Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structures of crotonaldehyde semicarbazone and crotonaldehyde thiosemicarbazone from X-ray powder diffraction data

Atef Arfan and Mwaffak Rukiah*

Department of Chemistry, Atomic Energy Commission of Syria (AECS), PO Box 6091, Damascus, Syrian Arab Republic. *Correspondence e-mail: cscientific@aec.org.sy

Received 22 December 2014
Accepted 13 January 2015

Edited by V. V. Chernyshev, Moscow State University, Russia

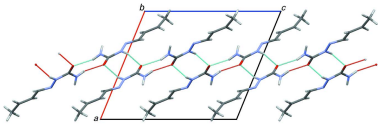
Keywords: crystal structure; crotonaldehyde; semicarbazone; thiosemicarbazone; powder X-ray diffraction; supramolecular structure; hydrogen bond; one-dimensional chain; two-dimensional networks

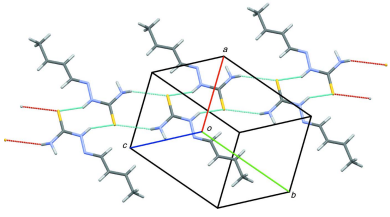
CCDC references: 1043290; 1043289
Supporting information: this article has supporting information at journals.iucr.org/e

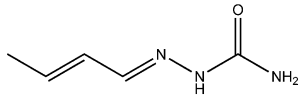
Crotonaldehyde semicarbazone {systematic name: (*E*)-2-[(*E*)-but-2-en-1-ylidene]hydrazinecarboxamide}, $C_5H_9N_3O$, (I), and crotonaldehyde thiosemicarbazone {systematic name: (*E*)-2-[(*E*)-but-2-en-1-yldene]hydrazinecarbothioamide}, $C_5H_9N_3S$, (II), show the same *E* conformation around the imine C=N bond. Compounds (I) and (II) were obtained by the condensation of crotonaldehyde with semicarbazide hydrochloride and thiosemicarbazide, respectively. Each molecule has an intramolecular N—H···N hydrogen bond, which generates an *S*(5) ring. In (I), the crotonaldehyde fragment is twisted by 2.59 (5)° from the semicarbazide mean plane, while in (II) the corresponding angle (with the thiosemicarbazide mean plane) is 9.12 (5)°. The crystal packing is different in the two compounds: in (I) intermolecular N—H···O hydrogen bonds link the molecules into layers parallel to the *bc* plane, while weak intermolecular N—H···S hydrogen bonds in (II) link the molecules into chains propagating in [110].

1. Chemical context

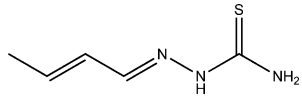
The chemistry of semicarbazones and thiosemicarbazones is especially interesting due to their special role in biological applications such as anti-proliferative, anti-tumoral, anti-convulsant, anti-trypanosomal, herbicidal and biocidal activities (Beraldo *et al.*, 2002; Kasuga *et al.*, 2003; Teixeira *et al.*, 2003; Beraldo & Gambino, 2004; Mikhaleva *et al.*, 2008; de Oliveira *et al.*, 2008; Alomar *et al.*, 2012; Gan *et al.*, 2014). They are also important intermediates in organic synthesis, mainly for obtaining heterocyclic rings, such as thiazolidones, oxadiazoles, pyrazolidones, and thiadiazoles (Greenbaum *et al.*, 2004; Küçükgüzel *et al.*, 2006). Semicarbazones and thiosemicarbazones have received considerable attention in view of their simplicity of preparation, various complexing abilities and coordination behavior that can be used in analytical applications (Garg & Jain, 1988; Casas *et al.*, 2000). They are of interest from a supramolecular point of view since they can be functionalized to give different supramolecular arrays.







(I)



(II)

2. Structural commentary

Compounds (I) and (II) crystallize in centrosymmetric space groups $P2_1/c$ and $P\overline{1}$, respectively, with one molecule in the asymmetric unit. Each molecule has an intramolecular N—H···N hydrogen bond (Tables 1 and 2), which forms an *S*(5)

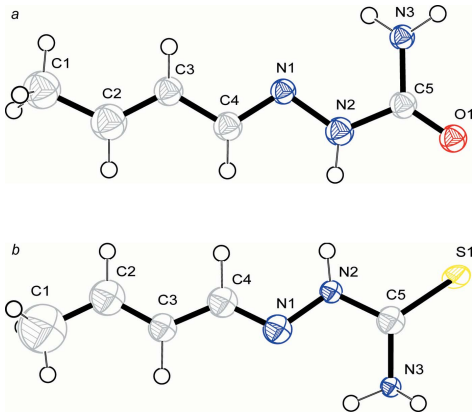


Figure 1
The molecular structures of (*a*) (I) and (*b*) (II), showing the atom-labelling schemes. Displacement spheres (and the ellipsoid for S1) are drawn at the 50% probability level.

ring. The semicarbazone and thiosemicarbazone fragments in the compounds show an *E* conformation around the imine C=N bond. The molecules (Fig. 1) are approximately planar, with a dihedral angle of 2.59 (5)° between the C1/C2/C3 crotonaldehyde plane and the mean plane of the C4/N1/N2/C5/O1/N3 semicarbazone fragment for (I), and of 9.12 (5)° between the C1/C2/C3 crotonaldehyde plane and the mean plane of the C4/N1/N2/C5/S1/N3 thiosemicarbazone fragment for (II). All bond lengths and angles in (I) and (II) are normal and correspond well to those observed in the crystal structures of related semi- and thiosemicarbazone derivatives, *viz*. acetone semicarbazone and benzaldehydesemicarbazone (Naik & Palenik, 1974), 3,4- methylenedioxybenzaldehydesemicarbazone (Wang *et al.*, 2004), isatin 3-semicarbazone and 1-methylisatin 3-semicarbazone (Pelosi *et al.*, 2005), 4-(methylsulfanyl)benzaldehydethiosemicarbazone (Yathirajan *et al.*, 2006), 4-(methylsulfanyl)benzaldehydesemicarbazone (Sarojini *et al.*, 2007), 5-hydroxy-2-nitrobenzaldehyde thiosemicarbazone (Reddy *et al.*, 2014) and 1-(4-formylbenzylidene) thiosemicarbazone (Carballo *et al.*, 2014).

3. Supramolecular features

As a result of the presence of potential hydrogen-donor sites in molecules (I) and (II), supramolecular hydrogen-bonding interactions are observed in both compounds (Tables 1 and 2). In the crystal of (I), molecules are linked by pairs of N—H···O hydrogen bonds, forming inversion dimers with $R_2^2(8)$ ring motifs (Fig. 2*a*). The resulting dimers are connected through N—H···O hydrogen bonds, forming layers parallel to *bc* plane. In the crystal of (II), molecules are linked by weak N—H···S hydrogen bonds, forming chains propagating in [110] (Fig. 2*b*).

4. Synthesis and crystallization

All reactions and manipulations were carried out in air with reagent grade solvents. The IR spectra were recorded on a Jasco FT–IR 300E instrument. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker Bio spin 400 spectrometer. Microanalysis was performed using EURO EA. Powder X-ray diffraction data were collected with Stoe Transmission diffractometer (Stadi P).

For the synthesis of (I), a mixture of semicarbazide hydrochloride (CH_5N_3O·HCl; 0.5 g, 4.5 mmol) and sodium acetate (CH_3COONa; 0.75 g, 9.1 mmol) in 10 ml water was agitated well and crotonaldehyde (0.5 g, 7.1 mmol) was added slowly with stirring. On completion of the addition, the reaction mixture was agitated for 24 h at room temperature. The solid product which formed was separated by filtration and washed with water and finally recrystallized from absolute

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H2N3···N1	0.87	2.33	2.629 (19)	100
N2—H1N2···O1^{i}	0.88	2.07	2.910 (11)	158
N3—H1N3···O1^{ii}	0.91	2.04	2.914 (18)	162

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

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H2N3···N1	0.89	2.17	2.641 (14)	112
N2—H1N2···S1^{i}	0.86	2.83	3.473 (11)	133
N3—H1N3···S1^{ii}	0.87	2.77	3.398 (11)	130

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

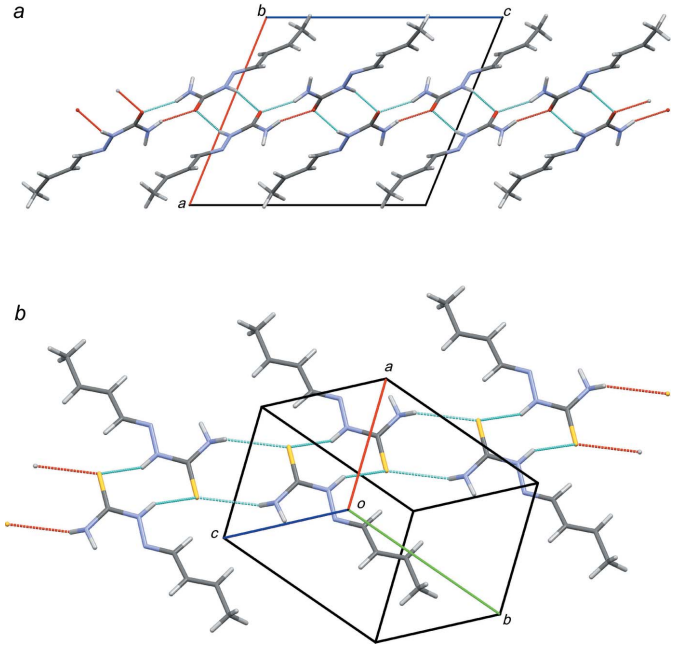


Figure 2
(*a*) A portion of the crystal packing of (I) viewed down the *b* axis (parallel to the hydrogen-bonded layer). (*b*) A portion of the crystal packing of (II), showing the hydrogen-bonded chain of the molecules. Thin dotted lines denote intermolecular hydrogen bonds.

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_5H_9N_3O$	$C_5H_9N_3S$
M_r	127.15	143.21
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\overline{1}$
Temperature (K)	298	298
a, b, c (Å)	11.1646 (3), 5.13891 (9), 13.0301 (2)	5.86650 (17), 8.0313 (2), 9.0795 (4)
α, β, γ (°)	90, 112.3496 (11), 90	104.1407 (18), 101.0403 (19), 106.3511 (17)
V (Å^3)	691.43 (3)	382.15 (2)
Z	4	2
Radiation type	Cu $K\alpha_1$, λ = 1.5406 Å	Cu $K\alpha_1$, λ = 1.5406 Å
μ (mm^{-1})	0.74	3.11
Specimen shape, size (mm)	Flat sheet, 8 × 8	Flat sheet, 8 × 8
Data collection		
Diffractometer	Stoe transmission Stadi-P	Stoe transmission Stadi-P
Specimen mounting	Powder loaded into two Mylar foils	Powder loaded into two Mylar foils
Data collection mode	Transmission	Transmission
Scan method	Step	Step
2θ values (°)	$2\theta_{min}$ = 5 $2\theta_{max}$ = 80 $2\theta_{step}$ = 0.02	$2\theta_{min}$ = 4.980 $2\theta_{max}$ = 79.960 $2\theta_{step}$ = 0.02
Refinement		
R factors and goodness of fit	R_p = 0.027, R_{wp} = 0.036, R_{exp} = 0.029, $R(F^2)$ = 0.02795, χ^2 = 1.613	R_p = 0.033, R_{wp} = 0.043, R_{exp} = 0.034, $R(F^2)$ = 0.02670, χ^2 = 1.664
No. of data points	3750	3750
No. of parameters	121	114
No. of restraints	0	1
H-atom treatment	H-atom parameters not refined	H-atom parameters not refined

Computer programs: *WinXPOW* (Stoe & Cie, 1999), *EXPO2014* (Altomare *et al.*, 2013), *GSAS* (Larson & Von Dreele, 2004), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2006) and *publCIF* (Westrip, 2010).

ethanol to produce the product (I) (white powder; m.p. 481–482 K) in 55.5% yield.

IR (KBr, ν, cm^{-1}): 3456, 3281, 3192 (NH_2), (1668–1638) (C═O); ^{1}H NMR (400 MHz, CD_3OD) δ p.p.m. 1.76 (*d*, *J* = 4.42 Hz, 3H, –CH_3), 6.43–5.46 (*m*, 2H, –HC═CH–), 7.39 (*d*, *J* = 7.19 Hz, 1H, HC═N–).^{13}C NMR (100 MHz, CD_3OD) δ p.p.m. 18.52 (CH_3), 130.01 (–HC═CH–), 137.62 (–HC═CH–), 145.64 (N═C), 160.19 (C═O). Analysis calculated for (I): C, 47.23; H, 7.13; N, 33.05, 12.58 O%. Found: C, 46.43; H, 6.08; N, 34.69%

For the synthesis of (II), crotonaldehyde (0.5 g, 7.1 mmol) was added to thiosemicarbazide (CH_5N_3S; 0.65 g, 7.1 mmol) in 5 ml water and the mixture was stirred at room temperature for 24 h. The product was separated by filtration and recrystallized from absolute ethanol to produce the product (II) (white powder; m.p. 435–436 K) in 72.5% yield.

IR (KBr, ν, cm^{-1}): 3323, 3244, 3164 (NH_2), 1650(C═S). ^{1}H NMR (400 MHz, $CDCl_3$) δ p.p.m. 1.90 (*d*, *J* = 5.86 Hz, 3H, –CH_3), 6.07–6.27 (*m*, 2H, –HC═CH–), 6.49 (*sb*, 1H), 7.10 (*sb*, 1H) 7.60 (*d*, *J* = 8.57 Hz, 1H, HC═N–), 10.10 (*sb*, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$) 18.73 (CH_3), 127.70 (–HC═CH–), 140.58 (–HC═CH–), 146.21 (N═C), 177.95 (C═S). Analysis calculated for (II): C, 41.93; H, 6.33; N, 29.34.05, 22.39 S%. Found: C, 41.89; H, 6.25; N, 31.88%.

5. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3. Compounds (I) and (II) crystallized in the form of a very fine white powder. Since no single crystals of sufficient size and quality could be obtained, the crystal structures of both compounds were determined from X-ray powder diffraction patterns. The powder samples of (I) and (II) were lightly ground in a mortar, loaded into two Mylar foils and fixed onto the sample holder with a mask of suitable internal diameter (8.0 mm). The powder X-ray diffraction data were collected at room temperature with a STOE transmission STADI-P diffractometer using monochromatic Cu K_{a1} radiation (λ= 1.54060 Å) selected with an incident beam curved-crystal germanium Ge(111) monochromator with a linear position-sensitive detector (PSD). The patterns were scanned over the angular range 5.0–80.0° (2θ). For pattern indexing, the extraction of the peak positions was carried out with the program *WinPLOTR* (Roisnel & Rodríguez-Carvajal, 2000). Pattern indexing was performed with the program *DICVOL4.0* (Boultif & Louër, 2004). The first 20 lines of the powder pattern were indexed completely on the basis of a monoclinic cell for (I) and a triclinic cell for (II). The figures of merit (de Wolff *et al.*, 1968; Smith & Snyder, 1979) are sufficiently acceptable to support the obtained indexing results [$M(20)$ = 50.5, $F(20)$ = 71.9 (0.0034, 83)] for (I) and [$M(20)$ = 61.8, $F(20)$ = 96.0 (0.0051, 41)] for (II). The best estimated space groups were $P2_1/c$ in the monoclinic system for (I) and $P\overline{1}$ in the triclinic system for (II).

The whole powder diffraction patterns from 5 to 80° (2θ) for the two compounds (I) and (II) were subsequently refined with cell and resolution constraints (Le Bail *et al.*, 1988) using the profile-matching option of the program *FULLPROF*

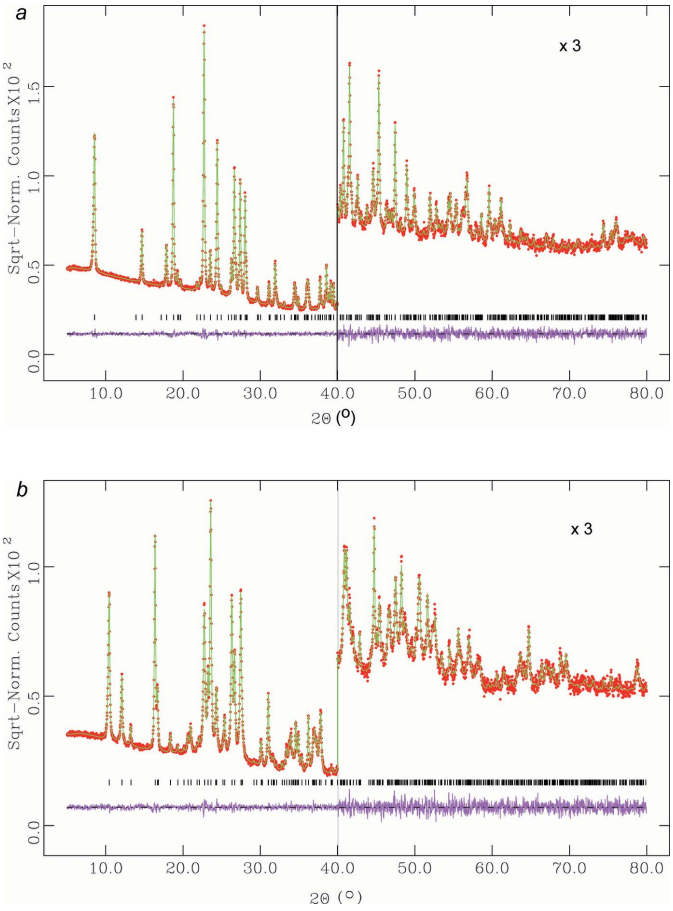


Figure 3
The final Rietveld plots for (*a*) (I) and (*b*) (II). Experimental intensities are indicated by dots and the best-fit profile (upper trace) and difference pattern (lower trace) are shown as solid lines. The vertical bars indicate the calculated positions of the Bragg peaks.

(Rodríguez-Carvajal, 2001). The number of molecules per unit cell was estimated to be $Z = 4$ for (I) and $Z = 2$ for (II). The initial crystal structures for (I) and (II) were determined by direct methods using the program *EXPO2014* (Altomare *et al.*, 2013). The models found by this program were introduced into the program *GSAS* (Larson & Von Dreele, 2004) implemented in *EXPGUI* (Toby, 2001) for Rietveld refinement. During the Rietveld refinements, the background was refined using a shifted Chebyshev polynomial with 20 coefficients. The effect of asymmetry of low-order peaks was corrected using a pseudo-Voigt description of the peak shape (Thompson *et al.*, 1987), which allows for angle-dependent asymmetry with axial divergence (Finger *et al.*, 1994) and microstrain broadening, as described by Stephens (1999). The two asymmetry parameters of this function, S/L and D/L, were both fixed at 0.022 during this refinement. Intensities were corrected from absorption effects with a function for a plate sample in transmission geometry with a $\mu \cdot d$ value of 0.15 for (I) and 0.72 for (II) (μ is the absorption coefficient and d is the sample thickness). These $\mu \cdot d$ values were determined experimentally.

Before the final refinement, all H atoms were introduced in geometrically calculated positions. The coordinates of these H atoms were refined with strict restraints on bond lengths and angles until a suitable geometry was obtained, after that they were fixed in the final stage of the refinement. No soft restraints were imposed for (I), while for (II) the CH_3—CH bond was clearly stretched (close to 1.6 Å), therefore a single soft restraint was carried out to obtain a normal value (1.49 Å). The final refinement cycles were performed using isotropic atomic displacement parameters for the C, N and O atoms, an anisotropic atomic displacement parameter for S atom in (II) and a fixed global isotropic atomic displacement parameter for the H atoms. The preferred orientation was modelled with 12 coefficients using a spherical harmonics correction (Von Dreele, 1997) of intensities in the final refinement. The use of the preferred orientation correction leads to a better molecular geometry with better agreement factors. The final Rietveld plots of the X-ray diffraction patterns for both (I) and (II) are given in Fig. 3.

Acknowledgements

The authors thank Professor I. Othman, Director General, and Professor Z. Ajji, Head of the Chemistry Department, for their support and encouragement during this work. We also thank Miss D. Naima for her kind assistance.

References

Alomar, K., Gaumet, V., Allain, M., Bouet, G. & Landreau, A. (2012). *J. Inorg. Biochem.* **115**, 36–43.
Altomare, A., Cuocci, C., Giacovazzo, C., Moliterni, A., Rizzi, R., Corriero, N. & Falcicchio, A. (2013). *J. Appl. Cryst.* **46**, 1231–1235.
Beraldo, H. & Gambinob, D. (2004). *Mini Rev. Med. Chem.* **4**, 31–39.
Beraldo, H., Sinisterra, R. D., Teixeira, L. R., Vieira, R. P. & Doretto, M. C. (2002). *Biochem. Biophys. Res. Commun.* **296**, 241–246.
Boultif, A. & Louër, D. (2004). *J. Appl. Cryst.* **37**, 724–731.
Carballo, R., Pino-Cuevas, A. & Vázquez-López, E. M. (2014). *Acta Cryst.* E**70**, o970.
Casas, J. S., Garc\?ía-Tasende, M. S. & Sordo, J. (2000). *Coord. Chem. Rev.* **209**, 197–261.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Finger, L. W., Cox, D. E. & Jephcoat, A. P. (1994). *J. Appl. Cryst.* **27**, 892–900.
Gan, C., Cui, J., Su, S., Lin, Q., Jia, L., Fan, L. & Huang, Y. (2014). *Steroids*, **87**, 99–107.
Garg, B. S. & Jain, V. K. (1988). *Microchem. J.* **38**, 144–169.
Greenbaum, D. C., Mackey, Z., Hansell, E., Doyle, P. S., Gut, J., Caffrey, C. R., Lehrman, J., Rosenthal, P. J., McKerrow, J. H. & Chibale, K. (2004). *J. Med. Chem.* **47**, 3212–3219.
Kasuga, N. C., Sekino, K., Ishikawa, M., Honda, A., Yokoyama, M., Nakano, S., Shimada, N., Koumo, C. & Nomiya, K. (2003). *J. Inorg. Biochem.* **96**, 298–310.
Küçükgüzel, G., Kocatepe, A., De Clercq, E., Şahin, F. & Güllüce, M. (2006). *Eur. J. Med. Chem.* **41**, 353–359.
Larson, A. C. & Von Dreele, R. B. (2004). *GSAS*. Report LAUR 86-748. Los Alamos National Laboratory, New Mexico, USA.
Le Bail, A., Duroy, H. & Fourquet, J. L. (1988). *Mater. Res. Bull.* **23**, 447–452.
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.
Mikhaleva, A. I., Ivanov, A. V., Vasil'tsov, A. M., Ushakov, I. A., Ma, J. S. & Yang, G. (2008). *Chem. Heterocycl. Compd*, **44**, 1117–1122.
Naik, D. V. & Palenik, G. J. (1974). *Acta Cryst.* B**30**, 2396–2401.

Oliveira, R. B. de, de Souza-Fagundes, E. M., Soares, R. P. P., Andrade, A. A., Krettli, A. U. & Zani, C. L. (2008). *Eur. J. Med. Chem.* **43**, 1983–1988.
Pelosi, G., Pelizzi, C., Belicchi Ferrari, M., Rodríguez-Argüelles, M. C., Vieito, C. & Sanmartín, J. (2005). *Acta Cryst.* C**61**, o589–o592.
Reddy, M. S., Sarala, Y., Jagadeesh, M., Das, S. K. & Ammireddy, V. R. (2014). *Acta Cryst.* E**70**, o846.
Rodríguez-Carvajal, J. (2001). *Commission on Powder Diffraction (IUCr) Newsletter*, **26**, 12–19.
Roisnel, T. & Rodríguez-Carvajal, J. (2000). *Mater. Sci. Forum*, **378–381**, 118–123.
Sarojini, B. K., Narayana, B., Bindya, S., Yathirajan, H. S. & Bolte, M. (2007). *Acta Cryst.* E**63**, o2946.
Smith, G. S. & Snyder, R. L. (1979). *J. Appl. Cryst.* **12**, 60–65.
Stephens, P. W. (1999). *J. Appl. Cryst.* **32**, 281–289.
Stoe & Cie (1999). *WinXPOW*. Stoe & Cie, Darmstadt, Germany.
Teixeira, L. R., Sinisterra, R. D., Vieira, R. P., Doretto, M. C. & Beraldo, H. (2003). *J. Incl. Phenom. Macrocycl. Chem.* **47**, 77–82.
Thompson, P., Cox, D. E. & Hastings, J. B. (1987). *J. Appl. Cryst.* **20**, 79–83.
Toby, B. H. (2001). *J. Appl. Cryst.* **34**, 210–213.
Von Dreele, R. B. (1997). *J. Appl. Cryst.* **30**, 517–525.
Wang, J.-L., Jia, Y.-J. & Yu, M. (2004). *Acta Cryst.* E**60**, o662–o663.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Wolff, P. M. de (1968). *J. Appl. Cryst.* **1**, 108–113.
Yathirajan, H. S., Bindya, S., Narayana, B., Sarojini, B. K. & Bolte, M. (2006). *Acta Cryst.* E**62**, o5925–o5926.

supporting information

Acta Cryst. (2015). E**71**, 168-172 [doi:10.1107/S2056989015000663]

Crystal structures of crotonaldehyde semicarbazone and crotonaldehyde thiosemicarbazone from X-ray powder diffraction data

Atef Arfan and Mwaffak Rukiah

Computing details

For both compounds, data collection: *WinXPOW* (Stoe & Cie, 1999). Data reduction: *WinXPOW* (Stoe & Cie, 1999) for (I). For both compounds, program(s) used to solve structure: *EXPO2014* (Altomare *et al.*, 2013); program(s) used to refine structure: *GSAS* (Larson & Von Dreele, 2004); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

(I) (*E*)-2-[(*E*)-But-2-en-1-ylidene]hydrazinecarboxamide

Crystal data

$C_5H_9N_3O$
M_r = 127.15
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 11.1646 (3) Å
b = 5.13891 (9) Å
c = 13.0301 (2) Å
β = 112.3496 (11)°
V = 691.43 (3) Å^3
Z = 4
$F(000)$ = 272
D_x = 1.222 Mg m^{-3}
Cu $K\alpha_1$ radiation, λ = 1.5406 Å
μ = 0.74 mm^{-1}
T = 298 K
Particle morphology: fine powder
white
flat sheet, 8 × 8 mm

Data collection

Stoe transmission Stadi-P diffractometer
Radiation source: sealed X-ray tube
Ge 111 monochromator
Specimen mounting: Powder loaded into two Mylar foils
Data collection mode: transmission
Scan method: step
$2\theta_{min}$ = 5°, $2\theta_{max}$ = 80°, $2\theta_{step}$ = 0.02°

Refinement

Least-squares matrix: full
R_p = 0.027
R_{wp} = 0.036
R_{exp} = 0.029
$R(F^2)$ = 0.02795
χ^2 = 1.613
3750 data points

Profile function: CW Profile function number 4 with 21 terms Pseudovoigt profile coefficients as parameterized in (Thompson *et al.*, 1987) Asymmetry correction of Finger *et al.*, 1994. Microstrain broadening by P.W. Stephens, (1999. #1(GU) = 0.000 #2(GV) = 0.000 #3(GW) = 10.054 #4(GP) = 0.000 #5(LX) = 2.972 #6(ptec) = 0.00 #7(trns) = 0.00 #8(shft) = 0.0000 #9(sfec) = 0.00 #10(S/L) = 0.0220 #11(H/L) = 0.0220 #12(eta) = 0.6000 #13(S400) = 2.1E-01 #14(S040) = 3.3E-01 #15(S004) = 4.2E-02 #16(S220) = 2.1E-02 #17(S202) = 4.8E-03 #18(S022) = 8.7E-02 #19(S301) = -3.5E-03 #20(S103) = 5.2E-02 #21(S121) = 5.4E-02 Peak tails are ignored where the intensity is below 0.0010 times the peak Aniso. broadening axis 0.0 0.0 1.0
121 parameters
0 restraints
H-atom parameters not refined
Weighting scheme based on measured s.u.'s
$(\Delta/\sigma)_{max}$ = 0.03
Background function: GSAS Background function number 1 with 20 terms. Shifted Chebyshev function of 1st kind 1: 983.478 2: -916.772 3: 421.914 4: -92.3775 5: -9.18321 6: 30.2365 7: -2.25826 8: -10.7421 9: -19.9256 10: 25.6982 11: -24.5216 12: 4.20376 13: 6.93721 14: -3.88406 15: -7.36711 16: 7.71847 17: -1.82508 18: -0.259371 19: -0.220296 20: 0.765767

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.935 (2)	0.8319 (18)	0.3282 (11)	0.057 (5)*
H1a	0.88432	0.92372	0.25964	0.075*
H1b	0.96701	0.95714	0.38819	0.075*
H1c	1.00844	0.74948	0.31821	0.075*
C2	0.855 (2)	0.6310 (16)	0.3552 (13)	0.052 (4)*
H2	0.8297	0.48475	0.30627	0.075*
C3	0.8056 (15)	0.6448 (14)	0.4352 (9)	0.033 (4)*
H3	0.80211	0.8092	0.46492	0.05*
C4	0.7367 (18)	0.4405 (17)	0.4558 (11)	0.032 (4)*
H4	0.73987	0.27746	0.42622	0.075*
N1	0.7027 (14)	0.4632 (13)	0.5417 (7)	0.025 (3)*
N2	0.6313 (12)	0.2520 (15)	0.5530 (7)	0.031 (3)*
H1n2	0.60928	0.12885	0.50191	0.05*
C5	0.5708 (15)	0.252 (2)	0.6285 (11)	0.029 (4)*
O1	0.5060 (12)	0.0728 (12)	0.6388 (6)	0.029 (3)*
N3	0.6041 (15)	0.4651 (13)	0.6956 (9)	0.024 (3)*

H1n3	0.55477	0.51321	0.73425	0.05*
H2n3	0.67532	0.55182	0.70648	0.05*

Geometric parameters (Å, º)

C1—C2	1.493 (17)	C4—H4	0.928
C1—H1a	0.978	N1—N2	1.387 (11)
C1—H1b	0.970	N2—H1n2	0.883
C1—H1c	0.975	N2—C5	1.390 (10)
C2—C3	1.353 (11)	C5—O1	1.210 (11)
C2—H2	0.956	C5—N3	1.361 (11)
C3—C4	1.387 (13)	N3—H1n3	0.911
C3—H3	0.936	N3—H2n3	0.875
C4—N1	1.317 (11)		
H1a—C1—H1b	108.9	C3—C4—N1	117.2 (12)
H1a—C1—H1c	108.1	H4—C4—N1	120.1
H1a—C1—C2	111.0	C4—N1—N2	112.5 (9)
H1b—C1—H1c	109.0	N1—N2—H1n2	119.2
H1b—C1—C2	109.9	N1—N2—C5	121.9 (9)
H1c—C1—C2	109.9	H1n2—N2—C5	117.6
C1—C2—H2	115.9	N2—C5—O1	123.3 (11)
C1—C2—C3	126.9 (9)	N2—C5—N3	111.6 (11)
H2—C2—C3	116.9	O1—C5—N3	124.8 (11)
C2—C3—H3	117.3	C5—N3—H1n3	119.9
C2—C3—C4	121.8 (10)	C5—N3—H2n3	121.6
H3—C3—C4	119.4	H1n3—N3—H2n3	118.4
C3—C4—H4	119.5		
C4—N1—N2—C5	−171.0 (13)	N1—N2—C5—N3	−7.4 (18)
N2—N1—C4—C3	178.3 (13)	C1—C2—C3—C4	−177.3 (16)
N1—N2—C5—O1	178.6 (13)	C2—C3—C4—N1	174.0 (15)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H2N3···N1	0.87	2.33	2.629 (19)	100
N2—H1N2···O1^{i}	0.88	2.07	2.910 (11)	158
N3—H1N3···O1^{ii}	0.91	2.04	2.914 (18)	162

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

(II) (*E*)-2-[(*E*)-But-2-en-1-yldene]hydrazinecarbothioamide

Crystal data

$C_5H_9N_3S$	*b* = 8.0313 (2) Å
M_r = 143.21	*c* = 9.0795 (4) Å
Triclinic, $P\overline{1}$	α = 104.1407 (18)°
Hall symbol: -P 1	β = 101.0403 (19)°
a = 5.86650 (17) Å	γ = 106.3511 (17)°

V = 382.15 (2) Å^3
Z = 2
F(000) = 152
D_x = 1.245 Mg m^{-3}
Cu $K\alpha_1$ radiation, λ = 1.5406 Å

μ = 3.11 mm^{-1}
T = 298 K
Particle morphology: fine powder
white
flat sheet, 8 × 8 mm

Data collection

Stoe transmission Stadi-P diffractometer
Radiation source: sealed X-ray tube
Ge 111 monochromator

Specimen mounting: Powder loaded into two Mylar foils
Data collection mode: transmission
Scan method: step
$2\theta_{min}$ = 4.980°, $2\theta_{max}$ = 79.960°, $2\theta_{step}$ = 0.02°

Refinement

Least-squares matrix: full
R_p = 0.033
R_{wp} = 0.043
R_{exp} = 0.034
$R(F^2)$ = 0.02670
χ^2 = 1.664
3750 data points

Profile function: CW Profile function number 4 with 21 terms Pseudovoigt profile coefficients as parameterized in (Thompson *et al.*, 1987) Asymmetry correction of Finger *et al.*, 1994. #1(GU) = 0.000 #2(GV) = 0.000 #3(GW) = 2.793 #4(GP) = 0.000 #5(LX) = 5.477 #6(ptec) = 2.45 #7(trns) = 0.00 #8(shft) = 0.0000 #9(sfec) = 0.00 #10(S/L) = 0.0220 #11(H/L) = 0.0220 #12(eta) = 0.6000 Peak tails are ignored where the intensity is below 0.0010 times the peak Aniso. broadening axis 0.0 0.0 1.0
114 parameters
1 restraint
H-atom parameters not refined
$(\Delta/\sigma)_{max}$ = 0.03
Background function: GSAS Background function number 1 with 20 terms. Shifted Chebyshev function of 1st kind 1: 590.360 2: -469.557 3: 198.126 4: -45.2586 5: -2.75624 6: 13.8508 7: 4.35563 8: -5.95029 9: -12.8815 10: 35.6051 11: -12.9276 12: -11.1488 13: 8.85293 14: -2.01034 15: -0.496121 16: 8.39616 17: -2.33367 18: -5.14527 19: 10.5079 20: -3.85249

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.184 (2)	0.841 (2)	0.515 (2)	0.103 (6)*
H1A	0.15342	0.79934	0.39748	0.12*
H1B	0.2323	0.97016	0.55142	0.12*
H1C	0.02574	0.78525	0.53491	0.12*
C2	0.370 (2)	0.7688 (17)	0.5865 (18)	0.054 (5)*
H2	0.53963	0.83335	0.59455	0.055*
C3	0.325 (2)	0.6393 (16)	0.6524 (15)	0.034 (5)*
H3	0.14582	0.56255	0.63049	0.055*
C4	0.487 (3)	0.5747 (19)	0.7264 (19)	0.039 (5)*
H4	0.66632	0.65671	0.74816	0.055*
N1	0.4514 (17)	0.4461 (12)	0.7878 (15)	0.035 (4)*
N2	0.6486 (16)	0.4005 (12)	0.8462 (13)	0.021 (4)*

H1n2	0.79218	0.45838	0.841	0.05*
C5	0.611 (3)	0.2572 (16)	0.907 (2)	0.034 (4)*
N3	0.3681 (15)	0.1560 (12)	0.8849 (13)	0.017 (4)*
H1n3	0.34725	0.13246	0.97116	0.05*
H2n3	0.26401	0.20773	0.84645	0.05*
S1	0.8446 (6)	0.1980 (5)	0.9772 (6)	0.04081

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.032 (4)	0.039 (5)	0.082 (8)	0.026 (4)	0.043 (5)	0.035 (5)

Geometric parameters (Å, º)

C1—H1A	0.999	C4—N1	1.274 (12)
C1—H1B	0.946	N1—N2	1.361 (10)
C1—H1C	0.983	N2—H1n2	0.856
C1—C2	1.49 (2)	N2—C5	1.377 (13)
C2—H2	0.963	C5—N3	1.376 (13)
C2—C3	1.311 (13)	C5—S1	1.638 (13)
C3—H3	1.008	N3—C5	1.376 (13)
C3—C4	1.352 (14)	N3—H1n3	0.872
C4—H4	1.024	N3—H2n3	0.894
H1A—C1—H1B	109.0	C3—C4—N1	130.8 (16)
H1A—C1—H1C	106.2	H4—C4—N1	116.8
H1A—C1—C2	108.5	C4—N1—N2	118.6 (11)
H1B—C1—H1C	110.2	N1—N2—H1n2	119.6
H1B—C1—C2	113.8	N1—N2—C5	119.2 (10)
H1C—C1—C2	108.8	H1n2—N2—C5	121.2
C1—C2—H2	115.8	N2—C5—N3	115.6 (12)
C1—C2—C3	125.6 (13)	N2—C5—S1	120.4 (11)
H2—C2—C3	118.2	N3—C5—S1	123.5 (9)
C2—C3—H3	116.8	C5—N3—H1n3	110.5
C2—C3—C4	128.4 (15)	C5—N3—H2n3	112.2
H3—C3—C4	113.9	H1n3—N3—H2n3	113.2
C3—C4—H4	111.8		
C4—N1—N2—C5	−177.4 (14)	N1—N2—C5—N3	8.0 (19)
N2—N1—C4—C3	175.6 (15)	C1—C2—C3—C4	−176.2 (15)
N1—N2—C5—S1	179.6 (11)	C2—C3—C4—N1	−177.6 (16)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H2N3···N1	0.89	2.17	2.641 (14)	112

N2—H1N2···S1^{i}	0.86	2.83	3.473 (11)	133
N3—H1N3···S1^{ii}	0.87	2.77	3.398 (11)	130

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