One-dimensional organization of free radicals via halogen bonding

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1. Synthesis

Synthesis of diiodooctafluorobiphenyl (I₂F₈bph). Diiodooctafluorobiphenyl was synthesised using a method adapted from one used to synthesize monoiodoperfluoroarenes.^{S1} 2,3,5,6,2',3',5',6'-octafluorobiphenyl (152 mg, 0.52 mmol) was dissolved in 4 mL of tetrahydrofuran (dried by storing it over 3Å molecular sieves), under nitrogen. The solution was cooled in an acetone/dry ice bath and a solution of *n*-butylithium in hexane (1.6 M, 0.78 mL, 1.25 mmol) was slowly added over 15 min. After 10 min., I₂ was added (326 mg, 1.28 mmol) and after 30 min the cold bath was removed and solution left to warm to room temperature. The reaction mixture was then treated with 5 mL of water and 10 mL of dichloromethane and transferred to a separating funnel. The aqueous phase was extracted four times with dichloromethane (50 mL overall). The organic phase was then treated with 5 mL of a concentrated solution of sodium thiosulphate, washed twice with 15 mL of water and dried on sodium sulphate. The solution was then evaporated to dryness at the rotary evaporator, the resulting off-white solid was collected and weighed, resulting in 196 mg of product (0.356 mmol, 69.9% yield). ¹⁹F NMR (CD₃OD): -118.4 ppm, m; -135.9 ppm, m. ESI-MS (MeOH, negative ions), m/Z: 580.8 ([M·MeO]⁻), 422.9 (M⁻-I).

2. Characterization

Structural characterization. Single crystals of compounds 1 and 2 were mounted on glass fibres using a viscous hydrocarbon oil to coat the crystal and then transferred directly to the cold nitrogen stream for data collection. X-ray data were collected at 120 K on a Supernova diffractometer equipped with a graphite-monochromated Enhance (Mo) X-ray Source ($\lambda = 0.71073$ Å). The program CrysAlisPro, Oxford Diffraction Ltd. was used for cell refinements and data reduction of the compound. Empirical absorption correction was performed using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Crystal structures were solved and refined against all F^2 values using the SHELXTL suite of programs.^{S2} Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions that were refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. A summary of the data collection and structure refinements is provided in Table S.1. CCDC-886501 (1), and -886502 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

The powder diffraction pattern of the bulk sample was consistent with the pattern calculated from single-crystal data (see Figure S3), thus confirming the phase purity of the samples.

Physical measurements. Infrared spectra were recorded on a Perkin-Elmer model 1320 spectrometer (KBr disk, 400-4000 cm⁻¹). The TG measurements were performed on a Mettler Toledo TGA/SDTA 851e under nitrogen gas flow (30 mL/min). Samples were heated from room temperature to 800 °C at a heating rate of 10 °C/min.

Magnetic measurements. Magnetic susceptibility measurements were performed on polycrystalline samples using a magnetometer (Quantum Design MPMS-XL-5) equipped with a SQUID sensor. Variable-temperature measurements were carried out in the temperature range 2-300 K. Electron paramagnetic resonance spectroscopy was recorded with a Bruker ELEXYS E580 spectectrometer operating in the X-band (9.47 GHz).

Compound	1	2
Empirical formula	$C_{19}H_{17}F_{4}I_{2}N_{2}O_{2}$	$C_{25}H_{17}F_8I_2N_2O_2$
Formula weight	635.15	783.21
Crystal color	blue	blue
Temperature	120(2) K	120(2) K
Crystal size	$0.20 \times 0.20 \times 0.03$	$0.18 \times 0.12 \times 0.04$
Crystal system, Z	Triclinic, 2	Monoclinic, 4
Space group	<i>P</i> -1	$P2_{1}/c$
<i>a</i> (Å)	10.0452(5)	11.1945(2)
<i>b</i> (Å)	10.8471(4)	14.5047(3)
<i>c</i> (Å)	11.3100(5)	16.7801(3)
α (°)	109.224(4)	90
β (°)	106.972(4)	95.577(2)
γ (°)	100.343(4)	90
$V(\text{\AA}^3)$	1059.84(10)	2711.74(9)
ρ calc (Mg/m ³)	1.990	1.918
$\mu(Mo_{K\alpha}) (mm^{-1})$	3.019	2.401
θ range (°)	2.26–27.51	2.90-25.03
Refins collected	27906	19964
Independent reflns, n , (R_{int})	4688 (0.0730)	4786 (0.0504)
Reflns used in refinement	4688	4786
L. S. parameters/ restraints	262/0	356/0
$R1(F),^{[a]}I > 2\sigma(I)$]	0.0312	0.0324
$wR2(F^2)$, ^[b] all data	0.0679	0.0644
$S(F^2)$, ^[c] all data	0.959	1.060

 Table S.1. Crystallographic data for compounds 1 and 2.

 $[a] R1(F) = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|; [b] wR2(F^2) = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma wF_0^4]^{\frac{1}{2}}; [c] S(F^2) = [\Sigma w(F_0^2 - F_c^2)^2/((n + r) - p)]^{\frac{1}{2}}$

3. Additional Figures



Figure S.1. Relative orientation of the PhNN radicals that form the magnetic chain in 1; left: centroid-to-centroid distance of 5.6495(2) Å; right: centroid-to-centroid distances of 5.7483(3) Å.



Figure S.2. Relative orientation of the PhNN radicals that form the magnetic chain in **2**; left: centroid-to-centroid distance of 5.2462(2) Å; right: centroid-to-centroid distances of 7.3292(2) Å.



Figure S3. Observed and calculated powder diffraction patterns of compounds 1 (left) and 2 (right), using $\lambda_{Mo} = 0.71073$ Å. The observed pattern is shown in red and the calculated pattern with full width at half maximum set to 0.2° is shown in black.



Figure S.4. Thermogravimetric analysis (TGA) of PhNN (red line), I_2F_4bz (green line), 1 (blue line) and 2 (black line) showing the thermal stability of the compounds.



Figure S.5. IR spectra of PhNN, I_2F_4bz , 1 and 2 .

4. References

- S1. T. Rausis and M. Schlosser, Eur. J. Org. Chem., 2002, 3351
- S2. G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112.