Solid-State [4+4] Cycloaddition and Cycloreversion with Use of Unpaired Hydrogen-Bond Donors to Achieve Solvatomorphism and Stabilization

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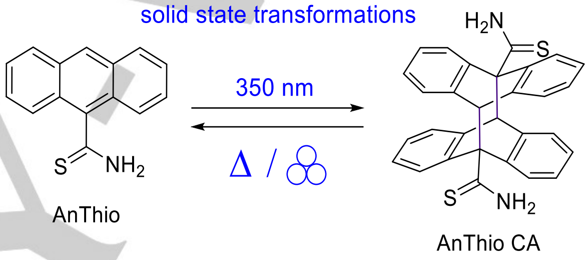
Abstract: The crystal structure of a commercially available anthracene derivative, anthracene-9-thiocarboxamide, is reported here for the first time, and we demonstrate that the compound undergoes a [4+4] cycloaddition in the solid state to afford facile synthesis of the cycloadduct (CA). The cycloaddition is also reversible in the solid state using heat or mechanical force. Due to the presence of unpaired, strong hydrogen-bond donor atoms on the CA, significant solvatomorphism is achieved, and components of the solvatomorphs self-assemble into four different classes of supramolecular structures. The CA readily crystallizes with a variety of structurally-diverse solvents including those containing oxygen-, nitrogen-, or pi-acceptors. Some of the solvents the CA crystallized with include thiophene, benzene, and the three xylene isomers; thus, we employed the CA in industrially-relevant solvent separation. However, in competition studies, the CA did not exhibit selectivity. Lastly, we demonstrate that the CA crystallizes with vinyl-containing monomers and is currently the only compound that crystallizes with both widely used monomers 4-vinylpyridine and styrene. Solid-state complexation of the CA with the monomers affords over a 50 °C increase in the monomer's thermal stabilities. We expect the strategy of designing molecules with unused donors can be applied to achieve separations or volatile liquid stabilization.

Introduction

Solid-state reactions are an important class of chemical transformations because they are green[1] (no solvent required, atom efficient) and often provide regio- or stereo-control over product formation.[2] Depending on the type of reaction, mild external stimuli, such as heat or light, may be the only requirement for the reaction to proceed.[3] Although solid-state reactions have clear advantages, the toolbox of molecules and reactions that can be conducted in the solid phase are significantly less numerous when compared to liquid-phase reactions. Simultaneously expanding the solid-state toolbox[4] and performing reactions efficiently would be beneficial for both organic synthesis and for preparing novel materials with unique applications (e.g., ligands, photo-responsive actuators).[5]

Schmidt proposed requirements that should generally be met for reactions to occur in the solid state, namely that the reacting atoms lie nearly coplanar and be separated by 4.2 Å or less.[6] Although there are exceptions to these rules,[7] they serve as good guidelines for investigating solid-state reactions. While some molecules happen to crystallize in arrangements that are suitable for solid-state reactions,[8] many molecules do not. Thus, templating strategies have been developed to direct the self-assembly of reactive functional groups into the proper orientation for reactions to occur.[9]



Scheme 1. Molecular structures of AnThio and solid-state [4+4] photocycloaddition reaction to the corresponding cycloadduct, AnThio CA. The cycloreversion occurs with heat or mechanical force, also in the solid state.

We sought to investigate the solid-state [4+4] cycloaddition reactivity of the compound anthracene-9-thiocarboxamide (AnThio, Scheme 1). Although AnThio is commercially available, we were surprised that the X-ray crystal structure of the compound was unknown.[10] Upon characterizing AnThio by single-crystal X-ray diffraction, we found that the molecule crystallized in an arrangement suitable for a [4+4] cycloaddition, without a need to use templating strategies. We show that AnThio undergoes the solid-state cycloaddition to near quantitative yield and further demonstrate that the cyclization is reversible using heat or mechanical force. Recrystallization of the CA to confirm molecular structure demonstrated that AnThio CA is highly solvatomorphic due to the availability of unused strong hydrogen-bond donors, which form hydrogen bonds with solvent molecules. Due to the wide range of solvents that the CA crystallizes with, we investigated the possibility of industrially-relevant separations,[11] and found that the CA crystallizes with thiophene, benzene, and xylene isomers. Moreover, we show that the CA can thermally stabilize liquid compounds that are not typically used as solvents, such as vinyl-containing monomers.

Results and Discussion

Solid-state structure and reactivity of AnThio

Commercially-obtained AnThio was recrystallized from ethyl acetate to obtain single crystals suitable for single-crystal X-ray diffraction analysis. AnThio crystallized in the triclinic space group, $P\bar{1}$, with two unique molecules in the asymmetric unit. The thiocarboxamide group of AnThio forms a hydrogen-bonded dimer,[12] and there is an extra hydrogen-bond-donor (NH) on each group that does not participate in the dimer, similar to amide functional groups. In accordance with Etter's rules,[13] all strong hydrogen-bond donors and acceptors should be used in hydrogen-bonding interactions. In the case of AnThio, this additional hydrogen-bond donor interacts with the pi system of a neighboring anthracene moiety as there is no steric hindrance around the thiocarboxamide group (Figure 1). AnThio likely crystallized with two unique molecules in the asymmetric unit because the pi systems of each unique molecule serve as acceptors for the two unused NH groups. Each AnThio molecule engages in discrete face-to-face pi-stacks, and forms a dimer with a neighboring AnThio molecule, and the thiocarboxamide groups are oriented head-to-tail. The separation between the reactive carbons is ca. 3.69 and 3.66 Å, which is favorable for a solid-state reaction to occur (Figure 1).

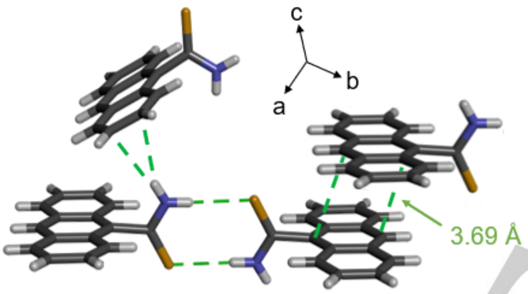


Figure 1. X-ray crystal structure of AnThio at 300 K highlighting the thiocarboxamide dimer, π-π distance, and the interaction of the additional hydrogen-bond donor (NH) with the pi system.

To determine if AnThio would undergo a [4+4] cycloaddition, both single crystals and a crystalline powder were placed in a photoreactor and exposed to 350 nm light. After six hours, a noticeable color change from bright yellow to orange-brown was observed (Figure 2). The single crystals did not retain crystallinity during the reaction. The powder was mixed ca. every four hours to ensure adequate exposure to light. Comparison of the ^{1}H NMR spectra of AnThio and the powder after exposure to UV light over the course of two days indicated that a solid-state [4+4] cycloaddition reaction had occurred (Figures S1-S4), affording a nearly quantitative yield of the anthracene-9-thiocarboxamide cycloadduct (AnThio CA, Scheme 1). This transformation could also be conducted using sunlight but required a longer reaction time (ca. 72 hours).

Spectroscopic and thermal characterization

AnThio CA was characterized using ^{13}C NMR spectroscopy (Figure S5). AnThio and AnThio CA were also characterized by infrared (IR) spectroscopy (Figure S9) and thermal methods (Figures S10-S12). The key structural change from AnThio to AnThio CA involves two sp^2 hybridized carbons converting to sp^3 hybridized carbons. This conversion is clearly shown in the ^{13}C NMR spectrum for AnThio CA, with peaks at 57 and 70 ppm that correspond to the dearomatized carbons. Furthermore, in the IR spectrum of the CA, the appearance of a small signal at 2944 cm^{-1} indicated the presence of a Csp^3-H bond. From thermogravimetric analysis (TGA), AnThio exhibits a decomposition onset at 209 °C, while the onset of decomposition for AnThio CA is lower (182 °C, Figure S10). From the differential thermal analysis (DTA) data, AnThio shows two exothermic signals at 229 °C and 288 °C (Figure S11), corresponding to the melting point and the decomposition of the material, respectively. AnThio CA shows three signals in the DTA, an endothermic signal at 191 °C, and two exothermic signals at 216 °C and 253 °C (Figure S12), with the exotherms exhibiting similar shape and temperature range to the exotherms for AnThio.

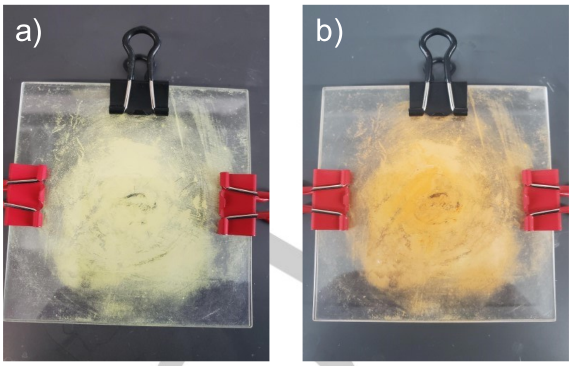


Figure 2. Image of the AnThio powder a) before and b) after exposure to UV light (350 nm) for six hours.

Cycloreversion

We determined that the endothermic signal in the DTA experiment corresponded to the cycloreversion (as follows). A powder sample of AnThio CA was placed in an aluminum pan and heated to 190 °C for 10 minutes using the DTA instrument. The resulting material appeared black, which is due to partial decomposition because of the overlap of the endotherm and decomposition onset temperatures. ^{1}H NMR spectroscopy performed on the material demonstrated reversion of AnThio CA to AnThio. The NMR spectrum also contained an impurity, which coincides with that from the bottle of the manufacturer (Figures S1, S6). This impurity is likely 9-anthracenecarbonitrile, as thiocarboxamides have been shown to undergo dehydrosulfurization to afford cyano groups.[14] Moreover, when we conducted long crystallization experiments using AnThio from the bottle, occassionally the corresponding nitrile was obtained.

Given the use of anthracene cycloadducts as mechanophores for force-induced chain scission of polymers,[15] we also exposed AnThio CA to milling. Indeed, the cycloreversion also occurs with application of mechanical force (Figure S6). Importantly the [4+4] cycloaddition and cycloreversion can both be conducted in the solid state, i.e., the reactions are green transformations. However, the material is unable to go through multiple cycles of dimerization and reversion because crystallinity is not retained through the process.

Behavior of 9-substituted anthracenes and their cycloadducts

The [4+4] cycloadditions of 9-substituted anthracene derivatives have been investigated for several decades. Specifically, two derivatives stand out as being structurally analogous to AnThio because the functional groups engage in hydrogen-bonded dimers, namely, anthracene-9-carboxylic acid and anthracene-9-carboxamide. In the case of anthracene-9-carboxylic acid, in the solid-state, the acid group engages in a discrete hydrogen-bonded dimer and the anthacenes form infinite pi stacks with acid groups arranged head-to-head. Irradiation of anthracene-9-carboxylic acid in the solid-state leads to formation of a metastable head-to-head CA that dissociates back into starting material.[5a, 16] On the other hand, the solution-state cycloaddition of anthracene-9-carboxylic acid affords the head-to-tail CA.[17] In the solid state, the compound anthracene-9-carboxamide has the amide groups arranged head-to-tail and reacts to afford the head-to-tail CA.[17] Only the unit cell parameters for anthracene-9-carboxamide are available, and the X-ray structure for anthracene-9-carboxamide CA is unknown; thus, although the amide groups would be expected to engage in hydrogen-bonded dimers, complete structural data is not available.

Crystallization of AnThio CA to confirm connectivity demonstrated that the cycloadduct lies in the head-to-tail geometry and is highly solvatomorphic (16 obtained solvatomorphs total, vide infra). AnThio CA contains two thiocarboxamide groups per molecule; thus, there are two additional NH donors on the molecule (instead of one in AnThio). The presence of unused donors adjacent to the dimer leads to solvatomorphism.

Solvatomorphism has been observed for anthracene-9-carboxylic acid CA with solvents that contain oxygen atoms.[18] The non-solvated form of the anthracene-9-carboxylic acid CA has also been successfully obtained, and the acid groups engage in hydrogen-bonded dimers to form 1D chains. The difference between the anthracene-9-carboxylic acid CA and AnThio CA is that carboxylic acid dimers can form without any donor atoms left unused. Here, AnThio CA contains two thiocarboxamide groups; thus, there are two unused NH donors on the molecule. The presence of unused donors adjacent to the dimer leads to significant solvatomorphism because a variety of solvent molecules are able to access the sterically-hindered, unused NH groups to act as hydrogen-bond acceptors. To follow Etter's rules,[13] a non-solvated structure of AnThio CA would likely require a group on a symmetry generated molecule (e.g., sulfur, pi) to interact with the unused NH;[19] however, the sterics of the CA make this challenging.

Solvatomorphism of AnThio CA

Crystallization of AnThio CA yielded solvated crystals (Figures S15-S31) upon crystallization from solvents with oxygen acceptors (THF, 1,4-dioxane, DMF, DMSO (three different DMSO forms: α, β, and hydrate)), nitrogen acceptors (pyridine and pyrimidine), and pi acceptors (toluene, chlorobenzene, bromobenzene, benzene, thiophene, *o*-xylene, *m*-xylene, and *p*-xylene) (Figure 3). We isolated a total of 16 solvatomorphs from 14 different solvents that included AnThio CA. Attempts were made to crystallize AnThio CA from acetone, ethyl acetate, diethyl ether, furan, and ethylbenzene, but experiments did not afford crystalline material.

The solvatomorphic structures with AnThio CA can be broken down into four different classes based on their supramolecular structures: linear one-dimensional (1D) thiocarboxamide dimer chains, non-linear 1D thiocarboxamide dimer chains, hydrogen-bonded networks, and interstitial solvent channels (Figure 3). Similar to AnThio and other molecules with a thiocarboxamide functional group,[12b] the thiocarboxamide dimer is persistent in nearly all of the AnThio CA solvatomorph structures.

For the first supramolecular class, linear 1D thiocarboxamide dimer chains, the AnThio CA molecules self-assemble into an infinite 1D chain sustained by thiocarboxamide dimers. The free NH hydrogen-bond donor interacts with either a heteroatom on the solvent molecule or the pi system of the solvent (Figure 4). In this packing motif, solvatomorphs with THF, dioxane, DMF, DMSO (β form, formula AnThio CA·2DMSO), benzene, thiophene, and *p*-xylene were found (Figures S32-S37). In the THF, dioxane, DMF, and DMSO solvatomorphs, the oxygen atoms of each solvent interact with the unused NH group of the AnThio CA. In the case of dioxane that has two heteroatoms capable of interacting with the NH, the second oxygen participates in C-H···O hydrogen bonds with an adjacent dioxane molecule (Figure S38).‡,[10] In the benzene, thiophene, and *p*-xylene solvatomorphs, the free NH group interacts with the pi system of each solvent, and interstitial solvent is also present in these solids.

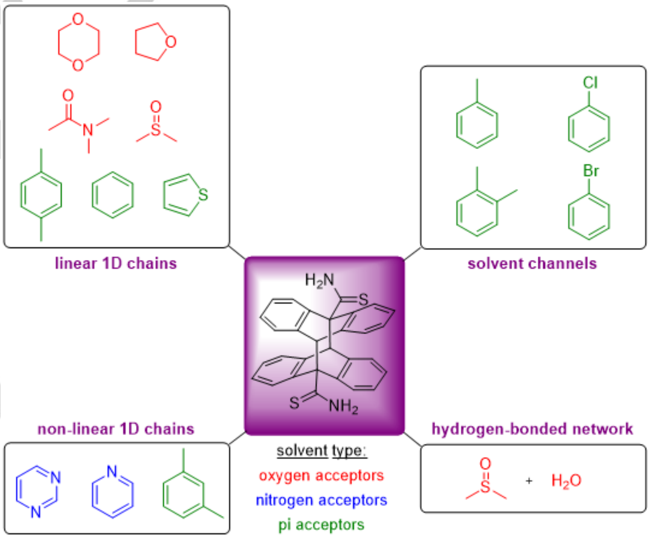


Figure 3. Supramolecular structure class and acceptor type for each solvatomorph.

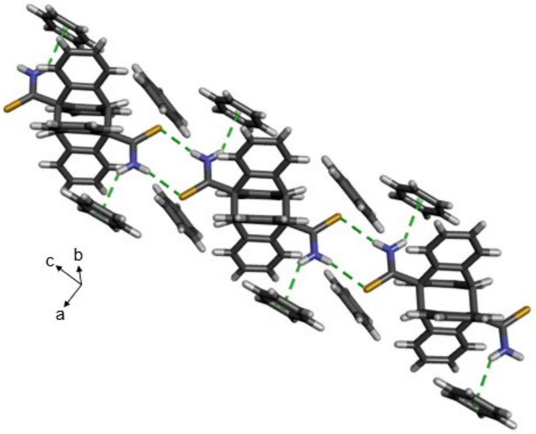


Figure 4. General crystal packing of the linear 1D thiocarboxamide dimer chain structure shown with benzene as an example, which also includes interstitial solvent.

The second supramolecular class is based on non-linear 1D thiocarboxamide dimer chains. This class is nearly identical to the first class; however, the CAs are rotated from linearity by 56-68°, depending on the solvent (Figure 5). The solvatomorphs that crystallize in this motif are pyridine, pyrimidine, and *m*-xylene (Figures S39-S40). In the case of pyrimidine, which has two heteroatoms capable of participating in hydrogen bonds, the second nitrogen atom engages in a C-H···N hydrogen bond with an adjacent pyrimidine molecule, similar to the behavior of dioxane (Figure S41).

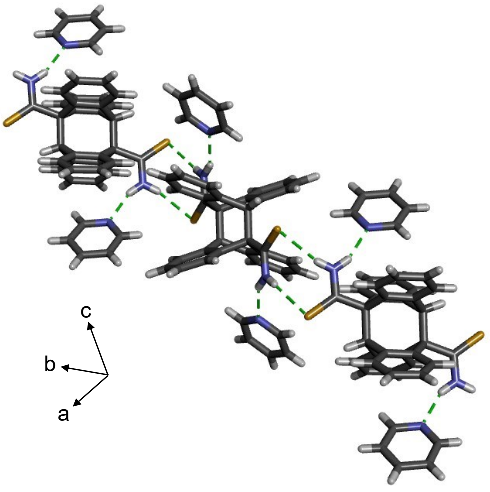


Figure 5. General crystal packing of the non-linear 1D thiocarboxamide dimer chain structure shown with pyridine as an example.

The third supramolecular class is based on hydrogen-bonded networks. Only the solvatomorphs with DMSO crystallized in this motif, specifically the α form (formula AnThio CA·2DMSO) and the hydrate form (formula AnThio CA·4DMSO·0.3H_2O). Unexpectedly, the thiocarboxamide dimer is completely absent in this structural motif. Instead, an $R_4^2(8)$ hydrogen-bonded ring involving the thionyl group of DMSO and the amine group of the thiocarboxamide forms (Figure 6). In the α form, the CAs are rotated from linearity by 15.3°, while the hydrate form is linear. In the hydrate form, DMSO molecules and partially occupied water lie on each side of the hydrogen-bond network, which form a solvent channel running nearly parallel to the crystallographic *b* axis (Figure S42).

The final supramolecular structure is based on interstitial solvent channels. In this structure class, the solvent does not interact with the free NH hydrogen-bond donor. Instead, the solvent fills interstitial space, which allows the free NH to interact with the pi system of a neighboring CA (Figure S43), similar to the structure of AnThio (Figure 7). The solvatomorphs in this class include toluene, chlorobenzene, bromobenzene, and o-xylene (Figures S44-S46). To visualize the channels, they are shown with voids in Figure S47.

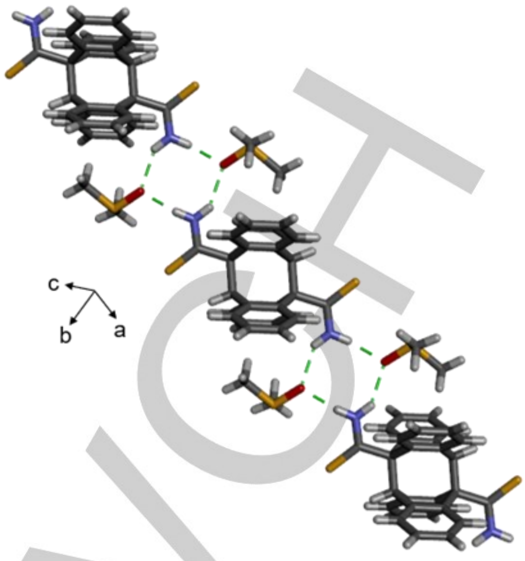


Figure 6. Crystal packing for the third supramolecular structure with DMSO, showing the hydrogen-bonded network facilitated through the thionyl and amine groups.

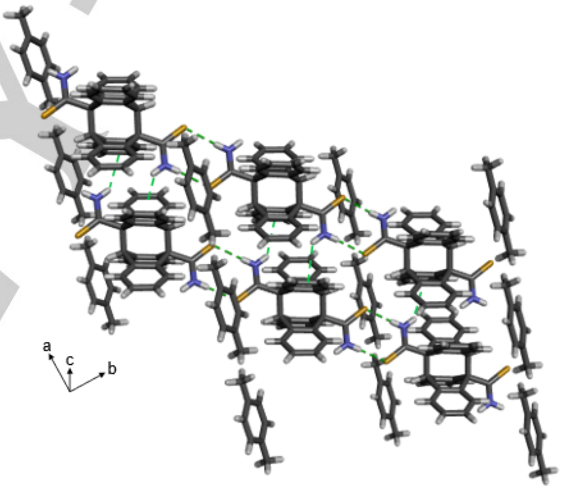


Figure 7. General crystal packing of the interstitial solvent structures with toluene as an example. The toluene sits on an inversion center, so each methyl group is only half occupied.

Solvent separation experiments

Given the highly solvatomorphic nature of AnThio CA, we sought to determine if selective crystallization with benzene or thiophene, as well as xylene isomers was possible. The solvatomorphs with benzene and thiophene both fall into the first class, linear 1D thiocarboxamide dimer chains that contain interstitial solvent. Interestingly, a CSD search for thiophene demonstrated that there have only been ca. 25 organic molecules shown to crystallize with thiophene, whereas over 3,300 have been shown to crystallize with benzene.[10] This is clearly due to the more common use of benzene as a solvent, but it is interesting to note that AnThio CA crystallizes with both.

When AnThio CA was dissolved in an equimolar mixture of benzene and thiophene, the CA crystallizes unselectively with either solvent as evidenced by ^1H NMR spectroscopy (Table S8).

Upon filtration of the solid, addition of more AnThio CA, heating, and recrystallization, the solution still showed a nearly equimolar mixture of benzene and thiophene (Figures S7-S8, Table S8).

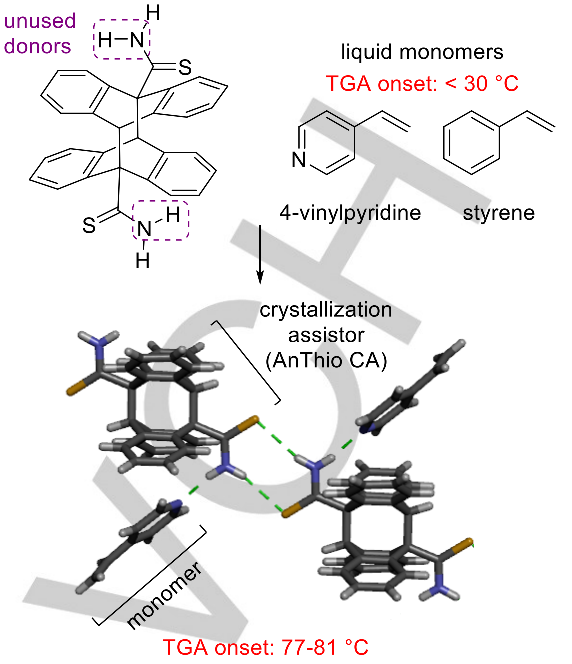
The solvatomorphs with the xylene isomers fall into three different classes, which we anticipated may result in selectivity of one or two of the xylene solvatomorphs due to differences in packing associated with the different classes. When AnThio CA was dissolved in an equimolar mixture of *o*-, *m*-, and *p*-xylene, no selectivity was observed. Only a few very small crystals formed, which could not be characterized by SCXRD. Overlap of xylene isomer peaks in the ^{1}H NMR spectra also prohibited determination of separation. Additionally, when two of the three xylene isomers were used, only a few of the same type of small crystals formed.

Volatile liquid stabilization

Lastly, we sought to determine if we could thermally stabilize other liquids through crystallization that are not typically used as solvents[20] (Scheme 2). We chose the monomers styrene and 4-vinylpyridine. A CSD search for organic compounds demonstrated that there are only nine crystal structures that include 4-vinylpyridine and only 15 that include styrene, although there is no report of a material that crystallizes with both 4-vinylpyridine and styrene. Indeed, crystallization of the two liquids with AnThio CA was successful, making it the first compound to form complexes with both monomers into a solid phase. The complex with 4-vinylpyridine falls into class 1 (linear 1D thiocarboxamide dimer chains), while the complex with styrene falls into class 4 (interstitial solvent channels) (Figures S48-S49). TGA data conducted for the monomer-included complexes demonstrated that the loss of monomer from the crystal lattice occurred at ca. 52-56 °C higher than the decomposition onset of free monomer (Figures S13-S14). Thus, AnThio CA serves to thermally stabilize both monomers by preventing volatilization.

Conclusion

Herein, we have determined the X-ray crystal structure of commercially-available anthracene-9-thiocarboxamide for the first time. The anthracene moieties are properly aligned for a solid-state [4+4] cycloaddition reaction. We demonstrated near quantitative yield via exposure to UV light, which affords the corresponding AnThio CA in a green reaction. Moreover, the photocycloaddition is reversible, albeit with slight product decomposition, using either heat or force in the solid state. Furthermore, we demonstrated that AnThio CA crystallizes with a wide variety of structurally-diverse solvents that act as hydrogen-bond acceptors due to the presence of two sterically-hindered and unused strong hydrogen-bond donor groups. Based on the wide range of solvents the CA crystallizes with, we attempted separation of difficult-to-separate solvents. Although no preference for solvents was achieved, we expect that similar materials with unused hydrogen-bond donors could be tuned to achieve separations. We also showed that AnThio CA can thermally stabilize liquid monomers in the crystalline state. The facile synthesis, reversibility, strong hydrogen bond donors, and unique solvatomorphic properties of AnThio CA make it an interesting candidate for incorporation into framework or polymer materials, as well as multi-component solids.



Scheme 2. General strategy toward employing unused donor groups to aid in crystallization and thermal stabilization of volatile, non-solvent liquids, e.g., monomers.

Experimental Section

Materials: Anthracene-9-thiocarboxamide (AnThio), 1,4-dioxane (dioxane), o-, m-, and p-xylene were purchased from Oakwood Chemical. Ethyl acetate, tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), toluene, and chlorobenzene were purchased from Fisher Chemical. Pyridine (anhydrous), pyrimidine, thiophene (benzene free), styrene, and 4-vinylpyridine were purchased from Acros Organics. Dimethylsulfoxide was purchased from Calbiochem. Benzene was purchased from EMD Millipore. Bromobenzene was purchased from Sigma-Aldrich. All reagents were used as received.

Instrumentation for Synthesis and Characterization: Single crystal X-ray data were collected on a Rigaku XtaLAB Synergy-iKappa diffractometer equipped with a PhotonJet-i X-ray source operated at 50 W (50 kV, 1 mA) to generate Cu Kα radiation (λ = 1.54178 Å), and a HyPix-6000HE HPC (hybrid photon counting) detector. NMR data was collected using a JOEL ECS 400 MHz Spectrometer. FTIR spectra were recorded on a Nicolet iS10 infrared spectrometer using an ATR attachment equipped with a diamond crystal. TGA and DTA data were collected simultaneously on a Shimadzu DTG-60H instrument. Optical images were collected on a Leica DM2700 M microscope equipped with a Leica MC170 HD microscope camera. A FlackTek SpeedMixer 330-100 SE purchased from FlackTek manufacturing was used for milling. Experiments were conducted in 15 mL stainless steel jars with two 7 mm stainless steel grinding balls using a custom holder acquired from FlackTek.

Crystallization of AnThio: Single crystals were grown using the slow evaporation method with ethyl acetate. 40 mg of AnThio was dissolved in 4 mL of ethyl acetate. The vial was left in the dark and allowed to slowly evaporate over the course of 5 days, after which time crystallization of AnThio was complete.

Cycloaddition Reactions: Cycloaddition reactions were conducted by placing approximately 40 mg of powder of crystalline AnThio (either from the manufacturer's bottle or recrystallized from ethyl acetate) between two 3"x3" quartz glass plates and then exposed to light using either a Rayonet photoreactor equipped with 300, 350, or 419 nm lamps, or using sunlight. Reactions using the photoreactor took approximately 12 hours (with occasional rearrangement to expose all material to light), whereas reactions using sunlight took ca. 72 hours of exposure to sunlight. The cycloadduct was typically used without purification, except for characterization, where the material was washed with ethyl acetate and allowed to dry.

General Procedure for Crystallization of Solvatomorphs: Single crystals of each solvatomorph were grown by dissolving approximately 0.0150 g of AnThio CA in 2-3 mL of the respective solvent. The solutions were heated to near the boiling point of the solvent to dissolve the solid, and any remaining solid was filtered through a pipette with a cotton plug. The vials were sealed tightly and left undisturbed for approximately 24 hours. After this time, the vials were inspected, and typically single crystals suitable for X-ray diffraction had formed.

Notes on AnThio CA·DMSO β Solvatomorph: AnThio CA·DMSO β solvate crystals were grown by dissolving approximately 0.0150 g of cycloadduct in 2-3 mL of moist DMSO. Solutions were gently heated to dissolve the solid, and any remaining solid was filtered through a pipette with a cotton plug. The vial was sealed tightly and left undisturbed for approximately 24 hours. After this time, the vials were inspected for single crystals suitable for X-ray diffraction. This form seems to be metastable, where the crystals will redissolve and then reform as the hydrated DMSO solvate.

Notes on AnThio CA Monomer Crystallizations: For both styrene and 4-vinylpyridine crystals, approximately 0.0150 g of cycloadduct was dissolved in 2-3 mL of the respective solvent. The solutions were gently heated at ca. 40° C for 5 minutes to dissolve the solid but to minimize any potential polymerization. After this time the solution was filtered through a pipette with a cotton plug to remove any undissolved solid. The vials were tightly capped and covered with aluminum foil to prevent any possible polymerization. After 24-48 hours, single crystals suitable for X-ray diffraction had formed.

Ball Milling for Cycloreversion: Approximately 20 mg of AnThio CA was placed in a stainless-steel jar. The compound was milled at 1500 rpm for a period of 5 or 15 min.

Supporting Information

See the Supporting Information for the preparation and characterization of all compounds, X-ray data, IR spectra, NMR spectra, thermal data, optical microscope images, and additional crystal packing figures.

Deposition Numbers 2259231-2259249 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe https://www.ccdc.cam.ac.uk/structures. The authors have cited additional references within the Supporting Information.[21]

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Conflicts of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: crystal engineering • cycloaddition • solid-state reaction • solvatomorphs • supramolecular

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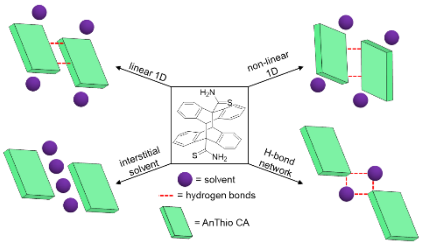

The solid-state [4+4] cycloaddition of a commercially available anthracene derivative affords facile synthesis of a cycloadduct. The cycloaddition is reversible in the solid-state using heat or mechanical force. The cycloadduct is highly solvatomorphic due to presence of unused, strong hydrogen-bond donors and is applied to the thermal stabilization of monomers.

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