

Amidinium...Phosphonate Charge Assisted Hydrogen-bonded Organic Frameworks : Influence of Diverse Intermolecular Interactions

Asia R.Y. Almuhana, Sarah L. Griffin and Neil R. Champness

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Experimental

General procedures

All chemicals were obtained from commercial suppliers, (Alfa Aesar, Fisher Scientific, Sigma-Aldrich, or VWR international) and used without further purification. Reactions sensitive to air and moisture were performed using a standard Schlenk line, with nitrogen as the inert gas. Glassware was flame dried under vacuum and backfilled with dinitrogen.

¹H and ¹³C NMR experiments were carried out using Bruker DPX (400 MHz), Bruker AV(III)400hd (400 MHz), Bruker AV(III) 400 or AV(III) 500 MHz instrument at room temperature. Chemical shifts are reported with respect to the CDCl₃ residual peak at 7.26 ppm (¹H) and 77.00 ppm (¹³C) or DMSO-*d*₆ residual peak at 2.50 ppm. For ¹H spectroscopy, splitting patterns are described in brackets after the chemical shift as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, or qd = quartet of doublets.

Electrospray ionisation (ESI) spectra were recorded on a Bruker MicroTOF II spectrometer operating in Flow Injection mode, using methanol or acetonitrile as the solvent. Nominal mass matrix-assisted laser desorption/ionisation (MALDI) spectra were recorded with a Bruker Ultraflex III mass spectrometer using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) as the matrix.

Powder X-ray diffraction (PXRD) data were collected using The Panalytical Empyrean. The data was collected at room temperature equipped with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) operating at 40 kV and 40 mA and on a diffracted-beam graphite monochromator and in the 2 θ range from 3 to 50 ° with a step size of 0.02 °. The data were corrected for background noise by subtracting the background using HighScore Plus software.^{S1}

Thermogravimetric analysis (TGA)

Data were collected using PerkinElmer TGA8000. The sample was heated to 1000 °C under the flow of N₂, at a rate of 10 °C/min from room temperature.

X-ray Crystallography

Data were collected using a Rigaku Synergy-S dual source (Cu and Mo) with a PhotonJet-S X-ray source and a HyPix-6000 detector. Crystals were mounted in fomblin oil and collected at 100 K using an Oxford Cryosystems cryostream. Using Olex2,^{S2} the structure was solved with

the ShelXT⁵³ structure solution program using Intrinsic Phasing and refined with the ShelXL⁵⁴ refinement package using Least Squares minimisation. Atoms other than hydrogen were refined anisotropically, hydrogen atoms were incorporated as constants according to geometric calculations. When necessary, a solvent mask was applied. The number of electrons in voids were calculated per unit cell and this figure related to the number of disordered molecules. Further details of the refinement are given in the relevant cif.

Molecular Hirshfeld Surfaces

CrystalExplorer⁵⁵ was used to generate the molecular Hirshfeld surfaces at a standard (high) surface resolution. The 3D d_{norm} surfaces were mapped over a fixed color scale of -0.680 (red) to 4.030 a.u. (blue). The short contacts on the d_{norm} surface are highlighted in red, the longer contacts in blue, and the contacts around the sum of Van der Waals radii are displayed in white.

Synthesis

Synthesis of N,N'-di(4-benzylphosphonic acid diethyl ester) 1,4,5,8-naphthalenetetracarboxylic diimide (2)

The synthesis of this compound was carried out according to a literature procedure with some minor modifications.⁵⁶ A mixture of 1,4,5,8-naphthalenetetracarboxylic dianhydride (0.500 g, 1.87 mmol), diethyl 4-aminobenzylphosphonate (1.36 g, 5.60 mmol) and N, N'-dimethyl acetamide (DMA) (10 mL) was refluxed at 120 °C for 18 h under an inert atmosphere. The mixture was allowed to cool to RT and poured into cooled 2M HCl (50 mL). The precipitate was filtered under reduced pressure and washed with water (100 mL). The organic layer was extracted twice with CH₂Cl₂ and then washed with brine. The organic layer was dried over anhydrous MgSO₄ prior to the removal of the solvent via rotary evaporation, providing a yellow powder (1.00 g, 70%).

MS (MALDI-TOF) m/z [M]⁻: 718.2. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.75 (s, 4H), 7.45 (dd, J = 8.4, 2.5 Hz, 4H), 7.24 – 7.19 (d, J = 8.1 Hz, 4H), 4.08 – 3.94 (m, 8H), 3.21 (s, 2H), 3.16 (s, 2H), 1.22 (t, J = 7.1 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 162.90, 134.80, 133.46, 131.46, 131.00, 130.93, 128.61, 127.22, 127.03, 62.39, 62.32, 34.32, 32.46, 16.40, 16.40. ³¹P NMR (162 MHz, CDCl₃) δ (ppm): 25.62.

References

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