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Twin Triptycyl Spinning Tops: A Simple Case of Molecular Gearing with Dynamic C_2 Symmetry

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Lithiation and subsequent oxidation of the recently described prototype molecular paddlewheel 9-(2-indenyl)triptycene (**1**) leads to the *racemic* dimer 2,2′-bis(9-triptycyl)-1,1′-biindenyl (**4**). In the solid state this very congested molecule adopts a conformation in which the two triptycenyl paddlewheel fragments are attached to the C_2-symmetric biindenyl core. However, the orientation of the triptycene blades, dictated by their size and shape, is gear-like and breaks the nascent C_2-symmetry of the whole molecule. Nevertheless, effective C_2-symmetry is restored in solution when the triptycene paddlewheels, although apparently tightly interlocked, undergo rapid contra-rotation on the NMR time-scale. The analogous reaction of (2-phenylindenyl)lithium (**6**), likewise yields *racemic* (*RR*/*SS*) 2,2′-diphenyl-1,1′-biindenyl(**7**). Interestingly, although the treatment of **6** with a Cu^{II} salt leads to both *rac*-**7** and its diastereomer *meso*-**7**, the reaction of **6** and 2-phenylindenyl bromide furnishes selectively *rac*-**7**. Overall, these data suggest that the oxidative dimerisation to yield *racemic* products occurs through a nucleophilic substitution mechanism.

Introduction

Two-fold symmetric molecules are often readily accessible, in racemic form, by the dimerisation of achiral starting materials. For instance, we recently reported the [2+2] cyclodimerisation of a series of fluorenylidene-allenes leading to an interesting family of *trans*-3,4-diaryl-1,2-bis(fluorenylidene)cyclobutanes that are rendered C_2-symmetric as a result of the twisting and overlapping of the fluorenylidene moieties with their very large wingspans.[1] Alternatively, the dimerisation of free radicals derived from a prochiral centre can lead to a mixture of the C_2-symmetric (*R*,*R* and *S*,*S*) enantiomers as well as the *meso* (*R*,*S*) product. The product distribution may be dictated by such factors as accessibility of the reaction centre and total steric strain.

In this short paper we focus on the dimerisation of the recently prepared molecular pro-gearing system 9-(2-indenyl)-triptycene (**1**).[2] Because the barrier to rotation about the single bond connecting the indenyl and triptycyl moieties in **1** is low ($< 9\ kcal\,mol^{-1}$), it was tempting to investigate how dimerisation, if it were to occur, could affect or even arrest internal rotation in such a picturesque structure.

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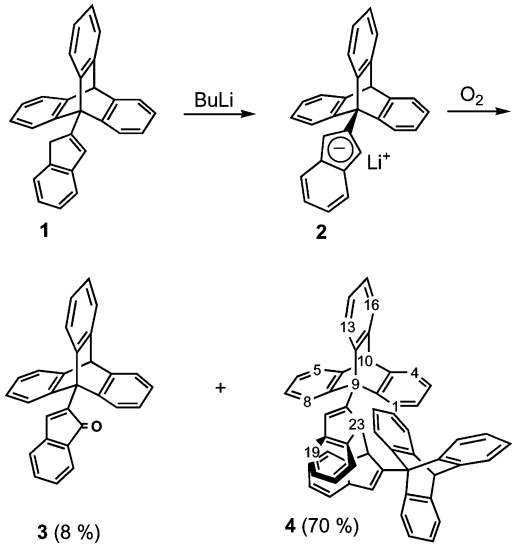
Results and Discussion

The appeal of the triptycene system to molecular mechanical engineering is based on several factors: (a) the threefold symmetry of its aromatic blades, (b) the rigidity of its bicyclo[2.2.2]octatriene core, and (c) the proximity of any substituent at C(9) to the H(1), H(8) and H(13) sites on the blades. When connected by a short rigid moiety, e.g. a methylene bridge or an ether linkage, two triptycyl moieties readily form so-called "molecular gears".[3–7] In such systems, two or more triptycyl units are positioned so closely to each other that internal disrotatory motion about the linking bonds is rapid and mutually correlated. However, we are unaware of any examples in which correlated rotation was observed between two triptycyl units connected by a flexible linker.

In continuation of our quest for an organometallic derivative that might lead to restricted rotation about the triptycyl-indenyl C(9)–C(17) single bond,[2] we were investigating the chemistry of the cyclopentadiene ring in **1** which, as expected, can be deprotonated by a strong base. Despite its sparing solubility in diethyl ether (less than 0.01 M at ambient temperature), when treated with *n*-butyllithium for 1 h, **1** forms the lithium derivative **2**, which upon the addition of a deuteriated solvent regenerates the 1-deuterated hydrocarbon **1**-d.

However, when left at ambient temperature for an extended period of time, the lithium salt **2** was gradually oxidised by the slow diffusion of air into the reaction vessel, and the oxidation products were separated by chromatog-

raphy and characterised. While the minor product was identified as 2-(9-triptycyl)-1-indenone (**3**), the major product, **4**, displayed a ^{1}H NMR spectrum very similar to that of the starting material, **1**. The most obvious difference was the loss of the singlet resonance at δ = 4.36 ppm attributable to the indene CH_2, and appearance of a new singlet at δ = 6.01 ppm with intensity corresponding to only one H per indenyl moiety. These data, together with a comparison of the ^{13}C NMR spectra of **1** and **4**, indicated the formation of the dimer 2,2′-bis(9-triptycyl)-1,1′-biindenyl (**4**) (Scheme 1).



Scheme 1. Oxidation of the lithium derivative **2** leading to the dimer **4**.

The structure of **4** was unequivocally established by X-ray crystallography which revealed that the unit cell contains enantiomeric pairs of (1*R*,1′*R*) and (1*S*,1′*S*) molecules. Careful scrutiny of the molecular structure of *racemic* **4** (Figure 1, a) shows that the molecule is not strictly C_2-symmetric in the solid state: while the core 1,1′-biindenyl moiety has a local C_2 axis, the C_s-type orientation of the intermeshed triptycene blades breaks this symmetry, as illustrated by the space-filling representations in Figure 1, b and Figure 1, c, respectively. The overall geometry of the biindenyl moiety is very reminiscent of bifluorenyl which adopts a *gauche* conformation such that the central H–C–C–H dihedral angle is 60°;[8,9] in *rac*-**4**, the corresponding torsion angle, H–C(23)–C(46)–H, is 73°. As suggested previously,[8] the rationale for the favoured *gauche* conformation in bifluorenyl (and presumably also in the biindenyl dimer) is based on the "back-clamping" which disallows aryl ring stacking. In the *anti* conformation, the hydrogen atoms in the 1,8 positions of one fluorenyl are forced to point directly at their counterparts in the other half of the molecule. These severe H···H nonbonded interactions are greatly relieved in the *gauche* conformation, and contrast with the situation for unclamped tetraarylethanes, which uniformly favour the *anti* conformation.

Both triptycyl units are very severely distorted from their normal threefold symmetry, as indicated by the interplanar angles between the blades (124.9°, 120.0°, 114.9° and

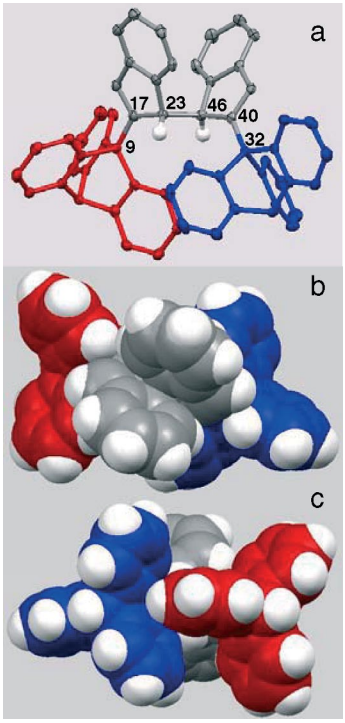


Figure 1. (a) Mercury[10] representation of the X-ray crystal structure of 2,2′-bis(9-triptycyl)-1,1′-biindenyl (*rac*-**4**); aromatic hydrogen atoms have been removed for clarity; (b) space-filling view of *rac*-**4** showing the C_2 character of the indenyl orientations. (c) space-filling view of *rac*-**4** showing the gear-meshing of the triptycyl groups.

135.1°, 122.2°, 102.7°). This exceeds the perturbation of interplanar angles previously seen in 3-(9-triptycyl)indene when one of the blades bears a $Cr(CO)_3$ substituent (126°, 126°, 108°),[11] or in (η^6-triptycene)$Co_4(CO)_9$ (124.1°, 118.9°, 117.0°).[12] Moreover, the degree of intramolecular overcrowding is even more evident in the angle distortions about the bridgehead carbon atoms, C(9) and C(32) of the triptycyl fragments, away from the normal tetrahedral value: C(17)–C(9)–C(9a) 121.5°, C(17)–C(9)–C(8a) 112.8°, C(17)–C(9)–C(12) 108.9°; C(40)–C(32)–C(31a) 120.0°, C(40)–C(32)–C(24a) 117.2°, C(40)–C(32)–C(35) 106.9°. Furthermore, the indenyl–triptycyl bonds are now somewhat longer in **4** [1.528(4) and 1.529(4)] than in **1** [1.514(4) Å]; even more striking is the length of the central C(23)–C(46) linkage at 1.580(4) Å. Finally, it is important to reiterate that the configurations of the directly connected stereogenic C(23) and C(46) centres are identical, i.e. the dimer **4** is chiral.

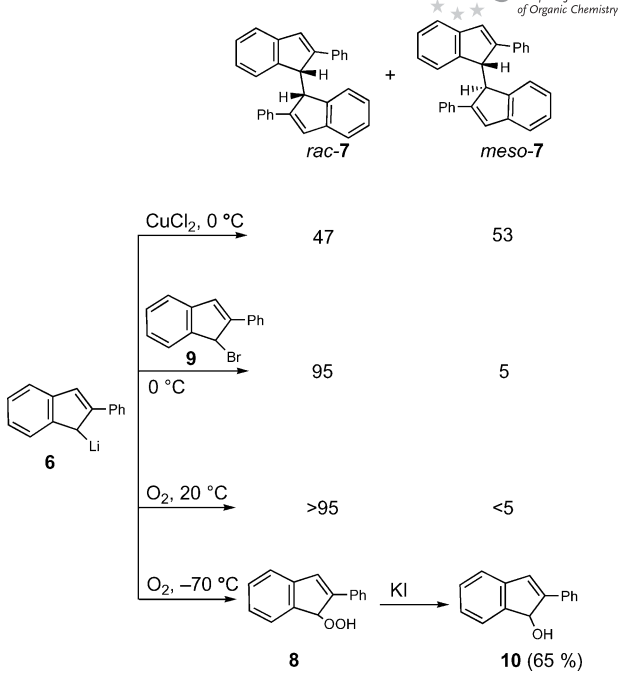
Remarkably, despite the severe steric congestion in *rac*-**4**, the rotation about the C(9)–C(17) and C(40)–C(32) indenyl–triptycenyl single bonds in solution is apparently almost unhindered, as evidenced by the simplicity of its ^{1}H and ^{13}C NMR spectra in which all six triptycyl blades are equivalent at room temperature. Moreover, even at 193 K, the 500 MHz ^{1}H and 125 MHz ^{13}C NMR spectra exhibit only minimal peak broadening, and fully decoalesced spectra cannot be obtained. However, to provide an approximate value for the rotational barrier, one could assume a

similar chemical shift separation (ca. 1.3 ppm) between the H^1/H^8 and H^{13} sites as was observed in 3-indenyltriptycene at low temperature[11] and, estimating the maximum coalescence temperature as 183 K, the barrier would appear to be no more than 9 kcal mol^{-1}. Evidently, in solution the molecular gearing system *rac*-**4** exhibits *dynamic* C_2-symmetry because of the low triptycyl rotation barrier, and the intrinsic C_2-symmetry of the interconnecting biindenyl moiety. Examination of the space-filling representation in Figure 1, c, or of scale molecular models, suggests that the triptycyl units must execute correlated disrotatory motion with concomitant interplanar bending to compensate for the unusually large range of angles (from 103° to 135°) between the blades of the paddlewheels.

Interestingly, when kept in solution for a prolonged period of time, the gradually changing NMR spectra indicated the conversion of *rac*-**4** into a closely related product in which all the triptycyl blades were again equivalent. The ^1H and ^{13}C NMR and mass spectra indicated that this product was the alcohol 2-(9-triptycyl)inden-1-ol (**5**), presumably arising from homolysis of the long C(23)–C(46) central linkage. This is supported by the presence of a strong OH absorption band in the IR spectrum of **5**.

To probe the generality of these interesting observations, 2-phenylindene was converted into its lithium derivative **6** (Scheme 2) under an atmosphere of nitrogen, and air was allowed to diffuse in slowly. The only dimeric product was *rac*-2,2′-diphenyl-1,1′-biindenyl, *rac*-**7**, as confirmed by X-ray crystallography (Figure 2, a). As with the di-triptycyl system *rac*-**4**, the molecule adopted the *gauche* conformation; however, in the case of *rac*-**7**, the H–C(1)–C(14)–H dihedral angle was 64° and the central C(1)–C(14) bond length was a more normal 1.549(2) Å. The torsion angle between the local C_2-axes of the phenyl groups in *rac*-**7** is 86°, implying much less steric strain than in *rac*-**4** for which the corresponding angle between the local C_3 axes of the triptycenes is only 30°. We note that an energy-minimised geometry calculation at the B3LYP/6-31G** level[13] also predicts that *rac*-**7** should adopt a *gauche* conformation, with a H–C(1)–C(14)–H dihedral angle of 70°. Furthermore, the calculated structure has a C(1)–C(14) bond length of 1.568 Å, and a torsion angle of 77° between the local C_2-axes of the phenyl groups.

The initial exclusive formation of the *racemic* dimers derived from the 2-(9-triptycyl)indenide and 2-phenylindenide



Scheme 2. Reactions of **6** leading to *rac*-**7**, *meso*-**7**, and the alcohol **10**.

anions in the presence of oxygen raises interesting mechanistic questions. Moreover, in marked contrast to the preceding result, the treatment of (2-phenylindenyl)lithium **6** with a Cu^{II} salt – a typical radical process[14] – led to both *rac*-**7** and *meso*-**7** isomers in a 47:53 ratio. These observations suggest that the exclusive formation of *rac*-**4** and *rac*-**7** does not arise from a simple radical dimerisation process.

X-ray crystallographic data were acquired on several samples of *meso*-**7**; however, because of the insufficient quality of the crystals, the molecular parameters cannot be quoted with a high degree of accuracy, except that the molecule clearly adopts a *gauche* conformation (Figure 3, a) with a dihedral angle of ca. 70°. Gratifyingly, the DFT calculated energy-minimised molecular geometry at the B3LYP/6-31G** level also yields a *gauche* structure with a dihedral angle of 73° (Figure 3, b). However, unlike dimeric *rac*-**7** that retains its C_2-symmetry whatever the rotamer conformation, *meso*-**7** loses all symmetry elements unless the central H–C–C–H dihedral angle is 0° or 180°, giving rise to either a single mirror plane, (C_s) or an inversion centre (C_i),

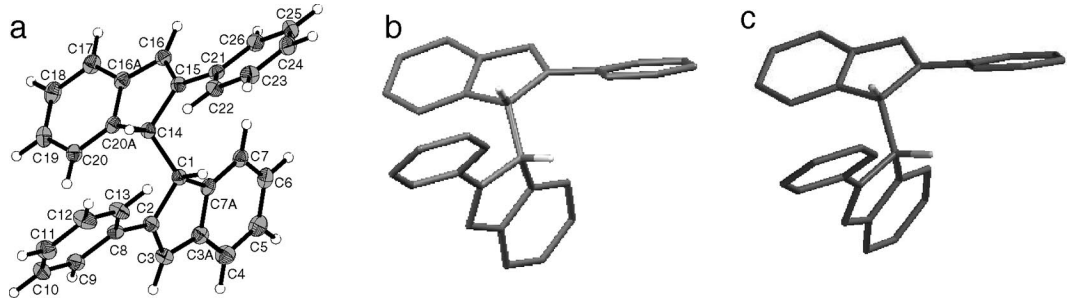


Figure 2. (a) X-ray crystal structure of *rac*-**7**; (b) Mercury[10] representation of *S*,*S*-**7**; (c) DFT energy-minimised structure of *S*,*S*-**7**.

respectively. Consequently, the indenyl moieties and the phenyl substituents in *meso*-**7** become non-equivalent, and this is reflected in its variable-temperature NMR spectra which reveal very significant line broadening in the carbon spectra at room temperature, and gradual sharpening of those signals as temperature is raised to 80 °C. Evidently, the steric crowding in *meso*-**7** causes restricted rotation about the C^1–C^{14} central single bond on the NMR timescale, thus indicating atropisomerism.

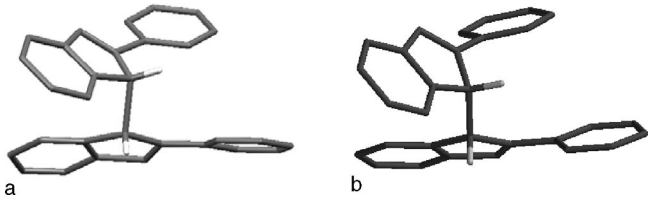
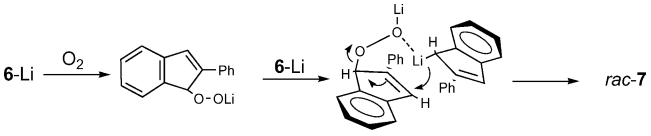


Figure 3. (a) X-ray crystal structure of *meso*-**7**, showing the molecular connectivity; (b) DFT energy-minimised structure of *meso*-**7**.

Although the barrier to interconversion of the enantiomers of *meso*-**7** was not accessible experimentally, it was probed computationally by calculating the relative energies of the energy-minimised ground state, and both the mirror-symmetric (C_s) and centrosymmetric (C_i) potential transition states, all at the B3LYP/6-31G** level. In the former, the barrier was evaluated as ca. 20 kcal mol^{-1}, and the central carbon–carbon bond, C^1–C^{14}, appears to have lengthened somewhat (from 1.57 Å to 1.64 Å) as it passes through the C_s structure. An imaginary frequency was found (25*i* cm^{-1}), and its vibrational twist motion is consistent with enantiomer conversion via this mirror-symmetric transition state. In the latter case, the C_i structure lies only ca. 11 kcal mol^{-1} above the ground state; however, during the rotation about the central C–C bond required to attain this geometry, both phenyl substituents would have to rotate simultaneously so as to avoid a steric confrontation with the indenyl moiety in the other half of the molecule, thus raising the barrier substantially and making this a rather unlikely eventuality.

In the light of these observations, one might envisage at least two viable scenarios to rationalise predominant formation of the racemic products in the presence of oxygen. Firstly, one could invoke initial reaction of the 2-substituted indenyllithium with dioxygen to form the corresponding peroxide; subsequent S_N2 displacement of the peroxide ion by a second anion *of the opposite configuration*, would thus generate an *R*,*R* (or *S*,*S*) product. A second, and in some ways more attractive proposal, that might alleviate the severe steric problems that would be encountered in a normal S_N2 reaction could proceed instead via an S_N2' mechanism. In the latter case, the incoming nucleophile (which must again adopt *the opposite configuration* to that of the peroxide-bearing carbon centre) approaches the indenyl-C(3) position in a *syn* fashion, possibly involving an interaction of its lithium cation with a peroxide oxygen (Scheme 3). Furthermore, in cases where it has been possible to determine the stereochemistry of the S_N2' process, the *syn* approach predominates.[15] Clearly, the stereochemistry of the nucleophilic displacement process must be heavily influenced by the steric hindrance arising from the bulky substituent at the indenyl-C(2) position. Moreover, because both dimers, *rac*- and *meso*-**7**, adopt stable *gauche*-conformations, it is not unreasonable to assume that the phenylindenyl moieties also favour a *gauche*-orientation in the transition state. Consideration of the least hindered possible approach trajectories for both S_N2 and S_N2' mechanisms led to the conclusion that the formation of *rac*-**7** is the more favourable.



Scheme 3. A possible mechanistic representation of an S_N2' route to *rac*-**7**.

In seeking precedents for such proposals, we note not only the reaction of indenyllithium with oxygen to form the corresponding hydroperoxide,[16] but also the report by Abeles[17] on the mechanism of action of dioxygenases in the methionine salvage pathway whereby a crucial step involves attack by a carbanion on dioxygen to form the corresponding alkyl peroxide anion. Although peroxide has frequently been used as an attacking nucleophile,[18] there are also examples where peroxide (or hydroperoxide) can be a leaving group, but we are well aware that cleavage of the oxygen–oxygen bond is the more normal observation.[19]

Following the method described by Hock,[16b] we attempted the oxidation of (2-phenylindenyl)lithium **6** with dioxygen at –70 °C. As anticipated, acidic workup yielded the hydroperoxide **8**, for which iodometric titration indicated a 65% yield. This correlates with the isolation of 2-phenyl-1-indenol (**10**), in 65% yield, thereby establishing that **6** readily forms the corresponding peroxide when treated with dioxygen.

To further test the plausibility of a non-radical nucleophilic pathway leading to dimers **7**, the cross-coupling of 1-bromo-2-phenylindene (**9**) with the lithium derivative **6** was studied (Scheme 2). It transpired that, when this reaction was carried out at 0 °C in ether, it resulted in the selective formation of *rac*-**7** in 72% yield while *meso*-**7** was formed in just 4% yield, i.e. a 95:5 ratio. Accordingly, it can be concluded that a nucleophilic mechanism is responsible for the selective formation of *rac*-dimers in the oxidative dimerisation of lithiated indenes and, possibly, other substrates. We envisage further applications of this significant finding in the area of selective syntheses of chiral, sterically hindered C_2-symmetrical molecules, and trust that these observations prompt others to undertake more detailed studies to verify, or modify, these mechanistic proposals.

Conclusions

The oxidative dimerisation of 2-substituted lithiated indenes leads to racemic hydrocarbons with a C_2-symmetric

bis-1,1′-indenyl core. The sterically constrained triptycene derivative, **4**, can be prepared by an oxidative dimerisation of 2-(9-triptycyl)indene. In solution, the molecule **4** undergoes correlated gear-like contra-rotation with a low activation energy leading to NMR equivalence of its "cogs" thus resulting in *dynamic* C_2-symmetry. However, in the solid state, the intermeshing of the pairs of triple paddlewheels breaks the C_2-symmetry of the system and gives rise to severe geometric perturbations. The analogous oxidative dimerisation of 2-phenylindenyl-lithium, **6**, likewise furnished the dimer *rac*-**7**, whereas the reaction with cupric chloride led to the formation of both *rac*- and *meso*-**7** dimers. Evidence for the possible involvement of a nucleophilic displacement, rather than a simple radical dimerisation pathway, leading to the formation of *rac*-**4** and *rac*-**7** is presented.

Experimental Section

General: All reactions were carried out under a nitrogen atmosphere unless otherwise stated. Column chromatography separations were carried out with a Buchi Sepacor machine with UV absorbance detector using silica gel particle size 40–63 mm. NMR spectra were acquired with Varian Inova 400 or 500 MHz spectrometers. Assignments were based on standard ^{1}H-^{1}H and ^{1}H-^{13}C two-dimensional techniques, and NOE measurements. 2-(9-Triptycenyl)indenyl (**1**), was prepared by benzyne addition to 9-(2-indenyl)anthracene[20] according to the previously described procedure.[2] Infrared spectra were recorded with a Perkin–Elmer Paragon 1000 FT-IR spectrometer and were calibrated with polystyrene. Melting points were determined with an Electrothermal ENG instrument and are uncorrected. Elemental analyses were carried out by the Microanalytical Laboratory at the University College Dublin.

***rac*-2,2′-Bis(9-triptycyl)-1,1′-biindenyl (*rac*-4):** A suspension of 9-(2-indenyl)-triptycene (**1**) (37 mg, 0.1 mmol) in diethyl ether (6 mL) was transferred under a nitrogen atmosphere to a round-bottom flask (25 mL) equipped with a rubber septum. Then, a solution of *n*BuLi (0.2 mmol) in hexanes was added, and the reaction mixture was stirred for 1 d while the nitrogen inlet was removed. The mixture was quenched with methanol (1 mL), extracted with dichloromethane and separated by chromatography by eluting with 5% dichloromethane in cyclohexane to give ketone **3** (5 mg, 8%) as a yellow glassy solid, and **4** (23 mg, 70%) as a white solid, m.p. 222–224 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, numbering in accord with Scheme 1, only positions C^1–C^{23} listed): δ = 7.84 (d, J = 7.3 Hz, 2 H, H^{19}), 7.70 (s, 2 H, H^{18}), 7.56 (d, J = 7.7 Hz, 6 H, $H^{1,8,13}$), 7.36 (d, J = 7.4 Hz, 2 H, H^{22}), 7.31 (d, J = 7.3 Hz, 6 H, $H^{4,5,16}$), 7.25 (t, J = 7.4 Hz, 2 H, H^{20}), 7.05 (t, J = 7.1 Hz, 2 H, H^{21}), 6.84, (t, J = 7.3 Hz, 6 H, $H^{3,6,15}$), 6.54 (t, J = 7.7 Hz, 6 H, $H^{2,7,14}$), 6.01 (s, 2 H, H^{23}), 5.29 (s, 2 H, H^{10}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 147.0 ($C^{4a,10a,11}$), 146.3 ($C^{8a,9a,12}$), 142.4 (C^{18a}), 144.6 (C^{17}), 145.3 (C^{22a}), 141.1 (C^{18}), 123.0 (C^{20}), 124.6 ($C^{2,7,14}$), 125.0 (C^{21}), 125.1 ($C^{3,6,15}$), 123.5 ($C^{4,5,16}$), 122.6 (C^{19}), 61.7 (C^9), 55.5 (C^{10}), 54.5 (C^{23}) ppm. MS (ES): m/z = 735 [MH^+]. $C_{58}H_{38}{\cdot}CH_2Cl_2$ (819.87): calcd. C 86.43, H 4.92; found C 85.90, H 5.01.

Ketone 3: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, numbering as for **4**): δ = 8.53 (s, 1 H, H^{18}), 7.60 (d, J = 7.4 Hz, 1 H, H^{22}), 7.49 (t, J = 7.4 Hz, 1 H, H^{20}), 7.40 (d, $H^{4,5,16}$, J = 7.3 Hz, 3 H, d), 7.37 (t, J = 7.1 Hz, 2 H, H^{21}), 7.34 (d, J = 7.7 Hz, 3 H, $H^{1,8,13}$), 7.29 (d, J = 7.3 Hz, 1 H, H^{19}), 7.00, (t, J = 7.3 Hz, 3 H, $H^{3,6,15}$), 6.95 (t, J = 7.7 Hz, 3 H, $H^{2,7,14}$), 5.40 (s, 2 H, H^{10}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 197.4 (C^{23}), 148.6 (C^{18}), 145.9 ($C^{8a,9a,12}$), 145.6 ($C^{4a,10a,11}$), 143.9 (C^{22a}), 137.1 (C^{17}), 134.5 (C^{21}), 130.0 (C^{18a}), 129.6 (C^{20}), 124.8 ($C^{2,7,14}$), 125.5 ($C^{3,6,15}$), 123.9 ($C^{4,5,16}$), 122.5 (C^{19}), 55.9 (C^9), 55.0 (C^{10}) ppm. MS (ES): m/z = 383.1 (100) [M + H]. IR (KBr): $\tilde{\nu}$ = 1714 cm^{-1}.

2-(9-Triptycyl)inden-1-ol (5): When a solution of **4** (23 mg) in dichloromethane was maintained under ambient conditions in air for 10 d, the products were purified to yield **5** (20 mg, 80%) as a yellow solid; m.p. 188–189 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, atom numbering as for **4**): δ = 7.20 (d, J = 7.3 Hz, 1 H, H^{19}), 7.09 (s, 1 H, H^{18}), 7.58 (d, J = 7.6 Hz, 3 H, $H^{1,8,13}$), 6.30 (d, J = 7.4 Hz, 1 H, H^{22}), 7.42 (d, J = 7.2 Hz, 3 H, $H^{4,5,16}$), 7.06 (t, J = 7.4 Hz, 1 H, H^{20}), 6.34 (t, J = 7.3 Hz, 1 H, H^{21}), 6.97, (t, J = 7.3 Hz, 3 H, $H^{3,6,15}$), 6.85 (t, J = 6.5 Hz, 3 H, $H^{2,7,14}$), 6.50 (s, 1 H, H^{23}), 5.43 (s, 1 H, H^{10}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.1 ($C^{4a,10a,11}$), 146.5 ($C^{8a,9a,12}$), 141.0 (C^{18a}), 139.8 (C^{17}), 142.6 (C^{22a}), 139.9 (C^{18}), 128.2 (C^{20}), 124.6 ($C^{2,7,14}$), 126.2 (C^{21}), 125.2 ($C^{3,6,15}$), 123.3 ($C^{4,5,16}$), 120.6 (C^{19}), 88.2 (C^{23}), 58.7 (C^9), 55.2 (C^{10}) ppm. MS (ES): m/z = 367 (65) [M – OH]. IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1}.

***rac*-2,2′-Diphenyl-1,1′-biindenyl (*rac*-7):** 2-Phenylindene (38 mg, 0.2 mmol) and ether (6 mL) were transferred under a nitrogen atmosphere to a round-bottom flask (25 mL) equipped with a rubber septum. A solution of *n*BuLi (0.2 mmol) in hexanes was then added to the flask. After 1 h, a clear solution of 2-phenylindenyllithium (**6**) was formed. The reaction mixture was stirred for 1 d while the nitrogen inlet was removed. The mixture was quenched with methanol (1 mL), extracted with dichloromethane and separated by chromatography by eluting with 5% dichloromethane in cyclohexane to give *rac*-**7** (9.6 mg, 25%) as a white solid, m.p. 191 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, numbering in accord with Figure 2, a): δ = 7.84 (d, J = 6.8 Hz, 4 H, $H^{9,13,22,26}$), 7.58 (t, J = 7.4 Hz, 4 H, $H^{10,12,23,25}$), 7.40 (t, J = 7.4 Hz, 2 H, $H^{11,24}$), 7.19 (s, 2 H, $H^{3,16}$), 7.14 (d, J = 7.3 Hz, 2 H, $H^{4,17}$), 7.00 (t, J = 7.3 Hz, 2 H, $H^{5,18}$), 6.99 (d, J = 7.3 Hz, 2 H, $H^{7,20}$), 6.81 (t, J = 7.3 Hz, 2 H, $H^{6,19}$), 4.49 (s, 2 H, $H^{1,14}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.6 ($C^{2,15}$), 143.8 ($C^{3a,16a}$), 143.4 ($C^{7a,20a}$), 136.0 ($C^{8,21}$), 129.2 ($C^{3,10,12,16,23,25}$), 127.7 ($C^{11,24}$), 127.2 ($C^{9,13,22,26}$), 126.7 ($C^{5,18}$), 126.2 (C^{21}), 124.1 ($C^{6,19}$), 122.9 ($C^{7,20}$), 120.7 ($C^{4,17}$), 49.3 ($C^{1,14}$) ppm. $C_{30}H_{22}$ (382.51): calcd. C 94.20, H 5.80; found C 94.14, H 5.84. No isomeric dimer, *meso*-**7**, was found indicating that its yield was below 1%.

***meso*-2,2′-Diphenyl-1,1′-biindenyl (*meso*-7):** A solution of **6** (0.4 mmol) in diethyl ether (6 mL) was added slowly to a cold (–20 °C) suspension of cupric chloride (54 mg, 0.4 mmol) in THF (3 mL). The mixture was warmed to 0 °C and stirred for 15 h after which it was quenched with methanol (0.5 mL), extracted with dichloromethane and separated by chromatography by eluting with 5% dichloromethane in cyclohexane to give *meso*-**7** (18 mg, 23%) as a white solid, m.p. 181–182 °C. $C_{30}H_{22}{\cdot}0.2C_4H_{10}O$ (397.33): calcd. C 93.11, H 6.09; found C 93.53, H 5.94. ^{1}H NMR (500 MHz, $(CDCl_2)_2$, 80 °C, numbering as in *rac*-**7**): δ = 7.30 (d, J = 7.3 Hz, 4 H, $H^{9,13,22,26}$), 7.28 (m, 4 H, $H^{4,17,6,19}$), 7.24 (d, J = 7.5 Hz, 2 H, $H^{7,20}$), 7.15 (t, J = 7.5 Hz, 2 H, $H^{5,18}$), 7.05 (br. s, 4 H, $H^{10,12,23,25}$), 7.00 (br. s, 2 H, $H^{11,24}$), 6.58 (s, 2 H, $H^{3,16}$), 4.69 (s, 2 H, $H^{1,14}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.3 ($C^{2,15}$), 145.5 ($C^{7a,20a}$), 144.3 ($C^{3a,16a}$), 136.0 ($C^{8,21}$), 128.2 ($C^{3,16}$), 127.7 ($C^{6,19}$), 127.2 ($C^{4,17,10,12,23,25}$), 127.0 ($C^{9,13,22,26}$), 124.5 ($C^{5,18}$), 122.6 ($C^{11,24}$), 120.8 ($C^{7,20}$), 50.2 ($C^{1,14}$); and *rac*-**7** (16 mg, 20%) ppm.

Coupling of 6 with 1-Bromo-2-phenylindene (9):[21] A solution of **9** (108 mg, 0.4 mmol) in diethyl ether (1 mL) was added to a stirred

solution of **6** (0.4 mmol) at –20 °C. The mixture was treated as above to give *rac*-**7** (110 mg, 72%) and *meso*-**7** (6 mg, 4%).

2-Phenyl-1-indenol (10): A solution of **6** (0.4 mmol) was cooled to –70 °C and the nitrogen was replaced with dioxygen for 4 h after which diluted hydrochloric acid (0.8 mL, 1 M) was added. The mixture was extracted at 5 °C with ether, the organic layer was treated with an excess potassium iodide and titrated with a sodium thiosulfate solution indicating the presence of 0.26 mmol (65%) of the peroxide **8**. The residue was separated by chromatography to give the alcohol **10** (54 mg, 65%) as a white solid; m.p. 150–151 °C, lit. 152 °C.[22]

X-ray Measurements for *rac*-4, *rac*-7: Crystal data were collected with a Bruker SMART APEX CCD area detector diffractometer, and are listed in Table 1. A full sphere of the reciprocal space was scanned by phi-omega scans. Pseudo-empirical absorption correction based on redundant reflections was performed by the program SADABS.[23] The structures were solved by direct methods using SHELXS-97[24] and refined by full-matrix least-squares on F^2 for all data using SHELXL-97.[25] All hydrogen atoms, except for the ones of solvent molecules, were located in the difference Fourier map and allowed to refine freely with isotropic thermal displacement factors. Hydrogen atoms of the solvents were added at calculated positions and refined using a riding model. Their isotropic displacement parameters were fixed to 1.2 times the equivalent isotropic displacement parameters of the parent carbon atom. Anisotropic temperature factors were used for all non-hydrogen atoms.

Table 1. Crystallographic data for *rac*-**4** and *rac*-**7**.

	rac-**4**	*rac*-**7**
Formula	$C_{58}H_{38}{\cdot}2CH_2Cl_2$	$C_{30}H_{22}$
M	907.74	382.48
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)
a [Å]	19.2854(13)	8.7327(7)
b [Å]	14.3423(10)	10.8598(9)
c [Å]	15.9639(11)	21.6999(18)
α [°]	90	90
β [°]	90.129(2)	94.226(2)
Γ [°]	90	90
V [Å^3]	4415.6(5)	2052.3(3)
Z	4	4
$\rho_{calcd.}$ [g cm^{-3}]	1.361	1.238
T [K]	100(2)	100(2)
μ [mm^{-1}]	0.311	0.070
$2\theta_{max}$ [°]	49.58	52.00
Reflns. measured	33803	17291
Reflns. used	7571	4025
R_{int}	0.0416	0.0239
Parameters	729	359
Final R values [$I>2\sigma(I)$]:		
R_1	0.0542	0.0366
wR_2	0.1322	0.0896
R values (all data):		
R_1	0.0673	0.0415
wR_2	0.1401	0.0930
GOF on F^2	1.042	1.029

CCDC-677070 (for *rac*-**4**) and CCDC-677071 (for *rac*-**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details: Computational geometry optimisations were carried out using B3LYP (a density functional theory method) for determining equilibrium geometries of *rac*-**7** and *meso*-**7**, and for calculating the barrier to interconversion of the enantiomers of *meso*-**7**. This interconversion barrier was calculated from the relative energies of the energy-minimised ground state, and the mirror-symmetric and centrosymmetric transition states. The basis set 6-31G** was employed for all calculations, and the software package used was Titan (Jaguar, version 3.5).[13]

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[1] E. V. Banide, B. C. Molloy, Y. Ortin, H. Müller-Bunz, M. J. McGlinchey, *Eur. J. Org. Chem.* **2007**, 2611–2622.
[2] K. Nikitin, H. Müller-Bunz, Y. Ortin, M. J. McGlinchey, *Org. Biomol. Chem.* **2007**, *5*, 1952–1960.
[3] H. Iwamura, K. Mislow, *Acc. Chem. Res.* **1988**, *21*, 175–182.
[4] S. Brydges, L. E. Harrington, M. J. McGlinchey, *Coord. Chem. Rev.* **2002**, *233*, 75–105, and references therein.
[5] F. Chiaravalloti, L. Gross, K.-H. Rieder, S. M. Stojkovic, A. Gourdon, C. Joachim, F. Moresco, *Nat. Mater.* **2007**, *6*, 30–33.
[6] R. E. Bulo, F. Allaart, A. W. Ehlers, F. J. J. de Kanters, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, *J. Am. Chem. Soc.* **2006**, *128*, 12169–12173.
[7] E. R. Kay, D. A. Leigh, F. Zerbetto, *Angew. Chem. Int. Ed.* **2007**, *46*, 72–191.
[8] D. A. Dougherty, F. M. Llort, K. Mislow, J. F. Blount, *Tetrahedron* **1978**, *34*, 1285–1300.
[9] L. E. Harrington, J. F. Britten, M. J. McGlinchey, *Tetrahedron Lett.* **2003**, *44*, 8057–8060.
[10] *Mercury* 1.4.2, available free from http://www.ccdc.cam.ac.uk/mercury
[11] L. E. Harrington, L. S. Cahill, M. J. McGlinchey, *Organometallics* **2004**, *23*, 2884–2891.
[12] R. A. Gancarz, J. F. Blount, K. Mislow, *Organometallics* **1985**, *4*, 2028–2032.
[13] Titan. Wavefunction Inc. Irvine, CA and Schrödinger Inc. Portland, OR, USA.
[14] a) P. Nicolet, J. Y. Sanchez, A. Benaboura, M. J. M. Abadie, *Synthesis* **1987**, 202–203; b) U. Simmross, K. Müllen, *Chem. Ber.* **1993**, *126*, 969–973.
[15] J. March, *Advanced Organic Chemistry*, 4th ed., John Wiley & Sons, New York, **1992**, pp. 328–329.
[16] a) E. C. Friedrich, D. B. Taggart, *J. Org. Chem.* **1975**, *40*, 720–723; b) H. Hock, F. Ernst, *Chem. Ber.* **1959**, *92*, 2723.
[17] Y. Dai, T. C. Pochapsky, R. H. Abeles, *Biochemistry* **2001**, *40*, 6379–6387.
[18] B. Plesničar in *The Chemistry of the Functional Groups, Peroxides* (Ed.: S. Patai), John Wiley & Sons, New York, **1983**, ch. 17, pp. 521–584.
[19] G. Merényi, J. Lind, *J. Am. Chem. Soc.* **1991**, *113*, 3146–3153.
[20] D.-W. Lee, J. Yun, *Bull. Korean Chem. Soc.* **2004**, *25*, 29–30.
[21] P. C. Jocelyn, *J. Chem. Soc.* **1954**, 1641–1642.
[22] a) T. Matsuda, M. Makino, M. Murakami, *Chem. Lett.* **2005**, *34*, 1416–1417; b) D. Kuck, T. Lindenthal, A. Schuster, *Chem. Ber.* **1992**, *125*, 1449–1460.
[23] G. M. Sheldrick, *SADABS*, Bruker AXS Inc., Madison, WI 53711, **2000**.
[24] G. M. Sheldrick, *SHELXS-97*, University of Göttingen, **1997**.
[25] G. M. Sheldrick, *SHELXL-97-2*, University of Göttingen, **1997**.

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