Struct Chem (2010) 21:995–1003
DOI 10.1007/s11224-010-9637-3

ORIGINAL RESEARCH

Synthesis, spectroscopic characterization, crystal structures, and theoretical studies of (*E*)-2-(2,4-dimethoxybenzylidene) thiosemicarbazone and (*E*)-2-(2,5-dimethoxybenzylidene) thiosemicarbazone

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Received: 5 January 2010 / Accepted: 11 June 2010

Abstract Two thiosemicarbazones, (*E*)-2-(2,4-dimethoxybenzylidene)thiosemicarbazone (24-MBTSC (**1**)) and (*E*)-2-(2,5-dimethoxybenzylidene)thiosemicarbazone (25-MBTSC (**2**)), derived from 2,4-dimethoxybenzaldehyde and 2,5-dimethoxybenzaldehyde, respectively, with thiosemicarbazide have been synthesized and their structures were characterized by elemental analyses, FT-IR, ^{1}H NMR spectroscopy, and X-ray single-crystal diffraction analysis. Molecular orbital calculations have been carried out for **1** and **2** by using an ab initio method (HF) and also density functional method (B3LYP) at 6-31G basis set. Compound **1** crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 8.1342(5)$ Å, $b = 18.1406(10)$ Å, $c = 8.2847(6)$ Å, $\beta = 109.7258(17)°$, $V = 1150.75(12)$ Å^3, and $Z = 4$, whereas compound **2** crystallizes in the orthorhombic system, space group *Pbca*, with $a = 11.0868(6)$ Å, $b = 13.1332(6)$ Å, $c = 15.9006(8)$ Å, $V = 2315.2(2)$ Å^3, and $Z = 8$. The compounds **1** and **2** displays a *trans*-configuration about the C=N double bond.

Keywords Thiosemicarbazone · 2,4-Dimethoxybenzaldehyde · 2,5-Dimethoxybenzaldehyde · Crystal structure · Configuration · HF · Density functional theory (DFT)

Introduction

Thiosemicarbazide $H_2N–NH–C(=S)–NH_2$ is a promising unit to synthesize new polyfunctional organic compounds, named as thiosemicarbazone, that are used as a precursor to produce new transition metal complexes with a wide range of application in recent years [1]. They have been evaluated over the last 50 years as antiviral, antibacterial, and anticancer therapeutics, and biological activities of them are a function of parent aldehyde or ketone moiety [2–7]. Thiosemicarbazone is an important group of multidentate ligands and usually coordinates with the metal through the imine nitrogen and sulfur atom [8–24] (Scheme 1).

Although a series of free thiosemicarbazone compounds and their complexes have been investigated crystallographically [25–27], herein, we report the syntheses, characterization, and crystal structure of two thiosemicarbazone compounds derived from 2,4-dimethoxybenzaldehyde and 2,5-dimethoxybenzaldehyde (Scheme 2). The structural analyses were carried out utilizing elemental analyses (CHN), FT-IR and ^{1}H NMR spectroscopy and X-ray diffraction techniques.

Experimental

All reagents and solvents for synthesis and analysis were commercially available and used as-received. Infrared spectra were recorded as KBr pellets on a FT-IR Perkin-Elmer

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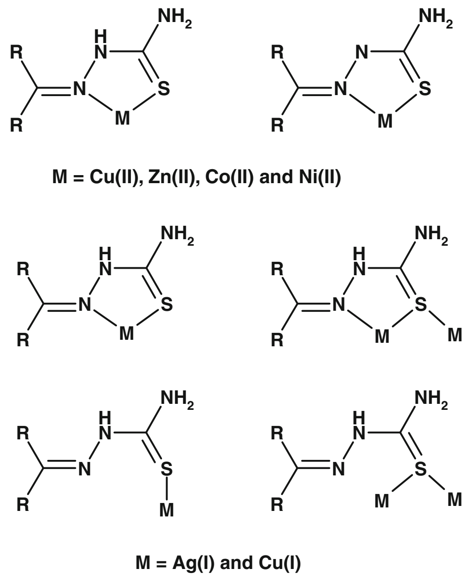
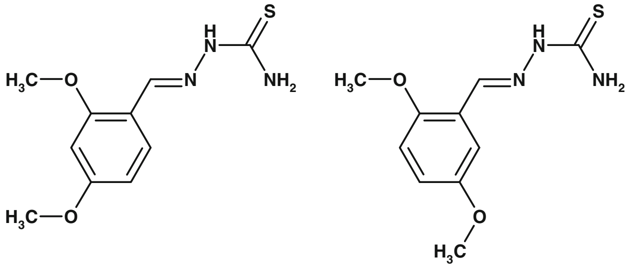


Scheme 1 Different modes of thiosemicarbazone in transition metal complexes


24-MBTSC (1) **25-MBTSC (2)**

Scheme 2 Chemical structure of the title compounds

spectrophotometer. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer. ^{1}H NMR spectra were measured on a BRUKER DRX-250 AVANCE spectrometer at 250 MHz and all chemical shifts are reported in δ units downfield from TMS.

Synthetic procedures of 24-MBTSC (1) and 25-MBTSC (2)

Compounds **1** and **2** were synthesized by addition of the 2,4-dimethoxybenzaldehyde or 2,5-dimethoxybenzaldehyde (0.2 mmol, in 5 mL ethanol) to a solution of thiosemicarbazide (0.2 mmol, 10 mL ethanol). The resulted solution was stirred in air at 323 K for about 1.5–2 h and then was left at room temperature for several days without disturbance to yield single crystals of compounds. The obtained crystals were filtered off, washed with EtOH.

24-MBTSC (**1**): Reactant materials: Thiosemicarbazide, 2,4-dimethoxybenzaldehyde. Colorless crystals. Yield: 88%. *Anal.* Calc. for $C_{10}H_{13}N_3O_2S$: C, 50.20; H, 5.48; N, 17.56%. Found: C, 49.58; H, 5.35; N, 18.0%. IR (KBr pellet, cm^{-1}): υN–H: 3443, 3243, 3139, υC–H (aromatic): 3009, υC–H (aliphatic): 2967, υC–H (imine): 2826, υC=N (imine) 1613, υC–C and C–N: 1429–1590, υC–O: 1323, υC=S: 1210. ^{1}H NMR (DMSO, δ(ppm)): 11.26 (s, 1H, N–H); 8.26 (s, 1H, –CH=N–); 7.99 (s, 1H, NH_2); 7.96 (s, 1H, NH_2); 7.82 (s, 1H, Ar–H); 6.54 (t, 2H, Ar–H), 3.77 (s, 6H, $2CH_3$–O–).

25-MBTSC (**2**): Reactant materials: Thiosemicarbazide, 2,5-dimethoxybenzaldehyde. Colorless crystals. Yield: 90%. *Anal.* Calc. for $C_{10}H_{13}N_3O_2S$: C, 50.20; H, 5.48; N, 17.56%. Found: C, 50.10; H, 5.37; N, 17.58%. IR (KBr pellet, cm^{-1}): υN–H: 3432, 3316, 3175, υC–H (aromatic): 3014, υC–H (aliphatic): 2963, υC–H (imine): 2837, υC=N (imine): 1610, υC–C, and C–N: 1431–1597, υC–O: 1364, υC=S: 1222. ^{1}H NMR (DMSO, δ(ppm)): 11.39 (s, 1H, N–H); 8.35 (s, 1H, –CH=N–); 8.15 (s, 1H, NH_2); 8.05 (s, 1H, NH_2); 7.61 (s, 1H, Ar–H); 6.94 (t, 2H, Ar–H), 3.73 (s, 6H, $2CH_3$–O–).

X-ray structure analysis

Crystallographic measurements for both compounds were done with Rigaku RAXIS-RAPID II diffractometer, with graphite monochromataed Mo Kα radiation ($\lambda = 0.71075$ Å) at 180 K. The crystal structures were solved by direct methods using program SHELXS97 [28] and refined by full-matrix least-squares technique (SHELXL97 [28]) based on F^2 with atomic anisotropic thermal parameters for all non-hydrogen atoms. The molecular structure plots were prepared by using the ORTEP-3 [29]. C-bound H atoms were placed in geometrically idealized positions (C–H = 0.95 or 0.98 Å) and allowed to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C). Crystallographic data and details of the data collection and structure refinements are listed in Table 1.

Theoretical methods

Molecular parameters (bond distances, torsion and bond angles, and the theoretically structures) of the title compounds 24-MBTSC (**1**) and 25-MBTSC (**2**) have been computed in an ab initio comparative study involving HF and density functional theory (DFT) calculations. The 6-31G basis set was employed. Several useful concepts derived from DFT have been applied to the study of the chemical reactivity of the more stable forms of the isomeric thiosemicarbazone. The parameters have been obtained from calculations made in the context of the Hartree–Fock and nonlocal (B3LYP) density functional approximations. The results were compared with the

Table 1 Crystal structure and refinement of 24-MBTSC (**1**) and 25-MBTSC (**2**)

	1	**2**
Empirical formula	$C_{10}H_{13}N_3O_2S$	$C_{10}H_{13}N_3O_2S$
Formula weight	239.29	239.29
Crystal system, space group	Monoclinic, $P2_1/c$	Orthorhombic, *Pbca*
a (Å)	8.1342(5)	11.0868(6)
b (Å)	18.1406(10)	13.1332(6)
c (Å)	8.2847(6)	15.9006(8)
α	90.00	90.00
β	109.7258(17)	90.00
γ	90.00	90.00
V (Å^3)	1150.75(12)	2315.2(2)
Z	4	8
Crystal size (mm^3)	0.35 × 0.30 × 0.21	0.35 × 0.35 × 0.15
ρ_{calc} (g/cm^3)	1.381	1.373
μ (mm^{-1})	0.271	0.269
Index ranges	$-11 \leq h \leq 11$	$-15 \leq h \leq 15$
	$-23 \leq k \leq 25$	$-16 \leq k \leq 18$
	$-11 \leq l \leq 11$	$-22 \leq l \leq 22$
Reflection number, total	18734, 3354	43088, 3369
R_{int}	0.0213	0.0163
Number of parameters	157	157
Goodness-of-fit on F^2	1.064	1.039
Final R indices [$I > 2\sigma$ (I)]	$R_1 = 0.0315$, $wR_2 = 0.0845$	$R_1 = 0.0315$, $wR_2 = 0.0876$
Final R indices (all data)	$R_1 = 0.0343$, $wR_2 = 0.0866$	$R_1 = 0.0339$, $wR_2 = 0.0895$

24-MBTSC (**1**) $w = 1/[s^2(F_o^2) + (0.0499P)^2 + 0.2515P]$ $P = (F_o^2 + 2F_c^2)/3$

25-MBTSC (**2**) $w = 1/[s^2(F_o^2) + (0.0543P)^2 + 0.5575P]$ $P = (F_o^2 + 2F_c^2)/3$

existing experimental evidence on thiosemicarbazone and related compound. The results indicate that B3LYP with the 6-31G basis set is a useful method [30–33]. All HF and DFT calculations were performed using the Gaussian 98 R−A.9 package [34].

Results and discussion

Synthesis

Both compounds **1** and **2** were prepared in yield 88 and 90%, respectively, by reaction of 2,4-dimethoxybenzaldehyde or 2,5-dimethoxybenzaldehyde and thiosemicarbazide in at mild condition in ethanolic solution. They are air-stable in the solid state for several months. The stability of dissolved compound is very much shorter than in the solid state and depends on the nature of the solvent. The title compounds **1** and **2** are very slightly soluble in common organic solvents such as acetonitrile, methanol, chloroform, and dichloromethane but completely soluble in DMF and DMSO.

FT-IR spectra

The FT-IR data of the compounds are given in "Experimental" section and summarized in Table 2. Vibration bands with the wave numbers of 3443, 3243, 3139 and 3432, 3316, 3175 cm^{-1} (υN–H), 1323 and 1364 cm^{-1} (υC–O), 1210 and 1222 cm^{-1} (υC=S) were observed for compounds **1** and **2**, respectively. The difference between these bands shows the presence of different hydrogen bonds in these compounds. Strong vibration band at 1613 and 1610 cm^{-1} was observed in **1** and **2**, respectively, which is accountable for the existence C=N imine bond.

^{1}H NMR spectra

The ^{1}H NMR spectra of the title compounds **1** and **2** were recorded using DMSO as the solvent and the data were summarized in "Experimental" section, and are depicted in Fig. 1. The N–H and azomethine protons are observed as a singlet at 11.26 and 8.26 ppm, respectively, for compound **1** and 11.39 and 8.325 ppm, respectively, for compound **2**. The two amine protons (NH_2) have different hydrogen bonds as observed at 7.99 and 7.96 ppm for compound **1** and 8.15 and 8.05 ppm for compound **2**. The phenyl protons are observed as two groups; the first group observed as a singlet bands at 7.82 ppm for compound **1** and 7.61 ppm compound **2,** and the second group observed as a triplet bands at 6.54 ppm for compound **1** and 6.94 ppm compound **2**. All the aliphatic protons (CH3–O– groups) in the

Table 2 Selected vibration bands of 24-MBTSC (**1**) and 25-MBTSC (**2**)

Vibration bands	**1**	**2**
υN–H	3443, 3243, 3139	3432, 3316, 3175
υC–H (aromatic)	3009	3014
υC–H (aliphatic)	2967	2963
υC–H (imine)	2826	2837
υC=N (imine)	1613	1610
υC–C and C–N	1429–1590	1431–1597
υC–O	1323	1364
υC=S	1210	1222

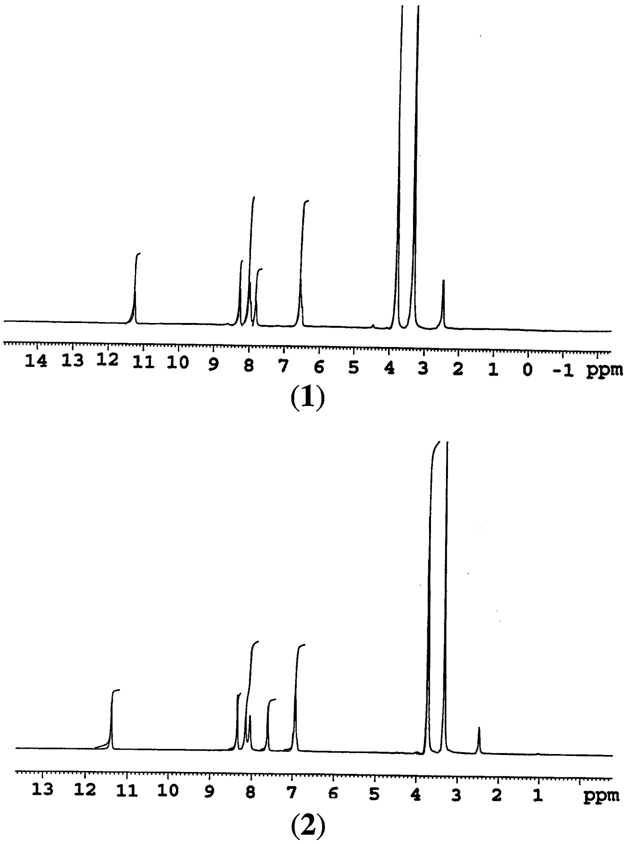


Fig. 1 ^{1}H NMR spectra of the title compounds **1** and **2**

title compounds **1** and **2** as a singlet bands are observed at 3.77 ppm for compound **1** and 3.73 ppm for compound **2**.

Crystal structures of 1 and 2

Figures 2 and 3 depict the molecular structures of **1** and **2**, respectively. Bond distances, bond, and torsion angles are given in Tables 3, 4, and 5, respectively. The benzene ring (C1–C6) and the thiosemicarbazide fragment (C9/N1/N2/C10/S1/N3) in the title molecules **1** and **2** are essentially coplanar, the dihedral angles between them being 2.98(4)° and 9.04(4)°, respectively, for **1** and **2**, so that the structure provides π-conjugation between the benzene ring and the thiosemicarbazide fragment of the compounds.

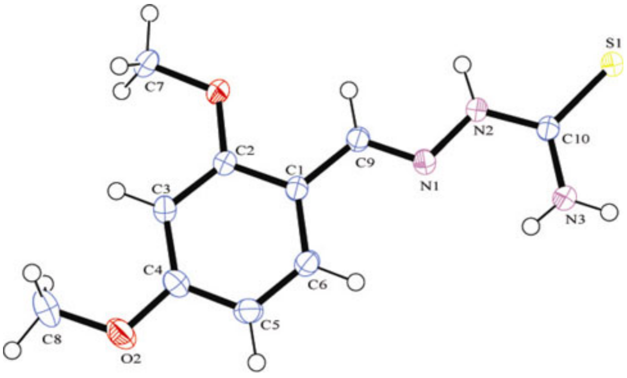


Fig. 2 ORTEP-3 drawing of **1** with the atom numbering scheme. The thermal ellipsoids are drawn at the 50% probability level

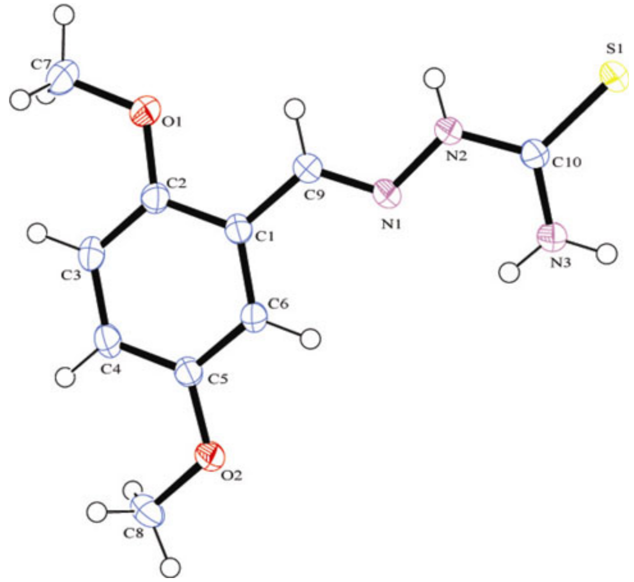


Fig. 3 ORTEP-3 drawing of **2** with the atom numbering scheme. The thermal ellipsoids are drawn at the 50% probability level

The C1–C9 bond length of **1** and **2** are 1.4566(12) and 1.4636(12) Å, which are shorter than the corresponding bond in other uncoordinated thiosemicarbazone (1.498(3) Å, [35]) but is almost similar to ones in other uncoordinated thiosemicarbazone (1.445(3) Å [26] and 1.468(2) Å [27]). The C10–S1 bond distance of 1.6961(9) Å in **1** and 1.6950(9) Å in **2** is almost similar to those in other uncoordinated thiosemicarbazone (1.674(2) Å [26], 1.690(1) Å [27]) and is intermediate between the values of 1.82 Å for a C–S single bond and 1.56 Å for C=S double bond. The terminal nitrogen atoms N1 and N3 of the thiosemicarbazide fragment are in an antiperiplanar conformation with respect to the C10–N2, whereas the middle nitrogen atom N2 of the thiosemicarbazide and C1 of the benzaldehyde fragment are in a *trans*-configuration with respect to the imine C9=N1. Structural data show that the N1–C9 distance is 1.2866(11) Å in **1** and 1.2809(12) Å in **2**, which is longer or shorter than the distance for C=N double bond in some thiosemicarbazone compounds, 1.276(3) Å [26] and 1.330(2) Å [27], but well in the range of C=N double bond distance found in some thiosemicarbazone compound, 1.281(3) Å [35]. The N2–C10 bond length 1.3467(11) Å in **1** and 1.3507(11) Å in **2** is shorter or longer than the distance for C=N double bond in some thiosemicarbazone compounds, 1.360(2) Å [26], 1.353(3) Å [35], and 1.342(3) Å [27]. The bond angle C1–C9–N1 is 120.81(8)° in **1** and 120.20(8)° in **2**, and they are consistent with the sp^2 hybrid character for

Table 3 Bond distances of 24-MBTSC (**1**) and 25-MBTSC (**2**)

	1	HF/6-31G	B3LYP/6-31G	**2**	HF/6-31G	B3LYP/6-31G
S1–C10	1.6961(9)	1.746	1.730	1.6950(9)	1.736	1.728
O1–C2	1.3625(11)	1.367	1.380	1.3679(11)	1.363	1.385
O1–C7	1.4273(11)	1.433	1.453	1.4203(12)	1.427	1.450
O2–C4	1.3582(12)	1.364	1.385	1.3772(11)	1.375	1.393
O2–C8	1.4339(14)	1.431	1.453	1.4298(11)	1.425	1.450
N1–C9	1.2866(11)	1.269	1.289	1.2809(12)	1.267	1.298
N1–N2	1.3836(11)	1.375	1.380	1.3772(10)	1.370	1.376
N2–C10	1.3467(11)	1.342	1.371	1.3507(11)	1.344	1.371
N3–C10	1.3259(12)	1.327	1.348	1.3259(12)	1.326	1.347
C1–C6	1.4008(13)	1.387	1.404	1.3941(12)	1.392	1.400
C1–C2	1.4039(12)	1.403	1.421	1.4099(12)	1.401	1.417
C1–C9	1.4566(12)	1.461	1.454	1.4636(12)	1.466	1.463
C2–C3	1.3972(12)	1.379	1.392	1.3890(13)	1.388	1.394
C3–C4	1.3909(13)	1.390	1.403	1.3943(14)	1.392	1.393
C4–C5	1.3990(14)	1.387	1.402	1.3892(13)	1.380	1.386
C5–C6	1.3788(14)	1.386	1.395	1.3907(12)	1.386	1.393

Table 4 Bond angles of 24-MBTSC (**1**) and 25-MBTSC (**2**)

	1	HF/6-31G	B3LYP/6-31G	**2**	HF/6-31G	B3LYP/6-31G
C2–O1–C7	117.75(7)	121.78	119.26	117.86(8)	121.47	118.98
C4–O2–C8	117.67(9)	121.84	118.65	–	–	–
C5–O2–C8	–	–	–	117.52(7)	118.20	118.54
C9–N1–N2	115.14(8)	118.32	117.55	115.60(8)	118.46	117.99
C10–N2-N1	119.33(8)	121.20	121.19	119.08(8)	121.10	121.06
C6–C1–C2	117.68(8)	117.94	117.65	119.40(8)	118.42	118.14
C6–C1–C9	121.96(8)	122.52	122.72	121.38(8)	121.95	122.14
C2–C1–C9	120.36(8)	119.53	119.61	119.22(8)	119.07	119.23
O1–C2–C3	122.86(8)	122.90	123.18	124.78(8)	123.83	123.90
O1–C2–C1	115.93(8)	116.10	115.14	115.48(8)	116.10	115.83
C3–C2–C1	121.21(8)	121.55	121.77	119.73(8)	119.78	119.75
C4–C3–C2	119.23(8)	119.60	119.62	–	–	–
O2–C4–C3	123.74(9)	115.51	115.11	–	–	–
O2–C4–C5	115.63(9)	124.36	124.85	–	–	–
C3–C4–C5	120.63(8)	120.11	120.03	–	–	–
C6–C5–C4	119.14(9)	118.74	118.65	–	–	–
C5–C6–C1	122.07(9)	122.86	122.46	–	–	–
C2–C3–C4	–	–	–	120.42(8)	120.36	120.39
C5–C4–C3	–	–	–	119.84(8)	119.91	119.91
O2–C5–C4	–	–	–	123.97(8)	123.54	124.48
O2–C5–C6	–	–	–	115.79(8)	115.67	115.50
C4–C5–C6	–	–	–	120.23(8)	119.59	120.53
C5–C6–C1	–	–	–	120.34(8)	121.55	121.63
N1–C9–C1	120.81(8)	122.20	122.13	120.20(8)	121.83	121.24
N3–C10–N2	117.48(8)	116.96	115.48	116.91(8)	116.63	116.27
N3–C10–S1	122.98(7)	123.01	124.43	123.54(7)	123.37	124.56
N2–C10–S1	119.53(7)	120.02	122.08	119.54(7)	119.99	119.95

Table 5 Torsion angles of 24-MBTSC (**1**) and 25-MBTSC (**2**)

	1	HF/6-31G	B3LYP/6-31G	**2**	HF/6-31G	B3LYP/6-31G
C9–N1–N2–C10	−179.00(8)	−180.00	179.99	175.39(9)	−179.99	179.99
C7–O1–C2–C3	2.53(13)	0.02	0.02	3.14(15)	0.03	0.01
C7–O1–C2–C1	−177.80(8)	−179.90	179.99	−177.96(9)	179.99	179.98
C6–C1–C2–O1	−178.29(8)	179.38	177.83	179.50(8)	180.00	180.00
C9–C1–C2–O1	1.33(12)	0.00	0.00	−0.56(12)	0.00	0.00
C6–C1–C2–C3	1.39(13)	0.872	1.03	−1.55(13)	0.89	0.00
C9–C1–C2–C3	−178.98(8)	−180.00	−180.00	178.40(9)	−180.00	−180.00
O1–C2–C3–C4	178.67(8)	179.82	178.76	−179.59(9)	−178.42	−180.00
C1–C2–C3–C4	−0.99(14)	0.09	0.34	1.56(15)	0.23	0.00
C8–O2–C4–C3	2.82(15)	−179.21	−179.97	–	–	–
C8–O2–C4–C5	−177.72(9)	1.08	0.43	–	–	–
C2–C3–C4–O2	179.20(9)	−179.92	−179.93	–	–	–
C2–C3–C4–C5	−0.23(14)	0.36	0.5	–	–	–
O2–C4–C5–C6	−178.48(9)	179.70	179.82	–	–	–
C3–C4–C5–C6	0.99(15)	0.02	0.31	–	–	–
C2–C3–C4–C5	–	–	–	−0.08(15)	0.65	0.00
C8–O2–C5–C4	–	–	–	5.75(13)	0.04	0.00
C8–O2–C5–C6	–	–	–	−174.43(8)	179.92	−180.00
C3–C4–C5–O2	–	–	–	178.39(9)	179.92	180.00
C3–C4–C5–C6	–	–	–	−1.43(15)	1.081	0.00
O2–C5–C6–C1	–	–	–	−178.40(8)	−179.08	−180.00
C4–C5–C6–C1	−0.56(15)	0.81	0.74	1.43(14)	1.25	0.00
C2–C1–C6–C5	−0.61(14)	1.24	1.5	0.06(13)	1.64	0.00
C9–C1–C6–C5	179.77(9)	178.70	179.42	−179.89(8)	178.85	180.00
N2–N1–C9–C1	−179.32(8)	−180.00	−179.97	−178.53(8)	−178.98	−179.98
C6–C1–C9–N1	−1.59(14)	0.02	0.04	8.70(14)	0.01	0.01
C2–C1–C9–N1	178.80(8)	−179.99	−179.96	−171.25(9)	−179.99	−179.99
N1–N2–C10–N3	1.90(13)	0.02	0.02	3.09(13)	0.01	0.01
N1–N2–C10–S1	−176.70(6)	−179.98	−179.98	−175.94(7)	−179.99	−179.99

C9 atom (123.3(2)° [26], 118.89(11)° [27], and 114.93(18)° [35]).

The geometrical details of hydrogen bonds in **1** and **2** are summarized in Table 6. In each compound, there is an intramolecular N–H···N hydrogen bond (N3–H3A···N1), which supports an antiperiplanar conformation of N1 and N3 atoms with respect to the C10–N2 bond. In the crystal structure of **1**, the molecules are connected by N–H···S hydrogen bonds (N2–H2···S1 and N3–H3B···S1) to form a chain running along the *c*-axis (Fig. 4). Between the chains, the molecules are arranged in an antiparallel manner (Fig. 5), but no significant interaction is observed. In the structure of **2**, the primary intermolecular interaction is formed between the amide and methoxyl groups (N3–H3B···O2), which leads to a different molecular packing from **1**. The N–H···S hydrogen bonds are also observed but

Table 6 Hydrogen bonds of 24-MBTSC (**1**) and 25-MBTSC (**2**)

D–H···A	*D*–H	H···A	*D*···A	*D*–H···A
24-MBTSC (**1**)				
N3–H3A···N1	0.820(18)	2.269(16)	2.6368(12)	107.7(13)
N2–H2···S1^{i}	0.909(15)	2.511(15)	3.4159(9)	173.5(13)
N3–H3B···S1^{ii}	0.865(16)	2.594(16)	3.4465(9)	168.7(15)
25-MBTSC (**2**)				
N3–H3A···N1	0.871(15)	2.254(13)	2.6212(12)	105.2(11)
N3–H3B···O2^{iii}	0.871(15)	2.155(15)	2.9745(11)	156.6(14)
N2–H2···S1^{iv}	0.849(14)	2.718(14)	3.5439(8)	165.0(13)
N3–H3A···S1^{v}	0.871(15)	2.825(15)	3.5318(9)	139.3(11)
C4–H4···O1^{vi}	0.95	2.51	3.3200(13)	143

Symmetry codes: (i) *x*, ½ − *y*, 1/2 + *z*; (ii) *x*, ½ − *y*, −1/2 + *z*; (iii) −1/2 + *x*, 3/2 − *y*, 1 − *z*; (iv) −*x*, 1 − *y*, 1 − *z*; (v) 1/2 + *x*, 3/2 − *y*, 1 − *z*; (vi) 1/2 + *x*, *y*, ½ − *z*

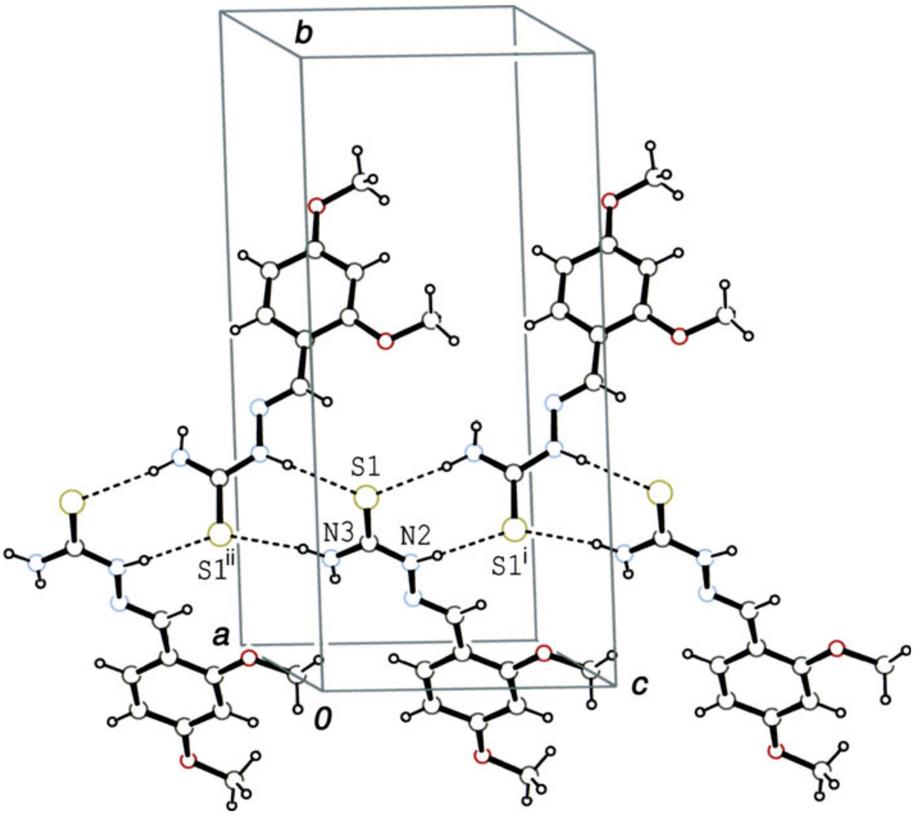


Fig. 4 A partial packing diagram of **1**, showing a molecular chain formed by the intermolecular N–H···S hydrogen bonds (*dashed lines*). Symmetry codes: (i) *x*, ½ − *y*, 1/2 + *z*; (ii) *x*, ½ − *y*, −1/2 + *z*

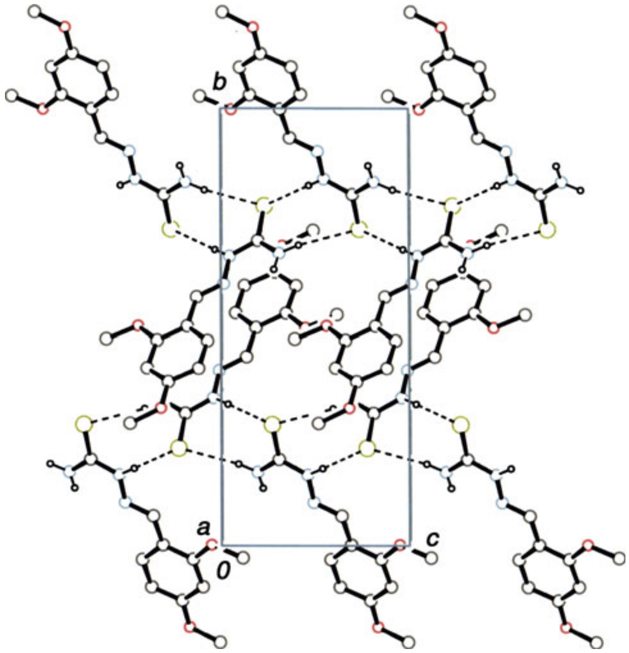


Fig. 5 A packing diagram of **1**, viewed along the *a*-axis. H atoms except N-bound ones have been omitted. The N–H···S hydrogen bonds are indicated by *dashed lines*

rather weak as compared with those in **1**. The molecules are linked through the N–H···O and N–H···S hydrogen bonds (N3–H3B···O2 and N3–H3A···S1), forming a zigzag chain along the *a*-axis (Fig. 6). The chains related by an inversion center are connected by a pair of N–H···S interactions (N2–H2···S1) to form a layer expanding parallel to the *ab* plane (Fig. 7). The layers are further lined by C–H···O interactions (C4–H4···O1).

Theoretical studies

The B3LYP/6-31G optimized structure of the title compounds **1** and **2** discussed during the computational investigations is presented in Figs. 8 and 9, respectively. Some optimized geometric parameters are also listed in Tables 2–4. However, the theoretical calculations are performed in gaseous phase and the experimental results are in a solid state, comparing the theoretical with the experimental values of **1** and **2** shows that there is quite resemblance in the structural parameters (such as bond distances, bond angles, etc.) of the title compounds obtained theoretically and experimentally obtained by X-ray crystallography.

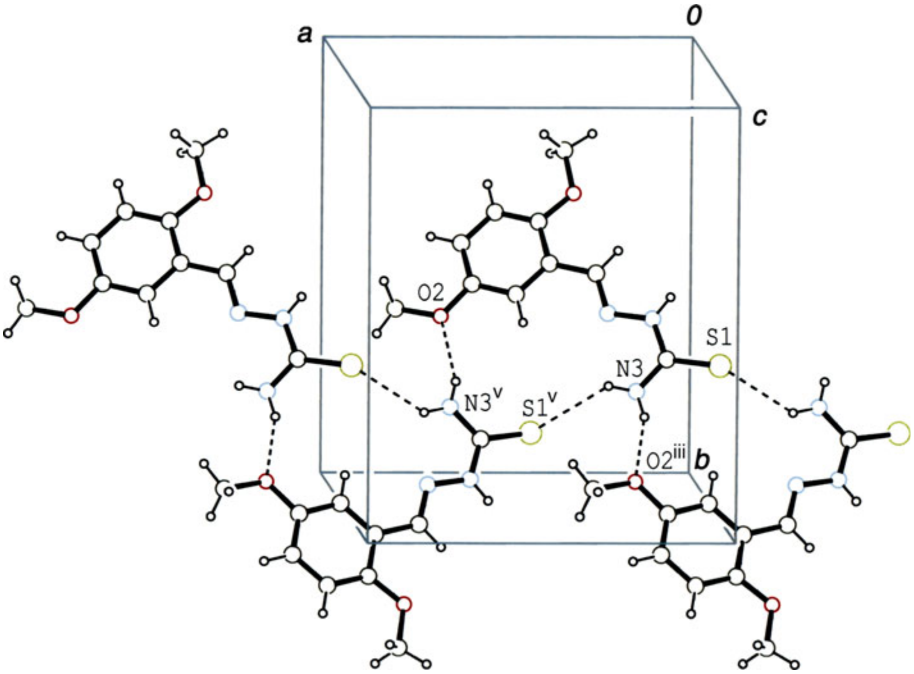


Fig. 6 A partial packing diagram of **2**, showing a molecular chain formed by the intermolecular N–H···O and N–H···S hydrogen bonds (*dashed lines*). Symmetry codes: (iii) $-1/2 + x$, $3/2 - y$,$1 - z$; (v) $1/2 + x$, $3/2 - y$, $1 - z$

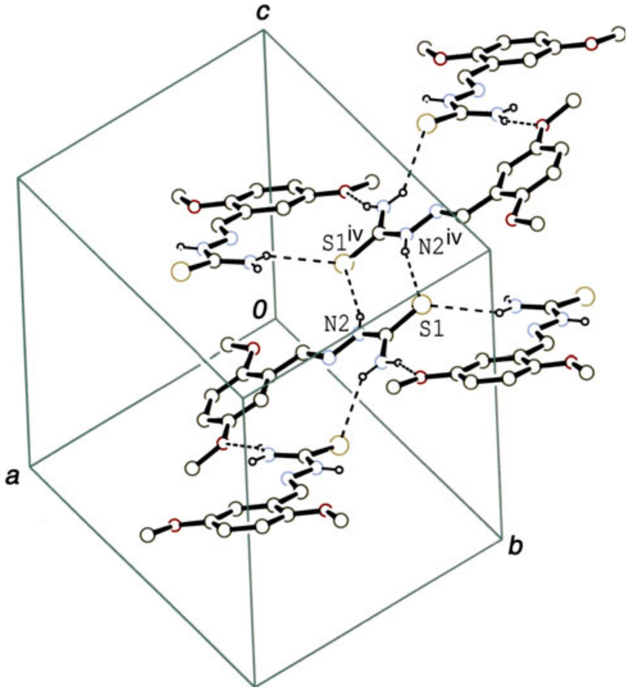


Fig. 7 A partial packing diagram of **2**, showing N–H···S hydrogen bonds (*dashed lines*) formed between the molecular chains. Symmetry code: (iv) $-x$, $1 - y$, $1 - z$

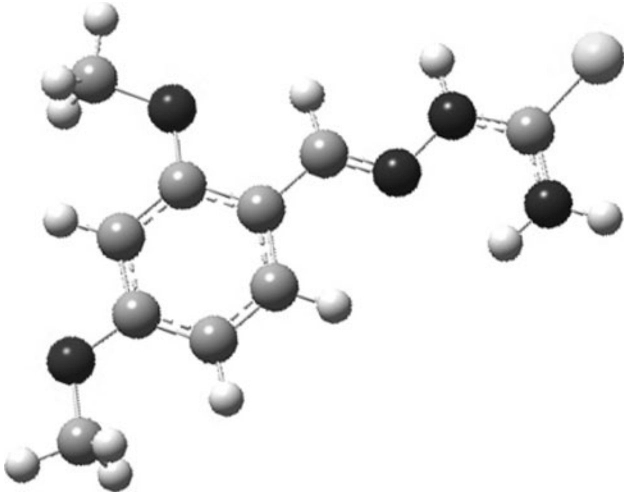


Fig. 8 The B3LYP/6-31G optimized structure of **1**

Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Center, CCDC Nos. 757173 (**1**) and 757174 (**2**). Copies of the data can be

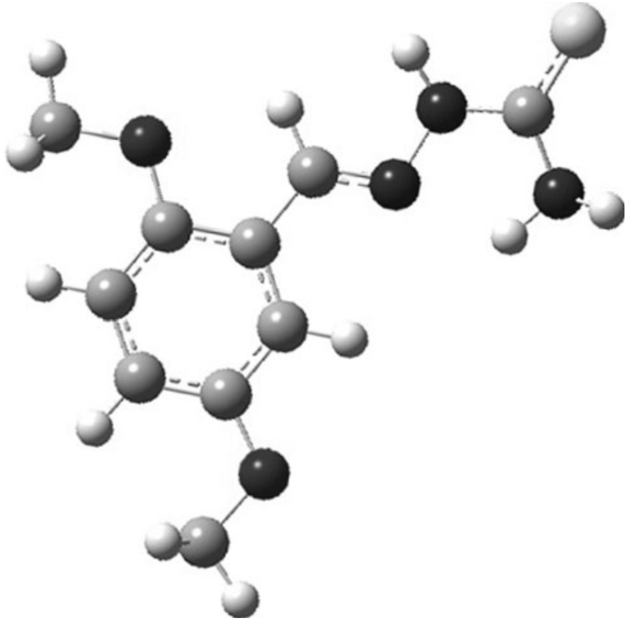


Fig. 9 The B3LYP/6-31G optimized structure of **2**

obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

Acknowledgments We acknowledge Golestan University (GU) and Damghan University (DU) for partial support of this study and Okayama University (OU) for X-ray analysis.

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