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Self-assembly of aromatic sulfonamide–amide hybridized molecules: formation of 2D layers and 3D microporous networks in the solid state

Zhi-Qiang Hu and Chuan-Feng Chen*

Laboratory of Chemical Biology, Institute of Chemistry, Chinese Academy of Sciences, Center for Molecular Science, Beijing 100080, China

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Abstract—Three sulfonamide–amide hybridized molecules and one cyclic analogue were synthesized and their assembling behaviors in the solid state were investigated by X-ray crystallography. The results showed that the hybridized molecules could be not only induced to take up helical secondary structures by a network of intramolecular hydrogen bonds, but also utilized as useful building blocks for assembling into 1D zigzag chains and superhelices, 2D layers and further 3D networks. Moreover, it was found that the multiple C–H···O═S hydrogen bonds played an important role in the assembling processes.

1. Introduction

There has been intense interest in designing molecules that can assemble into molecular crystals.[1,2] Some recent efforts in this field have focused on the assembly of organic molecule[3] through the non-covalent interactions and these organic crystals with predefined solid state structures can find many important applications for developing new materials with nonlinear optical properties or other functions.[4] Because of high selectivity and directionality, hydrogen bonds are the most widely used interactions.[5] Recently, weaker interactions have received increasing interest in self-assembly of organic molecules.[6] The properties of the materials are determined by three-dimensional array of individual molecules, so it is important to construct higher order superstructures, such as microporous networks[7] with potential applications as materials in selective separation, gas absorption, and heterogeneous catalysis. However, current works in assembling molecular solids focus mainly on one-dimensional aggregates such as chains[8] because controlling the crystal architecture in all three dimensions is difficult.

Discovery of molecular building block bearing different functional groups that can assemble to form higher order superstructures is of paramount importance in the controlled assembly of solid-state structures for developing new materials. Being easy to form hydrogen bonds, the assemblies of organic molecules containing amide group have been widely investigated to form superstructure such as superhelice[9] and layers.[10] Compared with the wide application of organic amides in different assembling systems, little is known[11] about the assembly of organic molecules bearing sulfonamide groups although organic molecules bearing $RNHSO_2NHR$ groups can self-assemble into robust two-dimensional molecular layers through H···O═S hydrogen bonds network.[12]

Different from the planar amide group, the sulfonamide group adopts tetrahedral geometry and O atoms in sulfonamide group are easier to form hydrogen bonds in higher dimensions. This makes organic molecules containing sulfonamide group to be potential building blocks for controlled assembly into higher order superstructure. Moreover, the sulfonamide is a stronger hydrogen-bond donor than the amide. Sulfonamide group also shows a small rotational barrier of the S–N bond and one of the H–N–S═O torsion angles is near 0°.[13] With these different structural features from those of the amide, we envisioned that a rational designed aromatic sulfonamides could be a useful building block for self-assembly along different directions into unique highly ordered supramolecular architectures through hydrogen bonds and π–π stacking interactions. Herein, we described that aromatic sulfonamide–amide hybridized molecules **1**–**3** with helical secondary structures and the cyclic analogue **4** could serve as units to assemble into 2D layers and 3D microporous

Keywords: Sulfonamide; Self-assembly; Superhelice; 2D Layer; 3D Microporous network; Hydrogen bond.
* Corresponding author. Tel.: +86 10 62588936; fax: +86 10 62554449; e-mail: cchen@iccas.ac.cn

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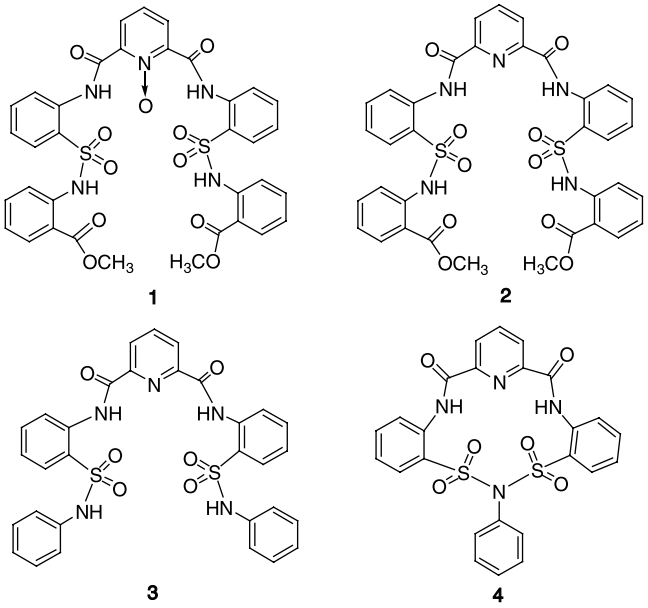
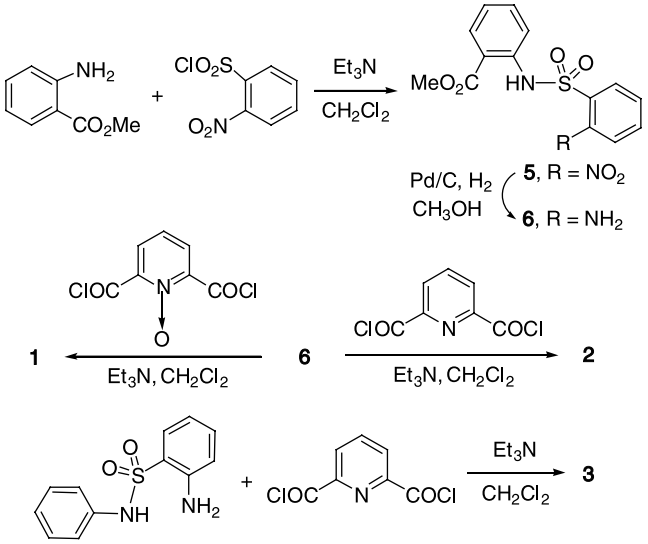
networks in the solid state. Moreover, the hydrogen bonds involving sulfonamide groups played an important role in the assembling processes.



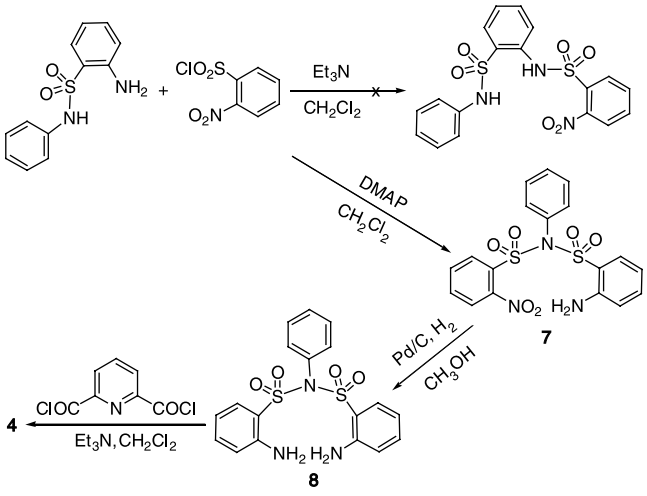
2. Results and discussion

Synthesis of **1**–**3** was depicted in Scheme 1. Compound **1** was readily synthesized by the reaction of 2,6-bis(chloroformyl)pyridine *N*-oxide with intermediate **6**, *N*-(2-methoxycarbonylphenyl)-2-amino-benzenesulfonamide, in the presence of Et_3N. **6** was prepared by treatment of 2-nitrobenzenesulfonyl chloride with methyl anthranilate in the presence of Et_3N, followed by catalytic hydrogenation. Under the similar reaction conditions, compounds **2** and **3**[14] were synthesized by the reactions of 2,6-bis(chloroformyl)-pyridine with **6** and *N*-phenyl-2-amino-benzenesulfonamide, respectively.



Scheme 1. Synthesis of compounds **1**–**3**.

When we intended to synthesize the oligosulfonamide through coupling *N*-phenyl-2-aminobenzenesulfonamide with 2-nitrobenzenesulfonyl chloride in the presence of Et_3N, it was found that no reaction occured. The same result was obtained by replacing Et_3N with Na_2CO_3. This might be due to the electron withdrawing effect of sulfonamide group and intramolecule hydrogen bond between NH_2 and SO_2 groups. When the stronger base, 4-dimethylamino-pyridine (DMAP), was used, we found that 2-nitrobenzenesulfonyl chloride reacted with NH in sulfonamide group rather than NH_2 group, which resulted in **7**. Compound **7** was reduced by catalytic hydrogenation in methanol to yield **8** in quantitative yield, which was further reacted with 2,6-bis(chloroformyl) pyridine to give a cyclic compound **4** (Scheme 2).



Scheme 2. Synthesis of compound **4**.

The assemblies of **1**–**4** in the solid states were investigated through X-ray diffraction analysis.

We first obtained crystals of **1** suitable for X-ray analysis from a mixture of CH_2Cl_2/CH_3OH. The crystal named as crystal **I** belonged to *P*2/*n* space group. As expected, bifurcated intramolecular hydrogen bonds involving both pyridine *N*-oxide O6 and sulfonyl inward O4 atoms as acceptors (N2···O6, 2.58 Å and N2···O4, 2.88 Å) were existed in the crystal **I** (Fig. 1a). Pyridine ring and two adjacent benzene rings were not planar, and the two benzene rings were above and below the plane of pyridine ring about 30°. With the torsion angle of H–N1–S–O4 of 9.51° and O3 atoms outward, the terminal rings were far apart and positioned above and below the respective adjacent ring of all 67°. The results led to molecule **1** to take up a 'Gelander' helical conformation,[15] which was different from that of oligoanthranilamides.[16]

As shown in Figure 1b, **1** in the crystal **I** could assemble along the [1 0 1] direction into a twisted zigzag structure. The main driving forces were the C11–H···O4 hydrogen bonds (H···O, 2.63 Å) and the π–π stacking interactions between the benzenesulfonamide rings of adjacent molecules with centroid distance of 3.94 Å.

Interestingly, we found that the assembled zigzag chains could further associate into higher order supramolecular structures

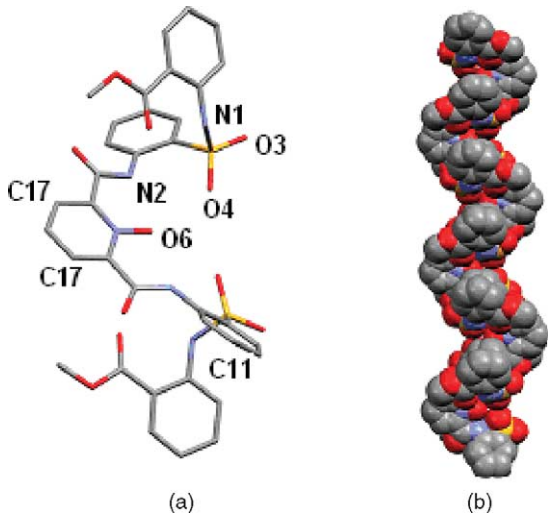


Figure 1. (a) X-ray crystal structure of **1** in the crystal **I**. Hydrogen atoms were omitted for clarity. (b) Side view of the assembled zigzag chain.

through π–π stacking interactions and C–H···O═S hydrogen bonds. Firstly, the zigzag structures assembled along the *b*-axis into a 2D layer through (C17) H···O3 (H···O, 2.57 Å) hydrogen bonds between 3 and 5-protons of pyridine rings in a zigzag chain and sulfonyl outward O atoms of the adjacent zigzag chain (Fig. 2a and b). Then, the 2D layers stack along [$\bar{1}$01] direction into 3D microporous networks through π–π stacking interactions between the terminal rings of **1** with the centroid distance of 3.67 Å. When it was viewed along the [101] direction (Fig. 3a), there were channels formed by the interlocked zigzag chains with the size of ca. 7.5×16.6 Å and carbonate groups occupied inside. When it was viewed along the [$\bar{1}$01] direction (Fig. 3b), there was another kind of channels with size of ca. 6.5×7.4 Å, in which CH_2Cl_2 molecules were positioned.

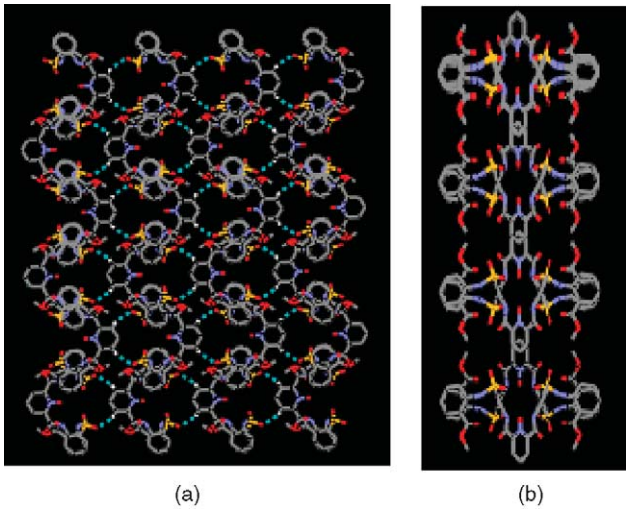


Figure 2. (a) Side view of a 2D layer along *a*-axis. Dashed lines represent the C–H···O═S hydrogen bonds. (b) Top view of a 2D layer.

To investigate the effect of environment on the assembly of **1**, another kind of crystal of **1** was obtained from a mixture of CH_2Cl_2/*n*-C_6H_{14} and named as crystal **II**. Interestingly, we found that the crystal **II** belonged to the non-centrosymmetric space group of $P2_12_12_1$.[17] As shown in Figure 4a, **1** also takes up a 'Gelander'helical secondary structure in the crystal **II**, which is stabilized by a network of intramolecular hydrogen bonds (N1···O2, 2.60 Å; N2···O4, 2.90 Å; N2H···O6, 2.61 Å; N3···O6, 2.61 Å; N3···O8, 2.90 Å; N4···O10, 2.61 Å).

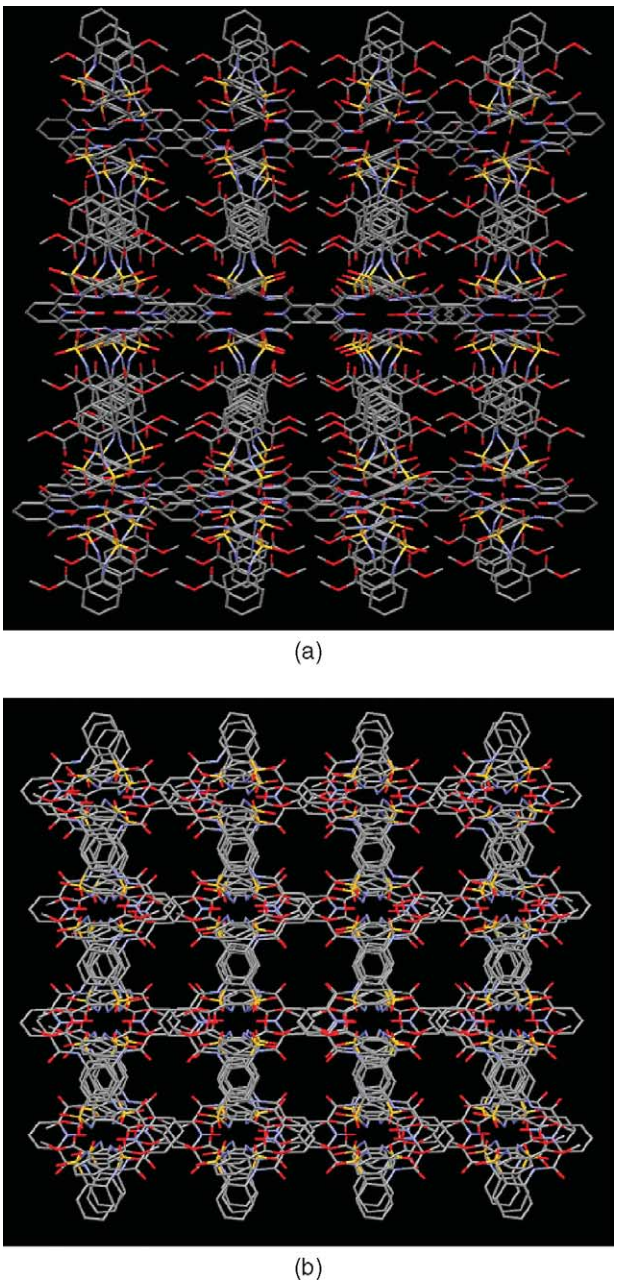


Figure 3. View of microporous networks presented in the crystal **I** (a) along [101] direction; (b) along [$\bar{1}$01] direction. Hydrogen atoms and solvent molecules were omitted for clarity.

Different from the assembling way in crystal **I**, **1** in the crystal **II** could assemble along the *b*-axis to form a helical superstructure (Fig. 4b). In view of the occurrence of helical structures and superstructures[18] in many biological systems and their importance in biomimetic and material sciences, this may be important. In the superhelice, two kinds of C–H···O═S (H···O, 2.50 and 2.72 Å) hydrogen bonds were existed

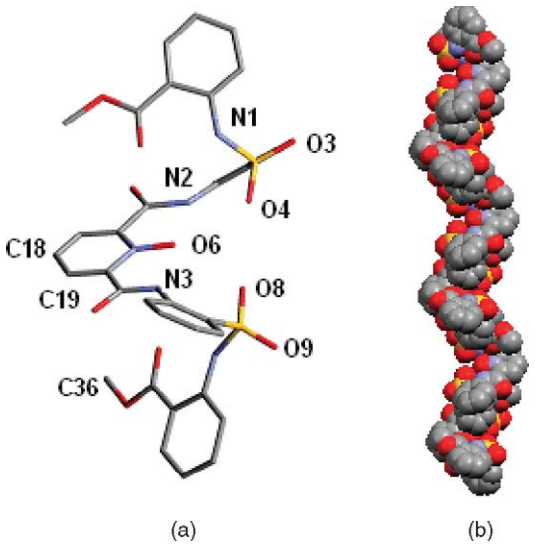


Figure 4. (a) X-ray crystal structure of **1** in the crystal **II**. Hydrogen atoms are omitted for clarity. (b) Side view of the assembled superhelice.

between the sulfonyl inward O atoms of one molecule and the 5-protons of the terminal benzene ring of its adjacent two molecules. Also, two kinds of π–π stacking interactions were present between the benzenesulfonamide rings of one molecule and the terminal rings of its adjacent two molecules with the centroid distances of 3.71 and 3.85 Å, respectively. In addition, C–H···O═C (H···O, 2.59 Å) hydrogen bond was existed between a carbonate O atom of a molecule and 4-proton of a terminal ring of the adjacent molecule. The pitch of superhelice was 20.79 Å.

Further assembly of the helical structure is very important. Although more and more efforts to self-assembled superhelices[9,19] have been made, most of them were still limited to one dimension along the helical axis.[20] We found that the superhelices in crystal **II** can further assemble to form highly ordered architectures. Firstly, they associate along the *c*-axis resulting in formation of 2D layers, in which a network of intermolecular C–H···O═S hydrogen bonds (C18H···O8, 2.45 Å; C18H···O4, 2.48 Å; C19H···O3, 2.67 Å; C36H···O3, 2.69 Å) were utilized as main driving forces (Fig. 5a and b). Secondly, through the π–π stacking

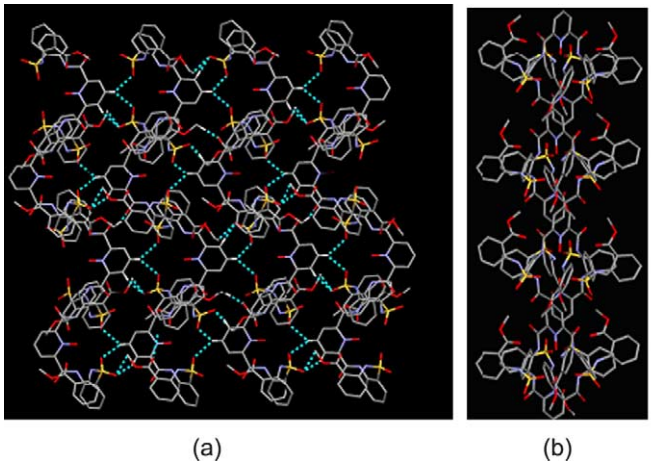


Figure 5. (a) Side view of a 2D layer. Dashed lines represent the C–H···O═S hydrogen bonds. (b) Top view of a 2D layer.

interactions between the benzene rings not involved in formation of the superhelice with the centroid distances of 3.71 and 3.85 Å, the 2D layers were then stacked along [$\bar{1}$01] direction into a 3D microporous network with channels of ca. 5.3×8.0 Å (Fig. 6), in which water molecules[21] were located.

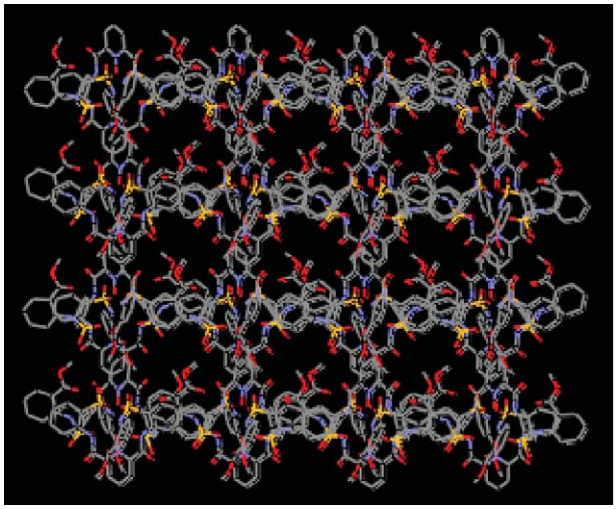


Figure 6. View of a microporous network along [110] direction.

The X-ray crystal structure of **2** confirmed that it took up a similar conformation with **1** in the solid state (Fig. 7a), and the helical arrangement of the rings was also stabilized by a network of intramolecular hydrogen. Similar to the case of **1** in the crystal **I**, molecule **2** could assemble into zigzag structure (Fig. 7b). It could also further assemble into 2D layers along the *a*-axis (Fig. 8a and b) and then 3D networks along the *c*-axis (Fig. 9), in which the C–H···O═S hydrogen bonds also played an important role. In the 3D microporous network, there existed the channels of ca. 7.5×16.6 Å, in which $CHCl_3$ molecules were included.

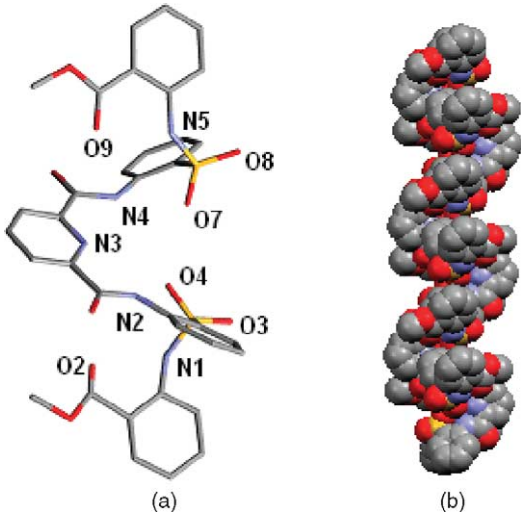


Figure 7. (a) X-ray crystal structure of **2** in the crystal. (b) Side view of the assembled zigzag chain. Hydrogen atoms were omitted for clarity.

The single crystal of **3** obtained from a mixture of CH_2Cl_2/CH_3OH had similar helical secondary structure with **2**. The

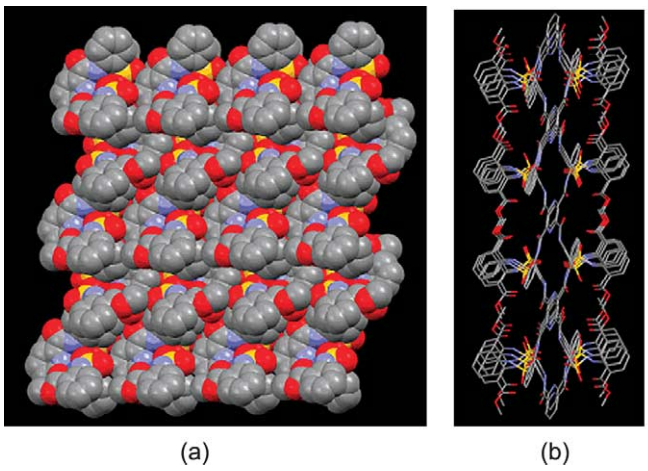


Figure 8. (a) Side view and (b) top view of a 2D layer. Hydrogen atoms were omitted for clarity.

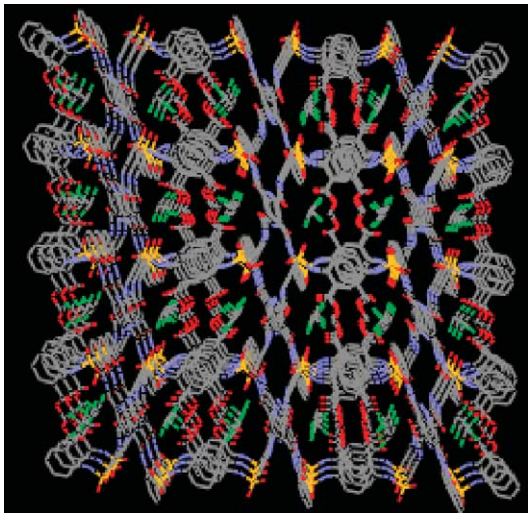


Figure 9. View of a microporous network along the *c*-axis with $CHCl_3$ molecules included in the channels. Hydrogen atoms were omitted for clarity.

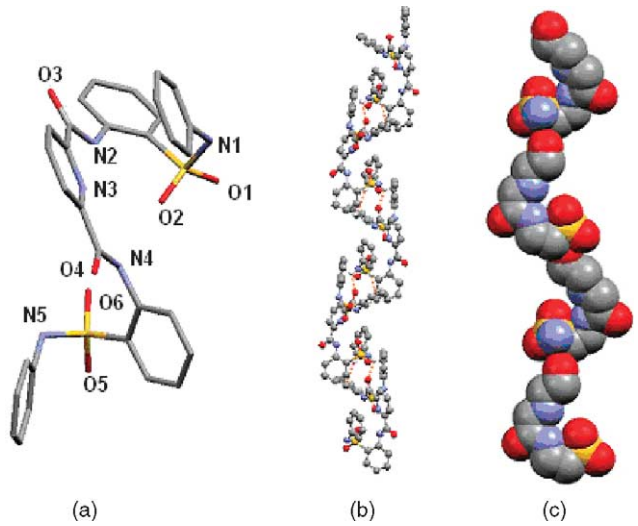


Figure 10. (a) X-ray crystal structure of **3**. Hydrogen atoms were omitted for clarity. (b) View of assembled superhelices. along *b*-axis. (c) View of assembled superhelice along *b*-axis; only the atoms in track of helice were shown.

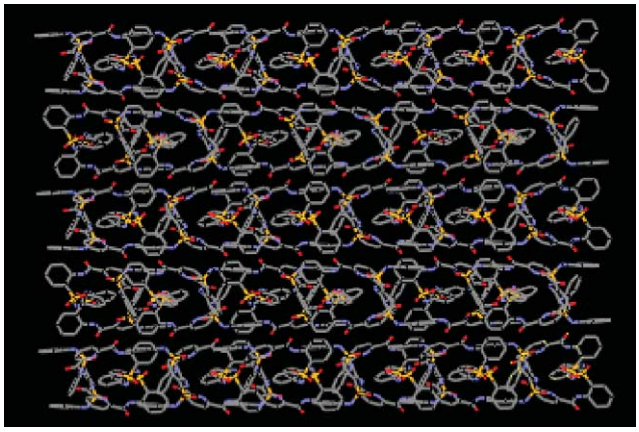


Figure 11. View of 3D array along *c*-axis. Hydrogen atoms were omitted for clarity.

only difference was almost parallel to pyridine ring because of π–π stacking interactions with centroid distance of 3.88 Å and dihedral angle between them was 4.4° (Fig. 10a). This difference led to the assembly of **3** in the solid state in the different way from that of **2**.

Firstly, **3** assembled along *a*-axis to form superhelices (Fig. 10b and c) mainly through complementary hydrogen bonds between one of O atoms in carboxamide groups and one of H atoms in sulfonamide groups (N1···O4, 2.80 Å). In addition, there existed C–H···π interactions ($d_{H\cdots\pi}$ is 2.88 Å) to stabilize this structure. The superhelices could further associate to form 2D layers through C–H···O═S hydrogen bonds (C29H···O6, 2.63 Å). All of other O atoms (O3) in carboxamide groups pointed outward the layer. The layers stacked with two adjacent layers in opposite direction along *c*-axis to form 3D array (Fig. 11) through the complementary hydrogen bonds between the O3 and another H atoms in sulfonamide groups (N5···O3, 2.81 Å), C–H···O═S hydrogen bonds (C15H···O6, 2.60 Å) and C–H···π interactions ($d_{H\cdots\pi}$ is 2.89 Å). As above mentioned, sulfonamide group is a strong hydrogen-bond donor and carboxamide group is a strong hydrogen bond acceptor, and this kind of complementary hydrogen bonds between sulfonamides and carboxamides may be important in future design of molecular crystal.[13b,22]

Furthermore, we found the cyclic compound **4** could also assemble into highly ordered architectures in the solid state and C–H···O═S hydrogen bonds played an important role in the assembling process. The crystals of **4** were obtained from a mixture of CH_2Cl_2/CH_3OH. There were two crystallographically independent molecules of **4** in the crystal named as A and B. They adopted similar helical conformations but their chiralities were opposite. A was right-handed with dihedral angles between pyridine ring and two adjacent benzene rings about 15.3 and 19.4°, but B was left-handed with two dihedral angles about 13.7 and 21.2° (Fig. 12).

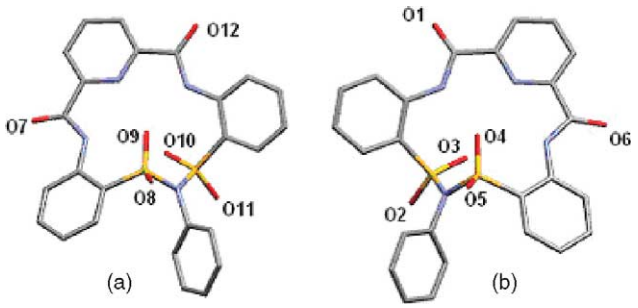


Figure 12. Two crystallographically independent molecules with opposite chirality of **4** in the crystal: A was right-handed, and B was left-handed. Hydrogen atoms were omitted for clarity.

A and B were alternated to connect each other along *b*-axis to form chain structures. The connection was driven by π–π stacking interactions between the pyridine ring of A or B and one of benzene rings adjacent to pyridine ring of B or A with centroid distances of 3.67 and 3.62 Å, and C–H···O═S hydrogen bonds (H···O, 2.59 Å and H···O, 2.67 Å) between O atoms in sulfonamide groups of A or B and H atoms in 3 and 4 position of pyridine rings of B and A. The cavities of A and B were located in two sides of the chain, respectively (Fig. 13a).

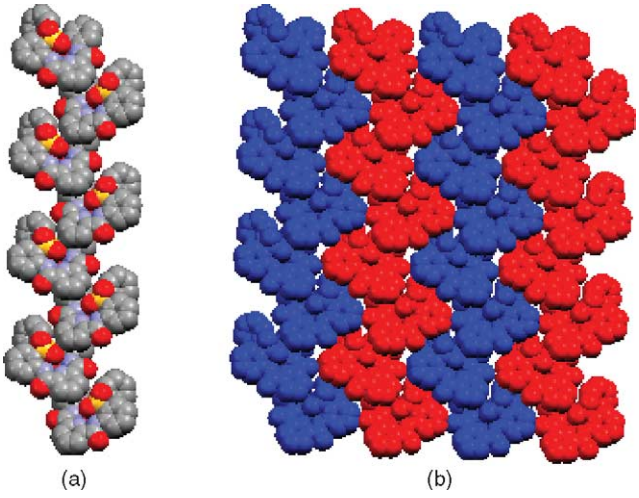


Figure 13. (a) View of assembled chain structure along *c*-axis. (b) View of a 2D layer along *c*-axis. Hydrogen atoms were omitted for clarity.

The chains were interlocked each other like zippers through π–π stacking interactions and C–H···O hydrogen bonds along *a*-axis to form 2D layers (Fig. 13b). The π–π stacking interactions were present between the benzene rings connecting with *N* atoms in sulfonamide group of one chain and benzene ring adjacent to the pyridine ring of another chain with centroid distance about 4.48 and 4.56 Å. The layers were consisted of two planes with S–N bonds as 'pillar'. The first plane named as plane **I** was made up with all pyridine rings and one of benzene rings adjacent to them and O6 and O7 atoms in carboxamide groups pointing outward this plane. The second plane named as plane **II** was made up of the rest two benzene rings in all constituent molecules and O2 and O10 atoms in sulfonamide groups pointing out this plane (Fig. 14a).

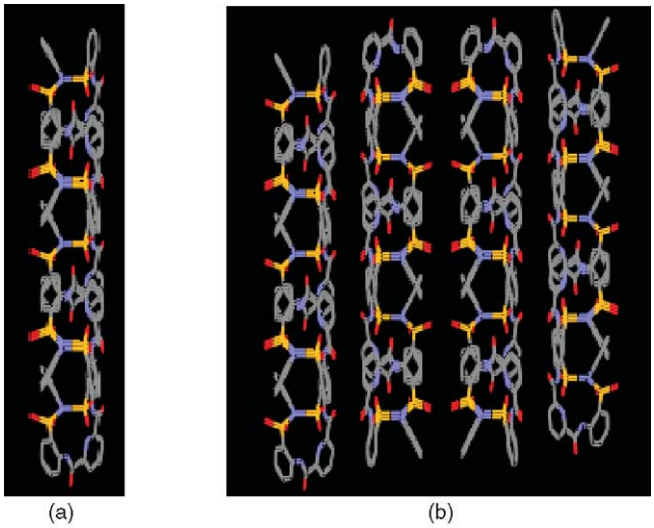


Figure 14. View of 2D layers (a) and the crystal lattic along the *a*-axis of the cell (b) of **4**, hydrogen atoms were omitted for clarity.

The layers were further associated along *c*-axis to form 3D array in two fashions (Fig. 14b). The first was through the interactions between plane **I** of two layers. The interactions included π–π stacking interactions between the pyridine rings in one layer and benzene rings adjacent to pyridine rings in another layer with centroid distance about 3.74 and 3.97 Å, and the C–H···O hydrogen bonds (H···O, 2.48 Å) between the O6 and O7 atoms of carboxamide groups in one layers and aromatic H atoms in other layers. The second was through the interactions between plane **II** of two layers, which was mainly through C–H···O hydrogen bonds (H···O, 2.62 Å) between the O2 and O10 atoms of sulfonamide groups in one layer and aromatic H in another layer.

3. Conclusions

In conclusion, we have synthesized three sulfonamide–amide hybridized molecules and one cyclic analogue, and demonstrated that aromatic sulfonamide-based subunits could be induced to take up helical secondary structures by a network of intramolecular hydrogen bonds. In particular, the helical molecules could be utilized as useful building blocks for assembly into not only 1D zigzag chains and superhelices, but also 2D layers and 3D microporous networks in the solid state. Moreover, we found that the multiple C–H···O═S hydrogen bonds and other hydrogen bonds involving sulfonamide groups played an important role in the assembling processes, which would be helpful for design and construction of other unique supramolecular architectures. The further studies on sulfonamide-based building blocks for the assembly into new highly order structures are under the way.

4. Experimental

4.1. General

Melting points were measured on a micro melting-point apparatus and uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM300 (300 MHz, chemical shifts in

ppm relative to internal TMS, *J* in Hertz). Mass spectra were obtained by EI and MALDI-TOF techniques. Elemental analyses were performed on a Vario ELIII and Carlo Erba 1106 analytical instrument. Solvents were dried and distilled before use according to standard procedures. *N*-Phenyl-2-aminobenzenesulfonamide[23] was prepared according to the published procedure.

4.1.1. Compound 5. To a solution of methyl anthranilate (1 mmol) and Et_3N (1.2 mmol) in CH_2Cl_2 (10 mL) at 0 °C, 2-nitrobenzenesulfonyl chloride (1.2 mmol) in CH_2Cl_2 (5 mL) was added dropwise. The reaction mixture was stirred at room temperature for 10 h and then washed with 2 N HCl and water. The organic phase was dried over anhydrous $MgSO_4$ and then concentrated. The crude product was purified by flash chromatography (1:1 DCM/petroleum ether) to give the product **5** as a white solid (218 mg, 65%). Mp 143–144 °C. ^{1}H NMR ($CDCl_3$): δ 11.18 (s, 1H), 8.16 (m, 1H), 7.98 (d, J=8.0 Hz, 1H), 7.83–7.78 (m, 2H), 7.74–7.69 (m, 2H), 7.49 (t, J=8.0 Hz, 1H), 7.08 (t, J=7.8 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 167.9, 148.2, 139.3, 134.5, 134.2, 132.9, 132.4, 131.6, 131.3, 125.4, 123.2, 117.9, 116.3, 52.8; EI-MS: *m*/*z* 336 $[M]^+$; elemental analysis calcd (%) for $C_{14}H_{12}N_2O_6S$: C 50.00, H 3.60, N 8.33; found: C 50.03, H 3.60, N 8.24.

4.1.2. Compound 6. A mixture of compound **5** (1 mmol) dissolved in CH_3OH (15 mL) and 10% Pd/C (10 mg) was stirred at ambient temperature under an atmosphere of hydrogen for 10 h. The reaction mixture was filtered through Celite and CH_3OH was evaporated to afford **6** as a white solid in quantitative yield. The product was pure and used without further purification. Mp 164–165 °C. ^{1}H NMR ($CDCl_3$): δ 10.85 (s, 1H), 7.91 (d, J=8.0 Hz, 1H), 7.71 (d, J=8.0 Hz, 1H), 7.62 (d, J=8.3 Hz, 1H), 7.42 (t, J=7.8 Hz, 1H), 7.23 (t, J=8.5 Hz, 1H), 7.00 (t, J=7.7 Hz, 1H), 6.71–6.65 (m, 2H), 4.88 (broad, 2H), 3.88 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 168.3, 145.5, 148.5, 140.4, 134.5, 134.4, 131.1, 130.1, 122.6, 120.3, 118.4, 117.6, 117.2, 115.7, 52.5; EI-MS: *m*/*z* 306 $[M]^+$; elemental analysis calcd (%) for $C_{14}H_{14}N_2O_4S$: C 54.89, H 4.61, N 9.14; found: C 54.72, H 4.65, N 9.13.

4.1.3. Compound 1. A solution of 2,6-pyridinedicarboxylic acid *N*-oxide (1 mmol) in excess $SOCl_2$ was refluxed for 2 h, $SOCl_2$ was then removed by reduced pressure. The acid chloride obtained was dissolved in anhydrous CH_2Cl_2 (10 mL), and added dropwisely over a period of 10 min to a solution of **6** (1 mmol) and Et_3N (3 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The mixture was stirred at room temperature for 4 h. The organic phase was washed with 2 N HCl twice, and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was purified by flash chromatography (20:1 DCM/EA) to give desired product **1** as a white solid (342 mg, 45%). Mp 268–270 °C. ^{1}H NMR (DMSO-d_6): δ 13.11 (s, 2H), 10.78 (s, 2H), 8.61 (d, J=8.0 Hz, 2H), 8.14 (d, J=8.0 Hz, 2H), 8.03 (d, J=7.8 Hz, 2H), 7.96 (t, J=7.9 Hz, 1H), 7.79–7.72 (m, 4H), 7.56–7.41 (m, 6H), 7.07 (t, J=7.4 Hz, 2H), 3.48 (s, 6H). ^{13}C NMR (DMSO-d_6): δ 167.3, 167.2, 157.9, 157.8, 140.8, 138.6, 138.4, 134.5, 134.4, 134.3, 134.1, 131.6, 131.0, 129.9, 129.7, 129.6, 128.9, 126.5, 126.4, 125.6, 123.8, 119.2, 116.7, 52.1; MALDA-TOF MS: *m*/*z* 758.3 $[M-H]^+$; elemental analysis calcd (%) for $C_{35}H_{29}N_5O_{11}S_2$: C 55.33, H 3.85, N 9.22; found: C 55.33, H 3.97, N 8.92.

4.1.4. Compound 2. Following the method described above for **1**, **2** was obtained in 54% yield by the reaction of 2,6-pyridinedicarboxylic acid with **6**. Mp 256–258 °C. ^{1}H NMR ($CDCl_3$): δ 11.37 (s, 2H), 10.65 (s, 2H), 8.49 (d, J=7.8 Hz, 2H), 8.27 (d, J=7.3 Hz, 2H), 8.18 (t, J=7.8 Hz, 1H), 7.83 (d, J=8.0 Hz, 2H), 7.76 (d, J=8.0 Hz, 2H), 7.64–7.55 (m, 4H), 7.33 (t, J=7.5 Hz, 2H), 7.18 (t, J=7.6 Hz, 2H), 6.96 (t, J=7.1 Hz, 2H), 3.66 (s, 6H). ^{13}C NMR (DMSO-d_6): δ 166.9, 161.2, 161.1, 147.9, 140.4, 137.7, 137.6, 135.0, 134.8, 134.6, 134.0, 130.7, 129.8, 129.3, 129.1, 129.0, 125.4, 125.2, 125.1, 125.0, 124.95, 124.89, 124.4, 121.1, 118.4, 52.2; MALDA-TOF MS: *m*/*z* 766.3 $[M+Na]^+$; elemental analysis calcd (%) for $C_{35}H_{29}N_5O_{10}S_2$: C 56.52, H 3.93, N 9.42; found: C 56.54, H 3.92, N 9.33.

4.1.5. Compound 7. To a solution of *N*-phenyl-2-aminobenzenesulfonamide (1 mmol) and DMAP (1.2 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added 2-nitrobenzenesulfonyl chloride (1.2 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was refluxed for 10 h and then washed with 2 N HCl and water. The organic phase was dried over anhydrous $MgSO_4$ and then concentrated. The crude product was purified by flash chromatography (1:1 DCM/petroleum ether) to give desired product **7** as a white solid (294 mg, 68%). Mp 138–140 °C. ^{1}H NMR ($CDCl_3$): δ 8.44–8.41 (m, 1H), 7.78–7.75 (m, 2H), 7.67–7.65 (m, 1H), 7.49 (d, J=8.3 Hz, 1H), 7.41–7.38 (m, 1H), 7.34–7.26 (m, 5H), 6.64–6.57 (m, 2H), 4.88 (broad, 2H). ^{13}C NMR ($CDCl_3$): δ 148.2, 147.1, 136.1, 135.1, 132.8, 132.7, 132.66, 132.1, 132.0, 131.3, 130.6, 129.1, 124.3, 117.4, 117.0, 116.7; MALDA-TOF MS: *m*/*z* 432.4 $[M-H]^-$; elemental analysis calcd (%) for $C_{18}H_{15}N_3O_6S_2$: C 49.88, H 3.49, N 9.69; found: C 49.75, H 3.49, N 9.75.

4.1.6. Compound 8. A mixture of compound **7** (1 mmol) dissolved in CH_3OH (25 mL) and 10% Pd/C (15 mg) was stirred at ambient temperature under an atmosphere of hydrogen for 10 h. The reaction mixture was filtered through Celite and CH_3OH was evaporated to afford **8** as a white solid in quantitative yield. The product was pure and used without further purification. Mp 162–164 °C. ^{1}H NMR ($CDCl_3$): δ 7.49 (d, J=8.2 Hz, 2H), 7.38–7.15 (m, 7H), 6.70–6.61 (m, 4H), 4.86 (broad, 4H). ^{13}C NMR ($CDCl_3$): δ 146.4, 135.6, 133.8, 132.0, 131.3, 130.2, 128.9, 119.0, 117.4, 116.7; MALDA-TOF MS: *m*/*z* 404.3 $[M+H]^+$; elemental analysis calcd (%) for $C_{18}H_{17}N_3O_4S_2$: C 53.58, H 4.25, N 10.41; found: C 53.38, H 4.31, N 10.21.

4.1.7. Compound 4. Following the method described for **1**, compound **4** was obtained as a white solid in 71% yield by the reaction of 2,6-pyridinedicarboxylic acid with **8**. Mp > 300 °C. ^{1}H NMR ($CDCl_3$): δ 12.70 (s, 2H), 8.98 (d, J=8.2 Hz, 2H), 8.42 (d, J=7.7 Hz, 2H), 8.22 (t, J=7.7 Hz, 1H), 7.71 (t, J=7.9 Hz, 2H), 7.61–7.50 (m, 3H), 7.40–7.35 (m, 4H), 7.17 (t, J=7.7 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 160.8, 147.8, 140.5, 136.9, 136.0, 134.3, 132.3, 131.2, 129.6, 126.9, 124.8, 123.5, 121.3; EI-MS: *m*/*z* 534 $[M]^+$; elemental analysis calcd (%) for $C_{25}H_{18}N_4O_6S_2$: C 56.17, H 3.39, N 10.48; found: C 55.96, H 3.36, N 10.39.

4.2. X-ray crystallographic study

Data were collected using a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα

(λ=0.71073 Å) radiation, and were corrected for Lorentzian, polarization, and absorption. Structures were solved by direct methods, and refined by full matrix least-squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were placed in calculated position. CCDC-259979 (**1**–**I**), CCDC-259977 (**1**–**II**), CCDC-259978 (**2**), CCDC-264356 (**3**) and CCDC-264357 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk).

Compound **1** *(crystal I)*. $C_{37}H_{29}Cl_4N_5O_{13}S_2$, *M* 957.57, crystal dimensions 0.80×0.50×0.10 mm^3, monoclinic, space group *P*2/*n*, *a*=15.053(3) Å, *b*=9.810(2) Å, *c*=16.063(3) Å, *V*=2190.1(8) Å^3, D_c=1.452 Mg m^{-3}, *Z*=2, 19578 reflections collected, 4853 independent [*R*(int)=0.0426], giving R_1=0.1003 for observed unique reflection [$F^2>2s(F^2)$] and wR_2=0.3697 for all data.

Compound **1** *(crystal II)*. $C_{35}H_{31}N_5O_{12}S_2$, *M* 777.77, crystal dimensions 0.51×0.49×0.09 mm^3, orthorhombic, space group *P*2(1)2(1)2(1)*c*, *a*=14.4682(7) Å, *b*=14.9321(9) Å, *c*=18.4391(10) Å, *V*=7970(3) Å^3, D_c=1.297 Mg m^{-3}, *Z*=4, 25091 reflections collected, 5026 independent [*R*(int)=0.0973], giving R_1=0.0793 for observed unique reflection [$F^2>2s(F^2)$] and wR_2=0.2259 for all data.

Compound **2**. $C_{36}H_{30}Cl_3N_5O_{10}S_2$, *M* 863.12, crystal dimensions 0.34×0.16×0.09 mm^3, triclinic, space group *P*-1, *a*=9.5294(19) Å, *b*=13.151(3) Å, *c*=16.255(3) Å, α=87.84(3)°, β=80.53(3)°, γ=85.97(7)°, *V*=2003.6(7) Å^3, D_c=1.431 Mg m^{-3}, *Z*=2, 17719 reflections collected, 6715 independent [*R*(int)=0.0972], giving R_1=0.089 for observed unique reflection [$F^2>2s(F^2)$] and wR_2=0.2018 for all data.

Compound **3**. $C_{32}H_{27}Cl_2N_5O_6S_2$, *M* 712.61, crystal dimensions 0.672×0.393×0.288 mm^3, orthorhombic, space group *Pbca*, *a*=18.967(4) Å, *b*=17.030(3) Å, *c*=20.597(4) Å, *V*=6653(2) Å^3, D_c=1.423 Mg m^{-3}, *Z*=8, 52803 reflections collected, 7568 independent [*R*(int)=0.0512], giving R_1=0.0680 for observed unique reflection [$F^2>2s(F^2)$] and wR_2=0.2164 for all data.

Compound **4**. $C_{25.5}H_{26}N_4O_{7.5}S_2$, *M* 572.62, crystal dimensions 0.55×0.52×0.24 mm^3, triclinic, space group *P*-1, *a*=12.3181(7) Å, *b*=14.1384(7) Å, *c*=16.2761(8) Å, α=110.964(2)°, β=107.2170(18)°, γ=90.150(2)°, *V*=2509.6(2) Å^3, D_c=1.516 Mg m^{-3}, *Z*=4, 11070 reflections collected, 7138 independent [*R*(int)=0.0532], giving R_1=0.0698 for observed unique reflection [$F^2>2s(F^2)$] and wR_2=0.1959 for all data.

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