

## Polymorphism and solvolysis of 2-cyano-3-[4-(*N,N*-diethylamino)- phenyl]prop-2-enethioamide

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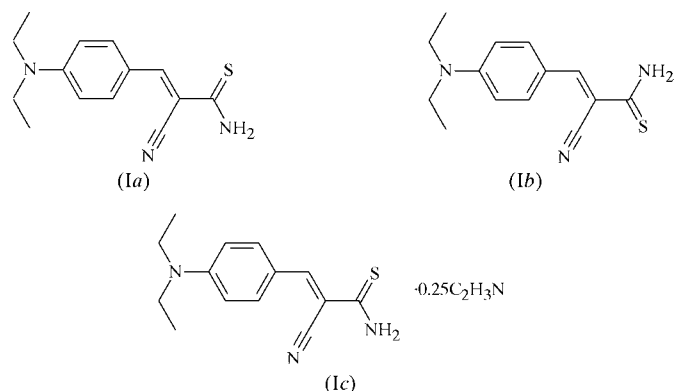
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Two new polymorph forms, (*Ia*) and (*Ib*), of the title compound,  $C_{14}H_{17}N_3S$ , and its solvate with acetonitrile,  $C_{14}H_{17}N_3S \cdot 0.25C_2H_3N$ , (*Ic*), have been investigated. Crystals of the two polymorphs were grown from different solvents, *viz.* ethanol and *N,N*-dimethylformamide, respectively. The polymorphs have different orientations of the thioamide group relative to the CN substituent, with *s-cis* and *s-trans* geometry of the  $C=C-C=S$  diene fragment, respectively. Compound (*Ic*) contains two independent molecules, *A* and *B*, with *s-cis* geometry, and the solvate molecule lies on a twofold axis. The core of each molecule is slightly non-planar; the dihedral angles between the conjugated  $C=C-CN$  linkage and the phenyl ring, and between this linkage and the thioamide group are  $13.4(2)$  and  $12.0(2)^\circ$  in (*Ia*),  $14.0(2)$  and  $18.2(2)^\circ$  in (*Ib*),  $2.3(3)$  and  $12.7(4)^\circ$  in molecule *A* of (*Ic*), and  $23.2(3)$  and  $8.1(4)^\circ$  in molecule *B* of (*Ic*). As a result of strong conjugation between donor and acceptor parts, the substituted phenyl rings have noticeable quinoid character. In (*Ib*), there exists a very strong intramolecular steric interaction ( $H \cdots H = 1.95 \text{ \AA}$ ) between the bridging and thioamide parts of the molecule, which makes such a form less stable. In the crystal structure of (*Ia*), intermolecular  $N-H \cdots N$  and  $N-H \cdots S$  hydrogen bonds link molecules into infinite tapes along the  $[1\bar{1}0]$  direction. In (*Ib*), such intermolecular hydrogen bonds link molecules into infinite (101) planes. In (*Ic*), intermolecular  $N-H \cdots N$  hydrogen bonds link molecules *A* and *B* into dimers, which are connected *via*  $N-H \cdots S$  hydrogen bonds and form infinite chains along the *c* direction.

### Comment

The present investigation is a continuation of a project that includes syntheses and structural studies of polar conjugated organic compounds that crystallize in non-centrosymmetric space groups (Antipin *et al.*, 1998; Nesterov *et al.*, 1998, 2000; Nesterov, Antipin, Nesterov, Moore *et al.*, 2004; Nesterov, Antipin, Nesterov, Penn *et al.*, 2004). These compounds may

find applications in non-linear optical materials (Zyss, 1994; Kuzyk & Dirk, 1998) and in the syntheses of hetero-



cyclic compounds (Brunskill *et al.*, 1984; Nesterov *et al.*, 2002). Moreover, related compounds have found applications as potential antitumor drugs (Hutchinson *et al.*, 2001; Thacher *et al.*, 2001; Wermuth, 2004). During thorough and systematic work, we have found many compounds that crystallize in different space groups and reveal polymorphism (Timofeeva *et al.*, 2000; Timofeeva, Nesterov *et al.*, 2003; Timofeeva, Kuhn *et al.*, 2003; Wang *et al.*, 2001). Thus, cocrystallization of such compounds with chiral molecules can build non-centrosymmetric crystalline structures or polymorphs (Timofeeva *et al.*, 2000), and polymorphism is a very important phenomenon in

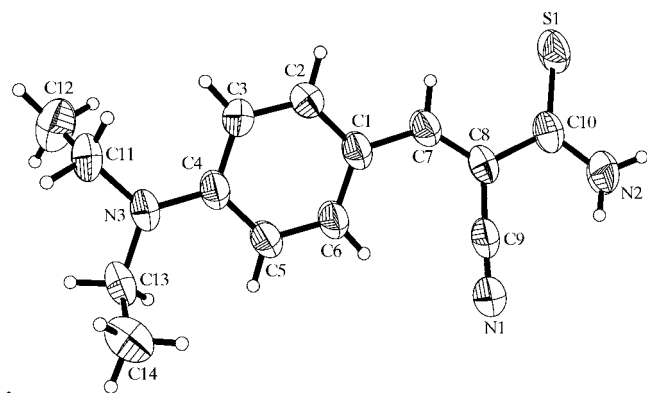


Figure 1

A view of polymorph (*Ia*), showing the atom numbering used. Non-H atoms in Figs. 1–3 are shown with displacement ellipsoids drawn at the 50% probability level.

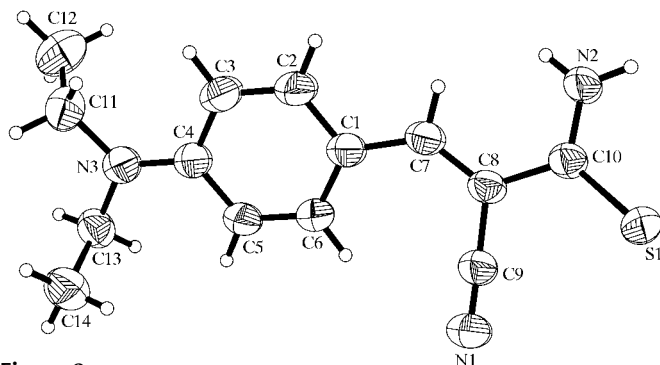
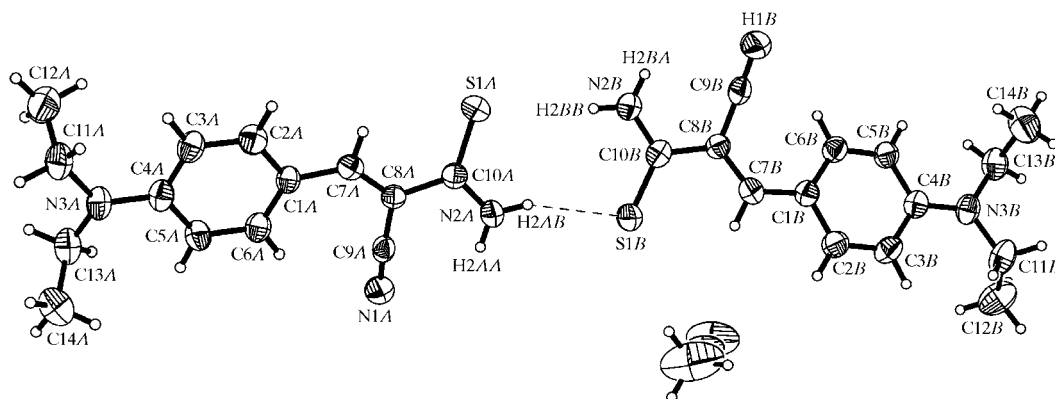
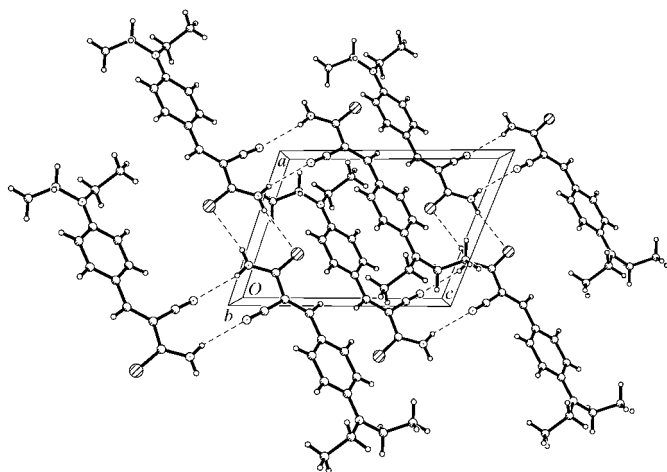


Figure 2

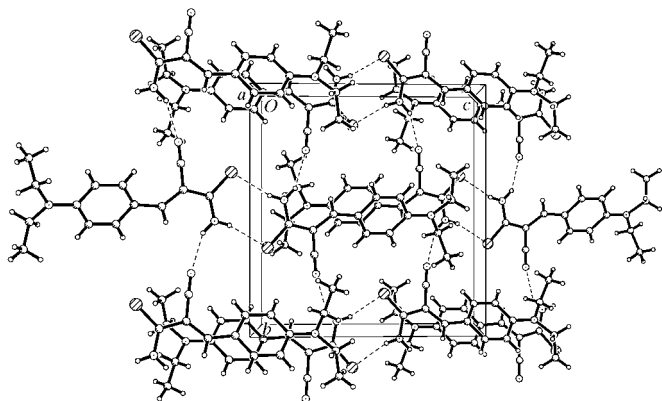
A view of polymorph (*Ib*), showing the atom numbering used.



**Figure 3**  
A view of adduct (Ic), showing the atom numbering used. The dashed line represents the intermolecular N—H...S hydrogen bond.



**Figure 4**  
A projection of the crystal packing of (Ia) along the *b* axis. Dashed lines represent intermolecular N—H...N and N—H...S hydrogen bonds.



**Figure 5**  
A projection of the crystal packing of (Ib) along the *a* axis. Dashed lines represent intermolecular N—H...N and N—H...S hydrogen bonds.

the pharmaceutical industry (Davey *et al.*, 1997; Bernstein, 2002).

In this paper, we present interesting results that were obtained working with the title compound, (I). X-Ray struc-

tural investigations have been carried out for two polymorphs, *viz.* orange triclinic (Ia) and red monoclinic (Ib) (Figs. 1 and 2), and for a complex, (Ic) (Fig. 3), of (I) with acetonitrile. In an attempt to find other crystalline forms, crystals of (I) have been grown from several solvents, including ethanol, propan-2-ol, acetonitrile, toluene, chloroform, and their mixtures. In almost all cases, we obtained crystals of (Ia), and only from acetonitrile did we obtain complex (Ic). Starting with (I), we have synthesized several thiazole derivatives using dimethylformamide (DMF) as a solvent. In one case, crystals with different shapes were separated from the reaction mixture, *viz.* red prisms (several crystals) and orange plates. The former were another monoclinic form, (Ib), of the starting material, while the latter crystals were the thiazole product. According to the Cambridge Structural Database (CSD; Allen, 2002), the structure of another monoclinic modification, (Id), of (I) has been investigated (Brunskill *et al.*, 1984). All our attempts to obtain complexes of (I) with L-proline and L-tartaric acid, using different solvents and different crystallization conditions, gave only good crystals of polymorph (Ia).

As can be seen in Figs. 1 and 2, the main distinction between (Ia) and (Ib) is the different orientation of the thioamide group relative to the CN substituent (two rotamers). In accordance with the results of Brunskill *et al.* (1984), in these cases we obtained two forms, with *s-cis* and *s-trans* geometry of the C=C—C=S fragment. Although conformer (Id) has a structure similar to that of (Ib), the values of the C7—C8—C10—S1 torsion angles are different [159.37 (13)° in (Ib) and -158.5° in (Id)]. In both independent molecules, A and B, of (Ic), the orientation of this substituent is similar to that in (Ia) (Fig. 3), but compounds (Ic) and (Ia) also have different dihedral angles (see below). The rotation of the thioamide group about the C8—C10 single bond is a possible reason for the existence of the three forms.

Most of the geometric parameters in the investigated molecules (Ia)–(Ic) are very similar. The molecular skeleton of each molecule is slightly non-planar; the dihedral angles between the conjugated linkage (C=C—CN) and the phenyl ring, and between this linkage and the thioamide group are 13.4 (2) and 12.0 (2)° in (Ia), 14.0 (2) and 18.2 (2)° in (Ib),

2.3 (3) and 12.7 (4)° in molecule *A* of (*Ic*), and 23.2 (3) and 8.1 (4)° in molecule *B* of (*Ic*). Such slight non-planarity is not sufficient to preclude conjugation between aryl and CN groups via a C=C-bridged fragment. Because of the strong conjugation between donor and acceptor parts in these molecules, the substituted phenyl rings have a noticeably quinoid character (Tables 1, 3 and 5). Moreover, the dihedral angles between the trigonal diethylamine substituent [in all structures, the sum of the bond angles around the N atom is 359.5 (2)°] and the phenyl ring are small [5.6 (2)° in (*Ia*), 10.7 (2)° in (*Ib*), and 10.6 (4) and 10.4 (4)° in molecules *A* and *B* of (*Ic*)]. In all compounds, the N3—C4 bond length [range 1.351 (4)–1.369 (4) Å] is comparable to the average conjugated C—N single bond (1.370 Å) and is distinctly shorter than the average non-conjugated C—N single bond (1.430 Å) found in the CSD. Furthermore, the C1—C7 and C7=C8 bond lengths also have noticeable differences in comparison with standard distances (Allen *et al.*, 1987).

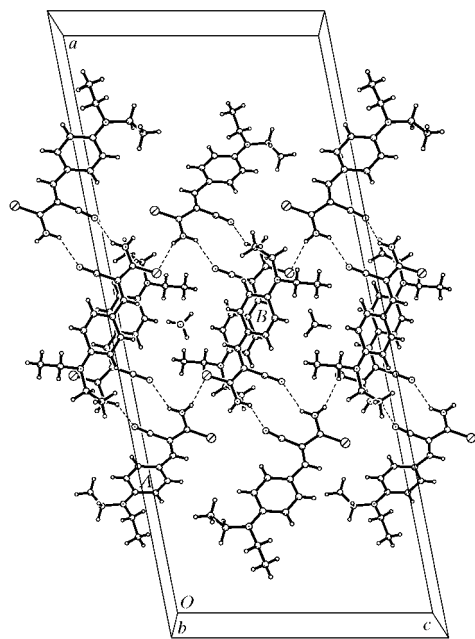
As can be seen in Tables 1, 3 and 5, all of the molecules possess a strong conjugation in the thioamide fragment. The C=S bond lengths are distinctly elongated, while the C—N bonds have a partial double-bond character. In our previous work (Nesterov *et al.*, 1986), we have analyzed such conjugation in the thioamide fragments. As mentioned above, the deviations of the thioamide groups in (*Ia*)–(*Ic*) from the bridged plane are not significant, but the C8—C10 bond lengths are equal or slightly elongated compared with the conjugated C—C bond (1.470 Å; Allen *et al.*, 1987).

The planarity of the molecules leads to the existence of shortened H···CH intramolecular contacts [H6A···C9 =

2.38 Å and H2A···C9 = 2.28 Å in (*Ia*), H6A···C9 = 2.52 Å and H7A···H2A = 1.95 Å in (*Ib*), H6AA···C9A = 2.44 Å and H2AA···C9A = 2.25 Å in molecule *A* of (*Ic*), and H6BA···C9B = 2.48 Å and H2BA···C9B = 2.33 Å in molecule *B* of (*Ic*)]. In (*Ib*), there exists a very strong steric H···H interaction between the bridging and thioamide parts of the molecule. The same short steric contact is also found in the monoclinic form (*Id*) at 2.04 Å. Probably, the presence of such short contacts indicates that polymorphs (*Ib*) and (*Id*) are energetically less stable than (*Ia*). This is perhaps the reason that we were unable to obtain polymorphs (*Ib*) and (*Id*) again in our work. Such intramolecular interactions are the reason for the elongation of the C8—C10 bond lengths.

The crystal packings of (*Ia*) and (*Ib*) are different. In (*Ia*), intermolecular N—H···N and N—H···S hydrogen bonds link molecules in two centrosymmetric dimers to build infinite tapes along the  $[1\bar{1}0]$  direction (Fig. 4 and Table 2). However, in (*Ib*), such hydrogen bonds link molecules into infinite (101) planes (Fig. 5 and Table 4). In the case of (*Ic*), intermolecular N—H···N hydrogen bonds link molecules *A* and *B* into dimers, which are connected via N—H···S hydrogen bonds and form infinite chains along the *c* direction (Fig. 6 and Table 6). In molecule *B*, one atom of the NH<sub>2</sub> group (H2BB) does not participate in hydrogen bonding. The intermolecular distance between atoms H2BB and S1A of molecules *A* and *B* (3.05 Å) is greater than the sum of the van der Waals radii of these atoms (Rowland & Taylor, 1996).

According to the foregoing results, previously studied compounds (Nesterov *et al.*, 2003) having 4-diethylamino substituents that occupy different positions relative to the phenyl ring (two CH<sub>3</sub> groups above a plane or disordered) might also yield polymorphic forms.



**Figure 6**

A projection of the crystal packing of (*Ic*) along the *b* axis. Dashed lines represent intermolecular N—H···N and N—H···S hydrogen bonds.

## Experimental

Compound (*I*) was synthesized by the reaction of 4-(diethylamino)-benzaldehyde with 2-cyanothioacetamide in the presence of a catalytic amount of morpholine in ethanol at room temperature. The precipitate was separated from the solution, and the structure and purity were investigated by NMR (m.p. 421–425 K, yield 83%). The large melting interval is probably a result of the mixture of isomers present. After recrystallization from ethanol, only crystals of (*Ia*) (m.p. 424–425 K) were found. Crystals of (*Ic*) were obtained by slow isothermal evaporation from an acetonitrile solution of (*I*). Compound (*I*) was used to synthesize a 2,4-disubstituted thiazole derivative, using DMF as solvent. From one such reaction mixture were extracted two types of crystals with different shapes. X-Ray analysis revealed that one of these forms was the thiazole derivative and the other was a monoclinic polymorph, (*Ib*). All attempts to reobtain polymorph (*Ib*), complex (*Ic*) and the literature polymorph (*Id*), using exactly the same conditions and variations of them, gave only (*Ia*). Polymorph (*Ia*) is probably the most stable energetically. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.65 (s, 1H, C7H), 7.96 (d, 2H, *J* = 9.2 Hz, C2, C6), 7.57 (br s, 1H, NH), 7.36 (br s, 1H, NH), 6.69 (d, 2H, *J* = 9.2 Hz, C3, C5), 3.47 (q, 4H, *J* = 7.1 Hz, 2CH<sub>2</sub>), 1.24 (t, 6H, *J* = 7.2 Hz, 2CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 193.6 (C=S), 158.1 (C7), 152.0 (C4), 134.9 (C2, C6), 119.3 (C1), 118.3 (C9), 111.3 (C3, C5), 98.7 (C8), 44.8 (2CH<sub>2</sub>), 12.5 (2CH<sub>3</sub>).

**Polymorph (Ia)**

*Crystal data*

C<sub>14</sub>H<sub>17</sub>N<sub>3</sub>S  
*M<sub>r</sub>* = 259.38  
 Triclinic, *P*1̄  
*a* = 8.753 (3) Å  
*b* = 8.890 (3) Å  
*c* = 10.830 (4) Å  
 α = 85.44 (3)°  
 β = 69.76 (2)°  
 γ = 63.65 (3)°  
*V* = 705.8 (5) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.220 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 24 reflections  
 θ = 11–12°  
 μ = 0.22 mm<sup>-1</sup>  
*T* = 298 (2) K  
 Plate, orange  
 0.50 × 0.40 × 0.20 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer  
 θ/2θ scans  
 2639 measured reflections  
 2465 independent reflections  
 1811 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.016  
 θ<sub>max</sub> = 25.1°  
*h* = 0 → 10  
*k* = -9 → 10  
*l* = -12 → 12  
 3 standard reflections every 97 reflections  
 intensity decay: 3%

*Refinement*

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.035  
*wR*(*F*<sup>2</sup>) = 0.098  
*S* = 1.00  
 2465 reflections  
 165 parameters  
 H-atom parameters constrained  
*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.06*P*)<sup>2</sup>]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> < 0.001  
 Δρ<sub>max</sub> = 0.15 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.18 e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °) for polymorph (Ia).

S1–C10	1.669 (2)	C7–C8	1.358 (2)
N1–C9	1.145 (2)	C8–C9	1.428 (3)
N2–C10	1.330 (2)	C8–C10	1.476 (2)
N3–C4	1.361 (2)		
C8–C7–C1	131.08 (16)	N1–C9–C8	177.31 (18)
C2–C1–C7–C8	167.98 (17)	C9–C8–C10–N2	-10.0 (2)
C1–C7–C8–C10	-177.86 (16)	C7–C8–C10–S1	-13.1 (2)

**Table 2**

Hydrogen-bonding geometry (Å, °) for polymorph (Ia).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N2–H2 <i>A</i> ...N1 <sup>i</sup>	0.86	2.35	3.069 (2)	141
N2–H2 <i>B</i> ...S1 <sup>ii</sup>	0.86	2.66	3.481 (2)	160

Symmetry codes: (i) 2 - *x*, 1 - *y*, -*z*; (ii) 3 - *x*, -*y*, -*z*.

**Polymorph (Ib)**

*Crystal data*

C<sub>14</sub>H<sub>17</sub>N<sub>3</sub>S  
*M<sub>r</sub>* = 259.38  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 9.1670 (18) Å  
*b* = 13.023 (3) Å  
*c* = 12.172 (2) Å  
 β = 93.97 (3)°  
*V* = 1449.6 (5) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.189 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 24 reflections  
 θ = 11–12°  
 μ = 0.21 mm<sup>-1</sup>  
*T* = 295 (2) K  
 Prism, red  
 0.50 × 0.35 × 0.25 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer  
 θ/2θ scans  
 3307 measured reflections  
 3114 independent reflections  
 2316 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.027  
 θ<sub>max</sub> = 27.0°  
*h* = 0 → 11  
*k* = 0 → 16  
*l* = -15 → 15  
 3 standard reflections every 97 reflections  
 intensity decay: 3%

*Refinement*

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.038  
*wR*(*F*<sup>2</sup>) = 0.113  
*S* = 1.03  
 3114 reflections  
 165 parameters  
 H-atom parameters constrained  
*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.06*P*)<sup>2</sup> + 0.25*P*]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> < 0.001  
 Δρ<sub>max</sub> = 0.21 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.15 e Å<sup>-3</sup>

**Table 3**

Selected geometric parameters (Å, °) for polymorph (Ib).

S1–C10	1.6723 (15)	C7–C8	1.366 (2)
N1–C9	1.137 (2)	C8–C9	1.433 (2)
N2–C10	1.3270 (19)	C8–C10	1.467 (2)
N3–C4	1.362 (2)		
C8–C7–C1	132.68 (14)	N1–C9–C8	178.70 (18)
C2–C1–C7–C8	170.58 (19)	C9–C8–C10–N2	164.83 (16)
C1–C7–C8–C10	-179.09 (17)	C7–C8–C10–S1	159.37 (13)

**Table 4**

Hydrogen-bonding geometry (Å, °) for polymorph (Ib).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N2–H2 <i>A</i> ...N1 <sup>iii</sup>	0.86	2.20	2.989 (2)	152
N2–H2 <i>B</i> ...S1 <sup>iv</sup>	0.86	2.58	3.421 (2)	167

Symmetry codes: (iii) ½ - *x*, ½ + *y*, ¾ - *z*; (iv) -*x*, 1 - *y*, 2 - *z*.

**Compound (Ic)**

*Crystal data*

C<sub>14</sub>H<sub>17</sub>N<sub>3</sub>S·0.25C<sub>2</sub>H<sub>3</sub>N  
*M<sub>r</sub>* = 269.64  
 Monoclinic, *C*2/*c*  
*a* = 39.370 (8) Å  
*b* = 8.8800 (18) Å  
*c* = 17.056 (3) Å  
 β = 101.19 (3)°  
*V* = 5850 (2) Å<sup>3</sup>  
*Z* = 16  
*D<sub>x</sub>* = 1.225 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 24 reflections  
 θ = 10–11°  
 μ = 0.21 mm<sup>-1</sup>  
*T* = 298 (2) K  
 Plate, orange  
 0.50 × 0.40 × 0.20 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer  
 θ/2θ scans  
 5506 measured reflections  
 5423 independent reflections  
 2754 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.050  
 θ<sub>max</sub> = 25.5°  
*h* = 0 → 47  
*k* = 0 → 10  
*l* = -20 → 20  
 3 standard reflections every 97 reflections  
 intensity decay: 3%

## Refinement

Refinement on  $F^2$ 

$$R[F^2 > 2\sigma(F^2)] = 0.050$$

$$wR(F^2) = 0.149$$

$$S = 0.99$$

5423 reflections

344 parameters

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$$

**Table 5**Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (Ic).

S1A–C10A	1.671 (3)	S1B–C10B	1.662 (3)
N1A–C9A	1.148 (4)	N1B–C9B	1.144 (4)
N2A–C10A	1.320 (4)	N2B–C10B	1.328 (4)
N3A–C4A	1.369 (4)	N3B–C4B	1.351 (4)
C7A–C8A	1.355 (4)	C7B–C8B	1.363 (4)
C8A–C9A	1.422 (4)	C8B–C9B	1.422 (4)
C8A–C10A	1.484 (4)	C8B–C10B	1.473 (4)
C8A–C7A–C1A	132.1 (3)	C8B–C7B–C1B	131.4 (3)
N1A–C9A–C8A	175.4 (3)	N1B–C9B–C8B	176.8 (4)
C2A–C1A–C7A–C8A	176.7 (3)	C2B–C1B–C7B–C8B	165.7 (3)
C1A–C7A–C8A–C10A	–178.3 (3)	C1B–C7B–C8B–C10B	177.1 (3)
C9A–C8A–C10A–N2A	–12.4 (4)	C9B–C8B–C10B–N2B	7.9 (4)
C7A–C8A–C10A–S1A	–13.0 (4)	C7B–C8B–C10B–S1B	2.0 (4)

**Table 6**Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ) for (Ic).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2A–H2AA $\cdots$ N1B <sup>v</sup>	0.86	2.26	2.990 (4)	143
N2A–H2AB $\cdots$ S1B	0.86	2.48	3.293 (4)	158
N2B–H2BA $\cdots$ N1A <sup>vi</sup>	0.86	2.43	3.133 (4)	139

Symmetry codes: (v)  $x, 1 - y, z - \frac{1}{2}$ ; (vi)  $x, 1 - y, \frac{1}{2} + z$ .

For all molecules of (Ia)–(Ic), H atoms were placed in calculated positions and included in the refinement using a riding model, with C–H or N–H distances of 0.93  $\text{\AA}$  for aromatic H atoms, 0.97  $\text{\AA}$  for CH<sub>2</sub> atoms and 0.86  $\text{\AA}$  for NH<sub>2</sub> atoms [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ ], and with C–H distances of 0.96  $\text{\AA}$  for CH<sub>3</sub> groups [ $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ ]. The H atoms in the disordered acetonitrile molecule (which lies on a twofold axis) were found from a difference Fourier map and included using an AFIX 33 command (SHELXL97; Sheldrick, 1997), with an occupancy of 0.5 and with C–H = 0.96  $\text{\AA}$  and  $U_{\text{iso}}(\text{H})$  values of  $1.5U_{\text{eq}}(\text{C})$ .

For all determinations, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *SHELXTL-Plus* (Sheldrick, 1994); program(s) used to solve-structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1169). Services for accessing these data are described at the back of the journal.

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