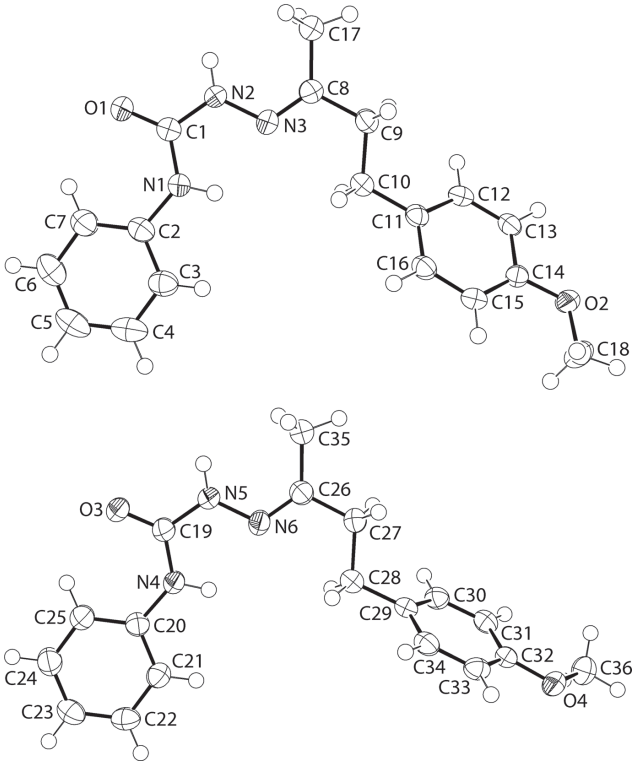
Ming Yueh Tan, Karen A. Crouse, Thahira B.S.A. Ravoof and Edward R.T. Tiekink*

Crystal structure of 1-[(*Z*)-[4-(4-methoxyphenyl) butan-2-ylidene]amino]-3-phenylurea, $C_{18}H_{21}N_3O_2$



https://doi.org/10.1515/ncrs-2017-0415
Received December 19, 2017; accepted March 16, 2018; available online March 27, 2018

Abstract

$C_{18}H_{21}N_3O_2$, triclinic, $P\bar{1}$ (no. 2), $a = 8.5155(4)$ Å, $b = 10.6415(4)$ Å, $c = 19.0732(10)$ Å, $\alpha = 80.918(4)°$, $\beta = 89.689(4)°$, $\gamma = 80.666(4)°$, $V = 1683.74(14)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.055$, $wR_{ref}(F^2) = 0.133$, $T = 100$ K.

CCDC no.: 1830404

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.44 × 0.29 × 0.10 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	0.8 cm^{-1}
Diffractometer, scan mode:	SuperNova Dual, ω scans
$2\theta_{max}$, completeness:	55°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	15637, 7710, 0.040
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4964
$N(param)_{refined}$:	431
Programs:	Agilent [1], SHELX [2, 3], ORTEP [4]

The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

To a solution of 4-phenylsemicarbazide (0.151 g, 1 mmol) in heated absolute ethanol (20 mL) was added slowly a heated ethanol solution (20 mL) of 4-methoxy-2-butanone (0.102 g, 1 mmol) while stirring for 20 min. The white precipitate was filtered, washed with cold ethanol and dried in vacuo. Single crystals were grown at room temperature from slow evaporation of a mixture of ethanol and acetonitrile (1:1 *v*/*v*). IR (cm^{-1}) 3338 (N—H), 1665 (C=O), 1597 (C=N), 1239 (C—N), 1025 (C=S). MS: *m*/*z* 311.25 $[M]^+$.

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95—0.99 Å) and refined as riding with U_{iso}(H) = 1.2–1.5 U_{eq}(C). The N-bound H-atoms were located in a difference Fourier map but were refined with a distance restraint of N—H = 0.88 ± 0.01 Å, and with U_{iso}(H) set to 1.2 U_{eq}(N).

Comment

It is well known that the condensation of semicarbazides with aldehydes/ketones gives rise to a class of potential Schiff base ligands. These molecules attract interest in

***Corresponding author: Edward R.T. Tiekink,** Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, e-mail: edwardt@sunway.edu.my
Ming Yueh Tan: Department of Physical Science, Faculty of Applied Sciences, Tunku Abdul Rahman, University College, 50932 Setapak, Kuala Lumpur, Malaysia
Karen A. Crouse: Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor Darul Ehsan, Malaysia; and Department of Chemistry, St. Francis Xavier University, P.O. Box 5000, Antigonish, NS B2G 2W5, Canada
Thahira B.S.A. Ravoof: Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor Darul Ehsan, Malaysia

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

Atom	x	y	z	U_{iso}*/U_{eq}
O1	0.62938(16)	0.17977(12)	0.45757(7)	0.0325(4)
O2	0.20571(15)	0.95078(12)	−0.03809(6)	0.0274(3)
N1	0.65711(19)	0.26364(15)	0.34056(8)	0.0265(4)
H1N	0.621(2)	0.3328(14)	0.3101(9)	0.032*
N2	0.4832(2)	0.37184(15)	0.41117(8)	0.0278(4)
H2N	0.437(2)	0.3733(18)	0.4526(7)	0.033*
N3	0.44148(18)	0.46161(14)	0.35062(8)	0.0240(4)
C1	0.5933(2)	0.26540(17)	0.40598(10)	0.0252(4)
C2	0.7657(2)	0.16579(17)	0.31674(10)	0.0250(4)
C3	0.8087(2)	0.18784(19)	0.24596(10)	0.0288(5)
H3	0.7658	0.2666	0.2167	0.035*
C4	0.9134(2)	0.0962(2)	0.21768(12)	0.0353(5)
H4	0.9415	0.1122	0.1692	0.042*
C5	0.9768(3)	−0.0181(2)	0.25965(12)	0.0380(5)
H5	1.0492	−0.0810	0.2405	0.046*
C6	0.9343(3)	−0.04031(19)	0.32977(12)	0.0378(5)
H6	0.9779	−0.1194	0.3586	0.045*
C7	0.8291(2)	0.05033(18)	0.35935(11)	0.0315(5)
H7	0.8010	0.0336	0.4078	0.038*
C8	0.3416(2)	0.56302(17)	0.35577(10)	0.0239(4)
C9	0.2972(2)	0.65680(17)	0.28843(9)	0.0239(4)
H9A	0.3307	0.7399	0.2933	0.029*
H9B	0.1799	0.6727	0.2823	0.029*
C10	0.3715(2)	0.61082(17)	0.22189(9)	0.0238(4)
H10A	0.4886	0.5933	0.2288	0.029*
H10B	0.3366	0.5282	0.2170	0.029*
C11	0.3316(2)	0.70338(16)	0.15329(9)	0.0211(4)
C12	0.1768(2)	0.76840(16)	0.13697(9)	0.0213(4)
H12	0.0956	0.7563	0.1705	0.026*
C13	0.1385(2)	0.84978(16)	0.07345(9)	0.0215(4)
H13	0.0326	0.8937	0.0641	0.026*
C14	0.2555(2)	0.86751(16)	0.02301(9)	0.0211(4)
C15	0.4095(2)	0.80246(16)	0.03690(10)	0.0231(4)
H15	0.4896	0.8123	0.0026	0.028*
C16	0.4454(2)	0.72220(17)	0.10202(10)	0.0235(4)
H16	0.5516	0.6789	0.1116	0.028*
C17	0.2642(2)	0.59499(18)	0.42328(10)	0.0302(5)
H17A	0.1897	0.5354	0.4386	0.045*
H17B	0.2064	0.6836	0.4149	0.045*
H17C	0.3461	0.5868	0.4604	0.045*
C18	0.3235(2)	0.9762(2)	−0.08930(10)	0.0324(5)
H18A	0.4076	1.0111	−0.0676	0.049*
H18B	0.2746	1.0390	−0.1295	0.049*
H18C	0.3694	0.8959	−0.1060	0.049*
O3	0.33971(16)	0.34631(12)	0.54839(7)	0.0327(4)
O4	0.82627(15)	−0.44318(12)	1.03135(7)	0.0284(3)
N4	0.32024(18)	0.26414(14)	0.66636(8)	0.0252(4)
H4N	0.361(2)	0.1956(14)	0.6972(9)	0.030*
N5	0.48823(19)	0.15496(15)	0.59335(8)	0.0268(4)
H5N	0.537(2)	0.1558(18)	0.5519(7)	0.032*
N6	0.53493(18)	0.06471(14)	0.65343(8)	0.0245(4)
C19	0.3792(2)	0.26156(17)	0.59999(10)	0.0251(4)
C20	0.2120(2)	0.36143(17)	0.69096(10)	0.0231(4)
C21	0.1890(2)	0.34831(18)	0.76388(10)	0.0259(4)
H21	0.2450	0.2756	0.7942	0.031*
C22	0.0855(2)	0.44006(18)	0.79290(10)	0.0283(4)
H22	0.0713	0.4302	0.8428	0.034*
C23	0.0029(2)	0.54582(18)	0.74927(11)	0.0295(5)
H23	−0.0687	0.6087	0.7688	0.035*
C24	0.0255(2)	0.55916(19)	0.67699(11)	0.0323(5)
H24	−0.0312	0.6319	0.6470	0.039*
C25	0.1297(2)	0.46828(18)	0.64711(10)	0.0289(5)
H25	0.1443	0.4792	0.5972	0.035*
C26	0.6373(2)	−0.03487(17)	0.64658(10)	0.0243(4)
C27	0.6851(2)	−0.13092(17)	0.71260(9)	0.0246(4)
H27A	0.8021	−0.1428	0.7188	0.030*
H27B	0.6570	−0.2149	0.7057	0.030*
C28	0.6084(2)	−0.09378(17)	0.78052(10)	0.0266(4)
H28A	0.6317	−0.0079	0.7865	0.032*
H28B	0.4915	−0.0868	0.7757	0.032*
C29	0.6656(2)	−0.18903(17)	0.84620(9)	0.0224(4)
C30	0.6270(2)	−0.31287(17)	0.85763(10)	0.0252(4)
H30	0.5632	−0.3376	0.8232	0.030*
C31	0.6792(2)	−0.40153(17)	0.91802(10)	0.0249(4)
H31	0.6523	−0.4858	0.9242	0.030*
C32	0.7710(2)	−0.36547(17)	0.96925(10)	0.0219(4)
C33	0.8103(2)	−0.24187(17)	0.95914(10)	0.0241(4)
H33	0.8729	−0.2165	0.9938	0.029*
C34	0.7577(2)	−0.15610(17)	0.89839(10)	0.0250(4)
H34	0.7853	−0.0721	0.8921	0.030*
C35	0.7140(3)	−0.06337(19)	0.57839(10)	0.0321(5)
H35A	0.6314	−0.0586	0.5421	0.048*
H35B	0.7772	−0.1501	0.5863	0.048*
H35C	0.7835	0.0000	0.5624	0.048*
C36	0.7948(3)	−0.57233(18)	1.04164(11)	0.0332(5)
H36A	0.6798	−0.5715	1.0446	0.050*
H36B	0.8472	−0.6199	1.0858	0.050*
H36C	0.8360	−0.6144	1.0016	0.050*

terms of potential biological activity, most notably in the context of their anti-convulsant properties with the 4-(4-fluorophenoxy)benzaldehyde semicarbazone being the subject of considerable investigations in this regard [5]. In connection with on-going studies of the biological activity of transition metal thiosemicarbazone complexes [6], recently the synthesis and characterization of a new Schiff base ligand, derived from the reaction of aryl semicarbazide and vanillylacetone, was described [7]. In continuation of these studies, the title Schiff base molecule was characterized.

Two independent molecules comprise the asymmetric unit of the title compound. As seen from the Figure (70% displacement ellipsoids), the molecules present many similarities but, with the obvious difference related to the relative disposition of the methoxyphenyl residues. The molecule comprises a di-substituted urea residue. At one end, there is a phenyl ring while at the other, an imine (*Z*-configuration) group connects the urea residue to the 4-methoxyphenyl ring

via an ethane link. The four atoms of the urea core are strictly planar with a r.m.s. deviation of 0.0004 Å for the fitted atoms [0.0014 Å for the O3-molecule]. The amine-N—H and imine-N atoms are syn, a disposition that enables the formation of intramolecular amine-N–H···N(imine) hydrogen bonds [N1—H1n···N3: 2.111(16) Å and 113.8(14)°; N4—H4n···N6: 2.125(16) Å and 113.7(13)°]. The dihedral angle between the CN_2O plane and the adjacent phenyl ring is 3.85(13)° [7.54(12)°], consistent with a co-planar relationship. The dihedral angles between the outer phenyl rings are 37.56(8) and 66.56(5)° for the O1- and O3-molecules, respectively.

The most prominent feature of the molecular packing is the formation of an eight-membered $\{\cdots HNCO\}_2$ amide synthon formed between the two independent molecules comprising the asymmetric unit [N2—H2n···O3: 2.001(14) Å and 171.0(18)°; N5—H5n···O1: 1.956(14) Å and 172.8(17)°].

There is a sole literature precedent for molecules of this type as discussed recently [7]. The structure of this molecule, derived from the reaction of semicarbazide and vanillylacetone, presents very similar features to that described above.

Acknowledgements: We thank the staff of the University of Malaya's X-ray diffraction laboratory for the data collection. The Universiti Putra Malaysia, under the research University Grant Scheme (RUGS Nos. 9199834 and 9174000), and the Malaysian Ministry of Science, Technology and Innovation (Grant No. 09-02-04-0752-EA001) are thanked for support.

References

1. Agilent: Agilent Technologies, Yarnton, England (2011).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A71** (2015) 3–8.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. **C71** (2015) 3–8.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Cryst. **45** (2012) 849–854.
5. Pandeya, S. N.: Semicarbazone – a versatile therapeutic pharmacophore for fragment based anticonvulsant drug design. Acta Pharm. **62** (2012) 263–286.
6. Yusof, E. N. M.; Ravoof, T. B. S. A.; Tiekink, E. R. T.; Veerakumarasivam, A.; Crouse, K. A.; Tahir, M. I. M.; Ahmad, H.: Synthesis, characterization and biological evaluation of transition metal complexes derived from N, S bidentate ligands. Int. J. Mol. Sci. **16** (2015) 11034–11054.
7. Tan, M. Y.; Crouse, K. A.; Ravoof, T. B. S. A.; Jotani, M. M.; Tiekink, E. R. T.: 3-{(E)-[4-(4-Hydroxy-3-methoxyphenyl)butan-2-ylidene]amino}-1-phenylurea: crystal structure and Hirshfeld surface analysis. Acta Crystallogr. **E74** (2018) 21–27.