

Synthesis and Structure of 2,2'-Spirobi(1,3-benzodioxole) Derivative Prepared from 3,5-Di(*tert*-butyl)-1,2-benzoquinone

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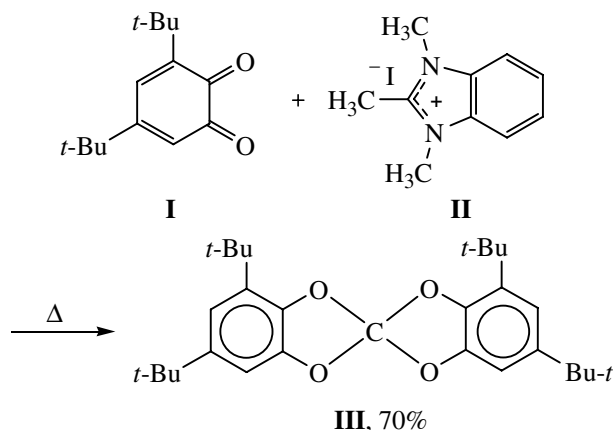
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Abstract—3,5-Di(*tert*-butyl)-1,2-benzoquinone reacted with 1,2,3-trimethylbenzimidazolium iodide led to the formation of 2,2'-spirobi[4,6-di(*tert*-butyl)-1,3-benzodioxole]. The reaction mechanism was suggested. The structure of 2,2'-spirobi[4,6-di(*tert*-butyl)-1,3-benzodioxole] was established by means of X-ray diffraction analysis.

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The chemistry of sterically-hindered *O*-quinones is versatile and rich in unexpected paths in reactions with methylene-active compounds. We recently revealed that the reaction of the sterically-hindered *O*-quinones with quinaldine derivatives resulted in the formation of (quinolin-2-yl)-1,3-tropolones [1–3]. Reactions of 3,5-di(*tert*-butyl)-1,2-benzoquinone with 2-methylbenzimidazole derivatives gave rise to polycyclic isoquinoline derivatives [4]. We extended this reaction to benzimidazolium salts, and the study of reaction products obtained from 3,5-di(*tert*-butyl)-1,2-benzoquinone (**I**) and a salt of 1,2,3-trimethylbenzimidazolium **II** by X-ray diffraction analysis demonstrated the formation of 2,2'-spirobi[4,6-di(*tert*-butyl)-1,3-benzodioxole] (**III**) in considerably high yield (65–70%) (Scheme 1).

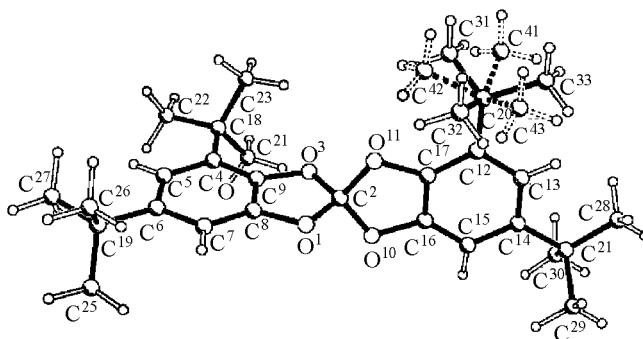
Scheme 1.



The structure of 2,2'-spirobi[4,6-di(*tert*-butyl)-1,3-benzodioxole] (**III**) has been established by X-ray crystallography and is shown on the figure. The main interatomic distances and bond angles are compiled in the table.

The presumed mechanism of compound **III** formation is given in Scheme 2.

In the first stage of the reaction quinone **I** adds to the N-methyl group of the benzimidazolium resulting in the formation of adduct **A**, whose oxidation with initial quinone **I** may give 3-[4,6-di(*tert*-butyl)-1,3-benzodioxol-2-yl]-1,2-dimethyl-3*H*-benzimidazolium iodide **B**. Further transformation occurs probably through the addition of the second quinone **I** molecule to salt **B** leading to intermediate compound **C** followed by elimination of a molecule of 1,2-dimethylbenzimidazolium iodide (**IV**) and thus giving rise to reaction product **III**.

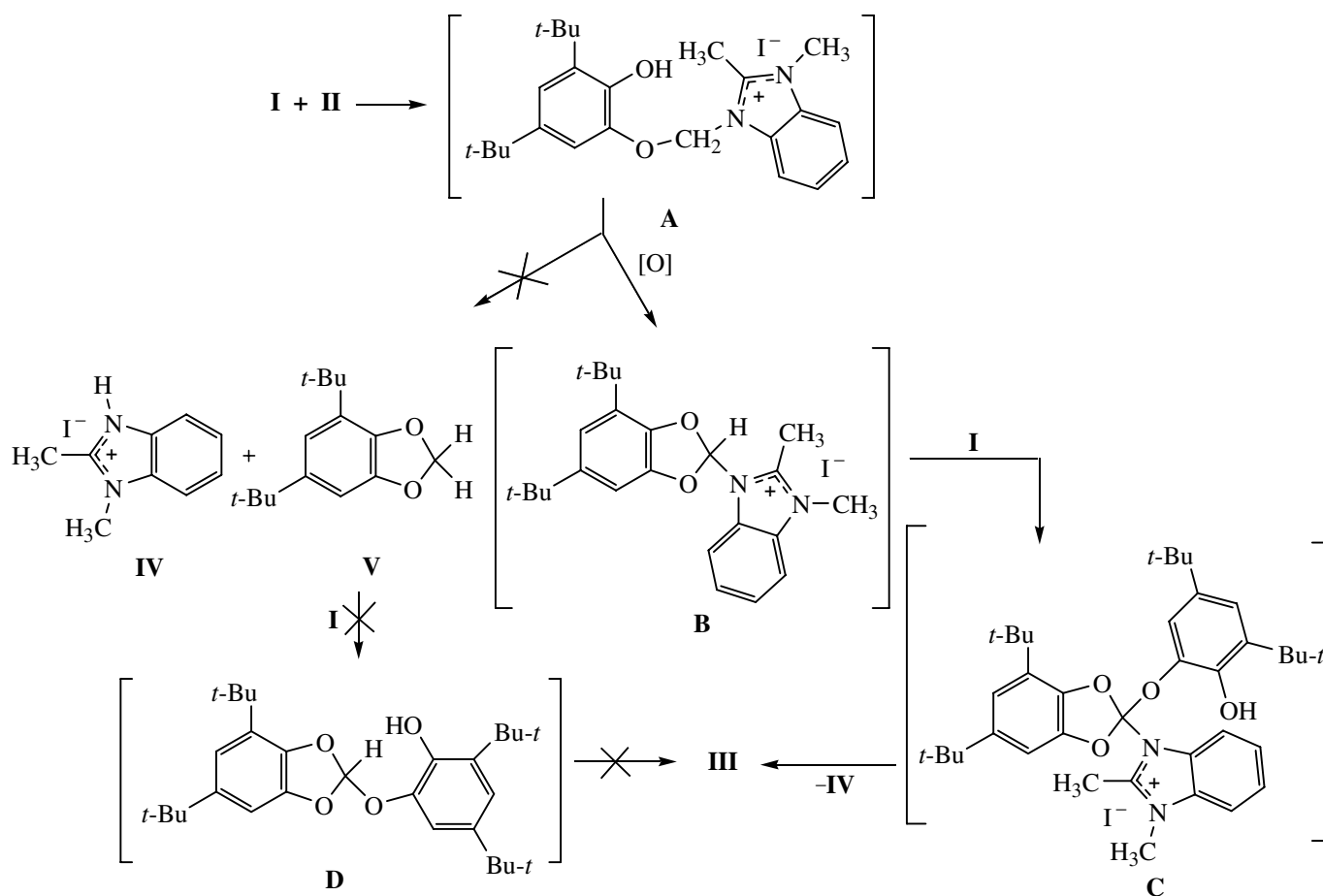


Molecular structure of 2,2'-spirobi[4,6-di(*tert*-butyl)-1,3-benzodioxole] (**III**).

Bond lengths and bond angles in the molecule of compound **III**

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å	Angle	φ, deg	Angle	φ, deg
O ¹ C ⁸	1.388(2)	O ¹ C ²	1.397(3)	C ⁸ O ¹ C ²	106.8(2)	C ⁹ O ³ C ²	107.2(2)
O ³ C ⁹	1.391(2)	O ³ C ²	1.395(3)	C ¹⁶ O ¹⁰ C ²	107.1(2)	C ¹⁷ O ¹¹ C ²	107.2(2)
O ¹⁰ C ¹⁶	1.384(2)	O ¹⁰ C ²	1.401(3)	O ³ C ² O ¹	108.4(2)	O ³ C ² O ¹⁰	110.2(2)
O ¹¹ C ¹⁷	1.391(2)	O ¹¹ C ²	1.403(3)	O ¹ C ² O ¹⁰	110.0(2)	O ³ C ² O ¹¹	110.2(2)
C ⁴ C ⁹	1.373(3)	C ⁴ C ⁵	1.401(3)	O ¹ C ² O ¹¹	110.3(2)	O ¹⁰ C ² O ¹¹	107.8(2)
C ⁴ C ¹⁸	1.527(3)	C ⁵ C ⁶	1.393(3)	C ⁹ C ⁴ C ⁵	113.3(2)	C ⁹ C ⁴ C ¹⁸	122.6(2)
C ⁶ C ⁷	1.389(3)	C ⁶ C ¹⁹	1.542(3)	C ⁵ C ⁴ C ¹⁸	124.1(2)	C ⁶ C ⁵ C ⁴	124.8(2)
C ⁷ C ⁸	1.362(3)	C ⁸ C ⁹	1.368(3)	C ⁷ C ⁶ C ⁵	118.8(2)	C ⁷ C ⁶ C ¹⁹	118.9(2)
C ¹² C ¹⁷	1.372(3)	C ¹² C ¹³	1.410(3)	C ⁵ C ⁶ C ¹⁹	122.3(2)	C ⁸ C ⁷ C ⁶	116.9(2)
C ¹² C ²⁰	1.523(3)	C ¹³ C ¹⁴	1.389(3)	C ⁷ C ⁸ C ⁹	123.3(2)	C ⁷ C ⁸ O ¹	127.5(2)
C ¹⁴ C ¹⁵	1.400(3)	C ¹⁴ C ²¹	1.525(3)	C ⁹ C ⁸ O ¹	109.2(2)	C ⁸ C ⁹ C ⁴	122.9(2)
C ¹⁵ C ¹⁶	1.360(3)	C ¹⁶ C ¹⁷	1.366(3)	C ⁸ C ⁹ O ³	108.4(2)	C ⁴ C ⁹ O ³	128.7(2)
				C ¹⁷ C ¹² C ¹³	113.2(2)	C ¹⁷ C ¹² C ²⁰	124.2(2)
				C ¹³ C ¹⁴ C ¹⁵	118.2(2)	C ¹³ C ¹⁴ C ²¹	122.7(2)
				C ¹⁵ C ¹⁶ C ¹⁷	123.8(2)	C ¹⁵ C ¹⁶ O ¹⁰	126.8(2)
				C ¹⁷ C ¹⁶ O ¹⁰	109.3(2)	C ¹⁶ C ¹⁷ C ¹²	122.8(2)
				C ¹⁶ C ¹⁷ O ¹¹	108.5(2)	C ¹² C ¹⁷ O ¹¹	128.7(2)

Scheme 2.



Compound **III** may also form by an alternative route: 1,2-dimethylbenzimidazolium iodide (**IV**) might be eliminated from the condensation product **A** providing 4,6-di(*tert*-butyl)-1,3-benzodioxole (**V**). The second molecule of quinone **I** then adds to compound **V** giving second condensation product **D** that suffers dehydration by quinone **I** resulting in cyclization into spiro compound **III**. To prove the above assumptions we prepared compound **V** by modified procedure [5]. However the reaction of 4,6-di(*tert*-butyl)-1,3-benzodioxole (**V**) with quinone **I** failed to give rise to compound **III**.

It was presumable that 1,2-dimethylbenzimidazolium salt **IV** reacts with quinone **I** like salt **II** transforming into compound **III** (Scheme 3). We found, that the reaction between compounds **IV** and **I** led to the formation of only traces of compound **III**.

2-Methylbenzimidazolium iodide (**VI**) can react with quinone **I** forming polycyclic isoquinoline derivatives [4] whose traces were found in the reaction mixture. The side reactions of salts **IV** and **VI** with the initial quinone decrease the yield of target product **III**, therefore the raising of the yield requires the application of a considerable excess of quinone **I**. Compound **III** can be obtained in over 80% yield by the reaction of 3,5-di(*tert*-butyl)pyrocatechol with trichloromethylisocyanide dichloride by procedure [6].

The structure of 2,22-spiro[4,6-di(*tert*-butyl)-1,3-benzodioxole] (**III**) was established by X-ray crystallography and additionally characterized by ^1H , ^{13}C , UR, and mass spectra. X-ray diffraction analysis revealed in the crystals disordering by two positions in 2:1 ratio of one among four *tert*-butyl groups (the less populated group is shown by dotted line on the figure). This fact distorts the C_2 -symmetry of the molecule in the single crystal. According to ^1H NMR spectrum the C_2 -symmetry is conserved in solution. The proton signals of *tert*-butyl groups have double integral intensity and appear in the region 1–2 ppm, and the aromatic proton signals are observed in the region 6–7 ppm. The spirocyclic carbon gives rise to a signal in ^{13}C NMR spectrum at 139 ppm.

The other structural details of the left and right part of the molecule under study are identical. The atoms of

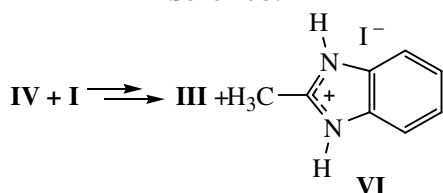
1,3-benzodioxole fragments are located in the corresponding planes within 0.006 and 0.009 Å, the angle between the planes at the spiro atom C^2 equals 90.1° . The endocyclic angles at C^2 are $108.4(2)$ and $107.8(2)^\circ$, the other bond angles at C^2 are in the range 110.0 – 110.3° . The equivalent distances in the five-membered 1,3-dioxole fragments between C^2 atom and oxygens lie in the range $1.395(3)$ – $1.403(3)$ Å, the valence distances between oxygens and the corresponding carbons in the aromatic part of the molecule amount to $1.384(3)$ – $1.391(3)$ Å, endocyclic angles are in the range $106.8(2)$ – $108.2(2)^\circ$. The analysis of valence bond lengths in the benzene fragment of molecule **III** reveals regular redistribution of their values: decrease in the distances C^7 – C^8 , C^8 – C^9 , C^9 – C^4 , C^{15} – C^{16} , C^{16} – C^{17} , and C^{12} – C^{17} to $1.360(3)$ – $1.373(3)$ Å accompanied with the increase in peripheral distances of the aromatic rings to $1.389(3)$ – $1.410(3)$ Å. It is presumable, that this redistribution of the bond lengths is caused by the interaction between the π -orbitals of the benzene fragment and the π -orbitals of two nearest oxygen atoms. The more thorough analysis of the diminished distances suggests a conclusion that in every 4,6-di(*tert*-butyl)-1,3-benzodioxole fragment in the chain $C^7C^8C^9C^4$ and its analog the mentioned redistribution occurs fairly characteristically: the shortest distances C^7 – C^8 and C^{15} – C^{16} [$1.362(3)$ and $1.360(3)$ Å], next in values C^8 – C^9 and C^{12} – C^{17} [$1.368(3)$ and $1.366(3)$ Å], then C^4 – C^9 and C^{12} – C^{17} [$1.373(3)$ and $1.372(3)$ Å]. It is presumable that this regularity in redistribution of the shortened distances is due to the unsymmetrical position of two *tert*-butyl groups in each 4,6-di(*tert*-butyl)-1,3-benzodioxole fragment.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were registered on a spectrometer Varian Unity-300. IR spectra were recorded on a spectrophotometer 75IR from mulls in mineral oil. Mass spectra were measured on Finnigan MAT INCOS-50 instrument.

X-ray diffraction analysis. Unit cell parameters of a crystal of compound **III** and a three-dimensional set of reflections intensities were obtained using a diffractometer Kuma-Diffraction KM-4 (MoK_α radiation, graphite monochromator) from an isometric single crystal of low quality, arbitrary form of a radius ~ 0.23 mm. Compound $\text{C}_{29}\text{H}_{40}\text{O}_4$, crystal triclinic, unit cell parameters a 9.448(2), b 11.458(2), c 12.815(3) Å, α 84.95(2), β 81.50(2), γ 84.91(2)°, V 1362.7(5) Å³, M 452.6, space group $P-1$, Z 2, d_{calc} 1.103 g/cm³. The intensities of 3765 reflections

Scheme 3.



($2\theta \leq 44.96^\circ$) were measured by $\omega/2\theta$ scanning. After exclusion of the systematically extinguished reflections the operating set of measured reflections was 3509 with $I > 3\sigma(I)$. The structure was solved by the direct method and refined by a least-squares full-matrix procedure with respect to F^2 by SHELXL-97 software [7] in anisotropic approximation for nonhydrogen atoms. All hydrogens in the structure were found from difference synthesis save the hydrogens at the disordered carbon atoms. The final value of R -factor was 4.7%, "good. of fit" parameter equaled 1.04.

2,2'-Spirobi[4,6-di(*tert*-butyl)-1,3-benzodioxole] (III). A solution of 0.72 g (2.5 mmol) of 1,2,3-trimethylbenzimidazolium iodide (II) and 4.95 g (22.5 mmol) of 3,5-di(*tert*-butyl)-1,2-benzoquinone (I) in 7 ml of dimethylformamide was heated for 12 h maintaining the temperature of the reaction mixture at 140–150°C. On cooling the separated precipitate of compound III was filtered off, washed with DMF (~10 ml) and petroleum ether (~20 ml), dried, dissolved in a minimum quantity of chloroform, and the solution was passed through a column (70×2 cm) packed with aluminum oxide, eluent chloroform–petroleum ether, 1:1, collecting the first colorless fraction. On evaporating the solvent we obtained 0.75 g of colorless compound III. Recrystallization from a mixture toluene–2-propanol, 1:3. Yield 66%. Colorless crystals, mp 228–230°C. IR spectrum, cm^{-1} : 1647, 1606, 1500, 1460, 1500, 1460, 1406, 1366, 1286 (C–O–C), 1260 (C–O–C), 1100, 1040 (C–O–C), 1020 (C–O–C). ^1H NMR spectrum (CDCl_3), δ , ppm: 1.30 s [18H, 6(6')-C(CH₃)₃], 1.38 s [18H, 4(4')-C(CH₃)₃], 6.92 d (2H, H^{5(5')}, J 1.7 Hz), 6.95 d (2H, H^{7(7')}, J 1.7 Hz). ^{13}C NMR spectrum (CDCl_3), δ , ppm: 29.541 (C¹³), 31.692 (C¹²), 34.159 (C¹⁰), 34.995 (C¹¹), 104.031 (C⁴), 116.254 (C⁶), 131.891 (C⁷), 139.612 (C²), 139.751 (C⁸), 144.301 (C⁹), 145.607 (C⁵). Mass spectrum, m/z (I_{rel} , %): 452 (95) [M]⁺, 437 (100), 233 (10), 211 (30), 57 (30), 41 (15). Found, %: C 77.28; H 8.64. C₂₉H₄₀O₄. Calculated, %: C 76.95; H 8.91. M 452.29.

4,6-Di(*tert*-butyl)-1,3-benzodioxole (V). In 100 ml of anhydrous DMSO 20 g of sodium hydroxide was heated at 100°C. At vigorous stirring a solution of 11 g

(0.05 mol) of 3,5-di(*tert*-butyl)pyrocatechol in 50 ml of dichloromethane was added slowly within 2 h to the above mixture, and the stirring was continued for 2 h. The formed precipitate was filtered off, the mother liquor was diluted with water (~200 ml). The water layer was decanted from the oily layer, and 50 ml of chloroform was added. The chloroform solution was washed with water (~100 ml), dried over sodium sulfate, and passed through a column (50×4 cm) packed with aluminum oxide, eluent chloroform, collecting the first colorless fraction. On evaporating the solvent we obtained 8 g (69%) of compound V. Colorless oily substance, slightly yellowish, bp 141–142°C [8]. IR spectrum, cm^{-1} : 1633, 1593, 1487, 1460, 1410, 1393, 1367, 1286, 1260, 1233 (1625, 1590, 1480, 1460 [8]). ^1H NMR spectrum (CDCl_3), δ , ppm: 1.30 s [18H, 6-C(CH₃)₃], 1.36 s [18H, 4-C(CH₃)₃], 5.91 s (2H, H²), 6.80 s (2H, H^{5,7}). Found, %: C 76.42; H 9.34. C₁₅H₂₂O₂. Calculated, %: C 76.88; H 9.46. M 234.16.

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