consequential reaction from **12c** by elimination of the amino function. Thus, treatment of **12a** with $BF_3 \cdot OEt_2$ at room temperature for 24 h led to **16a** in 85% yield. The structures of the steroid azacycles **12a–d**, **13**, and **14** were determined by NMR spectroscopy[7] based on an X-ray crystal structure analysis of **15**.[8]

We assume that during the reaction of the imines **7a–c**, **8**, and **9** with the Lewis acid $BF_3 \cdot OEt_2$ first an iminium ion **10** is formed. This undergoes a 1,5-hydride shift to give **11**, which contains a secondary amine moiety and a carbocation. A 1,2- or a 1,3-hydride shift is not observed, which was to be expected because of the higher activation energy of these rearrangements. Addition of the amino group to the carbocationic center in **11** then yields **12a–c**, **13**, or **14**, The proposed mechanism is consistent with the lower reactivity of **9** compared to that of **7** and **8**, which can easily be explained by a reduced stabilization of the intermediately formed benzylic cation **11**. This again is consistent with the observation that the *p*-methoxybenzyl group, which is used as a protecting group,[9] can easily be removed by an oxidative hydride transfer by using cerium ammonium nitrate (CAN) or other oxidants, whereas a benzyl group without an electron-donating group does not undergo this reaction.

To the best of our knowledge the described domino process is a new type of transformation, though the opposite reaction, namely the formation of an iminium ion from an amine and a carbocation, is a well known process.[10] In addition, examples of a formal insertion of an iminium ion derived from an oxime into a suitably oriented C–H bond have been described.[11] According to the electrophilicity scale, which has recently been published by Mayr and Ofial,[12] the iminium ion **10** is comparable with the tropylium cation and the phenyldiazonium ion. Therefore it is not unexpected that iminium ions obtained from **3a** and an aniline derivative containing an electron-donating group in *para* position such as **6d** gave the corresponding steroid alkaloids **12d** with only 2% yield. Reactions of **3a** with *ortho*-substituted anilines did not lead to the desired products at all, presumably due to steric reasons.

Experimental Section

12a: A mixture of **3a** (298 mg, 1 mmol), freshly distilled aniline (0.9 mL, 1 mmol), and molecular sieves (4 Å, 150 mg) in dichloromethane (10 mL) was stirred under an argon atmosphere for 4 h at 40 °C. After filtration $BF_3 \cdot OEt_2$ (0.15 mL, 0.5 mmol) in dichloromethane (1 mL) was added slowly at room temperature, and stirring was continued for 12 h. After a addition of further $BF_3 \cdot OEt_2$ (0.15 mL, 0.5 mmol) in dichloromethane (1 mL) and stirring until completion (TLC), the reaction was quenched by adding ice-cold 1N NaOH (30 mL). The organic phase was separated, the aqueous phase extracted with dichloromethane (3×30 mL), and the combined organic phases washed with brine and dried over Na_2SO_4. Evaporation in vacuo and purification of the residue by chromatography (silica gel, *tert*-butyl methyl ether/petroleum ether = 1:4) afforded **12a** (319 mg, 85%).

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[7] **12a:** M.p. 61–63 °C; $[\alpha]_D^{20} = +373.9$ ($c = 1.0$, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 0.92$ (t, 3H, $J = 7.2$ Hz, 16a-H_3), 0.93 (s, 3H, 18-H_3), 1.10–1.95 (m, 11H), 2.52 (m, 1H), 2.85 (m, 2H, 6-H_2), 2.94 (dd, 1H, $J = 9.4$ Hz, $J = 2.8$ Hz, N-$CH_{2,ax}$), 3.52 (d, 1H, $J = 9.4$ Hz, N-$CH_{2,eq}$), 3.75 (s, 3H, 3-OMe), 6.31 (d, 2H, $J = 8.3$ Hz, 2′- and 6′-H), 6.52 (m, 2H, 2- and 4′-H), 6.64 (d, 1H, $J = 2.6$ Hz, 4-H), 6.86 (m, 3H, 1-, 3′- and 5′-H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 14.9$ (C-16a), 22.3, 23.7 (C-18), 26.3, 28.6, 30.5, 33.4, 34.3, 35.0, 46.5 (C-14), 48.8 (C-8), 55.1 (3-OMe), 57.7 (C-9), 61.5 (N-CH_2), 111.8 (C-2), 113.2 (C-4), 116.9 (C-4′), 118.2 (2C, C-2′ and C-6′), 127.6 (2C, C-3′ and C-5′), 129.9 (C-1), 131.7 (C-10), 138.8 (C- 5), 149.1 (C-1′), 158.1 (C-3). **12b**: M.p. 127–129 °C; $[\alpha]_D^{20} = +307.1$ ($c = 1.0$, $CHCl_3$). **12c**: Oil; $[\alpha]_D^{20} = +610.4$ ($c = 1.0$, $CHCl_3$).
[8] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-102885. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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Peryleneimidazoloimides: Highly Fluorescent and Stable Replacements of Terrylene**

Heinz Langhals*, Harald Jaschke, Ulrike Ring, and Petra von Unold

Terrylene[1] (**1**) is an important compound for physicochemical investigations,[2] for example for single-molecule spectroscopy,[3] because its UV/Vis absorption spectrum closely matches the operation region of the easily controllable rhodamine 6G dye laser (about 555–560 nm). The preparation of terrylene is however laborious, high purification very difficult, and the chemical persistency low. Moreover, the

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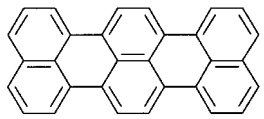

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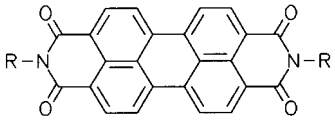

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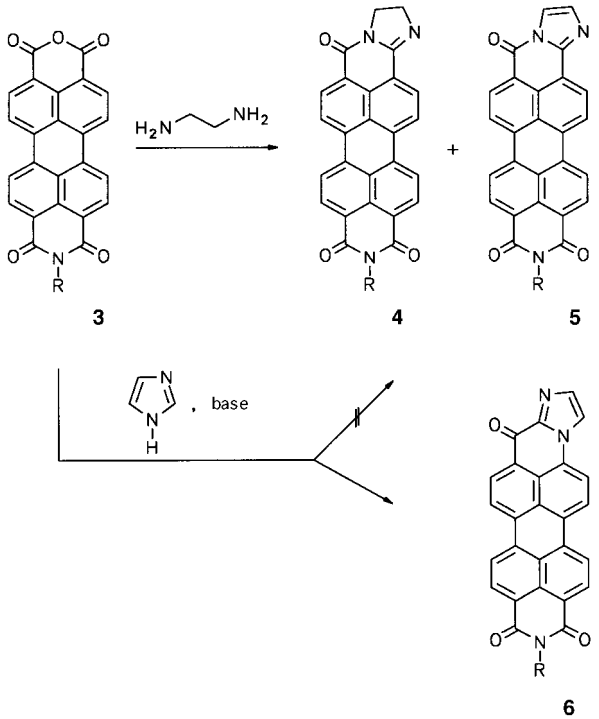
solubility is low, it has no anchor group for linkage to substrates and the fluorescence quantum yield Φ is only 45 %.[4] An easily accessible replacement of terrylene for the same spectral region would be of general interest and importance.

The perylene-3,4:9,10-bis(carboximide)s[5] (perylene dyes, **2**) are notable because of their high chemical and photochemical persistency, high fluorescence quantum yields, and high molar absorptivities. However, their absorption spectra are more hypsochromic than **1**. We wanted to match the spectrum to **1** by replacement of one of the carbonyl groups of **2** ($R = CH(C_6H_{13})_2$ with a ketimine function through the condensation of an imidazole ring. Because the free *cis*-1,2-diaminoethylene is unknown we firstly condensed **3** with 1,2-diaminoethane to **4** so that **5** could be obtained by oxidation (Scheme 1). The latter reaction proved to be difficult because of the persistency of **4**. However, the condensation of **3** with 1,2-diaminoethane



Scheme 1. Syntheses of **4**–**6** ($R = CH(C_6H_{13})_2$).

forms an easily separable mixture of **4** and **5**. The ratio of **4** and **5** can be controlled by the amount of 1,2-diaminoethane used: 18 equivalents of 1,2-diaminoethane favors the formation of **4** (30 %; 39 % **5**), whereas 50 equivalents gave mainly **5** (75 %). We tried to avoid the separation of **4** and **5** by the in situ generation of an equivalent of *cis*-1,2-diaminoethylene and its condensation with **3**. To this end, imidazole was treated with noncondensing amines such as 4-dimethylaminopyridine (DMAP[6]) in the presence of **3**. Surprisingly, the reaction product was not **5**, but the isomer **6**. A reaction according to Regel's mechanism[7–10] may be therefore responsible.

The exchange of a carbonyl group of **2** for the ketimine group in **4** causes a bathochromic shift (11 nm), which is increased (32 nm) by the extension of the π system in **5**, so that the working region of the laser is reached (Figure 1).

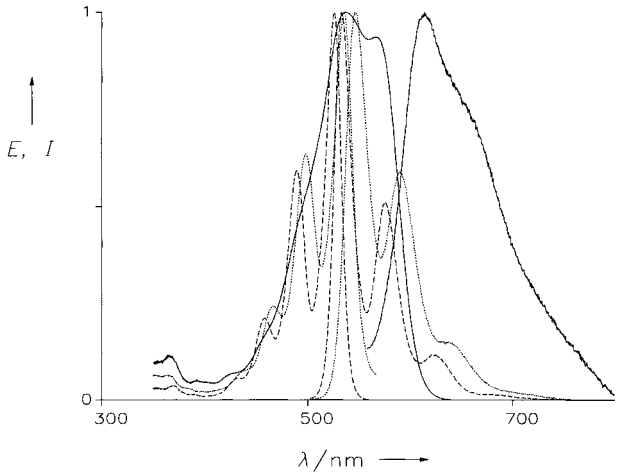


Figure 1. UV/Vis absorption and fluorescence spectra of **2** (– – –), **4** (···) (color coordinates: $x = 0.3646$, $y = 0.2817$, $Y = 65.24$, $T_{min} = 0.1$, 2°, normlight C), and **5** (—) ($x = 0.3414$, $y = 0.1904$, $Y = 30.66$) in chloroform.

Dye **4** exhibits an intense fluorescence (97 % quantum yield). However, the extension of the π system lowers the quantum yield (16 %). The isomeric dye **6**, however, exhibits optimal properties such as a strong pink fluorescence with 84 % quantum yield (in chloroform). Moreover, the absorption spectrum of **6** is nearly congruent with the spectrum of **1** (Figure 2) so that it is a replacement of terrylene, but with better properties. The higher fluorescence quantum yield of **6**

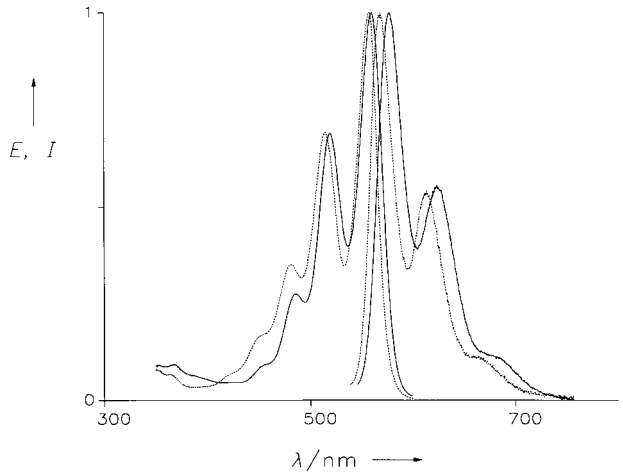


Figure 2. UV/Vis absorption and fluorescence spectra of **6** (—) (color coordinates: $x = 0.3452$, $y = 0.2343$, $Y = 50.55$, $T_{min} = 0.1$, 2°, normlight C) compared to **1** (···) ($x = 0.3663$, $y = 0.2619$, $Y = 51.27$) in chloroform.

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is remarkable as well as its high chemical and photochemical persistency.[11] Moreover, further properties of **6** can be controlled by the substituent R. For example, **6a** exhibits a high solubility relative to **1** by the action of the "swallow-tail" substituent.[12] On the other hand, R may contain, for example, an anchor group for the linkage of **6** to solid surfaces.

Compound **6** is a suitable dye for single-molecule spectroscopy (Figure 3). One observes for example a line with a half-width (FWHM) of 51 MHz in a polyethylene matrix, whereas a line with 39 MHz half-width was described for **1** in hexadecane.[2] Further details of the spectroscopic investigations will be described elsewhere.[13]

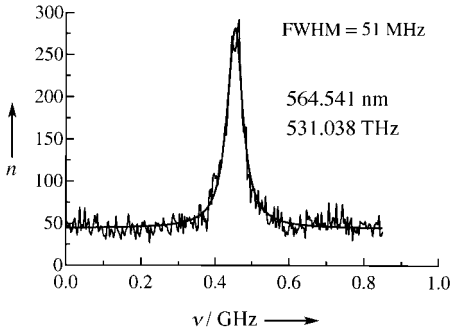

Figure 3. Single-molecule spectrum of **6** in a polyethylene matrix. Laser power 0.7 nW per 5-μm spot. Abscissa: laser detuning in GHz. Ordinate: counts in 90 ms.

Experimental Section

Condensation of **3a** with 1,2-diaminoethane: **3a** (100 mg, 0.17 mmol), 1,2-diaminoethane (0.20 mL, 3.0 mmol), and quinoline (10 mL) were heated at 180 °C for 2 h and poured while still warm into a mixture of ethanol (25 mL) and 2 N hydrochloric acid (50 mL). The violet precipitate was collected by vacuum filtration (D4 glass filter) after 1 h stirring for aging, dried (12 h, 100 °C), and purified by column chromatography (silica gel, chloroform/acetone 5/1). First fraction: 14 mg (7 %) of 1,2-bis-[*N*-(1-hexylheptyl)perylene-3,4:9,10-bis(carboximide)s-*N*′-yl]ethane; R_f (silica gel, $CHCl_3$/acetone 5/1) = 0.94; elemental analysis calcd for $C_{76}H_{74}N_4O_8$ (1170.6): C 77.92, H 6.37, N 4.78; found: C 77.41, H 6.28, N 4.74. Second fraction: 40 mg (39 %) of **5a**, m.p. 324 °C; R_f (silica gel, $CHCl_3$/acetone 5/1) = 0.49; IR (KBr): $\tilde{\nu}$ = 1697, 1658, 1593, 1349, 1282, 807, 741 cm^{-1}; UV/Vis($CHCl_3$): λ_{max} (ε) = 568.6 nm (50420), 540.3 (53100), 427.1 (sh) (5540), 364.7 nm (9070 $L\,mol^{-1}\,cm^{-1}$); fluorescence ($CHCl_3$) λ_{max} = 607, 654 nm (sh); Φ = 16 % ($c = 4.48 \cdot 10^{-7}$ M in $CHCl_3$; **6a**: Φ = 84 %, $\lambda_{excit.}$ = 537 nm);[14] ^{1}H NMR ($CDCl_3$): δ = 8.61 (d, 1H, J = 8 Hz), 8.54 (s, 2H), 8.51 (d, 1H, J = 8 Hz), 8.47 (d, 1H, J = 8 Hz), 8.45 (d, 1H, J = 8 Hz), 8.42 (d, 1H, J = 8 Hz), 8.40 (d, 1H, J = 8 Hz), 7.78 (d, 1H, J = 1.7 Hz), 7.33 (d, 1H, J = 1.6 Hz), 5.11 (m_c, 1H), 2.21 (m_c, 2H), 1.83 (m_c, 2H), 1.26 (m, 16H), 0.77 (t, 6H, J = 5 Hz); ^{13}C NMR ($CDCl_3$): δ = 158.5, 144.8, 132.5, 132.4, 131.3, 129.4, 126.8, 126.7, 125.8, 125.7, 123.8, 123.2, 122.6, 122.4, 122.2, 121.5, 115.2, 55.2, 32.4, 31.8, 29.3, 26.9, 22.6, 14.1; MS (70 eV): *m/z* (%): 596 (16), 595 (37) [M^+], 578 (5), 413 (100), 368 (9); elemental analysis calcd for $C_{39}H_{37}N_3O_3$ (595.7): C 78.63, H 6.26, N 7.05; found: C 78.49, H 6.05, N 7.13. Third fraction: yield 31 mg (30 %) of **4a**, m.p. 308 °C; R_f (silica gel, $CHCl_3$/acetone 5/1) = 0.24; IR (KBr): $\tilde{\nu}$ = 2927, 1697, 1658, 1596, 1356, 1347, 809 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 536.2 (73290), 489.9 (46940), 467.1 (17870), 439.3 nm (sh) (5680 $L\,mol^{-1}\,cm^{-1}$); fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 551 nm (1.00), 587 (0.59), 641 (0.14); Φ = 97 % ($c = 1.01 \cdot 10^{-6}$ M in $CHCl_3$; **2a** Φ = 100 %, $\lambda_{excit.}$ = 494 nm);[14] ^{1}H NMR ($CDCl_3$): δ = 8.60 (m_c, 8H), 5.23 (m_c, 1H), 4.34 (d, 2H, J = 7.9 Hz), 4.27 (d, 2H, J = 7.8 Hz), 2.30 (m_c, 2H), 1.87 (m_c, 2H), 1.35 (m, 16H), 0.87 (t, 6H, J = 5 Hz); ^{13}C NMR ($CDCl_3$): δ = 164.2, 163.4, 158.9, 153.6, 134.3, 134.0, 132.9, 132.0, 131.1, 130.5, 129.6, 129.3, 128.3, 126.5, 126.2, 125.7, 124.8, 122.9, 122.6, 121.9, 121.7, 121.6, 54.8, 54.3, 43.9, 32.4, 31.8, 29.3, 29.2, 27.1, 27.0, 22.6, 14.0; MS (70 eV): *m/z* (%): 597 (21) [M^+], 595 (29), 416 (31), 415 (66), 414 (79), 413 (100), 270 (20), 182 (30); elemental analysis calcd for $C_{39}H_{39}N_3O_3$ (597.8): C 78.29, H 6.52, N 7.03; found C 77.95, H 6.55, N 6.93.

6a: Compound **3a** (250 mg, 0.436 mmol) and imidazole (1.00 g, 14.7 mmol) were homogenized (mortar). The mixture was heated at 170 °C for 3 h (autoclave) after the addition of 4-dimethylaminopyridine (1.06 g, 8.68 mmol). Ethanol (100 mL) and 2 N hydrochloric acid (150 mL) were added to the still warm (ca. 60 °C) mixture, which was then stirred for more than 1 h for aging. The black precipitate was collected by vacuum filtration and purified by column chromatography (silica gel, $CHCl_3$/acetone 5/1). Yield. 130 mg (51 %) of **6a**, m.p. > 315 °C; R_f (silica gel, $CHCl_3$/acetic acid 20/1) = 0.21; IR (KBr): $\tilde{\nu}$ = 1697, 1653, 1592 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 561.5 (86800), 520.7 (60360), 486.7 nm (25050 $L\,mol^{-1}\,cm^{-1}$); fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 575.5 nm (1.00), 616.5 (0.55), 682 (sh) (0.11); Φ = 84 % ($c = 1.11 \cdot 10^{-6}$ M in $CHCl_3$; **2a**: Φ = 100 %, $\lambda_{excit.}$ = 485 nm);[14] ^{1}H NMR ($CDCl_3$): δ = 0.76 (t, 6H), 1.12 – 1.32 (m, 16H), 1.76 – 1.87 (m, 2H), 2.13 – 2.24 (m, 2H), 5.11 (m, 1H), 7.58 (d, 1H), 7.82 (d, 1H), 7.84 (d, 1H), 8.43 (d, 1H), 8.44 (d, 1H), 8.48 (d, 1H), 8.54 (d, 1H), 8.56 (d, 1H), 8.59 (d, 1H), 8.69 (d, 1H); ^{1}H NOESY NMR ($CDCl_3$): δ = (7.82, 7.84); ^{13}C NMR ($CDCl_3$): δ = 13.96, 22.58, 27.02, 29.22, 31.79, 32.52, 54.90, 115.22, 115.50, 122.00, 122.67, 123.30, 123.36, 123.96, 125.92, 128.12, 128.25, 129.22, 129.61, 130.01, 130.23, 134.22, 134.52, 134.63, 135.69, 141.62, 171.65; MS (70 eV): *m/z* (%): 595 (24) [M^+], 415 (12), 414 (50), 413 (100), 85 (18), 83 (28); HR-MS calcd for $C_{39}H_{37}N_3O_3$: 595.2835; found 595.2825; elemental analysis calcd for $C_{39}H_{37}N_3O_3$: C 78.63, H 6.26, N 7.05; found: C 77.75, H 7.05, N 7.03.

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