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Helical Atropisomers of Strained Phenanthrenes by Photochemistry of Aromatic Pauson–Khand Cycloadducts

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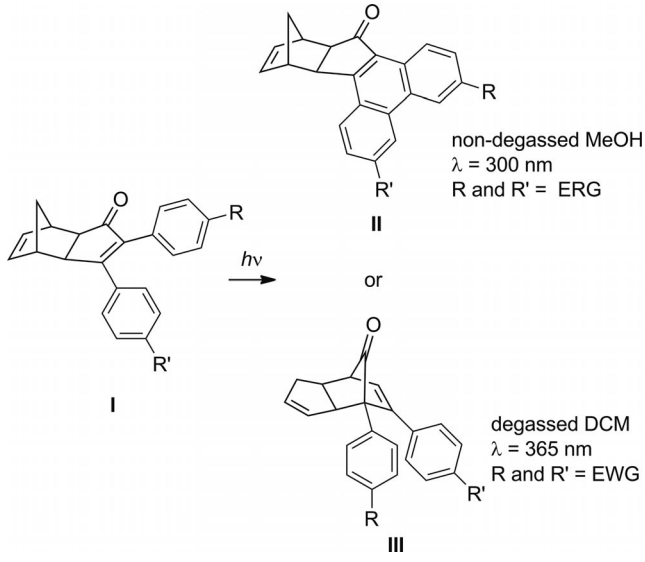
Norbornene and norbornadiene Pauson–Khand adducts of bis(3,5-dimethylphenyl)acetylene and bis(3,4,5-trimethylphenyl)acetylene were prepared. These compounds were subjected to a photochemical 6π-electrocyclic oxidative aromatization reaction to give the corresponding phenanthrene compounds in satisfactory yield in the case of norbornene derivatives. The helical twist imposed by the methyl groups at the 3- and 5-positions on the aromatic rings led to two atropisomers as a result of the non-planar helical phenanthrene structure. The molecular structures and conformational stabilities of these atropisomers were examined by X-ray crystallography and variable temperature NMR studies.

Introduction

Photochemical reactions are among the most convenient tools for the synthesis of strained compounds. During the last decade, we have uncovered several photochemical reactions involving cyclopentenones obtained from Pauson–Khand reactions (PKRs).[1,2] We have recently studied[2] the photochemistry of aromatic cycloadducts **I**, which, by choosing suitable reaction conditions, can selectively provide either electrocyclized (**II**) or photorearranged (**III**) products (Scheme 1). The starting cyclopentenones are easily obtained either in racemic or enantioenriched form[3] by Pauson–Khand cycloaddition of bis-aromatic acetylenes with norbornadiene.

The straightforward access to phenanthrene compounds **II** from diaryl acetylenes led us to study the synthetic applications of compounds **II** further. We envisioned that a suitable substitution pattern in the 3- and 5-positions or the 3-, 4-, and 5-positions of the aryl groups would result in conformationally restricted phenanthrene compounds. A relatively bulky alkyl group (R) would cause severe van der Waals repulsion between the two closely arranged substituents in the 3- and 5-positions, and distortion of the aromatic plane would be expected in order to relieve such steric congestion. If this occurred, the molecule would adopt a helical structure, leading to two possible isomers ($\mathbf{V_M}$ and $\mathbf{V_P}$; Scheme 2). Thus, if the interconversion barrier between the two conformers, which in turn is dependent on the steric volume of the alkyl groups, is high enough, the stereoisomers could be separated, thus leading to compounds with helical chirality.



Scheme 1. Electrocyclization or photorearranged products arising from aromatic cycloadducts **I**.

Helicenes[4,5] have attracted increasing attention because of their extraordinary optical[6] and electronic properties,[4c,4d,7] which are closely associated with their helically chiral structure. Therefore, we addressed whether the chirality of the bicyclic cyclopentenone skeleton could be transmitted to the putative helicenic chirality of the phenanthrene, thus allowing atropisomeric compounds $\mathbf{V_M}$ and $\mathbf{V_P}$ to be formed in a stereoselective way (Scheme 2).[8] In other words, we aimed to determine whether the electrocyclic

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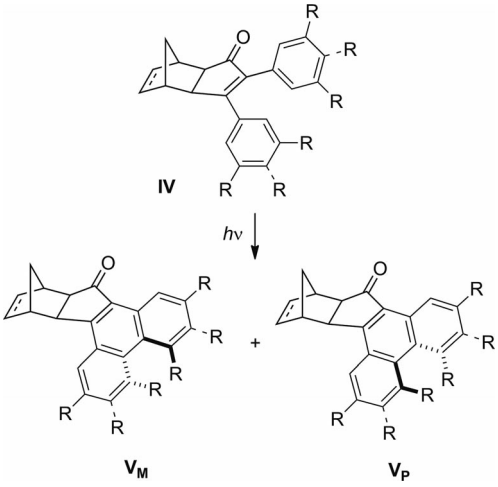
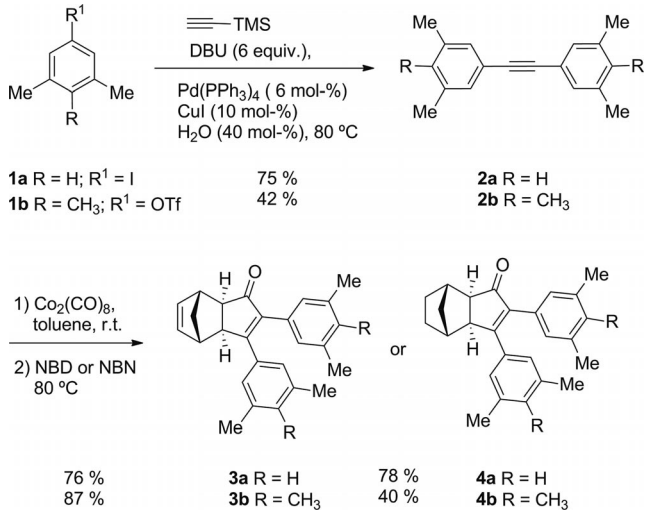
photochemical reaction[9] of adducts **IV** would allow a new mode of access to helicene-like molecules. In this paper, we describe the synthesis and structural study of phenanthrene derivatives **V** with methyl substituents.



Scheme 2. Atropisomers $\mathbf{V_M}$/$\mathbf{V_P}$ formed in a photochemical reaction.

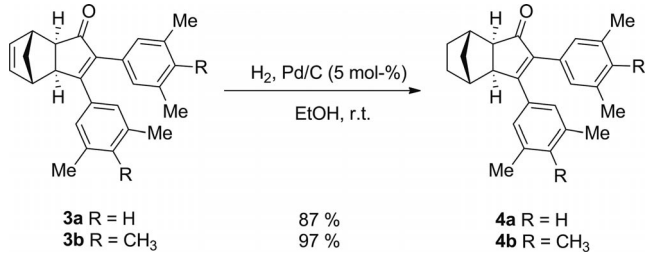
Results and Discussion

Bis(3,5-dimethylphenyl)acetylene (**2a**) and bis(3,4,5-trimethylphenyl)acetylene (**2b**) were prepared in satisfactory yields from the corresponding aryl iodide or aryl triflate by modified Sonogashira coupling reactions.[2] The PKRs using norbornene (NBN) or norbornadiene (NBD) gave the corresponding cyclization products **3a**–**b** or **4a**–**b**, respectively, in medium to excellent yields (Scheme 3). Products **4a**–**b** were also obtained directly by hydrogenation of NBD cycloadducts **3a**–**b** (Scheme 4).



Scheme 3. Synthesis of NBN and NBD cycloadducts; DBU = 1,8-diazabicycloundec-7-ene.

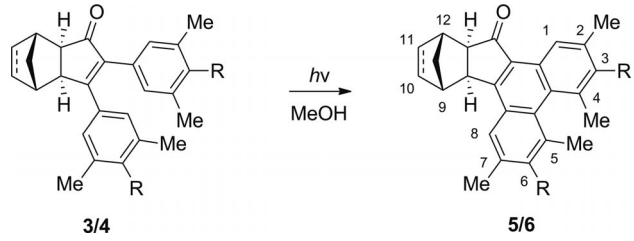
With cyclopentenones **3a**–**b** and **4a**–**b** in hand, we started the study of the photochemical reactions. Irradiation of



Scheme 4. Reduction of NBD cycloadducts **3a/3b**.

NBD derivative **3a** in methanol solution at 300 nm in a Rayonet apparatus (16 lamps) gave phenanthrene compound **5a** in a yield of only 33% after 10 d (Table 1, entry 1). The presence of the additional methyl groups in compound **3b** further hampered the reaction, giving less than a 13% yield of **5b** after 6 d of irradiation. Under the same conditions, compound **4a** behaved similarly (Table 1, entry 3). All these reactions gave crude product mixtures that were difficult to purify.

Table 1. Synthesis of phenanthrene compounds **5** and **6**.



Entry	Starting material	R	Light [nm]	Oxidant	Time	Product	Yield [%]
1	**3a**	H	300 [a]	O_2	10 d	**5a**	33
2	**3b**	Me	300 [a]	O_2	6 d	**5b**	13
3	**4a**	H	300[[a]	O_2	12 d	**6a**	22
4	**4a**	H	365[b]	I_2	7 d	**6a**	96
5	**4b**	Me	365[b]	I_2	10 d	**6b**	64
6	**4a**	H	300 [a]	I_2	36 h	**6a**	96
7	**4b**	Me	300 [a]	I_2	53 h	**6b**	94

[a] 16 lamps. [b] 8 lamps.

To improve the reaction conditions, we added an external oxidant to the photochemical reaction. We focused on compounds **4a**–**b** derived from NBN, which lacked the olefinic bond, and thus we avoided addition of iodine to the double bond. In the presence of iodine, the photochemical reaction gave much better results. Irradiation of **4a** at 365 nm in methanol with 1 equiv. I_2 gave **6a** cleanly in 96% yield (Table 1, entry 4) after 7 d of irradiation. Under the same conditions, **4b** gave **6b** in moderate yield after 10 d of irradiation (Table 1, entry 5). The reactions, especially in the case of **4b**, were extremely slow (10 d to completion). This difference in reactivity is consistent with the fact that the placement of an extra methyl group enhances the steric crowding by "buttressing" the methyl groups located at the 4- and 5-positions.[9] Irradiation with 16 lamps at 300 nm, also using iodine as oxidant, allowed a reduction of the reaction times to 1–2 d, giving compounds **6a** and **6b** cleanly in excellent yields (Table 1, entries 5 and 6).

As expected, photochemical product **6a** was found to be mixture of atropisomers. The isomeric ratio was determined to be 3:1 by ^{1}H NMR spectroscopy. Crystallization of the mixture from DMSO allowed us to obtain a single crystal that was suitable for X-ray diffraction.[10] The molecular structure of this crystal is shown in Figure 1. The phenanthrene fragment was completely distorted, with the methyl substituents in the 4- and 5-positions being displaced out of the mean plane of the aromatic system as a result of steric hindrance. The twist (dihedral angle C^4–C^{4a}–C^{4b}–C^5) between the mean planes of the aromatic rings was 32.3° (Figure 1). The configuration of this atropisomer was M. The bond angles C^{4a}–C^4–CH_3 and C^{4b}–C^5–CH_3 were 123.0 and 123.6°, respectively. The steric repulsion between the methyl groups in the 4- and 5-positions was released not only by the dihedral distortions but also by a widening of these bond angles from the theoretical 120°. The ^{1}H NMR spectrum of the crystals showed that a rapid equilibration took place in solution. Variable temperature NMR studies indicated that the coalescence of the two atropisomers **6a$_M$** and **6b$_P$** took place at 70.15 °C (Figure 2). The Gibbs free energy of activation ($\Delta_r G^{\neq}$) was calculated to be endoergic by +17.4 kcal mol^{-1}.

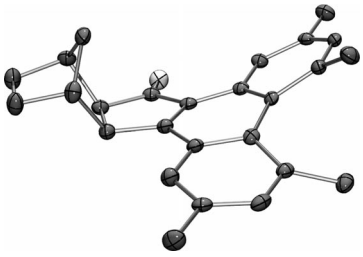


Figure 1. X-ray diffraction structure[10] of major atropisomer **6a$_M$**.

The geometry and energy of the atropisomers **6a$_M$** and **6a$_P$** were calculated by ab initio DFT molecular orbital calculations (RB3LYP 6-31G*//6-311+G**).[11] The enthalpy of formation of the major atropisomer **6a$_M$** was found to be 0.5 kcal mol^{-1} lower than that of **6a$_P$**. The optimized geometry of **6a$_M$** was very close to that observed by X-ray diffraction. The dihedral angle C^4–C^{4a}–C^{4b}–C^5 between the mean planes of the aromatic rings was 33.7° (vs. 32.3° in the X-ray structure). Since the most stable isomer was the major and crystalline one, we concluded that the atropisomeric equilibrium is controlled by the thermodynamic stability of the two isomers. The transition state of the interconversion between the two atropisomers was also located and geometry-optimized. The energy of the transition state was found to be 17.2 kcal mol^{-1} higher than that of **6a$_M$**. This energy difference perfectly matches the experimental value of the activation energy. The bond angles C^{4a}–C^4–CH_3 and C^{4b}–C^5–CH_3 were 129.9 and 129.5°, respectively, reflecting that the steric repulsion between the methyl groups was released by widening the bond angles.

In the case of photoadduct **6b**, derived from bis(3,4,5-trimethylphenyl)acetylene (**2b**), the ^{1}H NMR spectrum showed a 6:1 mixture of atropisomers. The extra methyl

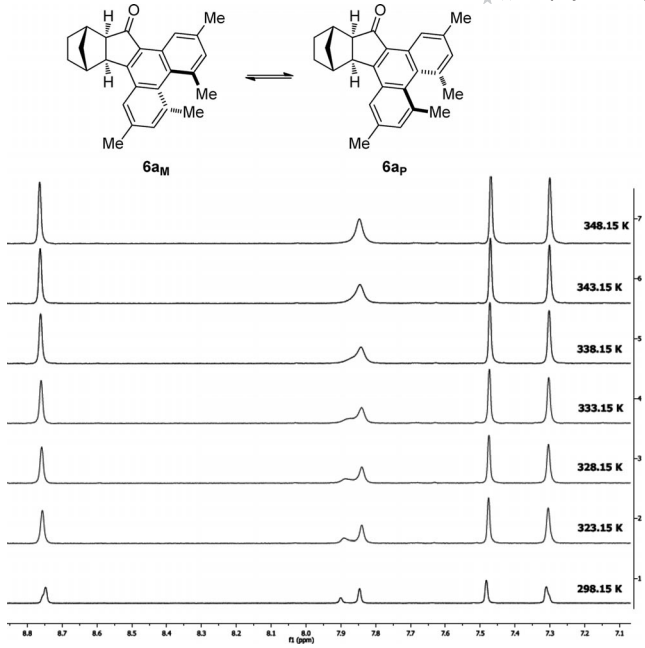


Figure 2. Variable temperature ^{1}H NMR spectra of **6b**, showing the coalescence temperature of the two atropisomers.

groups not only lowered the rate of the photochemical reaction, but also increased the atropisomeric ratio of the mixture. Both isomers were isolated sequentially by crystallization from a mixture of CH_2Cl_2/MeOH, and when analyzed by ^{1}H NMR spectroscopy, they revealed high purities of 99 and 98%, respectively (Figure 3).

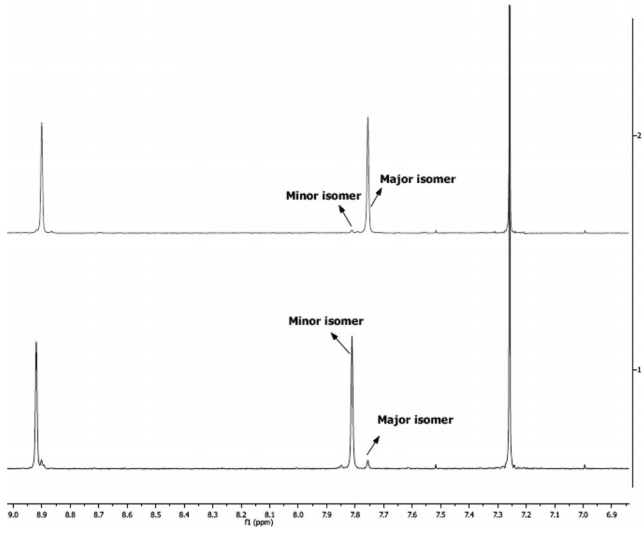


Figure 3. Aromatic region of the ^{1}H NMR spectra of atropisomers **6b$_M$** and **6b$_P$**.

A crystal of the major isomer was also analyzed by X-ray diffraction. The structure obtained revealed that this was again the M atropisomer (i.e., **6b$_M$**), and it revealed a distorted phenanthrene moiety with a significantly larger twist angle (35.9° vs. 32.1°) than that seen in **6a$_M$** (Figure 4). The larger dihedral angle was due to the strain arising from the extra methyl groups placed between the other two (i.e.,

at positions 3 and 6 of the phenanthrene fragment; 4 and 4' of the starting acetylene). The main effect of the extra methyl groups is to prevent the widening of the bond angles, since the methyl groups at positions 3 and 6, increase the steric repulsion when these bond angles widen. This effect can be clearly appreciated in the X-ray structure. The bond angles C^{4a}–C^{4}–CH_3 and C^{4b}–C^{5}–CH_3 in $\mathbf{6b_M}$ are 121.7 and 120.6°, respectively, much closer to the theoretical 120° than those in $\mathbf{6a_M}$. Therefore, the buttressing effect is due to the energy penalty paid in any widening of the methyl bond angles. The repulsion should be much bigger in the transition state, which should result in a higher energy barrier for the interconversion between atropisomers $\mathbf{6b_M}$ and $\mathbf{6b_P}$.

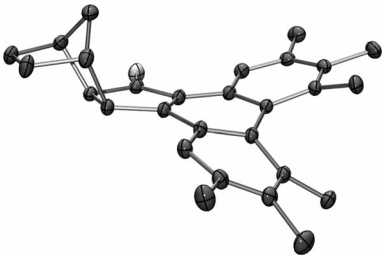


Figure 4. X-ray diffraction structure[10] of atropisomer $\mathbf{6b_M}$.

The higher conformational rigidity of **6b** relative to **6a** was confirmed by variable temperature NMR spectroscopy. A mixture of the two atropisomers was heated in DMSO solution up to 125 °C, but a coalescence point could not be reached. However, on heating up a solution of a pure isomer, it slowly isomerized to give a 2.5:1 thermodynamic mixture (Figure 5). This observation indicated the need for bulkier substituents to achieve stable atropisomers. The synthesis of more strained compounds of this type is currently being pursued in our laboratory. The results will be reported in due course.

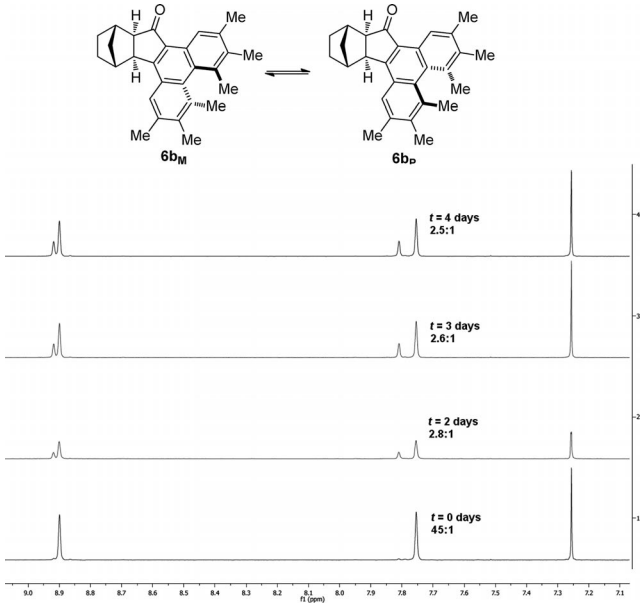


Figure 5. Isomerization of atropisomer $\mathbf{6b_M}$.

Conclusions

In summary, in this paper, we report the preparation of methyl-substituted phenanthrene compounds by photochemical electrocyclization of Pauson–Khand adducts of bis(3,5-dimethylphenyl)acetylene and bis(3,4,5-trimethylphenyl)acetylene. These electrocyclized products have been fully characterized by X-ray crystallography and NMR spectroscopy. The repulsion between the two methyl groups in the 4- and 5-positions of the phenanthrene systems causes a helical distortion of the planar aromatic system, thus yielding two atropisomers. The placement of extra methyl groups in the 3- and 6-positions enhances the steric crowding by "buttressing" the methyl groups, which results in more strained and helically distorted phenanthrenes. As a result, it has been possible to isolate the two atropisomers of **6b** by crystallization. However, the steric repulsion was not enough to prevent equilibration in solution. Our findings pave the way for the preparation of configurationally stable helicenic compounds.

Experimental Section

3,4,5-Trimethylphenyl Trifluoromethansulfonate (1b): Trifluoromethanesulfonic anhydride (0.95 mL, 5.56 mmol) was added dropwise to a solution of 3,4,5-trimethylphenol (0.5 g, 3.3 mmol) and triethylamine (1.5 mL) in CH_2Cl_2 (17 mL) at –15 °C under an inert atmosphere. The reaction was left overnight and was then quenched with H_2O and brine. The aqueous phase was extracted with CH_2Cl_2 (× 3). The combined organic extracts were dried with $MgSO_4$ and concentrated. Purification by flash chromatography (SiO_2, hexanes) gave **1b** (0.88 g, 99%) as a colorless oil. IR (film): $\tilde{\nu}$ = 3052, 1420, 1209, 1142, 1014, 956, 842 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.15 (s, 3 H, CH_3), 2.31 (s, 2 H, 2 CH), 6.91 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.09 (CH_3), 20.80 (2 CH_3), 117.25 (C), 119.99 (2 CH), 135.58 (C), 138.67 (2 C), 146.77 (C) ppm. MS: *m/z* = 269.6 $[M + H]^+$.

Bis(3,5-dimethylphenyl)acetylene (2a): $Pd(PPh_3)_4$ (223 mg, 0.19 mmol), CuI (62 mg, 0.32 mmol) and 3,5-dimethyl-1-iodobenzene (0.47 mL, 3.23 mmol) were placed into a Schlenk tube under a nitrogen atmosphere. While stirring, dry toluene (16 mL) was added to give a solution with a starting material concentration of 0.20 M. Nitrogen-sparged DBU (2.96 mL, 19.4 mmol) was then added, and then the reaction tube was purged with nitrogen. Distilled water (24 μL, 1.29 mmol) and ice-chilled trimethylsilylacetylene (234 μL, 1.6 mmol) were added sequentially, and then the tube was capped tightly. The mixture, protected from light, was stirred and heated at 80 °C for 18 h. The reaction mixture was then cooled to room temperature and partitioned between diethyl ether and distilled water. The organic phase was washed with 10% HCl (× 3) and brine, dried with $MgSO_4$, and evaporated in vacuo. Product **2a** (451 mg, 75%) was isolated by flash chromatography as a white solid; m.p. 123 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 12 H, CH_3), 6.93 (s, 2 H, CH), 7.14 (s, 4 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.08, 88.02, 123.00, 129.22, 130.00, 137.78 ppm. GC-MS: *m/z* (%) = 234 (100) $[M]^+$. $C_{28}H_{18}$ (354.45): calcd. C 92.26, H 7.74; found C 92.33, H 7.72.

Bis(3,4,5-Trimethylphenyl)acetylene (2b): The procedure described for the synthesis of **2a** was followed using: $Pd(PPh_3)_4$ (141 mg, 0.12 mmol), CuI (38 mg, 0.2 mmol), (3,4,5-trimethylphenyl)triflate

(540 mg, 2.0 mmol), DBU (1.83 mL, 12 mmol), distilled water (15 μL, 0.81 mmol), ice-chilled (trimethylsilyl)acetylene (145 μL, 1.0 mmol), and toluene (10 mL). The reaction mixture was heated at 65 °C for 18 h. Product **2b** (110 mg, 42%) was isolated as a white solid by trituration with methanol. IR (film): $\tilde{\nu}$ = 2923, 1460 1377, 1211, 1144, 960 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.18 (s, 6 H, CH_3), 2.27 (s, 12 H, CH_3), 7.18 (s, 4 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.38 (2 CH_3), 20.37 (4 CH_3), 97.13 (2 C), 119.23 (2 C), 130.39 (4 CH), 136.40 (2 C), 137.28 (4 C) ppm. ESI-HRMS: calcd. for $C_{20}H_{23}$ $[M + H]^+$ 263.1794; found 263.1795; calcd. for $C_{40}H_{45}$ $[2M + H]^+$ 525.3515; found 525.3519.

General Procedure for the Thermal PKRs: Octacarbonyldicobalt (1.1 equiv.) was added to a solution of alkyne (1 equiv.) in hexane or toluene (with the alkyne at a concentration of 0.02 M). The reaction mixture was stirred, and evolution of CO was monitored by a bubbler connected to an outlet. After 1 h of stirring, the alkene (10 equiv.) was added, the mixture was then heated, and the reaction was monitored by TLC. When no remaining starting complex was observed, the reaction mixture was allowed to cool and the flask was opened to air and stirred for 30 minutes. The crude product was filtered through a SiO_2 pad, evaporated, and purified by flash chromatography to give the corresponding cyclopentenone.

(1*S,2*S**,6*R**,7*R**)-4,5-Bis(3,5-dimethylphenyl)tricyclo[5,2,1,$0^{2,6}$]-deca-4,8-dien-3-one (3a):** Following the general procedure, bis(3,5-dimethylphenyl)acetylene (0.27 mL, 1.14 mmol), dicobalt octacarbonyl (429 mg, 1.25 mmol), and norbornadiene (0.95 mL, 11.39 mmol) were used. The reaction mixture was stirred overnight at 80 °C. Purification by flash chromatography on SiO_2 (Combiflash®, hexanes/EtOAc gradient) gave **3a** (309 mg, 76%) as a white solid; m.p. 187 °C. IR (film): $\tilde{\nu}$ = 2916, 1694, 1601, 1351, 1243, 685 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.44 (AB, J = 9 Hz, 1 H, CH_2), 1.48 (AB, J = 9 Hz, 1 H, CH_2), 2.22 (s, 6 H, CH_3), 2.24 (s, 6 H, CH_3), 2.57 (d, J = 5 Hz, 1 H, CH), 2.63 (s, 1 H, CH), 3.10 (s, 1 H, CH), 3.31 (d, J = 5 Hz, 1 H, CH), 6.31 (AB, J = 5, 3 Hz,, 1 H, CH), 6.34 (AB, J = 5, 3 Hz, 1 H, CH), 6.79 (s, 2 H, CH), 6.90 (s, 1 H, CH), 6.92 (s, 2 H, CH), 6.96 (s, 1 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4 (2 CH_3), 21.4 (2 CH_3), 42.0 (CH_2), 43.6 (CH), 44.3 (CH), 50.3 (CH), 52.8 (CH), 126.4 (2 CH), 127.0 (2 CH), 130.0 (CH), 131.4 (CH), 132.3 (C), 135.0 (C), 137.8 (2 C), 137.8 (2 C), 138.0 (CH), 138.5 (CH), 144.1 (C), 169.9 (C), 207.8 (C=O) ppm. $C_{30}H_{34}O{\cdot}0.25H_2O$: calcd. C 86.99, H 7.44; found C 86.88, H 7.47. ESI-HRMS: calcd. for $C_{26}H_{27}O$ $[M + H]^+$ 355.2062; found 355.2064; calcd. for $C_{52}H_{52}O_2Na$ $[2M + Na]^+$ 731.3865; found 731.3882.

(1*S,2*S**,6*R**,7*R**)-4,5-Bis(3,4,5-Trimethylphenyl)tricyclo[5,2,1,$0^{2,6}$]-deca-4,8-dien-3-one (3b):** Following the general procedure, bis(3,4,5-trimethylphenyl)acetylene (110 mg, 0.42 mmol), dicobalt octacarbonyl (175 mg, 0.46 mmol), and norbornadiene (0.45 mL, 4.20 mmol) were used. The reaction mixture was stirred for 24 h at 80 °C. Purification by flash chromatography on SiO_2 (hexanes/EtOAc gradient) gave **3b** (153 mg, 87%) as a white solid; m.p. 188 °C. IR (film): $\tilde{\nu}$ = 2916, 1692, 1502, 1245, 731 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.42 (AB, J = 9 Hz, 1 H, CH_2), 1.47 (AB, J = 9 Hz, 1 H, CH_2), 2.16 (s, 3 H, CH_3), 2.16 (s, 3 H, CH_3), 2.18 (s, 6 H, CH_3), 2.21 (s, 6 H, CH_3), 2.56 (d, J = 5 Hz, 1 H, CH), 2.65 (s, 1 H, CH), 3.09 (s, 1 H, CH), 3.31 (d, J = 5 Hz, 1 H, CH), 6.30 (AB, J = 5, 3 Hz, 1 H, CH), 6.34 (AB, J = 5, 3 Hz, 1 H, CH), 6.83 (s, 2 H, CH), 7.01 (s, 2 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.4 (CH_3), 15.7 (CH_3), 20.7 (2 CH_3), 20.8 (2 CH_3), 42.1 (CH_2), 43.8 (CH), 44.2 (CH), 50.0 (CH), 52.6 (CH), 127.9 (2 CH), 128.3 (2 CH), 129.6 (C), 131.9 (C), 134.7 (C), 136.4 (4 C), 137.3 (C), 138.0 (CH), 138.5 (CH), 143.5 (C), 169.1 (C), 208.3 (C=O) ppm. $C_{28}H_{30}O{\cdot}0.25H_2O$: calcd. C 86.89, H 7.94; found C 86.83, H 8.08. ESI-HRMS: calcd. for $C_{28}H_{31}O$ $[M + H]^+$ 383.2375; found 383.2372; calcd. for $C_{56}H_{60}O_2Na$ $[2M + Na]^+$ 787.4491; found 787.4506.

(1*S,2*S**,6*R**,7*R**)-4,5-Bis(3,5-dimethylphenyl)tricyclo[5,2,1,$0^{2,6}$]-deca-4-en-3-one (4a):** Pd/C (10%; 29 mg, 0.03 mmol) was added to a solution of Pauson–Khand adduct **3a** (191 mg, 0.54 mmol) in ethanol (5 mL)) under nitrogen. The flask was flushed with hydrogen, and the mixture was stirred under a hydrogen atmosphere until the total disappearance of the starting material was observed. The solution was filtered through a Celite pad and rinsed with methanol. Concentration of the filtrate under reduced pressure gave **4a** (166 mg, 87%) as a white solid. The product was also obtained by PKR of **2a** with norbornene following the general procedure (78%); m.p. 162 °C (methanol/CH_2Cl_2). IR (film): $\tilde{\nu}$ = 2956, 1693, 1601, 1352, 1249, 852 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.00 (d, J = 10 Hz, 1 H, CH_2), 1.24 (d, J = 10 Hz, 1 H, CH_2), 1.36–1.46 (m, 2 H, CH_2), 1.62–1.70 (m, 2 H, CH_2), 2.13 (s, 1 H, CH), 2.21 (s, 6 H, CH_3), 2.23 (s, 6 H, CH_3), 2.46 (d, J = 5 Hz, 1 H, CH), 2.58 (s, 1 H, CH), 3.17 (d, J = 6 Hz, 1 H, CH), 6.78 (s, 2 H, CH), 6.90 (s, 1 H, CH), 6.91 (s, 2 H, CH), 6.94 (s, 1 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4 (2 CH_3), 21.4 (2 CH_3), 29.1 (CH_2), 29.2 (CH_2), 31.8 (CH_2), 38.6 (CH), 39.7 (CH), 50.8 (CH), 54.1 (CH), 126.5 (2 CH), 127.0 (2 CH), 129.5 (CH), 131.3 (CH), 132.5 (C), 135.2 (C), 137.8 (2 C), 137.8 (2 C), 143.0 (C), 170.0 (C), 209.2 (C=O) ppm. $C_{26}H_{28}O$ (356.51): calcd. C 87.60, H 7.92; found C 87.73, H 8.02.

(1*S,2*S**,6*R**,7*R**)-4,5-Bis(3,4,5-Trimethylphenyl)tricyclo[5,2,1,$0^{2,6}$]-deca-4-en-3-one (4b):** Compound **4b** was obtained following the procedure described for **4a**, but starting from **3b** (153 mg, 0.42 mmol) and Pd/C (10%; 22 mg, 0.02 mmol). After stirring at room temperature for 2 d, **4b** (149 mg, 97%) was obtained as a white solid. It was also prepared by PKR of **2b** following the general procedure (40%); m.p. 207 °C (methanol/CH_2Cl_2). IR (film): $\tilde{\nu}$ = 2955, 1691, 1453, 1352, 1199, 1015 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.99 (d, J = 10 Hz, 1 H, CH_2), 1.23 (d, J = 10 Hz, 1 H, CH_2), 1.36–1.47 (m, 2 H, CH_2), 1.61–1.69 (m, 2 H, CH_2), 2.15 (s, 1 H, CH), 2.15 (s, 6 H, CH_3), 2.17 (s, 6 H, CH_3), 2.21 (s, 6 H, CH_3), 2.44 (d, J = 5 Hz, 1 H, CH), 2.57 (s, 1 H, CH), 3.17 (d, J = 6 Hz, 1 H, CH), 6.82 (s, 2 H, CH), 6.97 (s, 2 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.4 (CH_3), 15.7 (CH_3), 20.7 (2 CH_3), 20.8 (2 CH_3), 29.1 (CH_2), 29.3 (CH_2), 31.8 (CH_2), 38.9 (CH), 39.6 (CH), 50.4 (CH), 54.0 (CH), 128.1 (2 CH), 128.3 (2 CH), 129.8 (C), 132.0 (C), 134.6 (C), 136.3 (2 C), 136.4 (2 C), 137.2, (C) 142.4 (C), 169.2 (C), 209.4 (C=O) ppm. $C_{28}H_{32}O$ (384.56): calcd. C 87.45, H 8.39; found C 87.27, H 8.61.

General Procedure for the Photochemical Reactions: A solution of PK adducts (1 equiv.) and I_2 (1 equiv.) in methanol (with the PK adduct at a concentration of 0.018 M) was placed into a flask provided with magnetic stirring. The solution was irradiated at 300 nm in a Rayonet reactor equipped with 8 or 16 lamps, in the presence of oxygen at room temperature. The reaction was monitored by TLC. After completion of the reaction, a solution of $Na_2S_2O_3$ was added, and the aqueous phase was extracted with CH_2Cl_2 (×2). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude reaction product was purified by flash chromatography on SiO_2 (Combiflash®, hexanes/EtOAc gradient).

(8c*R,9*S**,12*R**,12a*S**)-8c,9,10,11,12,12a-Hexahydro-9,12-methano-2,4,5,7-tetramethyl-13*H*-indeno[1,2-*l*]phenanthren-13-one (6a):** Following the general procedure, compound **4a** (50 mg, 0.14 mmol) and I_2 (50 mg, 0.24 mmol) were used. The reaction was irradiated

in the presence of oxygen for 36 h. Flash chromatography on SiO_2 (Combiflash®, hexanes/EtOAc gradient) gave **6a** (48 mg, 96%) as a white solid; m.p. 206 °C. IR (film): $\tilde{\nu}$ = 2955, 1686, 1609, 1451, 1247, 731 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) (mixture of atropisomers): δ = 0.98 (br. s, 2 H, CH_2, maj. + min.), 1.44–1.52 (m, 1 H, CH_2, min. + maj.), 1.62–1.69 (m, 1 H, CH_2, min. + maj.), 1.70–1.85 (m, 2 H, CH_2, min. + maj.), 2.51 (s, 3 H, CH_3, min.), 2.53 (s, 3 H, CH_3, maj.), 2.53 (s, 3 H, CH_3, maj.), 2.54 (s, 3 H, CH_3, maj. + min.), 2.55 (s, 3 H, CH_3, min.), 2.58 (s, 3 H, CH_3, maj. + min.), 2.60–2.70 (m, 3 H, CH, maj. + min.), 3.35 (d, J = 6 Hz, 1 H, CH, min.), 3.41 (d, J = 6 Hz, 1 H, CH, maj.), 7.26 (s, 1 H, CH, maj.), 7.26 (s, 1 H, CH, min.), 7.39 (br. s, 1 H, CH, maj. + min.), 7.74 (s, 1 H, CH, maj.), 7.79 (s, 1 H, CH, min.), 8.90 (s, 1 H, CH, maj.), 8.91 (s, 1 H, CH, min.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4 (min., CH_3), 21.5 (maj., CH_3), 21.5 (min., CH_3), 21.6 (maj., CH_3), 21.7 (maj., CH_3), 21.8 (maj., CH_3), 21.8 (min., CH_3), 21.8 (min., CH_3), 28.7 (min., CH_2), 29.0 (maj., CH_2), 29.7 (maj., CH_2), 29.8 (min., CH_2), 32.5 (CH_2), 39.2 (min., CH), 39.9 (maj., CH), 40.1 (maj., CH), 41.1 (min., CH), 46.0 (maj., CH), 46.6 (min., CH), 56.6 (maj., CH), 57.1 (min., CH), 121.0 (maj., CH), 121.2 (min., CH), 122.3 (maj., CH), 122.6 (min., CH), 128.4 (C), 128.6 (maj., C), 128.6 (min., C), 130.1 (min., C), 130.6 (maj., C), 130.6 (CH), 132.0 (maj., C), 132.2 (min., C), 132.4 (maj., C), 132.6 (min., C), 133.1 (min., CH), 133.3 (maj., CH), 135.3 (maj., C), 135.3 (min., C), 135.9 (C), 136.4 (min., C), 136.5 (maj., C), 136.9 (maj., C), 136.9 (min., C), 160.2 (min., C), 160.3 (maj., C), 208.8 (min., C=O) 208.9 (maj., C=O) ppm. $C_{26}H_{26}O \cdot 1/3H_2O$: calcd. C 86.63, H 7.46; found C 86.61, H 7.43. ESI-HRMS: calcd. for $C_{26}H_{27}O$ $[M + H]^+$ 355.2062; found 355.2068; calcd. for $C_{52}H_{53}O_2$ $[2M + H]^+$ 709.4046; found 709.4033.

(8c*R,9*S**,12*R**,12a*S**)-8c,9,10,11,12,12a-Hexahydro-9,12-methano-2,3,4,5,6,7-tetramethyl-13*H*-indeno[1,2-*l*]phenanthren-13-one (6b):** Following the general procedure, compound **4b** (50 mg, 0.13 mmol) was irradiated in the presence of I_2 (33 mg, 0.13 mmol). After 54 h, the crude product was purified by flash chromatography on SiO_2 (Combiflash®, hexanes/EtOAc gradient) to give **6b** (45 mg, 93%) as a mixture of atropisomers; m.p. 219 °C. IR (film): $\tilde{\nu}$ = 2915, 1681, 1649, 1443, 1380, 733 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) $\mathbf{6b_M}$: δ = 0.96 (s, 2 H, CH_2), 1.43–1.50 (m, 1 H, CH_2), 1.72 (dt, J = 12, 4 Hz, 1 H, CH_2), 1.76–1.85 (m, 2 H, CH_2), 2.38 (s, 3 H, CH_3), 2.41 (s, 3 H, CH_3), 2.42 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3), 2.52 (s, 3 H, CH_3), 2.56 (s, 3 H, CH_3), 2.60 (br. s, 1 H, CH), 2.61 (br. s, 1 H, CH), 2.64 (d, J = 3 Hz, 1 H, CH), 3.39 (d, J = 6 Hz, 1 H, CH), 7.76 (s, 1 H, CH), 8.90 (s, 1 H, CH) ppm. ^1H NMR (400 MHz, $CDCl_3$) $\mathbf{6b_P}$: δ = 0.95 (s, 2 H, CH_2), 1.43–1.50 (m, 1 H, CH_2), 1.59–1.66 (m, 1 H, CH_2), 1.67–1.83 (m, 2 H, CH_2), 2.38 (s, 3 H, CH_3), 2.39 (s, 3 H, CH_3), 2.43 (s, 6 H, CH_3), 2.52 (s, 3 H, CH_3), 2.56 (s, 3 H, CH_3), 2.63 (d, J = 6 Hz, 1 H, CH), 2.66 (d, J = 3 Hz, 1 H, CH), 2.69 (d, J = 4 Hz, 1 H, CH), 3.35 (d, J = 6 Hz, 1 H, CH), 7.81 (s, 1 H, CH), 8.92 (s, 1 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) mixture $\mathbf{6b_M}$ (major)/$\mathbf{6b_P}$ (minor): δ = 16.5 (maj., CH_3), 16.8 (min., CH_3), 16.9 (maj., CH_3), 21.2 (maj., CH_3), 21.2 (maj., CH_3), 21.3 (maj., CH_3), 21.4 (maj., CH_3), 21.5 (min., CH_3), 28.8 (min., CH_2), 29.0 (maj., CH_2), 29.7 (maj., CH_2), 29.8 (min., CH_2), 32.5 (maj., CH_2), 39.1 (min., CH), 39.8 (maj., CH), 40.1 (maj., CH), 41.1 (min., CH), 45.9 (maj., CH), 46.5 (min., CH), 59.8 (maj., CH), 59.2 (min., CH), 121.7 (maj., 2 CH), 121.8 (min., 2 CH), 122.9 (maj., 2 CH), 123.3 (min., 2 CH), 126.2 (maj., C), 127.7 (min., C), 128.3 (maj., C), 129.3 (maj., C), 131.3 (maj., C), 133.1 (maj., C), 133.4 (min., C), 134.0 (maj., C), 134.7 (maj., C), 135.1 (min., C), 135.2 (maj., C), 135.3 (maj., C), 136.1 (maj., C), 137.8 (min., C), 138.0 (maj., C), 159.4 (min., C), 159.6 (maj., C), 208.9 (maj., C=O) ppm. $C_{28}H_{30}O \cdot 0.2H_2O$: calcd. C 87.09, H 7.94; found C 87.31, H 7.97. ESI-HRMS: calcd. for $C_{28}H_{31}O$ $[M + H]^+$ 383.2375; found 383.2369.

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra for all new compounds. Calculated geometries of both atropisomers of **6a** and **6b** and the transition state of the interconversion between $\mathbf{6a_M}$ and $\mathbf{6a_P}$. X-ray diffraction data for $\mathbf{6a_M}$ and $\mathbf{6b_M}$.

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Photochemical Atropisomer Formation

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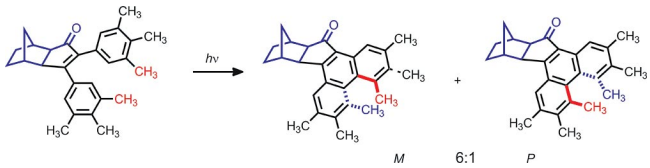
Helical Atropisomers of Strained Phenanthrenes by Photochemistry of Aromatic Pauson–Khand Cycloadducts

Keywords: Photochemistry / Electrocyclic reactions / Chirality / Atropisomerism / Helical structures



Norbornene and norbornadiene Pauson–Khand adducts of bis(3,5-dimethylphenyl)-acetylene and bis(3,4,5-trimethylphenyl)-acetylene were subjected to a photochemical 6π-electrocyclic oxidative aromatization reaction to give the corresponding phenanthrene compounds. The helical twist imposed by the methyl groups at the 3- and 5-positions on the aromatic rings led to two atropisomers as a result of the nonplanar helical phenanthrene structure.

