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Hydrogen-bond network in isomeric phenylenedipropynoic acids and their DABCO salts. Water mediated helical hydrogen bond motifs

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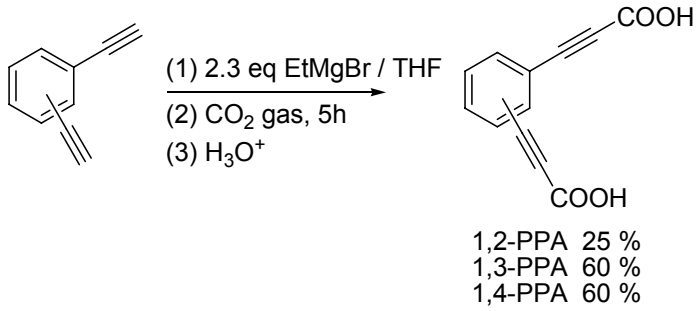
Synthesis of isomeric phenylenedipropynoic acids:

The acids were synthesized from the corresponding diethynylbenzenes as shown in Scheme 1 and characterized by spectroscopic data.



Scheme 1. Synthesis of isomeric phenylenedipropynoic acids

General procedure: Mg (0.46 g, 19.0 g atom) and THF (20 ml) were taken in a flask maintained at nitrogen atmosphere. Ethyl bromide (2.08 g, 19.0 mmol) was added and then mixture was allowed to stir at room temperature for 1.5 h to yield ethyl magnesium bromide. Diethynylbenzene (1.0 g, 7.93 mmol) was added to the reaction and stirring was continued for 15 min. Dry CO_2 gas was bubbled through the reaction mixture for 5 h at room temperature upon which a pale yellow precipitate was obtained. The reaction mixture was acidified by the addition of 5% HCl until the aqueous layer was acidic to litmus paper. THF layer was separated, dried over anhydrous Na_2SO_4 and THF was removed under reduced pressure. The dicarboxylic acids were obtained as pale yellow solid. Recrystallization from methanol afforded colorless crystals.

1,2-PPA: yield 70%, mp 195-197 ^oC (lit. 210 ^oC)[1] , IR (KBr) 2931 (broad), 2209, 1681 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.74 (m, 2H), 7.60 (m, 2H), 3.90 (broad, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.0, 133.5, 131.0, 122.4, 85.5, 81.3.

1,3-PPA: yield 60%, mp 209 ^oC (lit. 209 ^oC)[2], IR (KBr) 2923 (broad), 2958, 2220, 1715, 1659 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.64 (m, 1H), 7.55 (dd, 2H, J = 1.5, 8.2 Hz), 7.34, (t, 1H, J = 8.2 Hz), 3.40 (broad, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.9, 135.7, 134.5, 129.8, 120.0, 82.56, 82.47.

1,4-PPA: yield 60%, mp >250 ^oC (lit 266 ^oC dec)[3], IR (KBr) 2858 (broad), 2549, 2204, 1686, 1606 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.75 (s, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.0, 132.9,

121.1, 83.9, 82.2.

Synthesis of DABCO salts of 1,2- and 1,4-phenylenedipropynoic acids:

Mixing equimolar solutions of 1,2-PPA (50 mg, 0.23 mmol) and DABCO (26 mg, 0.23 mmol) in methanol (2 ml) gave colorless crystals of the salt after standing at room temperature for 2 days. The crystals thus obtained were suitable for single crystal X-ray crystallographic analysis. In the case of 1,4-PPA mixing of equimolar solutions of 1,4-PPA (50 mg, 0.23 mmol) and DABCO (26 mg, 0.23 mmol) in methanol (2 ml) gave a yellow precipitate. It was dissolved by addition of water (1 ml) and allowed to stand at room temperature for 15 days to yield single crystals suitable for X-ray analysis.

[1,2-PPA – DABCO]: IR (KBr) 2204, 1601 cm^{-1}, ^{1}H NMR (400 MHz, D_2O) 7.65 (broad, s, 2H), 7.50 (broad, s, 2H), 3.24 (12H, s); ^{13}C (100 MHz, D_2O) 160.7, 129.8, 123.5, 88.2, 78.6, 43.9.

[1,4-PPA – DABCO]: IR (KBr) 2203, 1620 cm^{-1}, ^{1}H NMR (400 MHz, D_2O) δ 7.76 (s, 4H), 4.70 (broad), 3.25 (s, 12H); ^{13}C NMR (100 MHz, D_2O) δ 135.3, 124.7, 89.0, 85.0, 83.0, 46.8.

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