A photochemical electrocyclization of the indolinylphenylethenes involving a C-N bond formation

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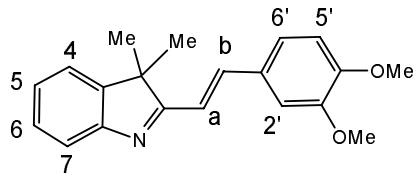
Supporting Information Available.

Synthetic procedure.

2-[(*E*)-2-(3,4-Dimethoxyphenyl)-1-ethenyl]-3,3-dimethyl-3H-indole (**1**).



A mixture of 2-methylbenzothizole 0.16g (10 mmol), 4'-formyl-benzo-15-crown-5-ether 0. 17g (10 mmol), and NaOMe 0.054g (10 mmol) in anhydrous DMSO (2 ml) was kept at ambient temperature for 24 hours. After addition of distilled water (10 ml), the product was extracted with benzene and was purified by column chromatography on aluminium oxide (eluent: benzene-MeCN from 10:1 to 1:1) followed by crystallization from C_6H_6. The yield of 1 was 0.03g (10%); m.p. 115°C; ^{1}H NMR (DMSO-d_6): 1.41 (s, 6 H, 2 CH_3), 3.81 and 3.85 (2 s, 6 H, 2 OCH_3), 7.00 (d, 1 H, H-5', J = 8.3), 7.15 (d, 1 H, H-b, J = 16.3), 7.20 and 7.30 (2 m, 2 H, H-5, H-6), 7.29 (br.d, 1 H, H-6', J = 8.3), 7.42 (d, 1 H, H-2', J = 1.5), 7.45 and 7.49 (2 d, 2 H, H-4, H-7, J = 7.2, J = 7.6), 7.68 (d, 1 H, H-a, J = 16.3); MS, *m/z* (I_{rel}): $[M+H]^+$ - 308 (12), 306 (100), 292 (30), 291 (34), 277 (11), 117 (14), 115 (16), 103 (15), 91 (14), 77 (16), 58 (16); Calcd for $C_{20}H_{21}NO_2$ (%): C 78.15, H 6.89, N 4.56; Found (%): C 78.12 , H 6.79, N 4.39 .

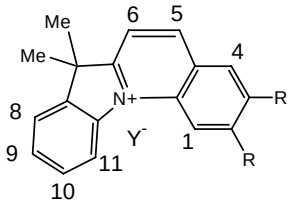
Synthesis of **2** was described in[17].

Reaction of *trans-cis*-isomerization. The 0.6 ml solution of *E*-**2** in CD_3CN (7 mMol/L) was irradiate with light (365 nm) for 25min. The resulting photostationary mixture was analyzed by using of COSY and NOESY spectroscopy. According the obtained results the mixture was consisted from *E*- and *Z*-isomers in ration 1:1.

(*E*)-**3,3-Dimethyl-2-[2-(6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxa-benzocyclopentadecen-2-yl)-vinyl]-3H-indole (*E*-2)** ^{1}H NMR (CD_3CN): 1.46 (s, 6 H, 2 CH_3), 3.67 (m, 8 H, 4 OCH_2), 3.84 (m, 4 H, 2 OCH_2), 4.14 (м, 2 H, ArOC$\underline{H}_2$), 4.19 (м, 2 H, ArOC$\underline{H}_2$), 6.97 (d, 1 H, H-5', J = 8.3), 7.07 (d, 1 H, H-b, J = 16.3), 7.26 (m, 2 H, H-5, H-6'), 7.35 (m, 2 H, H-2', H-6), 7.42 (m, 2 H, H-4), 7.53 (d, 1 H, H-7, J = 7.7), 7.68 (d, 1 H, H-a, J = 16.3).

(*Z*)-**3,3-Dimethyl-2-[2-(6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxa-benzocyclopentadecen-2-yl)-vinyl]-3H-indole (*E*-2)** ^{1}H NMR (CD_3CN): 1.36 (s, 6 •, 2 • •$_3$), 3.67 (m, 8 H, 4 OCH_2), 3.84 (m, 4 H, 2 OCH_2), 4.14 (•, 2 H, ArOC$\underline{H}_2$), 4.19 (•, 2 H, ArOC$\underline{H}_2$), 6.32 (d, 1 H, H-b, J = 13.3), 6.89 (d, 1 H, H-a, J = 13.3), 6.92 (d, 1 H, H-5', J = 8.3), 7.26 (m, 1 H, H-5), 7.35 (m, 3 H, H-2', H-6', H-6), 7.42 (m, 1 H, H-4), 7.56 (d, 1 H, H-7, J = 7.7).

Synthesis of 3, 4 (General procedure).



Method A. The acetonitrile solution of 1 mmol *E*-**1, 2** were irradiated with the unfiltered output of a 120 watt high-pressure Hg arc lamp and simultaneous bubbling of air for 16 minutes, the solvent was removed in vacuum, the residue was crystallized from MeOH with addition of $HClO_4$.

Method B. The acetonitrile solution of 1 mmol *E*-**1,2** with 1 mmol I_2 or mixture of 1mmol I_2 and 2mmol $AgClO_4$ was irradiated with filtered light of a DRK-120 mercury lamp at λ = 365 nm. Individual line of this lamp (365 nm) was isolated with the use of glass filters. When the all starting material was consumed (monitored by UV-vis spectroscopy), the solvent was removed in vacuum, the residue was crystallized from MeOH with addition of $HClO_4$.

2,3-Dimethoxy-7,7-dimethyl-7H-indolo[1,2-a]quinolinylium perchlorate (**3**): m.p. 228-230°C, DMSO-d_6: 1.75 (s, 6 H, 2 CH_3), 4.06 and 4.28 (2 s, 6 H, 2 OCH_3), 7.76 (m, 2 H, H-9, H-10), 7.97 (s, 1 H, H-4), 8.02 (d, 1 H, H-8, J = 6.6), 8.31 (s, 1 H, H-1), 8.39 (d, 1 H, H-6, J = 8.5), 8.78 (d, 1 H, H-11, J = 7.9), 9.08 (d, 1 H, H-5, J = 8.4). Ananl. Calcd. for $C_{20}H_{20}NO_6Cl$: C59.19, H 4.97, N 3.45. Found: C 59.29, H 5.05, N 3.25.

17,17-Dimethyl-2*H*,3*H*,5*H*,6*H*,8*H*,9*H*,11*H*,12*H*,17*H*-indolo[1,2-*a*][1,4,7,10,13]pentaoxacyclopentadecino[2,3-*g*]quinolin-22-ium Perchlorate (**4**): m.p. 256-257 °C, DMSO -d_6: 1.74 (s, 6 H, 2 CH_3), 3.68 (m, 8 H, 4 OCH_2), 3.90 (m, 2 H, OCH_2), 3.96 (m, 2 H, OCH_2), 4.32 (m, 2 H, ArOC$\underline{H}_2$), 4.61 (m, 2 H, ArOC$\underline{H}_2$), 7.75 (m, 2 H, H-9, H-10), 7.93 (s, 1 H, H-1), 8.01 (m, 1 H, H-8), 8.28 (s, 1 H, H-4), 8.38 (d, 1 H, H-6 J = 8.4), 8.79 (m, 1 H, H-11), 9.04 (d, 1 H, H-5, J = 8.4). Ananl. Calcd. for $C_{26}H_{30}NO_9Cl$: C58.26, H 5.64, N 2.16. Found: C 58.19, H 5.77, N 2.05.