JOC The Journal of Organic Chemistry

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Thermal Generation of Pentacenes from Soluble 6,13-Dihydro-6,13-ethenopentacene Precursors by a Diels–Alder-retro-Diels–Alder Sequence with 3,6-Disubstituted Tetrazines

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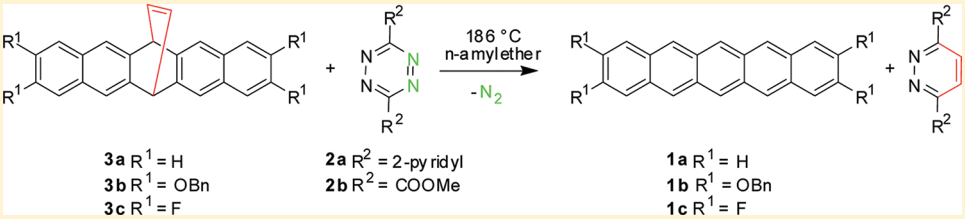
Supporting Information



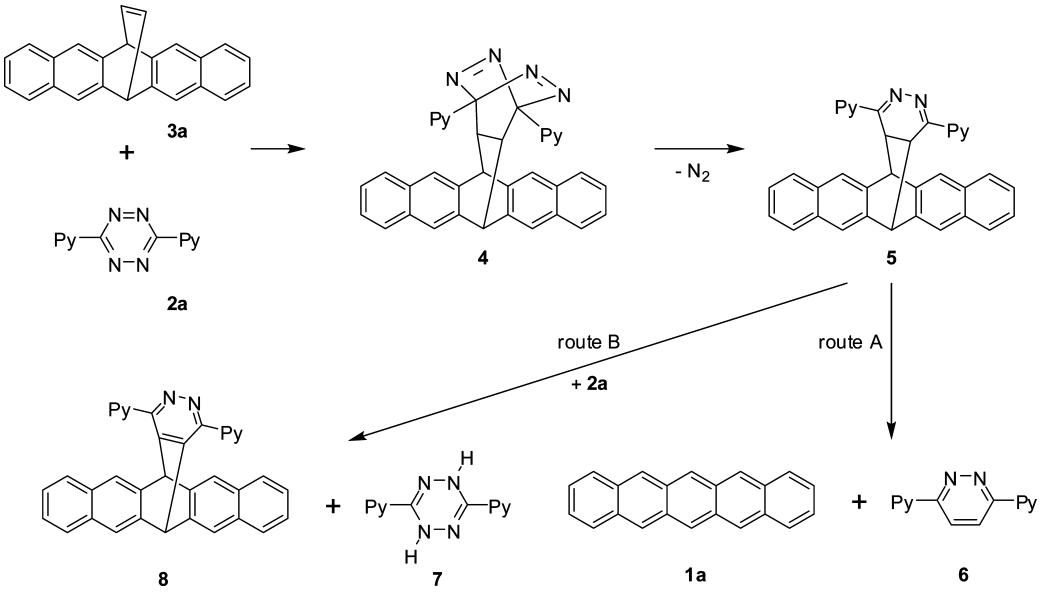
ABSTRACT: 3,6-Substituted tetrazines **2** (**a**: R^2 = 2-pyridyl or **b**: CO_2Me) react with 2,3,9,10-$(R^1)_4$-dihydro-6,13-ethenopentacene **3** in solution at elevated temperature to the corresponding pentacene **1** (**a**: R^1 = H, **b**: OBn, **c**: F).

Pentacene is a promising molecule for application as an organic semiconductor.[1−5] Because of its high degree of crystallinity in the solid state, pentacene has high charge carrier mobility in thin films, and therefore it is an ideal p-type semiconductor in organic thin-film transistors (OTFT).[1−5] Thin films of pentacene show mobilities greater than 1.5 $cm^2/(V\ s)$,[6] and even values greater than 5 $cm^2/(V\ s)$[7] have been reported. The mobility depends critically on the crystal morphology.[8−11] The OTFT devices are generally constructed by vapor-phase deposition of pentacene under high vacuum. The low air stability and the low solubility of pentacene in most solvents is the major problem that limits solution processing in the fabrication of OTFTs.[8−11] Many groups have described soluble pentacene precursors to solve the problem in fabrication of devices by spin coating.[12−16] Solid precursor films were created and underwent a chemical reaction by light or heat to gain a pentacene thin film.[17,18] Ono et al. were the first to use a pentacene precursor containing an α-diketo-bridge.[19] This precursor undergoes photoinduced elimination of two molecules of carbon monoxide, known as Strating–Zwanenburg reaction,[20] to yield pentacene. The α-diketone is availble from a 6,13-dihydro-6,13-ethenopentacene[19,21] in two steps by *cis*-dihydroxylation followed by Swern or Anelli oxidation. The photobisdecarbonylation was applied several times for synthesis of substitueted pentacenes,[17,18,22−26] but this procedure may be of limited use for pentacene derivatives with photolabile or strongly absorbing substituents. Herwig and Müllen generated a soluble pentacene precursor by reacting 6,13-dihydro-6,13-ethenopentacene with tetrahalothiophenedi-oxide in a Diels–Alder cycloaddition at high pressure (6 kbar).[21] Removal of the cyclohexadiene bridge at temperatures below 180 °C allowed generation of pentacene films on glass after spin coating.[21] Another way to remove etheno units is treatment with 3,6-disubstituted 1,2,4,5-tetrazines at elevated temperatures.[27−30] After a Diels–Alder reaction between the ethene unit and the tetrazine and loss of N_2, a subsequent retro-Diels–Alder step results in elimination of the etheno unit as part of pyridazine. We investigate the feasibility of this Diels–Alder-retro-Diels–Alder sequence to synthesize pentacenes from 6,13-dihydro-6,13-ethenopentacenes. This approach has been used previously for the synthesis of naphthalene and anthracene subunits.[27] In view of the quickly increasing Diels–Alder reactivity in the acene series, it is not clear if a cycloreversion reaction to a pyridazine can be employed for generating the pentacene π-system at all. Refluxing **3a** at 186 °C with an equimolar amount of 3,6-di(2-pyridyl)tetrazine **2a** in dipentylether for 2 h gave a dark blue solid upon cooling that was isolated in a yield of 28%. This was identified as pentacene **1a** by comparison of its MS and UV–vis spectral properties with an authentic sample, and by ^1H and ^{13}C NMR spectroscopy at elevated temperature. The low yield of 28% is due to a side reaction. The retro-Diels–Alder reaction of intermediate **5** can compete with dehydrogenation by an unreacted tetrazine molecule (Scheme 1).[31] This produces pyridazine **8** and 1,4-dihydro-3,6-(2-pyridyl)tetrazine **7**.[32] The latter, along with unreacted **1a**, could by identified by EI-MS and ^1H NMR from the reaction solution. To demonstrate the dehydrogenation of **5** to the side product **8**, we refluxed 2 equiv of tetrazine **2a** with 1 equiv of dienophile **3a** in 1,4-dioxane. Under these conditions the reaction produced **8** and **7** in a yield of 48%.

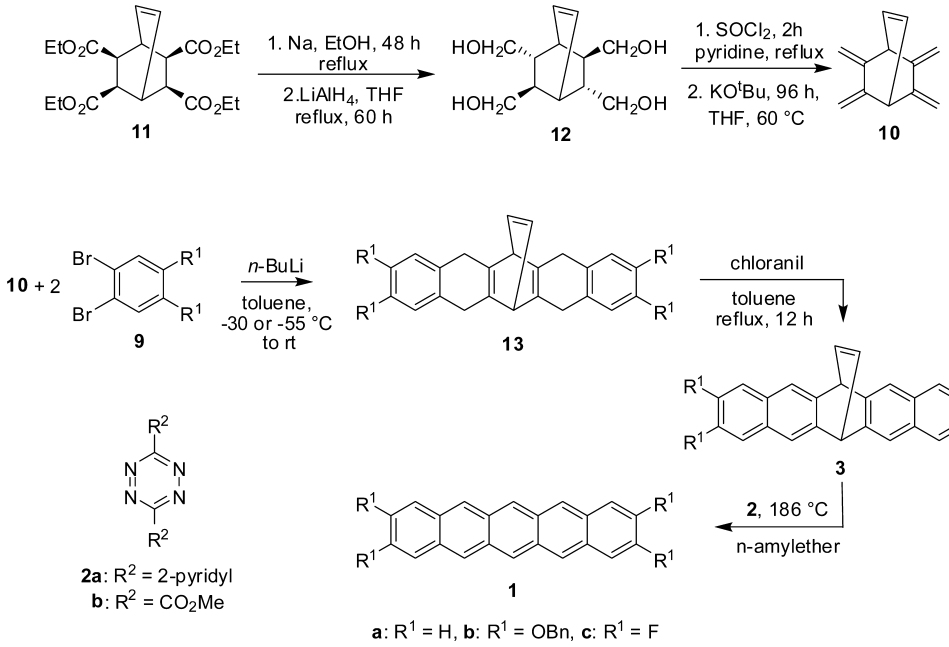
Side product **8** does not react in a retro-Diels–Alder sequence, neither in solution nor in the solid phase (heated up

Received: November 29, 2011
Published: March 23, 2012

Scheme 1. Diels–Alder-retro-Diels–Alder Sequence for Formation of Pentacene 1a from 3a and 2a (Route A) and the Proposed Side Reaction (Route B)



Scheme 2. Synthesis of Pentacenes



to 250 °C), to form the target acene. As it was not possible to increase the yields by changing the reaction conditions, we reasoned that a more reactive tetrazine is required to keep its concentration low and thus suppress the dehydrogenation pathway. 3,6-Di(carboxylic acid methyl ester)tetrazine **2b** is more reactive in cycloaddition reactions than **2a** by 3 orders of magnitude.[33] In the reaction of pentacene precursor **3a** with the more reactive tetrazine **2b** the yield increases to 48% at a decreased reaction time of only 2 min. Such yields are typically reported for the removal of etheno units using tetrazines in the literature.[27] To investigate the scope of the reaction we studied the formation of donor substituted 2,3,9,10-tetra(benzyloxy)-pentacene **1b** and acceptor substituted 2,3,9,10-tetrafluoropentacene **1c**. We generate the required substituted 6,13-dihydro-6,13-ethenopentacene **3b** and **3c** in two steps (14% and 49% yield over both steps for **3b** and **3c**, respectively) starting with the 1,2-bis(benzyloxy)-4,5-dibromobenzene **9b**[34,35] or 1,2-dibromo-4,5-difluorobenzene **9c** and 2,3,5,6-tetrakis-(methylene)bicyclo[2.2.2]oct-7-ene **10**[36] (Scheme 2). In the synthesis of **10** we obtained crystals structures of the all-*trans* ethylester precusor **11** and the alcohol **12** (see Supplementary Figures S25 and S26) that were of sufficient quality for X-ray crystallography. The bond distances and bond angles are quite similar to published molecules.[37,38] For example, **12** forms H-bridges in the crystal with O–O distances (2.711(5)–2.776(5) Å) similar to Iwasaki's 2,3-di-*tert*-butyl-5,6,7,8-endotetrakis-(hydroxymethyl)bicyclo[2.2.2]oct-2-ene (O···H–O distances 1.96(5)–2.04(4) Å).[37]

The formation of **1b** from **3b** proceeds with higher yields than that of parent pentacene with both tetrazines **2a** and **2b**.

dx.doi.org/10.1021/jo202450u | J. Org. Chem. 2012, 77, 3538–3542

With the more reactive **2b** the pentacene **1b** is formed in 62% yield. The tetrafluoro pentacene **1c**, on the other hand, is formed from **3c** with tetrazine **2b** with a lower yield of only 13%. Due to the low solubility of **1b** and **1c** at room temperature, NMR spectra were obtained in 1,1,2,2-tetrachloroethane (TCE) at 120 °C. Only a ^{1}H NMR spectrum could be obtained for **1c**; its solubility in TCE was too low to measure a ^{13}C NMR spectrum even at 120 °C.

In the UV−vis spectrum of **1b** and **1c** (in CH_2Cl_2 solution at room temperature, Figure 1) the p and the α bands show the typical vibrational fine structure of pentacenes. The recorded UV−vis spectrum of **1b** is very similar to that reported for 2,3,9,10-tetramethoxypentacene.[23] The longest wavelength absorption of the p band system in **1b** undergoes a red-shift of 5 nm compared to 2,3,9,10-tetramethoxypentacene, and the longest wavelength absorption of the α band is red-shifted by only 2 nm. In pentacene **1c** the longest wavelength absorption of the p band system is blue-shifted by 15 nm and the β band by 4 nm compared to **1a**.

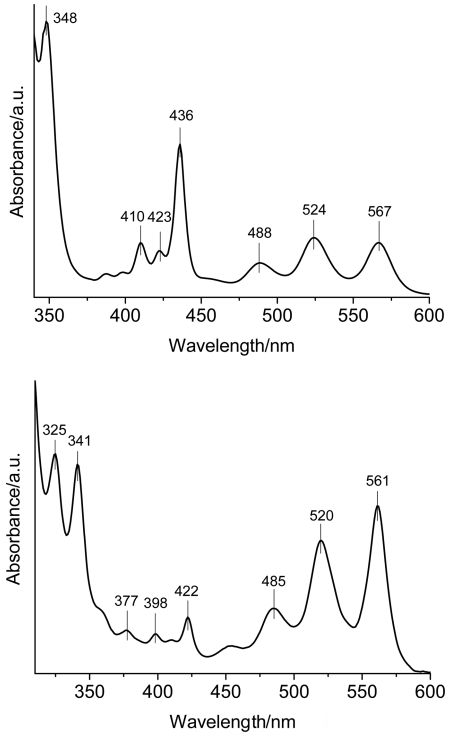


Figure 1. UV−vis spectrum (in CH_2Cl_2 solution at room temperature) of **1b** (top) and **1c** (bottom).

In summary, our study shows that the aromatic pentacene core can be obtained from 6,13-dihydro-6,13-ethenopentacene by a Diels−Alder-retro-Diels−Alder sequence employing tetrazines in moderate yields. We expect that the tetrazine route may be useful in case where the photobisdecarbonylation strategy of Ono et al. is not feasible for pentacene generation.

EXPERIMENTAL SECTION

All commercially available reagents were used as received. Compound **10** was prepared following a literature procedure[36] (yield 16% over 5 steps), and compound **9b** was prepared by following literature procedures[34,35] (54%, over two steps), and compound **3a** was prepared following literature procedures[19,21] (30% over two steps). Air- and/or water-sensitive reactions were carried under N_2 in oven-dried glassware. Dry solvents (hexane, toluene, and dichlormethane) were taken from a MBraun MB SPS-800 (solvent purification system). Methanol and dipenthylether were stored over N_2 and molecular sieves (3 Å). ^{13}C{^{1}H} NMR spectra of **1a** and **1b** were measured at 120 °C using the UDEFT pulse sequence.[39]

2,3,9,10-Tetrabenzyloxy-5,6,7,12,13,14-hexahydro-6,13-ethenopentacene (13b). To a solution of 4.1 g (9.19 mmol) of 1,2-dibenzyloxy-4,5-dibromobenzene (**9b**) and 0.7 g (4.48 mmol) of 2,3,5,6-tetrakis(methylene)bicyclo[2.2.2]oct-7-ene (**10**) at −30 °C in 80 mL of toluene was added dropwise a solution of 6 mL of *n*-BuLi (1.6 M in *n*-hexane) diluted in 20 mL of *n*-hexane over 2 h. After the addition the reaction mixture was stirred 2 h at −30 °C and at room temperature overnight and then quenched with methanol. After the solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica; DCM) to obtain 1.585 g (48%) of a white solid. Mp 161 − 163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.45 (s, 8H), 4.22 (m, 2H), 5.10 (s, 8H), 6.66 (s, 4H), 6.81 (m, 2H) 7,36 (m, 20H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 32.8, 54.2, 71.6, 115.4, 127.1, 127.3, 127.7, 128.4, 137.5, 139.2, 140.2, 147.2. Mass spectrum (EI) *m*/*z* M$^+$ 732.4 (7), 642.4 (15), 552.4 (13), 390.3 (15), 300.2 (7), 91.2 (100). HREI $C_{52}H_{44}O_4$ calcd *m*/*z* 732.323960, measured *m*/*z* 732.32235.

2,3,9,10-Tetrabenzyloxy-6,13-dihydo-6,13-ethenopentacene (3b). A 1.5 g (2.05 mmol) portion of **13b** and 1.043 g (4.24 mmol) of chloranil in 100 mL of toluene were heated under reflux overnight. After cooling to room temperature a part of **3b** precipitated and was collected by filtration followed by washing with *n*-hexane. The filtrate was washed three times with 20% aqueous NaOH (3 × 100 mL) and two times with water (2 × 100 mL). After drying over $MgSO_4$ the solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica; DCM). Total yield: 0.774 g (50%). Mp 216−219 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17 (m, 2H), 5.22 (s, 8H), 6.98 (m, 2H), 7.08 (s, 4H), 7.45 (m, 24H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 50.2, 71.1, 110.0, 120.2, 127.2, 127.3, 128.0, 128.7, 137.4, 138.7 141.4, 148.8. Mass spectrum (EI) *m*/*z* M$^+$ 728.5 (40), 638.4 (10), 610 (5), 581.4 (5), 91.2 (100). HREI $C_{52}H_{40}O_4$ calcd *m*/*z* 728.29266, measured *m*/*z* 728.29398.

2,3,9,10-Tetra(benzyloxy)pentacene (1b). *Method A.* A 40 mg (0.055 mmol) portion of **3b** in dipentylether (10 mL) was brought to reflux, and 14.2 mg (0.06 mmol) of 3,6-di(2-pyridyl)tetrazine (**2a**) was added. The violet mixture was heated under reflux for 2 h. After cooling to room temperature, a red solid formed. The solid was collected by filtration and washed with dipentylether (10 mL), methanol (20 mL,) and *n*-hexane (20 mL). Yield: 13.1 mg (38%)

Method B. A 50 mg (0.069 mmol) portion of **3b** in dipentylether (10 mL) was brought to reflux, and 13.6 mg (0.069 mmol) of 3,6-di(carboxylic acid methyl ester)tetrazine (**2b**) was added. The red mixture was heated under reflux for 1.5 min. The reaction was stopped by quickly immersing the reaction flask into an ice bath (0 °C). The red solid was collected by filtration and washed with dipentylether (10 mL), methanol (20 mL), and *n*-hexane (20 mL). Yield: 28.9 mg (62%) ^{1}H NMR (250 MHz, d_2-TCE, 120 °C) δ 5.26 (s, 8H), 7.21 (s, 4H), 7.27−7.40 (m, 12H), 7.47−7.54 (m, 8H), 8.33 (s, 4H), 8.65 (s, 2H). ^{13}C{^{1}H} NMR (126 MHz, d_2-TCE, 120 °C) δ 71.5, 108.2, 123.7, 124.8, 127.5, 128.1, 128.7, 129.4, 129.9, 137.5, 150.6. Mass spectrum (EI) *m*/*z* M$^+$ 91 (100), 207 (18), 432 (4), 522 (8), 613 (18), 702 (19). HREI $C_{50}H_{38}O_4$ calcd *m*/*z* 702.277010, measured *m*/*z* 702.27647.

2,3,9,10-Tetrafluoro-5,6,7,12,13,14-hexahydro-6,13-ethenopentacene (13c). To a solution of 2.7 g (10.08 mmol) of 1,2-dibrom-4,5-difluorbenzene (**9c**) and 0.75 g (4.8 mmol) of 2,3,5,6-tetrakis-(methylene)bicyclo[2.2.2]oct-7-ene (**10**) at −55 °C in 100 mL of toluene was added dropwise a solution of 7.5 mL of *n*-BuLi (1.6 M in *n*-hexane) diluted in 20 mL of *n*-hexane over 2 h. After the addition the reaction mixture was stirred for 2 h at −55 °C and at room temperature overnight and then quenched with methanol. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (silica; *n*-hexane/DCM, 5/1) to obtain 1.08 g (51%) bright yellow solid. Mp 113.5 − 114.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.53 (s, 8H), 4.27 (m, 2H), 6.84−6.90 (m, 6H);

dx.doi.org/10.1021/jo202450u | J. Org. Chem. 2012, 77, 3538−3542

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 32.8, 54.0, 116.8 (t), 130.6, 139.5, 140.2, $^{19}F\{^1H\}$ NMR (400 MHz, $CDCl_3$) δ −141.8. Mass spectrum (EI) m/z M^+ 380.1 (100), 350.1 (22), 337.1.4 (15), 319.1 (5), 251.1 (15), 239.1 (55), 214.1 (70), 203.2 (80), 177.1 (95), 164.0 (45), 151.0 (25), 140.1 (10). HREI $C_{24}H_{16}F_4$ calcd m/z 380.118813, measured m/z 380.11841.

2,3,9,10-Tetrafluoro-6,13-dihydo-6,13-ethenopentacene (3c). One gram (2.63 mmol) of **13c**, 1.92 g (7.89 mmol) of chloranil, and 1.45 g of K_2CO_3 in 150 mL toluene were heated under reflux overnight. The reaction mixture was washed three times with 20% aqueous NaOH (3 × 100 mL) and two times with water (2 × 100 mL). After drying over $MgSO_4$ the solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica; *n*-hexane/DCM, 4/1). Total yield: 960 mg (96%). Mp 218.1 − 223.2 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 5.29 (m, 2H), 7.03 (m, 2H), 7.43 ($t_{Axx'}$, J = 9 Hz, 4H), 7.63 (s, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 49.9, 113.4, 120.9, 128.4 (t), 138.3, 142.6, 148.6 - 151.3 (m), $^{19}F\{^1H\}$ NMR (400 MHz, $CDCl_3$) δ −138.0. Mass spectrum (EI) m/z M^+ 376.2 (90), 375.1 (100), 357.1 (20), 214.1 (8), 187.1 (45), 178 (40), 162.8 (15). HREI $C_{24}H_{12}F_4$ calcd m/z 376.087513, measured m/z 376.08776.

Pentacene (1c). *Method B.* A 100 mg (0.266 mmol) portion of **3c** in dipentylether (10 mL) was brought to reflux, and 52.7 mg (0.266 mmol) of 3,6-di(carboxylic acid methyl ester)-tetrazine (**2b**) was added. The red mixture was heated under reflux for 1.5 min. The reaction was stopped by quickly immersing the reaction flask into an ice bath (0 °C). The blue solid was collected by filtration and washed with DCM (20 mL) and *n*-hexane (20 mL). Yield: 12.1 mg (13%) ^1H NMR (250 MHz, d_2-TCE, 120 °C) δ 7.61 ($t_{Axx'}$, J = 10 Hz, 4H), 8.53 (s, 4H), 8.82 (s, 4H). $^{19}F\{^1H\}$ NMR (400 MHz, $CDCl_3$) δ −134.83. Mass spectrum (EI) m/z M^+ 165 (10), 175 (40), 330 (10), 350 (100). HREI $C_{22}H_{10}F_4$ calcd m/z 350.071863, measured m/z 350.07152.

Pentacene (1a). *Method A.* A 100 mg (0.32 mmol) portion of **3a** in dipentylether (10 mL) was brought to reflux, and 78 mg (0.33 mmol) of 3,6-di(2-pyridyl)tetrazine (**2a**) was added. The violet mixture was heated under reflux for 2 h. After cooling to room temperature a dark solid formed. The solid was collected by filtration and washed with dichloromethane (20 mL) and hexane (20 mL). Yield: 25.6 mg (28%).^1H NMR (250 MHz, d_2-TCE, 120 °C) δ 7.26−7.31 (m, 4H), 7.87−7.91 (m, 4H), 8.61 (s, 4H), 8.91 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, d_2-TCE, 120 °C) δ 120.0, 124.6, 125.7, 125.8, 127.8, 137.8. Mass spectrum (EI) m/z M^+ 278.2 (100), 276.2 (15), 139.3 (10). From the dichloromethane washing solution bright yellow crystals could be collected after removal of solvent. These were identified as **7** by ^1H NMR spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (ddd, 2 × 5-Py), 7.76 (dt, 2 × 4-PyH), 8.04 (ddd, 2 × 3-PyH), 8.53−8.56 (m, 2 × 6-PhH and 2 × CNH). After removal of the dipentylether from the first washing solution a mixture of **3a** (m/z 304.2), **7** (m/z 238.2), **8** (m/z 510.2), and **6** (m/z 234.3) could be identified by mass spectrometry.

Method B. A 50 mg (0.16 mmol) portion of **3a** in dipentylether (10 mL) was brought to reflux, and 33 mg (0.166 mmol) of 3,6-di(carboxylic acid methyl ester)tetrazine (**2b**) was added. The red mixture was heated under reflux for 1.5 min. The reaction was stopped by quickly immersing the reaction flask into an ice bath (0 °C). The dark solid was collected by filtration and washed with dichlormethane (20 mL) and hexane (20 mL). Yield: 22 mg (48%). Mass spectrum (EI) m/z M^+ 278.2 (100), 276.2 (15), 139.3 (10).

6,13-Dihydro-6,13-[4′,5′]-3′,6′-(di-2″-pyridyl)pyridazino-pentacene 8. A 40 mg (0.131 mmol) portion of **3a** in 1,4-dioxane (15 mL) was brought to reflux, and 62.1 mg (0.263 mmol) of 3,6-di(2-pyridyl)tetrazine (**2a**) was added. The violet mixture was heated under reflux overnight. After cooling to room temperature the solvent was removed, and the crude product was purified by column chromatography (silica, DCM/acetone 9/1) to gain 13.1 mg of **7** (second fraction) and 28.1 mg of **8** (48%, third fraction). **8**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 2H), 7.36−7.40 (m 4H), 7.51 (ddd, 2H), 7.95 (m, 6H), 8.41 (ddd, 2H), 9.05 (ddd, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 48.4, 123.5, 124.0, 124.6, 126.1, 127.8, 132.2, 137.2, 139.9, 145.2, 149.1, 153.2, 156.0; mass spectrum (EI) m/z M^+ 510 (90), 432 (100), 405 (28), 327 (17), 302 (5), 278 (85), 255 (25), 239 (15), 202 (10); HREI: $M^{+\bullet}$ ($C_{36}H_{22}N_4$) calcd 510.18444, measured 510.18131.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H and ^{13}C NMR and mass spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by DFG Fonds der Chemischen Industrie. We thank Prof. Dr. K.-P. Zeller for helpful discussion concerning the mass spectrum of acene **1b**.

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