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Crystal structure and supramolecular assembly of a hydrogen-bonded cocrystal of 2-fluoro-*N*-(pyrrolidine-1-carbonothioyl)benzamide and 1,3,5-triazinane-2,4,6-trithione

 Ahmad Yahaya ¹, Ummuhan Solmaz ^{1,2,*} and Hakan Arslan ¹
¹ Department of Chemistry, Faculty of Science, Mersin University, Mersin TR 33343, Türkiye² Department of Chemistry and Chemical Processing Technologies, Technical Science Vocational School, Mersin University, Mersin TR 33343, Türkiye

* Corresponding author at: Department of Chemistry and Chemical Processing Technologies, Technical Science Vocational School, Mersin University, Mersin TR 33343, Türkiye.

e-mail: ummuhan.solmaz@mersin.edu.tr (U. Solmaz).

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ABSTRACT

An unexpected 1:1 cocrystal of 2-fluoro-*N*-(pyrrolidine-1-carbonothioyl)benzamide and 1,3,5-triazinane-2,4,6-trithione (trithiocyanuric acid, TTCA) was isolated during an attempted synthesis of the single-component benzoylthiourea derivative and characterized by single-crystal X-ray diffraction. The compound crystallizes in the triclinic space group *P*-1 with one molecule of each component in the asymmetric unit. The fluorinated benzamide derivative adopts a non-planar conformation in which the carbonyl-bearing fragment is twisted relative to the aromatic ring, while the pyrrolidine ring is puckered. The trithione component is nearly planar and displays narrow ranges of C-S and C-N distances, consistent with delocalization within the heterocyclic framework. A nearly linear N3-H3...O1 hydrogen bond [N...O = 2.932(3) Å, N-H...O = 171(3)°] forms a heteromolecular associate. Further N-H...S contacts connect symmetry-related components, producing an extended hydrogen-bonded arrangement supplemented by weaker C-H...S and C-H...F contacts. The crystal packing is governed by cooperative N-H...O and N-H...S interactions.

KEYWORDS

 Cocrystal
 Trithione
 Acylthiourea
 Hydrogen bonding
 Supramolecular assembly
 Single-crystal X-ray diffraction
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1. Introduction

Acylthioureas are versatile sulfur- and nitrogen-containing molecular frameworks whose carbonyl, thiocarbonyl, and N-H sites support extensive conformational and supramolecular diversity. Their structural chemistry has been reviewed in the context of synthesis, coordination behavior, molecular recognition, and applications [1-4]. The competition and cooperation between N-H...O and N-H...S hydrogen bonds are particularly important because small changes in substitution, conformation, or coformer identity can redirect the resulting crystal packing.

Crystallographic studies of acylthiourea derivatives show that classical hydrogen bonds are commonly accompanied by C-H...O, C-H...S, C-H...π, and other weak contacts, producing diverse supramolecular assemblies [5-8]. Fluoro substitution and cyclic N-substitution can modify the conformational preferences of benzoylthiourea derivatives [7].

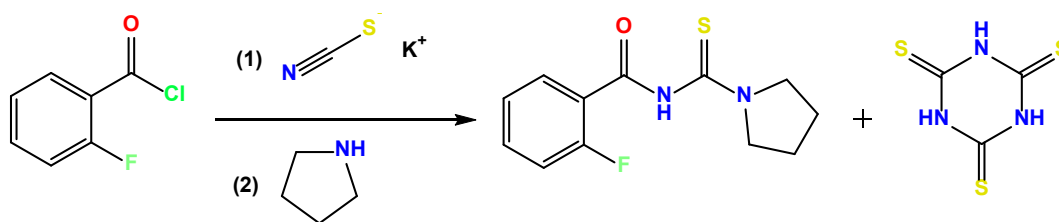
Trithiocyanuric acid (TTCA; 1,3,5-triazinane-2,4,6-trithione), in its neutral all-thione form, presents three N-H donors and three thione-S acceptor sites in a compact, approximately planar framework. Its crystal chemistry is dominated by self-complementary N-H...S association, frequently through

centrosymmetric $R_2^2(8)$ motifs, while one or more donors may engage coformer acceptors [9-13]. Pairing this sulfur-rich coformer with a fluorinated acylthiourea therefore provides multiple, chemically differentiated hydrogen-bonding possibilities.

The possible formation of TTCA from thiocyanate-derived species has a historical chemical basis. Martin et al. described cyclotrimerization within the thiocyanic acid/isothiocyanic acid system to 1,3,5-triazine-2,4,6-trithiol, which is tautomeric related to the all-thione TTCA form observed crystallographically [14]. Competition with linear polymerization was also reported; these data establish chemical feasibility but do not define the reaction pathway under the present conditions.

TTCA forms multicomponent crystals with diverse N- and O-donor coformers while retaining recurrent N-H...S motifs [11,12,15]. The carbonyl and thiocarbonyl groups of the target benzoylthiourea provide complementary recognition sites for TTCA in the crystalline phase.

Accordingly, the present study examines the tautomeric form of TTCA, the donor-acceptor contacts defining the 1:1 assembly, and the conformational consequences of ortho fluorination and cyclic N-substitution relative to the closest reported benzoyl-



Scheme 1. Synthesis of the cocrystal (TTCA and 2-fluoro-*N*-(pyrrolidine-1-carbonothioyl)benzamide).

thiourea·TTCA analogue [13].

A particularly relevant precedent is the 1:1 cocrystal of *N*-carbamothioylbenzamide and TTCA reported by Aziz *et al.* [13]. That structure contains the same benzoylthiourea carbonyl/thiocarbonyl recognition platform and the same TTCA coformer as the present crystal, but lacks the ortho-fluoro substituent and cyclic *N*-substitution. It therefore provides a close reference for evaluating how fluorination and incorporation of pyrrolidine alter conformation, hydrogen-bond geometry, and crystal symmetry.

The synthetic procedure was undertaken to prepare 2-fluoro-*N*-(pyrrolidine-1-carbonothioyl)benzamide through sequential formation of the corresponding 2-fluorobenzoyl isothiocyanate intermediate from 2-fluorobenzoyl chloride and potassium thiocyanate, followed by reaction with pyrrolidine. The intended outcome was the discrete, single-component benzoylthiourea derivative, and TTCA was not introduced as a reagent or cocrystal coformer at any stage of the synthesis or crystallization. However, single-crystal X-ray diffraction of a crystal obtained from the recrystallized material established that the target benzoylthiourea had co-crystallized with 1,3,5-triazine-2,4,6-trithione in a 1:1 stoichiometric ratio.

2. Experimental

2.1. Instrumentation and materials

All chemicals and solvents were of commercial grade and were used without further purification. The isolated product was characterized by spectroscopic and crystallographic methods. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III Ultrashield Plus 400 spectrometer operating at 400 and 100 MHz, respectively. FT-IR spectra were recorded using a PerkinElmer Spectrum 100 spectrometer, and the UV-Vis absorption spectrum was measured on a Shimadzu UV-3100 spectrophotometer. The UV-Vis spectrum was recorded in DCM at a concentration of 4.66×10^{-5} mol L^{-1} using a 1-cm quartz cuvette. Single-crystal X-ray diffraction instrumentation and data-processing details are given in Section 2.3.

2.2. Synthesis and crystallization

The benzoylthiourea component was prepared by a one-pot, stepwise acyl isothiocyanate procedure derived from the classical synthesis of mono- and disubstituted benzoylthioureas [16]. Potassium thiocyanate (5.14 mmol, 1.10 equiv.) was introduced into anhydrous acetone (100 mL) in a two-necked flask, and the mixture was heated under reflux for 30 min. 2-Fluorobenzoyl chloride (4.7 mmol, 1.00 equiv.) was then added dropwise, and the mixture was maintained under reflux for 240 min to generate the corresponding benzoyl isothiocyanate intermediate in situ. Pyrrolidine (4.7 mmol, 1.00 equiv.) was added slowly, after which the reaction mixture was maintained at 50 °C for 120 min and subsequently stirred for a further 24 h. The reaction mixture was poured into 0.1 M aqueous HCl (500 mL). The resulting solid was isolated and washed five times with distilled water. The product was recrystallized from a 1:1 (v/v)

mixture of dichloromethane and ethanol at room temperature. Single crystals suitable for X-ray diffraction were obtained after 2 days (Scheme 1).

Cocrystal (TTCA and 2-fluoro-*N*-(pyrrolidine-1-carbonothioyl)benzamide): Isolated solid yield: 17% (based on 2-fluorobenzoyl chloride). FT-IR (ATR, cm^{-1}): 3277, 3129 $\nu(\text{N-H})$; 3095, 3038 $\nu(\text{C-H})_{\text{ar}}$; 2967, 2949, 2871 $\nu(\text{C-H})_{\text{aliph}}$; 1667 $\nu(\text{C=O})$; 1577, 1537, 1376, 1124 (characteristic vibrations of the thione form of TTCA); 1330, 1290, 1257, 1244 (coupled $\nu(\text{C-N})/\nu(\text{C=S})$); 1175, 1156 ($\nu(\text{C-F})/\nu(\text{C-N})$). ^1H NMR (400 MHz, acetone- d_6 , δ , ppm): 12.46 (s, 3H, NH_{TTCA}), 9.55 (s, 1H, NH), 7.85 (tt, $J = 7.6, 1.7$ Hz, 1H, Ar-H), 7.64 (dddd, $J = 8.3, 7.2, 5.2, 1.9$ Hz, 1H, Ar-H), 7.38–7.33 (m, 1H, Ar-H), 7.32–7.26 (m, 1H, Ar-H), 3.80–3.73 (m, 4H, N- CH_2), 2.07–2.03 (m, 4H, CH_2 ; overlapped with residual acetone- d_6). ^{13}C NMR (100 MHz, acetone- d_6 , δ , ppm): 176.29 (C=S, TTCA), 171.48 (C=S), 160.33 (C=O), 160.24 (d, $J = 250.2$ Hz, Ar-C-F), 133.91 (d, $J = 8.8$ Hz, Ar-C), 122.28 (d, $J = 13.1$ Hz, Ar-C), 116.23 (d, $J = 23.0$ Hz, Ar-C), 53.87, 52.05 (N-C), 25.89, 24.39 (CH_2).

2.3. Single-crystal X-ray diffraction

A colorless block-shaped crystal with dimensions $0.322 \times 0.185 \times 0.174$ mm was selected for diffraction analysis. Intensity data were collected at 298.15 K on a Bruker D8 VENTURE diffractometer equipped with a PHOTON 100 CMOS detector using Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å) and ω/ϕ scans. The data were reduced with SAINT v8.37A. A multi-scan absorption correction was applied with SADABS-2014/5, giving $T_{\text{min}} = 0.7018$ and $T_{\text{max}} = 0.7454$.

The structure was solved with SHELXT 2014/5 in the Olex2 environment [17,18] and refined by full-matrix least squares on F^2 with SHELXL 2013/4 [19]. All non-hydrogen atoms were refined anisotropically. Carbon-bound H atoms were placed in calculated positions and refined using riding models, whereas the N-bound H atoms were located and refined with individual isotropic displacement parameters. The final refinement used 3705 reflections, 252 parameters, and no restraints. Crystal data, data-collection parameters, and refinement statistics are summarized in Table 1.

2.4. Hirshfeld surface and interaction-energy calculations

Hirshfeld surface analysis was performed with CrystalExplorer 21 for the 2-fluoro-*N*-(pyrrolidine-1-carbonothioyl)benzamide component in its crystallographic environment [20,21]. Surfaces mapped over d_{norm} , d_i , d_e , curvedness, and shape index were examined together with two-dimensional fingerprint plots. The relative contributions of individual $\text{X}\cdots\text{Y}$ contacts were obtained by decomposition of the fingerprint plot. Contact enrichment ratios, $E_{\text{XY}} = C_{\text{XY}}/R_{\text{XY}}$, were calculated from the observed contact contribution C_{XY} and the corresponding random-contact proportion R_{XY} derived from the elemental surface fractions [22].

Table 1. Crystal data and structure-refinement parameters for the title cocrystal.

Parameter	Value
Empirical formula	C ₁₅ H ₁₆ FN ₅ OS ₄
Formula mass	429.57
Temperature (K)	298.15
Crystal habit / color	Block / colorless
Crystal size (mm)	0.322 × 0.185 × 0.174
Crystal system	Triclinic
Space group	<i>P</i> -1 (No. 2)
<i>a</i> (Å)	7.7315(3)
<i>b</i> (Å)	10.3242(4)
<i>c</i> (Å)	12.7277(5)
α (°)	84.532(2)
β (°)	80.022(2)
γ (°)	70.547(2)
<i>V</i> (Å ³)	942.69(6)
<i>Z</i> / <i>Z'</i>	2 / 1
ρ _{calc} (Mg m ⁻³)	1.513
μ (mm ⁻¹)	0.529
<i>F</i> (000)	444
Radiation	Mo Kα, λ = 0.71073 Å
Scan mode	ω and φ
θ range (°)	2.924–26.021
Index ranges	−9 ≤ <i>h</i> ≤ 9; −12 ≤ <i>k</i> ≤ 12; −15 ≤ <i>l</i> ≤ 15
Measured reflections	33,250
Independent reflections	3,705
Observed reflections	2,694 [<i>I</i> > 2σ(<i>I</i>)]
Rint / Rσ	0.0714 / 0.0338
Completeness	0.999
<i>T</i> _{min} / <i>T</i> _{max}	0.7018 / 0.7454
Data/restraints/parameters	3,705/0/252
Goodness-of-fit on <i>F</i> ²	1.020
<i>R</i> ₁ , <i>I</i> > 2σ(<i>I</i>)	0.0364
<i>wR</i> ₂ , all data	0.0876
Largest diff. peak/hole (e Å ⁻³)	+0.264 / −0.327

Pairwise intermolecular interaction energies were calculated in CrystalExplorer 21 using the B3LYP model at the B3LYP/6-31G(d,p) level [7,21]. The electrostatic, polarization, dispersion, and exchange-repulsion terms were scaled by 1.057, 0.740, 0.871, and 0.618, respectively. The molecular-pair table reports the color used in the cluster diagram, the number of symmetry-equivalent neighbors (*N*), the symmetry operation, and the centroid-to-centroid separation (*R*), following the reporting scheme used for the related fluoro-substituted benzoylthiourea [7].

3. Results and discussion

3.1. Synthetic outcome and cocrystal formation

The synthesis was undertaken to prepare 2-fluoro-*N*-(pyrrolidine-1-carbonothioyl)benzamide as a single-component benzoylthiourea derivative. In the stepwise one-pot route, reaction of potassium thiocyanate with 2-fluorobenzoyl chloride generated the corresponding benzoyl isothiocyanate intermediate, which subsequently reacted with pyrrolidine to afford the target acylthiourea framework. The reaction mixture was subjected to acidic work-up, and the isolated material was recrystallized at room temperature. Although TTCA was not intentionally introduced as a reagent or coformer, single-crystal X-ray diffraction showed that the selected crystal contained the target benzoylthiourea and TTCA in a 1:1 ratio. The crystallographically examined product is therefore assigned as a benzoylthiourea-TTCA cocrystal formed during the overall reaction, work-up, and crystallization sequence. An analogous unintended outcome was reported by Aziz *et al.*, who obtained an *N*-carbamothioylbenzamide-TTCA cocrystal although the synthesis was directed toward *N*-carbamothioylbenzamide [13]. This precedent demonstrates that unplanned TTCA incorporation can also occur in related thiocyanate-based acylthiourea syntheses.

A plausible origin of the TTCA component involves residual thiocyanate carried into the acidic precipitation step. Protonation

of SCN[−] after addition of HCl can generate the tautomeric thiocyanic acid/isothiocyanic acid system (HSCN/HNCS). Martin *et al.* reported that aqueous thiocyanic acid can undergo cyclotrimerization to 1,3,5-triazine-2,4,6-trithiol, the thiol tautomer of TTCA [14]. Their review also documented competition with linear polymerization; in the single in situ example discussed, 23% of the thiocyanic-acid-derived material formed the cyclic trimer and 77% formed a linear polymer [14]. These data establish the chemical feasibility of TTCA formation but do not define the product distribution or mechanism under the present experimental conditions. If generated during acidic work-up, reaction-derived TTCA could be incorporated into the crystalline phase through complementary N-H⋯O and N-H⋯S recognition, consistent with its established cocrystal chemistry [11,12,15].

The FT-IR spectrum of the cocrystal exhibits characteristic absorptions attributable to both the benzoylthiourea and TTCA components (Figure 1). The bands observed at 3277 and 3129 cm^{−1} are assigned to N-H stretching vibrations. The relatively low-frequency N-H absorption is consistent with the involvement of the N-H groups in hydrogen-bonding interactions, in agreement with the N-H⋯O and N-H⋯S contacts identified by single-crystal X-ray diffraction. Similar lowering of the N-H stretching frequency has been reported for acylthiourea derivatives containing intramolecular and intermolecular hydrogen bonds [23]. The absorptions at 3095 and 3038 cm^{−1} are assigned to aromatic C-H stretching vibrations of the benzoylthiourea component, whereas the bands at 2967, 2949, and 2871 cm^{−1} are predominantly associated with the aliphatic C-H stretching vibrations of the pyrrolidine ring. The strong band at 1667 cm^{−1} is assigned to ν(C=O) of the benzoylthiourea unit, consistent with hydrogen-bonded acylthiourea systems [23]. Notably, the bands at 1577, 1537, 1376, and 1124 cm^{−1} are characteristic of the thione form of TTCA, consistent with previous vibrational studies [24,25]. The bands in the 1330–1244 cm^{−1} region are attributed to coupled C-N/C=S vibrations, in accordance with the reported vibrational behaviour of TTCA [26].

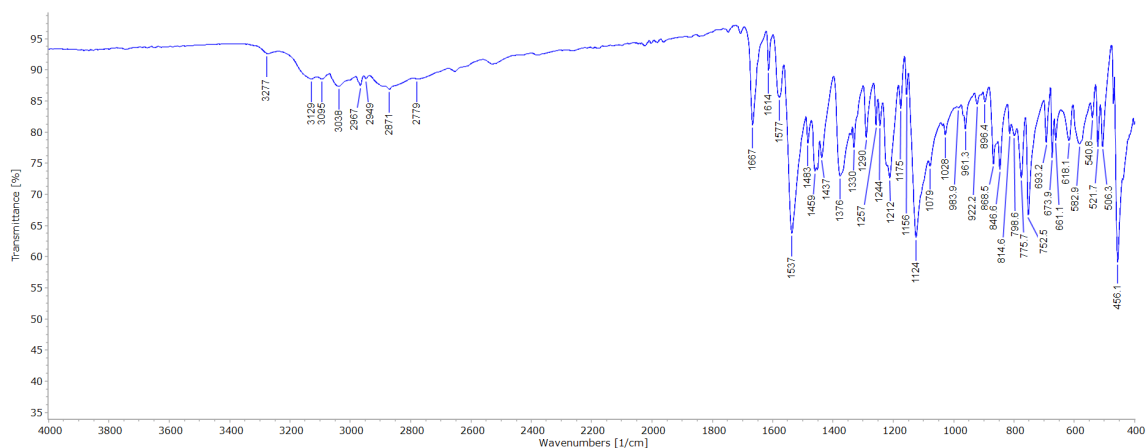


Figure 1. FT-IR spectrum of the cocrystal (TTCA and 2-fluoro-*N*-(pyrrolidine-1-carbonothioyl)benzamide).

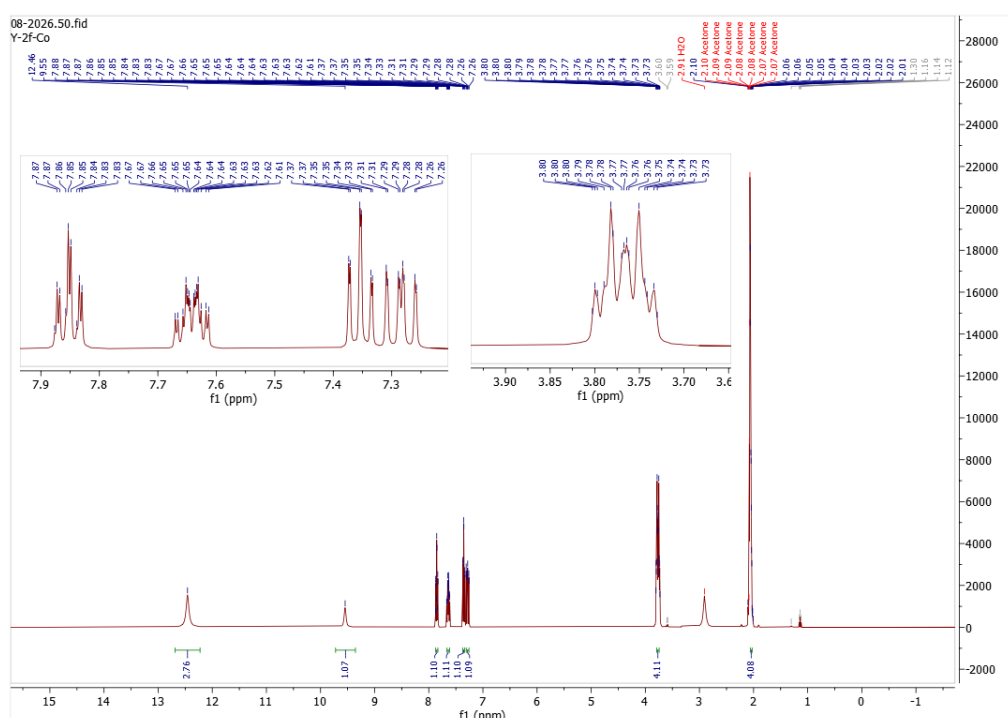


Figure 2. ^1H NMR spectrum of the isolated solid sample (TTCA and 2-fluoro-*N*-(pyrrolidine-1-carbonothioyl)benzamide).

The spectroscopic features are consistent with the molecular structure and hydrogen-bonding pattern established by single-crystal X-ray diffraction.

The ^1H NMR spectrum of the isolated sample recorded in acetone- d_6 displays a markedly downfield singlet at δ 12.46 ppm integrating for three protons, assigned to the three N-H protons of the TTCA component (Figure 2). Their appearance as a single resonance is consistent with the solution-state behaviour reported for TTCA, in which the three N-H protons are observed as an equivalent set [25]. The benzoylthiourea N-H proton appears separately at δ 9.55 ppm, clearly distinguishing the N-H environments of the two cocrystal components. The four aromatic protons of the 2-fluorophenyl ring resonate in the δ 7.85–7.26 ppm region with complex splitting patterns arising from combined H–H and H–F couplings. The pyrrolidine N-CH $_2$ protons are observed as a multiplet at δ 3.80–3.73 ppm (4H), whereas the remaining CH $_2$ protons occur at δ 2.06–2.03 ppm. Although partially obscured by the residual acetone- d_6 signal,

this resonance is assigned to the remaining pyrrolidine CH $_2$ protons.

The ^{13}C NMR spectrum of the isolated sample further confirms the presence of both TTCA and benzoylthiourea components (Figure 3). The resonance at δ 176.29 ppm is assigned to the equivalent C=S carbons of TTCA, whereas the thiocarbonyl carbon of the benzoylthiourea unit appears at δ 171.48 ppm. The carbonyl carbon resonates at δ 160.33 ppm. The ipso carbon bonded to fluorine is observed at δ 160.24 ppm as a doublet with a large $^1\text{J}(\text{C},\text{F})$ coupling constant of 250.2 Hz, characteristic of a directly bonded Ar–C–F carbon. The remaining fluorinated aromatic carbons appear at δ 133.91, 122.28, and 116.23 ppm and display smaller C–F coupling constants ($J = 8.8$ –23.0 Hz), consistent with longer-range $^2\text{J}/^3\text{J}(\text{C},\text{F})$ interactions. The pyrrolidine carbons directly attached to nitrogen resonate at δ 53.87 and 52.05 ppm, while the remaining aliphatic carbons are observed at δ 25.89 and 24.39 ppm.

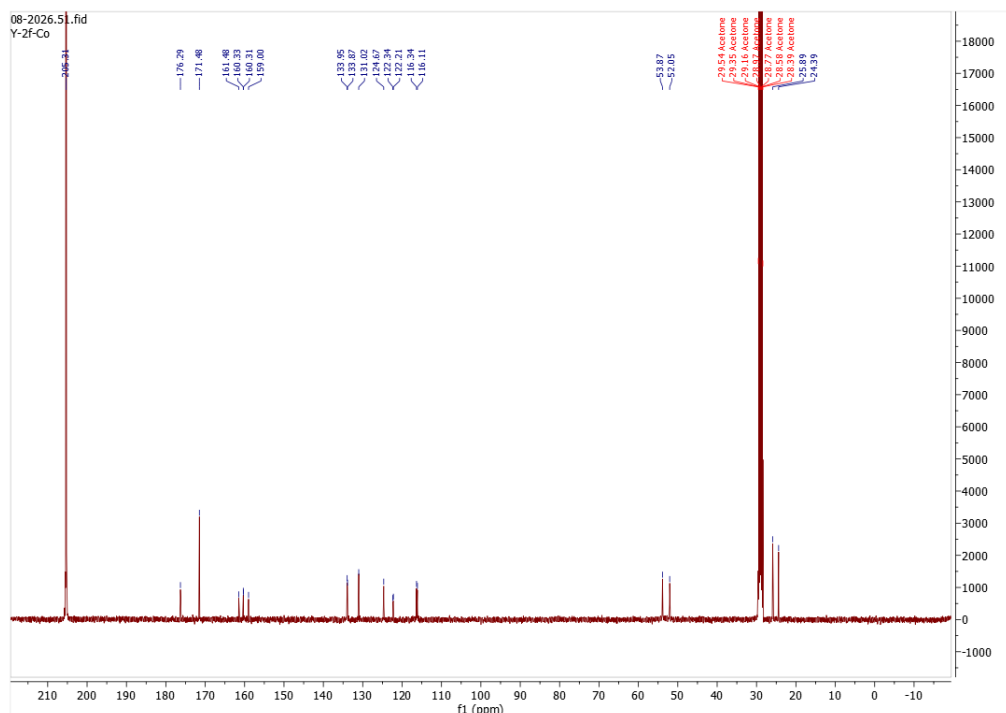


Figure 3. ^{13}C NMR spectrum of the isolated solid sample (TTCA and 2-fluoro-*N*-(pyrrolidine-1-carbonothioyl)benzamide).

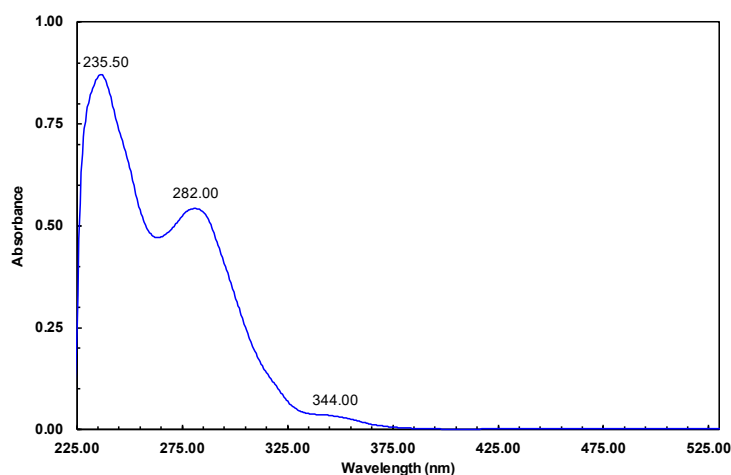


Figure 4. UV-Vis spectrum of the isolated solid sample (TTCA and 2-fluoro-*N*-(pyrrolidine-1-carbonothioyl)benzamide).

The UV-Vis spectrum of the cocrystal exhibits absorption maxima at 235.5 and 282.0 nm, together with a weak broad feature near 344 nm (Figure 4). The intense band at 235.5 nm is assigned predominantly to $\pi \rightarrow \pi^*$ transitions within the aromatic and conjugated framework [27]. The absorption at 282.0 nm is consistent with an intraligand transition involving the acylthiourea chromophore, with contributions from both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ excitation remaining possible [28,29]. The weak broad feature near 344 nm may involve a lower-energy $n \rightarrow \pi^*$ transition associated with the carbonyl and thiocarbonyl chromophores; however, its assignment remains tentative [28,29].

3.2. Crystal structure description

The cocrystal has the composition $\text{C}_{12}\text{H}_{13}\text{FN}_2\text{OS} \cdot \text{C}_3\text{H}_3\text{N}_3\text{S}_3$ and crystallizes in *P*-1. One molecule of each component is present in

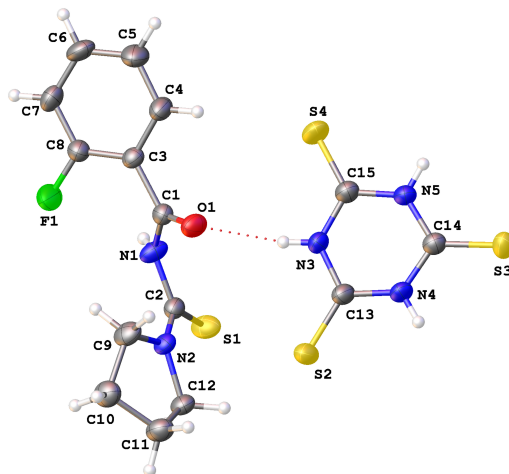
the asymmetric unit ($Z' = 1$), and inversion generates the second formula unit in the unit cell. The molecular structures and atom-numbering scheme are shown in Figure 5.

Within the benzoylthiourea component, the $\text{C1}=\text{O1}$ and $\text{C2}=\text{S1}$ distances are 1.222(3) and 1.673(2) Å, respectively. The $\text{N2}-\text{C2}$ distance of 1.312(3) Å is shorter than $\text{N1}-\text{C2}$ [1.402(3) Å], consistent with unequal delocalization across the substituted thiourea unit. The $\text{O1}-\text{C1}-\text{N1}$ and $\text{O1}-\text{C1}-\text{C3}$ angles are 122.7(2) and 122.0(2)°, respectively.

The short $\text{N2}-\text{C2}$ bond is consistent with conjugation between the pyrrolidine nitrogen and the $\text{C}=\text{S}$ group. In contrast, the longer $\text{N1}-\text{C2}$ bond and the $\text{C1}-\text{N1}-\text{C2}-\text{S1}$ torsion show that conjugation across the complete $\text{O}=\text{C}-\text{N}-\text{C}(=\text{S})-\text{N}$ sequence is interrupted by twisting. This conformation is associated with *N*-substitution and the ortho-fluorobenzoyl environment.

Table 2. Selected bond lengths, bond angles, and torsion angles for the title cocrystal ($\text{\AA}$, $^\circ$).

Parameter	Value	Parameter	Value
O1-C1	1.222(3)	C2-N1-C1-O1	3.2(4)
S1-C2	1.673(2)	C1-N1-C2-S1	-130.7(2)
N2-C2	1.312(3)	C12-N2-C2-S1	1.5(3)
N1-C1	1.363(3)	O1-C1-C3-C4	35.4(3)
N1-C2	1.402(3)	F1-C8-C3-C4	-179.8(2)
F1-C8	1.355(3)	N2-C9-C10-C11	36.2(2)
S2-C13	1.642(2)	C9-C10-C11-C12	-40.8(3)
S3-C14	1.643(2)	C10-C11-C12-N2	29.0(2)
S4-C15	1.628(2)	S2-C13-N4-C14	-175.5(2)
N5-C14	1.356(3)	N5-C14-N4-C13	-6.2(4)
O1-C1-N1	122.7(2)	N2-C2-S1	123.88(17)
N2-C2-N1	117.4(2)	N1-C2-S1	118.60(17)

**Figure 5.** Molecular structures and atom-numbering scheme of the two components in the asymmetric unit of the 1:1 cocrystal. Displacement ellipsoids are drawn at the 50% probability level. The N3-H3...O1 heteromolecular hydrogen bond is shown as a dashed line.

The six-membered aromatic ring is essentially planar. The fluorine substituent lies close to the ring plane, as shown by $\text{F1-C8-C3-C4} = -179.8(2)^\circ$. In contrast, the benzamide carbonyl group is rotated relative to the ring: O1-C1-C3-C4 and N1-C1-C3-C8 are $35.4(3)$ and $38.4(3)^\circ$, respectively. This twist reduces coplanarity between the carbonyl fragment and the aromatic ring and may reflect the combined steric requirements of the ortho-fluoro substituent and the attached thiourea group.

The trithione cofomer is nearly planar and adopts the neutral all-thione tautomer, with all three H atoms bonded to ring nitrogen atoms. Its C-S distances span $1.628(2)$ – $1.643(2)$ $\text{\AA}$ and the ring C-N distances $1.356(3)$ – $1.371(3)$ $\text{\AA}$, consistent with delocalization over the $\text{C}_3\text{N}_3\text{S}_3$ framework. The C-N distances closely match those of a reported triclinic TTCA polymorph, whereas the C-S distances are slightly shorter than the ca $1.658(7)$ $\text{\AA}$ value reported for that structure [30]. These metrics fall within the structural variability reported for neutral all-thione TTCA derivatives [10-12,30,31].

3.3. Conformational analysis

The acylthiourea chain is not globally planar. The O1-C1-N1-C2 torsion of $3.2(4)^\circ$ shows that the carbonyl group and the N1-C2 bond are approximately synperiplanar, whereas $\text{C1-N1-C2-S1} = -130.7(2)^\circ$ demonstrates a marked rotation of the thione group about the N1-C2 bond. On the N2 side, $\text{C12-N2-C2-S1} = 1.5(3)^\circ$ and $\text{C9-N2-C2-S1} = -166.86(18)^\circ$ indicate that C2=S1 is approximately coplanar with the immediate N2 substituent environment.

The pyrrolidine ring adopts a twist conformation about C10-C11 , with Cremer-Pople parameters $Q(2) = 0.397(3)$ $\text{\AA}$ and $\varphi(2) = 81.2(3)^\circ$ and pseudorotation parameters $P = 242.8(2)^\circ$ and $\tau(M) = 41.1(1)^\circ$. Selected bond lengths, bond angles, and torsion angles are collected in Table 2.

3.4. Hydrogen bonding and noncovalent interactions

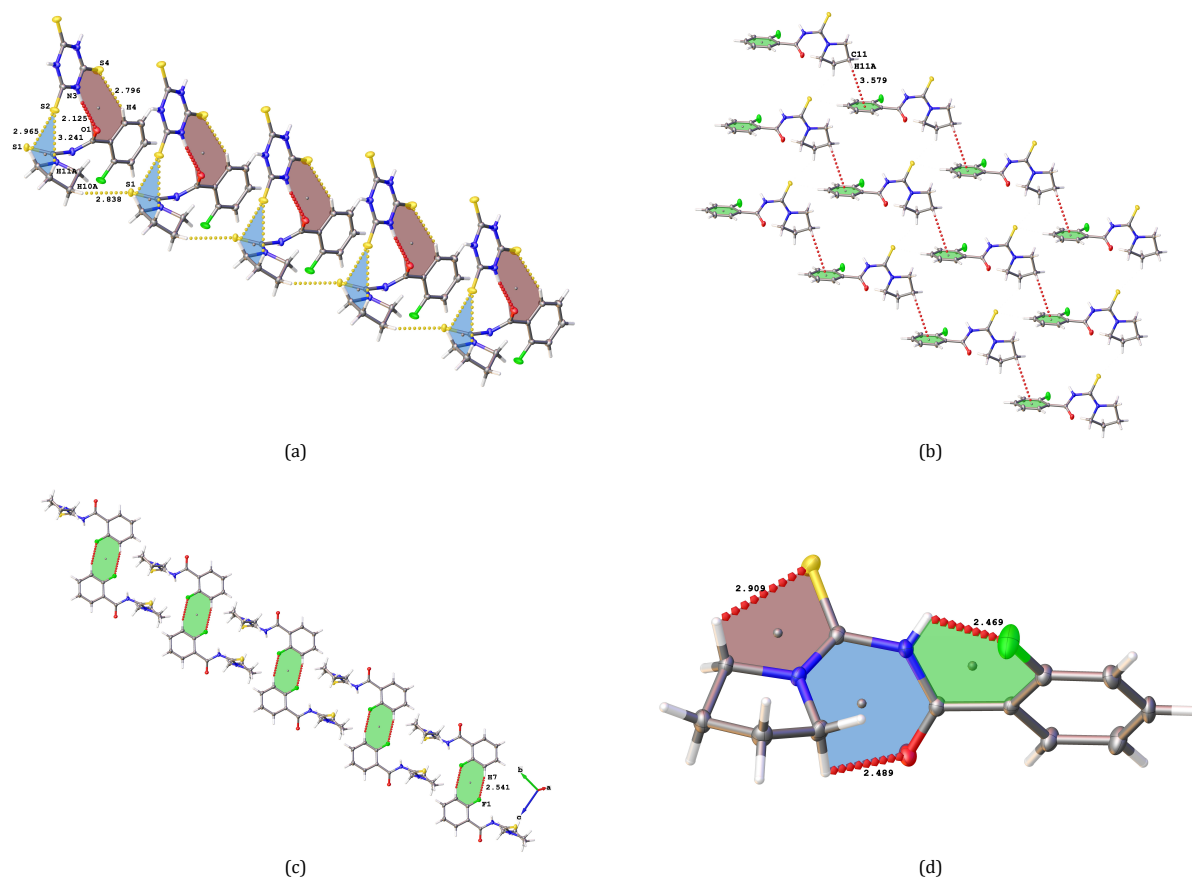
The crystal packing is governed by a combination of classical and non-classical hydrogen-bonding interactions involving both components of the cocrystal. Within the asymmetric unit, the nearly linear $\text{N3-H3}\cdots\text{O1}$ hydrogen bond [$\text{H}\cdots\text{O} = 2.13(3)$ $\text{\AA}$, $\text{N}\cdots\text{O} = 2.932(3)$ $\text{\AA}$, $\text{N-H}\cdots\text{O} = 171(3)^\circ$] establishes the principal heteromolecular contact between the N-H donor of 1,3,5-triazine-2,4,6-trithione (TTCA) and the carbonyl group of the benzoylthiourea component (Figure 5). The remaining N-H donor sites participate predominantly in $\text{N-H}\cdots\text{S}$ interactions, including $\text{N5-H5A}\cdots\text{S1}$ between TTCA and the acylthiourea thione group and $\text{N4-H4A}\cdots\text{S2}$ between symmetry-related TTCA molecules, while $\text{N1-H1}\cdots\text{S3}$ provides an additional, more angular connection between the acylthiourea and TTCA (Table 3). Collectively, these interactions demonstrate the simultaneous involvement of the carbonyl and thiocarbonyl functionalities in the organization of the two components. The hydrogen-bonded framework is further supported by weaker C-H-based contacts (Table 3). In addition, the benzene and trithione ring centroids are separated by $4.2764(14)$ $\text{\AA}$ with an interplanar angle of $23.59(13)^\circ$, suggesting an offset arrangement rather than a conventional face-to-face $\pi\cdots\pi$ interaction. Weak $\text{C=S}\cdots\pi$ and $\text{C=O}\cdots\pi$ approaches involving symmetry-related aromatic and trithione rings provide additional secondary contributions to the overall packing. Against this interaction-rich background, specific combinations of the weaker contacts generate well-defined supramolecular synthons and recurring packing motifs, as discussed below.

The cocrystal of 2-fluoro-*N*-(pyrrolidine-1-carbonothioyl) benzamide and TTCA displays two distinct supramolecular synthons arising from complementary hydrogen-bonding interactions between the two components (Figure 6a).

Table 3. Hydrogen-bond geometry and selected Y-X...Cg contacts in the title cocrystal (Å, °) *.

D-H...A	D-H	H...A	D...A	Angle
N1-H1...F1	0.76(3)	2.47(3)	2.740(3)	103(2)
N1-H1...S3 ⁱ	0.76(3)	2.87(3)	3.492(2)	141(2)
N3-H3...O1	0.82(3)	2.13(3)	2.932(3)	171(3)
N4-H4A...S2 ⁱⁱ	0.81(3)	2.56(3)	3.368(2)	170(3)
N5-H5A...S1 ⁱ	0.84(3)	2.46(3)	3.296(2)	176(2)
C4-H4...S4	0.93	2.80	3.649(2)	153
C7-H7...F1 ⁱⁱⁱ	0.93	2.54	3.454(3)	167
C9-H9B...O1	0.97	2.49	2.955(3)	109
C10-H10A...S1 ^{iv}	0.97	2.84	3.608(3)	137
Y-X...Cg	X...Cg (Å)	X-perp (Å)	γ (°)	Y-X...Cg (°)
C14=S3...Cg2 ⁱ	3.9751(14)	3.604	24.97	104.23(9)
C15=S4...Cg3 ⁱ	3.6828(14)	3.614	11.12	99.88(9)
C1=O1...Cg3 ^v	3.4491(19)	3.194	22.16	112.00(14)

* Symmetry codes: (i) 1 - x, 1 - y, 1 - z; (ii) 1 - x, -y, 1 - z; (iii) -x, 2 - y, -z; (iv) x - 1, y, z; (v) -x, 1 - y, 1 - z. Cg2 and Cg3 are the centroids of the C3-C8 benzene and N3-C13-N4-C14-N5-C15 trithione rings, respectively.

**Figure 6.** Supramolecular features of the cocrystal: (a) $R_2^2(9)$ and $R_2^2(5)$ synthons; (b) C-H... π interactions; (c) $R_2^2(8)$ homosynthon formed by C-H...F interactions; and (d) fused five-, six- and seven membered pseudorings. TTCA has been omitted from (b-d) for clarity.

The first is an $R_2^2(9)$ heterosynthon, generated through a pair of complementary N-H...O and C-H...S interactions. In this motif, the N3-H3 donor of TTCA interacts with the carbonyl O1 atom of the benzoylthiourea molecule [$H\cdots O = 2.125$ Å], while the C4-H4 group of the latter is directed towards the S4 atom of TTCA [$H\cdots S = 2.796$ Å]. These two contacts close a nine-membered hydrogen-bonded ring, giving rise to the $R_2^2(9)$ heterosynthon. A second, smaller $R_2^2(5)$ synthon is established through two C-H...S contacts involving the S2 atom of TTCA, which acts as a bifurcated acceptor towards the C12-H12A and C11-H11A groups of the benzoylthiourea component, with $H12A\cdots S2$ and $H11A\cdots S2$ separations of 2.965 and 3.241 Å, respectively. Although these contacts are relatively weak, their geometric arrangement closes a five-membered ring and therefore defines an $R_2^2(5)$ supramolecular synthon. In contrast, the C-H...S and N-H...O interaction links symmetry-related TTCA molecules into the more robust $R_2^2(9)$ heterosynthon, which represents the

dominant structure-directing motif of the TTCA substructure. This assignment agrees with the self-complementary N-H...S association reported for TTCA polymorphs and cocrystals [9-13]. The carbonyl-directed N-H...O contact incorporates the benzoylthiourea component into the same supramolecular framework. The resulting packing thus combines TTCA self-association with heteromolecular N-H...O and N-H...S recognition.

As shown in Figure 6b, the thiourea molecules are organized through intermolecular C-H... π interactions involving the aliphatic C11-H11A group and the aromatic π -system of a neighbouring molecule, with an $H11A\cdots Cg$ separation of 3.579 Å. Repetition of these contacts generates an extended supramolecular arrangement in which the interacting thiourea molecules adopt an approximately parallel orientation. Notably, the C-H... π contacts themselves are also propagated in a nearly parallel fashion throughout the packing, reinforcing the regular

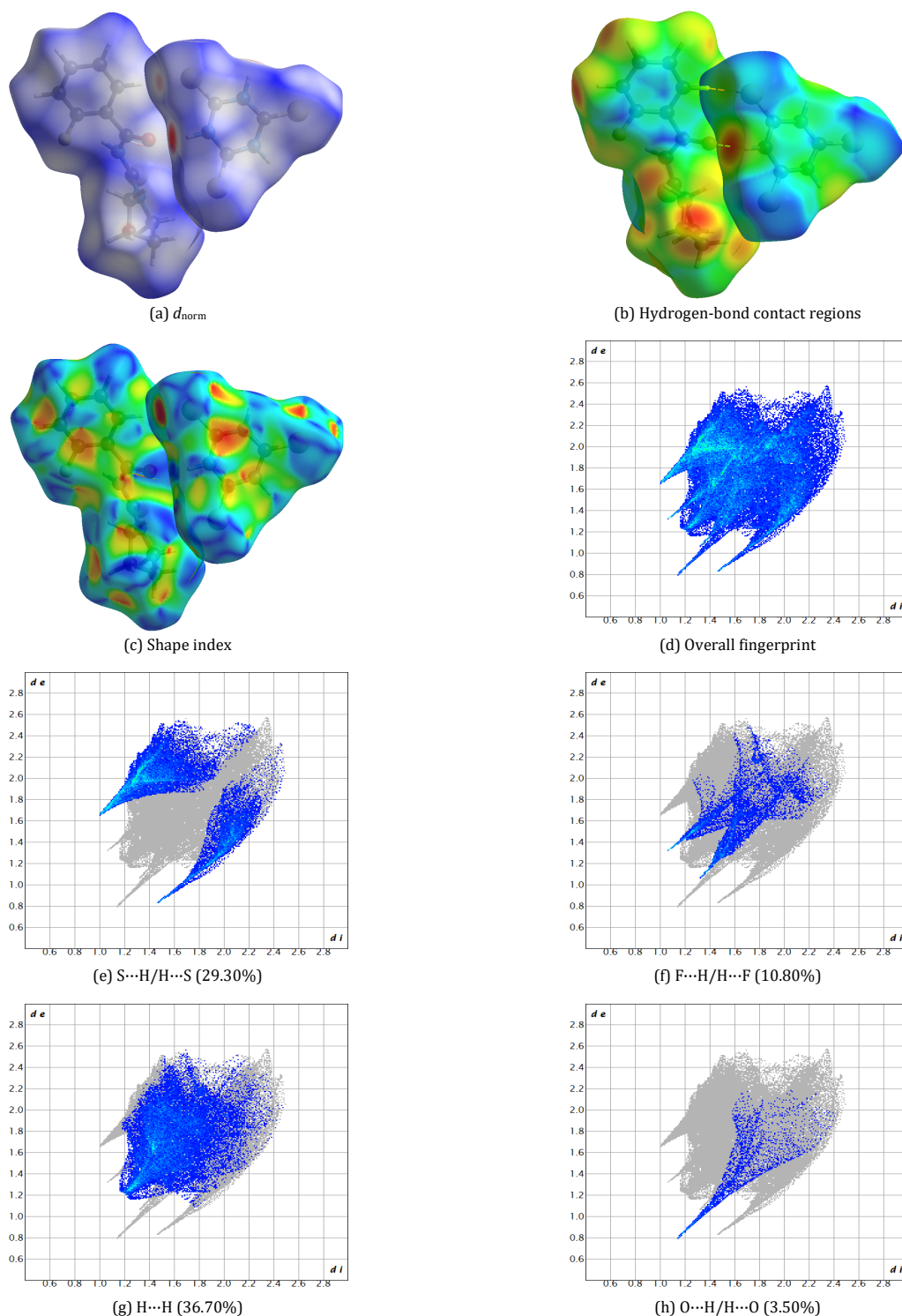


Figure 7. Hirshfeld surface and two-dimensional fingerprint analysis of the 2-fluoro-*N*-(pyrrolidine-1-carbonothioyl) benzamide component in the cocrystal: (a) d_{norm} surface, (b) highlighted close-contact regions, (c) shape-index surface, (d) overall fingerprint plot, and fingerprint contributions from (e) S...H/H...S, (f) F...H/H...F, (g) H...H, and (h) O...H/H...O contacts.

organization of the thiourea molecules. TTCA has been omitted from Figure 6b for clarity, allowing this parallel arrangement and the recurring C-H... π interactions to be visualized more clearly.

A further characteristic feature of the crystal packing is the formation of an $R_2^2(8)$ homosynthon generated by a pair of reciprocal C7-H7...F1 contacts, with an H7...F1 separation of 2.541 Å (Figure 6c). The repeated occurrence of this eight-membered synthon propagates the thiourea molecules into a

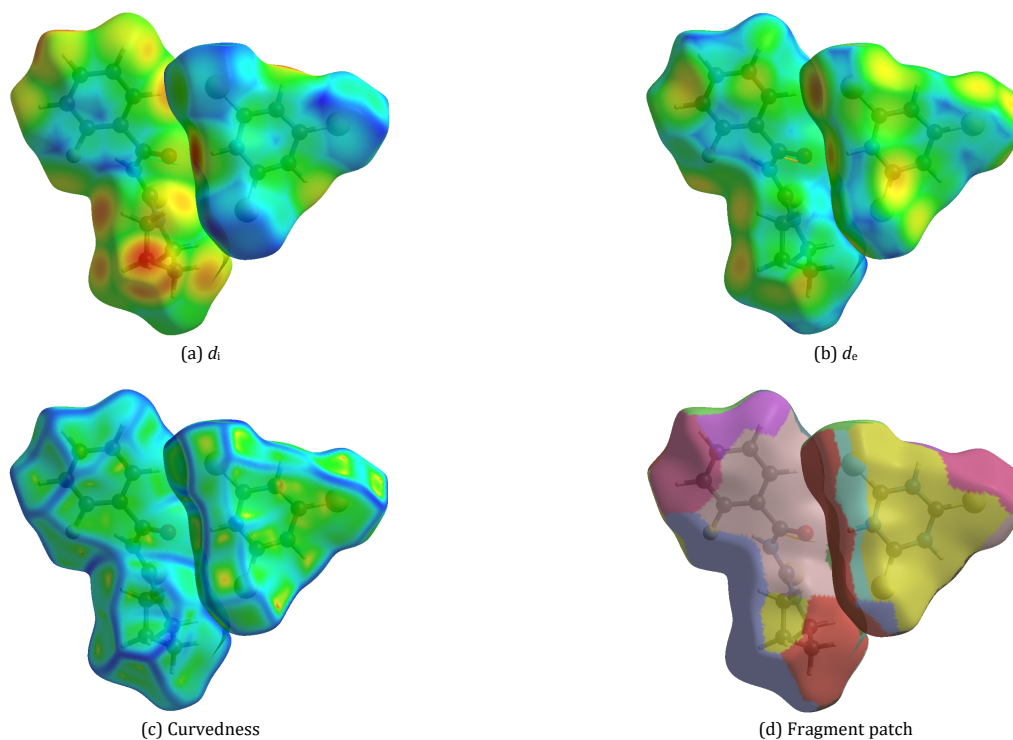
one-dimensional supramolecular chain, indicating that C-H...F interactions serve as an important structure-directing element in the crystal.

The molecular conformation of the benzoylthiourea component displays three intramolecular contacts that generate fused five-, six-, and seven-membered pseudorings (Figure 6d).

Table 4. Hirshfeld contact surfaces C_{XY} (%), proportions of chemical types on the molecular surface S_X (%), random contacts R_{XY} (%), and enrichment ratios E_{XY} for the 2-fluoro-*N*-(pyrrolidine-1-carbonothioyl)benzamide component of the title cocrystal *.

Atoms	S	F	O	N	H	C
S	0.00					Contacts
F	0.30	0.00				
O	0.00	0.00	0.00			
N	0.80	0.00	1.00	0.00		
H	29.30	10.80	3.50	1.30	36.70	
C	3.50	0.00	0.80	0.80	9.60	1.60
Surface %	16.95	5.55	2.65	1.95	63.95	8.95
S	2.87			Random	Contacts	(%)
F	1.88	0.31				
O	0.90	0.29	0.07			
N	0.66	0.22	0.10	0.04		
H	21.68	7.10	3.39	2.49	40.90	
C	3.03	0.99	0.47	0.35	11.45	0.80
S	0.00					Enrichment
F	0.16	/				
O	/	/	/			
N	/	/	/	/		
H	1.35	1.52	1.03	0.52	0.90	
C	1.15	0.00	/	/	0.84	/

* C_{XY} is the observed contact contribution, S_X is the proportion of chemical type X on the molecular surface, R_{XY} is the random-contact proportion, and $E_{XY} = C_{XY}/R_{XY}$. Enrichment ratios were not calculated when R_{XY} was lower than 0.9%; these entries are indicated by a slash in Table 4.

**Figure 8.** Additional Hirshfeld surface properties of the benzoylthiourea component: (a) d_i , (b) d_e , (c) curvedness, and (d) fragment-patch maps.

The five-membered pseudoring is formed through an C–H $\cdots$ S interaction (H $\cdots$ S = 2.909 Å), while the adjacent six-membered ring is closed by an N–H $\cdots$ F interaction (H $\cdots$ F = 2.469 Å). A further C–H $\cdots$ O contact (H $\cdots$ O = 2.489 Å) generates the seven-membered pseudoring.

3.5. Hirshfeld surface, fingerprint, and interaction-energy analysis

The Hirshfeld surface of the benzoylthiourea component has a volume of 288.36 Å³ and an area of 271.90 Å², with globularity and asphericity values of 0.776 and 0.221, respectively. Red regions on the d_{norm} surface coincide with the short contacts identified crystallographically, most prominently the carbonyl-directed N3–H3 $\cdots$ O1 contact and the N–H $\cdots$ S links involving the thione acceptor sites (Figure 7a,b). The shape-index map does not display the broad complementary red-blue pattern expected

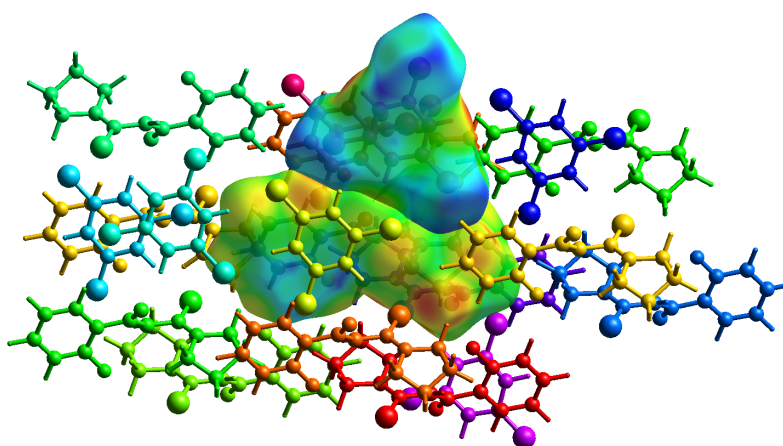
for dominant face-to-face π stacking, consistent with the offset ring geometry described above (Figure 7c).

The complementary d_i and d_e maps describe the nearest internal and external distances across the molecular surface, respectively, while the curvedness and fragment-patch maps show the local surface morphology and the partitioning of the surface among neighboring molecular fragments (Figure 8).

The fingerprint decomposition is dominated by H $\cdots$ H (36.70%) and S $\cdots$ H/H $\cdots$ S (29.30%) contacts, followed by F $\cdots$ H/H $\cdots$ F (10.80%) and C $\cdots$ H/H $\cdots$ C (9.60%) contacts (Table 4). The O $\cdots$ H/H $\cdots$ O contribution is smaller (3.50%) but contains the sharp fingerprint feature associated with the short carbonyl-directed hydrogen bond. The high H $\cdots$ H percentage largely reflects the hydrogen-rich surface (63.95%); its enrichment ratio of 0.90 shows that this contact is not preferential relative to a random distribution.

Table 5. B3LYP interaction energies of molecular pairs in the energy-framework cluster (kJ mol⁻¹).

Color	N	Symmetry	R (Å)	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}
Red	1	-x, -y, -z	7.040	-1.507	-0.836	-23.641	11.773	-15.526
Orange	2	x, y, z	7.730	-6.629	-1.910	-8.855	11.741	-8.881
Yellow	2	x, y, z	10.320	0.593	-0.578	-11.719	6.071	-6.256
Light Green	1	-x, -y, -z	8.860	-5.436	-0.603	-9.761	9.480	-8.837
Green	2	x, y, z	10.640	-9.605	-2.120	-10.711	9.771	-15.015
Light Blue	1	-x, -y, -z	11.260	-1.317	-0.453	-6.161	2.095	-5.798
Blue	1	—	9.270	-0.750	-0.033	-0.599	0.000	-1.339
Light Cyan	1	—	11.010	0.593	-0.578	-11.719	6.071	-6.256
Cyan	1	-x, -y, -z	12.880	0.212	-0.319	-4.343	0.000	-3.794
Dark Blue	1	—	9.380	-9.605	-2.120	-10.711	9.771	-15.015
Purple	1	-x, -y, -z	5.920	-11.505	-6.358	-35.350	25.104	-32.145
Dark Purple	1	—	8.290	-1.507	-0.836	-23.641	11.773	-15.526
Magenta	1	—	5.710	2.721	-0.285	-2.113	0.000	0.827
Red	1	—	5.170	-6.629	-1.910	-8.855	11.741	-8.881

**Figure 9.** Color-coded molecular pairs surrounding the reference benzoylthiourea component used in the CE-B3LYP interaction-energy calculation. Colors correspond to the molecular-pair entries in Table 5.

The preferential character of the polar contacts is more clearly expressed by the enrichment ratios. F...H/H...F and S...H/H...S are enriched, with E values of 1.52 and 1.35, respectively, while O...H/H...O is close to the random expectation ($E = 1.03$). The F...H enrichment is consistent with the propensity of fluorine to contact surface hydrogen atoms, but it does not by itself establish a strong classical hydrogen bond [22]. Following the criterion used for the related fluoro-substituted benzoylthiourea [7], enrichment ratios were not evaluated when R_{XY} was below 0.9%, because division by such small random-contact proportions produces numerically large but poorly robust values.

Relative to the structurally related ortho-fluoro benzoylthiourea T1 [7], the present benzoylthiourea surface shows a smaller H...H contribution (36.70 versus 43.70%) but substantially larger S...H/H...S (29.30 versus 11.80%) and F...H/H...F contributions (10.80 versus 1.30%). The enhanced sulfur-associated contribution is consistent with incorporation of the sulfur-rich TTCA cofomer, while the strong increase in F...H contacts shows that the cofomer also changes the local environment of the ortho-fluoro substituent. The prominence of sulfur-associated contacts is consistent with the Hirshfeld analysis of the *N*-carbamothioylbenzamide-TTCA cocrystal, in which H...S/S...H contacts constitute the dominant contribution (40.8%) [13].

The most stabilizing individual pair is the purple-coded neighbor at $R = 5.92$ Å, for which $E_{tot} = -32.15$ kJ mol⁻¹; its E_{ele} , E_{pol} , E_{dis} , and E_{rep} components are -11.51, -6.36, -35.35, and +25.10 kJ mol⁻¹, respectively (Table 5). The color-coded molecular-pair cluster is shown in Figure 9, and the corresponding electrostatic, dispersion, and total-energy frameworks are shown in Figure 10. The directional hydrogen bonds define the principal geometrical organization of the cocrystal, whereas the energy analysis

quantifies the substantial dispersive contribution from the broader molecular environment.

3.6. Comparison with related structures

The closest structural analogue is the 1:1 *N*-carbamothioyl benzamide-TTCA cocrystal (CCDC 2232631), reported in monoclinic $P2_1/c$ [13]. Both structures are organized by extensive N-H...S association, including a centrosymmetric $R_2^2(8)$ TTCA motif. Their carbonyl-recognition patterns differ: the analogue contains an intramolecular N-H...O contact within the *N*-carbamothioylbenzamide component, whereas the present structure contains the intermolecular TTCA N3-H3...O1 contact. The fluoro-pyrrolidinyl derivative also crystallizes in triclinic $P-1$ and displays a more strongly twisted acylthiourea fragment.

In the *N*-carbamothioylbenzamide-TTCA analogue, the $\text{NH}_2\text{C}(\text{S})\text{NHC}(\text{O})$ fragment is approximately planar and inclined to the phenyl ring [13]. The present O1-C1-C3-C4 torsion of 35.4(3)° and C1-N1-C2-S1 torsion of -130.7(2)° demonstrate greater carbonyl rotation and internal twisting in the present structure.

The intramolecular N-H...O contact in the analogue is shorter and more bent than the intermolecular N3-H3...O1 contact in the present cocrystal [13]. The present N-H...S distances nevertheless overlap those of the analogue and other TTCA structures [9-13], indicating retention of the characteristic sulfur-directed recognition mode despite the altered carbonyl-recognition pattern.

The C-N/C-S metrics and planar ring geometry likewise retain the neutral all-thione TTCA framework reported for TTCA polymorphs and cocrystals [10-12,30]. In the present lattice, the TTCA N-H donors participate in carbonyl-directed heteromolecular recognition, TTCA self-association, and binding

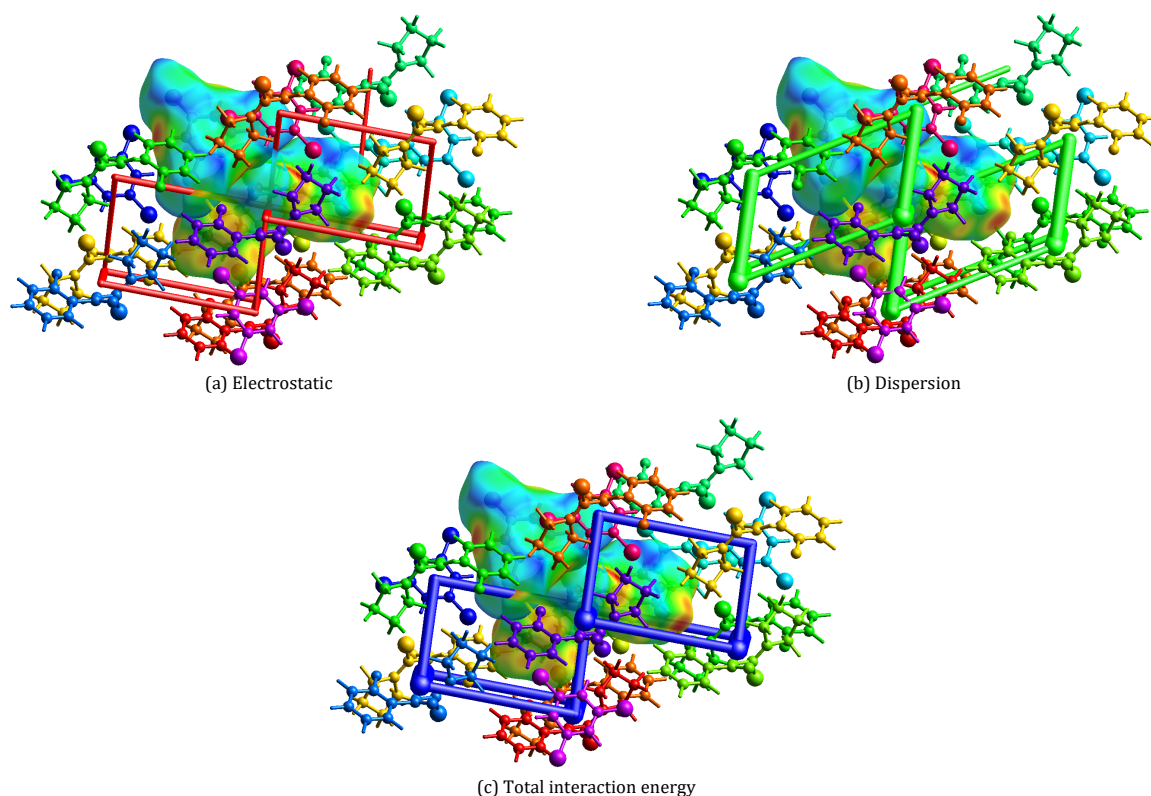


Figure 10. Energy frameworks calculated at the B3LYP/6-31G(d,p) level: (a) electrostatic, (b) dispersion, and (c) total interaction-energy frameworks.

binding to the acylthiourea thione group, illustrating the adaptability of the recurrent TTCA hydrogen-bonding platform.

Aziz *et al.* assigned TTCA⋯TTCA π stacking in the analogue, with a centroid separation of 4.0010(9) Å [13]. In the present structure, the 4.2764(14) Å benzene–trithione centroid separation and 23.59(13)° interplanar angle instead describe an offset secondary contact rather than conventional face-to-face stacking.

4. Conclusions

Although the synthesis was intended to yield only the benzoylthiourea derivative, single-crystal X-ray diffraction established a 1:1 cocrystal of 2-fluoro-*N*-(pyrrolidine-1-carbonothioyl)benzamide and 1,3,5-triazinane-2,4,6-trithione in triclinic *P*-1. The acylthiourea component is more strongly twisted than in the related *N*-carbamothioylbenzamide·TTCA cocrystal, whereas TTCA retains its planar all-thione geometry. A nearly linear N3–H3⋯O1 contact defines the heteromolecular associate, which is extended through N–H⋯S interactions. Hirshfeld analysis of the benzoylthiourea component identifies H⋯H and S⋯H/H⋯S as the largest surface contributions, while the enrichment analysis emphasizes the preferential H⋯F and H⋯S contacts. B3LYP interaction energies show that dispersion makes the largest attractive contribution to the strongest molecular pair, complementing the directional hydrogen-bond description of the lattice.

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Supporting information

CCDC-2582113 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, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement

Conflict of interest: The authors report no competing interests related to this work.

Sample availability: The compounds described in this work are available from the authors upon reasonable request.

CRediT authorship contribution statement

Conceptualization: Hakan Arslan, Ahmad Yahaya; Methodology: Hakan Arslan, Ahmad Yahaya, Ummuhan Solmaz; Validation: Ahmad Yahaya, Ummuhan Solmaz; Formal Analysis: Hakan Arslan, Ahmad Yahaya, Ummuhan Solmaz; Investigation: Hakan Arslan, Ahmad Yahaya, Ummuhan Solmaz; Resources: Hakan Arslan, Ahmad Yahaya, Ummuhan Solmaz; Data Curation: Hakan Arslan, Ahmad Yahaya, Ummuhan Solmaz; Writing - Original Draft: Ahmad Yahaya, Ummuhan Solmaz; Writing - Review and Editing: Hakan Arslan, Ahmad Yahaya, Ummuhan Solmaz; Visualization: Ahmad Yahaya, Ummuhan Solmaz; Funding acquisition: Hakan Arslan; Supervision: Hakan Arslan; Project Administration: Hakan Arslan.

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Mersin University
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ORCID and Email

Ahmad Yahaya
 ahmad.yahaya.ng@gmail.com
 <https://orcid.org/0009-0009-7164-9724>

Ummuhan Solmaz

 ummuhansolmaz@mersin.edu.tr <https://orcid.org/0000-0002-3697-577X>

Hakan Arslan

 hakan.arslan@mersin.edu.tr <https://orcid.org/0000-0003-0046-9442>

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