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CHEMISTRY

Synthesis and Structure of 5,7-Di(*tert*-butyl)-2-(8-methanesulfonyloxyquinolin-2-yl)-1,3-tropolone

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Abstract—5,7-Di(*tert*-butyl)-2-(8-methanesulfonyloxyquinolin-2-yl)-1,3-tropolone whose structure was established by X-ray diffraction analysis and confirmed by ^{1}H and ^{13}C NMR, IR spectroscopy, and mass spectrometry, was obtained by the reaction of 2-methyl-8-methanesulfonyloxyquinoline with 3,5-di(*tert*-butyl)-1,2-benzoquinone. According to X-ray diffraction study, this sulfonyloxyquinolinotropolone exists in the NH tautomeric form with methanesulfonyloxy group in the *exo* position to the tropolone ring and the six-membered chelate ring produced by the quinoline and tropolone moieties stabilized by strong intramolecular hydrogen bond. The strong intramolecular hydrogen bond between the phenolic oxygen atom and the six-membered chelate ring provides supplementary contribution to the stabilization of the NH tautomeric form.

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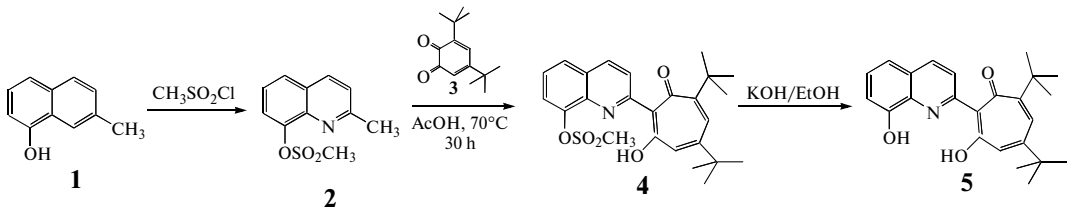
Chelate ligand systems based on 8-hydroxyquinoline and its derivatives are widely used in analytical chemistry for separation and determination of different metal cations [1], for preparation of highly efficient photo- and electroluminescent compounds [2, 3], highly selective fluorescent chemosensors [4], and in medicine due to their high and diverse pharmacological activity [5]. Good structural variability of this heterocyclic system provides a possibility to design on its basis materials with properties useful for practical applications [6–8]. Therefore, it is an urgent task to extend the scope of such compounds, establish their structure, and study their properties.

We prepared 5,7-di(*tert*-butyl)-2-(8-methanesulfonyloxyquinolin-2-yl)-1,3-tropolone **4** by the reaction of 2-methyl-8-methanesulfonyloxyquinoline **2** with 3,5-di(*tert*-butyl)-1,2-benzoquinone **3** via condensation of methylene active nitrogen heterocycles with 1,2-benzoquinones resulting in the expansion of *o*-quinone ring [9–11]. The alkaline hydrolysis of sulfonyloxyquinolinotropolone **4** led to 8-hydroxyquinoline ligand system **5** with the 1,3-tropolone moiety in the second position of the quinoline ring but in higher total yield (20%) than in the case when 2-methyl-8-arylsulfonyloxyquinolines were used as initial compounds (6–11%) [10].



The employment of 2-methyl-8-hydroxyquinoline **1** in this acid-catalyzed reaction instead of its alkyl(aryl)sulfonyloxy derivatives **2** leads to resinification of the initial reagents rather than the target products of type **4**.

The structure of sulfonyloxyquinolinotropolone **4** was established by X-ray diffraction analysis and confirmed by ^{1}H and ^{13}C NMR, IR spectroscopy, and mass spectrometry.

The X-ray diffraction data (figure) show that compound **4** exists as an *E* isomer at the C(2)–C(2') bond with hydrogen H(1') localization at the N(1') nitrogen

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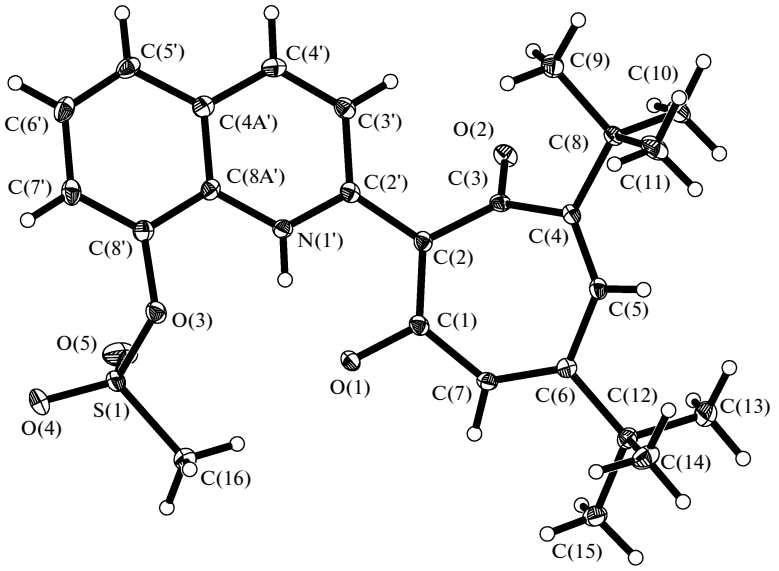

Molecular structure of 5,7-di(*tert*-butyl)-2-(8-methanesulfonyloxyquinolin-2-yl)-1,3-tropolone **4** according to X-ray diffraction study. The O(1)···N(1') distance is 2.446(4) Å. Selected bond lengths (Å): O(1)–C(1), 1.307(2); O(2)–C(3), 1.227(2); N(1')–H(1'), 0.86(1); N(1')–C(2'), 1.340(2); C(1)–C(2), 1.411(2); C(2)–C(3), 1.475(2); C(3)–C(4), 1.497(2); C(4)–C(5), 1.344(2); C(5)–C(6), 1.455(2); C(6)–C(7), 1.355(2); C(1)–C(7), 1.452(2); C(2)–C(2'), 1.450(2); C(2')–C(3'), 1.431(2). Selected bond angles (deg): C(1)–O(1)–H(1'), 101.9(1); O(1)–C(1)–C(2), 121.59(16); C(2')–N(1')–H(1'), 118.3(1); C(1)–C(2)–C(2'), 120.16(15);O(2)–C(3)–C(2), 122.31(15); C(1)–C(2)–C(3), 120.09(16); N(1')–C(2')–C(2), 116.44(15).

atom, which leads to the formation of strong intramolecular hydrogen bond of the N(1')–H(1')···O(1) type.

The N(1')–H(1') distance in structure **4** is 0.86(1) Å, while H(1')···O(1) = 1.72(1) Å, ∠N(1')H(1')O(1) = 149.7(1)°, the distance O(1)···N(1') = 2.446(4) Å is 0.5 Å shorter than the corresponding van der Waals contact and is the shortest for all known systems with strong intramolecular hydrogen bonds of this kind. The proton of the N–H group producing strong intramolecular hydrogen bond in compound **4** is strongly deshielded and has an extremely downfield shift in ^{1}H NMR spectra ($CDCl_3$, 19.03 ppm). The six-membered ring of the strong intramolecular hydrogen bond, quinoline fragment, and C(1)–C(3), C(7) atoms of the tropolone ring lie in the common plane (with slight deviations for the C(7) atom), while the tropolone ring is slightly distorted at the C(3)–C(7) line (dihedral angle between the C(3)C(2)C(1)C(7) and C(4)C(5)C(6)C(7) planes is 30.3(15)°).

Quinolinotropolone **5** [10] has a similar structure where phenolic hydroxyl like methanesulfonyloxy group in compound **4** is located in the *exo* position to the tropolone moiety; however, the replacement of phenolic group proton by the methanesulfonyl substituent leads to the enhancement of interaction between the phenolic oxygen and the N–H proton in **4** as compared with structure **5**. This is evidenced by a decrease in the C(8A')N(1')H(1') and N(1')H(1')O(1) angles from 124.2(1)° and 146.1(1)° to 118.3(1)° and 140.7(1)°, as well as the H(1')···O(3) distances from 2.39(1) Å to 2.35(1) Å in quinolinotropolones **4** and **5**, respectively. Moreover, the H(1')···O(1) distance in **4** (1.72(1) Å) is longer than in compound **5** (1.64(1) Å) because of the stronger interaction between H(1') and O(3) in the sulfonyloxy derivative. All these features lead to supplementary deshielding of the N–H proton in **4** strongly bound to three heteroatoms in the coordination core and to the downfield shift of proton signal in ^{1}H NMR by 0.52 ppm as compared with compound **5**.

The ^{1}H NMR spectrum of compound **4** shows proton signals of the tropolone ring as two doublets at 6.76 ppm (J = 1.7 Hz) and 6.66 ppm (J = 1.7 Hz), while the signal of the proton in the 3'-position of the quinoline ring is shifted downfield (8.15 ppm) as compared with the corresponding signal in the spectrum of initial quinoline **2** (7.33 ppm). The signal of the N–H proton producing strong intramolecular hydrogen bond with the tropolone oxygen that closes the six-membered chelate ring is observed in the downfield region at 19.03 ppm as a narrow singlet peak.

^{13}C NMR spectrum of compound **4** shows 21 signal, including signals at 30.4, 31.5 ppm and 37.6, 38.8 ppm from the methyl groups and quaternary carbon atoms of the *tert*-butyl substituents, respectively. Fourteen signals of the tropolone ring and quinoline moiety appear in the region 115.5–157.3 ppm, while the signals of the carbonyl carbons of tropolone emerge at 174.3 and 195.4 ppm. The ^{1}H and ^{13}C NMR

spectra, the IR spectrum that displays characteristic bands of NH (3019–3069 cm^{-1}), C=O (1620, 1637 cm^{-1}) and SO_2 groups (1182, 1346 cm^{-1}), and mass spectrum confirm the structure of compound **4**.

Compound **4** can exist also in the OH tautomeric form resulting from intramolecular proton transfer from the pyridine nitrogen to the nearest carbonyl oxygen of tropolone. According to DFT B3LYP/6-311++G(d,p) quantum chemical computations for the gas phase with the use of Gaussian-09 program, these tautomeric forms correspond to minima on the potential energy surface. It was found that the NH form ($E_{ZPE} = -1799.03048$ au, $\omega_1 = 17$ cm^{-1}), whose geometrical parameters agree well with X-ray diffraction data, is only 0.6 kcal/mol more stable than the corresponding OH form ($E_{ZPE} = -1799.02955$ au, $\omega_1 = 14$ cm^{-1}), which does not exclude the presence of the OH form in solutions.

Thus, the new precursor of the polydentate 8-hydroxyquinoline ligand system with the 1,3-tropolone moiety in the 2-position of the heterocyclic ring was prepared by the reaction of 2-methyl-8-methanesulfonyloxyquinoline with 1,2-benzoquinone. It was shown that in crystal state it exists in the NH tautomeric form with methanesulfonyloxy group in the *exo* position to the tropolone ring, which is stabilized due to emergence of supplementary intramolecular hydrogen bond between the phenolic oxygen and the six-membered chelate ring formed by the quinoline and tropolone moieties.

EXPERIMENTAL

^1H and ^{13}C NMR spectra in $CDCl_3$ were recorded at 22°C on a Bruker DPX-250 spectrometer operating at 250.13 and 62.90 MHz, respectively. Chloroform signals ($\delta_H = 7.24$ ppm, $\delta_C = 77.00$ ppm) were used as an internal reference. IR spectra were recorded as thin films on a Varian Excalibur 3100 FT-IR spectrophotometer. Mass spectra were obtained on a Finnigan MAT INCOS 50 spectrometer by electron impact (ionizing voltage 70 eV). Elemental analysis was carried out on a KOVO CHN analyzer. Chromatography was conducted on columns filled with Brockmann activity grade II or III Al_2O_3. Melting points were determined on a Boetius hot stage apparatus.

X-ray diffraction data. Unit cell parameters for crystal and 3D set of intensities for compound **5** were obtained on an Xcalibur, Eos automated diffractometer (MoK_α radiation, graphite monochromator, 100 K). Yellow monoclinic crystals, chemical formula $C_{25}H_{29}NO_5S$, $M = 455.55$; $a = 5.8144(3)$ Å, $b = 11.3680(5)$, $c = 18.1682(9)$ Å, $\alpha = 97.648(4)°$, $\beta = 95.955(4)°$, $\gamma = 103.149(4)°$, $V = 1147.5(1)$ Å^3, $Z = 2$, $d_{calcd} = 1.318$ g/cm^3, space group *P-1*. Intensities of 8419 reflections were measured in the angle range ($2\theta \le 53°$) by *w* scanning. After averaging of intensities of equivalent reflections, the working body of measured $F^2(hkl)$ and $\sigma(F^2)$ consisted of 4738 independent reflections, of which 3782 with $F^2 > 4\sigma(F^2)$. The structure was solved by direct methods and refined by full-matrix least squares on F^2 in the anisotropic approximation for non-hydrogen atoms (hydrogen atoms were refined in the isotropic approximation as riding on their bonded atoms) with the use of the SHELXTL software [12]. The final refining parameters for compound **4**: $R_1 = 0.045$ for all observed reflections with $I \ge 2\sigma(i)$ and $R_1 = 0.061$ for all measured reflections, GOF = 1.040. Full tables of atomic coordinates, bond distances, bond angles, and thermal parameters of compound **4** are available from the authors on request (vatka@icp.ac.ru).

Initial compounds used were commercially available 2-methyl-8-hydroxyquinoline **1**, methanesulfonyl chloride, and 3,5-di(*tert*-butyl)-1,2-benzoquinone **3** from Aldrich.

2-Methyl-8-methanesulfonyloxyquinoline 4. A solution of 1.4 mL (0.18 mmol) of methanesulfonyl chloride in 10 mL of dry benzene was added dropwise on stirring to a solution of 2.4 g (15 mmol) of 2-methyl-8-hydroxyquinoline **1** and triethylamine (3.5 mL) in 20 mL of dry benzene at ambient temperature. The reaction mixture was kept at ambient temperature for one day and next heated under reflux for 1 h. After removal of the solvent on a water bath, the oily residue was cooled to ambient temperature and 50 g of crushed ice was added. The resulting white powder was separated by filtration, washed with cold water (2 × 15 mL), dried in air, and crystallized from ethanol. Colorless crystals, yield 3.36 g (95%), mp 114–116°C.

IR (thin film, ν, cm^{-1}): 1648 (C=N), 1629, 1607, 1585, 1508, 1346 (SO_2), 1314, 1182 (SO_2).

^1H NMR ($CDCl_3$, δ, ppm, *J*, Hz): 8.07 (d, 1H, $J = 8.5$, H_{quinol}), 7.72 (dd, 1H, $J = 8.2$, 1.3, H_{quinol}), 7.64 (dd, 1H, $J = 8.0$, 1.3, H_{quinol}), 7.46 (dd, 1H, $J = 8.0$, 7.9, H_{quinol}), 7.33 (d, 1H, $J = 8.5$, H_{quinol}), 3.48 (s, 3H, SO_2CH_3), 2.73 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, δ, ppm): 160.4, 145.6, 141.3, 136.6, 128.5, 127.3, 125.8, 124.2, 123.4, 39.7, 25.9.

MS (EI, 70 eV, m/z (I_{rel}, %)): 237 (M^+, 22), 159 (100), 130 (75), 103 (23), 77 (25), 63 (11), 51 (11), 39 (10).

For $C_{11}H_{11}NO_3S$ anal. calcd. (%): C, 55.69; H, 4.64; N, 5.91.

Found (%): C, 55.77; H, 4.58; N, 6.17.

5,7-Di(*tert*-butyl)-2-(8-methanesulfonyloxyquinolin-2-yl)-1,3-tropolone 4. A mixture of 1.18 g (5 mmol) of 2-methyl-8-methanesulfonyloxyquinoline **2** and 2.11 g (10 mmol) of 3,5-di(*tert*-butyl)-1,2-benzoquinone **3** in 5 mL of AcOH was kept at 65–67°C for 60 h (TLC monitoring). After reaction completion, the reaction mixture was diluted with cold water (250 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The organic fraction was dried with Na_2SO_4 and CH_2Cl_2 was removed. The product was isolated by column chromatography (Al_2O_3 sorbent, light petroleum ether + CH_2Cl_2 (1 : 1) as an eluent), yellow fraction with R_f = 0.33 was collected. After removal of the solvent, the solid residue was recrystallized from propan-2-ol. Yellow crystals, yield 1.09 g (24%), mp 218–219°C.

IR (thin film, ν, cm^{-1}): 3069–3019 (NH), 1637, 1620 (C=O); 1603, 1580, 1565, 1504, 1461, 1395, 1346 (SO_2), 1235, 1182 (SO_2), 1157, 1066, 1048, 868, 803, 754.

^1H NMR ($CDCl_3$, δ, ppm, *J*, Hz): 19.03 (s, 1H, OH), 8.15 (d, 1H, J = 9.3, H_{quinol}), 8.07 (d, 1H, J = 9.3, H_{quinol}), 7.74 (d, 1H, J = 7.9, H_{quinol}), 7.69 (d, 1H, J = 7.9, H_{quinol}), 7.47 (dd, 1H, J = 7.9, 7.9, H_{quinol}), 6.76 (d, 1H, J = 1.7, H_{trop}), 6.66 (d, 1H, J = 1.7, H_{trop}), 3.46 (s, 3H, CH_3), 1.38 (s, 9H, $C(CH_3)_3$), 1.24, (s, 9H, $C(CH_3)_3$).

^{13}C NMR ($CDCl_3$, δ, ppm): 195.4, 174.3, 157.3, 155.8, 154.7, 141.0, 137.6, 135.0, 127.6, 126.7, 126.0, 125.2, 124.0, 123.5, 121.7, 115.5, 39.3, 38.8, 37.6, 31.5 (3C), 30.4 (3C).

MS (EI, 70 eV, m/z (I_{rel}, %)): 427 (M^+–CO, 42), 412 (27), 384 (16), 332 (22), 318 (19), 292 (14), 248 (9), 204 (8), 156 (12), 105 (9), 91 (20), 79 (84), 57 (95), 41 (100).

For $C_{31}H_{33}NO_5S$ anal. calcd. (%): C, 70.03; H, 6.26; N, 2.63.

Found (%): C, 69.92; H, 6.33; N, 2.77.

5,7-Di(*tert*-butyl)-2-(8-hydroxyquinolin-2-yl)-1,3-tropolone 5. A solution of KOH (1 M, 3.0 mL) was added to a solution of 0.50 g of compound **4** in 15 mL of ethanol and heated under reflux on a water bath for 20 h. The reaction mixture was cooled to ambient temperature, diluted with 40 mL of water, acidified to neutral pH with 0.1 M HCl solution, the resulting yellow precipitate was separated by filtration, washed with water (3 × 30 mL) and recrystallized from toluene. Yield 0.36 g (87%), yellow crystals, mp 257–258°C (lit.: 257–258°C [10]).

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