ARYLATION OF CHROMENO[3,2-*b*]INDOLIZINE BY AROMATIC SUPERELECTROPHILES

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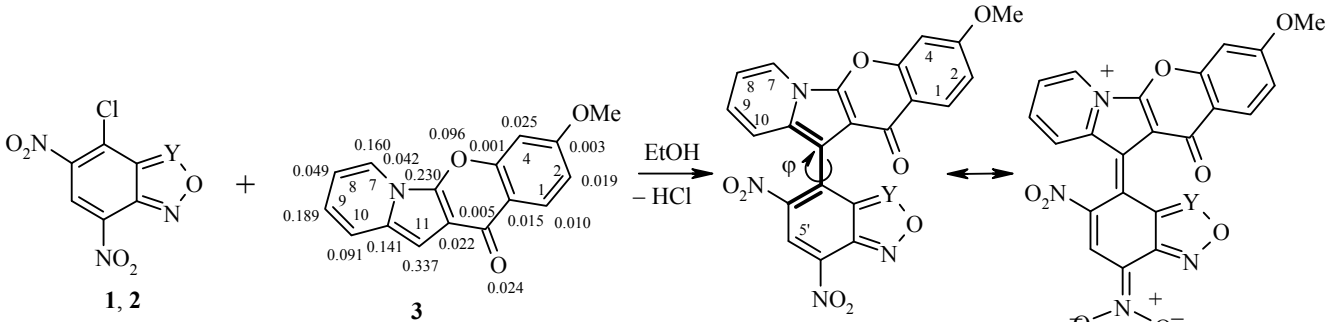
We have previously shown that the superelectrophilic halonitro-2,1,3-benzoxadiazoles **1** and **2** take part in an S_NAr-S_EAr reaction with an indolizine heteroaromatic system to form a structure with a strong intramolecular separation of charges [1]. Since the ease of the reaction occurrence and the degree of separation of the charges depends significantly on the ability of the electron-excessive fragment of the molecule to delocalize the generated positive charge [2] we have carried out the synthesis with the polyconjugated indolizine containing condensed system **3**.

The reaction of 3-methoxy-12H-chromeno[3,2-*b*]indolizin-12-one (**3**) with 7-chloro-4,6-dinitrobenzofurazan (**1**) and 7-chloro-4,6-dinitrobenzofuroxan (**2**) gave high yields of the deeply colored arylation products with structures **4** and **5**. It was found that substitution in the nucleophile occurs exclusively at position 11 and fully agrees with the distribution of localized index of nucleophilicity ω_k calculated by us using the Fukui [3] function for structure **3**.



				Torsional angle	Charge transfer	
1	Y = N	**4**	Y = N	φ = 47.5°	0.20 e	**6**
2	Y = N^+–O^-	**5**	Y = N^+–O^-	φ = 53°	0.21 e	**7**

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Evidence for a strong shift of electron density towards the dinitrobenzoxadiazole molecular fragment comes from an average 0.4 ppm low field shift of the aromatic protons of the indolizine fragment. This shift can be represented by the resonance structures **6** and **7**. The diaryls obtained absorb in the long wavelength part of the visible spectrum with λ_{max} = 643 nm (ε = 10300 l·mol^{-1}·cm^{-1}) for **4** and λ_{max} = 667 nm (ε = 9800 l·mol^{-1}·cm^{-1}) for **5** (acetone solvent). The N-oxide group causes a large acoplanarity in compound **5** when compared with **4** and so decreases the possibility of an intramolecular charge transfer. This leads to a smaller value of ε for compound **5**.

^{1}H NMR spectra were recorded on a Bruker DPX-250 spectrometer (250 MHz) using DMSO-d_6 with TMS as internal standard. Calculations were carried out by the B3LYP/6-31G(d) method using the Gaussian 03 Rev. E-01 program package.

Arylation of Chromeno[3,2-*b*]indolizines (General Method). An equivalent amount of 7-chloro-4,6-dinitrobenzofurazan (**1**) or 7-chloro-4,6-dinitrobenzofuroxan (**2**) was added to a solution of 3-methoxy-12H-chromeno[3,2-*b*]indolizin-12-one (**3**) [4] (0.13 g, 0.49 mmol) in ethanol (10 ml) and the mixture was stirred for a further 1 h. The precipitate obtained was filtered off, washed with ethanol (5 ml), and dried *in vacuo*.

3-Methoxy-11-(4',6'-dinitro-2',1',3'-benzoxadiazol-7'-yl)-12H-chromeno[3,2-*b*]indolizin-12-one (4). Dark-blue crystals. Yield 78%; mp 276ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.95 (3H, s, OCH_3); 7.12 (1H, dd, *J* = 9.0 and *J* = 2.2, H-2); 7.16 (1H, t, *J* = 6.9, H-8); 7.31 (1H, t, *J* = 9.4, H-9); 7.34 (1H, d, *J* = 2.2, H-4); 7.78 (1H, d, *J* = 9.4, H-10); 8.02 (1H, d, *J* = 9.0, H-1); 8.58 (1H, d, *J* = 6.9, H-7); 9.16 (1H, s, H-5'). Found, %: C 55.73; H 2.31. H 15.01. $C_{22}H_{11}N_5O_8$. Calculated, %: C 55.82; H 2.34; N 14.79.

3-Methoxy-11-(4',6'-dinitro-1'-oxido-2',1',3'-benzoxadiazol-7'-yl)-12H-chromeno[3,2-*b*]indolizin-12-one (5). Blue-green crystals. Yield 83%; mp 260ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.96 (3H, s, OCH_3); 7.15 (1H, dd, *J* = 8.7 and *J* = 1.8, H-2); 7.19 (1H, t, *J* = 7.2, H-8); 7.36 (1H, d, *J* = 1.8, H-4); 7.39 (1H, t, *J* = 8.9, H-9); 7.54 (1H, d, *J* = 8.9, H-10); 8.06 (1H, d, *J* = 8.7, H-1); 8.62 (1H, d, *J* = 7.2, H-7); 9.03 (1H, s, H-5'). Found, %: C 54.25; H 2.25; N 14.49. $C_{22}H_{11}N_5O_9$. Calculated, %: C 54.00; H 2.27; N 14.31.

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