Electronic Supplementary Material for CrystEngComm

Supporting Information

Attempted assembly of discrete coordination complexes into 1-D chains using halogen bonding or halogen•••halogen interactions

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Experimental

X-ray crystallography

2 The orthorhombic space group Pmn2(1) was chosen based on Laué symmetry and systematic absences. The molecule sits on a general position. A minor species (~40% occupancy) corresponding to the opposite sense of alkene placement was observed in the difference Fourier map. Geometries of the two species were restrained using the SAME command. The geometry of the substituted phenyl ring was restrained using selected DFIX commands on bond distances and 1,3-distances. The central alkene converged to an unrealistically short bond length and was restrained using a DFIX command. Attempts to refine the atoms anisotropically were unsuccessful: in all cases thermal parameters rapidly become non-positive definite.

3 The molecule sits on an inversion center. All non-hydrogen atoms were ordered and were refined using anisotropic thermal parameters.

4 The molecule sits on an inversion center. One of the two unique $-CF_3$ groups (on C31) was disordered and was modelled with three species. Occupancies for the three species were set with free variables, and the sum of these three variables was restrained to 100% by means of a SUMP command. Anisotropic thermal parameters for triplets of closely located fluorine atoms were constrained using the EADP command.

5 The molecule sits on an inversion center. One of the two unique $-CF_3$ groups (on C35) was disordered. Occupancy of the major & minor species was controlled with a free variable. Geometries of all three $-CF_3$ moieties (the ordered C31 group and the two C35 species) were restrained using the SAME command. The minor C35 species (occupancy ~13%) was given isotropic thermal parameters.

(a) SMART v5.060, © 1997 - 1999, Bruker Analytical X-ray Systems, Madison, WI.
(b) SAINT v6.02, © 1997 - 1999, Bruker Analytical X-ray Systems, Madison, WI.
(c) SHELXTL v5.10, © 1997, , Bruker Analytical X-ray Systems, Madison, WI.

Synthesis

Synthesis of 4'-bromo-2',3',5',6'-tetrafluorostilbazole, **1**[1]

Under a dinitrogen atmosphere, 4-bromo-2,3,5,6-tetrafluorobenzaldehyde (1.3 g, 5.0 mmol) and 4-picoline (0.625 mL, 6.5 mmol) were dissolved in acetic anhydride (8 mL), stirred and heated to 100 °C for 3 hours. Upon cooling, the reaction was poured into ice-water (50 mL) and basified by addition of a 20 % NaOH solution. The mixture was extracted with chloroform (3 x 100 mL), dried over $MgSO_4$ and reduced to dryness on a rotary evaporator, yielding a dark brown solid. The residue was chromatographed on

silica with a hexanes/ethyl acetate mixture (3:1) as the eluant. The product was isolated as a light yellow/white solid which was then recrystallized from a hexanes/chloroform mixture yielding off-white crystals (400 mg, 24 %). M.p. ºC; ^{1}H NMR (δ_H; 200 MHz, $CDCl_3$): 8.65 (d, J = 5.6 Hz, 2H), 7.41 (m, 3H), 7.18 (s, 1H); ^{13}C NMR (δ_C; 200 MHz, $CDCl_3$):; IR (KBr): cm^{-1}, MALDI-TOF / TOF-MS 334.2 and 332.2 (M+, Br isotopes)

Unsuccessful supramolecular synthesis

Synthesis of 4'-bromo-2',3',5',6'-tetrafluorostilbazole:copper(II) 1,1,1,5,5,5-hexafluoro-2,4-pentanedione:tetramethylpyrazine, **6**

4'-bromo-2',3',5',6'-tetrafluorostilbazole **1** (10 mg, 0.030 mmol), copper(II) 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (7 mg, 0.015 mmol), and tetramethylpyrazine (12 mg, 0.09) were added to a screw cap vial along with chloroform (2 mL). The mixture was heated gently until a clear homogeneous solution resulted. Green prism- shaped crystals formed after 1 day. Dec. 212 °C; IR (KBr pellet): υ 1651, 1614, 1482, 1265, 1203, 1132, 972, 787, 670, 589 cm^{-1}.

Synthesis of 4'-iodo-2',3',5',6'-tetrafluorostilbazole:copper(II) 1,1,1,5,5,5-hexafluoro-2,4-pentanedione:tetramethylpyrazine, **7**

4'-iodo-2',3',5',6'-tetrafluorostilbazole **2** (10 mg, 0.026 mmol), copper(II) 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (7 mg, 0.015 mmol), and tetramethylpyrazine (12 mg, 0.09 mmol) were added to a screw cap vial along with chloroform (2 mL). The mixture was heated gently until a clear homogeneous solution resulted. Green prism- shaped crystals resulted after 1 day. m.p. 220-222 °C; IR (KBr pellet): υ 1655, 1614, 1481, 1260, 1200, 1131, 970, 786, 672, 589 cm^{-1}.

Synthesis of 4'-iodo-2',3',5',6'-tetrafluorostilbazole:copper(II) 1,1,1,5,5,5-hexafluoro-2,4-pentanedione:4,4'-bipyridine, **8**

4'-iodo-2',3',5',6'-tetrafluorostilbazole **2** (10 mg, 0.026 mmol), copper(II) 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (7 mg, 0.015 mmol), and 4,4'-bipyridine (13 mg, 0.08 mmol) were added to a screw cap vial along with chloroform (2 mL). The mixture was heated gently until a clear homogeneous solution resulted. Green prism- shaped crystals resulted after 1 day. m.p. 220-222 °C; IR (KBr pellet): υ 1652, 1615, 1479, 1264, 1202, 1131, 970, 786, 674, 589 cm^{-1}.

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[1] A. C. B. Lucassen, M. Vartanian, G. Leitus and M. E. van der Boom, *Cryst. Growth Des*., 2005, **5**, 1671.