$_3$ − C =), 24.26 (2 × CH$_3$ − **CH**$_2$), 43.29 (methine C), 51.24 (2 × C 1), 55.40 (OCH_3), 106.73 (2 × C 4), 114.07 (C 3′, C 5″), 116.09 (2 × C 3′, 2 × C 5′), 124.70 (2 × C 7), 127.95 (2 × C 6), 128.94 (2 × C 1′), 130.97 (2 × C 2′, 2 × C 6′), 131.10 (C 2′, C 6″), 132.98 (2 × C 3), 137.56 (2 × C 7 a), 138.03 (C 1″), 146.07

(2 × C 2), 147.08 (2 × C 3 a), 154.86 (2 × C 5), 157.14 (2 × C 4′), 158.72 (C 4″). $C_{44}H_{42}O_5$ (650.82); calcd. C 81.20, H 6.51; found C 81.33, H 6.50.

6,6′-(4-Methoxybenzylidene)-bis[1-ethyl-5-methoxy-2-(4-methoxyphenyl)-3-methylindene] (**7b**)

1-Ethyl-5-methoxy-2-(4-methoxyphenyl)-3-methylindene (**3b**; 0.11 g, 0.37 mmol) was dissolved in 40 ml of ethanol. After addition of 10 ml of hydrochloric acid (25%; 2.5 g, 68.57 mmol) and 0.025 ml of 4-methoxybenzaldehyde (0.028 g, 0.21 mmol), the resultant mixture was heated at 100°C for 6 h. After extraction with 50 ml of dichloromethane, the organic phase was neutralised with $NaHCO_3$, dried with Na_2SO_4, filtered, and the filtrate was concentrated in preparation for an MPLC separation. The preconditioned Büchi column fitted with a pre-column was filled with silica gel LiChroprep® Si 60 and, with petroleum ether/ethyl acetate (70/30) as eluent and a pressure of 6 bar, exhibited a drop rate of 10 ml per 40 sec (duration: 90 min). The leukobase fractions obtained were concentrated and recrystallized to furnish a colourless crystalline powder. Yield: 10 mg (7.6%), m.p. decomposition at about 150°C.

^{1}H NMR ($CDCl_3$): δ (ppm) = 0.37 (3 × tc, ^3J = 7.23 Hz, 6 H, 2 × CH_3-CH_2), 2.20 (3 × dc, ^5J = 1.93 Hz, 6 H, 2 × $CH_3-C=$), 3.76 (5 × sc, 15 H, 5 × CH_3O), 3.82 (m, 2 H, 2 × C 1-H), 6.27 (3 × sc, 1 H, 2 × C 5′-H), 6.27 (3 × sc, 1 H, methine H), 6.77 (md, $^3J_{3,5}$ = 8.60 Hz, 6 H, 2 × C 4-H), 6.94 (m, 2 H, 2 × C 7-H), 7.24 (md, $^3J_{2,6}$ = 8.36 Hz, 6 H, 2 × C 2′-H, 2 × C 6′-H, C 2″-H, C 6″-H). ^{13}C NMR ($CDCl_3$): δ (ppm) = 8.45 (2 × CH_3-CH_2), 11.67 (2 × $CH_3-C=$), 55.20 (2 × CH_3O at C 4′ and C 5), 56.30 (CH_3O), 102.42 (2 × C 4), 113.27 (C 3″, C 5″), 113.77 (2 × C 3′, C 5′), 124.31 (2 × C 7), 129.53 (2 × C 1′), 129.71 (2 × C 6), 130.05 (2 × C 2′, C 6′), 130.19 (C 2″, C 6″), 133.14 (2 × C 3), 137.25 (2 × C 7 a), 137.77 (C 1″), C 6″), 133.14 (2 × C 3), 137.25 (2 × C 7 a), 137.77 (C 1″), 145.05 (2 × C 2), 145.99 (2 × C 3 a), 156.87 (2 × C 5), 157.50 (2 × C 4′), 158.27 (C 4″). $C_{48}H_{50}O_5$ (706.93); calcd. C 81.55, H 7.13; found C 81.27, H 6.99.

6,6′-(4-Methoxybenzylidene)-bis[1-ethyl-2-(4-hydroxyphenyl)-3-methylindan-5-ol] (**8**) *(Mixtures of Stereoisomers)*

The indan **4** (0.67 g, 2.5 mmol) was dissolved in 15 ml of ethanol. After addition of 10 ml of hydrochloric acid (25%; 2.50 g, 68.57 mmol) and 0.15 ml of 4-methoxybenzaldehyde (0.17 g, 1.25 mmol), the resultant mixture was heated for 1 h at 100°C on an oil bath. It was then successively extracted with 100 ml of dichloromethane, the extract was neutralized with $NaHCO_3$, and dried with Na_2SO_4. The concentrated, red-coloured filtrate was then subjected to an MPLC separation. Petroleum ether (40–60°C)/ethyl acetate (50/50) was used both for preconditioning the Büchi column filled with silica gel LiChroprep® Si 60 and fitted with a precolumn and also for elution. The duration of the separation amounted to 120 min at a pressure of 3–4 bar and a drop rate of 40 sec per 10 ml. After recrystallization of the fractions obtained from petroleum ether treated a small volume of acetone, a colourless crystalline powder was obtained. Yield: 85 mg (10.4%), m.p. decomposition at 140–150°C.

EI-MS (70 eV): *m/z* (%) = 654 (M^+, 17), 239 ($C_{16}H_{13}O_2^+$). ^{1}H NMR (acetone-d_6): δ (ppm) = 0.79 (3 × tc, ^3J = 7.27 Hz, 6 H, 2 × CH_3-CH_2), 0.90 (3 × dc, ^3J = 7.11 Hz, 6 H, 2 × CH_3-CH), 1.16 (m, 2 H, CH_3-CH_2), 1.67 (m, 2 H, CH_3-CH_2), 3.37 (q, ^3J = 6.42 Hz, 2 H, 2 × C 1-H), 3.55 (quint., ^3J = 6.89 Hz, 2 H, 2 × C 3-H), 3.74 (t, ^3J = 6.35 Hz, 2 H, 2 × C 2-H), 3.76 (s, 3 H, OCH_3), 6.28 (s, 1 H, methine H), 6.53 (3 × sc, 2 H, 2 × C 4-H), 6.60 (pseudo-t, 8 H, 2 × C 2′-H, 2 × C 3′-H, 2 × C 5′-H, 2 × C 6′-H), 6.72 (3 × sc, 2 H, 2 × C 7-H), 6.83 (dd, ^3J = 8.68 Hz, 2 H, C 3″-H, C 5″-H), 7.04 (dd, ^3J = 8.68 H, 2 H, C 2″-H, C 6″-H), 7.99 (s, 4 H, 4 × OH). ^{13}C NMR (acetone-d_6): δ (ppm) = 12.67 (2 × CH_3-CH_2), 14.48 (2 × CH_3-CH), 22.34 (2 × CH_3-CH_2), 43.24 (2 × C 1, methine C), 50.53 (2 × C 3), 55.37 (CH_3O), 56.06 (2 × C 2), 110.89 (2 × C 4), 114.05 (C 3″, C 5″), 115.11 (2 × C 3″, 2 × C 5″), 124.44 (2 × C 7), 129.22 (2 × C 6), 130.86 (C 2″, C 6″), 130.95 (2 × C 1′), 131.27 (2 × C 2′, 2 × C 6′), 137.66 (C 1″), 138.39 (2 × C 7 a), 147.68 (2 × C 3 a), 154.58 (2 × C 5), 156.65 (2 × C 4′), 158.68 (C 4″). $C_{44}H_{46}O_5$ (654.85); calcd. C 80.70, H 7.08; found C 81.09, H 6.89.

6,6'-(4-Methoxybenzylidene)-bis[5-acetoxy-2-(4-acetoxyphenyl)-1-ethyl-3-methylindene] (**9**)

The leukobase **7a** (38 mg, 0.06 mmol) was dissolved in 5 ml of acetic anhydride. After addition of 2 ml of pyridine the mixture was heated for 3 h at 100°C. The reaction mixture was then concentrated and the product recrystallized from petroleum ether (40–60°C) to furnish a colourless crystalline powder. Yield: 36 mg (73%), m.p. 95°C.

FD-MS (25–30 mA): *m/z* (%) = 819 (M^+, 2), 648 (1), 386 (9), 385 (7), 384 (14), 308 (24), 267 (13), 266 (100), 264 (32), 94 (47). ^{1}H NMR (acetone-d_6): δ (ppm) = 0.38 (t, ^3J = 7.57 Hz, 6 H, 2 × CH_3CH_2), 1.54 (m, 2 H, CH_2), 1.79 (m, 2 H, CH_2), 2.18 (s, 12 H, 4 × CH_3–COO), 2.27 (d, ^5J = 2.07 Hz, 6 H, CH_3–C=), 3.78 (s, 3 H, CH_3O), 3.95 (m, 2 H, 2 × C 1–H), 6.35 (s, 1 H, methine H), 6.85 (md, ^3J = 8.46 Hz, 6 H, 2 × C 3'-H, 2 × C 5'-H, C 3''-H, C 5''-H), 7.05 (s, 2 H, 2 × C 4-H), 7.14 (m, 2 H, 2 × C 7-H), 7.45 (md, ^3J = 8.32 Hz, 6 H, 2 × C 2'-H, 2 × C 6'-H, C 2''-H, C 6''-H). $C_{52}H_{50}O_9$ (818.97); calcd. C 76.26, H 6.16; found C 76.10, H 6.69.

Mixture of Configurational Isomers of 6,6'-(4-Methoxybenzylidene)-bis[1-ethyl-2-(4-hydroxyphenyl)-3-methylindan-5-ol] (**10**)

The bis[indenyl]arylmethane **7a** (30 mg, 0.05 mmol) was dissolved in 40 ml of ethanol. A hydrogenation mixture was prepared from 0.30 g of palladium/carbon (10% Pd), 50 ml of ethanol, and 1 ml of acetic acid. This mixture was saturated with 2 l of hydrogen and then mixed slowly with the ethanol solution of **7a**. After 30 min the catalyst was filtered off and the filtrate concentrated. The filtrate was treated with 50 ml of water and then extracted with 200 ml of dichloromethane. The organic layer was dried with Na_2SO_4 filtered, evaporated, and the residue was crystallized from petroleum ether (40–60°C)/acetone to furnish amorphous crystals. Yield: 31 mg (95%), m.p. decomposition at 140–145°C.

EI-MS (70 eV): *m/z* (%) = 654 (M^+, 17), 387 (73), 360 (11), 359 (42), 357 (16), 355 (21), 268 (31), 240 (19), 239 (100), 145 (37), 121 (84), 107 (44). ^{1}H NMR (acetone-d_6): δ (ppm) = 0.79 (t, ^3J = 7.27 Hz, 6 H, 2 × CH_3CH_2), 0.90 (d, ^3J = 7.11 Hz, 6 H, 2 × CH_3CH), 1.16 (m, 2 H, CH_2, 1.67 (m, 2 H, CH_2), 3.37 (q, ^3J = 6.89 Hz, 2 H, 2 × C 3-H), 3.74 (t, ^3J = 6.35 Hz, 2 H, 2 × C 2-H), 3.76 (s, 3 H, OCH_3), 6.28 (s, 1 H, methine H), 6.35 (s, 2 H, 2 × C 4-H), 6.60 (pseudo-t, 8 H, 2 × C 2'-H, 2 × C 3'-H, 2 × C 5'-H, 2 × C 6'-H), 6.72 (s, 2 H, 2 × C 7-H), 6.83 (dd, ^3J = 8.68 Hz, 2 H, C 3''-H, C 5''-H), 7.04 (dd, ^3J = 8.68 Hz, 2 H, C 2''-H, C 6''-H), 7.99 (s, 4 H, 4 × OH). $C_{44}H_{46}O_5$ (654.85); calcd. C 80.70, H 7.08; found C 80.92, H 6.72.

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