Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2,5-Diaminothiophene-3,4-dicarbonitrile

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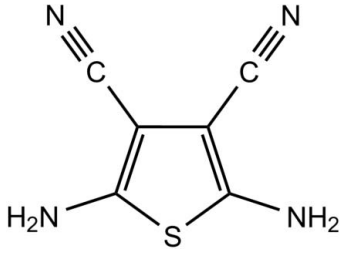
Received 12 July 2012; accepted 3 August 2012

Key indicators: single-crystal X-ray study; T = 123 K; mean σ(C–C) = 0.006 Å; R factor = 0.053; wR factor = 0.116; data-to-parameter ratio = 15.1.

In the title compound, $C_6H_4N_4S$, the planar molecule lies across a crystallographic mirror plane. In the crystal, the molecules form centrosymmetric dimers through cyclic amino N—H···N hydrogen-bonding associations with cyano N-atom acceptors [graph set $R_2^2(12)$] and these dimers are extended through amine–cyano N—H···N associations into a three-dimensional network.

Related literature

For the synthesis of this and related compounds *via* the reaction of tetracyanoethylene with hydrogen sulfide, see: Cairns *et al.* (1957); Middleton *et al.* (1958); Middleton (1959). For the use of this compound as a reagent, see: Nemykin *et al.* (2012). For graph-set analysis, see: Etter *et al.* (1990). For details of the weighting scheme, see: Prince (1982); Watkin (1994).



Experimental

Crystal data

$C_6H_4N_4S$
M_r = 164.19
Orthorhombic, *Pbcn*
a = 3.9231 (2) Å
b = 13.8213 (12) Å
c = 12.6465 (11) Å
V = 685.72 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.40 mm^{-1}
T = 123 K
0.41 × 0.24 × 0.16 mm

Data collection

Rigaku RAPID II diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.69, T_{max} = 0.94
2260 measured reflections
783 independent reflections
492 reflections with $I > 2\sigma(I)$
R_{int} = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.116
S = 0.99
769 reflections
51 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.63 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H2···N2^{i}	0.87	2.29	3.106 (5)	156
N1—H1···N2^{ii}	0.88	2.38	3.196 (5)	153

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+\frac{3}{2}, y+\frac{1}{2}, z$.

Data collection: *CrystalClear* (Rigaku, 2009); cell refinement: *HKL-2000* (Otwinowski & Minor, 1997); data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 2008); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

This study was supported by the National Science Foundation (grants CHE-0922366 and CHE-1110455).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZS2223).

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supporting information

Acta Cryst. (2012). E**68**, o2693 [doi:10.1107/S1600536812034678]

2,5-Diaminothiophene-3,4-dicarbonitrile

Christopher J. Ziegler and Victor N. Nemykin

S1. Comment

The synthesis of the title compound 2,5-diamino-3,4-dicyanothiophene, $C_6H_4N_4S$, and similar compounds has previously been reported (Cairns *et al.*, 1957; Middleton, 1959) and chemical transformations of this compound and its usage in macrocyclic chemistry have also been described (Middleton *et al.*, 1958; Nemykin *et al.*, 20120. In the structure of the title compound the planar molecule lies across a crystallograpic mirror plane (Fig. 1). The C—S bond length is 1.750 (4) Å and the C—C bond distances are unequal [1.358 (5) Å for C1—C2 and 1.458 (7) Å for C2—C2^{i} [for symmetry code (i): -*x*+2, *y*, -*z*+3/2]. The C—N_{amine} bond distance [1.358 (5) Å] shows some double-bond character and the C2—C3 bond length [1.422 (5) Å] is shorter than expected for a single bond. The cyanide C3—N2 bond length is 1.149 (5) Å.

In the crystal, the molecules form centrosymmetric cyclic dimers through amino N—H···N hydrogen-bonding associations with cyano N-atom acceptors (Table 1) [graph set $R^2_2(12)$ (Etter *et al.*, 1990)] and these dimers are extended into a three-dimensional structure through N—H···N amine···cyano group associations. The thiophene molecules form antiparallel stacks down *a*, with a thiophene-thiophene ring centroid separation of 3.923 (2) Å.

S2. Experimental

The title compound was prepared using an earlier published procedure via the reaction of tetracyanoethylene and hydrogen sulfide (Cairns *et al.*, 1957) and characterized by ^{1}H and ^{13}C NMR spectroscopy. The single crystal used for the X-ray analysis was obtained by slow cooling of a saturated solution in DMSO.

S3. Refinement

The H atoms were all located in a difference map. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (N—H in the range 0.86–0.89 Å) and U_{iso}(H) (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints. In the absence of significant anomalous scattering, Friedel pairs were merged.

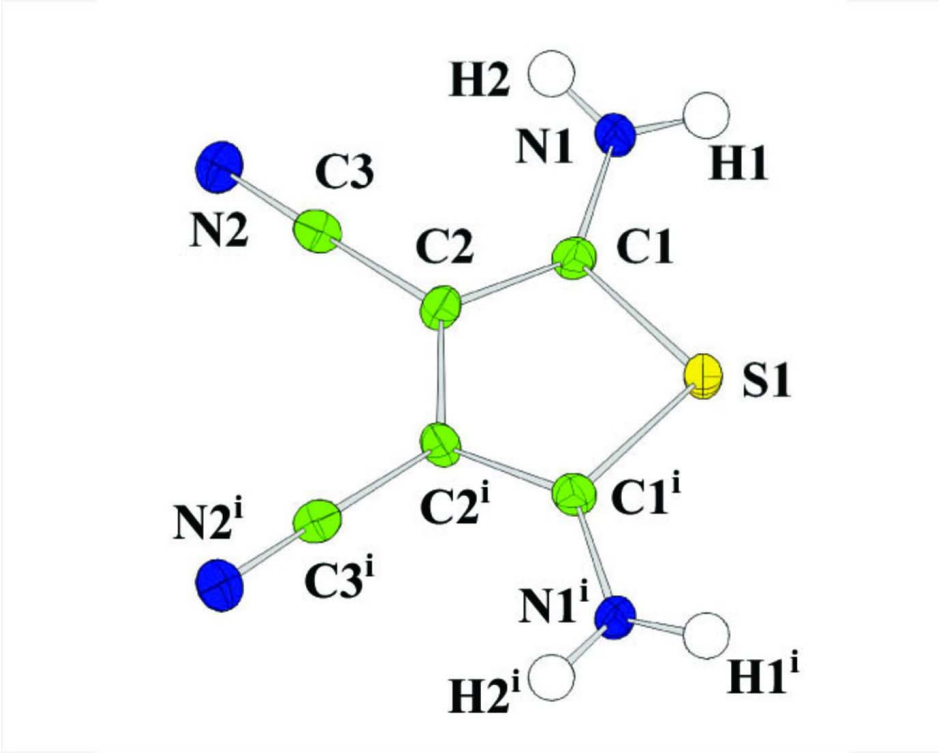

Figure 1

The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius. For symmetry code (i): -*x*+2, *y*, -*z*+3/2.

2,5-Diaminothiophene-3,4-dicarbonitrile

Crystal data

$C_6H_4N_4S$
M_r = 164.19
Orthorhombic, *Pbcn*
Hall symbol: -P 2n 2ab
a = 3.9231 (2) Å
b = 13.8213 (12) Å
c = 12.6465 (11) Å
V = 685.72 (9) Å^3
Z = 4
F(000) = 336

D_x = 1.590 Mg m^{-3}
Melting point: 513 K
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 783 reflections
θ = 2–27°
μ = 0.40 mm^{-1}
T = 123 K
Plate, brown
0.41 × 0.24 × 0.16 mm

Data collection

Rigaku RAPID II diffractometer
Radiation source: Mo Ka
Graphite monochromator
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.69, T_{max} = 0.94

2260 measured reflections
783 independent reflections
492 reflections with $I > 2\sigma(I)$
R_{int} = 0.054
θ_{max} = 27.5°, θ_{min} = 3.4°
h = −5→5
k = −13→17
l = −13→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.116$
$S = 0.99$
769 reflections
51 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
Method, part 1, Chebychev polynomial, (Watkin, 1994; *P*rince, 1982) [*w*eight] = $1.0/[A_0*T_0(x) + A_1*T_1(x) \cdots + A_{n-1}]*T_{n-1}(x)]$ where A_i are the Chebychev coefficients listed below and x = *F* /*F*max Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * [1-(delta*F*/6*sigma*F*)^2]^2 A_i are: 57.9 74.5 21.5
$(\Delta/\sigma)_{max} = 0.0000992$
$\Delta\rho_{max} = 0.65$ e Å^{-3}
$\Delta\rho_{min} = -0.63$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Rigaku XStream 2000 open-flow nitrogen cryostat with a nominal stability of 0.1 K.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	1.0000	0.75078 (10)	0.7500	0.0189
C1	0.8517 (10)	0.6628 (3)	0.6618 (3)	0.0184
N1	0.7035 (9)	0.6908 (2)	0.5697 (2)	0.0205
H2	0.6326	0.6473	0.5246	0.0500*
H1	0.6790	0.7530	0.5557	0.0500*
C2	0.9146 (10)	0.5716 (3)	0.6988 (3)	0.0188
C3	0.8190 (10)	0.4873 (3)	0.6416 (3)	0.0211
N2	0.7390 (11)	0.4203 (2)	0.5938 (3)	0.0286

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0243 (7)	0.0137 (5)	0.0188 (6)	0.0000	−0.0041 (6)	0.0000
C1	0.0202 (19)	0.0184 (17)	0.0166 (16)	−0.0027 (16)	0.0025 (15)	−0.0009 (13)
N1	0.0285 (19)	0.0152 (14)	0.0177 (14)	0.0003 (14)	−0.0060 (14)	0.0012 (11)
C2	0.023 (2)	0.0153 (16)	0.0181 (17)	−0.0018 (15)	0.0016 (16)	−0.0027 (14)
C3	0.024 (2)	0.0213 (19)	0.0176 (17)	0.0006 (17)	−0.0003 (16)	0.0021 (15)
N2	0.040 (2)	0.0205 (16)	0.0249 (17)	−0.0053 (17)	−0.0034 (18)	−0.0021 (13)

Geometric parameters (Å, º)

S1—C1^i	1.750 (4)	N1—H1	0.884
S1—C1	1.750 (4)	C2—C2^i	1.458 (7)
C1—N1	1.358 (5)	C2—C3	1.422 (5)
C1—C2	1.367 (5)	C3—N2	1.149 (5)
N1—H2	0.874		
C1^i—S1—C1	91.9 (3)	H2—N1—H1	120.2
S1—C1—N1	119.4 (3)	C2^i—C2—C1	112.8 (2)

S1—C1—C2	111.3 (3)	C2^{i}—C2—C3	125.0 (2)
N1—C1—C2	129.3 (3)	C1—C2—C3	122.3 (3)
C1—N1—H2	120.0	C2—C3—N2	178.6 (4)
C1—N1—H1	119.8		

Symmetry code: (i) $-x+2, y, -z+3/2$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H2···N2^{ii}	0.87	2.29	3.106 (5)	156
N1—H1···N2^{iii}	0.88	2.38	3.196 (5)	153

Symmetry codes: (ii) $-x+1, -y+1, -z+1$; (iii) $-x+3/2, y+1/2, z$.