J Therm Anal Calorim (2013) 111:597–603
DOI 10.1007/s10973-012-2309-3

# Bisthiourea: thermal and structural investigation

**Pramod B. Pansuriya · Hitesh M. Parekh ·
Holger B. Friedrich · Glenn E. M. Maguire**

Received: 16 November 2011 / Accepted: 3 February 2012 / Published online: 19 February 2012

**Abstract** Bisthiourea derivatives 1,1′-(ethane-1,2-diyl)-bis(3-phenylthiourea), 1,1′-(propane-1,3-diyl)bis(3-phenylthiourea), and 1,1′-(butane-1,4-diyl)bis(3-phenylthiourea) have been synthesized and characterized by IR, $^{1}$H NMR, and $^{13}$C NMR. Suitable crystals of 1,1′-(propane-1,3-diyl)-bis(3-phenylthiourea) were grown for single-crystal X-ray analysis and from the data it was observed that they organize into the *P*-1 space group. The thermal decomposition of these compounds has been studied by TG–DSC.

**Keywords** Bisthiourea derivatives · Crystal structure · Thermal decomposition

## Introduction

Urea and thiourea derivatives are conspicuous for their biological activity as they form strong hydrogen bonding interactions and coordinate metal ions [1–3]. In recent years, the use of urea and thiols as functionalized ligands has been extensively studied in catalytic reactions such as hydroformylation [4], hydrosilylation [5], asymmetric reduction [6], cyclization [7], hydrolytic kinetic resolution of epoxides [8], and hydrogenation [9]. Other applications include their use as synthetic cation–anion ionophores [10, 11], chromogenic and fluorogenic receptors [12], surfactant self-assemblies [13], and photo-dimerizing agents for coumarins [14]. A number of bisthiourea–urea single crystals have been studied for nonlinear optical properties [15–17]. Thermal analyses are especially useful for studying the chemical and physical behavior of catalysts. Owing to the different internal organization within the solid state, polymorphs may show different melting points, solubility, chemical reactivity, and stability. Variations in catalytic conditions can affect the state of a catalyst which in turn may have considerable effects on the rate, activity, selectivity, and turnover. It is thus important to study the thermal behavior of this type of ligand. Here, we report the synthesis (Scheme 1), crystal structure, spectroscopic elucidation, and thermal study of the bisthiourea derivatives 1,1′-(ethane-1,2-diyl)bis(3-phenylthiourea), 1,1′-(propane-1,3-diyl)bis(3-phenylthiourea), and 1,1′-(butane-1,4-diyl)-bis(3-phenylthiourea).

## Experimental

### Materials and synthesis

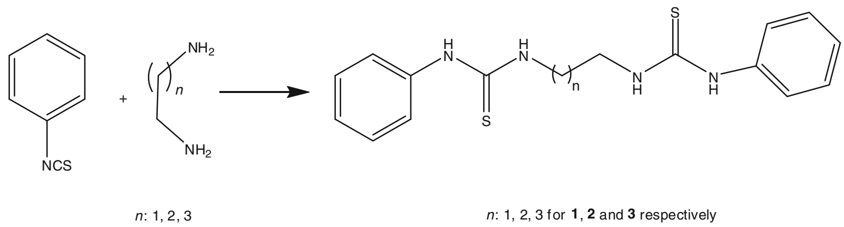
Three bisthiourea compounds were synthesized using phenyl isothiocynate (Merck Schuchardt), ethane-1,2-diamine (Saar Chem), propane-1,3-diamine (Aldrich), butane-1,4-diamine (Aldrich), diethylether (Merck), and isopropanol (Sigma Aldrich).

### Instruments and methods

The IR spectra were recorded using a Perkin Elmer Universal ATR spectrometer. NMR spectra were recorded employing a Bruker Avance 400 MHz instrument with either $CDCl_3$ or DMSO-$d_6$ as the solvent. Single-crystal X-ray diffraction data were collected with a Bruker KAPPA APEX II DUO diffractometer using graphite-monochromated Mo-K$\alpha$ radiation ($\chi = 0.71073$ Å). Data

---

P. B. Pansuriya · H. M. Parekh · H. B. Friedrich ·
G. E. M. Maguire (✉)
School of Chemistry, University of KwaZulu-Natal,
Westville Campus, Durban 4000, South Africa
e-mail: maguireg@ukzn.ac.za



**Scheme 1** Synthesis of bisthiourea derivatives

collection was carried out at 173(2) K. The temperature was controlled by an Oxford Cryostream cooling system (Oxford Cryostat). Cell refinement and data reduction were performed using the program SAINT [18]. The data were scaled and absorption correction performed using SADABS [18]. The structure was solved by direct methods using SHELXS-97 [19] and refined by full-matrix least-squares methods based on $F^2$ using SHELXL-97 [20]. The program OLEX2 was used to prepare molecular graphic images [21]. The powder X-ray diffraction was carried out using a Bruker D8 Advance instrument. The thermal characteristics of the samples were determined on a TA instruments differential scanning calorimeter. 8–10 mg samples were placed in a standard vessel and heated at a rate of 20 °C/min in the temperature range 30–1,000 °C under a nitrogen environment.

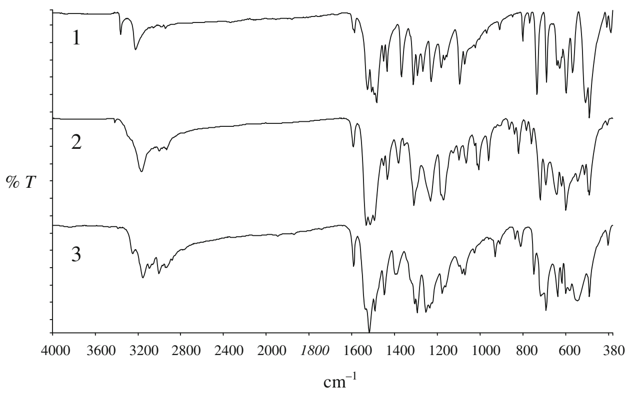


**Fig. 1** IR spectra of compounds **1**, **2**, and **3**

## Synthesis of 1,1′-(ethane-1,2-diyl)bis(3-phenylthiourea) (**1**)

A solution of phenyl isothiocyanate (6.75 g, 50 mmol) in diethyl ether (15 ml) was added dropwise at 15 °C to a vigorously stirred solution of anhydrous ethane-1,2-diamine (6.01 g, 100 mmol) in isopropyl alcohol (100 ml) over a period of 30 min. The reaction mixture was stirred for 2 h at room temperature and quenched with water (200 ml). The reaction mixture was kept overnight at room temperature, then acidified with conc. HCl up to pH 2.6. The solvents were evaporated under reduced pressure, the residue was then suspended in hot water for 30 min and the resulting precipitate was filtered under vacuum. The product was washed with ice-cold water and dried. The yield was 2.90 g (35%) **1**. Mp: 462 K.

$^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ (ppm): 9.5 (br.s., 2H, NH-CS), 7.37–7.39 (d, 4H, H-arom), 7.29–7.33 (t, 4H,

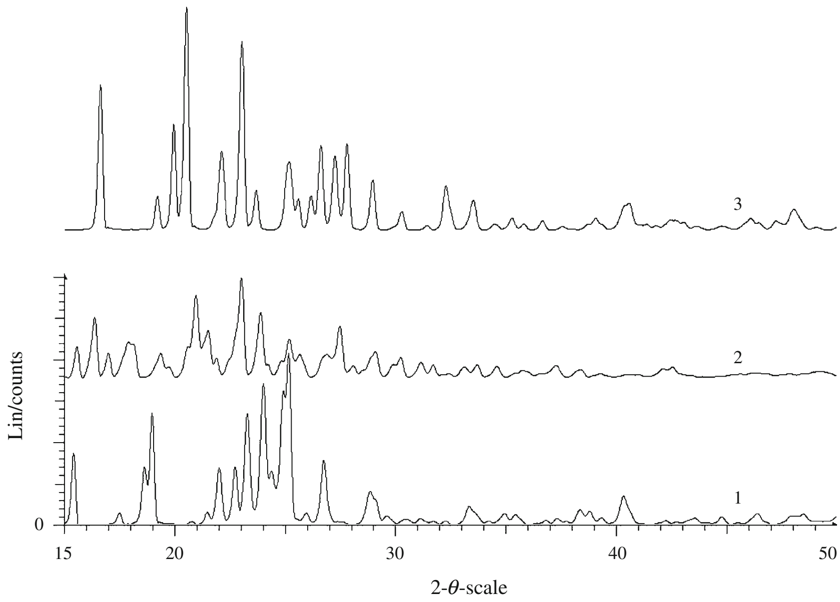


**Fig. 2** X-ray patterns of compounds **1**, **2**, and **3**

**Table 1** X-Ray diffraction data for bisthioureas

| **1** | | | | | **2** | | | | | **3** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2*θ*/° | *d*/Å | *h* | *k* | *l* | 2*θ*/° | *d*/Å | *h* | *k* | *l* | 2*θ*/° | *d*/Å | *h* | *k* | *l* |
| 15.2 | 5.8399 | – | – | – | 15.5 | 5.7000 | 0 | 2 | −1 | 15.4 | 5.7569 | 1 | 0 | −2 |
| 16.6 | 5.3355 | 1 | 1 | 2 | 17.6 | 5.0421 | – | – | – | 17.5 | 5.0744 | 1 | 1 | 1 |
| 18.5 | 4.7913 | – | – | – | 18.1 | 4.9036 | – | – | – | 18.6 | 4.7667 | 0 | 1 | 2 |
| 20.5 | 4.3279 | 2 | 1 | 1 | 20.6 | 4.3130 | 1 | 1 | 3 | 19.8 | 4.4820 | 1 | 1 | −2 |
| 22.1 | 4.0188 | 0 | 0 | 2 | 21.5 | 4.1322 | 1 | 3 | 1 | 22.0 | 4.0392 | 2 | 1 | 0 |
| 23.0 | 3.8609 | 1 | 0 | 4 | 23.9 | 3.7252 | – | – | – | 24.0 | 3.7066 | – | – | – |
| 25.6 | 3.4799 | 3 | 0 | 1 | 24.8 | 3.5836 | 3 | 1 | 0 | 24.4 | 3.6498 | 1 | 2 | 0 |
| 26.6 | 3.3484 | 2 | 2 | 1 | 26.9 | 3.3150 | 1 | −2 | −3 | 26.7 | 3.3324 | – | – | – |
| 27.2 | 3.2711 | 3 | 0 | 2 | 27.5 | 3.2450 | 3 | 2 | 2 | 27.4 | 3.2558 | 2 | 0 | 2 |
| 30.8 | 2.9034 | 0 | 2 | 4 | 29.1 | 3.0684 | 3 | 3 | 0 | 29.6 | 3.0165 | 2 | 2 | 0 |
| 33.5 | 2.6715 | 1 | 3 | 2 | 33.7 | 2.6578 | 3 | −2 | 2 | 33.6 | 2.6643 | 3 | 1 | 1 |
| 35.8 | 2.5054 | 4 | 0 | 2 | 36.6 | 2.4563 | 4 | 2 | 3 | 36.4 | 2.4660 | – | – | – |
| 39.4 | 2.2859 | 4 | 2 | 0 | 39.3 | 2.2918 | – | – | – | 40.3 | 2.2342 | 2 | 0 | 4 |
| 43.1 | 2.0989 | 5 | 0 | 1 | 43.4 | 2.0835 | 4 | −1 | −3 | 42.7 | 2.1144 | 3 | 1 | −5 |
| 48.1 | 1.8915 | 4 | 2 | 5 | 48.4 | 1.8778 | 1 | 6 | 4 | 48.5 | 1.8755 | 2 | 3 | 3 |

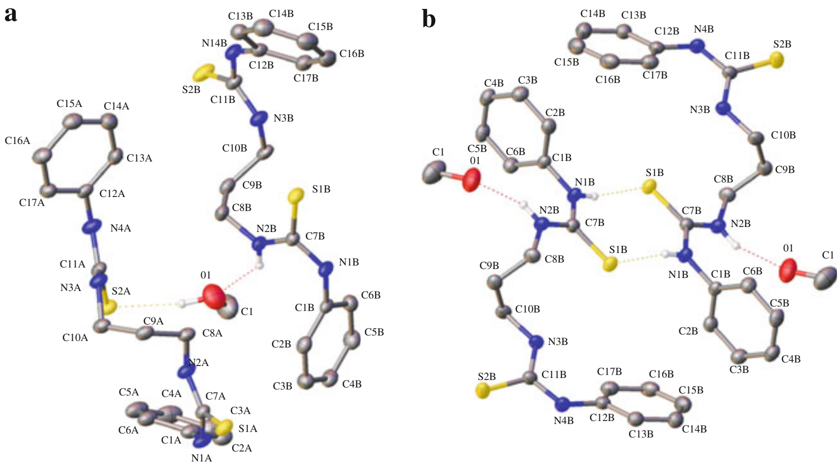


**Fig. 3** Single-crystal X-ray structure of **2**. **a** Projection of molecule **2** in plane *b* having 40% probability, all hydrogens have been removed for clarity, molecules A and B are linked via H-bonding N2B-H···O1 (2.872 Å), and O1-H···S2A (3.218 Å). **b** Projection of molecule **2** in plane a having 40% probability, all hydrogens have been removed for clarity, molecules B and B are linked via N1B-H-S1B (3.429 Å)

H-arom), 7.10–7.13 (t, 2H, H-arom), 7.82 (br.s., 2H, –NH–$CH_2$), 3.69 (s, 4H, –$CH_2$–$CH_2$).

$^{13}$C NMR (DMSO-$d_6$, 100 MHz): 43.14, 123.27, 124.33, 128.66, 138.92, 180.55.

IR. (*ν*, cm$^{-1}$): 3365, 3225, 1587, 1526, 1507, 1484, 1451, 1436, 1368, 1313, 1293, 1268, 1229, 1182, 1096, 1073, 909, 801, 769, 735, 691, 641, 599, 568, 508, 490, 408, 390.

### Synthesis of 1,1′-(propane-1,3-diyl)bis(3-phenylthiourea) (**2**)

The procedure for the preparation of **1** was repeated using phenyl isothiocyanate (6.75 g, 50 mmol) and propane-1,3-diamine (7.41 g, 100 mmol) to give 3.44 g (40%) **2**. Mp: 401 K.

$^1$H NMR ($CDCl_3$, 400 MHz) *δ* (ppm): 7.71 (br.s., 2H, NH-CS), 7.33–7.37 (m, 4H, H-arom), 7.19–7.24 (t, 2H, H-arom), 7.12–7.14 (d, 4H, H-arom), 6.69 (t, 2H, –NH–$CH_2$), 3.59 (q, 4H, –$CH_2$–$CH_2$), 1.73 (m, 2H, –$CH_2$–$CH_2$).

$^{13}$C NMR ($CDCl_3$, 100 MHz): 29.29, 41.55, 125.87, 127.72, 130.28, 135.57, 180.91.

IR. (*ν*, cm$^{-1}$): 3418, 3169, 3000, 1594, 1532, 1514, 1494, 1435, 1382, 1355, 1310, 1232, 1171, 1099, 1065, 1026, 1007, 961, 865, 840, 822, 761, 720, 694, 643, 600, 545, 489, 407.

### Synthesis of 1,1′-(butane-1,4-diyl)bis(3-phenylthiourea) (**3**)

The procedure for the preparation of **1** was repeated using phenyl isothiocyanate (6.75 g, 50 mmol) and butane-1,4-diamine (8.81 g, 100 mmol) to give 2.36 g (35%) **3**. Mp: 458 K.

$^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm): 7.64 (br.s., 2H, NH-CS), 7.40–7.46 (m, 4H, H-arom), 7.29–7.33 (t, 2H, H-arom), 7.19–7.21 (d, 4H, H-arom), 6.18 (br.s., 2H, –NH–$CH_2$), 3.65 (m, 4H, –$CH_2$–$CH_2$), 1.61 (m, 4H, –$CH_2$–$CH_2$).

$^{13}$C NMR ($CDCl_3$, 100 MHz): 26.12, 44.75, 125.45, 127.55, 130.34, 180.92.

IR. ($\nu$, $cm^{-1}$): 3251, 3155, 3095, 3005, 2933, 1591, 1518, 1492, 1447, 1396, 1306, 1294, 1254, 1178, 1084, 1071, 1027, 930, 811, 750, 718, 692, 639, 600, 549, 490, 402.

## Result and discussion

### IR and NMR spectra

IR spectra (Fig. 1) of the bisthiourea derivatives show bands at ~3,300 and ~1,590 $cm^{-1}$, which are assigned to NH stretching and bending vibrations, respectively. The absorptions observed at ~1,445 and ~735 $cm^{-1}$ correspond to C=S stretching and rocking, respectively. The absorptions recorded at ~1,490 and ~490 $cm^{-1}$ can be assigned to N–C–N stretching and bending vibrations, respectively. The peaks at ~1,090 and ~400 $cm^{-1}$ are due to the C–N stretch and the S–C–N stretch, respectively. For compounds **1**, **2**, and **3** absorptions for N–H–O hydrogen bonding can be seen around 3,169 $cm^{-1}$ and except for **1** weaker bands for the N–H–S interactions appear around 3,000 $cm^{-1}$.

The $^1$H NMR spectra of the thiourea derivatives show characteristic peaks for the aliphatic and aromatic protons. Signals associated with the secondary amines were also present and these peaks disappeared when $D_2O$ was added in a “shake” test. It should be noted that all the signals are sharp and the associated integration values correspond to the expected figures.

### X-Ray diffraction

The powder X-ray diffractograms of the compounds are shown in Fig. 2. All the three compounds show many reflection peaks ranging from $2\theta = 15°$ to 60°. This indicates that there are a number of classes of structures that are intermediate in the states between the crystalline and

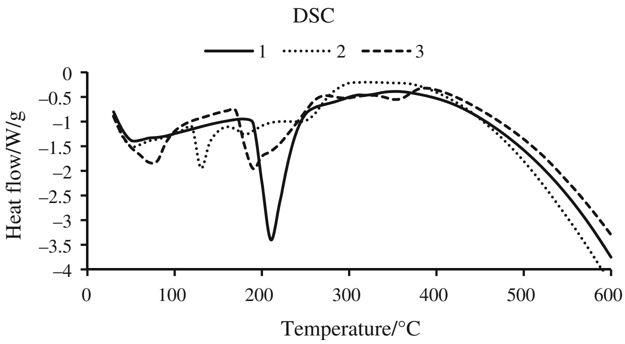


**Fig. 4** DSC results for compounds **1**, **2**, and **3**

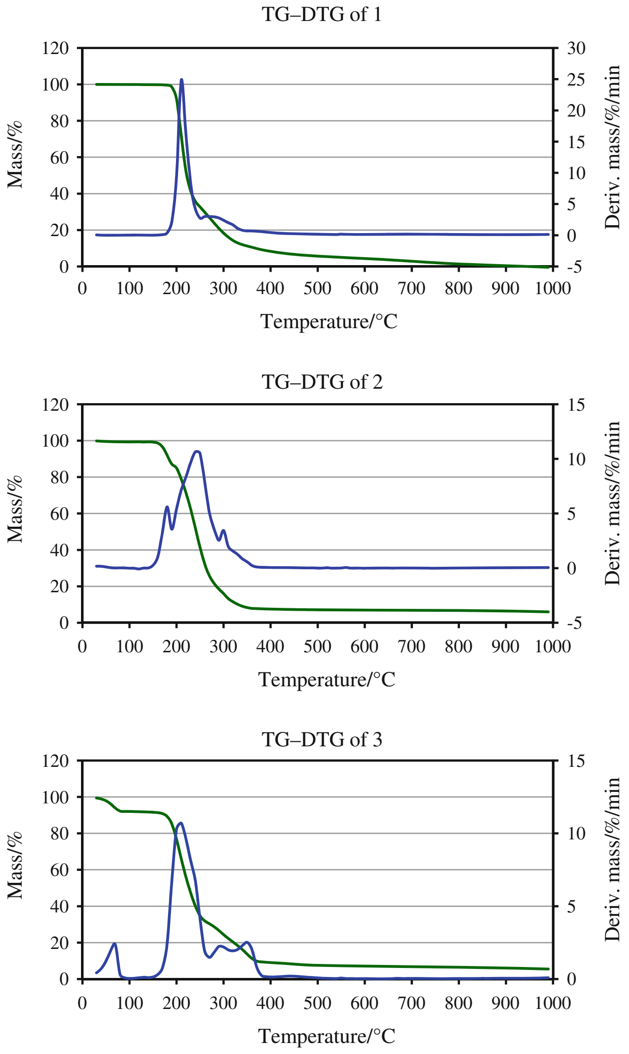
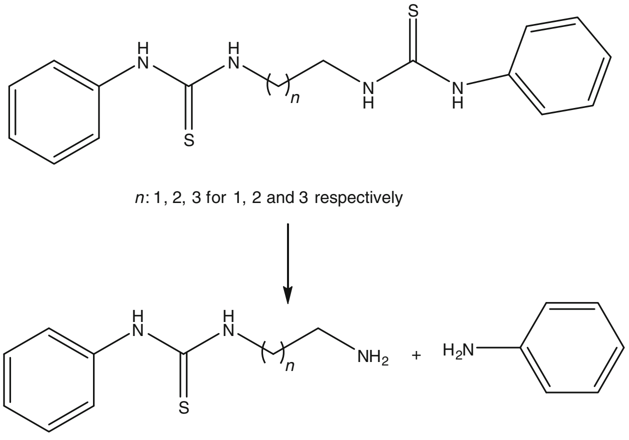


**Fig. 5** TG–DTG of compounds **1**, **2**, and **3**



**Scheme 2** Decomposition of bisthiourea derivatives

amorphous phases. Moreover, the presence of polar groups provides some order between two extents of crystallinity. As the length of the methylene spacer increases so too does the molecule's flexibility. The sharp reflections indicate an increase in associated crystallinity with this augmentation in flexibility [22, 23]. All the reflections in the powder X-ray diffractograms match the single crystal powder patterns. The resultant lattice parameters are summarized in Table 1.

The single-crystal X-ray structure of compound **1** was recently reported by our research group, the structure shows intermolecular hydrogen bonding interactions between N1–H1···S1 3.379(2) Å that creates layered sheets in the *ab* plane. The dihedral angle between the phenyl ring and the thiourea group is 52.9(4)° [24].

Crystals of compound **2** were grown from a solution of methanol:methylene chloride' (1:2 by volume) using the slow evaporation technique. The single-crystal lattice parameter values are *a*: 10.9393(8), *b*: 12.8867(9), and *c*: 13.7998(11) and hydrogen bonding occurs with methanol creating links between two molecules (Fig. 3). All non-hydrogen atoms were refined anisotropically. The hydroxyl hydrogen of methanol was located in the difference electron density maps and refined with a simple bond length constraint [d(O–H) = 0.97(1) Å] and with $U_{\text{iso}} = 1.2 \times U_{\text{eq}}$ (O). The rest of the hydrogen atoms were placed at calculated positions with attachment distances ranging from 0.95 to 0.99 Å and refined as riding on their parent atoms with $U_{\text{iso}}$ (H) = $1.2 \times U_{\text{eq}}$ (C) (CCDC: 853522).

The crystal structure of compound **3** shows two distinct intermolecular hydrogen bonding interactions [25]. The first occurs between N2–H2 and S1 2.713(16) Å that generates an infinite chain along the *a* axis. Due to these interactions an interlocking molecular structure is formed. The second occurs between N1–H1 and S1 2.508(18) Å that creates an infinite chain of molecules along the *b* axis [25].

All three compounds show a bent structure. Compound **1** is the most linear probably due to its lack of flexibility relative to the other molecules. It is also observed that all three derivatives show *transoid* arrangement of the two thiourea groups. This is atypical of previously reported structures of bisurea derivatives [26]. From the crystal structures, it appears that there is an infinite chain of molecules for **1** and **3**, while **2** has a cage-like structure. This is presumably because of the hydrogen bonding arrangement in this example.

**Table 2** Thermoanalytical data (TG, DSC) for bisthioureas

| Compound | TG–DTG | DSC | | Mass loss/% | | Probable decomposition assignment |
|---|---|---|---|---|---|---|
| | Range/°C | $\text{Peak}_{\text{max}}$/°C | Enthalpy/J/g | Obs | Cal | |
| 1 | 30–190 | (+)42.5 | – | 1.4 | – | Solvent or moisture |
| | 190–250 | (+)200.8 | 490.0 | 57.0 | 59.0 | 1-(2-Aminoethyl)-3-phenylthiourea |
| | 250–350 | – | – | 28.6 | 28.1 | Aniline |
| | 350–930 | (−)352.0 | – | 12.7 | – | – |
| 2 | 30–180 | (+)49.9,<br>(−)120.4,<br>(+)130.2,<br>(−)161.4,<br>(+)179.4 | 63.9 | 7.8 | – | Solvent or moisture |
| | 180–260 | – | 26.1 | 59.9 | 60.7 | 1-(3-Aminoethyl)-3-phenylthiourea |
| | 260–650 | (−)345.0 | – | 25.2 | 27.0 | Aniline |
| | 650–990 | – | – | 0.9 | – | – |
| 3 | 30–150 | (+)75.2 | 370.6 | 7.8 | – | Solvent or moisture |
| | 150–270 | (−)166.2,<br>(+)181.5, | 384.7 | 61.2 | 62.2 | 1-(4-Aminobutyl)-3-phenylthiourea |
| | 270–650 | (−)277.6,<br>(+)294.3,<br>(−)326.3,<br>(+)358.0,<br>(−)386.6 | 7.1 | 23.3 | 25.9 | Aniline |
| | 650–990 | – | 24.1 | 1.4 | – | – |

(+) endothermic, (–) exothermic

### Thermal analysis

All three compounds have two phenyl thiourea groups separated by a different number of methylene groups. The DSC traces of **1**–**3** (Fig. 4) show extensive decomposition concomitant with the melting process. The endo–exo–endo peak can be easily seen in the DSC traces, where the broad exothermic peak followed by the sharp endothermic peak, correspond to the melting process. The sharpness of this peak implies a significant degree of crystallinity for the samples. All the compounds **1**–**3** show similar DSC behavior, but **1** decomposes earlier and exhibits only one endothermic peak, while the other compounds possess multiple endothermic peaks due to polymorphism [27].

From the thermogravimetric analyses of the compounds from 30 and 1,000 °C (Fig. 5), it can be observed that **1** decomposes fully at 930 °C, while **2** and **3** decompose with up to 94.5% mass loss at this temperature. The measured decomposition range is in four steps. First, from 30 to 180 °C it is likely that all volatile and low molecular mass fragments of the derivatives are eliminated. In the second step, from 180 to 260 °C, the major part of the derivatives has decomposed. It may be the "aminoalkyl-3-phenylthiourea". The third step differs between **1** and **2**–**3**. For **1**, it occurs at 250–350 °C, while for **2** and **3** it is at 260–650 °C. This may be because of aniline decomposition (see Scheme 2). From the TG and DSC data compounds **2**–**3** (Table 2) follow similar thermal decomposition pathways. For **1**, the shorter distance between the two thiourea groups appears to have a substantive effect on its decomposition profile.

## Conclusions

Bisthiourea derivatives were synthesized and characterized by IR, NMR, and single-crystal X-ray crystallography. The single-crystal structure and powder data were compared. All the structures have bent *transoid* arrangements. These three bisthioureas also possess intermolecular hydrogen bonding arrangements. The structural behavior was studied by TG–DTG and the structures retain key properties up to 180 °C. This confirms thermal stability. The derivatives decompose stepwise as the spacer methylene groups between the two phenyl thiourea moieties increase. The compounds appear to mainly decompose into two fragments. From DSC data it was confirmed that multiple phases exist.

**Acknowledgements** The authors wish to thank Dr. Hong Su from the Chemistry Department of the University of Cape Town and Dr. Manuel Fernandes from the Chemistry Department of the University of the Witwatersrand for their assistance with the X-ray data collection and refinement and the DST—National Research Foundation, Centre of Excellence in Catalysis, c*change, for financial support. PBP would like to thank UKZN for funding his post-doctorate fellowship.

## References

1. Wittkopp A, Schreiner PR. Metal-free, noncovalent catalysis of Diels–Alder reactions by neutral hydrogen bond donors in organic solvents and in water. Chem Eur J. 2003;9(2):407–14.
2. Li X, Deng H, Luo S, Cheng J-P. Organocatalytic three-component reactions of pyruvate, aldehyde and aniline by hydrogen-bonding catalysts. Eur J Org Chem. 2008;25:4350–6.
3. Sharma SK, Wu Y, Steinbergs N, Crowley ML, Hanson AS, Casero RA, et al. (Bis)urea and (Bis)thiourea inhibitors of lysine-specific demethylase 1 as epigenetic modulators. J Med Chem. 2010;53(14):5197–212.
4. Abdallah R, Breuzard JAJ, Bonnet MC, Lemaire M. Phosphite and thiourea ligand synergy for rhodium catalyzed enantioselective hydroformylation of styrene. J Mol Catal A. 2006;249(1–2):218–22.
5. Karamé I, Lorraine Tommasino M, Lemaire M. N, N- and N, S-ligands for the enantioselective hydrosilylation of acetophenone with iridium catalysts. J Mol Catal A. 2003;196(1–2):137–43.
6. Nan Y, Miao H, Yang Z. A new complex of palladium–thiourea and carbon tetrabromide catalyzed carbonylative annulation of o-hydroxylarylacetylenes: efficient new synthetic technology for the synthesis of 2,3-disubstituted benzo[b]furans. Org Lett. 2000;2(3):297–9.
7. Breuzard JAJ, Tommasino ML, Touchard F, Lemaire M, Bonnet MC. Thioureas as new chiral ligands for the asymmetric hydroformylation of styrene with rhodium(I) catalysts. J Mol Catal A. 2000;156(1–2):223–32.
8. Park J, Lang K, Abboud KA, Hong S. Self-assembly approach toward chiral bimetallic catalysts: bis-urea-functionalized (salen)cobalt complexes for the hydrolytic kinetic resolution of epoxides. Chem Eur J. 2011;17(7):2236–45.
9. Tommasino ML, Casalta M, Breuzard JAJ, Lemaire M. Asymmetric hydrogenation of enamides with catalysts containing chiral thiourea ligands. Tetrahedron Asymmetry. 2000;11(24):4835–41.
10. Reinoso García MM, Verboom W, Reinhoudt DN, Malinowska E, Pietrzak M, Wojciechowska D. Heavy metal complexation by *N*-acyl(thio)urea-functionalized cavitands: synthesis, extraction and potentiometric studies. Tetrahedron. 2004;60(49):11299–306.
11. Leung AN, Degenhardt DA, Bühlmann P. Effect of spacer geometry on oxoanion binding by bis- and tetrakis-thiourea hosts. Tetrahedron. 2008;64(11):2530–6.
12. Ahmed N, Geronimo I, Hwang I-C, Singh NJ, Kim KS. Cyclobis(urea-3,6-dichlorocarbazole) as a chromogenic and fluorogenic receptor for anions and a selective sensor of zinc and copper cations. Chem Eur J. 2011;17(31):8542–8.
13. Vos MRJ, Leclere PELG, Meekes H, Vlieg E, Nolte RJM, Sommerdijk NAJM. Kinetic switching between two modes of bisurea surfactant self-assembly. Chem Commun. 2010;46(33):6063–5.
14. Dawn S, Dewal MB, Sobransingh D, Paderes MC, Wibowo AC, Smith MD, et al. Self-assembled phenylethynylene bis-urea macrocycles facilitate the selective photodimerization of coumarin. J Am Chem Soc. 2011;133(18):7025–32.
15. Mariappan M, Madhurambal G, Ravindran B, Mojumdar S. Thermal, FTIR and microhardness studies of bisthiourea-urea single crystal. J Therm Anal Calorim. 2011;104(3):915–21.
16. Ramamurthi K, Madhurambal G, Ravindran B, Mariappan M, Mojumdar S. The growth and characterization of a metal organic crystal, potassium thiourea thiocyanide. J Therm Anal Calorim. 2011;104(3):943–7.

17. Madhurambal G, Mariappan M, Ravindran B, Mojumdar S. Thermal and FTIR spectral studies in various proportions of urea thiourea mixed crystal. J Therm Anal Calorim. 2011;104(3):885–91.
18. Bruker. APEX2, SAINT and SAINT + (includes XPREP and SADABS). Bruker AXS Inc., Madison, WI, 2006.
19. Sheldrick GM. SHELXL97. Germany: University of Göttingen; 1997.
20. Sheldrick G. A short history of SHELX. Acta Cryst A. 2008;64(1):112–22.
21. Dolomanov OV, Bourhis LJ, Gildea RJ, Howard JAK, Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. J Appl Cryst. 2009;42(2):339–41.
22. Mandelkern L. Crystallization of polymers. New York: Mcgraw-Hill; 1964.
23. Aly KI. New polymer syntheses VIII. Synthesis, characterization and morphology of new unsaturated copolyesters based on dibenzylidenecycloalkanones. Polym Int. 1998;47(4):483–90.
24. Pansuriya PB, Friedrich HB, Maguire GEM. 1,1′-(Ethane-1,2-diyl)bis(3-phenylthiourea). Acta Cryst E. 2011;67(11):o2819.
25. Pansuriya P, Friedrich HB, Maguire GEM. 3,3′-Diphenyl-1,1′-(butane-1,4-diyl)dithiourea. Acta Cryst E. 2011;67(9):o2380.
26. Pansuriya P, Naidu H, Friedrich HB, Maguire GEM. 1,1′-(Propane-1,3-diyl)bis(3-phenylurea). Acta Cryst E. 2011;67(10):o2552.
27. Roviello A, Sirigu A. Poly[oxytetradecanedioyloxy-1,4-phenylene-(2-methylvinylene)-1,4-phenylene]. A polymer showing monotropic mesomorphism. Die Makromol Chem. 1979;180(10):2543–5.