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SHORT COMMUNICATIONS

New Heteroaromatic Bis-*peri*-fused Azoxonium Cation

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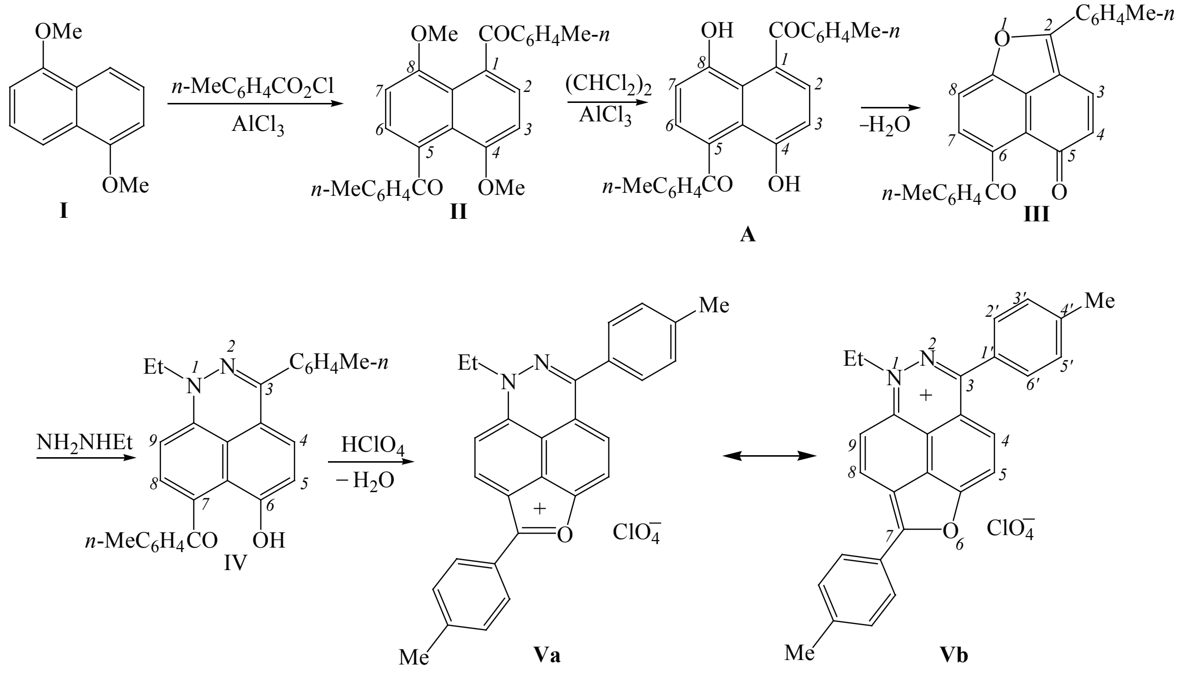
In continuation of the research on the chemistry of *peri*-fused heterocycles [1–3] we report here on the synthesis of a new bis-*peri*-fused heteroaromatic cation isolated as salt with perchlorate anion as the counter-ion.

The target product was obtained in several stages. The bis-acylation of 1,5-dimethoxynaphthalene (**I**) afforded compound **II** whose demethylation proceeded through intermediate **A** giving compound **III** with a methylenequinone structure which at heating both with 1 mol of ethylhydrazine and its double excess furnished monoheterocycle **IV**, whereas the 5-hydroxy-6-carbonyl *peri*-moiety was not affected in this process. This result seems rather unusual since the short heating in alcohol of *peri*-hydroxycarbonyl compounds with hydrazines is the easiest way of the preparation of *peri*-fused 1,2-diazines [4–6]. The short heating of diazine **IV** with perchloric acid in the acetic acid solution resulted in the dehydration of the *peri*-hydroxycarbonyl moiety with the closure of a five-membered ring and the formation of perchlorate **V**. The closure of the five-membered furylium ring and the formation of cation **V** is confirmed by the disappearance of the bands of carbonyl and hydroxy groups in the IR

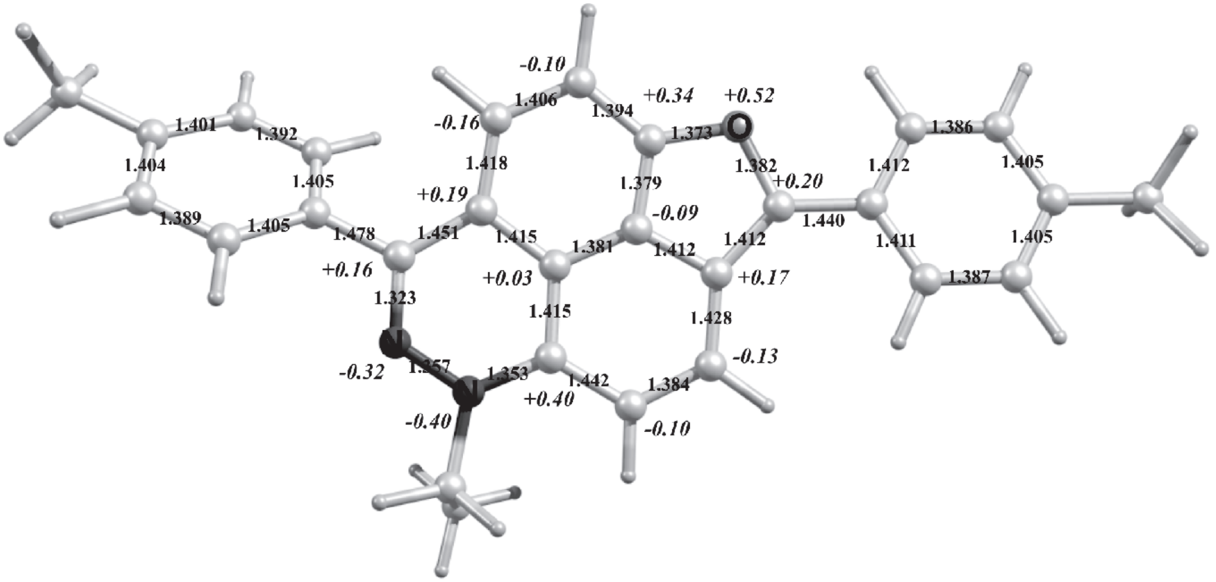


spectra, by the appearance of intensive yellow-orange fluorescence with λ_{max} 538 nm (quantum yield μ 0.65) at the irradiation with light of λ_{max} 320 nm, and also by the considerable downfield shift of all proton signals in its ^1H NMR spectrum compared to the spectra of precursor **IV** due to the formation of the 14π-electron heteroaromatic circuit on the periphery of the bis-*peri*-fused framework in cation **V**.

The quantum-chemical calculations by the method of functional density theory B3LYP/6-31G** [7] show that system **V** is stable and corresponds to the minimum on PES. The calculation shows that the central bis-*peri*-fused frame of molecule **V** is flat. Therewith the analysis of the electron density distribution demonstrated sufficiently weak delocalization of the positive charge along the π-system and its prevailing localization around the oxygen center of the molecule **Va**. The calculation data are shown on the figure.

1,5-Di(4-methylbenzoyl)4,8-dimethoxynaphthalene (II). To a slurry of 2.66 g (14 mmol) of 1,5-dimethoxynaphthalene (**I**) in 10 ml of 1,2-dichloroethane was added 4 g (30 mmol) of anhydrous aluminum chloride, the mixture was cooled to 0°C and thereto was added by small portions while stirring 4 ml (30 mmol) of *p*-toluic acid chloride. The mixture was stirred for 12 h at room temperature, then it was poured on ice with added 2–3 ml of hydrochloric acid, and it was left under hood till total evaporation of dichloroethane. The separated precipitate was filtered off, dried at 40–50°C, boiled for 4–5 min in ethyl acetate, the precipitate was filtered off. Yield 5.85 g (98%), yellow substance, mp 252–254°C (from benzene). IR spectrum, ν, cm^{-1}: 1655, 1605, 1591, 1551. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.35 s [6H, $(CH_3)_2$], 3.50 s [6H, $(OCH_3)_2$], 6.80 d (2H, $H^{3,7}$, *J* 8.0 Hz), 7.15 d (4H, H_{toluyl}, *J* 7.9 Hz), 7.33 d (2H, $H^{2,6}$, *J* 8.0 Hz), 7.55 d (4H, H_{toluyl}, *J* 7.9 Hz). Found, %: C 79.44; H 5.91. $C_{28}H_{24}O_4$. Calculated, %: C 79.23; H 5.70.

6-(4-Methylbenzoyl)-2-(4-methylphenyl)-5*H*-naphtho[1,8-*bc*]furan-5-one (III). Into a slurry of 2.07 g (5 mmol) of compound **II** in 48 ml of tetrachloroethane heated to 30–35°C was added by portions 3.25 g (25 mmol) of anhydrous aluminum chloride, and the reaction mixture was heated for 5 h on a boiling water bath. On cooling the mixture was poured on ice with added 2–3 ml of hydrochloric acid, the organic layer was separated, the solvent was removed by steam distillation to obtain 1.7 g of yellow substance, mp 160–170°C. On crystallization from benzene we obtained 1.47 g (83%) of chromatographically pure compound **III**, mp 214–216°C. IR spectrum, ν, cm^{-1}: 1665, 1637, 1605, 1576, 1556. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.35 s (3H, 2-$C_6H_4C\underline{H}_3$), 2.45 s (3H, 6-$COC_6H_4C\underline{H}_3$), 6.60 d (1H, H^8, *J* 9.4 Hz), 7.18 d (2H, 2-$C_6\underline{H}_4CH_3$, *J* 7.8 Hz), 7.38 d (2H, 6-$COC_6\underline{H}_4CH_3$, *J* 8.1 Hz), 7.45 d (1H, H^4, *J* 8.1 Hz), 7.68 d (2H, 2-$C_6\underline{H}_4CH_3$, *J* 7.8 Hz), 7.74 d (1H, H^3, *J* 8.1 Hz), 7.90–8.00 M (3H, 6-$COC_6\underline{H}_4CH_3$, H^7). Found, %: C 82.44; H 4.91. $C_{26}H_{18}O_3$. Calculated, %: C 82.52; H 4.79.



Results of calculation of cation **V** by the method B3LYP/6-31G**. Bond lengths are given in Å.

[1-Ethyl-6-hydroxy-3-(4-methylphenyl)-1*H*-benzo[*de*]cinnolin-7-yl](4-methylphenyl)methanone (IV). To a solution of 280 mg (0.7 mmol) of *peri*-oxoketone **III** in a mixture of 3 ml of ethanol and 2 ml of chloroform was added 55 mg (0.9 mmol) of ethylhydrazine, and the mixture was heated at reflux on a boiling water bath for 60–70 min. Then the reflux condenser was removed, and the solvent was partially evaporated till the precipitate started to separate. On cooling the solution 210 mg (75%) of dark-red precipitate was filtered off. After crystallization from acetic acid the precipitate was heated for 4 h at 40–50°C in the drying cabinet to obtain a substance of mp 234–236°C. IR spectrum, ν, cm^{-1}: 3052, 3025, 1607, 1585, 1546. UV spectrum, λ, nm (ε), in acetonitrile: 266 (13048), 363 (3929), 494 (9667). ^{1}H NMR spectrum (CD_2Cl_2), δ, ppm: 1.39 t (3H, $CH_2C\underline{H}_3$, *J* 7.5 Hz), 2.42 s (3H, $C_6H_4C\underline{H}_3$), 2.43 s (3H, $C_6H_4C\underline{H}_3$), 4.04 (2H, $C\underline{H}_2CH_3$, *J* 7.5 Hz), 6.07 d (1H, H^9, *J* 9.1 Hz), 7.16 d (1H, H^5 , *J* 8.3 Hz), 7.25–7.35 M (5H, 3-$C_6\underline{H}_4CH_3$, 7-$COC_6\underline{H}_4CH_3$, H^4), 7.48 d (2H, 3-$C_6\underline{H}_4CH_3$, *J* 8.0 Hz), 7.62 d (2H, 7-$COC_6\underline{H}_4CH_3$, *J* 8.0 Hz), 7.75 d (1H, H^9, *J* 9.1 Hz), 10.55 s (1H, OH). Found, %: C 79.64; H 5.91; N 6.34. $C_{28}H_{24}N_2O_2$. Calculated, %: C 79.98; H 5.75; N 6.66.

1-Ethyl-3,7-bis(4-methylphenyl)-1*H*-[1]-benzofuro[5,4,3-*def*]cinnolin-6-ium (V). In 6 ml of acetic acid was heated to complete dissolution 82 mg (0.2 mmol) of diazine **IV**, and 4 drops of 70% perchloric acid was added. On cooling the separated precipitate was filtered off, dried at 50°C to complete removal of acetic acid (monitoring by IR spectrum) to obtain 92 mg (93%) of dark-red perchlorate, mp 253–255°C. IR spectrum, ν, cm^{-1}: 1610, 1549, 1431, 1092 (ClO_4^-). UV spectrum, λ, nm (ε), in acetonitrile: 224 (28277), 287 (26278), 497 (45778). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.82 t (3H, $CH_2C\underline{H}_3$, *J* 7.1 Hz), 2.51 s (3H, $C_6H_4C\underline{H}_3$), 2.53 s (3H, $C_6H_4C\underline{H}_3$), 5.11 (2H, $C\underline{H}_2CH_3$, *J* 7.4 Hz), 7.52 d (4H, 3-$C_6\underline{H}_4CH_3$, *J* 8.1 Hz), 7.88 d (2H, 7-$COC_6\underline{H}_4CH_3$, *J* 8.1 Hz), 8.14 d (1H, H^9, *J* 9.1 Hz), 8.29 d (2H, 7-CO-$C_6\underline{H}_4CH_3$, *J* 8.1 Hz), 8.47 d (1H, H^5, *J* 8.8 Hz), 8.61 d (1H, H^4, *J* 8.8 Hz), 9.02 d (1H, H^8, *J* 9.1 Hz). Found, %: C 66.74; H 5.91; Cl 7.09; N 5.54. $C_{28}H_{27}ClN_2O_5$. Calculated, %: C 66.33; H 5.57; Cl 6.99; N 5.53.

^{1}H NMR spectra were registered on a spectrometer Bruker DPX-250 (250 MHz), internal reference TMS. IR spectra were obtained on a spectrophotometer Varian Excalibur 3100 FT-IR by the method of distorted complete internal reflection. Electronic spectra in acetonitrile were recorded on a spectrophotometer (Uv-Vis) Varian Cary 100 Scan, luminescence spectra (in acetonitrile), on a spectrofluorimeter Hitachi 6010.

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