

Unusual reactions of resorcinol and methylresorcinol with methylaminoacetaldehyde dimethyl acetal

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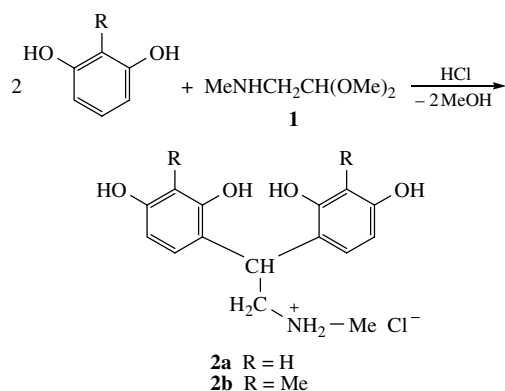
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The condensation of resorcinol or methylresorcinol with methylaminoacetaldehyde dimethyl acetal in an acid medium results in the formation of 2,2-bis[(2,4-dihydroxyaryl)ethyl]methylamine hydrochlorides.

The synthesis of calix[4]resorcinolarenes is performed by the condensation of resorcinol and its derivatives with aliphatic or aromatic aldehydes.^{1–3} Using phosphorylated acetals, calix[4]-resorcinolarenes with phosphinoylalkyl substituents were obtained.⁴ Their aminoalkyl analogues, which may be used (due to the participation of amino groups) in the synthesis of cavitands, container-like structures and nanotubes are of particular interest.^{5,6} We performed the condensation of resorcinol (or methylresorcinol) with methylaminoacetaldehyde dimethyl acetal **1** and unexpectedly obtained compounds **2a,b**. The structures of the compounds were found by physico-chemical methods[†] and X-ray diffraction analysis (for compound **2b**).[‡]

The monoclinic crystal of **2b** (space group *Cc*) contains one crystallographically independent anion–cation pair and a water molecule. The molecular structure of compound **2b** is shown in Figure 1. Two phenol rings of the molecule are almost orthogonal to each other (the dihedral angle between planes is 81.4°). In the crystal, different strong intermolecular hydrogen bonds (O–H...O, O–H...Cl and N–H...Cl) are formed. The analysis of the crystal packing demonstrated that chlorine anions and water molecules assemble molecules in hydrogen-bonded chains (channels) along the 0*z* crystallographic axis.

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[†] **2a**: 65% yield, mp > 300 °C. ¹H NMR (Bruker WM-250, 250 MHz, CD₃OD) δ: 2.74 (s, 3H, NMe), 3.64 (d, 2H, NCH₂, ³J 8.0 Hz), 4.89 (t, 1H, CH, ³J 7.9 Hz), 6.35 [d, 2H, C(5)H, ³J 8.2 Hz], 6.45 [s, 2H, C(3)H], 7.00 [d, 2H, C(6)H, ³J 8.2 Hz]. ¹³C NMR (101 MHz, CD₃OD) δ: 34.11 (CH), 37.19 (MeN), 53.60 (CH₂N), 103.82 [C(6)], 108.51 [C(5)], 118.45 [C(1)], 131.13 [C(3)], 156.22 [C(2)], 158.34 [C(4)]. Found (%): C, 57.42; H, 5.73; N, 4.71. Calc. for C₁₅H₁₈ClNO₄ (%): C, 57.79; H, 5.82; N, 4.49. MS, *m/z*: 553 (M⁺).

2b: 73% yield, mp > 300 °C. ¹H NMR (CD₃OD) δ: 2.16 (s, 6H, Me), 2.75 (s, 3H, NMe), 3.67 (d, 2H, NCH₂, ³J 7.9 Hz), 5.01 (t, 1H, CH, ³J 7.9 Hz), 6.44 [d, 2H, C(5)H, ³J 8.4 Hz], 6.89 [d, 2H, C(6)H, ³J 8.4 Hz]. ¹³C NMR (101 MHz, CD₃OD) δ: 8.99 [C(3)Me], 34.05 (CH), 36.75 (MeN), 53.72 (CH₂N), 108.35 [C(6)], 113.13 [C(5)], 119.82 [C(1)], 126.22 [C(3)], 154.43 [C(2)], 156.27 [C(4)]. MS, *m/z*: 595 (M⁺).

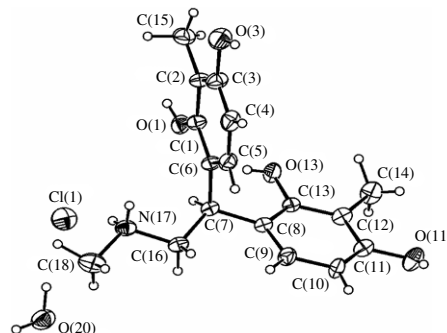


Figure 1 Molecular geometry of compound **2b** in a crystal. Main bond lengths (Å): C(7)–C(16) 1.520(4), C(7)–C(8) 1.525(4), C(6)–C(7) 1.529(4), N(17)–C(18) 1.485(5), N(17)–C(16) 1.495(4), O(1)–C(1) 1.366(4), O(3)–C(3) 1.376(4), O(11)–C(11) 1.379(3), O(13)–C(13) 1.360(3), C(12)–C(14) 1.509(5), C(2)–C(15) 1.495(5); valence angles (°): C(8)–C(7)–C(16) 112.2(2), C(6)–C(7)–C(16) 111.6(2), C(6)–C(7)–C(8) 110.0(2), C(16)–N(17)–C(18) 113.1(3), N(17)–C(16)–C(7) 110.5(2).

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[‡] X-Ray diffraction study of compound **2b**. Crystal of **2b**, C₁₇H₂₂NO₄⁺ H₂O, Cl[–], monoclinic, space group *Cc*. At 20 °C, *a* = 14.827(2), *b* = 11.751(4) and *c* = 10.581(3) Å, β = 104.25(1)°, *V* = 1787(1) Å³, *Z* = 4; *d*_{calc} = 1.33 g cm^{–3}, μ(Mo) = 0.24 mm^{–1}. The intensities of 2007 reflections were measured on an Enraf-Nonius CAD-4 diffractometer at 20 °C; of these, 1446 reflections with *I* ≥ 3σ were observed; 25 centered reflections gave the refined unit cell parameters. The structure was solved in the uniquely assignable space group *Cc* by direct methods using the SIR⁵ program and difference Fourier syntheses. The final divergence factors are *R* = 0.032, *R*_w = 0.039 based on 1446 reflections with *F*² ≥ 3σ. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were refined isotropically. All calculations were carried out on a DEC Alpha Station 200 computer with the MolEN⁶ system.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 244191. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2005.

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