Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

(*Z*)-Ethyl 2-cyano-3-(1-phenylethylamino)but-2-enedithioate

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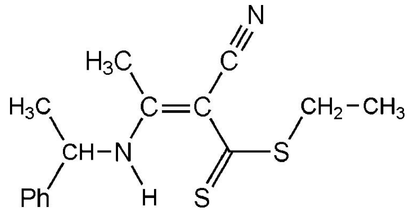
Received 30 March 2007; accepted 24 April 2007

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.003 Å; R factor = 0.043; wR factor = 0.122; data-to-parameter ratio = 17.1.

The title molecule, $C_{15}H_{18}N_2S_2$, adopts the Z configuration. The dihedral angle between the planes of the phenyl ring and the CH—NH—C═C(C≡N)—C(═S)—S fragment is 76.10 (5) Å. The molecular structure is stabilized by a weak intramolecular N—H···S hydrogen bond [H···S = 2.29 (3) Å, N···S = 2.981 (2) Å and N—H···S = 145 (2)°].

Related literature

For related literature, see: Belhadj-Tahar *et al.* (1996); Contreras *et al.* (2004); Feroci *et al.* (2000); Feroci *et al.* (2003); Hou *et al.* (2006); Jansons (1976); Laus *et al.* (2001); Szulzewsky *et al.* (1984); Toumi *et al.* (2007).



Experimental

Crystal data

$C_{15}H_{18}N_2S_2$
M_r = 290.43
Monoclinic, $P2_1/c$
a = 8.997 (3) Å
b = 10.645 (3) Å
c = 16.293 (3) Å
β = 95.97 (2)°
V = 1552.0 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.33 mm^{-1}
T = 298 (2) K
0.50 × 0.50 × 0.50 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.816, $T_{\max}$ = 0.847
4376 measured reflections
3386 independent reflections
2592 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.014
2 standard reflections
frequency: 120 min
intensity decay: 4%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.122
S = 1.02
3386 reflections
198 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.71 e Å^{-3}
$\Delta\rho_{\min}$ = −0.47 e Å^{-3}

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

The authors thank le Ministère de l'Enseignement Supérieur, de la Recherche Scientifique et de la Technologie for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2354).

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doi:10.1107/S1600536807020429

supplementary materials

Acta Cryst. (2007). E**63**, o2735   [**doi:10.1107/S1600536807020429**]

(*Z*)-Ethyl 2-cyano-3-(1-phenylethylamino)but-2-enedithioate

M. Toumi, F. Ben Amor, N. Raouafi, M. Bordeau, A. Driss and **K. Boujlel**

Comment

Dithiocarboxylic acid and its derivatives are good complexing agents for transition metal elements (Contreras *et al.*, 2004; Jansons, 1976). They exhibit antitumoral actvities (Hou *et al.*, 2006), and are useful in isotope labelling methods with radioactive nuclei (Belhadj-Tahar *et al.*, 1996). More recently, these compounds gained attention in polymer chemistry for their ability to control radical polymerization, especially the RAFT radical polymerization (Laus *et al.*, 2001).

The electolysis of acetonitrile under galvanostatic conditions in the presence of tetrabutylammonium perchlorate as a supporting electrolyte gives the cyanomethyl anion, a strong base, enough to deprotonate primary, secondary amines and amino alcohols to give the corresponding anions, useful intermediates for mild synthesis of alkyl carbamates, and oxazolinones by reaction with carbon dioxide (Feroci *et al.*, 2000; 2003).

Under these conditions, the electrolysis of 1-phenylethylamine followed by the addition of carbon disulfide and ethyliodide yields the title compound, (I). The product formation is a result of autocondensation of acetonitrile followed by removal of ammonia by nucleophilic substitution with 1-phenylethlyamine, finally reaction with CS_2 and EtI gives the compound (I). The structure of the N-unsbustituted compound (II) and its carboxylic analogue (III) have been reported (Szulzewsky *et al.*, 1984). Compound (II) was obtained as a by-product during the course of reaction.

The structure determination of (I) was undertaken as a part of our studies on the generation and use of electrogenerated base (EGB) in organic synthesis and their applications in order to access to dithiocarbamates, dithiocarboxylic, trithiocarbonate esters (Toumi *et al.*, 2007).

The molecular structure and labelling scheme are illustrated in Fig. 1. Atoms N1, N2, S1, S2, C1, C2, C3, C5 and C6 are coplanar, with an r.m.s deviation of 0.032 Å. The dihedral angle between the C8—C13 phenyl ring and the N1/N2/S1/S2/C1/C2/C3/C5/C6 plane is 76.10 (5) Å. The molecule adopts the Z configuration. The molecular structure is stabilized by an N2–H2···S1 intramolecular hydrogen bond [H2···S2 2.29 (3) Å, N2···S1 2.981 (2) Å and N2—H2···S1 145 (2)°].

Experimental

The title compound was obtained from the electrolysis of racemic 1-phenylethylamine (0.5 g, 4.1 mmol) under glavanostatic conditions (I = 80 mA, 6.0 h, Q = 2.0 F/mole) in anhydrous acetonitrile (80 ml) as solvent and reagent in the presence of tetrabutylammonium perchlorate (3.2 g, 8.0 mmol) as supporting electrolyte. At the end of electrolysis, carbon disulfide (0.38 g, 5.0 mmol) was added with stirring for 1 h and then ethyl iodide (0.78 g, 5.0 mmol) was added and the mixture was stirred overnight. After the removal of acetonitrile under reduced pressure, the residue was quenched with water and extracted with diethyl ether. The resulting product was chromatographed on silica gel (mesh 60, ethyl acetate/hexanes 30/70) to afford a pure product (yield: 73%, m.p. 354 K). Crystals suitable for X-ray analysis were grown by slow evaporation of a chloroform solution. The title compound was characterized by ^{1}H, ^{13}C NMR and MS spectra anlysis. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.30 (t, ^3J = 7 Hz, 3H); 1.60 (d, ^3J = 6 Hz, 3H); 2.36 (s, 3H); 3.20 (q, ^3J = 7 Hz, 2H); 5.2 (quint, ^3J = 6 Hz, 1H);7.20-7.50 (m, 5H, H$_{ar}$); 14.1 (br, d, ^{3}J = 6 Hz, 1H, intramolecularly bonded NH).^{13}C NMR (CDCl$_3$ + DMSO, 75 MHz) : 12.9; 19.2; 23.3; 27.6; 54.6; 93.5; 118.1; 125.9; 127.8; 128.9; 141.3; 167.5; 206.6. MS (EI, 70 eV): m/z (%): 290 (10) (M$^+$); 261 (6) (M - Et)$^+$; 229 (18) (M - SEt)$^+$; 196 (4); 185 (14) (M - CS$_2$Et)$^+$; 125 (13); 105 (100) (PhCHCH$_3$)$^+$; 77 (18) (Ph)$^+$; 42 (4). CI-HRMS (CH$_4$): 291.099 (M+H)$^+$. IR (NaCl): ν = 3150 (m, broad, intramolecularly bonded NH), 2195 (conjugated C≡N), 1600 (S, conjugated C=C, C$_{ar}$—C$_{ar}$), 1261 (S, conjugated C—N), 1240 (C—N), 1090 (C=S).

Refinement

The N-bound H atom was located in a difference Fourier map and refined freely. C-bound H atoms were placed in calculated positions and constrained to ride on their carrier atoms, with C—H = 0.95-0.98 Å; the isotropic displacement parameters of the H atoms were refined freely.

Figures

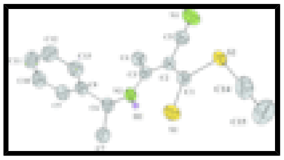


Fig. 1. The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

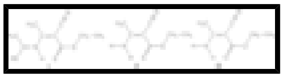


Fig. 2. Compounds (I)–(III).

(*Z*)-Ethyl 2-cyano-3-(1-phenylethylamino)but-2-enedithioate

Crystal data

C$_{15}$H$_{18}$N$_2$S$_2$

M_r = 290.43

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

a = 8.997 (3) Å

b = 10.645 (3) Å

c = 16.293 (3) Å

β = 95.97 (2)°

V = 1552.0 (7) Å^3

Z = 4

F_{000} = 616

D_x = 1.243 Mg m^{-3}

Mo Kα radiation
λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 11.8–14.5°

μ = 0.33 mm^{-1}

T = 298 (2) K

Prism, yellow

0.50 × 0.50 × 0.50 mm

Data collection

Enraf–Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 298(2) K

R_{int} = 0.014

θ$_{max}$ = 27.0°

θ$_{min}$ = 2.3°

h = −11→1

$\omega/2\theta$ scans	$k = -1 \rightarrow 13$
Absorption correction: ψ scan (North *et al.*, 1968)	$l = -20 \rightarrow 20$
$T_{\min} = 0.816$, $T_{\max} = 0.847$	2 standard reflections
4376 measured reflections	every 120 min
3386 independent reflections	intensity decay: 4%
2592 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2 + 0.7692P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.043$	$(\Delta/\sigma)_{\max} = 0.001$
$wR(F^2) = 0.122$	$\Delta\rho_{\max} = 0.71$ e Å^{-3}
$S = 1.02$	$\Delta\rho_{\min} = -0.47$ e Å^{-3}
3386 reflections	Extinction correction: none
198 parameters	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	
Hydrogen site location: inferred from neighbouring sites	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of F^2 > 2sigma(F^2) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
S1	0.15033 (7)	0.11219 (5)	0.04503 (4)	0.0524 (2)
S2	0.22913 (9)	0.36720 (5)	−0.01435 (4)	0.0638 (2)
N1	0.4329 (3)	0.3250 (2)	−0.1745 (1)	0.0734 (6)
N2	0.2968 (2)	−0.0649 (2)	−0.0632 (1)	0.0423 (4)
C1	0.2388 (2)	0.2010 (2)	−0.0191 (1)	0.0393 (4)
C2	0.3250 (2)	0.1568 (2)	−0.0825 (1)	0.0378 (4)
C3	0.3574 (2)	0.0289 (2)	−0.1003 (1)	0.0387 (4)
C4	0.4662 (3)	−0.0013 (2)	−0.1614 (1)	0.0529 (5)

H14	0.5581	−0.0355	−0.1323	0.11 (1)*
H24	0.4894	0.0753	−0.1909	0.09 (1)*
H34	0.4219	−0.0635	−0.2011	0.080 (9)*
C5	0.3862 (3)	0.2501 (2)	−0.1332 (1)	0.0483 (5)
C6	0.3188 (2)	−0.2004 (2)	−0.0763 (1)	0.0445 (5)
H6	0.4278	−0.2162	−0.0785	0.059 (7)*
C7	0.2692 (3)	−0.2692 (2)	−0.0012 (1)	0.0608 (7)
H17	0.3252	−0.2368	0.0492	0.067 (7)*
H27	0.2887	−0.3594	−0.0062	0.09 (1)*
H37	0.1621	−0.2556	0.0014	0.09 (1)*
C8	0.2339 (2)	−0.2475 (2)	−0.1568 (1)	0.0407 (4)
C9	0.2656 (3)	−0.3681 (2)	−0.1843 (1)	0.0502 (5)
H9	0.3402	−0.4173	−0.1538	0.067 (8)*
C10	0.1892 (3)	−0.4165 (2)	−0.2558 (2)	0.0584 (6)
H10	0.2110	−0.4989	−0.2735	0.066 (7)*
C11	0.0822 (3)	−0.3459 (3)	−0.3009 (1)	0.0610 (6)
H11	0.0315	−0.3787	−0.3504	0.084 (9)*
C12	0.0484 (3)	−0.2269 (3)	−0.2742 (1)	0.0613 (6)
H12	−0.0262	−0.1782	−0.3052	0.085 (9)*
C13	0.1233 (2)	−0.1782 (2)	−0.2020 (1)	0.0498 (5)
H13	0.0984	−0.0969	−0.1836	0.053 (6)*
C14	0.1419 (3)	0.4006 (2)	0.0788 (2)	0.0622 (6)
H114	0.0915	0.4833	0.0729	0.09 (1)*
H214	0.0645	0.3363	0.0855	0.073 (8)*
C15	0.2510 (4)	0.4020 (4)	0.1541 (2)	0.087 (1)
H15	0.2927	0.3176	0.1638	0.10 (1)*
H25	0.2002	0.4281	0.2017	0.12 (1)*
H35	0.3317	0.4612	0.1463	0.12 (1)*
H2	0.241 (3)	−0.047 (2)	−0.030 (2)	0.060 (8)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0661 (4)	0.0413 (3)	0.0534 (3)	−0.0013 (3)	0.0239 (3)	0.0014 (2)
S2	0.1007 (5)	0.0330 (3)	0.0607 (4)	−0.0001 (3)	0.0222 (3)	−0.0020 (2)
N1	0.095 (2)	0.056 (1)	0.074 (1)	−0.008 (1)	0.030 (1)	0.016 (1)
N2	0.048 (1)	0.0332 (9)	0.047 (1)	−0.0002 (7)	0.0095 (8)	−0.0036 (7)
C1	0.046 (1)	0.0322 (9)	0.038 (1)	−0.0009 (8)	−0.0010 (8)	−0.0012 (8)
C2	0.041 (1)	0.0347 (9)	0.0369 (9)	−0.0035 (8)	0.0023 (8)	0.0010 (8)
C3	0.038 (1)	0.041 (1)	0.0362 (9)	−0.0017 (8)	−0.0003 (8)	−0.0007 (8)
C4	0.051 (1)	0.054 (1)	0.055 (1)	0.003 (1)	0.016 (1)	−0.003 (1)
C5	0.056 (1)	0.042 (1)	0.047 (1)	−0.001 (1)	0.008 (1)	0.0033 (9)
C6	0.047 (1)	0.032 (1)	0.053 (1)	0.0032 (8)	−0.0013 (9)	−0.0027 (9)
C7	0.086 (2)	0.042 (1)	0.051 (1)	−0.004 (1)	−0.009 (1)	0.005 (1)
C8	0.042 (1)	0.035 (1)	0.046 (1)	−0.0002 (8)	0.0080 (8)	−0.0019 (8)
C9	0.048 (1)	0.041 (1)	0.062 (1)	0.004 (1)	0.009 (1)	−0.007 (1)
C10	0.063 (1)	0.049 (1)	0.066 (1)	−0.006 (1)	0.018 (1)	−0.021 (1)
C11	0.064 (1)	0.069 (2)	0.050 (1)	−0.013 (1)	0.008 (1)	−0.015 (1)

C12	0.060 (1)	0.065 (2)	0.056 (1)	0.003 (1)	−0.006 (1)	0.001 (1)
C13	0.054 (1)	0.042 (1)	0.053 (1)	0.005 (1)	0.002 (1)	−0.003 (1)
C14	0.069 (2)	0.048 (1)	0.070 (2)	0.001 (1)	0.013 (1)	−0.015 (1)
C15	0.090 (2)	0.102 (3)	0.071 (2)	−0.012 (2)	0.008 (2)	−0.026 (2)

Geometric parameters (Å, °)

S1—C1	1.671 (2)	C7—H37	0.98
S2—C1	1.773 (2)	C8—C13	1.388 (3)
S2—C14	1.815 (3)	C8—C9	1.398 (3)
N1—C5	1.151 (3)	C9—C10	1.388 (3)
N2—C3	1.315 (3)	C9—H9	0.95
N2—C6	1.474 (3)	C10—C11	1.373 (4)
N2—H2	0.80 (3)	C10—H10	0.95
C1—C2	1.434 (3)	C11—C12	1.384 (4)
C2—C3	1.428 (3)	C11—H11	0.95
C2—C5	1.437 (3)	C12—C13	1.394 (3)
C3—C4	1.502 (3)	C12—H12	0.95
C4—H14	0.98	C13—H13	0.95
C4—H24	0.98	C14—C15	1.489 (4)
C4—H34	0.98	C14—H114	0.99
C6—C7	1.531 (3)	C14—H214	0.99
C6—C8	1.532 (3)	C15—H15	0.98
C6—H6	1.00	C15—H25	0.98
C7—H17	0.98	C15—H35	0.98
C7—H27	0.98		
C1—S2—C14	105.0 (1)	H27—C7—H37	109.5
C3—N2—C6	127.5 (2)	C13—C8—C9	118.5 (2)
C3—N2—H2	117 (2)	C13—C8—C6	123.11 (18)
C6—N2—H2	115 (2)	C9—C8—C6	118.38 (19)
C2—C1—S1	126.4 (1)	C10—C9—C8	120.7 (2)
C2—C1—S2	113.0 (1)	C10—C9—H9	119.6
S1—C1—S2	120.6 (1)	C8—C9—H9	119.6
C3—C2—C1	126.61 (17)	C11—C10—C9	120.3 (2)
C3—C2—C5	116.29 (18)	C11—C10—H10	119.9
C1—C2—C5	117.10 (18)	C9—C10—H10	119.9
N2—C3—C2	121.83 (18)	C10—C11—C12	119.8 (2)
N2—C3—C4	118.16 (19)	C10—C11—H11	120.1
C2—C3—C4	119.99 (18)	C12—C11—H11	120.1
C3—C4—H14	109.5	C11—C12—C13	120.2 (2)
C3—C4—H24	109.5	C11—C12—H12	119.9
H14—C4—H24	109.5	C13—C12—H12	119.9
C3—C4—H34	109.5	C8—C13—C12	120.5 (2)
H14—C4—H34	109.5	C8—C13—H13	119.8
H24—C4—H34	109.5	C12—C13—H13	119.8
N1—C5—C2	178.9 (3)	C15—C14—S2	112.7 (2)
N2—C6—C7	107.36 (18)	C15—C14—H114	109.1
N2—C6—C8	112.45 (17)	S2—C14—H114	109.1
C7—C6—C8	111.51 (18)	C15—C14—H214	109.1

N2—C6—H6	108.5	S2—C14—H214	109.1
C7—C6—H6	108.5	H114—C14—H214	107.8
C8—C6—H6	108.5	C14—C15—H15	109.5
C6—C7—H17	109.5	C14—C15—H25	109.5
C6—C7—H27	109.5	H15—C15—H25	109.5
H17—C7—H27	109.5	C14—C15—H35	109.5
C6—C7—H37	109.5	H15—C15—H35	109.5
H17—C7—H37	109.5	H25—C15—H35	109.5

Fig. 1

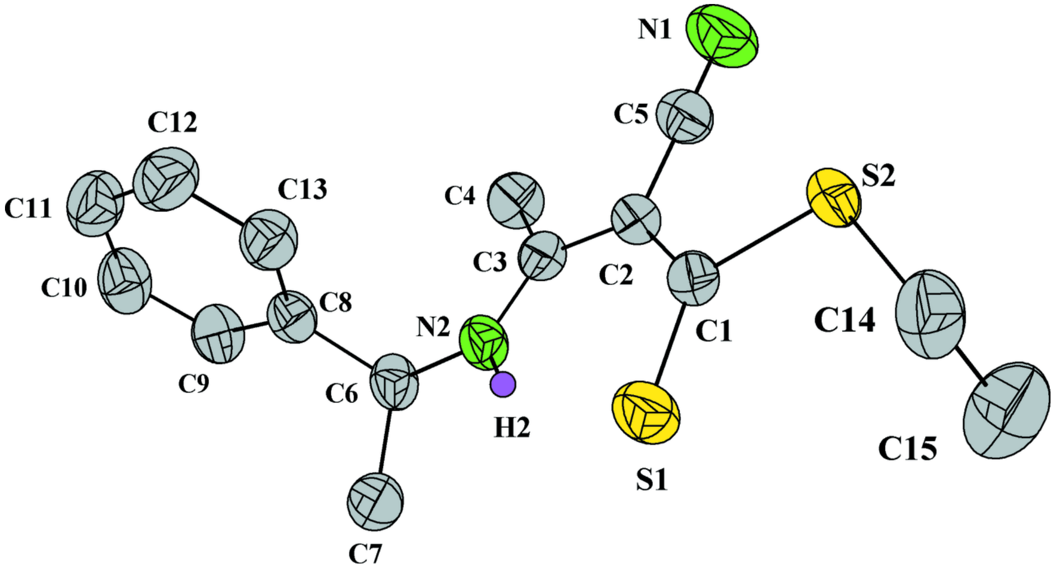
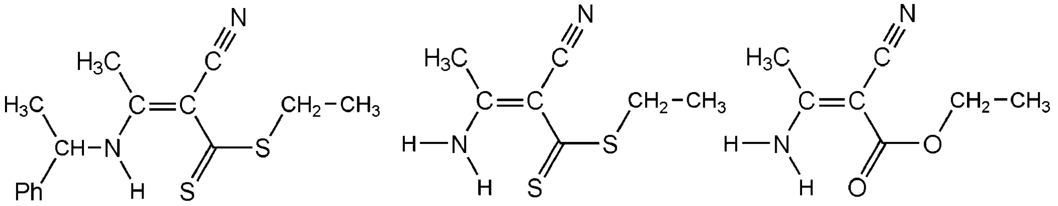


Fig. 2



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