Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

1,3-Dibenzoylimidazolidine-2-thione and 1,3-dibenzoyl-3,4,5,6-tetrahydropyrimidine-2(1*H*)-thione

Canan Kazak,[a] Veysel T. Yilmaz,[b]* Suleyman Servi,[c] Murat Koca[c] and Frank W. Heinemann[d]

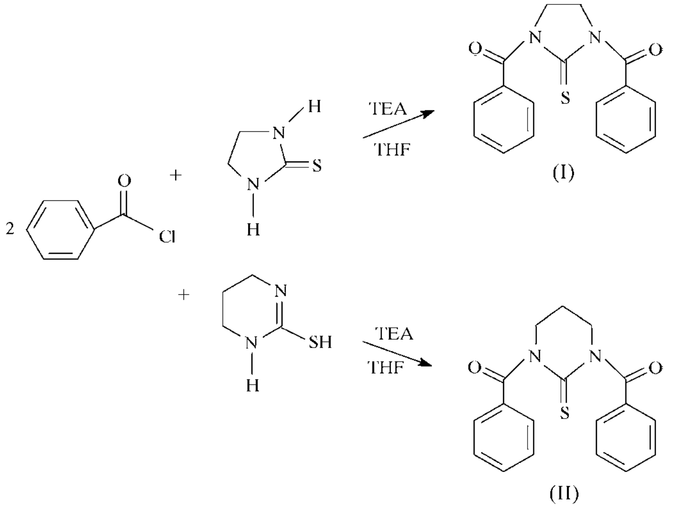
[a]Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayis University, 55139 Kurupelit, Samsun, Turkey, [b]Department of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayis University, 55139 Kurupelit, Samsun, Turkey, [c]Depart-of Arts and Sciences, Firat University, 23169 Elazig, Turkey, and [d]Institut für Anorganische Chemie, Universität Erlangen-Nürnberg, D-91058 Erlangen, Germany
Correspondence e-mail: vtyilmaz@omu.edu.tr

Received 12 January 2005
Accepted 29 March 2005
Online 13 May 2005

The title compounds, 1,3-dibenzoylimidazolidine-2-thione, $C_{17}H_{14}N_2O_2S$, (I), and 1,3-dibenzoyl-3,4,5,6-tetrahydropyrimidine-2(1*H*)-thione, $C_{18}H_{16}N_2O_2S$, (II), were obtained from the reactions of imidazolidine-2-thione and 1,4,5,6-tetrahydropyrimidine-2-thiol, respectively, with benzoyl chloride. Compounds (I) and (II) contain, respectively, imidazolidinethione [C=S = 1.6509 (14) Å] and pyrimidinethione [C=S = 1.6918 (19) Å] moieties bonded to two benzoyl rings. The molecules of (I) exhibit C_2 symmetry, the C=S bond lying along the twofold rotation axis, while the molecules of (II) have mirror symmetry (C_s). The imidazolidine ring in (I) is essentially planar, while the pyrimidine ring in (II) adopts a boat conformation. Molecules of (I) are linked by weak intermolecular C—H···O interactions, while molecules of (II) are held together by van der Waals interactions.

Comment

Heterocyclic thioamides usually occurring in their thioketo form are referred to as 'thiones'. Heterocyclic thiones have a wide range of applications as analytical reagents, as metal corrosion inhibitors and in the pharmaceutical field (Hussain *et al.*, 1990). These compounds are of particular interest in coordination chemistry because they display both hard and soft donor sites. In many instances, heterocyclic thiones behave as polyfunctional ligands, with monodentate, chelating and bridging coordination modes, and form a wide range of transition metal complexes, many of which have important chemical and biological properties (Raper, 1985, 1994, 1996, 1997; Akrivos, 2001). Furthermore, metal complexes of heterocyclic thiones exhibit interesting anticarcinogenic properties (Reedijk, 1992; van Boom & Reedijk, 1993; Barnham *et al.*, 1994) and are used in the treatment of rheumatoid arthritis (Haynes & Whitehouse, 1989). Metal complexes are also used as models to understand the electronic and structural properties of the active sites in metalloenzymes (Casella *et al.*, 1988; Gullotti, *et al.*, 1989) and metal–DNA interactions (Tran Qui & Bagieu, 1990). In the course of synthesizing new ligands suitable for coordination chemistry, we prepared two new heterocyclic thiones, namely 1,3-dibenzoylimidazolidine-2-thione, (I), and 1,3-dibenzoyl-3,4,5,6-tetrahydropyrimidine-2(1*H*)-thione, (II), from the reactions of imidazolidine-2-thione and 1,4,5,6-tetrahydropyrimidine-2-thiol, respectively, with benzoyl chloride.



Views of the molecules of (I) and (II), including the atom-numbering schemes, are shown in Figs. 1 and 2. Selected bond distances and angles are listed in Tables 1 and 3. Each compound exhibits a soft thione S-donor and three hard donor sites (a carbonyl O and two N atoms) and seems to act as a chelating or a bridging ligand. These compounds are also interesting building blocks for generating coordination polymers upon metal complexation. Both (I) and (II) consist of imidazolidinethione and pyrimidinethione moieties bonded to two benzoyl rings. The sulfur substituents exist in the thione form. The C=S bond lengths in (I) and (II) are consistent with

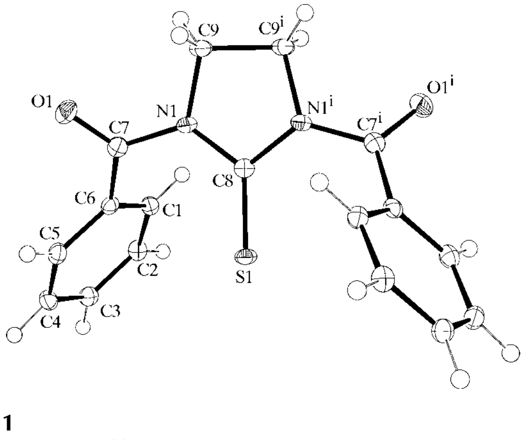


Figure 1
The molecule of (I), showing the atom-labelling scheme and 40% probability displacement ellipsoids.

DOI: 10.1107/S0108270105009844

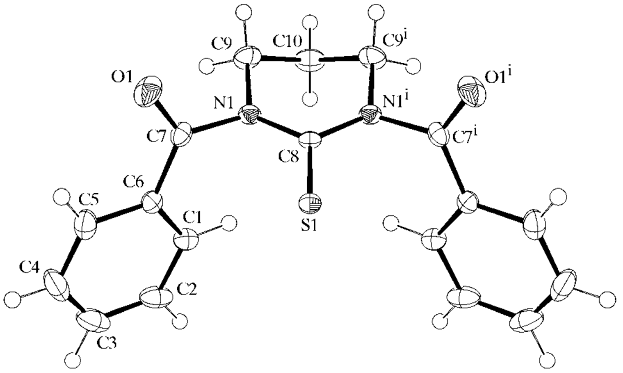


Figure 2
The molecule of (II), showing the atom-labelling scheme and 40% probability displacement ellipsoids. [Symmetry code: (i) $x, \frac{3}{2} - y, z$.]

a double bond and are similar to those in other reported heterocyclic thione derivatives containing imidazolethione and pyrimidinethione rings (Özbey *et al.*, 1991, 2004; Akkurt *et al.*, 1992, 2000; Cox *et al.*, 1996; Liu *et al.*, 2003; Brito *et al.*, 2004). The C8—N1 bond distances in both compounds are intermediate between standard single C—N (1.47 Å) and double C=N (1.28 Å) bonds, being significantly shorter than the C9—N1 bonds, because atom C8 is in an sp^2-hybridized state, while atom C9 is sp^3. The remaining bond lengths in both compounds show no unusual values.

The molecules of (I) show C_2 symmetry and the C8—S1 bond lies on the twofold rotation axis, while the molecules of (II) have mirror symmetry (C_s), with atoms S1, C8, C10, H10*A* and H10*B* situated on the mirror plane. The five-membered imidazolidine ring in (I) is essentially planar, with maximum deviations from the mean plane of −0.1418 (8) and 0.1397 (8) Å for atoms N1 and C9^i [symmetry code: (i) $-x + 1, -y + 2, z$], respectively. The six-membered pyrimidine ring in (II) adopts a half-boat conformation, in which atoms C8 and C10 are displaced from the mean plane by 0.0387 (10) and 0.2561 (13) Å. The benzoyl rings in (I) make dihedral angles of 76.55 (3) and 79.85 (3)° with the mean plane of the imidazole ring. The dihedral angle between the two planar benzoyl fragments is 75.92 (3)° in (I) and 61.08 (4)° in (II). A non-planar disposition of the three rings has been observed in other reported heterocyclic thione derivatives with similar compositions (Özbey *et al.*, 1991; Cox *et al.*, 1996; Akkurt *et al.*, 2000; Özçelik *et al.*, 2004).

The molecules of (I) are linked by weak intermolecular C—H···O interactions (Table 2). There are no π–π stacking interactions in (II). Examination of the structures with *PLATON* (Spek, 2003) indicates that there are no solvent-accessible voids in either (I) or (II).

Experimental

Triethylamine (TEA; 2.02 g, 20 mmol) was added to a solution of imidiazolidine-2-thione (1.02 g, 10 mmol) dissolved in tetrahydrofuran (100 ml) with stirring in an ice bath for 30 min. Benzoyl chloride (2.81 g, 20 mmol) was added to the reaction mixture dropwise and the resulting mixture was refluxed for 4 h. The solution was evaporated under vacuum to half the volume and then poured into ice water to precipitate. The residue was filtered off and single crystals of (I) suitable for X-ray measurements were obtained by crystallization from acetone. The procedure and molar quantities of the reactants for the preparation of (II) were the same as for (I), with 1,4,5,6-tetrahydropyrimidine-2-thiol replacing imidiazolidine-2-thione.

Compound (I)

Crystal data

$C_{17}H_{14}N_2O_2S$
$M_r = 310.36$
Orthorhombic, $P2_12_12$
$a = 11.8543$ (8) Å
$b = 5.7221$ (2) Å
$c = 10.6312$ (6) Å
$V = 721.13$ (7) Å^3
$Z = 2$
$D_x = 1.429$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 128 reflections
$\theta = 6.0–20.0°$
$\mu = 0.23$ mm^{-1}
$T = 100$ (2) K
Prism, yellow
0.37 × 0.16 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min} = 0.925$, $T_{max} = 0.967$
21 502 measured reflections
1864 independent reflections
1772 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 28.7°$
$h = -16 \rightarrow 16$
$k = -7 \rightarrow 7$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.059$
$S = 1.09$
1864 reflections
101 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0278P)^2 + 0.1874P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Absolute structure: Flack (1983), 757 Friedel pairs
Flack parameter: −0.03 (6)

Table 1
Selected geometric parameters (Å, °) for (I).

N1—C7	1.4073 (15)	O1—C7	1.2135 (16)
N1—C8	1.3766 (13)	S1—C8	1.6504 (14)
N1—C9	1.4777 (15)	C9—C9^i	1.530 (2)
C7—N1—C9	119.83 (9)	N1^i—C8—N1	106.48 (13)
C8—N1—C7	126.84 (10)	N1—C8—S1	126.76 (6)
C8—N1—C9	111.59 (9)		
C9—N1—C8—N1^i	−9.82 (6)	C8—N1—C9—C9^i	23.99 (13)
C9—N1—C8—S1	170.18 (6)	C7—N1—C9—C9^i	−170.02 (11)

Symmetry code: (i) $-x + 1, -y + 2, z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9*A*···O1^{ii}	0.99	2.47	3.2231 (16)	132

Symmetry code: (ii) $-x + 1, -y + 1, z$.

Compound (II)

Crystal data

$C_{18}H_{16}N_2O_2S$
$M_r = 324.39$
Orthorhombic, *Pnma*
$a = 8.6803\ (6)$ Å
$b = 21.946\ (1)$ Å
$c = 8.1845\ (9)$ Å
$V = 1559.1\ (2)$ Å^3
$Z = 4$
$D_x = 1.382$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 150 reflections
$\theta = 6.0–20.0°$
$\mu = 0.22$ mm^{-1}
$T = 100\ (2)$ K
Irregular, colourless
$0.23 \times 0.23 \times 0.16$ mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{\min} = 0.941$, $T_{\max} = 0.972$
22 525 measured reflections
2051 independent reflections
1707 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$
$\theta_{\max} = 28.7°$
$h = -11 \rightarrow 11$
$k = -24 \rightarrow 29$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.095$
$S = 1.09$
2051 reflections
109 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.7208P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

N1—C7	1.4537 (18)	O1—C7	1.2039 (17)
N1—C8	1.3478 (15)	S1—C8	1.6918 (19)
N1—C9	1.4760 (17)	C9—C10	1.5082 (19)
C7—N1—C9	115.08 (11)	N1$^{\rm iii}$—C8—N1	117.56 (16)
C8—N1—C7	119.80 (12)	N1—C8—S1	121.21 (8)
C8—N1—C9	123.87 (12)		
C7—N1—C8—N1$^{\rm iii}$	−173.28 (10)	C8—N1—C9—C10	32.02 (19)
C9—N1—C8—N1$^{\rm iii}$	−6.7 (2)	N1—C9—C10—C9$^{\rm iii}$	−54.9 (2)
C9—N1—C8—S1	172.02 (11)		

Symmetry code: (iii) $x, -y + \frac{3}{2}, z$.

All H atoms were refined using a riding model [C—H = 0.95 and 0.99 Å, and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$].

For both compounds, data collection: *COLLECT* (Bruker, 2002); cell refinement: *EVALCCD* (Bruker, 2002); data reduction: *EVALCCD*; structure solution: *SHELXTL* (Bruker, 2002); structure refinement: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors thank Ondokuz Mayis and Firat Universities for the financial support given to the study.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1118). Services for accessing these data are described at the back of the journal.

References

Akkurt, M., Guldeste, A., Soylu, H., Altural, B. & Saripinar, E. (1992). *Acta Cryst.* C**48**, 315–317.
Akkurt, M., Ozturk, S., Fun, H.-K., Onal, Z. & Altural, B. (2000). *Acta Cryst.* C**56**, e276–e277.
Akrivos, P. D. (2001). *Coord. Chem. Rev.* **213**, 181–210.
Barnham, K. J., Djuran, M. I., Del Socorro Murdoch, P. & Sadler, P. J. (1994). *Chem. Commun.* pp. 721–723.
Boom, S. S. G. E. van & Reedijk, J. (1993). *Chem. Commun.* pp. 1397–1398.
Brito, I., Cardenas, A., Lopez-Rodriguez, M., Gutierrez, C. & Reyes, A. (2004). *Acta Cryst.* E**60**, o2127–o2129.
Bruker (2002). *SADABS* (Version 2.06), *COLLECT*, *EVALCCD* and *SHELXTL* (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.
Casella, L., Gullotti, M. & Vigano, R. (1988). *Inorg. Chim. Acta*, **124**, 121–125.
Cox, P. J., Sohal, B., Skellern, G. G., Love, S. W. & Shankland, N. (1996). *Acta Cryst.* C**52**, 3152–3154.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Gullotti, M., Casella, P., Pinter, A., Suardi, E., Zanello, P. & Mangani, S. (1989). *J. Chem. Soc. Dalton Trans.* pp. 1979–1986.
Haynes, D. R. & Whitehouse, M. N. (1989). *New Developments in Anti-Rheumatic Therapy*, edited by K. D. Rainsforth & G. P. Velo, p. 207. Kluwer: Dordrecht.
Hussain, M. S., Al-Arfaj, A. R. & Hossain, M. L. (1990). *Transition Met. Chem.* **15**, 264–269.
Liu, Q., Shi, D., Yu, K. & Xu, J. (2003). *Acta Cryst.* E**59**, o356–o357.
Özçelik, S., Dincer, M., Yildirim, I. & Akcamur, Y. (2004). *Acta Cryst.* E**60**, o1123–o1125.
Özbey, S., Kendi, E., Akcamur, Y., Yildirim, I., Elerman, Y. & Soylu, H. (1991). *Acta Cryst.* C**47**, 1105–1106.
Raper, E. S. (1985). *Coord. Chem. Rev.* **61**, 115–184.
Raper, E. S. (1994). *Coord. Chem. Rev.* **129**, 91–156.
Raper, E. S. (1996). *Coord. Chem. Rev.* **153**, 199–255.
Raper, E. S. (1997). *Coord. Chem. Rev.* **165**, 475–567.
Reedijk, J. (1992). *Inorg. Chim. Acta*, **198**, 873–881.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Tran Qui, D. & Bagieu, M. (1990). *Acta Cryst.* C**46**, 1645–1647.