Electronic Supplementary Information for:

Open Network Structures from 2D Hydrogen Bonded Networks: Diaminotriazyl Tetraoxapentacenes

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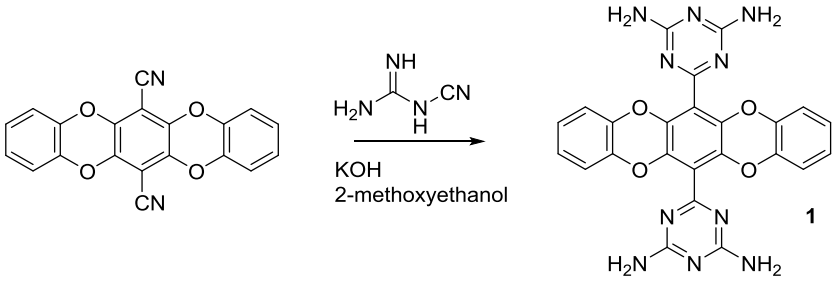
Contents:

Synthesis

All reagents and starting materials were purchased from Sigma-Aldrich and used as purchased. Anhydrous solvents were dispensed using a custom-built solvent system from Glasscontour (Irvine, CA) which used purification columns packed with activated alumina and supported copper catalyst. Oven-dried glassware was used for all reactions that were performed under nitrogen. High resolution mass spectra were recorded at the Centre Régional de Spectrométrie de Masse à l'Université de Montréal using an Agilent LC-MSD TOF spectrometer. ^{1}H and ^{13}C spectra were recorded on an Agilent Technologies 400 MHz Spectrometer using deuterated DMSO purchased from Sigma-Aldrich. Chemical shifts are reported in δ scale downfield from the peak for tetramethylsilane.

Synthesis of **1**.



3,13-dicyanobenzo-1,2,4',5'-bis(benzodioxane)[1] (1.00 g, 2.94mmol), dicyandiamide (0.988 g, 11.8 mmol), and potassium hydroxide (0.225 g, 4.00 mmol) were combined in 2-methoxyethanol (30 mL). The reaction mixture was heated at reflux overnight and then cooled to room temperature. The resulting precipitate was collected by suction filtration and air-dried. Recrystallization from DMSO/water yielded compound **1** as a white solid (1.20 g, 80%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 6.86 (m, 8H), 7.02 (br s, 8H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 121.7, 121.8, 129.8, 139.4, 145.5, 172.0, 172.1; HRMS (ASAP) calc'd for $C_{24}H_{17}N_{10}O_4$+H *m/z* 509.1434, found 509.1427.

[1] C. R. Mason, L. Maynard-Atem, N. M. Al-Harbi, P. M. Budd, P. Bernardo, F. Bazzarelli, G. Clarizia and J. C. Jansen, *Macromolecules*, 2011, **44**, 6471-6479.

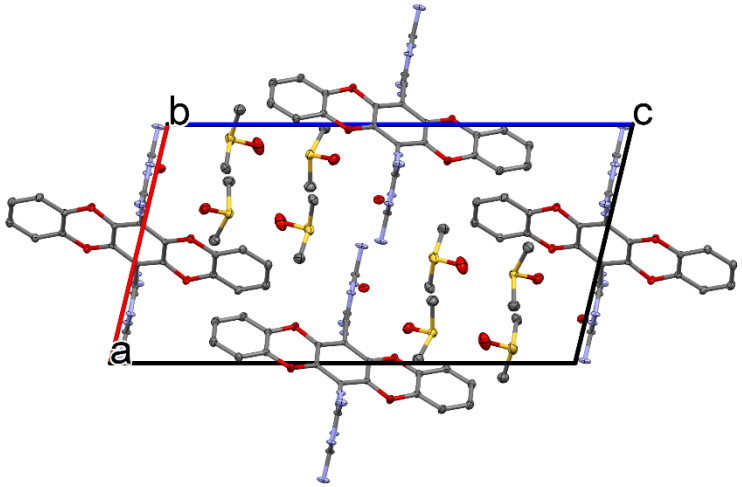


Figure S1: View down the c-axis of the structure of **1**·$(DMSO)_4(H_2O)_2$, with 50% displacement ellipsoids. Lattice solvent included to show how it is filling the open network formed by **1**. H-atoms omitted for clarity.

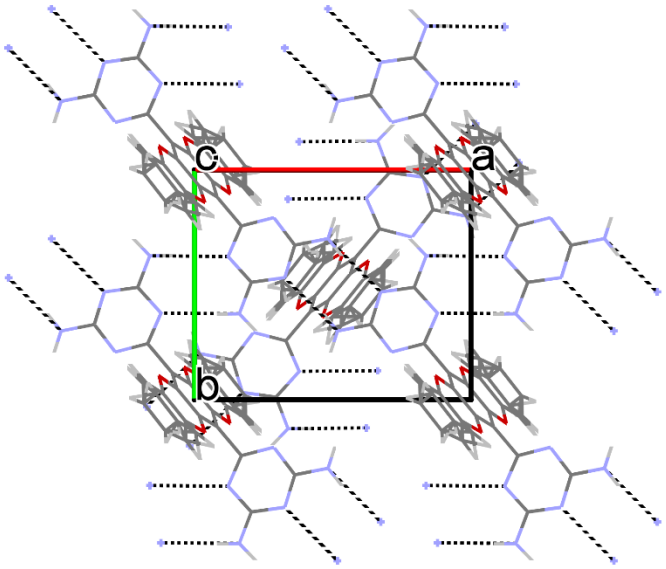


Figure S2: View down the c-axis of the structure of **1**·$(CH_3CN)_x$ showing the two dimensional hydrogen-bonded sheets. Main fragment disorder has been included.

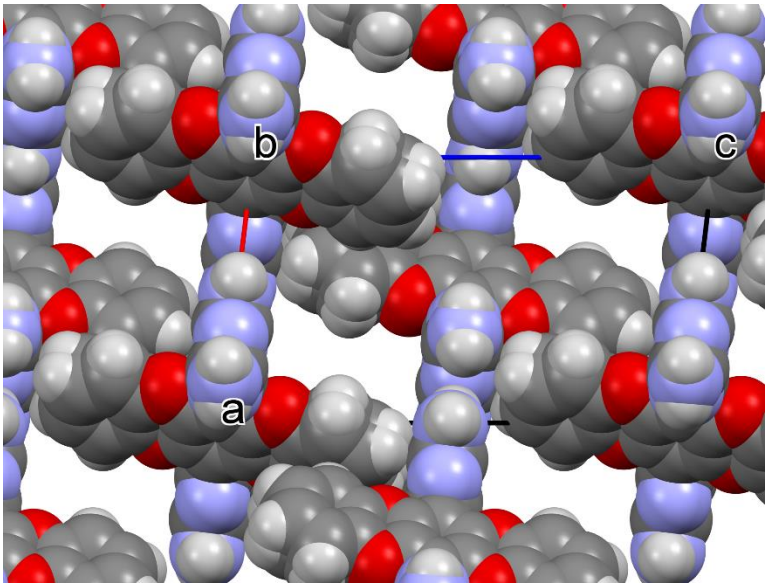


Figure S3: View of crystal structure (space filling model) of **1**·$(CH_3CN)_x$ along the b-axis.

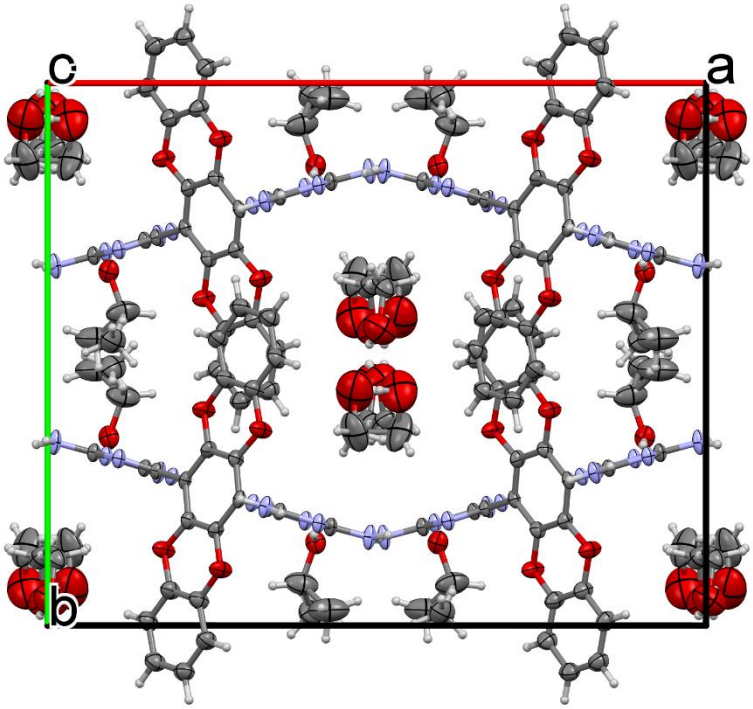
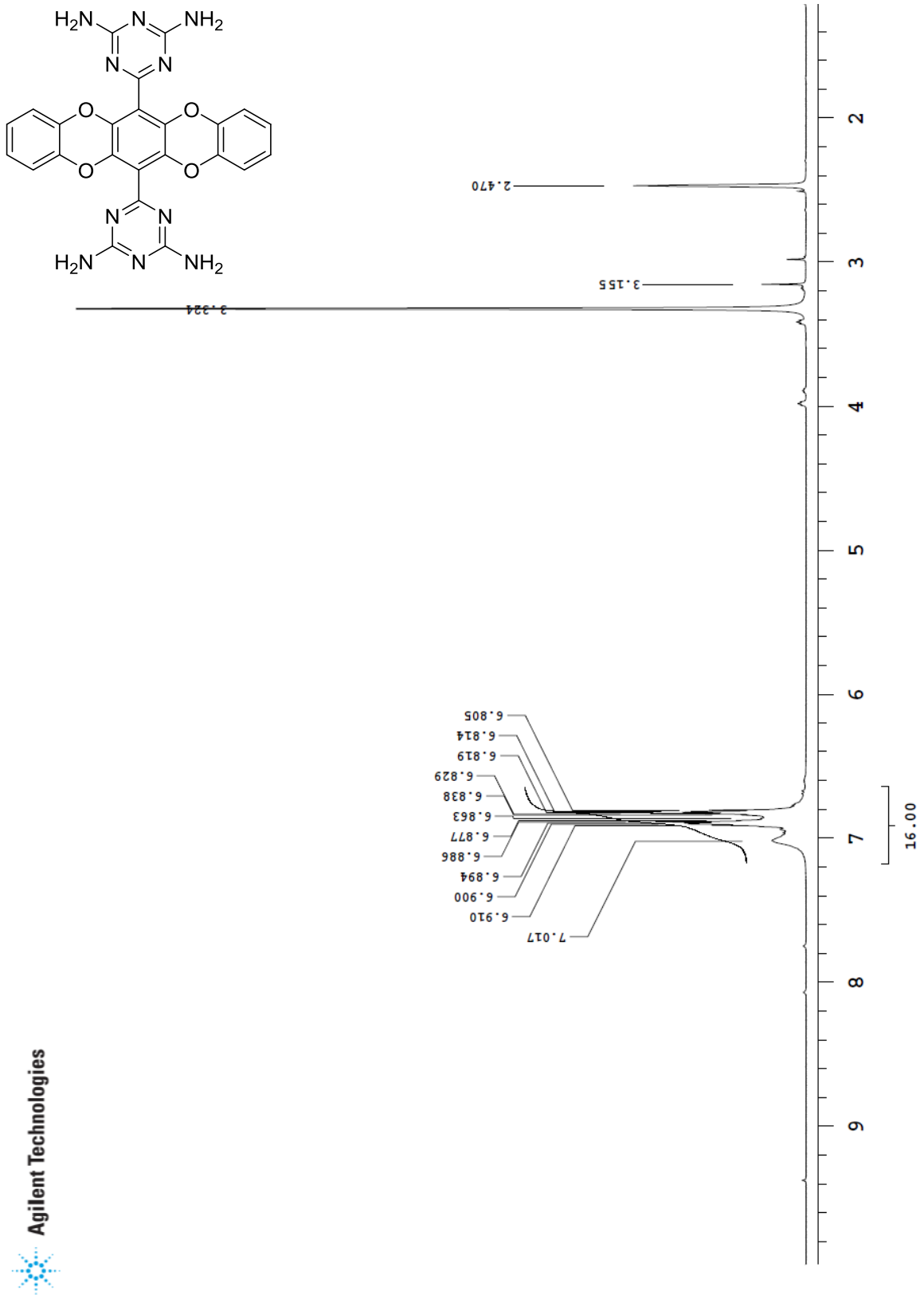
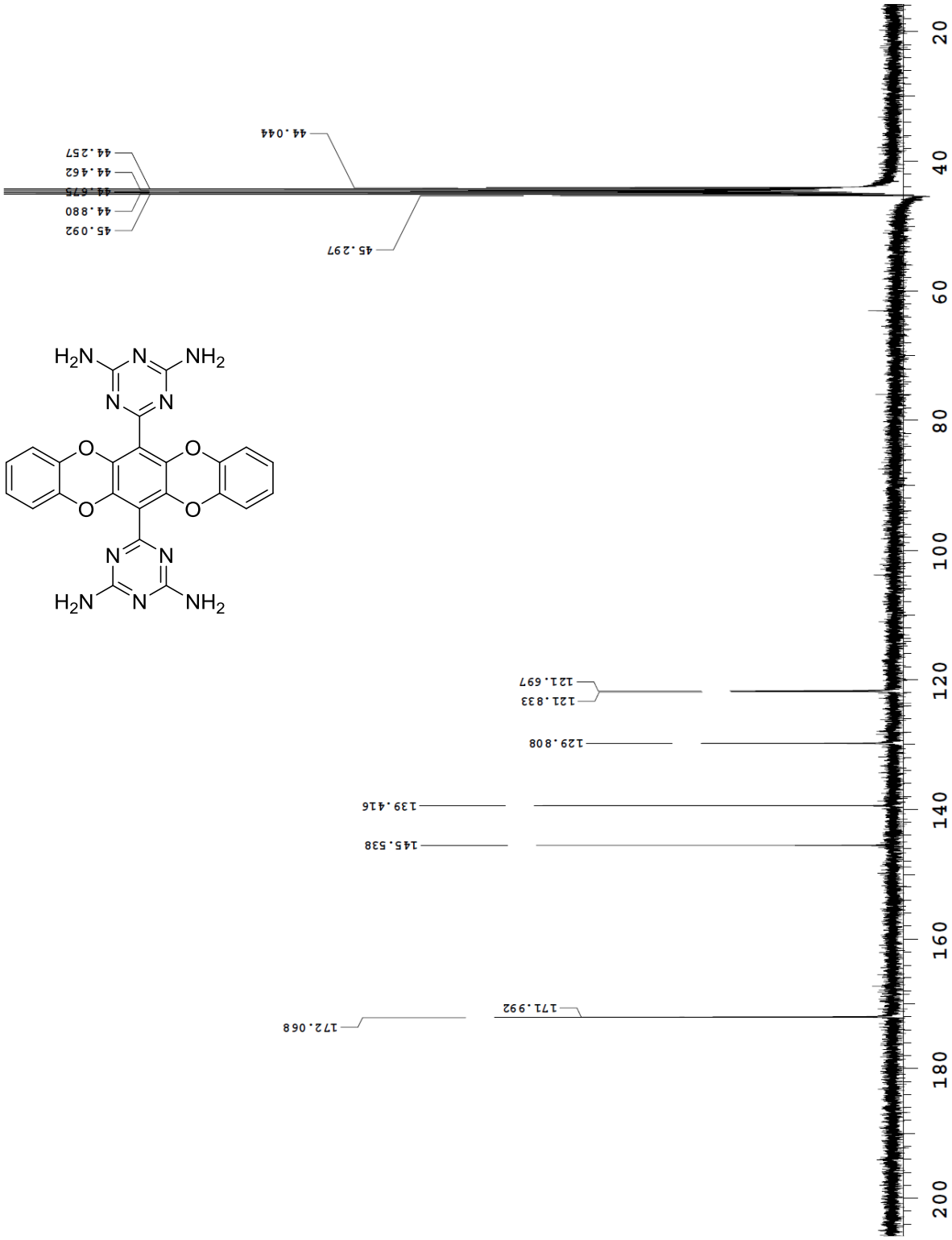


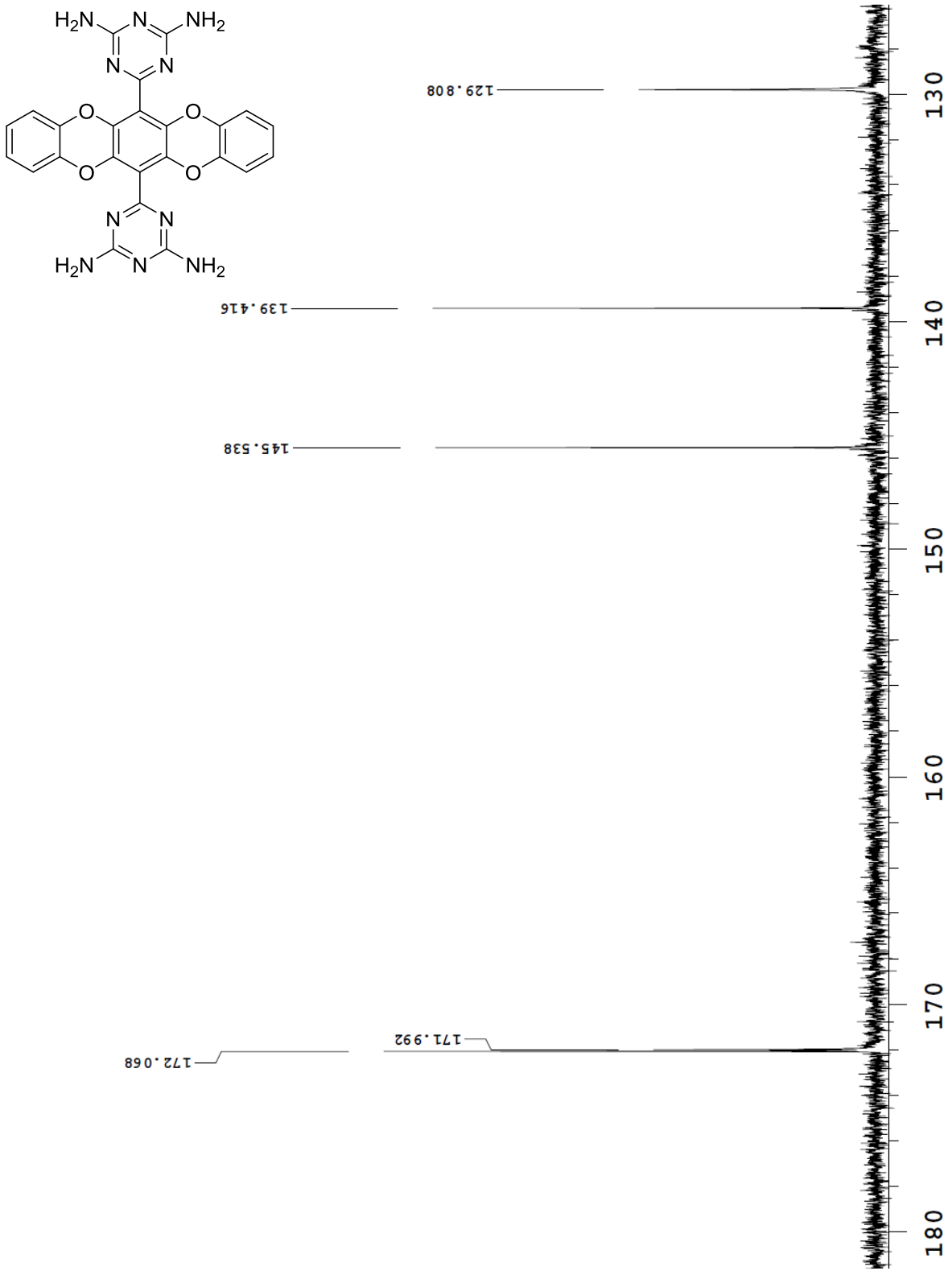
Figure S4: View down the c-axis of the structure of **1**·$(EtOH)_4$, with 50% displacement ellipsoids. Disordered lattice solvent included to show how it is filling the open network formed by **1**.



^{1}H NMR spectrum of **1** in DMSO-d_6.



^{13}C NMR spectrum of **1** in DMSO-d_6.



^{13}C NMR spectrum of **1** in DMSO-d_6 (expansion).