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Chirality and asymmetric transformations of axially chiral 4,5-disubstituted phenanthreneamides

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Abstract

We have investigated the rotation barriers of 4-carbamoylphenanthrene and 4-thiocarbamoylphenanthrene and the asymmetric transformations of the novel 4-carboxy-5-carbamoylphenanthrenes. The similar Ar–C and C–N barriers of 92 kJ/mol of 4-carbamoylphenanthrene indicate a strongly correlated process of both rotations. Only the corresponding thioamide could be separated on microcrystalline triacetylcellulose and a barrier of 115.6 kJ/mol was obtained from thermal racemization. Despite the large steric hindrance of the tightly interlocked substituents of the 4-carboxy-5-carbamoylphenanthrenes, the chirality became visible only at temperatures below −60°C by ^{1}H NMR spectroscopy. Only six of the eight possible stereoisomers, which may form four racemates, have been observed, namely two *anti* and one *syn* species. After the asymmetric transformation, one further *syn* arrangement is less populated or does not exist and the two *anti* isomers exist in an unequal ratio. Two orientations were found for the amide group: a major form A with the Me^E 'outside' and the carbonyl group 'inside' the bay-area and a minor form B with the reverse arrangement. The low barriers of 4-carboxy-5-carbamoylphenanthrenes indicate that steric hindrance and electrostatic repulsion in the transition state are compensated by correlated Ar–C and C–N rotations and by twisting the phenanthrene plane. In the transition state, the carbonyl group passes the bay area and the pyramidal amide group passes H^3 or H^6 of the phenanthrene ring.

1. Introduction

4,5-Disubstituted phenanthrenes exist in chiral non-planar conformations. Even phenanthrene itself can be considered the smallest helicene, because the steric hindrance of the hydrogens in position four and five causes a helical distortion of the phenanthrene skeleton in the crystal.[1,2] In 4,5-dimethylphenanthrene the steric hindrance is already large enough for the enantiomers to be separated at low temperature and an inversion barrier of 67.0 kJ/mol was determined.[3] Additional methyl groups in 3,4,5,6-tetramethylphenanthrene increased the racemization barrier

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to 95.8 kJ/mol and the enantiomers had already a half life of 1.5 h at room temperature.[4] The low barriers of 56–79 kJ/mol obtained for 4,5-diphenyltriphenylenes[5] and the estimated barrier of 25 kJ/mol for 4–phenylphenanthrenes[6] are due to correlated processes between helix inversion and rotations. However, in 1-phenylbenzo[*c*]phenanthrene derivatives, the barriers of two processes could be determined, a phenyl rotation of 54 kJ/mol and a rotation with simultaneous helix inversion of 67 kJ/mol.[6] Interconversion barriers of 62–76 kJ/mol have been obtained for phenanthrene-4,5-dicarboxylic acids and esters.[7] The successful separation of axially chiral benzene and naphthalene amides and thiomides[8–10] that allowed the subsequent determination of racemization barriers encouraged us to extend the investigations to the phenanthrene system.

2. Results and discussion

The 4-carboxyl-5-carbamoylphenanthrene system is described by an Ar–C amide rotation, an Ar–C ester rotation, a C–N amide rotation and an inversion of the phenanthrene helix. This leads to $2^4 = 16$ stereoisomers, i.e. eight racemic diastereomers are possible. For a symmetrically substituted dimethylamide the number of stereoisomers is reduced to eight (Fig. 1).

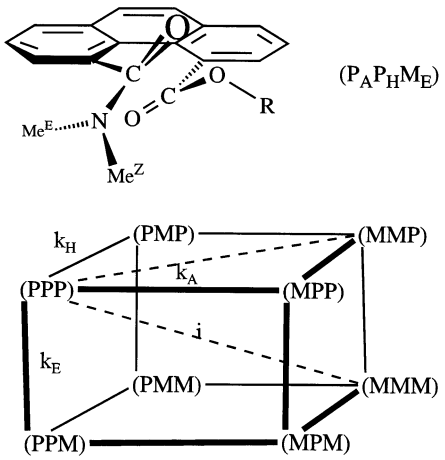
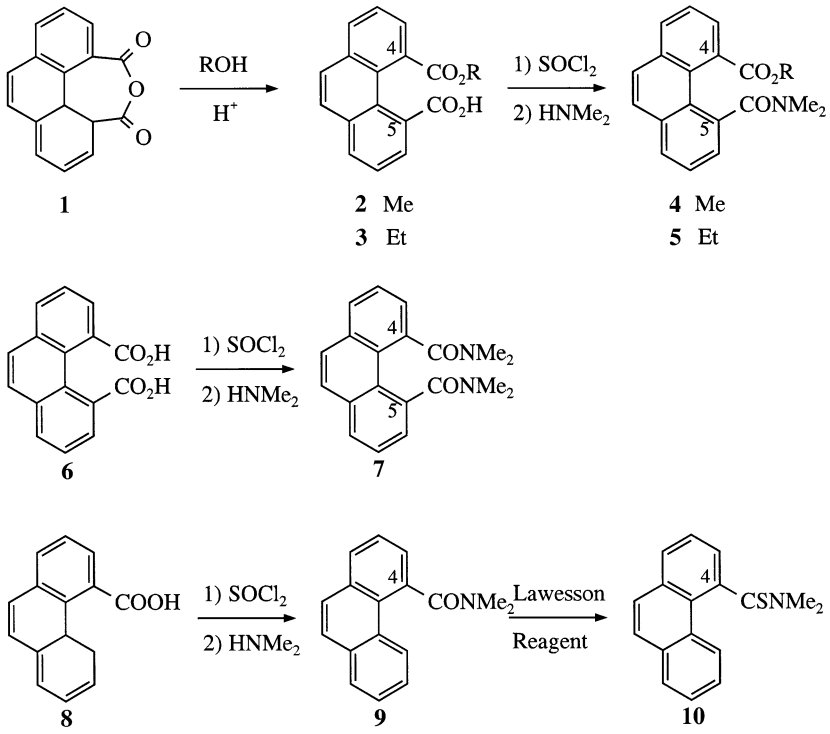


Figure 1. 4-Carboxy-5-carbamoylphenanthrenes can form 16 stereoisomers. With a symmetrical dimethylamide group, the stereoisomers are reduced to eight. Interconversions along any cube lines correspond to one motion and describe a diastereomerization, either by a rotation around the Ar–C_{amide} or Ar–C_{ester} bonds or by an inversion of the helix. The diagonals across squares describe a diastereomerization by two simultaneous motions. Enantiomers are at diagonally opposite corners with an inversion center *i* in the center of the cube. Enantiomerizations along the diagonals through space require three simultaneous motions. Parallel lines on the cube correspond to analogous motions. *Anti* and *syn* are used in the text to describe the orientations of the carbonyl group. k_A describes the Ar–C_{amide} rotation, k_H the helix inversion and k_E the Ar–C_{ester} rotation

The 4-carboxyl-5-carbamoylphenanthrenes **4** and **5** were synthesized by reaction of phenanthrene anhydride **1**[7,11] with ROH/H_2SO_4 to the monoesters **2** and **3**, which were transformed to the products by reaction with $SOCl_2/HNMe_2$ (Scheme 1). Tetramethyl-4,5-dicarbamoylphenanthrene **7** was synthesized by reaction of phenanthrene-4,5-dicarboxylic acid **6**[11,12] with $SOCl_2/HNMe_2$. 4-Dimethylcarbamoylphenanthrene **9** was obtained from phenanthrene-4-carboxylic acid **8**[13,14] with the same method and subsequently transformed into thioamide **10** with the Lawesson reagent.[9]



Scheme 1. Synthesis of the 4,5-disubstituted phenanthreneamides

2.1. Information on the ground state by NOE experiments

Broad signals were observed for Me^E and the methylene H-atoms of amide **5** indicating slow coalescence phenomena within the NMR time scale. The negative signal in the difference spectrum upon excitation of Me^E showed that there was already a magnetization transfer between Me^E and Me^Z at 24°C. The dominating NOE occurred at H^3 indicating that Me^E is closer to H^3 than to H^6 (Fig. 2). But there was also a significant NOE at H^6, which shows that at least two major amide orientations coexist in the ground state (Fig. 3). Excitation of the Me^Z signal showed similar NOE effects on H^3 and H^6, but the intensity at H^3 was smaller (Fig. 2). NOE effects at H^6 and Me^Z were found upon irradiation of the methylene H-atoms, which suggests that the methylene protons are closer to H^6 and that the conformation A in Fig. 3 is dominant. Further evidence that the substituents are twisted in the ground state came from the Me^E signal at 1.82 ppm, which was shifted to high field due to the anisotropy effect of the phenyl ring.

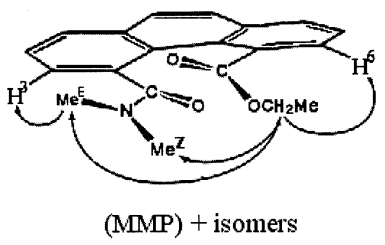


Figure 2. NOE experiments on amide **5**

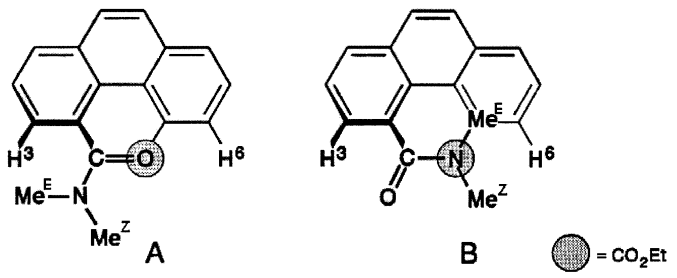


Figure 3. Major conformations A (Me^E 'outside' and the carbonyl group 'inside' the bay area) and minor conformation B (reverse orientation of A) of amide **5** according to the NOE experiments in Fig. 2. Only one of the enantiomers is shown

After cooling to low temperatures it was possible to see the diastereomers in the ^{1}H NMR spectra of **4** and **5** (Fig. 4). The eight possible diastereomers, that correspond to four racemates, should give 12 signals for the OMe and $CONMe_2$ groups in amide **4**. However, at −80°C only nine signals have been found indicating that only three of the four racemates are sterically and electrostatically possible. The same was found for amide **5**. The missing diastereomers are probably due to *syn* conformers, where the rotors are electrostatically strongly disfavored. In the case of 1,8-bis(dimethylcarbamoyl)naphthalene, dipole moment experiments showed that the *syn* conformer was missing.[15] Molecular models demonstrate that *anti*-orientations should be highly favored, whereas *syn* conformers are probably missing.

At room temperature the *anti* conformers were observed; only at very low temperatures the *syn* population appeared (Fig. 5). The ^{1}H NMR signals could be assigned to the *anti* and *syn* conformations (Fig. 4). In the *syn* conformation the Me^E and Me^Z signals were shifted to lower field relative to the *anti* species and the shift difference $\Delta\nu$ became smaller. Integration of the signals of amide **4** resulted in a 2.8:1 (*anti:syn*) ratio for the diastereomers at −80°C. The two *anti* populations are not equal but appear in a 1.4:1 ratio (Fig. 4). Integration of the signals of amide **5** resulted in a 1.9:1 (*anti:syn*) ratio at −80°C. Here the ratio of the two *anti* populations was 1.7:1. The integrals not only show that one *syn* racemate is missing but also that one *anti* isomer had been enriched at the expense of the other one, which corresponds to an asymmetric transformation of first kind.[16]

2.2. Dynamic processes

4-Thiocarbamoylphenanthrene **10** was successfully separated on microcrystalline triacetylcellulose and a barrier to racemization of 115.6 kJ/mol was determined (Table 1). This racemization process may represent the Ar–C rotation and/or the helix inversion. As the barriers of the latter process in 4,5-dicarboxyphenanthrenes **11** and **12** are much lower,[7] we can assign this barrier to the Ar–C rotation.

A barrier of >91.7 kJ/mol was determined for the Ar–C rotation and >92 kJ/mol for the C–N rotation in 4-carbamoylphenanthrene **9** by ^{1}H NMR. The similarity of these barriers strongly suggests a correlated process between the Ar–C and C–N rotations via a pyramidal amide

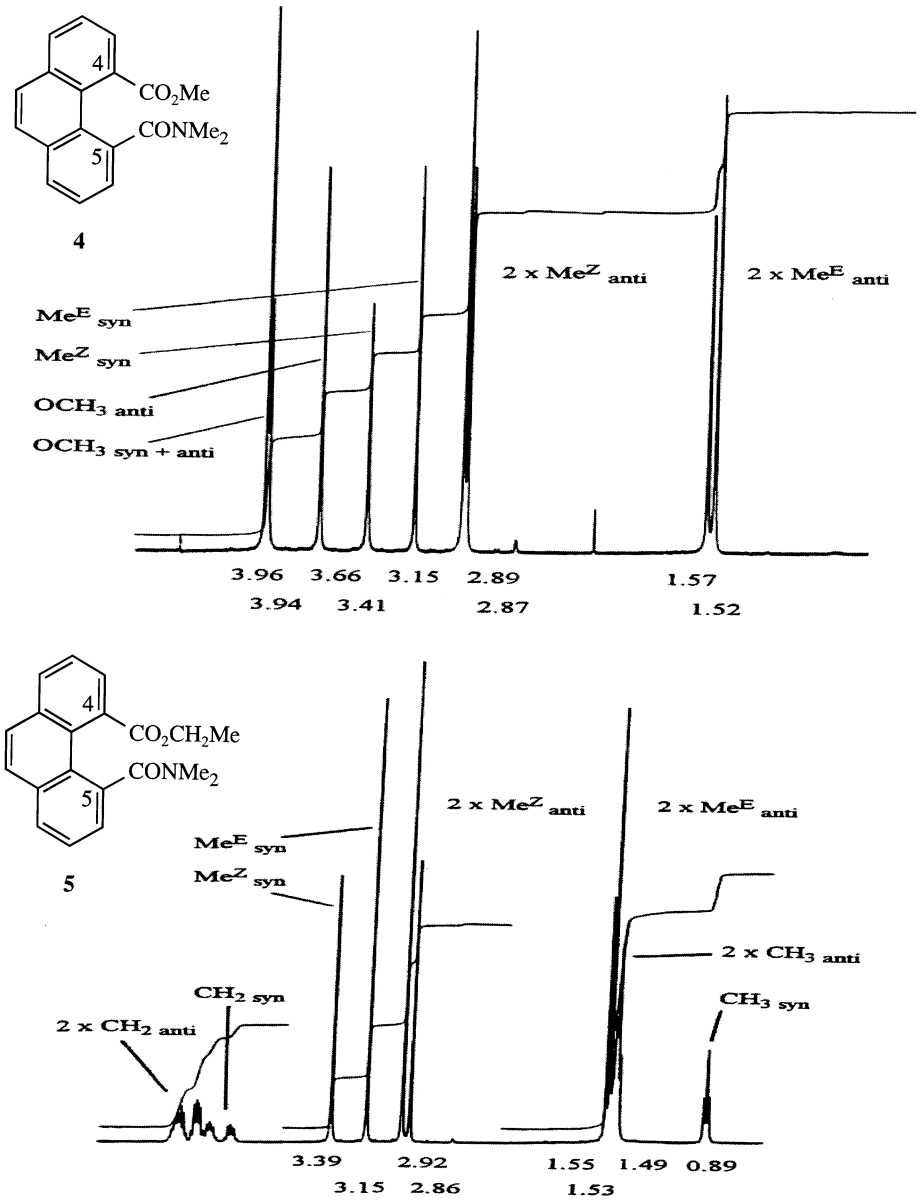
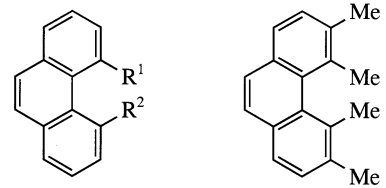


Figure 4. Diastereomers of **5** (below) and **4** (above) (CD_2Cl_2, 400 MHz, −80°C)

transition state[17,18] (Fig. 6). The half-life of the enantiomers of **9** at room temperature was not long enough to trap the enantiomers for thermal racemization. ^{1}H NMR coalescence experiments were performed to determine the Ar–C barrier using the NMe^Z signal, which split into two distinct signals in the presence of 0.28 equivalents of (+)-Eu(hfbc)$_3$. At 399.5 K there was no coalescence, but a single rounded-off peak was found at 400 K instead of a plateau; therefore a barrier of >91.7 kJ/mol was noted. For the amide barrier, the limit of the instrument was reached at coalescence. We could not get a spectrum above the coalescence temperature; therefore a barrier of >92 kJ/mol was noted.

Table 1
Barriers of rotation and helix inversion of phenanthrene compounds



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No.	R^1	R^2	Solvent	ν_o (MHz)	$\Delta\nu_c$ (Hz)	T_c (°C)	$\Delta G^{\neq}$ (kJ/mol)	Method/signals used	Type of motion
4	$CONMe_2$	CO_2Me	*o*-$C_6D_4Cl_2$	80	91.3	117	79.2 ± 0.6	$CONMe^{E/Z}$	C–N rot.
9	$CONMe_2$	H	$C_2D_2Cl_4$	250	<5.3	>126	$>91.7\pm0.7$	NMe^{Z} [a]	Ar–C rot.
			o-$C_6D_4Cl_2$	80	<57.5	>157	>92	$CONMe^{E/Z}$	C–N rot.
10	$CSNMe_2$	H	Diglyme	–	–	90.4	115.6 ± 0.2	Thermal rac.	Ar–C rot.
11	CO_2H	CO_2Bzl	Pyridine-d_5	60	–	16	62.4	CH_AH_BPh	Rot.–inv.[7]
			Pyridine-d_5	60	–	25	62.0		Helix–inv.[7]
12	CO_2CHMe_2	CO_2Me	$CDCl_3$	60	–	0	60.7	$CHMe_2$	Rot.–inv.[7]
			$CDCl_3$	60	–	25	59.9		Helix–inv.[7]
13	Me	Me	EtOH	–	–	25	67 ± 6	Thermal rac.	Helix–inv.[3]
14			EtOH	–	–	77.4	95.8 ± 0.2	Thermal rac.	Helix–inv.[4]

[a] Coalescence of NMe^{Z} signal in the presence of 0.28 equivalents of (+)-Eu(hfbc)$_3$ (hfbc = 3-heptafluorobutyryl-D-camphor).

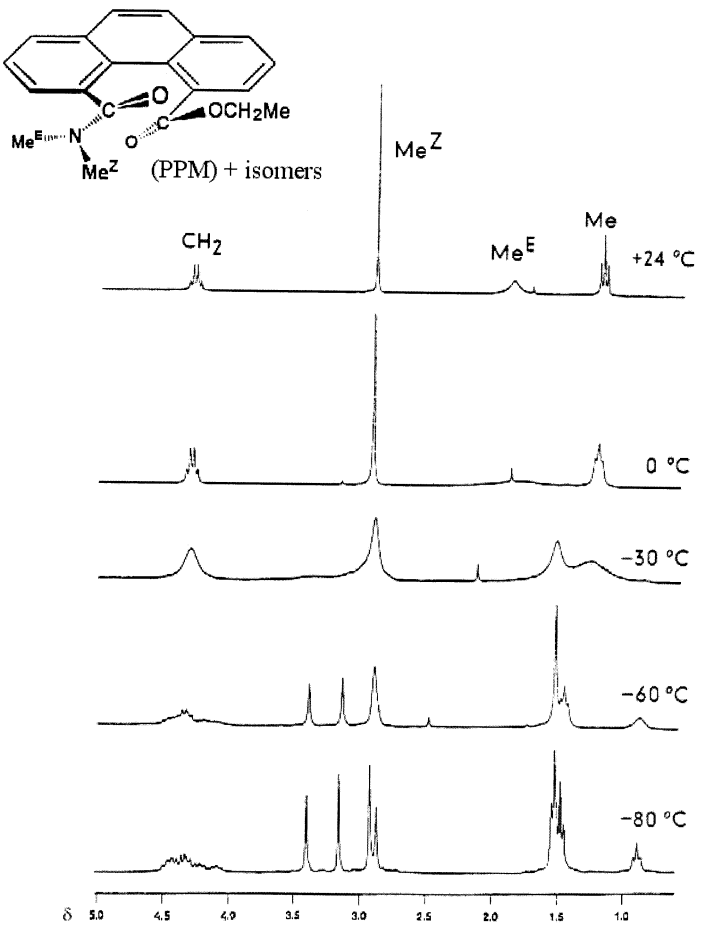

Figure 5. ^{1}H NMR spectra of amide **5** at various temperatures (250 MHz, $CDCl_3$)

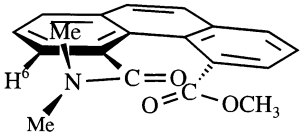

Figure 6. Transition state in phenanthreneamides. The carbonyl group passes through the bay area, whereas the pyramidal amide group passes H^6 of the phenanthrene ring

After introduction of ester groups in the 4-position of the 5-carbamoylphenanthrene, all attempts to separate enantiomers or diastereomers on non-racemic sorbents failed (microcrystalline triacetylcellulose and tribenzoylcellulose, (+)-poly(tritylmethacrylate)/SiO_2 and tris-(phenylcarbamoyl)cellulose/SiO_2), despite the increased steric hindrance. Obviously the carboxy-substituent in 4-position reduced the activation barriers and the change of the dipole moment reduced the interactions with the sorbent. Therefore we could only use NMR spectroscopy to investigate chirality and dynamic processes of these compounds.

Fig. 5 shows some ^{1}H NMR spectra of amide **5** at various temperatures. The different coalescence phenomena indicate slow interconversions within the NMR time scale. Due to the tightly interlocked system, we have to consider strongly correlated processes. In similar phenanthrene systems simultaneous changes of conformations were suggested.[5,6] The 4-methoxycarbonyl-5-carbamoylphenanthrene **4** shows an amide rotation barrier of 79 kJ/mol, 13 kJ/mol lower than the one of amide **9** (Table 1); this barrier is significantly smaller despite a larger substituent. The methyl ester group obviously destabilizes the amide ground state and favors the pyramidal NMe_2 amide transition state.

An increase of symmetry and a simplification of the spectra was attained by exchanging the ester for an amide group. In this case, cooling of **7** to lower temperatures did not lead to additional signals in the ^{1}H NMR spectra. Only a low-field shift of the amide signals and a strong temperature-dependence of the Me^E signal has been observed: (250 MHz, $CD_2Cl_2/CFCl_3$) 24°C, $\delta = 2.74$ Me^E, 3.03 Me^Z; −100°C, $\delta = 3.41$ Me^E, 3.18, Me^Z. Exact kinetic data for the Ar–C rotation by coalescence in the presence of (+)-(*S*)-1-(9-anthryl)-2,2,2-trifluoroethanol were not possible due to overlap of signals, but we estimated a barrier of $\sim$70 kJ/mol, which is even lower than the barriers of 4-carbamoylphenanthrene. The same overlap problems were obtained for the ethyl ester **5** and a barrier of $\sim$70 kJ/mol was measured.

The surprisingly low and similar amide rotation barriers of 70–79 kJ/mol for the amides **4**, **5**, **7** and **9**, despite different substituents, indicate that the steric hindrance and electrostatic repulsions in the transition states are compensated by twisting the phenanthrene plane and by a correlation of Ar–C and C–N rotations. In the transition state, the carbonyl group passes the twisted bay area; therefore the Ar–C barrier is more dependent on substituents there. The pyramidal amide group, however, passes H^3 and H^6 of the phenanthrene ring and therefore showed no dependence on substituents in the bay area (Fig. 6).

3. Conclusion

4,5-Disubstituted phenanthrenes exist in chiral non-planar conformations. We have investigated the rotation barriers and chirality of 4-carbamoyl- **9** and 4-thiocarbamoylphenanthrene **10** and the asymmetric transformations of the first kind of 4-carbonyl-5-carbamoylphenanthrenes **4** and **5**. Amide **9** showed a strongly correlated process of Ar–C and C–N rotation with a barrier of 92 kJ/mol. The enantiomers of 4-thiocarbamoylphenanthrene **10** could be separated on microcrystalline triacetylcellulose and a racemization barrier of 115.6 kJ/mol was determined. This barrier represents the Ar–C rotation as the helix inversion barriers are much smaller.[7]

After introduction of the 4-carboxy group, the stereoisomers could not be separated on non-racemic sorbents. Two orientations were found for the amide group: a major form A with the Me^E 'outside' and the carbonyl group 'inside' the bay-area and a minor form B with the reverse orientations. Despite the larger steric hindrance of the tightly interlocked substituents, chirality became visible by ^{1}H NMR spectroscopy at temperatures below −60°C. Only six of the eight possible stereoisomers, which form four racemates, have been observed, two *anti* and one *syn* population in a 2.8:1 (*anti*:*syn*) ratio for **4** and 1.9:1 ratio for **5**. Obviously one further *syn* conformation is sterically and electrostatically disfavored. The two *anti* isomers equilibrated to a 1.4–1.7:1 ratio, i.e. one conformer was enriched at the expense of another one. As the different diastereomers are not separable, the process is called an asymmetric transformation of the first kind.

4. Experimental

4.1. Spectroscopy and analysis

^{1}H NMR spectra were recorded on Bruker AW-80, WM-250 or ARX-400 instruments at 24°C with tetramethylsilane as internal standard. Temperatures were determined by samples of CH_3OH or 1,2-ethanediol.[19] Hexamethyldisilane or octamethylcycoltetrasiloxane served as internal standards for measurements at higher temperatures. The barriers were calculated with the coalescence method, where the NMR shift difference $\Delta\nu_c$ is extrapolated from the coalescence temperature, using the correction with the band width of the signals and the equilibrium constant. For an uncoupled AB: $k_c=(\pi/\sqrt{2})\Delta\nu_c$ with $b_E/\Delta\nu_c$ and K;[20] for a coupled AB: $k_c=(\pi/\sqrt{2})\sqrt{\Delta\nu^2+6J^2}$ with $b_E/\Delta\nu_c$ and $J_{AB}/\Delta\nu_c$.[21] IR spectra were measured on Beckman Acculab 1 or Jasco IR 810 spectrometers. UV spectra were recorded on a Hitachi U-2000. Melting points were determined on a Büchi SMP-20 or a SMP-530 apparatus and are corrected. Preparative column chromatography was carried out on ICN silica-gel $60F_{254}$ (63–200 μm). The thermal racemization of an enantiomer or an enriched sample was monitored via angle of rotation at a suitable fixed wavelength. The 10 cm quartz cell of the Perkin–Elmer 241 polarimeter was provided with a water jacket connected to a thermostat. First-order kinetics were obtained and evaluated with computer programs developed in our group.[22] The separation and enrichment of enantiomers was performed with microcrystalline triacetylcellulose (TAC).[23]

4.2. 4-Methoxycarbonyl-5-phenanthrenecarboxylic acid **2**

Reaction of anhydride **1**[11] with $MeOH/H_2SO_4$ was analogous to the literature.[7] Purification by liquid chromatography (petroleum ether/THF 1:1). Recrystallization from $MeOH/H_2O$ resulted in colorless crystals. Yield 75%. Mp 220–225°C. ^{1}H NMR (80 MHz, THF-d_8): $\delta=3.68$ (s, 3H, CO_2CH_3), 7.3–8.1 (m, 9H, 8 Ar–H and CO_2H). IR (KBr): $\nu=3300$–2500 (br, CO_2H), 1710 (C=O, ester), 1675 (C=O, acid), 1640, 1615, 1590 cm^{-1} ($C{=}C_{ar}$).

4.3. 4-Ethoxycarbonyl-5-phenanthrenecarboxylic acid **3**

Reaction of anhydride **1**[11] with $EtOH/H_2SO_4$ was analogous to **2**. After evaporation of the solvent, water was added and the colorless precipitate was isolated. Yield 67%. ^{1}H NMR (80 MHz, DMF-d_8): $\delta=1.2$ (t, 3H, $CO_2CH_2CH_3$), 4.25 (q, 2H, $CO_2CH_2CH_3$), 7.6–8.2 (m, 8H, Ar–H), 12.6 (br, s, 1H, CO_2H).

4.4. 4-Methoxycarbonyl-5-dimethylcarbamoylphenanthrene **4**

2.0 g (7.13 mmol) of monoester **2** was stirred in 50 ml of freshly distilled $SOCl_2$ for six hours at 40–60°C. Then non-reacted $SOCl_2$ was removed by vacuo and the precipitate was dissolved in dry THF. $HNMe_2$ was added until the forming of precipitate was finished. The precipitate was isolated, dissolved in CH_2Cl_2 (100 ml) and washed with water (3×50 ml). After drying the organic phase with $MgSO_4$, the solvent was removed and the product purified by liquid chromatography (petroleum ether/acetic ester 1:1). Recrystallization from MeOH resulted in colorless crystals. Yield 50%. Mp 123–125°C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=1.86$ (s, 3H,

CONMe^{E}), 2.91 (s, 3H, CONMe^{Z}), 3.81 (s, 3H, CO_2CH_3), 7.62 (dd, 1H, Ar–H^7), 7.64 (t, 1H, Ar–H^2), 7.68 (dd, 1H, Ar–H^3), 7.72 (AB, 1H, Ar–H$^{9/10}$), 7.79 (AB, 1H, Ar–H$^{9/10}$), 7.95 (dd, 1H, Ar–H^6), 7.97 (m, 1H, Ar–H^1), 7.99 (m, 1H, Ar–H^8), $^3J_{12}=7.4$, $^4J_{13}=1.8$, $^3J_{23}=7.3$, $^3J_{67}=7.3$, $^4J_{68}=1.8$, $^3J_{78}=7.9$, $^3J_{9,10}=8.7$ Hz. IR (KBr): $\nu=3070$, 3060, 3020 (C_{ar}–H), 2960, 2920, 2870 (C_{al}–H), 2830 (OCH_3), 1705 (C=O, ester), 1610 (C=O, amide), 1590 cm^{-1} (C=C_{ar}). $C_{19}H_{17}NO_3$ (307.35): calcd C, 74.24; H, 5.57; N, 4.55; found C, 74.28; H, 5.68; N 4.66.

4.5. 4-Ethoxycarbonyl-5-dimethylcarbamoylphenanthrene **5**

Reaction with $SOCl_2$/$HNMe_2$ analogous to amide **4**. The product was purified by liquid chromatography (petroleum ether/acetic ester 1:1). Recrystallization from the same mixture resulted in colorless crystals. Yield 49%. Mp 107–109°C. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta=1.21$ (t, 3H, OCH_2CH_3), 1.85 (br, s, 3H, CONCH$_3^E$), 2.92 (s, 3H, CONCH$_3^Z$), 4.29 (q, 2H, OCH_2CH_3), 7.62 (t, 1H, Ar–H^7), 7.64 (t, 1H, Ar–H^2), 7.68 (dd, 1H, Ar–H^3), 7.72 (AB, 1H, Ar–H$^{9/10}$), 7.79 (AB, 1H, Ar–H$^{9/10}$), 7.95 (dd, 1H, Ar–H^6), 7.97 (m, 1H, Ar–H^1), 8.00 (m, 1H, Ar–H^8), $^3J_{12}=8.3$, $^4J_{13}=1.5$, $^3J_{23}=7.3$, $^3J_{67}=7.4$, $^4J_{68}=1.8$, $^3J_{78}=7.4$, $^3J_{9,10}=8.7$ Hz. IR (KBr): $\nu=3030$, 3010 (C_{ar}–H), 2980, 2940 (C_{al}–H), 1700 (C=O, ester), 1630 (C=O, amide), 1595 cm^{-1} (C=C_{ar}). $C_{20}H_{19}NO_3$ (321.3): calcd C, 74.75; H, 5.96; N, 4.36; found C, 74.52; H, 6.03; N 4.18.

4.6. N,N,N′,N′-Tetramethyl-4,5-dicarbamoylphenanthrene **7**

Reaction of phenanthrene-4,5-dicarboxylic acid **6**[11,12] with $SOCl_2$ and $HNMe_2$ analogous to amide **4**. The product is purified by liquid chromatography (petroleum ether/acetic ester 1:1). Recrystallization from the same mixture resulted in colorless crystals. Yield 41%. Mp 215–219°C. ^{1}H NMR (250 MHz, CD_2Cl_2/$CFCl_3$ 1:1): $\delta=2.74$ (br.s, 3H, Me^E), 3.03 (s, 3H, Me^Z), 7.5–7.7 (m, 2H, Ar–H), 7.70 (s, 1H, Ar–H$^{9/10}$), 7.88 (dd, 1H, Ar–H). IR (KBr): $\nu=3050$, 3020, 3010 (C_{ar}–H), 2900 (C_{al}–H), 1600 (C=O), 1575 cm^{-1} (C=C). $C_{20}H_{20}N_2O_2$ (320.4): calcd C, 74.98; H, 6.29; N, 8.74; found C, 74.72; H, 6.31; N 8.69.

4.7. (±)-4-Dimethylcarbamoylphenanthrene **9**

Reaction of phenanthrene-4-carboxylic acid **8**[13,14] with $SOCl_2$/$HNMe_2$ analogous to amide **4**. The product was purified by distillation at 170°C, 0.1 torr. Recrystallization from ethanol/water resulted in colorless crystal plates. Yield 61%. Mp 119–121°C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=2.42$ (s, 3H, NMe^E), 3.17 (s, 3H, NMe^Z), 7.3–8.6 (m, 9H).

4.8. (±)-4-Dimethylthiocarbamoylphenanthrene **10**

Reaction of dimethylcarbamoylphenanthrene **9** with Lawesson's reagent was analogous to the literature.[9] The product was purified by liquid chromatography (CH_2Cl_2). Recrystallization from ethanol resulted in colorless, slightly yellow crystals. Yield 78%. Mp 169–170°C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=2.72$ (s, 3H, NMe^E), 3.71 (s, 3H, NMe^Z), 7.4–8.0 (m, 8H), 8.4–8.8 (m, 1H, H-5). UV ($CHCl_3$): λ_{max} (log ε) = 242 (4.51), 267 (4.52), 338 (2.87), 355 (2.85), 370 nm (2.73). $C_{17}H_{15}NS$ (265.4): calcd C, 76.94; H, 5.70; N, 5.28; found C, 76.70; H, 5.83; N, 5.28.

*4.8.1. $(+)_{436}$-4-Dimethylthiocarbamoylphenanthrene (+)-**10***

Mp 149.0–151.0°C. $[P]=76.0\%$; $[\alpha]_{436}^{22}=+341\pm13$; $k_2'=4.87$, 2nd enantiomer after separation with TAC (EtOH 96%, $T=20$°C, $p=25$ bar, flow = 2 ml/min). CD ($CHCl_3$): λ_{max} ($\Delta\varepsilon$) = 250(0), 240(14.5), 250(0), 266(−27.8), 283(0), 289(16.4), 305(0), 310(−2.0), 342(0), 377(4.1) nm (l mol^{-1} cm^{-1}).

*4.8.2. $(-)_{436}$-4-Dimethylthiocarbamoylphenanthrene (−)-**10***

Mp 151.0–153.0°C. $[P]=83.0\%$; $[\alpha]_{436}^{22}=-371\pm36$; $k_1'=2.58$. 1st enantiomer after separation with TAC (EtOH 96%, $T=20$°C, $p=25$ bar, flow = 2 ml/min).

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