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New bis-*o*-quinone with azine spacer and its cyclization into indazolo[2,1-*a*]indazole system

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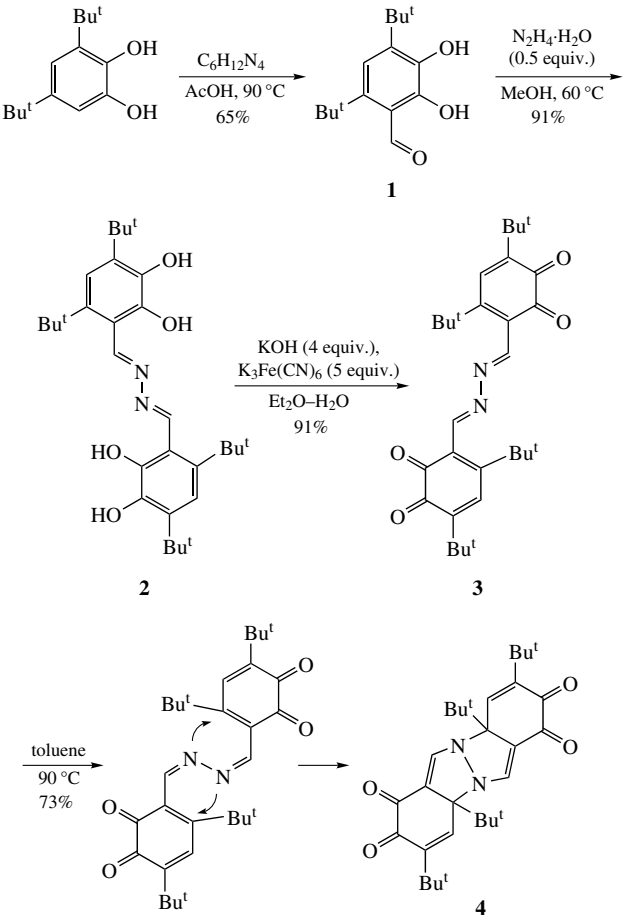
Reaction of 4,6-di-*tert*-butyl-2,3-dyhydroxybenzaldehyde with hydrazine gives a new sterically hindered bis-catecholimine which on oxidation and heating undergoes cyclization into indazolo[2,1-*a*]indazole derivative.

Redox-active ligands are employed for the preparation of transition and nontransition metal complexes useful in redox-switching catalysis,[1] redox-isomerism[2] and reversible addition of small molecules.[3] An important class of redox-active ligands is catechols and their oxidized form, *o*-quinones. These compounds can have different oxidative states in complexes such as catecholate dianion, *o*-semiquinonic and quinonic forms. Stability of such oxidative forms appreciably increases with insertion of one or two sterically hindered substituents, *e.g.*, *tert*-butyl group, into catechol molecule. Catechol derivatives without *tert*-butyl groups, especially catecholamides and catecholaldimines are well known as ligands for supramolecules (helicate structures and molecular tetrahedrones)[4] and bimetallic catalysts for the Mannich and Henry reactions,[5] however, these ligands do not have stable oxidative forms. Earlier we reported a three-step synthesis of catecholaldehyde **1** (4,6-di-*tert*-butyl-2,3-dihydroxybenzaldehyde) from 3,5-di-*tert*-butylcatechol.[6] Compound **1** is convenient block for the synthesis of sterically hindered bis-catecholaldimines.[7] Here we report on improved synthesis of **1**, synthesis of new sterically hindered bis-catecholaldimine with azine spacer and its oxidative cyclization.

Catecholaldehyde **1** was prepared in one step from 3,5-di-*tert*-butylcatechol[8] by the Duff reaction in 65% yield (Scheme 1).[†] Reaction of catecholaldehyde **1** with $N_2H_4·H_2O$ leads to bis-



Scheme 1

† *4,6-Di*-tert-*butyl-2,3-dihydroxybenzaldehyde* **1**. 3,5-Di-*tert*-butylcatechol (22.2 g, 0.1 mol) and urotropine (14 g, 0.1 mol) were dissolved in acetic acid (150 ml) under Ar atmosphere and heated at 120 °C for 2 h. The reaction mixture was then cooled to 40 °C and 50 ml of 50% aqueous H_2SO_4 solution was added. The precipitate was filtered and recrystallized from 250 ml MeOH. The product appeared as yellow crystals, yield 16.3 g (65%), mp 115–116 °C. IR (Nujol, ν/cm^{-1}): 3620 (nar.), 3529–3240 (br.), 1624 (C=O). ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.42 and 1.49 (2 s, 2×9 H, Bu^t), 5.99 (s, 1H, OH), 6.88 (s, 1H, H_{Ar}), 10.71 (s, 1H, CHO), 12.92 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 29.00, 33.76, 35.72, 35.75, 115.19, 115.99 (CH), 141.73, 141.77, 143.24, 151.93, 196.58. Found (%): C, 71.89; H, 8.90. Calc. for $C_{15}H_{22}O_3$ (%): C, 71.97; H, 8.86.

*6,6′-[(*E,E*)-2,3-Diazabuta-1,3-diene-1,4-diyl]bis(3,5-di*-tert-*butylcatechol)* **2**. Hydrazine hydrate (0.2 ml, 2 mmol) was added to methanol solution of compound **1** (2.0 g, 4 mmol), and the mixture was boiled for 3 h. The product was isolated as yellow powder (1.81 g, 91%). mp 290–291 °C. IR (Nujol, ν/cm^{-1}): 1567, 1606, 1619, 3496 (nar.). ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.45 and 1.49 (2 s, 2×18 H, Bu^t), 6.09 (s, 2H, OH), 6.93 (s, 2H, H_{Ar}), 9.49 (s, 2H, N=C–H), 12.98 (s, 2H, OH). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 29.22, 33.24, 35.44, 35.76, 112.07, 115.47, 138.34, 141.25, 141.82, 148.89, 163.67. UV [$CHCl_3$, λ_{max}/nm (log ε)]: 351 (4.73). Found (%): C, 72.53; H, 8.96; N, 5.60. Calc. for $C_{30}H_{44}N_2O_4$ (%): C, 72.55, H, 8.93; N, 5.64.

*6,6′-[(*E,E*)-2,3-Diazabuta-1,3-diene-1,4-diyl]bis(3,5-di*-tert-*butyl-*o*-*benzoquinone)* **3**. Water solution of $K_3Fe(CN)_6$ (3.28 g, 10 mmol) and KOH (0.11 g, 2 mmol) were added with stirring to solution of **2** (0.99 g, 2 mmol) in Et_2O (10 ml). The product was isolated by filtration as red-green powder. The yield was 0.89 g (91%). IR (Nujol, ν/cm^{-1}): 1618, 1659, 1685. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.27 and 1.33 (2 s, 2×18 H, Bu^t), 7.11 (s, 2H, C_q–H), 8.44 (s, 2H, N=C–H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 29.11 and 30.35 (Me, Bu^t), 35.61 and 38.46 (C, Bu^t), 129.79, 136.02, 149.57, 159.06, 160.02, 178.53, 180.70. UV [$CHCl_3$, λ_{max}/nm (log ε)]: 416 (3.75), 580 (2.30). Found (%): C, 73.10; H, 8.23; N, 5.60. Calc. for $C_{30}H_{40}N_2O_4$ (%): C, 73.14; H, 8.18; N, 5.69.

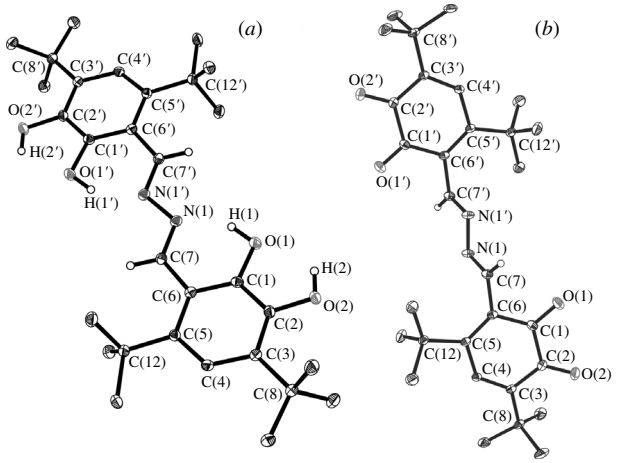


Figure 1 Molecular structures of (*a*) **2** and (*b*) **3**. Thermal ellipsoids are given with 30% probability. Hydrogens of Bu^t groups are not shown.

catecholaldimine **2**† in 91% yield. Catecholaldimines can in general exist in two tautomeric forms as quinonemethide or catecholic. Compound **2** exists in catecholic form both in solution and in solid. In the ^{1}H NMR spectrum of compound **2** in $CDCl_3$ the OH···N and OH···O signals are observed at 12.98 and 6.06 ppm, respectively. The signal of aldimine proton is located at 9.49 ppm. The IR spectrum of catecholaldimine **2** exhibits the strong absorption band of the OH stretch vibration at 3496 cm^{-1}. The molecular structure of **2** was confirmed by X-ray diffraction [Figure 1(*a*)].‡ The molecule of compound **2** is a centrosymmetrical monomer with inversion center at the middle of N(1)–N(1′) bond. The aldimine bonds C(7)–N(1) and C(7′)–N(1′) lie in the aromatic planes. This conformation is stabilized by intramolecular hydrogen bond O(1)H(1)···N(1) [1.72(2) Å]. So, the molecule of **2** has a common π-system. Intermolecular hydrogen bonds[7] typical of catecholimines are not observed in the crystal lattice of **2**.

Deprotonation of catecholaldimines leads to aldimine fragment rotation about C(6)–C(7) bond followed by the displacement of imine fragment out of the benzene plane and as a consequence by disturbance of molecule generalized π-system and localization of catecholate dianion.[4(*e*)–(*h*)] So, oxidation of catecholaldimines based on **1** should result in stable *o*-quinones like well known sterically hindered 3,5-di-*tert*-butylbenzoquinone. In fact, oxidation of bis-catecholaldimine **2** gives stable bis-*o*-quinone **3** in 91% yield.† Its IR spectrum contains the strong absorption bands of the *o*-quinone fragment: C=O and C=C stretch vibrations at 1618, 1659 and 1685 cm^{-1}. The C=O signals were observed in its ^{13}C NMR spectrum in $CDCl_3$ at 178.53 and 180.70 ppm. The UV spectrum of compound **3** in $CHCl_3$ is characterized by two bands at 416 nm (ε = 5660) typical of π→π* transition and at 578 nm (ε = 200) – of n→π* transition. Extinctions of both transitions are close to twofold values for *o*-quinone,[14] which evidences the nonplanar structure of **3** analogous to deprotonated form of catecholaldimines in solution. It is possible because aldimine substituent does not conjugate with *o*-benzoquinone fragment and consequently both benzoquinone fragments are independent. This nonplanar structure in solution is in agreement with molecular structure of **3**, determined by X-ray crystallography [Figure 1(*b*)].‡ Compound **3** has centrosymmetrical structure with inversion center at N(1)–N(1′) bond like compound **2**. Azine fragment C(7)N(1)N(1′)C(7′) possesses *trans*-conformation. Oxidation of bis-catechol **2** results in changes of the structure. Distances C(1)–O(1), C(2)–O(2) and C(7)=N(1) are shortened from 1.360(2), 1.372(2) and 1.290(2) Å (in **2**) to 1.208(2), 1.208(2) and 1.269(2) Å (in **3**), respectively. The N(1)–N(1′) bond distance is lengthened from 1.399(2) Å (in **2**) to 1.422(2) Å (in **3**). The intramolecular hydrogen bonds which stabilize planar structure disappear upon oxidation of **2**. The repulsion of electron pairs of atoms N(1) and O(1) [and N(1′) and O(1′)] breaks the generalized π-system of compound **3**. The N(1)···O(1) distance in molecule **3** [3.669(2) Å] is larger than that in molecule **2** [2.544(1) Å]. The dihedral angle C(5)C(6)C(7)N(1) in molecule **3** is –60.5(2)°, whereas in molecule **2** this angle is 174.8(1)°. Symmetrical *o*-quinone fragments are situated in the parallel planes [atoms C(1)–C(6), O(1) and O(2)], the distance between them being 2.2234(2) Å. Dihedral angle between quinone planes [C(1)–C(6), O(1), O(2)] and azine fragment [C(7)N(1)N(1′)C(7′)] is 55.6(1)°. *o*-Quinone fragments are not planar. The average deviation of C(1)–C(6), O(1) and O(2) atoms out of the mean plane is 0.072 Å and this value is larger than that in bis-catecholaldimine **2** (0.009 Å). Atoms C(7), C(8) and C(12) deviate from the mean plane C(1)–C(6), O(1), O(2) by 0.125(2), 0.086(2) and 0.065(2) Å (for **2**), and 0.150(2), 0.293(2) and 0.473(2) Å (for **3**), respectively. The *tert*-butyl groups [atoms C(12) and C(12′)] and imine fragment [atoms N(1) and N(1′)] are deviated from ring plane in opposite directions. It simplifies the nucleophilic attack to C(5) (see Scheme 1).

Intramolecular nucleophilic addition can occur within *o*-quinone **3** which turned thermally unstable. Heating of **3** in toluene leads to compound **4**.§ The latter, like *o*-quinone **3**, has two C=O groups (δ 175.36 and 183.40 ppm in ^{13}C NMR spectrum), but, in contrast to **3**, it has signal at δ 77.60 ppm distinctive for compounds with cyclohexadienone structure. It was confirmed by ^{1}H NMR data: a signal of one of *tert*-butyl groups is shifted to a strong field from 1.33 ppm for compound **3** to 1.04 ppm for **4**. Thus, compound **4** possesses indazoloindazole structure. This reaction can be considered a double nucleophilic addition or

‡ *Crystal data.* The crystals suitable for crystallographic work were grown from methanol (**2**) or hexane (**3**). The X-ray data were collected on automatic Bruker AXS SMART APEX (**2**) and APEX II D8 Quest (**3**) diffractometers (graphite-monochromated, MoKα radiation, ω-scan technique, λ = 0.71073 Å) at 100 K. The intensity data were integrated by SAINT (for **2**[9] and **3**[10]) programs. SADABS (for **2**[11] and **3**[12]) were used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and refined on F^2 using SHELXTL[13] package. All non-hydrogen atoms were found from Fourier syntheses of electron density and refined anisotropically. The most of H atoms in **2** and **3** were placed in calculated positions and refined in the riding model. The hydrogen atoms H(1A) and H(2A) in **2** and H(7A) in **2** and **3** were found from Fourier syntheses of electron density and refined isotropically.

For **2**: $C_{30}H_{44}N_2O_4$, M = 496.67, monoclinic, space group $P2_1/n$, at 100 K: a = 11.7066(8), b = 8.0811(6) and c = 15.6407(11) Å, β = 105.235(1)°, V = 1427.6(2) Å^3, Z = 2, d_{calc} = 1.155 g cm^{-3}, μ = 0.076 mm^{-1}, $F(000)$ = = 540, 2θ = 52°, R_{int} = 2800 (0.025), R_1 [$I > 2\sigma(I)$] = 0.0427, wR_2 (all data) = 0.1162. Largest diff. peak and hole, e/Å^3 = 0.285/–0.161.

For **3**: $C_{30}H_{40}N_2O_4$, M = 492.64, monoclinic, space group $P2_1/n$, at 100 K: a = 12.423(1), b = 6.3066(7) and c = 18.179(2) Å, β = 99.538(2)°, V = 1404.6(3) Å^3, Z = 2, d_{calc} = 1.165 g cm^{-3}, μ = 0.077 mm^{-1}, $F(000)$ = = 532, 2θ = 52°, R_{int} = 2750 (0.0367), R_1 [$I > 2\sigma(I)$] = 0.0412, wR_2 (all data) = 0.1041. Largest diff. peak and hole, e/Å^3 = 0.228/–0.161.

CCDC 1033937 and 1033938 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

§ *3,4a,9,10a-Tetra*-tert-*butylindazolo[2,1-*a*]indazole-1,2,7,8(4a*H*,10a*H*)-tetraone* **4**. Compound **3** (0.49 g, 1 mmol) in toluene (10 ml) was heated to 90 °C for 3 h. The reaction mixture was cooled and the product was isolated by filtration. Red-pink powder, yield 0.36 g (73%), decomposes without melting at 203 °C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.04 and 1.27 (s, 2×18 H, Bu^t), 6.95 (s, 2 H, CH), 7.58 (s, 2 H, NCH). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 25.33, 29.04, 35.80, 42.44, 77.60, 128.22, 129.03, 137.46, 143.91, 149.80, 175.36, 183.40. UV [$CHCl_3$, λ_{max}/nm (log ε)]: 276 (4.05), 448 (3.67), 488 (3.69). Found (%): C, 73.23; H, 8.15; N, 5.58. Calc. for $C_{30}H_{40}N_2O_4$ (%): C, 73.14; H, 8.18; N, 5.69.

[3 + 2] cycloaddition. The C(7)N(1)N(1′)C(7′) fragment in compound **3** has *trans*,*trans*,*trans* conformation, however, the mentioned transformation can be realized only from *cis*,*trans*,*cis* conformation of azine C(7)N(1)N(1′)C(7′) fragment (see Scheme 1) and probably thermal activation of **3** is necessary to change the conformation.

In summary, bis-*o*-quinone **3** with azine spacer is the first example of *o*-quinones formed from catecholaldimines. The X-ray data for **2** and **3** have demonstrated the structural changes which occur upon oxidation of catecholaldimine into its *o*-benzoquinone analogue.

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