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A new method for pyrrole *peri*-annulation: synthesis of 1*H*-1,5,7-triazacyclopenta[*c,d*]phenalenes from 1*H*-perimidines

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ABSTRACT

New methods for the synthesis of 1*H*-1,5,7-triazacyclopenta[*c,d*]phenalenes have been developed based on a sequence involving Schmidt reaction of keto-perimidines and acylation of the intermediate amides with 1,3,5-triazines or carboxylic acids. The same synthetic sequence starting from the corresponding alkylperimidine includes acylation with acetic acid as the first step.

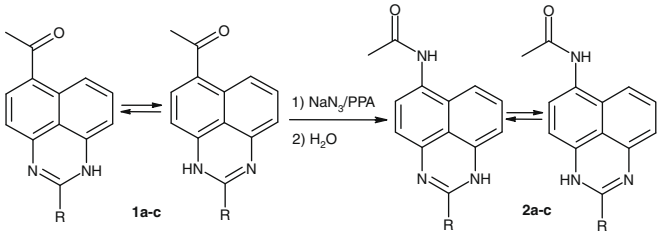
It is difficult to overestimate the significance of indole derivatives amongst biologically active substances. A special place is occupied by benzo[*c,d*]indoles, some of which have been shown to be effective inhibitors of thymidylate synthetase.[1]

A standard method for the synthesis of such compounds is via annulation of either a carbocycle[2a] or a pyrrole ring starting from 1-naphthylamines containing an adjacent carbonyl[2c] or nitrile group.[1,2c] If a donor substituent is present at position 5, a carbonyl group can be introduced during the course of the reaction.[2b,c]

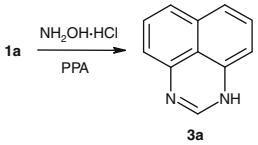
Prior to our work, benzo[*c,d*]indole perimidine derivatives were not widely known. This was due to the poor availability of perimidines containing an amino group at the *peri* positions; nitrations at these positions were low yielding.[3] In the current work we report synthetic methods for such compounds using the Schmidt reaction.

The Schmidt reaction cannot be implemented on acetylperimidines **1** using classical conditions. We have shown that amides **2** can be obtained in quantitative yields using sodium azide/polyphosphoric acid (PPA) (Scheme 1) provided that a 1.3-fold excess of NaN_3 is used in 80% PPA or a 1.07-fold excess of NaN_3 in 86% PPA.[4]

An attempt to carry out a Beckmann rearrangement did not succeed. The reaction of compound **1a** with hydroxyammonium chloride led to deacylation with the formation of perimidine **3a** (Scheme 2).



Scheme 1. The synthesis of amides **2a–c**.



Scheme 2. Reaction of acetylperimidine **1a** with hydroxyammonium chloride in PPA.

On the basis of our previous work,[5] we propose that *peri*-annulation of the pyrrole ring may be achieved using a Schmidt reaction and subsequent reaction with 1,3,5-triazines **4a–c**. Indeed, the reaction of acetylperimidines **1a–c** with NaN_3 in PPA at 55–60 °C for 1 h followed by the addition of the corresponding 1,3,5-triazine 4a–**c** and heating for an additional 3 h at 55–60 °C (**4a**) or

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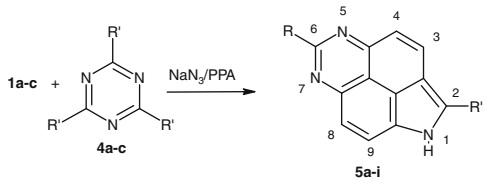


Scheme 3. The synthesis of 1*H*-1,5,7-triazacyclopenta[*c,d*]phenalenes **5a–i** using 1,3,5-triazines **4a–c**.

Table 1
The synthesis of 1*H*-1,5,7-triazacyclopenta[*c,d*]phenalenes **5a–i**

Entry	R	R′	Product	Yield (%), from			
				1 and **4**	**1** and R′COOH	**3** and **4**	**3** and R′COOH
1	H	H	**5a**	75	—	61	—
2	Me	H	**5b**	74	—	63	—
3	Ph	H	**5c**	77	—	68	—
4	H	Me	**5d**	68	81	58	67
5	Me	Me	**5e**	71	84	62	68
6	Ph	Me	**5f**	76	89	65	65
7	H	Ph	**5g**	65	72	—	59
8	Me	Ph	**5h**	67	81	—	65
9	Ph	Ph	**5i**	69	78	—	63

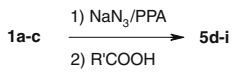
110–120 °C (**4b**,**c**) gave previously unknown 1*H*-1,5,7-triazacyclopenta[*c,d*]phenalenes **5a–i** (Scheme 3) in yields of 65–77% (Table 1).[6]

The process can be carried out as a three-component reaction using the same temperature regime. In this case the overall yields were almost the same.

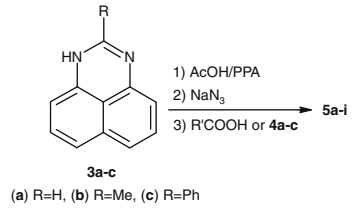
Furthermore, the synthesis of compounds **5d–i** could be accomplished by reaction with carboxylic acids **6a,b** (Scheme 4) to give the products in slightly higher yields (Table 1).[6]

Acetylperimidines **1a–c** may serve as starting compounds in reactions with triazines as well as with carboxylic acids regardless of the substituent at position 2 of products **5**.

It is known that acetylperimidines **1a–c** can be obtained by the reaction of perimidines **3a–c** with acetic acid in PPA.[7] Thus we have shown that the reaction of **3a–c** with a 1.2-fold excess of acetic acid proceeds at 50–55 °C in one hour followed by the treatment with sodium azide, and finally addition of the corresponding 1,3,5-triazine **4a–c** or carboxylic acid with heating for 3 h at 110–120 °C (90–100 °C in the case of **4a**) gave 1*H*-1,5,7-triazacyclopenta[*c,d*]phenalenes **5a–i** (Scheme 5) in good yields (Table 1).[8]



Scheme 4. The synthesis of 1*H*-1,5,7-triazacyclopenta[*c,d*]phenalenes **5d–i** using carboxylic acids.



Scheme 5. The synthesis of 1*H*-1,5,7-triazacyclopenta[*c,d*]phenalenes **5d–i** from perimidines **3a–c**.

The yields in this case were slightly lower due to the formation of 9-acetylperimidines during the first stage.[7]

In conclusion, the advantages of the described method for pyrrole *peri*-annulation include ready availability of the reagents, experimental simplicity and its applicability to the synthesis of a broad range of substituted 1*H*-1,5,7-triazacyclopenta[*c,d*]-phenalenes.

Acknowledgement

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4. *General procedure for the synthesis of amides* **2a–c**: a mixture of ketone **1a–c** (1 mmol), PPA (2–3 g) and sodium azide (1.3 mmol for 80% PPA) or (1.07 mmol for 86% PPA)[9] was heated at 55–60 °C with stirring for 1 h. The reaction mixture was poured into H_2O (50 ml) and neutralized with aq NH_3 solution. The precipitate was removed by filtration and the filtrate was extracted with butyl alcohol (3 × 30 ml). The solvent was evaporated in vacuo, the residue combined with the precipitate and purified by crystallization from EtOAc.
Data for 6(7)-acetoaminoperimidine (**2a**): mp 225–226 °C (EtOAc). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.08 (3H, s, COMe), 6.43 (2H, m, H-4(9), 9(4)), 7.03 (1H, d, J = 8.5 Hz, H-7(6)), 7.15 (1H, dd, J = 8.5, J = 7.3 Hz, H-8(5)), 7.24 (1H, d, J = 8.1 Hz, H-7(6)), 7.32 (1H, s, H-2), 9.21 (1H, br s, NHCO), 10.61 (1H, br s, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 23.11, 107.81, 108.12, 114.52, 114.73, 122.01, 125.19, 126.38, 128.92, 141.58, 154.66, 162.83, 169.54. ν_{max}(KBr)/cm^{-1} 3416 (NH), 3184 (NH), 1638 (CONH), 1602 (CONH). Anal. Calcd for $C_{13}H_{11}N_3O$: C, 69.32; H, 4.92; N, 18.65. Found: C, 69.45; H, 4.86; N, 18.61.
Data for 6(7)-acetoamino-2-methylperimidine (**2b**): mp 247–248 °C (EtOAc). ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.04 (3H, s, Me), 2.07 (3H, s, COMe), 6.43 (2H, br m, H-4(9), 9(4)), 7.02 (1H, d, J = 8.2 Hz, H-7(6)), 7.15 (1H, dd, J = 8.2, J = 7.3 Hz, H-8(5)), 7.24 (1H, d, J = 8.3 Hz, H-7(6)), 9.14 (1H, br s, NHCO), 10.5 (1H, br s, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.34, 23.41, 107.59, 107.63, 114.41, 114.64, 121.92, 125.14, 126.29, 128.75, 141.55, 154.58, 162.79, 169.22. ν_{max}(KBr)/cm^{-1} 3408 (NH), 3352 (NH), 1638 (CONH), 1612 (CONH). Anal. Calcd for $C_{14}H_{13}N_3O$: C, 70.28; H, 5.48; N, 17.56. Found: C, 70.43; H, 5.42; N, 17.52.
Data for 6(7)-acetoamino-2-phenylperimidine (**2c**): mp 302–303 °C (EtOAc). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.09 (3H, s, COMe), 6.67 (2H, br m, H-4(9), 9(4)), 7.11 (1H, d, J = 8.4 Hz, H-7(6)), 7.21 (1H, dd, J = 8.4, J = 7.3 Hz, H-8(5)), 7.34 (1H, d, J = 8.0 Hz, H-7(6)), 7.54 (3H, m, Ph-3,4,5), 8.03 (2H, d, J = 7.7 Hz, Ph-2,6), 9.19 (1H, br s, NHCO), 10.5 (1H, br s, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 23.26, 107.81, 108.34, 114.63, 114.91, 122.12, 125.22, 126.31, 127.83 (2C), 128.05 (2C), 128.99, 129.31, 139.88, 141.63, 154.89, 163.14, 169.73. ν_{max}(KBr)/cm^{-1} 3418 (NH), 3220 (NH), 1632 (CONH), 1598 (CONH). Anal. Calcd for $C_{19}H_{15}N_3O$: C, 75.73; H, 5.02; N, 13.94. Found: C, 75.91; H, 4.98; N, 13.89.
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6. *General procedure for the synthesis of 1H-1,5,7-triazacyclopenta[c,d]phenalenes* ***5a–i*** *from acetylperimidines* **1a–c**: a mixture of acetylperimidine **1a–c** (1 mmol) and sodium azide (1.07 mmol) in 86% PPA (2–3 g) was heated at 55–60 °C with stirring for 1 h. The 1,3,5-triazine **4a–c**[10] or carboxylic acid (1.5 mmol) was added to the reaction mixture. The temperature was increased to 110–120 °C (90–100 °C for **4a**) and stirring was continued for 3 h. The reaction mixture was poured into H_2O (30 ml) and neutralized with aq NH_3 solution. The precipitate was removed by filtration and the filtrate was extracted with toluene (6 × 30 ml). The precipitate was extracted with toluene (100 ml) in a Soxhlet apparatus for 5 h. The toluene fractions were combined and the solvent was evaporated in vacuo. The residue was purified by crystallization from toluene or toluene with petroleum ether.
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8. *General procedure for the synthesis of 1H-1,5,7-triazacyclopenta[c,d]phenalenes* ***5a–i*** *from perimidines* **3a–c**: a mixture of perimidine **3a–c** (1 mmol) and acetic acid (1.2 mmol) in 80% PPA (2–3 g) was heated at 55–60 °C with stirring for 1 h. Then sodium azide (1.3 mmol) was added and stirring was continued at the same temperature for 1 h. The 1,3,5-triazine **4a–c** or carboxylic acid (1.5 mmol) was added to the reaction mixture, the temperature was increased to 110–120 °C (90–100 °C for **4a**) and stirring was continued for 3 h. The reaction

mixture was poured into H_2O (30 ml) and neutralized with aq NH_3 solution. The precipitate was removed by filtration and the filtrate was extracted with toluene (6 × 30 ml). The precipitate was extracted with toluene (100 ml) in a Soxhlet apparatus for 5 h. The toluene fractions were combined and the solvent was evaporated in vacuo. The residue was purified by crystallization from toluene.

Data for 1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalene **(5a)**: mp 207–209 °C (toluene). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.70 (1H, d, J = 9.0 Hz, H-3), 7.91 (1H, d, J = 8.7 Hz, H-9), 8.45 (1H, d, J = 8.7 Hz, H-8), 8.46 (1H, s, H-2), 8.51 (1H, d, J = 9.0 Hz, H-4), 9.48 (1H, s, H-6), 13.2 (1H, br s, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 111.87, 112.86, 116.34, 120.09, 120.42, 120.56, 124.88, 131.06, 136.44, 147.82, 154.91, 163.04. ν_{max}(KBr)/cm^{-1} 3401 (NH). Anal. Calcd for $C_{12}H_7N_3$: C, 74.60; H, 3.65; N, 21.75. Found: C, 74.71; H, 3.58; N, 21.64.

Data for 6-methyl-1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalene **(5b)**: mp 237–238 °C (toluene). ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.93 (3H, s, Me), 7.65 (1H, d, J = 9.0 Hz, H-3), 7.82 (1H, d, J = 8.7 Hz, H-9), 8.42 (1H, d, J = 8.7 Hz, H-8), 8.46 (1H, s, H-2), 8.50 (1H, d, J = 9.0 Hz, H-4), 13.1 (1H, br s, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 26.91, 111.87, 112.94, 116.27, 119.91, 120.48, 120.64, 124.67, 130.82, 136.34, 147.83, 154.91, 162.99. ν_{max}(KBr)/cm^{-1} 3332 (NH). Anal. Calcd for $C_{13}H_9N_3$: C, 75.35; H, 4.38; N, 20.28. Found: C, 75.51; H, 4.33; N, 20.16.

Data for 6-phenyl-1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalene **(5c)** mp 201–203 °C (toluene). ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.57–7.63 (m, 3H, Ph(H-3,4,5)), 7.78 (d, J = 8.4 Hz, 1H, H-3), 7.96 (d, J = 8.5 Hz, 1H, H-9), 8.39 (s, 1H, H-2), 8.43 (d, J = 8.5 Hz, 1H, H-8), 8.51 (d, J = 8.4 Hz, 1H, H-4), 8.73 (d, J = 7.3 Hz, 2H, Ph(H-2,6)), 13.1 (br s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): 112.51, 112.88, 117.14, 120.51, 120.55, 120.72, 124.83, 128.08 (2C), 128.20 (2C), 129.32, 130.86, 136.28, 140.12, 147.93, 155.14, 160.14. ν_{max}(KBr)/cm^{-1} 3374 (NH). Anal. Calcd for $C_{18}H_{11}N_3$: C, 80.28; H, 4.12; N, 15.60. Found: C, 80.43; H, 4.03; N, 15.54.

Data for 2-methyl-1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalene **(5d)**: mp 259–260 °C (toluene). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.98 (3H, s, Me), 7.58 (1H, d, J = 9.0 Hz, H-3), 7.78 (1H, d, J = 8.7 Hz, H-9), 8.31 (1H, d, J = 8.7 Hz, H-8), 8.47 (1H, d, J = 9.0 Hz, H-4), 9.36 (1H, s, H-6), 13.1 (1H, br s, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 12.46, 112.02, 112.92, 116.28, 120.05, 120.45, 120.52, 124.65, 130.81, 136.21, 147.82, 154.98, 163.04. ν_{max}(KBr)/cm^{-1} 3398 (NH). Anal. Calcd for $C_{13}H_9N_3$: C, 75.35; H, 4.38; N, 20.28. Found: C, 75.54; H, 4.31; N, 20.15.

Data for 2,6-dimethyl-1*H*-1,5,7-triazacyclopenta[*c*,*d*] phenalene **(5e)**: mp 271–272 °C (toluene). ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.86 (3H, s, (2)Me), 2.92 (3H, s, (6)Me), 7.46 (1H, d, J = 9.0 Hz, H-3), 7.64 (1H, d, J = 8.7 Hz, H-9), 8.22 (1H, d, J = 8.7 Hz, H-8), 8.38 (1H, d, J = 9.0 Hz, H-4), 13.1 (1H, br s, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 12.42, 26.98, 111.98, 112.83, 116.20, 119.99, 120.35, 120.51, 124.58, 130.69, 136.14, 147.69, 154.88, 162.92. ν_{max}(KBr)/cm^{-1} 3408 (NH). Anal. Calcd for $C_{14}H_{11}N_3$: C, 76.00; H, 5.01; N, 18.99. Found: C, 76.18; H, 4.95; N, 18.87.

Data for 2-methyl-6-phenyl-1*H*-1,5,7-triazacyclopenta[*c*,*d*] phenalene **(5f)**: mp 245–246 °C (toluene–PE). ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.93 (s, 3H, (6)Me), 7.48–7.58 (3H, m, Ph(H-3,4,5)), 7.62 (1H, d, J = 9.0 Hz, H-3), 7.82 (1H, d, J = 8.7 Hz, H-9), 8.29 (1H, d, J = 8.7 Hz, H-8), 8.43 (1H, d, J = 9.0 Hz, H-4), 8.71 (2H, d, J = 8.4 Hz, Ph(H-2,6)), 13.1 (1H, br s, NH). ^{13}C NMR (100 MHz, DMSO-d_6): 12.38, 112.66, 112.94, 117.12, 120.54, 120.61, 120.65, 124.85, 128.05 (2C), 128.22 (2C), 129.36, 130.88, 136.20, 140.09, 147.88, 155.12, 159.64. ν_{max}(KBr)/cm^{-1} 3412 (NH). Anal. Calcd for $C_{19}H_{13}N_3$: C, 80.55; H, 4.62; N, 14.83. Found: C, 80.66; H, 4.56; N, 14.78.

Data for 2-phenyl-1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalene **(5g)**: mp 263–265 °C (toluene). ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.54 (3H, m, Ph(H-3,4,5)), 7.66 (1H, d, J = 9.0 Hz, H-3), 7.79 (1H, d, J = 8.7 Hz, H-9), 8.18 (2H, d, J = 7.7 Hz, Ph(H-2,6)), 8.33 (1H, d, J = 8.7 Hz, H-8), 8.69 (1H, d, J = 9.0 Hz, H-4), 9.33 (1H, s, H-6), 13.3 (1H, br s, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 112.03, 112.17, 117.87, 120.93, 121.15, 122.25, 126.21, 127.16 (2C), 128.51, 129.31 (2C), 129.43, 130.99, 132.16, 148.36, 154.55, 163.48. ν_{max}(KBr)/cm^{-1} 3293 (NH). Anal. Calcd for $C_{18}H_{11}N_3$: C, 80.28; H, 4.12; N, 15.60. Found: C, 80.39; H, 4.04; N, 15.57.

Data for 6-methyl-2-phenyl-1*H*-1,5,7-triazacyclopenta[*c*,*d*] phenalene **(5h)**: mp 291–292 °C (toluene). ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.91 (s, 3H, (6)Me), 7.49 (1H, t, J = 7.3 Hz, Ph(H-4)), 7.64 (2H, dd, J = 7.3, J = 7.7 Hz, Ph (H-3,5)), 7.68 (1H, d, J = 9.0 Hz, H-3), 7.77 (1H, d, J = 8.7 Hz, H-9), 8.18 (2H, d, J = 7.7 Hz, Ph(H-2,6)), 8.31 (1H, d, J = 8.7 Hz, H-8), 8.69 (1H, d, J = 9.0 Hz, H-4), 13.3 (1H, br s, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 26.95, 111.96, 112.14, 118.43, 120.97, 121.07, 122.22, 126.07, 127.14 (2C), 128.50, 129.13, 129.38 (2C), 131.19, 131.73, 148.27, 154.21, 163.30. ν_{max}(KBr)/cm^{-1} 3322 (NH). Anal. Calcd for $C_{19}H_{13}N_3$: C, 80.55; H, 4.62; N, 14.83. Found: C, 80.69; H, 4.55; N, 14.76.

Data for 2,6-diphenyl-1*H*-1,5,7-triazacyclopenta[*c*,*d*] phenalene **(5i)**: mp 169–171 °C (toluene–PE). ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.5–7.7 (6H, m, 2,6-Ph(H-3,4,5)), 7.85 (1H, d, J = 9.0 Hz, H-3), 7.98 (1H, d, J = 9.0 Hz, H-9), 8.21 (2H, d, J = 7.7 Hz, 2-Ph(H-2,6)), 8.41 (1H, d, J = 9.0 Hz, H-8), 8.73 (2H, d, J = 8.1 Hz, 6-Ph(H-2,6)), 8.81 (1H, d, J = 9.0 Hz, H-4), 13.0 (1H, br s, NH). ^{13}C NMR (100 MHz, DMSO-d_6): 112.31, 112.52, 117.73, 120.76, 120.86, 121.43, 125.51, 127.36 (2C), 128.11 (2C), 128.24 (2C), 128.36, 129.28, 129.47 (2C), 130.01, 131.29, 133.72, 140.14, 148.07, 154.69, 161.53. ν_{max}(KBr)/cm^{-1} 3412 (NH). Anal. Calcd for $C_{24}H_{15}N_3$: C, 83.46; H, 4.38; N, 12.17. Found: C, 83.62; H, 4.29; N, 12.09.

9. PPA containing 86% P_2O_5 was used; preparation according to: Uhlig, F. *Angew. Chem.* **1954**, *66*, 435.
10. The triazine **4a–c** may be added at the beginning of the reaction.