

Supporting Information

Design, Synthesis and Crystal structure of a multiple Donor-Acceptor Halogen Bonded Stilbazole: Assembly of Unimolecular Interconnected Helices

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Experimental section

THF was distilled from sodium benzophenone ketyl under N₂. Reaction flasks were washed with deionized water followed by acetone, and then oven-dried for at least 24 h at 130°C prior to use. ¹H and ¹³C{¹H}-NMR spectra were recorded at 500.1 and 125 MHz, respectively, on a Bruker Avance 500 NMR spectrometer. ¹H, ¹³C{¹H}, ¹⁹F{¹H} and ³¹P{¹H} spectra were recorded at 400.19, 100.6, 376.5 and 161.9 MHz, respectively, on a Bruker AMX 400 NMR spectrometer and at 250.17, 62.9, 235.0 and 101.3 MHz, respectively, on a Bruker DPX 250 NMR spectrometer. All chemical shifts (δ) are reported in ppm and coupling constants (J) are in Hz. The ¹H and ¹³C NMR chemical shifts are relative to tetramethylsilane; the resonance of the residual protons of chloroform were used as an internal standard for ¹H (δ 7.25 ppm) and all-d solvent peaks for ¹³C (δ 77.0 ppm). ¹⁹F NMR chemical shifts are relative to hexafluorobenzene in CDCl₃ at δ = -163.0 ppm (external reference). All room temperature measurements were carried out at 298 K. Mass spectrometry was carried out using a Micromass Platform LCZ 4000 mass spectrometer. Elemental Analyses were performed by H. Kolbe, Mikroanalytisches laboratorium, Mülheim an der Ruhr, Germany. 2,4,6-Trifluorobenzoic acid (**4**) was prepared from 1,3,5-trifluorobenzene (**3**) by lithiation with ⁿBuLi at -78°C followed by reaction with gaseous carbon dioxide according to a published procedure.¹

Preparation of 3,5-Diiodo-2,4,6-trifluorobenzoic acid (5). Periodic acid (6.80 g, 30 mmol) was added in portionwise sulfuric acid (60 mL). The mixture was cooled on an ice bath and freshly powdered KI (14.8 g, 90 mmol) was added over 15 min. Subsequently, 2,4,6-trifluorobenzoic acid (3.45 g, 20 mmol) was added over a period of 10 min. After the addition was completed, the ice bath was removed and the mixture was stirred at room temperature for 1 h. The mixture was poured on ice and was extracted with diethyl ether (4 $\times$ 75 mL). The combined layers were washed with 5% aqueous hydrochloric acid, followed

by washing with 5% Na₂S₂O₃ until all iodine was removed. After drying (Na₂SO₄) and evaporation of the solvent, the product **5** was obtained as a white solid (8.56 g, 90 %). Analyses correspond with literature values.²

Preparation of 3,5-Diiodo-2,4,6-trifluorobenzylalcohol (6).³ 3,5-Diiodo-2,4,6-trifluorobenzoic acid (4.85 g, 11.4 mmol) was dissolved in dry THF (25 mL) under Ar. The mixture was cooled in an ice bath and BH₃·THF (22 mL, 1 M in THF) was added by syringe. After addition, the mixture was allowed to attain room temperature and was then heated to a gentle reflux for 16 h. It was then cooled in an ice bath and excess borane was destroyed by careful addition of ice water (10 mL). The THF was removed on a rota-evaporator, 50 mL water was added and the mixture was extracted with CH₂Cl₂ (3 × 75 mL). The combined layers were washed once with water and dried (Na₂SO₄). Filtration and evaporation of the solvent gave 3.54 g crude product. Purification by column chromatography over silica gel (hexane:ethyl acetate = 6:1 to 4:1) yielded 2.90 g product (62 %). ¹H NMR (CDCl₃): 2.04 (br t, 1H, *J* = 6.0 Hz), 4.78 (d, 2H, *J* = 6.0 Hz). ¹⁹F{¹H} NMR: -69.6 (t, 1F, *J* = 3.8 Hz), -94.39 (d, 2F, *J* = 3.8 Hz). ¹³C{¹H} NMR: 53.5 (t, *J*_{CF} = 3 Hz, CH₂), 65.0 (t of d, *J*_{FC} = 34 Hz, ³*J*_{CF} = 2.8 Hz), 113.2 (t of d, *J*_{CF} = 23 Hz, ³*J*_{CF} = 4.4 Hz), 160.2 (t, *J* = 8.7 Hz), 160.6 (dd, *J* = 10.4 Hz, 7.55 Hz), 162.1 (t, *J* = 8.7 Hz), 162.6 (dd, *J* = 10.4 Hz, 7.55 Hz). Mass: 413. Elem.Anal.: Calculated for C₇H₃OF₃I₂ %C 20.31, %H 0.73. Found %C 20.48, %H 0.72.

Preparation of 3,5-diiodo-2,4,6-trifluorobenzaldehyde (7).⁴ A solution of 3,5-diiodo-2,4,6-trifluorobenzyl alcohol (1.03 g, 2.5 mmol) in CH₂Cl₂ (10 mL) was cooled in an ice bath. Trichloroisocyanuric acid (0.609 g, 2.62 mmol, 1.05 eq.) was added followed by TEMPO (4 mg, 0.025 mmol, 1 mol%). The mixture was stirred at 0°C and the reaction was monitored by TLC (hexane:ethyl acetate = 4:1). The reaction was complete within 15 min.

Subsequently, more CH₂Cl₂ was added and the mixture was filtered through celite (washed with CH₂Cl₂). The CH₂Cl₂ solution was washed with 5% Na₂CO₃ solution, water (3 × 50 mL) and brine. After drying (Na₂SO₄) and evaporation of CH₂Cl₂, 970 mg (quantitative yield) of compound **7** was obtained. ¹H NMR (CDCl₃): 10.16 (s, 1H). ¹⁹F{¹H} NMR (CDCl₃): -58.1 (t, 1F, *J* = 8.0 Hz), -92.56 (d, 2F, 8.0 Hz). ¹³C{¹H} NMR (CDCl₃): 66.7 (AB of doublets, C-I, *J*_{AB} = 32 Hz, *J* = 3.8 Hz), 111.3 (AB of doublets, C-CH=O, *J*_{AB} = 13.8, *J* = 3.8 Hz), 162.6 + 164.6 (doublet of triplets, *ortho*-F-C, *J* = 251 Hz, *J* = 8.0 Hz), 163.9 + 165.9 (doublet of triplets, *para*-F-C, *J* = 251 Hz, *J* = 8.0 Hz), 182.0 (d, *J* = 2.5 Hz, C=O). Mass: 410 (M-H), 285 (M-I). Elem.Anal.: Calculated for C₇HOF₃I₂ %C 20.41, %H 0.24. Found %C 20.49, %H 0.22.

Preparation of 3,5-Diiodo-2,4,6-trifluorostilbazole (2).⁵ A solution of 3,5-diiodo-2,4,6-trifluorobenzaldehyde (0.86 g, 2.1 mmol) and *γ*-picoline (0.21 mL, 2.2 mmol) in acetic anhydride (5 mL) was stirred at room temperature for 18 h under Ar. The reaction mixture was filtered on a sintered glass filter and the solid was washed thoroughly with water. It was subsequently dissolved in CH₂Cl₂ and the solution was washed with an aqueous solution of 5 % Na₂CO₃. The organic layer was dried (Na₂SO₄) and the solvent was evaporated. The obtained product was triturated with warm ethyl acetate (5 mL) yielding and off-white solid (410 mg, 40%). An analytical pure sample could be obtained by recrystallization from ethyl acetate/diisopropyl ether as colorless needles. ¹H NMR (CDCl₃): 7.23 (AB, 2H, *J*_{AB} = 4.5 Hz), 7.35 (m, 2H), 8.61 (m, 2H). ¹⁹F{¹H} NMR: -89.6 (d, 2F, *J* = 4.0 Hz), -69.5 (t, 1F, *J* = 4.0 Hz). ¹³C{¹H} NMR (CDCl₃): 65.7 (t of d, *J*_{CF} = 33.6 Hz, ³*J*_{CF} = 3.0 Hz, C-I), 111.0 (t of d, FC-C-CH=C, *J* = 18.3 Hz, ³*J*_{CF} = 4.8 Hz), 118.1 (d, *J* = 2.1 Hz, FC-C-CH=CH-), 121.0 (s, CH-CH-N), 133.6 (t of d, *J* = 8.6 Hz, ³*J* = 2.4 Hz, FC-C-CH=C), 144.0 (s, C-CH-CH-N), 150.3 (s, CH-N), 159.6 + 161.5 (d of triplets, *J* = 248 Hz, ³*J* = 8.7 Hz), 159.8 + 161.8 (d of dd, *J* = 248 Hz, *J* = 9.4 Hz, *J* = 7.6 Hz) Mass:

488.3 (M+1); 510.34 (M+Na). El.Anal.: Calculated for $C_{13}H_6F_3I_2N$: %C 32.06; %H 1.24; Found %C 32.26; %H 1.28.

X-ray Crystal Structure Analysis of Compound 2. Crystal data: $C_{13}H_6NF_3I_2$, colorless, needles, $0.5 \times 0.05 \times 0.05$ mm³, Orthorhombic, P2(1)2(1)2(1) (no. 19) $a = 4.229(1)$ Å, $b = 14.112(3)$ Å, $c = 23.312(5)$ Å, from 20 degrees of data, $T = 120(2)$ K, $V = 1391.3(5)$ Å³, $Z = 4$, $F_w = 486.99$, $D_c = 2.325$ Mg.m⁻³, $\mu = 4.539$ mm⁻¹. Data collection and processing: Nonius KappaCCD diffractometer, MoK α ($\lambda = 0.71073$ Å), graphite monochromator, $0 \leq h \leq 5$, $0 \leq k \leq 18$, $0 \leq l \leq 30$, frame scan width = 1.0°, scan speed 1.0° per 60 sec, typical peak mosaicity 0.31°, 6936 reflections collected, 3769 independent reflections ($R_{\text{int}} = 0.034$). The data were processed with Denzo-Scalepack. Solution and refinement: Structure solved by Patterson method with SHELXS-97. Full matrix least-squares refinement based on F^2 with SHELXL-97 173 parameters with 0 restraints, final $R_1 = 0.0294$ (based on F^2) for data with $I > 2\sigma(I)$ and, $R_1 = 0.0382$ on 1897 reflections, goodness-of-fit on $F^2 = 1.077$, largest electron density peak = 0.877 e.Å⁻³. Structural data for compound **2** has been deposited in the Cambridge Crystallographic Data Centre under CCDC 637114, and can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

Table S1. X-ray diffraction data for compound **2**

Formula	C ₁₃ H ₆ NF ₃ I ₂
Molecular Mass	486.99
Crystal color	white
Crystal dimensions	0.50 × 0.05 × 0.05 mm
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
a [Å]	4.2290(8)
b [Å]	14.112(3)
c [Å]	23.312(5)
α [°]	90
β [°]	90
γ [°]	90
Z	4
V [Å ³]	1391.3(5)
ρ _{calc} [Mg m ⁻³]	2.325
No. unique data	1897
R ₁	0.0294
wR ₂	0.0588
Goodness of fit (F ²)	1.077

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