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DERIVATIVES OF A NEW HETEROAROMATIC SYSTEM — 11-THIA-4*b*,6,10,12-TETRAAZAINDENO[2,1-*a*]-FLUORENE

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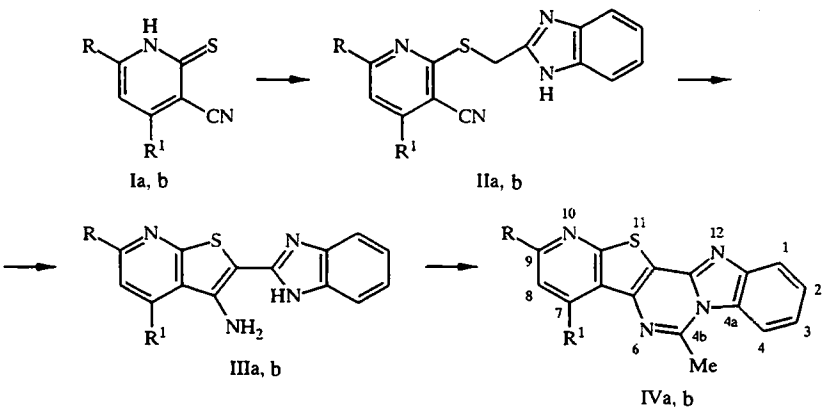
There have been no reports in the literature of the 11-thia-4*b*,6,10,12-tetraazaindeno[2,1-*a*]fluorene heteroaromatic system.

In a continuation of our work on the synthesis and alkylation of 3-cyano-2-pyridinethione derivatives (Ia, Ib) [1, 2], we synthesized 3-cyano-2-(benzimidazoylmethylthio)pyridines (IIa, IIb), which are smoothly converted in basic medium by the Thorpe–Ziegler isomerization into substituted thienopyridines IIIa and IIIb. In turn, IIIa and IIIb react with acetic anhydride to give high yields of the corresponding 11-thia-4*b*,6,10,12-tetraazaindeno[2,1-*a*]fluorene derivatives IVa and IVb.



Ia, b IIa, b IIIa, b IVa, b

I–IV a R = Me, R^1 = MeO; b R = MeO, R^1 = Me

The structure of IVa and IVb was demonstrated by physicochemical methods.

5,9-Dimethyl-7-methoxymethyl-11-thia-4*b*,6,10,12-tetraazaindeno[2,1-*a*]fluorene (IVa), mp 249-250°C (from ethanol). PMR spectrum in DMSO-d_6: 2.54 (3H, s, 9-CH_3), 3.13 (3H, s, 5-CH_3), 3.16 (3H, s, O–CH_3), 5.18 (2H, s, 7-CH_2–O), 7.34 (1H, s, 8-H), 7.42 (1H, d.d, 3-H), 7.58 (1H, d.d, 2-H), 7.83 (1H, d, 1-H), 8.15 ppm (1H, d, 4-H, J_{12} = 10.0, J_{23} = 9.0, J_{34} = 10.0 Hz). Found: C, 64.57; H, 4.12; N, 16.94, S, 9.72%. Calculated for $C_{18}H_{14}N_4OS$: C, 64.65; H, 4.22; N, 16.75; S, 9.59%.

5,7-Dimethyl-9-methoxymethyl-11-thia-4*b*,6,10,12-tetraazaindeno[2,1-*a*]fluorene (IVb), mp 246-247°C (from ethanol). PMR spectrum in DMSO-d_6: 2.93 (3H, s, 9-CH_3), 3.13 (2H, s, 5-CH_3), 3.42 (3H, s, O–CH_3), 4.52 (2H, s, 7-CH_2–O), 7.28 (1H, s, 8-H), 7.43 (1H, d.d, 3-H), 7.56 (1H, d.d, 2-H), 7.85 (1H, d, 1-H), 8.18 ppm (1H, d, 4-H, J_{12} = 10.0, J_{23} = 9.0, J_{34} = 10.0 Hz). Mass spectrum, *m/z*: 348 (M^+), 333 (M — 15), 318 (M — 2×15), 303 (M — 3 × 15). Found: C, 64.67; H, 4.30; N, 16.50; S, 9.68%. Calculated for $C_{18}H_{14}N_4OS$: C, 64.65; H, 4.22; N, 16.75; S, 9.59%.

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