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Planarity of heteroaryldithiocarbazic acid derivatives showing tuberculostatic activity. II. Crystal structures of 3-[amino(pyrazin-2-yl)methylidene]-2-methylcarbazic acid esters[1]

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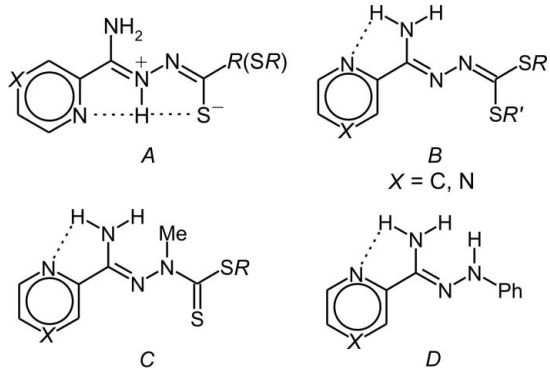
Four compounds showing moderate antituberculostatic activity have been studied to test the hypothesis that the planarity of the 2-[amino(pyrazin-2-yl)methylidene]dithiocarbazate fragment is crucial for activity. *N*′-Anilinopyrazine-2-carboximidamide, $C_{11}H_{11}N_5$, *D*1, and diethyl 2,2′-[({[amino(pyrazin-2-yl)methylidene]hydrazinylidene}methylidene)bis(sulfanediyl)]diacetate, $C_{14}H_{19}N_5O_4S_2$, *B*1, maintain planarity due to conjugation and attractive intramolecular hydrogen-bond contacts, while methyl 3-[amino(pyrazin-2-yl)methylidene]-2-methyldithiocarbazate, $C_8H_{11}N_5S_2$, *C*1, and benzyl 3-[amino(pyrazin-2-yl)methylidene]-2-methyldithiocarbazate, $C_{14}H_{15}N_5S_2$, *C*2, are not planar, due to methylation at one of the N atoms of the central N—N bond. The resulting twists of the two molecular halves (parts) of *C*1 and *C*2 are indicated by torsion angles of 116.5 (2) and −135.9 (2)°, respectively, compared with values of about 180° in the crystal structures of nonsubstituted compounds. As the methylated derivatives show similar activity against *Mycobacterium tuberculosis* to that of the nonsubstituted derivatives, maintaining planarity does not seem to be a prerequisite for activity.

Comment

The increasing resistance of *Mycobacterium tuberculosis* to existing agents and the resulting spread of the pathogen, in both developed and developing countries, makes the search for new tuberculostatics an important issue. 2-/3-/4-Pyridinecarbonimidoyldithiocarbazic acid esters and *N*′-thioamido-substituted pyrazinecarboxyamidrazones, of which many compounds have been synthesized by Foks and Orlewska and tested against standard *M. tuberculosis* strains (Foks & Janowiec, 1979; Foks *et al.*, 1992, 2002, 2004; Orlewska, 1996; Orlewska *et al.*, 1995, 2001), are one of the promising chemical classes showing action against tuberculosis.



Scheme 1

Our earlier studies of the crystal structures of the representatives of this class (*A* in Scheme 1), which all existed in a dipolar form, showed the same molecular features, of which the most significant was the bifurcated intramolecular hydrogen bond between protonated atom N3 as a donor and two acceptors, *viz.* the anionic S atom from the thioacid function and the N atom at the *ortho* position of the pyridine or pyrazine ring (Główka *et al.*, 2005; Olczak *et al.*, 2007; Orlewska *et al.*, 2001). A search of the Cambridge Structural Database (CSD, Version 5.31; Allen, 2002) succeeded in finding only two other similar structures (Bermejo *et al.*, 2001; Ketcham *et al.*, 2001) showing the features described above. The attractive intramolecular hydrogen-bond contacts and extensive conjugation, both present in these zwitterionic structures, keep all atoms of the molecules coplanar, except the terminal thioester or thioamide group (*A* in Scheme 1). In addition, in two crystal structures of *S*,*S*′-diesters of pyridinecarbonimidoyldithiocarbazic acid (*B* in Scheme 1) showing moderate activity against *M. tuberculosis* strains, coplanarity was also maintained despite the lack of an active H atom at N3 (Główka *et al.*, 1999).

An analysis of the data available at that time suggested that planarity of the pyridin-2-yl or pyrazin-2-ylformamide thiosemicarbazone fragment could be a prerequisite for tuberculostatic activity (Olczak *et al.*, 2007). To check the importance and generality of this observation, we have determined, and describe in this study, four crystal structures of other mono- and diesters of pyridine- or pyrazinecarbonimidoyldithiocarbazic acid derivatives, namely diethyl 2,2′-[({[amino(pyrazin-2-yl)methylidene]hydrazinylidene}methylidene)bis(sulfanediyl)]diacetate, *B*1, methyl 3-[amino(pyrazin-2-yl)methylidene]-2-methyldithiocarbazate, *C*1, benzyl 3-[amino(pyrazin-2-yl)methylidene]-2-methyldithiocarbazate, *C*2, and *N*′-anilinopyrazine-2-carboximidamide, *D*1, having the same pyridine- or pyrazineamidine fragment but lacking protonation on atom N3 and, as a consequence, lacking crucial intramolecular (bifurcated) hydrogen-bond contacts with N3—H as a donor.

[1] For Part I, see Olczak *et al.* (2007).

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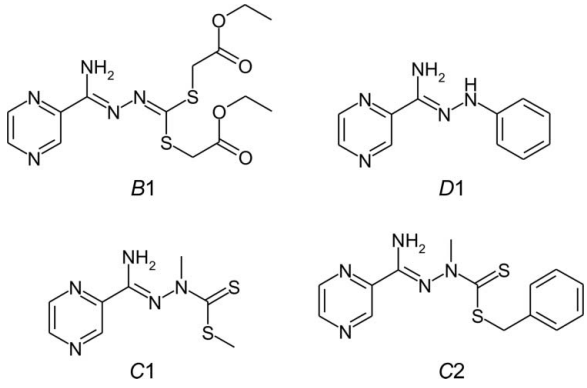
Together with six thioamide and thioester structures found in the CSD (Bermejo *et al.*, 2004, 2005*a*,*b*; Castiñeiras *et al.*, 2000; Labisbal *et al.*, 2002; West *et al.*, 1999), these compounds form a sufficient set for statistical analysis and verification of the hypothesis that the planarity of a whole molecule is correlated with activity, especially given that, in two structures presented here (*C*1 and *C*2), atom N2 has been substituted by a methyl group. The substitution introduces spatial repulsion between the methyl group at atom N2 and the neighbouring amine group at atom C4, and forces a twist at the N2—N3 bond (Figs. 1 and 2), which also excludes conjugations involving that bond. As a result, we expected a significant difference in their activities.



With the exception of the twist at the N2—N3 bond in structures *C*1 and *C*2, both halves of the molecules are planar. The coplanarity of the pyrazine ring and the neighbouring imide group in all structures determined in this work, as expected on the basis of known structures (Bermejo *et al.*, 2004, 2005*a*,*b*; Castiñeiras *et al.*, 2000; Główka *et al.*, 1999; Labisbal *et al.*, 2002; West *et al.*, 1999), is indicated by the C41—C4═N3—N2 torsion angles of −177.67 (12), −177.88 (13), 176.53 (12) and −178.18 (13)°, respectively, for *B*1, *C*1, *C*2 and *D*1 (Table 5). The coplanarity is obviously secured by the attractive intramolecular N5—H···N(pyridine) hydrogen-bond contact, characterized by H···N42 distances of 2.2–2.7 Å and angles at hydrogen of 101–112°, as no significant conjugation between the π systems of the pyrazine ring and imide group (Scheme 1) is observed. This observation

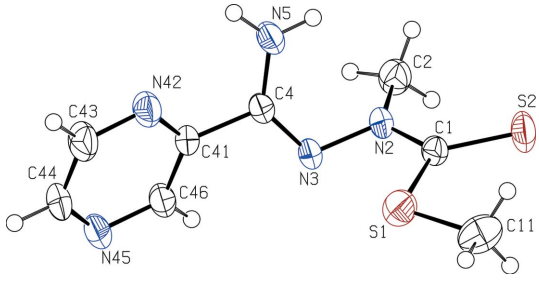


Figure 1
The molecular structure of *C*1, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

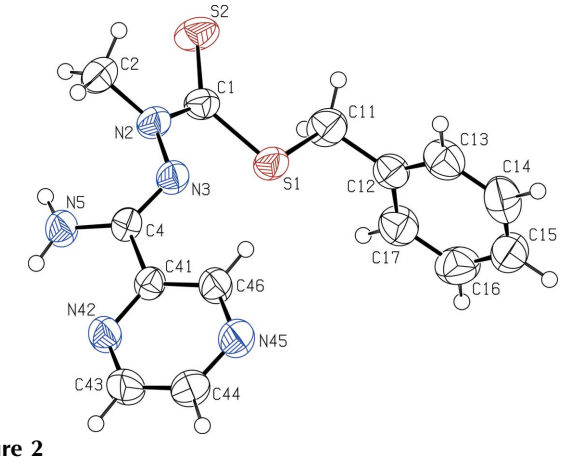


Figure 2
The molecular structure of *C*2, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

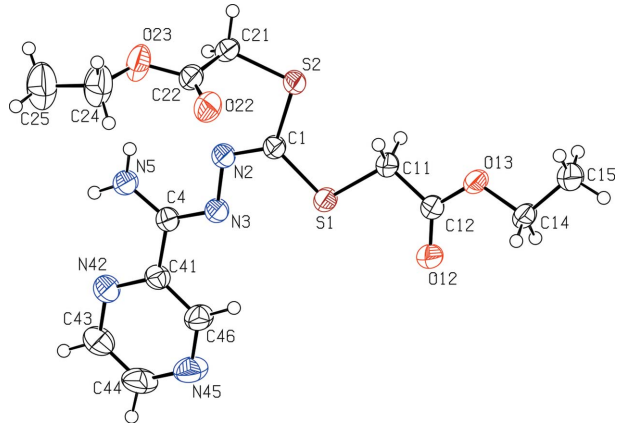


Figure 3
The molecular structure of *B*1, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

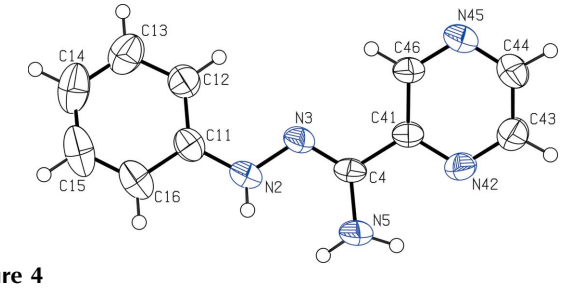


Figure 4
The molecular structure of *D*1, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

is confirmed by the lengths of the formally single bonds C4—C41 and C4—N5, in the ranges 1.473 (2)–1.493 (2) and 1.329 (2)–1.3577 (19) Å, respectively (Table 5). Instead, in *C*1 and *C*2, another conjugated system (S═C1—N2) is observed, resulting in the shortening of the C1—N2 bond to about 1.34 Å (Table 5), compared with 1.43–1.48 Å in similar fragments containing a tetrahedral C atom found in the CSD. As expected, the resulting twist around the N2—N3 bond in *C*1

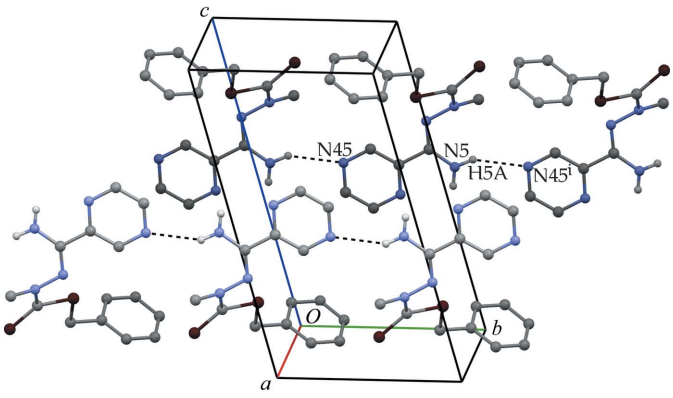


Figure 5
The intermolecular hydrogen bonds (dashed lines) in the crystal structure of *C*2, determining the packing of the molecules. Two *C*(6) chains (related by a centre of symmetry) parallel to [010] run in opposite directions. Symmetry codes are as given in Table 3.

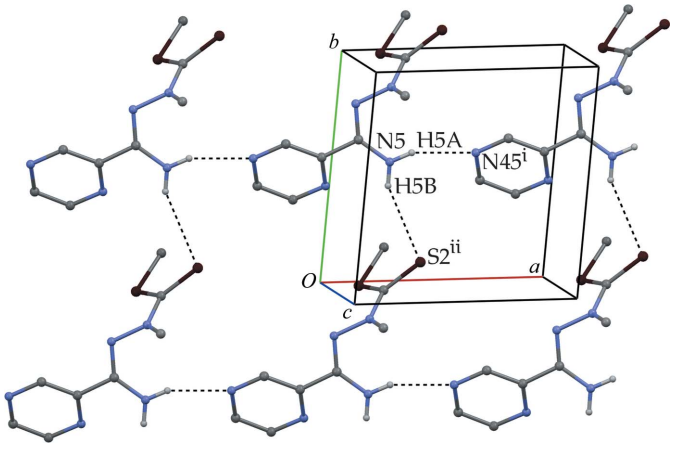


Figure 6
The intermolecular hydrogen bonds (dashed lines) in the crystal structure of *C*1, determining the packing of the molecules. Two chains, *C*(6) parallel to [100] and *C*(7) parallel to [010], form an $R_4^4(24)$ ring at the second level of graph-set theory. Symmetry codes are as given in Table 2.

and *C*2 breaks the coplanarity of the pyrazinamidrazone and thioacid fragments, which has been observed in all monoesters of heteroarylcarbonamidoyldithiocarbazic acids studied so far by X-ray diffraction. This is evidenced in this study by the torsion angle C1—N2—N3═C4 being 116.53 (16)° in *C*1 and −135.85 (15)° in *C*2, compared with the antiperiplanar conformation observed in *B*1 and *D*1 (Figs. 3 and 4) and 24 similar structures found in the CSD. The largest deviation of the C1—N2—N3═C4 torsion angle from 180° is 7.55 (13)° found in *B*1.

Surprisingly, as the tuberculostatic activities of the 'non-planar' compounds *C*1 and *C*2 against three selected strains of *Mycobacterium tuberculosis* are similar to those of other tested compounds (Zwolska, 2009), it seems that maintaining planarity of the whole molecule is not important for its biological action. However, the engagement of hydrophilic H atoms in the intramolecular hydrogen-bond contacts commonly observed in these compounds may facilitate the

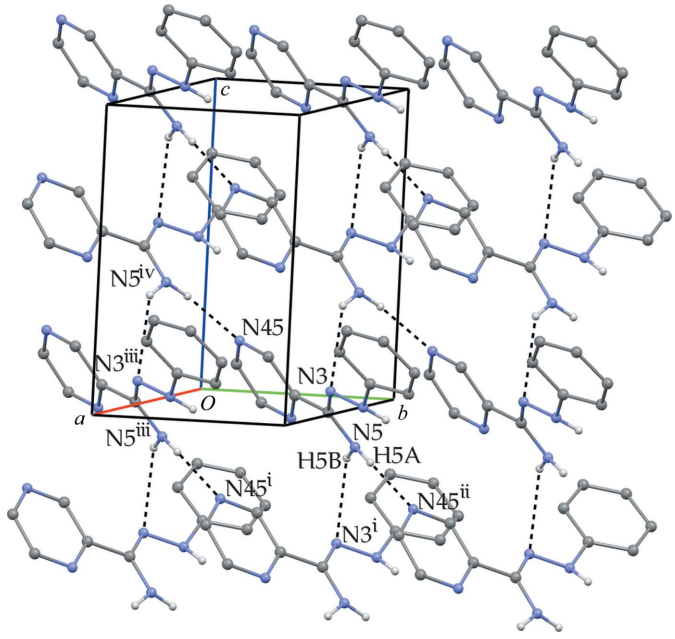


Figure 7
The intermolecular hydrogen bonds (dashed lines) in the crystal structure of *D*1, determining the packing of the molecules. *C*(6) chains parallel to [02$\bar{1}$] and *C*(4) chains parallel to [001] form $R_4^4(18)$ rings at the second level of graph-set theory. [Symmetry codes: (i) $-x+\frac{1}{2}, y, z-\frac{1}{2}$; (ii) $-x+\frac{1}{2}, y+1, z-\frac{1}{2}$; (iii) $x, y-1, z$; (iv) $-x+\frac{1}{2}, y-1, z+\frac{1}{2}$.]

smooth passage of the studied molecules through hydrophobic cell membranes, which may also affect their tuberculostatic activity.

Despite the differences in the chemical structures of the type *A*, *B*, *C* and *D* compounds, the intermolecular hydrogen-bond contacts observed in their crystal structures reveal a common motif, *viz.* a *C*(6) chain (Bernstein *et al.*, 1995) formed through an intermolecular N5—H5*A*···N45′ hydrogen bond (symmetry codes for acceptor atom N45′ are as in Tables 1–4). In *C*2 and *B*1, the chain runs parallel to the [010] direction, in *C*1 parallel to [100] and in *D*1 parallel to [02$\bar{1}$]. In *C*2 this is the only hydrogen-bond pattern formed (Fig. 5). The same phenomenon is observed in all structures bearing appropriate functions in analogous positions of the molecules (Olczak *et al.*, 2007; Zhang *et al.*, 2009). In *C*1, at the first level of graph-set theory, an additional motif is formed through an N5—H5*B*···S2(x, $y-1$, z) interaction (Table 2), namely a *C*(7) chain parallel to the [010] direction (Fig. 6). These two chains form a sheet parallel to the (001) plane in which (at the second level of graph-set theory) an $R_4^4(24)$ ring can be identified (Fig. 6). In *D*1, apart from the *C*(6) chain common to all studied structures, a new *C*(4) chain parallel to the [001] direction appears through an N5—H5*B*···N3($-x+\frac{1}{2}, y, z-\frac{1}{2}$) hydrogen bond (Fig. 7 and Table 4). These two chains at the second level of graph-set theory cause the appearance of an $R_4^4(18)$ ring (Fig. 7). The most complex hydrogen-bond pattern is found in *B*1 because of the existence of four different hydrogen bonds (Fig. 8). At the first level there are four chains: (*a*) *C*(6) parallel to [010], (*b*) *C*(4) parallel to [001], (*c*) *C*(13) parallel to [001] and (*d*) *C*(10) parallel to [001]. At the

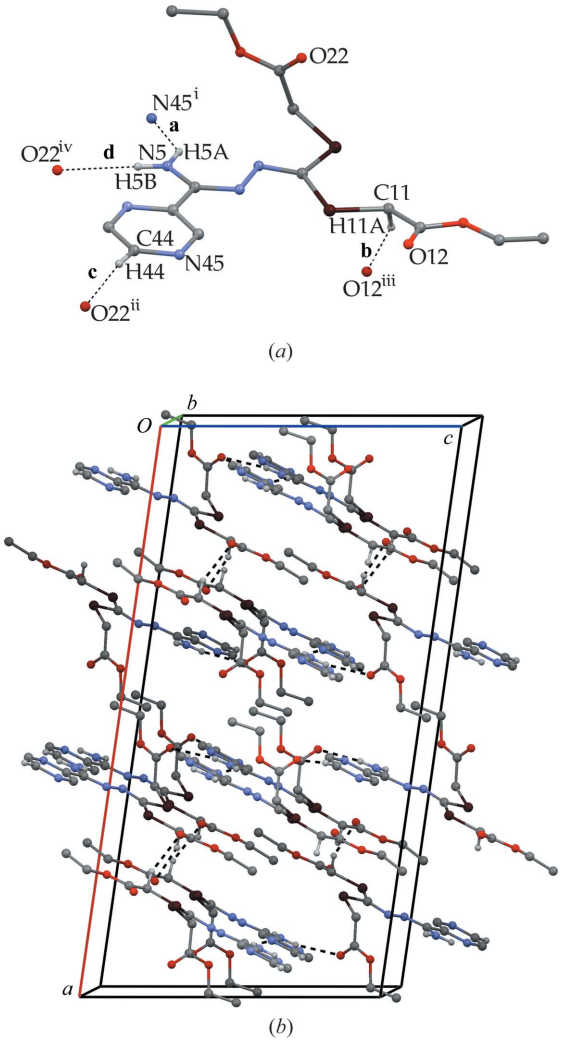


Figure 8
(*a*) The intermolecular hydrogen bonds (dashed lines) and (*b*) the packing of the molecules in the crystal structure of *B*1. The structure contains four distinct hydrogen bonds, designated **a** (N5—H5*A*···N45^{i}), **b** (C11—H11*A*···O12^{iii}), **c** (C44—H44···O22^{ii}) and **d** (N5—H5*B*···O22^{iv}). [Symmetry codes: (i) $x, y+1, z$; (ii) $x, -y, z-\frac{1}{2}$; (iii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x, -y+1, z-\frac{1}{2}$.]

second level, for each pair of hydrogen bonds the following rings can be identified: (*ab*) $R_3^3(24)$, (*ac*) $R_4^4(32)$, (*ad*) $R_4^4(30)$, (*bc*) $R_4^4(42)$, (*bd*) $R_4^4(36)$ and (*cd*) $R_4^3(32)$. The smallest rings observed at the third level are as follows: (*abc*) $R_5^5(32)$, (*abd*) $R_5^5(30)$, (*acd*) $R_3^2(7)$ and (*bcd*) $R_4^3(27)$. At the fourth level, $R_6^6(33)$ is the smallest ring which is formed in this structure.

Experimental

The syntheses of the title compounds were as described by Foks & Janowiec (1979) for *D*1, Foks *et al.* (1992) for *B*1, and Orlewska (1996) for *C*1 and *C*2.

Single crystals of compounds *B*1, *C*1, *C*2 and *D*1 suitable for X-ray diffraction were obtained from chloroform–ethanol (1:1 *v*/*v*), chloroform–ethanol (1:1 *v*/*v*), chlorobenzene and chloroform solutions, respectively, by slow evaporation of the solvents at room temperature.

Compound *B*1

Crystal data

$C_{14}H_{19}N_5O_4S_2$
$M_r = 385.46$
Monoclinic, $C2/c$
$a = 29.5249\ (14)$ Å
$b = 8.0969\ (9)$ Å
$c = 15.4717\ (6)$ Å
$\beta = 98.635\ (4)^\circ$
$V = 3656.7\ (5)$ Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.32$ mm^{-1}
$T = 291$ K
0.4 × 0.3 × 0.1 mm

Data collection

Kuma KM-4 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.729$, $T_{max} = 1.000$
21104 measured reflections
3722 independent reflections
3064 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.092$
$S = 1.05$
3722 reflections
227 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Compound *C*1

Crystal data

$C_8H_{11}N_5S_2$
$M_r = 241.34$
Triclinic, $P\overline{1}$
$a = 7.7213\ (1)$ Å
$b = 8.1004\ (1)$ Å
$c = 9.3331\ (1)$ Å
$\alpha = 87.9959\ (11)^\circ$
$\beta = 79.0802\ (12)^\circ$
$\gamma = 82.8402\ (10)^\circ$
$V = 568.67\ (1)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.44$ mm^{-1}
$T = 290$ K
0.3 × 0.3 × 0.3 mm

Table 1
Hydrogen-bond geometry (Å, °) for *B*1.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5*A*···N45^{i}	0.86	2.63	3.320 (2)	139
C44—H44···O22^{ii}	0.93	2.48	3.403 (2)	174
C11—H11*A*···O12^{iii}	0.97	2.55	3.473 (2)	159
N5—H5*B*···O22^{iv}	0.86	2.37	3.2002 (17)	164

Symmetry codes: (i) $x, y+1, z$; (ii) $x, -y, z-\frac{1}{2}$; (iii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x, -y+1, z-\frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °) for *C*1.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5*A*···N45^{i}	0.86	2.24	2.9975 (19)	147
N5—H5*B*···S2^{ii}	0.86	2.87	3.6387 (16)	149

Symmetry codes: (i) $x+1, y, z$; (ii) $x, y-1, z$.

Table 3
Hydrogen-bond geometry (Å, °) for *C*2.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5*A*···N45^{i}	0.86	2.39	3.135 (2)	146

Symmetry code: (i) $x, y+1, z$.

Table 4
Hydrogen-bond geometry (Å, °) for *D*1.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5*B*···N3^{i}	0.921 (18)	2.54 (2)	3.106 (2)	119.9 (15)
N5—H5*A*···N45^{ii}	0.894 (18)	2.135 (19)	3.005 (2)	164.1 (15)

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

Table 5
Selected bond lengths (Å) for the title structures, compared with data from the CSD, and absolute values of selected torsion angles (°).

Structure	C4—C41	C4—N5	N3—C4	N2—N3	C1(C11)—N2
*B*1	1.486 (2)	1.3389 (19)	1.2966 (17)	1.4079 (17)	1.2803 (17)
*C*1	1.4919 (19)	1.329 (2)	1.291 (2)	1.4215 (16)	1.334 (2)
*C*2	1.493 (2)	1.339 (2)	1.289 (2)	1.4180 (18)	1.341 (2)
*D*1	1.473 (2)	1.3577 (19)	1.287 (2)	1.3786 (17)	1.386 (2)
CSD	1.46–1.50	1.32–1.36	1.29–1.31	1.36–1.41	1.27–1.36

	N42—C—C—N5	C41—C—N—N2	C4—N—N—C1(C11)	C4—N—N—Me	N3—N—C—S2
*B*1	1.8 (2)	177.67 (12)	172.45 (13)		178.75 (10)
*C*1	27.4 (2)	177.88 (13)	116.53 (16)	78.19 (18)	168.75 (11)
*C*2	2.1 (2)	176.52 (12)	135.85 (15)	66.56 (18)	170.04 (11)
*D*1	5.7 (2)	178.18 (13)	174.58 (14)		

Data collection

Kuma KM-4 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.940, T_{max} = 1.000
7633 measured reflections
2319 independent reflections
2161 reflections with $I > 2\sigma(I)$
R_{int} = 0.009

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.095
S = 1.12
2319 reflections
138 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Compound *C*2

Crystal data

$C_{14}H_{15}N_5S_2$
M_r = 317.43
Triclinic, $P\overline{1}$
a = 7.2329 (1) Å
b = 7.9041 (1) Å
c = 14.0969 (2) Å
α = 105.717 (1)°
β = 91.368 (1)°
γ = 93.863 (1)°
V = 773.27 (2) Å^3
Z = 2
Cu $K\alpha$ radiation
μ = 3.12 mm^{-1}
T = 290 K
0.3 × 0.2 × 0.05 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.735, T_{max} = 1.000
8491 measured reflections
2647 independent reflections
2549 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.098
S = 1.06
2647 reflections
191 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Compound *D*1

Crystal data

$C_{11}H_{11}N_5$
M_r = 213.25
Orthorhombic, $Pca2_1$
a = 20.7274 (6) Å
b = 5.7456 (1) Å
c = 9.1455 (3) Å
V = 1089.15 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 290 K
0.4 × 0.3 × 0.05 mm

Data collection

Kuma KM-4 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.728, T_{max} = 1.000
15567 measured reflections
1415 independent reflections
1055 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.068
S = 0.90
1415 reflections
154 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.11 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}

H atoms were located in difference Fourier maps and subsequently geometrically optimized and allowed for as riding atoms, with C—H = 0.95 Å for aromatic CH groups, 0.97 Å for secondary CH_2 groups and 0.96 Å for methyl groups, and N—H = 0.86 Å, with U_{iso}(H) = 1.2U_{eq}(C,N). In the case of *D*1, the positions of all amine H atoms were refined freely. In the absence of significant anomalously scattering, atoms in the crystal of *D*1, Friedel pairs were merged before the final refinement and the absolute structure was assigned arbitrarily.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007) for *B*1, *C*1 and *D*1; *APEX2* (Bruker, 2002) for *C*2. Cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007) for *B*1, *C*1 and *D*1; *SAINT-Plus* (Bruker, 2003) for *C*2. Data reduction: *CrysAlis RED* for *B*1, *C*1 and *D*1; *SAINT-Plus* for *C*2. For all compounds, program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3209). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bermejo, E., Castiñeiras, A., Fostiak, L. M., García, I., Llamas-Saiz, A. L., Swearingen, J. K. & West, D. X. (2001). *Z. Naturforsch. Teil B*, **56**, 1297–1305.
Bermejo, E., Castiñeiras, A., García-Santos, I. & West, D. X. (2004). *Z. Anorg. Allg. Chem.* **630**, 1096–1109.
Bermejo, E., Castiñeiras, A., García-Santos, I. & West, D. X. (2005*a*). *Z. Anorg. Allg. Chem.* **631**, 728–738.
Bermejo, E., Castiñeiras, A., García-Santos, I. & West, D. X. (2005*b*). *Z. Anorg. Allg. Chem.* **631**, 2011–2019.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2002). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2003). *SAINT-Plus*. Version 6.45. Bruker AXS Inc., Madison, Wisconsin, USA.
Castiñeiras, A., García, I., Bermejo, E. & West, D. X. Z. (2000). *Z. Naturforsch. Teil B*, **55**, 511–518.
Foks, H. & Janowiec, M. (1979). *Acta Pol. Pharm.* **36**, 155–160.
Foks, H., Mieczkowska, J., Janowiec, M., Zwolska, Z. & Andrzejczak, Z. (2002). *Chem. Heterocycl. Compd*, **38**, 810–816.
Foks, H., Orlewska, C. & Janowiec, M. (1992). *Acta Pol. Pharm. Drug Res.* **49**, 47–50.
Foks, H., Trapkowska, I., Janowiec, M., Zwolska, Z. & Augustynowicz-Kopeć, E. (2004). *Chem. Heterocycl. Compd*, **40**, 1185–1193.
Główka, M. L., Martynowski, D., Olczak, A., Kozłowska, K., Ołubek, Z., Orlewska, C. & Foks, H. (1999). *Pol. J. Chem.* **73**, 845–851.
Główka, M. L., Martynowski, D., Olczak, A., Orlewska, C., Foks, H., Bojarska, J., Szczesio, M. & Gołka, J. (2005). *J. Chem. Crystallogr.* **35**, 477–480.
Ketcham, K. A., Swearingen, J. K., Castiñeiras, A., García, I., Bermejo, E. & West, D. X. (2001). *Polyhedron*, **20**, 3265–3273.
Labisbal, E., Sousa-Pedrares, A., Castiñeiras, A., Swearingen, J. K. & West, D. X. (2002). *Polyhedron*, **21**, 1553–1559.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Olczak, A., Główka, M. L., Gołka, J., Szczesio, M., Bojarska, J., Kozłowska, K., Foks, H. & Orlewska, C. (2007). *J. Mol. Struct.* **830**, 171–175.
Orlewska, C. (1996). PhD thesis, Medical University of Gdańsk, Poland.
Orlewska, C., Foks, H., Janowiec, M. & Zwolska-Kwiek, Z. (1995). *Pharmazie*, **50**, 565–566.
Orlewska, C., Foks, H., Sowiński, P., Martynowski, D., Olczak, A. & Główka, M. L. (2001). *Pol. J. Chem.* **75**, 1237–1245.
Oxford Diffraction (2007). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
West, D. X., Swearingen, J. K., Valdes-Martinez, J. & Hernandez-Ortega, S. (1999). *Polyhedron*, **18**, 2919–2929.
Zhang, Y.-W., Wang, J.-Q. & Cheng, L. (2009). *Acta Cryst.* E**65**, o1941.
Zwolska, Z. (2009). Personal communication.