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SYNTHESIS OF THE FIRST BIPOLAR SPIRO-σ-COMPLEXES OF DINITRO-BENZOFUROXAN WITH 2-(2'-AMINO-PHENYL)BENZIMIDAZOLES

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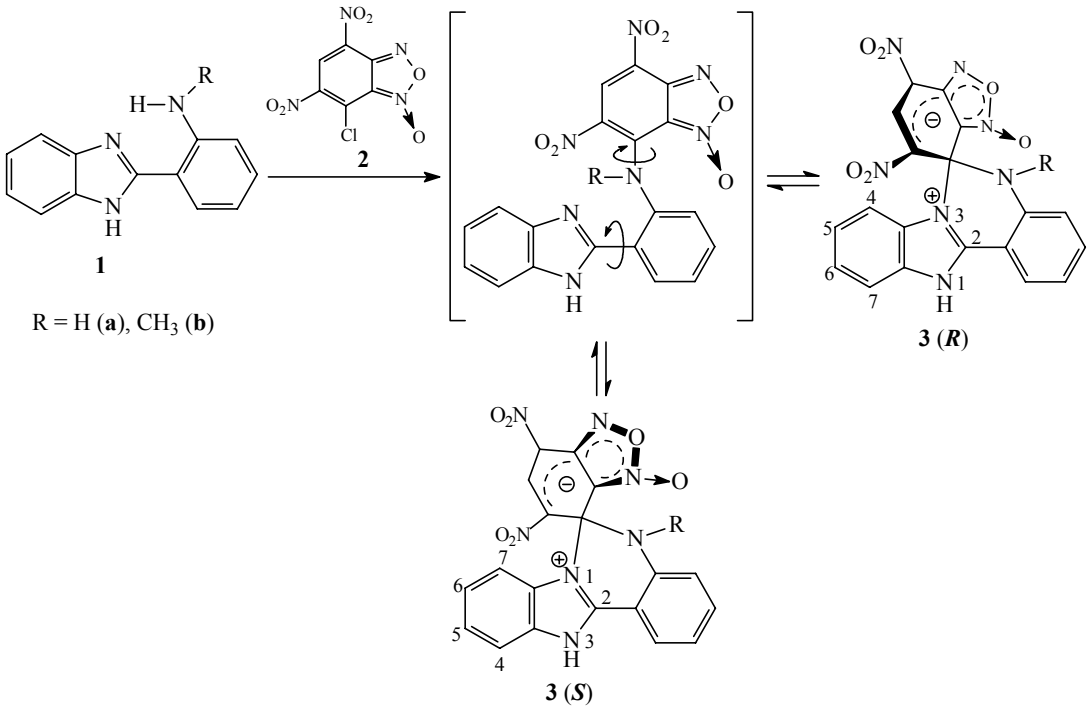
In a continuation of the study of the structural and stereoflexible derivatives of the superelectrophile 4,6-dinitrobenzofuroxan [1], we have synthesized the previously unknown bipolar spiro-σ-complexes **3** by the interaction of 2-(2'-aminophenyl)benzimidazole (**1**) with 4,6-dinitro-7-chlorobenzofuroxan (**2**).



1 a R = H, **b** R = Me

When solutions of compound **3** in DMSO-d_6 were heated, an exchange of the positions of the signals of protons 4, 7 and 5, 6 of the benzene ring of benzimidazole was observed (evolution of the spin multiplet $AA'BB' \rightleftarrows A_2B_2$) in the variable temperature ^{1}H NMR spectrum. The recyclization *R*-**3** ⇄ *S*-**3** includes opening

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of the C_{ipso}-$N_{(3)}$ bond, rotations relative to the $C_{(7)}$-benzofuroxan-N and $C_{(2)}$-benzimidazole-C-benzene bonds, and formation of the C_{ipso}-N_1 bond (**3a**: $\Delta G^{\neq}_{298}$ = 17.5, $\Delta H^{\neq}$ = 18.4, $\Delta S^{\neq}$ = 3 e.u., k_{298} = 0.8 s^{-1}; **3b**: $\Delta G^{\neq}_{298}$ > 30 kcal/mol).

2-(2-Aminophenyl)benzimidazoles 1 were made by fusing *o*-phenylenediamine with the corresponding anthranilic acid in the presence of P_2O_5 by a known method [2].

Synthesis of Spiro-σ-complexes 3 (General Method). 7-Chloro-4,6-dinitrobenzofuroxan [3] (0.25 g, 0.96 mmol) in MeCN (2 ml) was added to a solution of benzimidazole **1** (0.96 mmol) in MeCN (7 ml). The precipitate was removed by filtration, suspended in MeOH (5 ml), heated to boiling and filtered hot. This procedure was repeated 3 times.

5',7'-Dinitro-5,12-dihydro-5H-spiro[(benzoimidazo[1,2-*c*]-quinazolin)-6,4'-(benz-2,1,3-oxadiazol)]-3'-oxide (2a). Yield 0.11 g (53%); mp 278-282°C (dec.). ^{1}H NMR spectrum (DMSO-d_6, 250 MHz), δ, ppm, *J* (Hz): 6.71 (1H, d, *J* = 8.3, H-6'); 6.82-6.95 (2H, m, H-4', 7); 7.32 (1H, dd, *J* = 7.6, *J* = 8.0, H-5); 7.38-7.50 (2H, m, H-5',6); 7.77 (1H, d, *J* = 8.3, H-4); 7.97 (1H, d, *J* = 8.2, H-3'); 8.44 (1H, s, NH); 8.90 (1H, s, H-5''). Found, %: C 52.80; H 2.38; N 22.86. $C_{19}H_{11}N_7O_6$. Calculated, %: C 52.66; H 2.56; N 22.63.

5-Methyl-5',7'-dinitro-5,12-dihydro-5H-spiro[(benzoimidazo[1,2-*c*]-quinazolin)-6,4'-(benz-2,1,3-oxadiazol)]-3'-oxide (2b). Yield 0.12 g (56%); mp 254°C (dec.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J* (Hz): 2.77 (3H, s, CH_3); 6.83 (1H, d, *J* = 8.1, H-6'); 6.95-7.08 (2H, m, H-4', 7); 7.36 (1H, dd, *J* = 8.3, *J* = 7.3, H-5); 7.47 (1H, dd, *J* = 7.4, *J* = 7.4, H-6); 7.57 (1H, dd, *J* = 8.0, *J* = 7.9, H-5'); 7.80 (1H, d, *J* = 8.0, H-4); 8.13 (1H, d, *J* = 7.8, H-3'); 9.02 (1H, s, H-5''). Found, %: C 52.54; H 2.68; N 22.09. $C_{20}H_{13}N_7O_6$. Calculated, %: C 53.70; H 2.93; N 21.92.

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