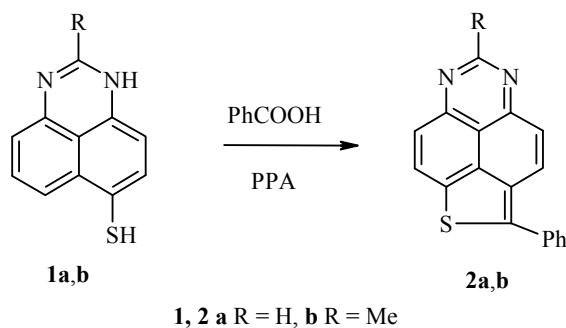


## SYNTHESIS OF 1-THIA-5,7-DIAZACYCLOPENTA- [c,d]PHENALENES, A NEW HETEROCYCLIC SYSTEM

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In previous work, we developed a number of methods for the *peri* annelation of the pyrrole ring to give perimidines [1, 2]. The considerable biological activity of thiophene derivatives has led us to develop a method for the *peri* annelation of the thiophene ring to give perimidines. Heating thiols **1** (1 mmol) and benzoic acid (0.244 g, 2 mmol) in PPA\* (2-3 g) at 100-110°C for 4 h with monitoring by thin-layer chromatography gave previously unreported 1-thia-5,7-diazacyclopenta[*c,d*]phenalenes **2a,b** in 78 and 82% yield, respectively.



The <sup>1</sup>H NMR spectra were taken on a Bruker WP-200 spectrometer at 200 MHz in DMSO-*d*<sub>6</sub> with TMS as the internal standard. The reaction course and purity of the products were monitored by thin-layer chromatography on Silufol UV-254 plates with ethyl acetate as the eluent.

The reaction mixture was treated with 50 ml water and brought to pH 8-9 by adding ammonium hydroxide. The precipitate formed was filtered off. The mother liquor was extracted with three 50-ml portions of hot benzene. The solvent was evaporated off and the residue was combined with the precipitate. The products obtained were purified by recrystallization.

\* The PPA sample used was prepared according to Uhlig [3] and contained 86% P<sub>2</sub>O<sub>5</sub>.

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**2-Phenyl-1-thia-5,7-diazacyclopenta[*c,d*]phenalene (2a)** was obtained in 78% yield (0.223 g); mp 283-285°C (dec., benzene). <sup>1</sup>H NMR spectrum, δ, ppm (*J*, Hz): 7.50 (3H, m, H-3, H-4, H-5 Ph); 7.81 (1H, d, *J* = 9.8, H-3); 7.95 (2H, d, *J* = 7.7, H-2, H-6 Ph); 8.15 (1H, d, *J* = 9.1, H-9); 8.53 (1H, d, *J* = 9.8, H-4); 8.91 (1H, d, *J* = 9.1, H-8); 9.58 (1H, s, H-6). Found, %: C 75.68; H 3.46; N 9.83. C<sub>18</sub>H<sub>10</sub>N<sub>2</sub>S. Calculated, %: C 75.50; H 3.52; N 9.78.

**6-Methyl-2-phenyl-1-thia-5,7-diazacyclopenta[*c,d*]phenalene (2b)** was obtained in 82% yield (0.246 g); mp >300°C (benzene). <sup>1</sup>H NMR spectrum, δ, ppm (*J*, Hz): 3.12 (3H, s, CH<sub>3</sub>); 7.50 (3H, m, H-3, H-4, H-5 Ph); 7.87 (1H, d, *J* = 9.8, H-3); 7.95 (2H, d, *J* = 7.7, H-2, H-6 Ph); 8.13 (1H, d, *J* = 9.1, H-9); 8.56 (1H, d, *J* = 9.8, H-4); 8.90 (1H, d, *J* = 9.1, H-8). Found, %: C 76.12; H 3.92; N 9.28. C<sub>19</sub>H<sub>12</sub>N<sub>2</sub>S. Calculated, %: C 75.97; H 4.03; N 9.33.

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