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Synthesis, structure and antimicrobial activity of sterically hindered bis-phosphonium derivatives of 2,6-di-*tert*-butyl-4-methylphenol

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Experimental section

General details

NMR spectra were recorded on the Bruker Avance III instrument with an operating frequency of 122.4 MHz for ^{31}P spectra (internal standard 85% H_3PO_4). IR spectra were recorded on the PerkinElmer UATR Two FT-IR Spectrometer (Spectrum Two). Thermal stability was studied using a STA 449C Jupiter synchronous microthermoanalyzer (Netzsch, Germany) at heating rate of 10 deg min^{-1} under argon atmosphere.

New compounds

*Synthesis of 4-bromomethyl-2,6-di-tert-butylphenol (**2**)* To a solution of 2,6-di-*tert*-butyl-4-methylphenol **1** (0.01 mol)in CCl_4 (20 ml) was added dropwise a solution of bromine (0.01 mol) in CCl_4 (20 ml) at such a rate that the color faded as bromine reacted. After completion of the reaction, the mixture was refluxed for one hour, and the solvent was removed *in vacuo*. The precipitated oily product was washed from the starting compounds and crystallized upon freezing. Yield 92%, mp. 56.3°C. IR (ν/cm^{-1}) 3301 (OH). ^1H NMR spectrum (CH_3OD) δ_H, ppm (*J*/Hz): 2.8 (s, 18H, $C(CH_3)_3$), 5.9 (s, 2H, $C\underline{H}_2Br$), 8.6 (s, 2H, $C^o\underline{H}$). $^{13}C\{^1H\}$ NMR spectrum (CH_3OD), δ_C, ppm, 100.6 MHz: 31.6 (s, $C(\underline{C}H_3)_3$), 34.1 (s, $\underline{C}H_2Br$), 34.6 (s, $\underline{C}(CH_3)_3$), 124.8 (s, C^4), 129.6 (s, C^3, C^5), 138.1 (s, C^2, C^6), 153.2 (s, C^1). Elemental analysis: $C_{15}H_{23}BrO$. Found, %: C 60.51, H 8.01. Calculated, %: C 60.20, H 7.75.

*Synthesis of ethane-1,2-diylbis[(3,5-di-tert-butyl-4-hydroxybenzyl)diphenylphosphonium] dibromide (**3a**)* To a solution of 4-bromomethyl-2,6-di-*tert*-butylphenol **2** (1 mmol) in diethyl ether (10 ml) was added 1,2-bis(diphenylphosphino)ethane (0.5 mmol) dissolved in acetonitrile (10 ml). The precipitate formed in 30 min was collected by filtration, washed with diethyl ether, and dried in air. Yield 93%, mp. 195°C (dec.). ^{31}P NMR spectrum (CH_3OD): δ 29.2 ppm. ^{1}H NMR spectrum (CH_3OD) δ_H, ppm (J/Hz): 2.8 (s, 18H, $C(CH_3)_3$), 5.9 (m, 4H, $C\underline{H}_2P$), 2.6 (m, 4H, P$\underline{-(CH_2)}_2$), 7.8-8.7 (m, 24H, $\underline{Ph}$). ^{13}C{^{1}H} NMR spectrum (CH_3OD), δ_C, ppm, 100.6 MHz: 12.1, 31.6, 34.6, 117.1, 124.2, 129.6, 133.1, 133.9, 135.1, 138.1, 153.2 (high viscosity of the sample made the observation of P-C coupling constants difficult). Found, %: C 67.53, H 7.14, P 6.20. $C_{56}H_{70}O_2P_2Br_2$. Calculated, %: C 67.47, H 7.08, P 6.21. The structure was confirmed by X-ray diffraction.

*Synthesis of propane-1,3-diylbis[(3,5-di-tert-butyl-4-hydroxybenzyl)diphenylphosphonium] dibromide (**3b**)* To a solution of 4-bromomethyl-2,6-di-*tert*-butylphenol **2** (1 mmol) in diethyl ether (10 ml) was added 1,3-bis(diphenylphosphino)propane (0.5 mmol) in acetonitrile (10 ml). The precipitate formed in 30 min was collected by filtration, washed with diethyl ether, and dried in air. Yield 90%, mp. 215°C (dec.). ^{31}P NMR spectrum (CH_3OD): δ 24.9 ppm. ^{1}H NMR spectrum (CH_3OD) δ_H, ppm (J/Hz): 1.5 (m, 2H, P-CH_2-$\underline{CH_2}$), 3.0 (m, 4H, P-$\underline{CH_2}$), 3.3 (s, 18H, $C(\underline{CH_3)}_3$), 4.7 (m, 4H, $\underline{CH_2}$-P), 7.8-8.7 (m, 24H, $\underline{Ph}$). ^{13}C{^{1}H} NMR spectrum (CH_3OD), δ_C, ppm, 100.6 MHz: 12.3, 16.1, 31.7, 34.8, 117.1, 124.2, 129.6, 133.1, 133.9, 135.1, 138.1, 153.2. (high viscosity of the sample made the observation of P-C coupling constants difficult). Found, %: C 67.74; H 7.25; P 6.20. $C_{57}H_{72}Br_2O_2P_2$. Calculated, %: C 67.72; H 7.18; P 6.13.

*Synthesis of hexane-1,6-diylbis[(3,5-di-tert-butyl-4-hydroxybenzyl)diphenylphosphonium] dibromide (**3c**)* To a solution of 4-bromomethyl-2,6-di-*tert*-butylphenol **2** (1 mmol) in diethyl ether (10 ml) was added 1,6-bis(diphenylphosphino)hexane (0.5 mmol) in benzene (10 ml). The reaction mixture was heated for 10 min. The precipitate formed in 30 min was collected by filtration, washed with diethyl ether, and dried in air. Yield 92%, mp. 162°C (dec.). ^{31}P NMR spectrum (C_2D_5OD): δ: 25.4 ppm. Found, %: C 68.65; H 7.51; P 5.94 $C_{60}H_{78}Br_2O_2P_2$. Calculated, %: C 68.54; H 7.47; P 5.88.

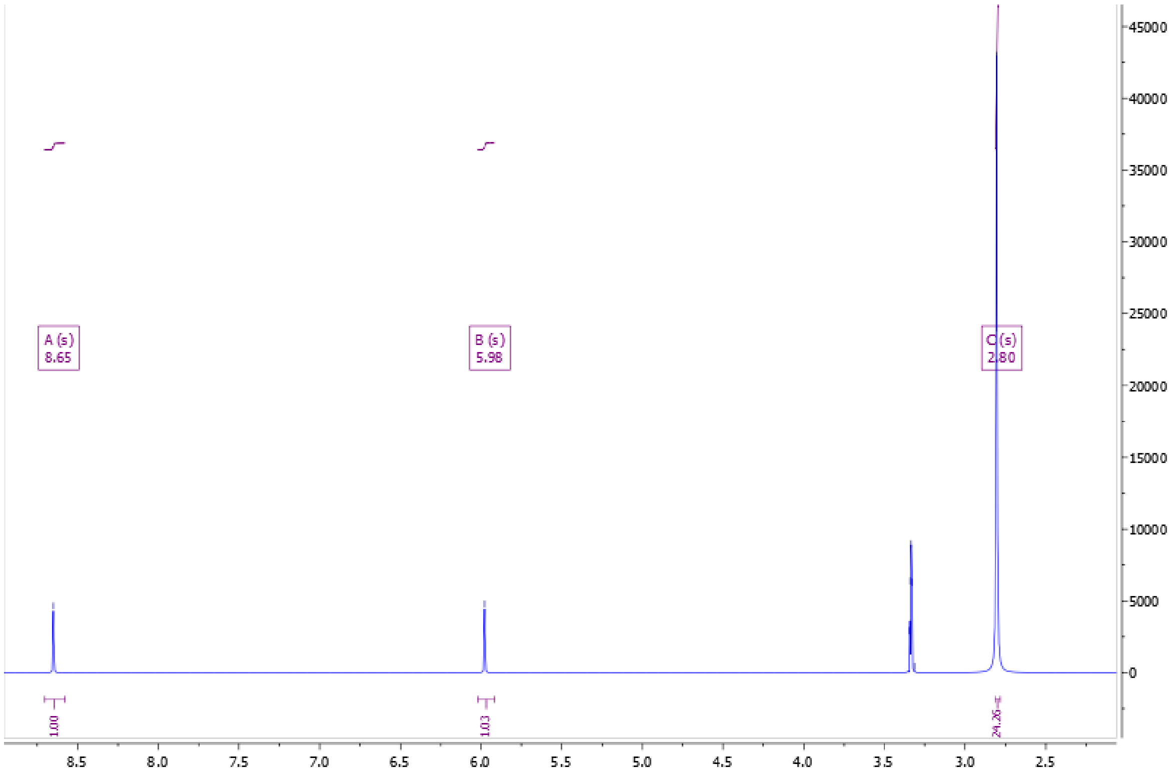

Figure S1 ^{1}H NMR spectrum of 4-bromomethyl-2,6-di-*tert*-butylphenol **2** (400 MHz, CH_3OD).

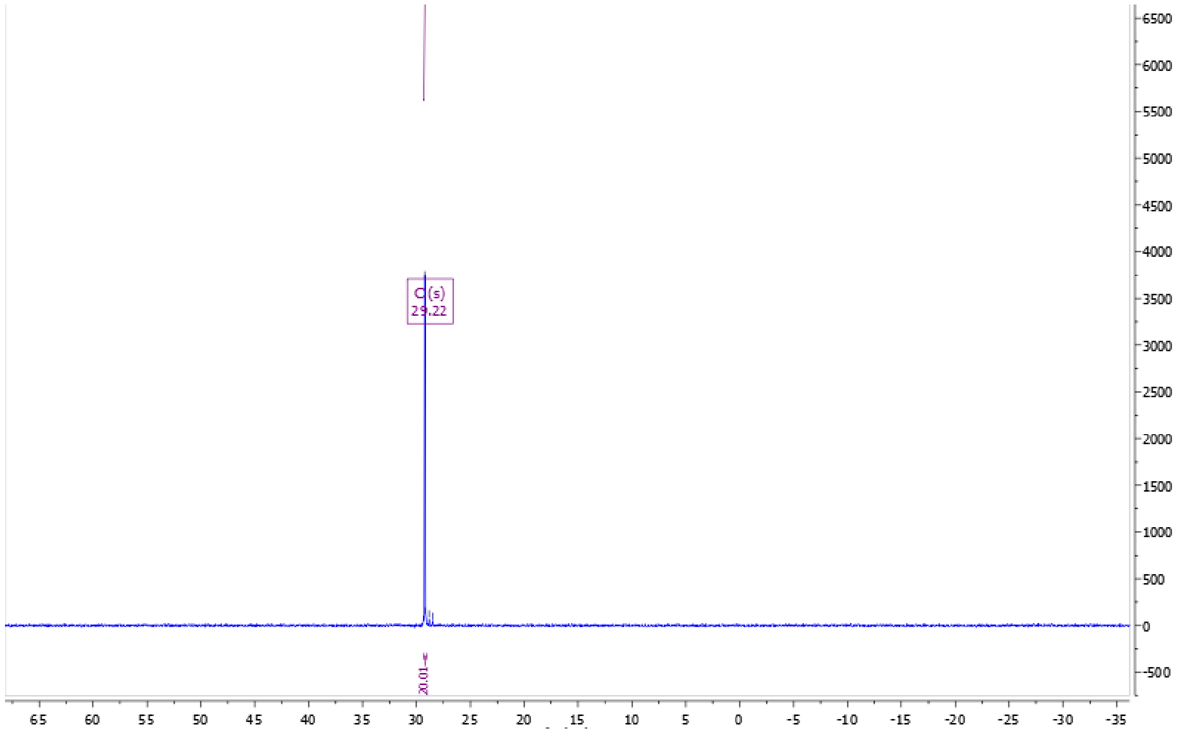

Figure S2 ^{31}P NMR spectrum of ethane-1,2-diylbis[(3,5-di-*tert*-butyl-4-hydroxybenzyl)-diphenylphosphonium]bromide **3a** (CH_3OD, 161.97 MHz).

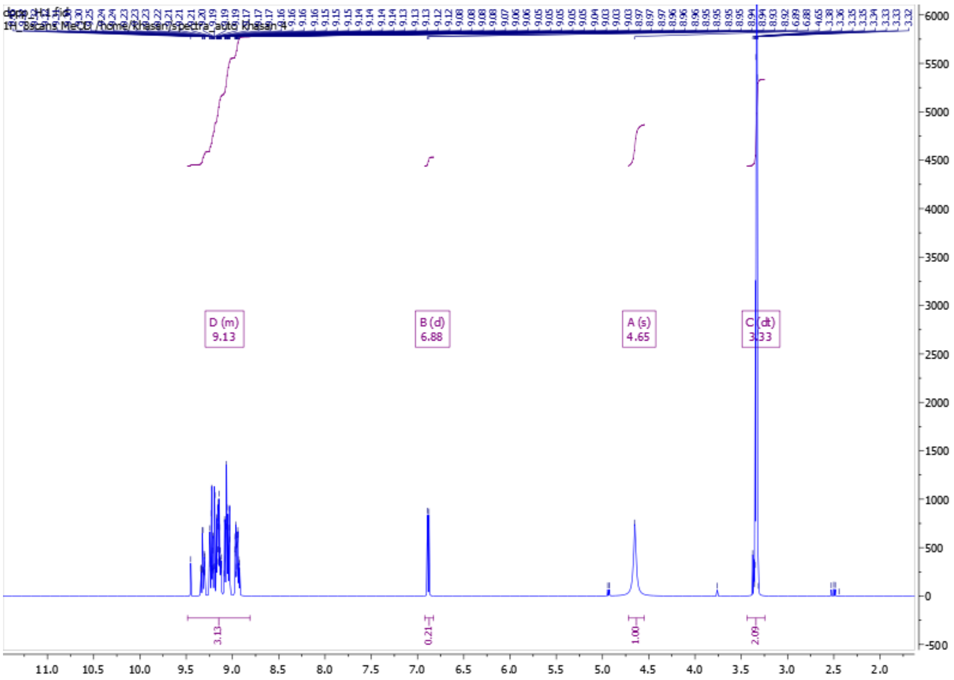

Figure S3 ^{1}H NMR spectrum of ethane-1,2-diylbis[(3,5-di-*tert*-butyl-4-hydroxybenzyl)-diphenylphosphonium]bromide **3a** (400 MHz, CH_3OD).

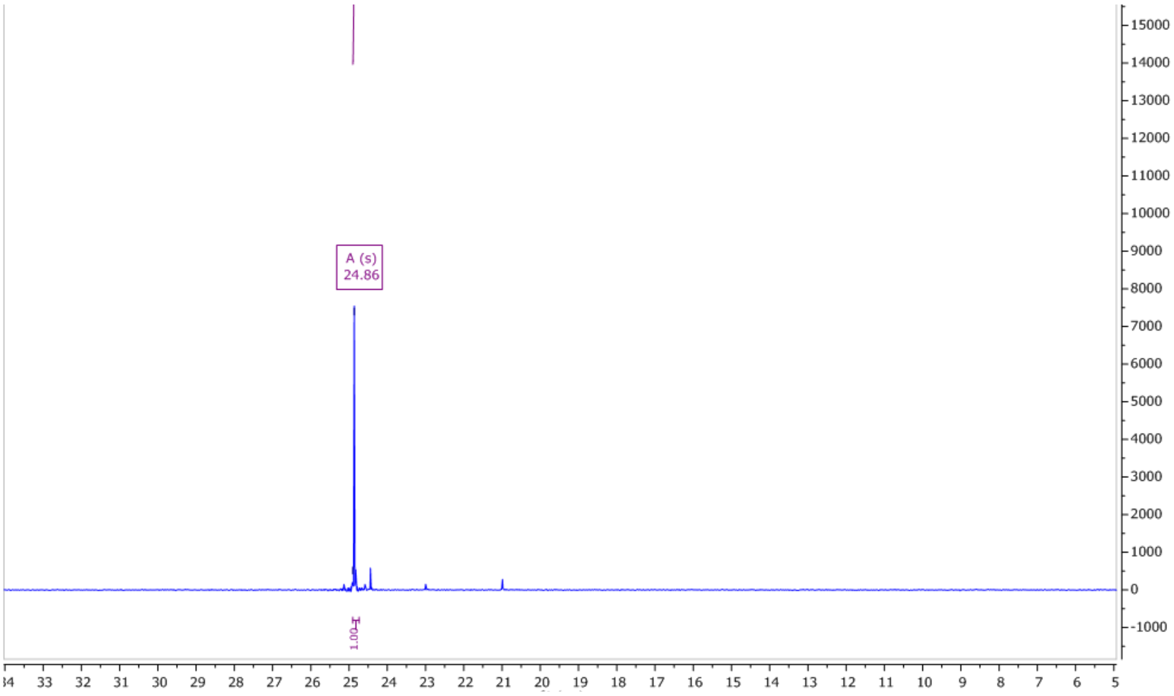

Figure S4 ^{31}P NMR spectrum of propane-1,3-diylbis[(3,5-di-*tert*-butyl-4-hydroxybenzyl)-diphenylphosphonium]bromide **3b** (CH_3OD, 161.97 MHz).

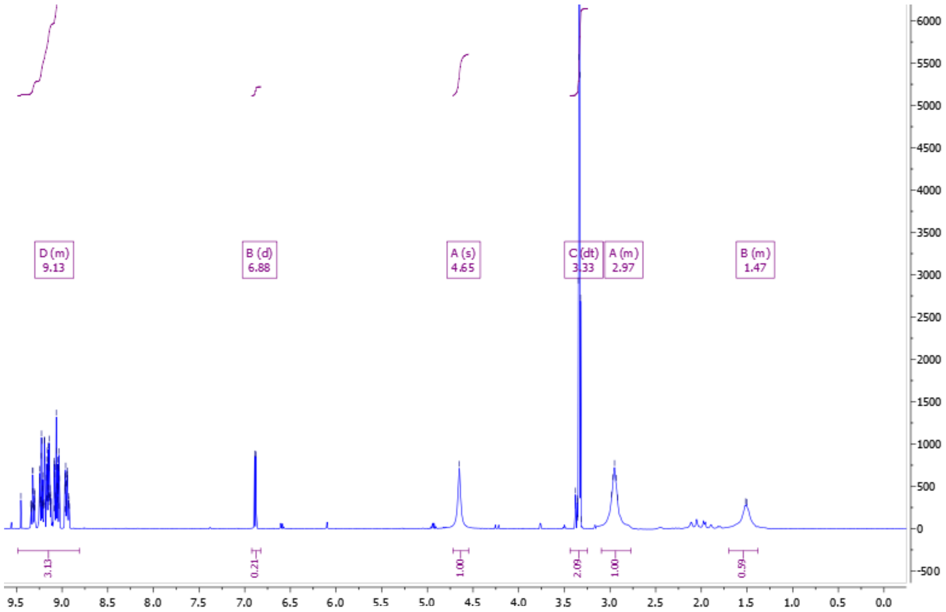

Figure S5 ^{1}H NMR spectrum of propane-1,3-diylbis[(3,5-di-*tert*-butyl-4-hydroxybenzyl)-diphenylphosphonium]bromide **3b** (400 MHz, CH_3OD).

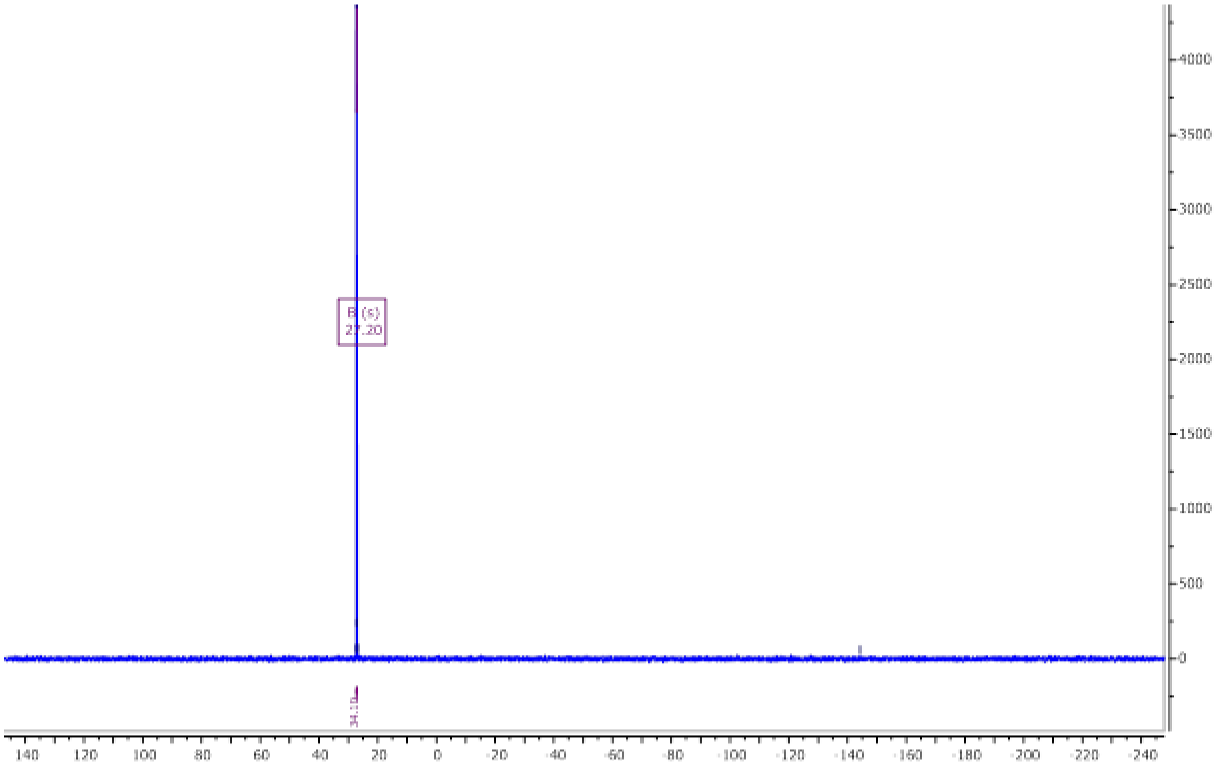

Figure S6 ^{31}P NMR spectrum of hexane-1,6-diylbis[(3,5-di-*tert*-butyl-4-hydroxybenzyl)-diphenylphosphonium]bromide **3c** (CH_3OD, 161.97 MHz).

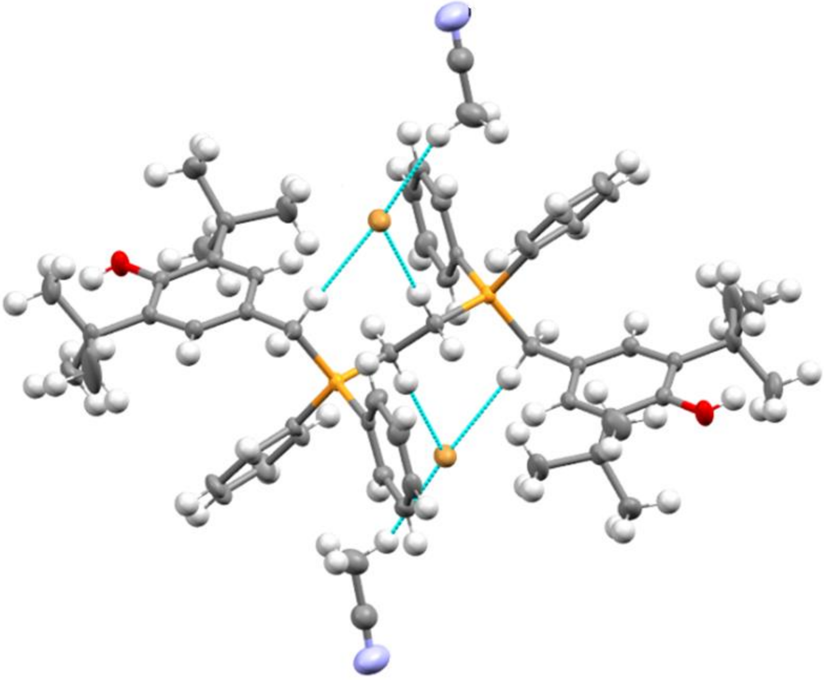

Figure S7 The structure of compound **3a** (solvate with MeCN) in the crystal. C-H…Br hydrogen bonds are shown by dashed lines.