CRYSTAL STRUCTURE OF *N*-{(1*Z*)-3-OXO-1-(THIOPHEN-2-YL)-3-[(2*E*)-2-(THIOPHEN-2-YLMETHYLIDENE)-HYDRAZINYL]PROP-1-EN-2-YL}BENZAMIDE: *N*,*N*-DIMETHYLFORMAMIDE (1:1) SOLVATE

Amit Kumar,[a] K. N. Subbulakshmi,[b,d] B. Narayana,[b] B. K. Sarojini,[c] László Kótai,[e] Sumati Anthal[a] and Rajni Kant[a]*

Keywords: Hydrazine; Intermolecular hydrogen bond; Crystal structure; Direct methods.

N-{(1*Z*)-3-Oxo-1-(thiophen-2-yl)-3-[(2*E*)-2-(thiophen-2-ylmethylidene)hydrazinyl]prop-1-en-2-yl}benzamide:*N*,*N*-dimethylformamide (1:1) solvate, ($C_{19}H_{15}N_3O_2S_2.C_3H_7NO$), crystallizes in the monoclinic space group C2/c with the following unit cell parameters: *a*= 21.111(3), *b*= 8.7685(8), *c*= 25.742(3) Å, *β*= 105.273(13)° and Z=8. The crystal structure was solved by direct methods and refined by full matrix least squares procedures to a final R value of 0.0962 for 2155 observed reflections. The crystal structure is stabilized by N–H···O and C–H···O hydrogen bonds. The DMF solvent gives rise to C10-H10···O3 intermolecular interaction.

* Corresponding Authors
Fax: +91 191 243 2051
E-Mail: rkant.ju@gmail.com
[a] X-ray Crystallography Laboratory, Post-Graduate Department of Physics & Electronics,
[b] Department of Chemistry, Mangalore University, Mangalagangothri-574199, D.K., Mangalore, India
[c] Department ofIndustrial Chemistry, Mangalore University, Mangalagangothri- 574 199, D.K., Mangalore, India
[d] Department of Chemistry, Shree Madhwa Vadiraja Institute of Technology and Management (VTU Belgaum), Vishwothama Nagar, Bantakal, Udupi-574115, Karnataka, India.
[e] Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Budapest, Hungary

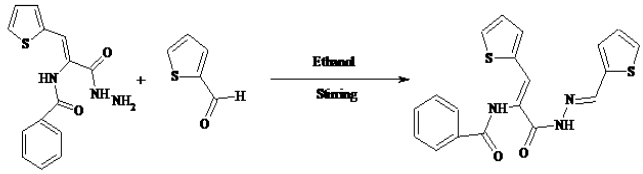
Introduction

Hydrazine derived from condensation of aldehyde with hydrazide have shown excellent biological activities such as, antimicrobial[1-2], antifungal[3], antitumor[4-5], anti-inflammetry[6], analgesic[7], antioxidant.[8] Crystal structure of some Schiff bases *viz*., 2-(1-phenylethylidene)hydrazinyl]-8-(trifluoromethyl)-quinoline, 2-[1-(3-bromophenyl)ethylidene]hydrazinyl}-8-(trifluoromethyl)-quinoline, 2-[-8-(trifluoromethyl)quinolin-4-yl]-hydrazinylidene}ethyl]-phenol hydrate, and 2-[1-(naphthalen-2-yl)ethylidene]-hydrazinyl}-8-(trifleoromethyl)quinolone[9], 2-phenyl-5-[(thiophen-2-yl)methylidene]-3-{[(*E*)-(thiophen-2-yl)methylidene]amino}-3,5-dihydro-4*H*imidazol-4-one[10], 1-(5-bromo-2-hydroxyphenyl)-ethylidene]benzohydrazide[11], 1-(2-hydroxyphenyl)ethylidene]-3-ethoxybenzohydrazide[12], 2-fluoro-N'-[(2-hydroxy-naphthalen-1-yl)-methylidene]benzohydrazide[13], (E)-3,4,5-trimethoxy-N'-[(6-methoxy-4-oxo-4H-chromen-3-yl)methylidene]benzohydrazide monohydrate[14] have been reported. Structural information of ′3-oxo-1-(thiophen-2-yl)-3-[(2*E*)-2-(thiophen-2-ylmethylidene)hydrazinyl]prop-1-en-2-yl}-benzamide is useful in developing the coordination properties of Schiff bases and to investigate new ligands.

Experimental

Synthesis

A mixture of 3-hydrazinyl-3-oxo-1-(thiophen-2-yl)prop-1-en-2-yl]benzamide (2.87 g, 0.01 mol) and thiophenaldehyde (1.12 g, 0.01 mol) in 20 ml ethanol were stirred 3-4 h.. The solid obtained was filtered washed with cold water, dried and recrystallized from ethanol. Single crystals were grown from methanol:1,4-dioxane(1:1) mixture by the slow evaporation method (M.P.435K-436K). The synthetic route for the compound is presented in Scheme 1.



Scheme 1. Synthesis of *N*-{(1*Z*)-3-oxo-1-(thiophen-2-yl)-3-[(2*E*)-2-(thiophen-2-ylmethylidene)hydrazinyl]prop-1-en-2-yl}benzamide:*N*,*N*-dimethylformamide (1:1) solvate

X-Ray structure determination

A crystal of dimensions 0.30x0.20x0.20 mm was used for data collection on X'calibur CCD area-detector single crystal X-ray diffractometer equipped with graphite monochromated MoKα radiation (λ=0.71073 Å). X-ray intensity data consisting of 9749 reflections were collected at 293(2) K and out of these reflections 4487 were found to be unique. The intensities were measured by ω–scan mode for θ ranging between 3.70 to 23.94°. A total number of 2155 reflections were treated as observed[$I>2\sigma(I)$]. Data were corrected for Lorentz-polarization and absorption factors. The structure was solved by direct methods using

SHELXS97.[15] All non-hydrogen atoms of the molecule were located in the best E-map. All the hydrogen atoms were geometrically fixed and allowed to ride on the corresponding non-H atoms with C-H= 0.93-0.96 Å, N-H= 0.86 Å and U_{iso}= 1.2 U_{eq}(C), except for the methyl groups where U_{iso}(H) = 1.5U_{eq}(C). The final refinement cycles converged to an R- factor of 0.0962 (w$R(F2)$ = 0.2459) for 2155 observed reflections. Residual electron density ranges from -0.739 to 0.796 eÅ^{-3}. Atomic scattering factors were taken from International Tables for X-ray Crystallography(1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4). The crystallographic data are summarized in Table 1.

Table 1. Crystal data and other experimental details

CCDC Number	1494776
Crystal description	Plate shape
Crystal size	0.30 x 0.20 x 0.10 mm
Empirical formula	$C_{22}H_{22}N_4O_3S_2$
Formula weight	454.6
Radiation, wavelength	MoK_α, 0.71073 Å
Unit cell dimensions	a = 21.111(3) Å, b = 8.7685(8) Å, c = 25.742(3) Å, α= 90.0º, β = 105.273(13)º, γ= 90.0º
Crystal system, space group	Monoclinic, C2/c
Unit cell volume	4596.8(9)Å^3
No. of molecules per unit cell, Z	8
Absorption coefficient	0.262 mm^{-1}
F(000)	1904
θ range for entire data collection	3.7090 < θ < 23.9430
Reflections collected / unique	9749/4487
Reflections observed $I > 2\sigma(I)$	2155
Range of indices	h= -16 to 26, k= -9 to 10, l= -31 to 31
No. of parameters refined	282
Final R-factor	0.0962
w$R(F2)$	0.2459
R_{int}	0.0351
R_σ	0.0713
Goodness-of-fit	1.019
(Δ/σ)max	0.001
Final residual electron density	-0.739 < Δρ > 0.796 eÅ^{-3}

Results and discussion

The molecule containing atomic labelling is shown in Figure 1 (ORTEP)[16] and the packing diagram as generated using PLATON[17] is shown in Figure 2. It consists of benzamide and two thiophene rings connected via methylidene hydrazinyl. There exists an independent moiety of DMF molecule. The structural parameters, including bond distances and angles show a normal geometry.[18] The benzene ring makes a dihedral angle of 76.14(2)^o with thiophene ring (A). The double bond C7=O1 and C13=O2 bond distance is confirmed by its respective distance of 1.227(5) Å and 1.226(5) Å, respectively. All the three rings are planar with maximum deviation of 0.0354(8) Å observed for C3 atom of the thiophene ring (A). The conformations of the N-H and C=O bonds are *anti* with respect to each other. Benzamide ring is twisted with respect to thiophene ring (A) with a torsion angle (C5-C6-N3-C13) of 75.6(6)°. Methylidene hydrazinyl chain is almost linear as indicated by the values of torsion angles C6-C7-N1-N2=-178.6(4)° and N1-N2-C8-C9= -179.0(4)°.

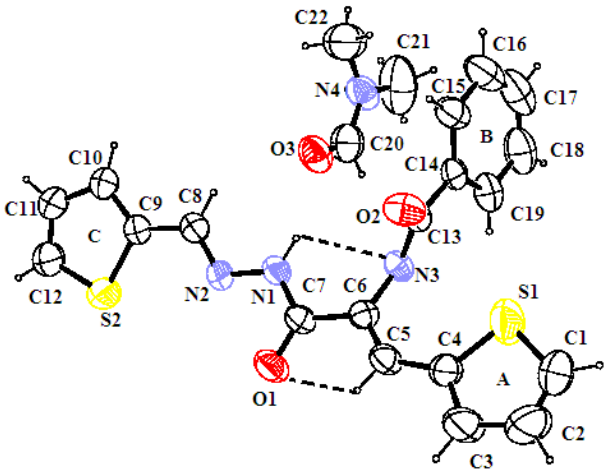


Figure 1. ORTEP view of the molecules with displacement ellipsoids drawn at 40 % probability level. H atoms are shown as small spheres of arbitrary radii.

Molecular packing in the unit cell is viewed down the b-axis is shown in Figure 2. There are two C–H···O, N-H···N and N-H···O intramolecular hydrogen bonds (Table 3). C5-H5···O1 results in the formation of a virtual five-membered ring with S(5) graph-set motif.[19] In the crystal structure, adjacent molecules are interconnected through N–H···O and C–H···O hydrogen bonds. DMF molecule is linked to molecule through C10-H10···O3 hydrogen bond.

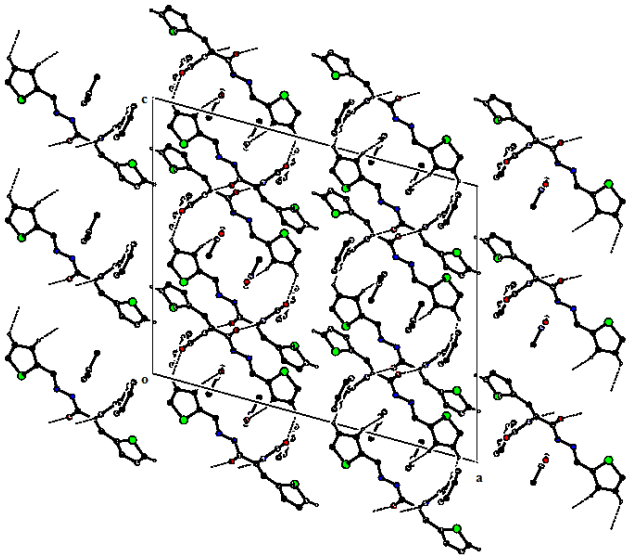


Figure 2. The crystal packing viewed down the b-axis.

Table 2. Selected bond lengths (Å), bond angles (º) and torsion angles(º) for non hydrogen atoms (e.s.d.'s are given in parentheses)

Bond distances		Bond angles		Torsion angles	
S1-C4	1.676(6)	C1-S1-C4	93.5(4)	S1-C4-C5-C6	-7.0(10)
N3-C6	1.415(6)	S1-C4-C5	127.8(4)	N2-N1-C7-C6	-178.6(4)
N1-N2	1.377(5)	N3-C6-C7	118.4(4)	O2-C13-C14-C19	29.9(7)
S2-C9	1.710(5)	C7-N1-N2	117.5(4)	N1-C7-C6-N3	16.2(6)
O2-C13	1.226(5)	O2-C13-C14	122.7(4)	C13-N3-C6-C5	75.6(6)
N2-C8	1.277(6)	O2-C13-N3	121.6 (4)	O1-C7-C6-C5	10.6(7)
O1-C7	1.227(5)	O1-C7-N1	122.4(5)	N1-C7-C6-C5	-167.0(5)
N2-C8	1.277(6)	O1-C7-C6	120.3(5)	N3-C6-C5-C4	-3.0(9)
N3-C13	1.360(5)	N3-C13-C14	115.7(4)	C4-S1-C1-C2	1.5(9)
S2-C9	1.710(5)	C8-N2-N1	117.3(4)	N2-C8-C9-S2	3.4(7)

Table 3. Geometry of intra and intermolecular hydrogen bonds

D-H…A	D-H, Å	H…A, Å	D…A, Å	θ[DH…A, º]
N1-H1...O3	0.86	2.08	2.897(6)	158
N1-H1...N3	0.86	2.47	2.799(5)	104
C5-H5...O1	0.93	2.32	2.736(6)	106
C8-H8...O3	0.93	2.49	3.246(6)	138
N3-H3...O1^{i}	0.86	1.99	2.782(5)	152
C10-H10...O3^{ii}	0.93	2.54	3.440(7)	162
C11-H11...O2^{ii}	0.93	2.51	3.198(8)	131

Symmetry code: (i) 1/2-*x*,-1/2+*y*,1/2-*z* (ii) -*x*,*y*,1/2-*z*

Acknowledgement

RK is thankful to DST, New Delhi for funding under research project no: EMR/2014/000467.

References

[1]El-Masry, A. H., Fahmy, H. H. and Abdelwahed. S. H. A., *Molecules.,* **2000**, *5*, 1429-1438.

[2]Pandey, S. N., Sriram, D., Nath, G. and De Clercq, E., *II Farmaco*. **1999**, *54*, 624-628.

[3]Singh, W. M. and Dash, B. C., *Pesticides*. **1988**, *22*, 33-37.

[4]Desai, S. B., Desai, P. B. and Desai, K. R. *Heterocycl. Commun*., **2001**, *7*, 83-90.

[5]Misra, V. S., Singh, S., Agrwal, R. and Chaudhary, K. C., *J. Chem. Soc. Pak*. **1981**, *3*, 209-213.

[6]Todeschini, R., De Miranda, A. L. P., Da Silva, K. C. M., Pamini, S. C. and Barreiero, E. J., *Eur. J. Med. Chem*., **1998**, *33*, 189-199.

[7]Sridar, S. K. and Ramesh, A., *Boil. Pharm. Bull.* **2001**, *24*, 1149-1152.

[8]Mamolo, M. G., Falagiaru, V., Zampieri, D., Vio, U., Banfi, E. and Scialino, G., *Farmaco. Sci*., **2003**, *58*, 631-637.

[9]Jasinskia, J. P., Butcher, R. J., Mayekar, A. N., Yathirajan, H. S., Narayana, B. and Sarojini, B. K., *J. Mol. Struct.*, **2010,** *980*, 178-181.

[10]Subbulakshmi, K. N., Narayana, B., Hemmige, S. Y., Akkurt, M., Celik, O., Ersanli, C. C. and Glidewell, C., *Acta Cryst*., **2015**, *C71*, 1-10.

[11]Zheng. C. Z., Ji. Y., Chang, X. and Zhang, L.,. *Acta Cryst*., **2008**, *E64*, o2487.

[12]Li, C. and Ban, H., *Acta Cryst*., **2009**, *E65*, o876.

[13]Wang, D., Meng, X. and Ma, J., *Acta Cryst*., **2012,** *E68*, 021.

[14]Ishikawa, Y. and Watanabe, K., *Acta Cryst*. **2014**, *E70*, o832.

[15]Sheldrick, G.M., *Acta Cryst*., **2008**, *A64*, 112.

[16]Farrugia, L.J., *J. Appl. Cryst*., **1997**, *30*, 565.

[17]Spek, A. L., *Acta Cryst*., **2009**, *D65*, 148.

[18]Allen, F. H., Kennard,O., Watson,D.G., Brammer,L., Orpen,A.G. and Taylor,R., *J. Chem. Soc., Perkin Trans-II.*, **1987**, S1.

[19]Bernstein, J., Davis, R. E., Shimoni, L. and Angew, N. L., *Chem. Int. Ed. Engl.*, **1995**, *34*, 1555.

Received: 22.09.2016.
Accepted: 02.10.2016.