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Short Note

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diyl)bis(4,1-phenylene))bis(oxy))-
bis(2,3,5,6-tetrafluoropyridine)



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4,4'-(((Perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(oxy))-bis(2,3,5,6-tetrafluoropyridine)

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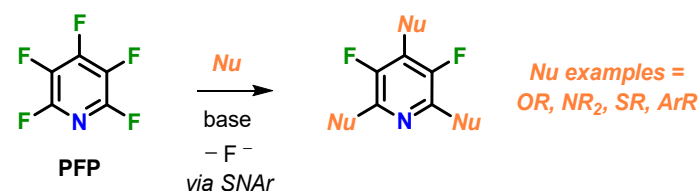
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Abstract: The title compound was synthesized in near-quantitative yield using nucleophilic aromatic substitution of 4,4'-(hexafluoroisopropylidene)diphenol (**BPAF**) with perfluoropyridine (**PFP**). The purity and structure were determined by NMR (^1H , ^{13}C , ^{19}F), GC-EIMS, and single-crystal X-ray crystallography.

Keywords: organo-fluorine; aryl ether; pentafluoropyridine; bisphenol; nucleophilic aromatic substitution

1. Introduction

Perfluoropyridine (**PFP**) is a versatile starting material for nucleophilic aromatic substitution (SNAr), reacting with a broad range of *O*-, *N*-, *S*, and *C*-nucleophiles via exclusive attack at the 4-*para*-position [1,2] (Scheme 1). Sequential addition to the 2,6-*ortho*-positions can also be accomplished leaving the 3,5-*meta*-fluorines intact. Furthermore, **PFP** has demonstrated utility as a protecting group for phenols [3,4], fluorinating reagent [5,6] and can also be defluorinated via site-selective catalysis [7,8]. Motivation for incorporating **PFP** into polymer frameworks led to the development of a pool of new fluoropolymer architectures, including highly processable polyarylethers, fluorosilicones, dendrimers, and high-char-yield resins for demanding aerospace applications [9], in addition to expanding the utility of hydrofluoroethers (HFEs) [10]. These unique materials have shown marked improvement over conventional state-of-the-art polymers in processability, mechanical strength, and compatibility with hybrid composites, while retaining high-temperature resistance. More recently, **PFP** was used for the mechanochemical synthesis of perfluoropolyether oligomers, which expands its utility for solvent-free polymerizations [11]. As an extension of this work, herein, we detail the synthesis and structural characterization of a **PFP** end-capped bisphenol, a new type of monomer for SNAr polymerizations.



Scheme 1. Perfluoropyridine as a regioselective electrophile.

2. Results and Discussion

The synthesis of 4,4'-(((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(oxy))-bis(2,3,5,6-tetrafluoropyridine) (**1**) was accomplished by nucleophilic aromatic substitution of pentafluoropyridine (**PFP**) with 4,4'-(perfluoropropane-2,2-diyl)diphenol (**BPAF**) using stoichiometric cesium carbonate in acetonitrile at room temperature (Scheme 2). Reaction monitoring by ^{19}F -NMR showed the regioselective quantitative conversion of the *para*-F ($\delta -130$ ppm)



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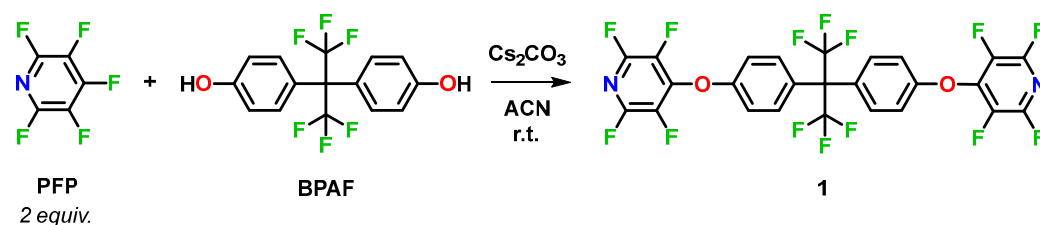
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from PFP exclusively to the set of *ortho*- and *meta*-F multiplets at δ -88.1 – 88.2 and δ -153.7 – 153.9 (see supplementary materials). Upon filtration of the carbonate salts followed by aqueous workup, compound **1** was obtained as a white, waxy solid in 95% overall isolated yield, requiring no further purification. GC–MS confirmed the purity $>98\%$ with an observed molecular ion at $[M - CF_3]^+$ at $m/z = 565$.



Scheme 2. Base-promoted synthesis of compound **1** from PFP and BPAF.

Crystals suitable for single-crystal X-ray diffraction were obtained by dissolution of **1** in hot ethanol followed by cooling and slow evaporation. The molecular structure of **1** (Figure 1) shows the expected BPAF core with two PFP groups attached via ether linkages. The least-squares planes of the rings of the BPAF core are inclined at an angle of 73.47° (0.04), with the attached PFP rings inclined at angles of 68.17° (0.04) (N1PFP) and 63.39° (0.04) (N2PFP) to their respective BPAF core rings.

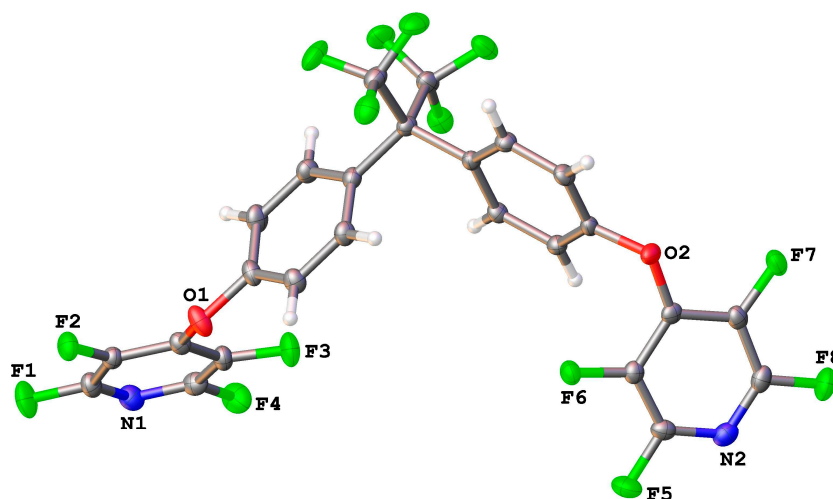


Figure 1. Molecular structure of **1**. Thermal ellipsoids are shown at the 50% probability level.

3. Materials and Methods

Chemicals and solvents were purchased as reagent grade through commercial suppliers. ^1H -, $^{13}\text{C}\{^1\text{H}\}$ -, and ^{19}F -NMR spectra were recorded on a Jeol 500 MHz spectrometer. Chemical shifts are reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform, $\text{C}\{\text{D}\}$ triplet, δ 77.0 ppm), and fluorine (CFCl_3 δ 0.00). NMR data are reported as follows: chemical shift, multiplicity, coupling constants (Hz), and integration. Gas chromatography/mass spectrometry (GC–MS) analysis was performed on an Agilent 7890 gas chromatograph coupled to an Agilent 5975C electron impact mass spectrometer with initial 2 min temperature hold at 80°C , followed by a temperature gradient of 80 to 250°C at $15^\circ\text{C}/\text{min}$.

3.1. Synthesis of 4,4'-(((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(oxy))-bis(2,3,5,6-tetrafluoropyridine) (**1**)

Cesium carbonate (10.7 g, 32.7 mmol), pentafluoropyridine (5.89 g, 34.8 mmol), and 4,4'-((perfluoropropane-2,2-diyl)diphenol) (4.97 g, 14.8 mmol) were combined in acetonitrile (30 mL) and allowed to stir for 48 h at room temperature. The reaction was monitored

by ^{19}F -NMR until 100% conversion of the desired product was observed. The solution was vacuum-filtered to remove carbonate salts and washed with diethyl ether (100 mL). The filtrate was combined with saturated ammonium chloride (100 mL) and the aqueous layer was extracted with diethyl ether (2×50 mL). The combined organic fractions were washed with saturated brine (1×100 mL), dried with magnesium sulfate, vacuum-filtered, concentrated using rotary evaporation, and placed under high vacuum, affording a white, waxy solid (8.89 g, 95%). ^1H -NMR (CDCl_3 , 500 MHz) δ 7.44–7.20 (d, $J = 9.0$ Hz, 4H), 7.10–7.08 (d, $J = 9.0$ Hz, 4H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz) δ 156.1, 145.3–145.1 (m), 143.6 (sept, $J = 11.1$ Hz, $(\text{CF}_3)_2\text{C}=\text{C}$), 144.5 (dtd, $J = 252, 16.2, 3.02$ Hz), 137.5–137.2 (m), 136.3 (ddt, $J = 252, 20.1, 6.05$ Hz), 132.1, 129.8, 123.0 (q, $J = 283$ Hz, $-\text{CF}_3$), 116.4; ^{19}F -NMR (CDCl_3 , 471 MHz) δ -64.2 (s, 6F) -88.1 – -88.2 (m, 4F) -153.7 – -153.9 (m, 4F); GC-EIMS (70 eV) m/z (% relative intensity) 565 ($[\text{M} - \text{CF}_3]^+$, 100), 379 (15), 330 (50), 233 (80), 201 (15), 183 (40), 152 (40), 138 (40), 100 (40), 69 (10).

3.2. Single-Crystal XRD Determination

The single crystal X-ray diffraction studies were carried out on a Rigaku Synergy-i single-crystal diffractometer equipped with a Mo $\text{K}\alpha$ radiation source ($\lambda = 0.71073$) and a Bantam HyPIX-3000 direct photon-counting detector. A $0.379 \times 0.298 \times 0.242$ mm³ translucent colorless prism crystal was mounted on a Cryoloop with Paratone-N oil. Data were collected in a nitrogen gas stream at 100.00(15) K using ω scans. The crystal-to-detector distance was 40 mm using an exposure time of 10 s with a scan width of 0.50° . Data collection was 100.0% complete to 25.242° in θ . A total of 81,813 reflections were collected. Of these, 5176 reflections were found to be symmetry-independent, with an R_{int} of 0.0340. Indexing and unit cell refinement indicated a primitive orthorhombic lattice. The space group was found to be Pbc_a. The data were integrated using the CrysAlisPro software program (Rigaku Oxford Diffraction, 2020, 1.171.42.49) and scaled using an empirical absorption correction implemented in the SCALE 3 ABSPACK software program, as well as a numerical absorption correction based on Gaussian integration over a multifaceted crystal model. Solution by direct methods (SHELXT-2014) produced a complete phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least squares (SHELXL-2008). All carbon bonded hydrogen atoms were placed using a riding model with their positions constrained relative to their parent atom using the appropriate HFIX command in SHELXL.

Supplementary Materials: The following supporting information is available online: ^1H -, ^{19}F -, and ^{13}C -NMR spectra and GC-MS for **1**.

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Data Availability Statement: CCDC 2238883 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44-1223-336033.

Conflicts of Interest: The authors declare no conflict of interest.

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