

# The role of the gauche effect and local 1,3-dipole-dipole interactions in stabilizing an unusual conformation of tartarodinitriles

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## SUPPLEMENTARY MATERIAL

### Synthesis of tartarodinitriles

**(*R,S*)-1,2-Dihydroxy-1,2-dicyanoethane (1a).** This product was obtained from glyoxal by a reported procedure (Grundmann, C. & Fulton, M.B. (1964) *Chem. Ber.*, **97**, 566-574). Yield 18%, m. p. 135-136 °C, <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>SO) δ 4.79 (s, 2H), 7.36 (s, 2OH), <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>SO) δ 62.8 (dd, *J*=156, 2.5 Hz, CH) 118.3 (s, CN), EI-MS 113 (*M*+1), 85, 67, 57, IR (KBr) 3394, 2267, 1084.

**(*R,S*)-1,2-Diacetoxy-1,2-dicyanoethane (1b).** Dinitrile **1a** (0.222 g, 1.98 mmol) was stirred at room temperature with acetic anhydride (1 ml) and pyridine (0.2 ml) overnight. The solution was poured onto ice, the precipitate was filtered off and the product was purified by column chromatography on silicagel (solvent CH<sub>2</sub>Cl<sub>2</sub>). Yield 0.247 g (63%), m. p. 77-79 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.3 (s, 6H), 5.75 (s, 2H), <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 20 (quartet, *J*= 131.6 Hz, CH<sub>3</sub>), 59.6 (dd, *J*=159, 4.5 Hz, CH), 112.1 (s, CN), 167.9 (s, C=O).

**(*R,S*)-1,2-Dibenzoyloxy-1,2-dicyanoethane (1c).** To a solution of dinitrile **1a** (0.23 g, 2.05 mmol) in  $\text{CHCl}_3$  (3 ml) at 0 °C was added pyridine (0.75 ml) and benzoyl chloride (0.5 ml, 0.6 g, 4.3 mmol). The mixture was stirred overnight and then extracted with 2M sulfuric acid, followed by water, saturated solution of sodium bicarbonate and water. The product was further purified by column chromatography on silicagel (eluent  $\text{CH}_2\text{Cl}_2$ -hexane 1:1 to 8:2). Yield 0.446 g (68%), m. p. 137-138 °C,  $^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{CO}$ )  $\delta$  6.6 (s, 2H), 7.58 (dd,  $J=7.42$ , 1.65 Hz, 4H), 7.74-7.79 (t,  $J=7.42$  Hz, 2H), 8.1 (d,  $J=1.37$  Hz, 4H),  $^{13}\text{C}$  NMR ( $(\text{CD}_3)_2\text{SO}$ )  $\delta$  62.2 (dd,  $J=162$ , 3.9 Hz, CH), 113.8 (s, CN), 128, 129, 130, 135 (Ph), 205.8 (s, C=O).

**(*S,S*)-1,2-Dihydroxy-1,2-dicyanoethane (2a).** A suspension of cyanuric chloride (0.380 g, 2 mmol) in TBME (10 ml) was added to a suspension of (*R,R*)-tartaric acid diamide (0.295 g, 2 mmol) in anhydrous DMF (3 ml). The suspension was stirred under argon at room temperature overnight. The reaction mixture was quenched with water (10 ml) and extracted with TBME, followed by water and purified by column chromatography on silicagel (solvent  $\text{CH}_2\text{Cl}_2$ -MeOH 98:2 to 9:1). The product is not stable at room temperature. Yield 0.075 g (34%),  $[\alpha]_{\text{D}}^{20} = +48.2$  ( $c=1.7$ , MeOH),  $^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{SO}$ )  $\delta$  4.8 (s, 2H), 7.3 (s, 2OH),  $^{13}\text{C}$  NMR ( $(\text{CD}_3)_2\text{SO}$ )  $\delta$  62.9 (d,  $J=156$ , 4.1 Hz, CH), 118.4 (s, CN).