
Azobenzene-based difunctional halogen-bond donor towards the engineering of photoresponsive co-crystals

Marco Saccone,^a Giancarlo Terraneo,^{a*} Tullio Pilati,^a Gabriella Cavallo,^{a*}

Arri Priimagi,^{b*} Pierangelo Metrangolo^a and Giuseppe Resnati^a

Supplementary Material

Synthesis of (*E*)-bis(2,3,5,6-tetrafluorophenyl)diazene (**1**)

2,3,5,6-tetrafluoroaniline (4 mmol) was dissolved in 10 mL of an ethanol-water (1:1) mixture. A solution of potassium hydroxide (10 mmol) in 10 mL of an 1:1 ethanol-water mixture was added at room temperature, followed by the slow addition of solid potassium ferricyanide (20 mmol). The mixture was refluxed overnight, filtered to remove the excess of oxidant and extracted with chloroform. The organic phase was washed twice with water, dried over anhydrous sodium sulfate and evaporated under reduced pressure. The resulting solid was *chromatographed* over silica gel using hexane/ethyl acetate (9/1) as the eluent, to obtain 0.22 mmol (11%) of (**1**) as orange powder. Melting point: 124-126°C. FT-IR ν_{\max} = 3095, 1709, 1607, 1499, 1409, 1378, 1278, 1257, 1178, 1130, 1068, 1036, 951, 855, 745, 716, 700 cm^{-1} . ^1H NMR (400 MHz, ppm, CDCl_3): 7.2-7.1 (m 2H). ^{13}C NMR (100 MHz, ppm, CDCl_3): 146.3 (d, $^1J_{\text{CF}} = 251$ Hz, 4C), 140.2 (d, $^1J_{\text{CF}} = 264$ Hz, 4C), 132.9-132.7 (m, 2C), 107.8 (t, $J = 16$ Hz, 2C). MS/ESI m/z 326.1 found 327.1 ($\text{M} + \text{H}^+$).

Synthesis of (*E*)-bis(4-iodo-2,3,5,6-tetrafluorophenyl)diazene (**2**)

4-iodo-2,3,5,6-tetrafluoroaniline (Meazza *et al.*, 2013) (2.5 mmol) was dissolved in 10 mL of an ethanol-water (1:1) mixture. A solution of potassium hydroxide (5 mmol) in 10 mL of an 1:1 ethanol-water mixture was added at room temperature, followed by the slow addition of solid potassium ferricyanide (10 mmol). The mixture was refluxed overnight, filtered to remove the excess of oxidant and extracted with chloroform. The organic phase was washed twice with water, dried over anhydrous sodium sulfate and evaporated under reduced pressure. The resulting solid was *chromatographed* over silica gel using hexane/ethyl acetate (95/5) as the eluent, to obtain 0.06 mmol (5%) of (**2**) as orange powder. Melting point: 203-207 °C (dec.). FT-IR ν_{\max} = 1621, 1583, 1468, 1405, 1380, 1279, 1135, 1034, 973, 802, 762, 634 cm^{-1} . ^{13}C NMR (100 MHz, ppm, CDCl_3) 148.4 (d, $^1J_{\text{CF}} = 246$ Hz, 4C), 140.3 (d, $^1J_{\text{CF}} = 265$ Hz, 4C), 133.1 (t, $J = 8.2$ Hz, 2C), 76.9 (t, $J = 28.4$ Hz, 2C). ^{19}F NMR (471 MHz, ppm, CDCl_3) -120.2 (m, 4F), -148.6 (m, 4F). MS/ESI m/z 578, found 579 ($\text{M} + \text{H}^+$).

Characterisation of (2):DMSO

Melting point: 210-212°C (dec). FT-IR ν_{\max} = 3000, 2921, 2850, 1621, 1581, 1466, 1420, 1375, 1276, 1034, 979, 913, 792, 793, 726, 534 cm^{-1} .

Characterisation of (2):BiPy

Melting point: 236-240 (dec.). FT-IR ν_{\max} = 3038, 1619, 1592, 1536, 1464, 1406, 1463, 1368, 1273, 1214, 1063, 993, 974, 807, 794, 760, 732 cm^{-1} .

Characterisation of (2):(StOMe)₂

Melting point: 210-214 (dec.). FT-IR ν_{\max} = 3026, 1620, 1590, 1576, 1510, 1463, 1420, 1405, 1361, 1308, 1282, 1175, 1146, 1066, 1045, 1024, 964, 933, 886, 799, 762, 635 cm^{-1} .