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Crystal structure, spectroscopic studies and theoretical studies of thiobarbituric acid derivatives: understanding the hydrogen-bonding patterns

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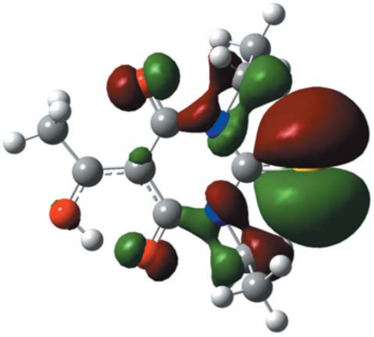
In addition to their wide-ranging applications in the pharmaceutical industry, thiobarbituric acid (TBA) derivatives are also known to possess applications in engineering and materials science. 20 TBA derivatives, with diversity at the N and C-5 positions through acylation, Schiff base formation, Knoevenagel condensation, thioamide and enamine formation, were studied. The absolute configurations for six derivatives, namely 5-acetyl-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione, $C_{10}H_{14}N_2O_3S$, **A01**, 1,3-diethyl-5-propionyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione, $C_{11}H_{16}N_2O_3S$, **A02**, *tert*-butyl [1-(1,3-diethyl-4,6-dioxo-2-thioxohexahydropyrimidin-5-yl)-3-methyl-1-oxobutan-2-yl]carbamate, $C_{18}H_{29}N_3O_5S$, **A06**, 1,3-diethyl-4,6-dioxo-2-thioxo-*N*-(*p*-tolyl)-hexahydropyrimidine-5-carbothioamide, $C_{16}H_{19}N_3O_2S_2$, **A13**, 5-(1-aminoethylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione, $C_{10}H_{15}N_3O_2S$, **A17**, and 5-(1-aminopropylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione, $C_{11}H_{17}N_3O_2S$, **A18**, were confirmed by single-crystal X-ray crystallography, which indicates the formation of intramolecular hydrogen bonding in all six cases and intermolecular hydrogen bonding for **A17**. In **A13**, the presence of two intramolecular hydrogen bonds was observed. The stabilization of the enol form over the keto form was confirmed by computation. In order to convert the keto form to the enol form, an energy barrier of 55.05 kcal mol^{-1} needs to be overcome, as confirmed by transition-state calculations.



1. Introduction

A prerequisite for rational drug design and structure-based functional studies is an accurate knowledge of the molecular structure, which is derived solely by X-ray crystallography (Aitipamula & Vangala, 2017; Deschamps, 2008; Zheng *et al.*, 2014). It is the most reliable technique available for determining a three-dimensional (3D) structure with the correct configuration of the molecule at the atomic level. As structure and function are related, configuration plays a critical role in biological systems, as changes in this may alter the response of the biologic system (Mason, 1983). Compounds containing the barbituric acid/thiobarbituric acid (BA/TBA) moiety (Fig. 1) play a vital role as anti-anxiety agents in the central nervous system by binding to the γ-aminobutyric acid (GABA) receptor (Kapoor *et al.*, 2016; Ahluwalia & Aggarwal, 1996).

Thiobarbituric acid (TBA) derivatives are privileged structures which display a broad range of biological activities,

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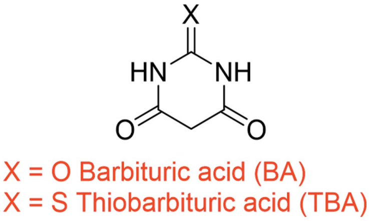

Figure 1
General structure of BA and TBA. The atom-labelling scheme is shown in Fig. 4.

including antiepileptic, anticancer, antioxidant, anticonvulsant, immuno-modulatory, gelatinase inhibiting, HIV integrase inhibiting, antifungal, antiviral, tyrosinase inhibiting, anti-inflammatory and antidiabetic effects (Agarwal *et al.*, 2006; Singh *et al.*, 2009; Khan *et al.*, 2008; Jursic & Neumann, 2001; Jursic *et al.*, 2003; Wang *et al.*, 2011; Rajamaki *et al.*, 2009; Lee *et al.*, 2011; Chen *et al.*, 2014; Penthala *et al.*, 2013). The bioactivity, however, differs from molecule to molecule depending on the tautomerization and the nature of the substituents (Chierotti *et al.*, 2010; Demeunynck *et al.*, 2006). Apart from their importance in the pharmaceutical industry, TBA derivatives are also known to possess nonlinear optical properties (NLO), corrosion inhibition properties, applications in analytical chemistry and they are suitable for crystal engineering materials possessing specific programmed properties due to their possessing both hydrogen-bond donors and acceptors (Ivanova & Spiteller, 2010; Özcan *et al.*, 2008; Roux *et al.*, 2012).

Protons at the C-5 position in TBA are highly acidic and hence undergo various reactions, including acylation and Knoevenagel condensation, among others (Faidallah & Khan, 2012). Substitution at C-5 increases lipophilicity and hence facilitates the transport of BA and TBA analogs towards their enzyme targets (Ahluwalia & Aggarwal, 1996). In view of the significance of TBA derivatives, we became interested in synthesizing new TBA derivatives with several C-5 substitutions, including amino acid–TBA conjugates, followed by density functional theory (DFT) calculations to understand the keto–enol conformation of the TBA derivatives.

2. Experimental

2.1. General

All reagents and solvents were purchased from commercial suppliers and were used without further purification, unless otherwise stated. Fourier transform infrared (FT–IR) spectra were recorded on a Bruker-ALPHA Spectrophotometer in the spectral range 400–4000 cm^{-1}. The electronic spectra of the studied compounds (1 mg in 50 ml solvent) were measured using a 3600 Series UV-Spectrophotometer in different solvents, such as acetonitrile, ethanol and dichloromethane. NMR spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Bruker AVANCE III 400 MHz spectrometer. Chemical shift values are expressed in parts per million (ppm). Analytical HPLC was performed on an Agilent 1100 system using a Phenomenax C$_{18}$ column (3 µm, 4.6 × 50 mm) and *Chemstation* software was used for data processing over a 5–95% gradient of CH$_3$CN (0.1% trifluoroacetic acid)/H$_2$O (0.1% trifluoroacetic acid) over a period of 15 min, with a flow rate of 1.0 ml min^{-1} and detection at 220 nm. High resolution mass spectrometry (HRMS) was performed using a Bruker ESI–QTOF mass spectrometer in positive-ion mode.

2.2. Synthesis of derivatives

Derivatives **A01**–**A20** were synthesized as reported previously by our group (Sharma *et al.*, 2018). Further characterizations are given in the following sections.

2.2.1. 5-Acetyl-1,3-diethyl-2-thioxodihydropyrimidine-4,6-(1*H*,5*H*)-dione (A01). Pale-white solid; 82% yield; m.p. 40–42 °C; HPLC t_R = 11.9 min; $\lambda_{\max}$ = 316 nm; IR (cm^{-1}): 1231 (C═S), 1685 (C═O); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.18 (*t*, *J* = 7 Hz, –CH$_3$), 2.65 (*s*, –CH$_3$), 4.40 (*q*, *J* = 7 Hz, –CH$_2$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 11.8, 24.5, 42.5, 78.9, 97.4, 177.1, 197.3. HRMS (*m*/*z*): calculated for C$_{10}$H$_{14}$N$_2$O$_3$S: 243.0798 [*M* + H]$^+$; found: 243.0811.

2.2.2. 1,3-Diethyl-5-propionyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (A02). Pale-white solid; 56% yield; m.p. 74–75 °C; HPLC t_R = 12.9 min; IR (cm^{-1}): 1227 (C═S), 1680 (C═O); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.14 (*t*, *J* = 7.4 Hz, –CH$_3$), 1.19 (*t*, *J* = 7.0 Hz, –CH$_3$), 3.11 (*q*, *J* = 7.4 Hz, –CH$_2$), 4.41 (*q*, *J* = 7.0 Hz, –CH$_2$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 8.9, 11.8, 30.7, 42.6, 96.6, 171.6, 177.0, 201.4. HRMS (*m*/*z*): calculated for C$_{11}$H$_{16}$N$_2$O$_3$S: 257.0954 [*M* + H]$^+$; found: 257.0966.

2.2.3. 5-Benzoyl-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (A03). Pale-white solid; 36% yield; m.p. 92–93 °C; HPLC t_R = 13.1 min; IR (cm^{-1}): 1287 (C═S), 1675 (C═O); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.18 (*t*, *J* = 7.0 Hz, –CH$_3$), 4.39 (*q*, *J* = 7.0 Hz, –CH$_2$), 7.4–7.6 (m, ArH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 12.1, 42.3, 96.3, 127.6, 128.4, 131.4, 137.1, 161.6, 167.3, 177.0, 192.3. HRMS (*m*/*z*): calculated for C$_{15}$H$_{16}$N$_2$O$_3$S: 305.0954 [*M* + H]$^+$; found: 305.0957.

2.2.4. *tert*-Butyl [1-(1,3-diethyl-4,6-dioxo-2-thioxohexahydropyrimidin-5-yl)-1-oxo-3-phenylpropan-2-yl]carbamate (A04). Pale-pink solid; 94% yield; m.p. 130–131 °C; HPLC t_R = 14.4 min; $\lambda_{\max}$ = 322 nm; IR (cm^{-1}): 1164 (C═S), 1682 (C═O), 3359 (N—H); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.18 (*t*, *J* = 7.2 Hz, –CH$_3$), 1.28 (*s*, –CH$_3$), 3.09–3.12 (m, –CH$_2$), 4.44 (*q*, *J* = 7.2 Hz, –CH$_2$), 5.52 (*t*, *J* = 7.8, –CH), 7.16 (*d*, *J* = 7.3 Hz, –NH), 7.21–7.33 (m, Ar-H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 12.4, 18.8, 28.1, 45.7, 60.2, 69.9, 71.9, 125.7, 127.7, 129.3, 138.9, 155.1, 177.1, 183.8, 216.1. HRMS (*m*/*z*): calculated for C$_{22}$H$_{29}$N$_3$O$_5$S: 448.1900 [*M* + H]$^+$; found: 448.1901.

2.2.5. 1,3-Diethyl-5-phenylalanyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (A05). Pale-pink gum; 98% yield; HPLC t_R = 7.6 min; $\lambda_{\max}$ = 308 nm; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.15 (*t*, *J* = 6.8 Hz, –CH$_3$), 3.08–3.12 (*m*, –CH$_2$), 4.20 (*t*, *J* = 5.5 Hz, –CH), 4.40 (*q*, *J* = 6.8 Hz, –CH$_2$), 7.23–7.30 (*m*, Ar-H), 7.72 (*bs*, –NH$_2$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 12.5, 41.5, 53.1, 58.5, 95.0, 128.4, 128.6, 129.4, 136.5, 160.2, 176.7, 189.6. HRMS (*m*/*z*): calculated for C$_{17}$H$_{21}$N$_3$O$_3$S: 348.1376 [*M* + H]$^+$; found: 348.1388.

2.2.6. *tert*-Butyl [1-(1,3-diethyl-4,6-dioxo-2-thioxohexahydropyrimidin-5-yl)-3-methyl-1-oxobutan-2-yl)carbamate (A06). Dark-pink solid; 92% yield; m.p. 100–101 °C; HPLC t_R = 14.1 min; λ_{max} = 320 nm; IR (cm^{-1}): 1105 (C═S), 1623 (C═O) 3369 (N—H); ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.81 (*d*, J = 6.8 Hz, –CH$_3$), 1.18 (*t*, J = 6.6 Hz, –CH$_3$), 1.37 (*s*, –CH$_3$), 3.06–3.11 (*m*, –CH), 3.80 (*s*, –CH), 4.41 (*q*, J = 6.8 Hz, –CH$_2$), 5.52 (*d*, J = 7.3 Hz, –CH), 6.87 (*s*, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 11.9, 28.1, 30.1, 42.6, 52.1, 58.9, 78.1, 139.1, 155.6, 168.7, 176.8, 199.5. HRMS (*m*/*z*): calculated for $C_{18}H_{29}N_3O_5S$: 400.1901 [*M* + H]$^+$; found: 400.1884.

2.2.7. 1,3-Diethyl-2-thioxo-5-valyldihydropyrimidine-4,6(1*H*,5*H*)-dione (A07). Dark-pink gum; 97% yield; HPLC t_R = 6.6 min; ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.76 (*d*, J = 7 Hz, –CH$_3$), 1.2 (*t*, J = 7 Hz, –CH$_3$), 2.16 (*m*, –CH), 3.10 (*m*, –CH), 4.37 (*q*, J = 7 Hz, –CH$_2$), 4.96 (*d*, J = 8.5 Hz, –CH), 7.66 (*bs*, NH$_2$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 12.5, 15.8, 19.6, 29.1, 41.5, 61.5, 160.1, 176.7, 190.5. HRMS (*m*/*z*): calculated for $C_{13}H_{21}N_3O_3S$: 300.1376 [*M* + H]$^+$; found: 300.1377.

2.2.8. (*E*)-1,3-Diethyl-5-{1-[(pyridin-2-ylmethyl)imino]ethyl}-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (A08). Pale-yellow solid (gummy at room temperature); 86% yield; HPLC t_R = 8.8 min; ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.22 (*t*, J = 7.0 Hz, –CH$_3$), 2.69 (*s*, –CH$_3$), 4.49 (*q*, J = 7.0 Hz, –CH$_2$), 4.75 (*d*, J = 5.6 Hz, –CH$_2$), 7.2–8.6 (*m*, Ar-H), 13.3 (*s*, –CH); ^{13}C NMR (100 MHz, CDCl$_3$): δ 11.4, 17.9, 41.8, 42.2, 48.2, 92.3, 120.4, 122.1, 136.3, 148.9, 153.3, 174.3, 176.6. HRMS (*m*/*z*): calculated for $C_{16}H_{20}N_4O_2S$: 333.1380 [*M* + H]$^+$; found: 333.1387.

2.2.9. (*E*)-1,3-Diethyl-5-{1-[(4-methoxybenzyl)imino]ethyl}-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (A09). White solid; 69% yield; m.p. 98–100 °C; HPLC t_R = 12.6 min; ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.21 (*t*, J = 6.9 Hz, –CH$_3$), 2.10 (*s*, –OCH$_3$), 2.66 (*s*, –CH$_2$), 3.75 (*s*, –CH$_3$), 4.47 (*q*, J = 7.0 Hz, –CH$_2$), 6.84–7.15 (*m*, Ar-H), 12.96 (*s*, –CH); ^{13}C NMR (100 MHz, CDCl$_3$): δ 11.4, 17.2, 41.8, 42.6, 46.8, 54.9, 113.7, 127.4, 130.1, 152.1, 154.4, 167.4, 173.6 HRMS (*m*/*z*): calculated for $C_{18}H_{23}N_3O_3S$: 362.1533 [*M* + H]$^+$; found: 362.1535.

2.2.10. 1,3-Diethyl-5-(4-fluorobenzylidene)-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (A10). Yellow solid; 70% yield; m.p. 180–182 °C; HPLC t_R = 11.9 min; λ_{max} = 287 nm, 361 nm; IR (cm^{-1}): 1108 (C═S), 1614 (C═O); ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.30 (*t*, J = 7.0 Hz, –CH$_3$), 4.59 (*q*, J = 7.0 Hz, –CH$_2$), 7.00–7.04 (*m*, Ar-H), 13.86 (*s*, –CH); ^{13}C NMR (100 MHz, CDCl$_3$): δ 12.1, 45.2, 97.4, 115.2, 115.4, 127.9, 128.0, 162.2, 163.7, 174.6. HRMS (*m*/*z*): calculated for $C_{15}H_{15}N_2O_2S$: 307.0911 [*M* + H]$^+$; found: 307.0908.

2.2.11. 5,5′-[(3,5-Dimethoxyphenyl)methylene]bis[1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione] (A11). Yellow solid; 74% yield; m.p. 150–151 °C; HPLC t_R = 13.2 min; λ_{max} = 284 nm, 366 nm; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.16 (*t*, J = 7.0 Hz, –CH$_3$), 3.44 (*m*, –CH), 3.62 (*s*, –OCH$_3$), 4.45 (*q*, J = 7.0 Hz, –CH$_2$), 6.10–6.26 (*m*, Ar-H), 8.10 (*d*, J = 6.6, –CH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 12.3, 18.5, 33.6, 42.8, 54.8, 96.3, 104.9, 145.2, 160.1, 161.1, 174.0. HRMS (*m*/*z*): calculated for $C_{25}H_{32}N_4O_6S_2$: 549.1836 [*M* + H]$^+$; found: 549.1821.

2.2.12. 5,5′-[(2,4-Dinitrophenyl)methylene]bis[1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione] (A12). Buff solid; 76% yield; m.p. 163–165 °C; HPLC t_R = 12.2 min; λ_{max} = 289 nm; IR (cm^{-1}): 1108 (C═S), 1611 (C═O); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.14 (*t*, J = 6.7 Hz, –CH$_3$), 4.40 (*q*, J = 6.7 Hz, –CH$_2$), 6.42 (*s*, –CH), 7.51–8.41 (*m*, Ar-H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 12.1, 32.3, 42.8, 94.2, 118.9, 125.6, 130.9, 143.4, 145.5, 149.3, 160.7, 174.4. HRMS (*m*/*z*): calculated for $C_{23}H_{26}N_6O_8S_2$: 579.1326 [*M* + H]$^+$; found: 579.1322.

2.2.13. 1,3-Diethyl-4,6-dioxo-2-thioxo–(*p*-tolyl)hexahydropyrimidine-5-carbothioamide (A13). Pale-yellow solid; 90% yield; m.p. 132–133 °C; HPLC t_R = 15.6 min; λ_{max} = 333 nm; IR (cm^{-1}): 1105 (C═S), 1645 (C═O); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.31 (*t*, J = 7.0 Hz, –CH$_3$), 2.39 (*s*, –CH$_3$), 4.58 (*q*, J = 7.0, –CH$_2$), 7.31–7.39 (*m*, Ar-H), 13.9 (*s*, –NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 11.6, 20.7, 43.8, 91.7, 125.2, 129.5, 134.5, 137.0, 174.3, 184.9, 202.9. HRMS (*m*/*z*): calculated for $C_{16}H_{19}N_3O_2S_2$: 350.0991 [*M* + H]$^+$; found: 350.0962.

2.2.14. 2-Thioxo-1,3-di-*p*-tolyldihydropyrimidine-4,6(1*H*,5*H*)-dione (A14). Yellow solid; 92% yield; m.p. 218–220 °C; HPLC t_R = 10.2 min; λ_{max} = 241 nm, 286 nm; IR (cm^{-1}): 1339 (C═S), 1700 (C═O); ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.27 (*s*, –CH$_3$), 7.12 (*d*, J = 8.1 Hz, Ar-H), 7.33 (*d*, J = 8.1 Hz, Ar-H), 9.58 (*s*, –CH$_2$,); ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.1, 40.6, 128.4, 129.5, 136.6, 137.9, 169.3, 174.2. HRMS (*m*/*z*): calculated for $C_{18}H_{16}N_2O_2S$: 325.1005 [*M* + H]$^+$; found: 325.1025.

2.2.15. 5-Acetyl-2-thioxo-1,3-di-*p*-tolyldihydropyrimidine-4,6(1*H*,5*H*)-dione (A15). Yellow solid; 45% yield; m.p. 185–186 °C; HPLC t_R = 12.0 min; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.34 (*s*, –CH$_3$), 2.65 (*s*, –CH$_3$), 7.15 (*d*, J = 8.2 Hz, Ar-H), 7.26 (*d*, J = 8.2 Hz, Ar-H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.7, 24.5, 98.2, 128.5, 129.5, 136.7, 137.6, 179.6, 196.3, 206.9. HRMS (*m*/*z*): calculated for $C_{20}H_{18}N_2O_3S$: 366.1077 [*M* + H]$^+$; found: 366.1100.

2.2.16. 5-Propionyl-2-thioxo-1,3-di-*p*-tolyldihydropyrimidine-4,6(1*H*,5*H*)-dione (A16). Yellow solid; 57% yield; m.p. 140–141 °C; HPLC t_R = 12.7 min; λ_{max} = 318 nm; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.14 (*t*, J = 7.4 Hz, –CH$_3$), 2.33 (*s*, –CH$_3$), 2.91 (*q*, J = 7.4 Hz, –CH$_2$), 7.08 (*d*, J = 8.2 Hz, Ar-H), 7.20 (*d*, J = 8.2 Hz, Ar-H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 10.1, 20.7, 30.1, 63.4, 128.5, 129.5, 137.6, 166.2, 170.6, 179.5, 187.6. HRMS (*m*/*z*): calculated for $C_{21}H_{20}N_2O_3S$: 381.1290 [*M* + H]$^+$; found: 381.1267.

2.2.17. 5-(1-Aminoethylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (A17). Yellow solid; m.p. 190–191 °C; HPLC t_R = 9.2 min; λ_{max} = 320 nm; IR (cm^{-1}): 1357 (C═S), 1613 (C═O) 3295 (N—H); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.14 (*t*, J = 7 Hz, –CH$_3$), 2.53 (*s*, –CH$_3$), 4.37 (*q*, J = 7 Hz, –CH$_2$), 9.7 (*s*, –NH$_2$), 11.1 (*s*, –NH$_2$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 12.1, 24.3, 42.0, 91.2, 175.8, 176.9, 197.3. HRMS (*m*/*z*): calculated for $C_{10}H_{15}N_3O_2S$: 242.0958 [*M* + H]$^+$; found: 242.0966.

2.2.18. 5-(1-Aminopropylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (A18). Yellow solid; m.p. 101–102 °C; HPLC t_R = 10.1 min; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.15 (*t*, J = 7.3 Hz, –CH$_3$), 1.16 (*t*, J = 6.9 Hz, –CH$_3$), 2.53 (*q*, J = 7.3 Hz, –CH$_3$), 4.40 (*q*, J = 6.9 Hz, –CH$_2$), 9.68 (*s*, –NH$_2$),

Table 1
Experimental details.

All determinations used a temperature of 100 K, a Bruker APEXII CCD diffractometer and a multi-scan (*SADABS*; Bruker, 2012) absorption correction.

	A01	**A02**	**A06**
Crystal data			
Chemical formula	$C_{10}H_{14}N_2O_3S$	$C_{11}H_{16}N_2O_3S$	$C_{18}H_{29}N_3O_5S$
M_r	242.29	256.32	399.50
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1$	Orthorhombic, $P2_12_12_1$
a, b, c (Å)	4.6212 (1), 12.5742 (4), 19.3936 (6)	4.9140 (1), 12.9450 (3), 9.7630 (3)	8.3816 (12), 9.6258 (14), 24.297 (3)
α, β, γ (°)	90, 92.869 (1), 90	90, 103.474 (1), 90	90, 90, 90
V (Å^3)	1125.51 (6)	603.95 (3)	1960.3 (5)
Z	4	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.28	0.27	0.20
Crystal size (mm)	0.29 × 0.23 × 0.12	0.19 × 0.14 × 0.07	0.33 × 0.25 × 0.21
Data collection			
$T_{\min}, T_{\max}$	0.911, 0.978	0.940, 0.991	0.925, 0.968
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	14896, 2704, 2309	8623, 8623, 8469	15360, 15360, 14556
R_{int}	0.016	0.000	0.000
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.667	0.650	0.654
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.030, 0.085, 1.05	0.027, 0.070, 1.09	0.028, 0.070, 1.04
No. of reflections	2704	8623	15360
No. of parameters	146	158	264
No. of restraints	0	1	5
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å^{-3})	0.40, −0.19	0.21, −0.26	0.47, −0.30
Absolute structure	–	Flack x determined using 1252 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons *et al.*, 2013)	Flack x determined using 1707 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	–	0.034 (16)	0.001 (2)

	A13	**A17**	**A18**
Crystal data			
Chemical formula	$C_{16}H_{19}N_3O_2S_2$	$C_{10}H_{15}N_3O_2S$	$C_{11}H_{17}N_3O_2S$
M_r	349.46	241.31	255.33
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Orthorhombic, $P2_12_12_1$
a, b, c (Å)	4.8156 (2), 21.7395 (7), 15.1912 (5)	12.8983 (4), 9.8458 (3), 18.2217 (6)	4.9625 (3), 10.6358 (7), 23.2402 (15)
α, β, γ (°)	90, 95.656 (1), 90	90, 98.250 (2), 90	90, 90, 90
V (Å^3)	1582.61 (10)	2290.10 (13)	1226.62 (14)
Z	4	8	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.35	0.27	0.26
Crystal size (mm)	0.19 × 0.12 × 0.11	0.19 × 0.13 × 0.09	0.25 × 0.11 × 0.09
Data collection			
$T_{\min}, T_{\max}$	0.925, 0.976	0.941, 0.985	0.924, 0.988
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	25387, 4036, 3430	14727, 5036, 4323	10534, 10534, 9991
R_{int}	0.027	0.024	0.000
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.675	0.642	0.649
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.031, 0.078, 1.04	0.033, 0.088, 1.03	0.032, 0.076, 1.04
No. of reflections	4036	5036	10534
No. of parameters	212	291	154
No. of restraints	0	3	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å^{-3})	0.38, −0.25	0.28, −0.27	0.28, −0.22
Absolute structure	–	–	Flack x determined using 1038 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	–	–	−0.02 (3)

Computer programs: *APEX2* (Bruker, 2008), *SAINT-Plus* (Bruker, 2008), *XPREP* (Bruker, 2008), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2016* (Sheldrick, 2015*b*), *ORTEP-3* (Farrugia, 2012) and *WinGX* (Farrugia, 2012).

11.18 (*s*, –NH$_2$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 12.2, 12.7, 29.2, 42.1, 90.3, 161.2, 176.9, 180.6. HRMS (*m*/*z*): calculated for $C_{11}H_{17}N_3O_2S$: 256.1080 $[M + H]^+$; found: 256.1096.

2.2.19. 5-(1-Aminoethylidene)-2-thioxo-1,3-di-*p*-tolyldihydropyrimidine-4,6(1*H*,5*H*)-dione (A19). Yellow solid; m.p. 198–200 °C; HPLC t_R = 9.9 min; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.23 (*s*, –CH$_3$), 2.33 (*s*, –CH$_3$), 7.07 (*d*, *J* = 8.2 Hz, Ar-H), 7.20 (*d*, *J* = 8.2 Hz, Ar-H), 9.69 (*s*, –NH$_2$), 10.9 (*s*, –NH$_2$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.8, 23.4, 101.2, 129.8, 132.4, 136.2, 137.3, 162.8, 167.3, 172.5. HRMS (*m*/*z*): calculated for $C_{20}H_{19}N_3O_2S$: 366.1282 $[M + H]^+$; found: 366.1271.

2.2.20. 5-(1-Aminopropylidene)-2-thioxo-1,3-di-*p*-tolyldihydropyrimidine-4,6(1*H*,5*H*)-dione (A20). Yellow solid; m.p. 159–160 °C; HPLC t_R = 10.6 min; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.14 (*t*, *J* = 7.4 Hz, CH$_3$), 2.33 (*s*, –CH$_3$), 2.91 (*q*, *J* = 7.4 Hz, CH$_2$), 7.08 (*d*, *J* = 8.2 Hz, Ar-H), 7.20 (*d*, *J* = 8.2 Hz, Ar-H), 9.62 (*s*, –NH$_2$), 10.97 (*s*, –NH$_2$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 9.8, 20.7, 24.5, 98.2, 128.5, 129.5, 136.7, 137.6, 162.4, 179.6, 196.3. HRMS (*m*/*z*): calculated for $C_{21}H_{21}N_3O_2S$: 380.1436 $[M + H]^+$; found: 380.1427.

2.3. Structure determination

Crystal data, data collection and structure refinement details are summarized in Table 1. All non-H atoms were first refined isotropically and then anisotropically with full-matrix least-squares based on F^2 using *SHELXL* (Sheldrick, 2015*b*). All H atoms were positioned geometrically, allowed to ride on their parent atoms and refined isotropically. In **A06**, the H atom of the enol unit was found to be disordered over two positions between the enol and one of the carbonyl groups of the thiobarbituric ring. Equal occupancies were used for the two components.

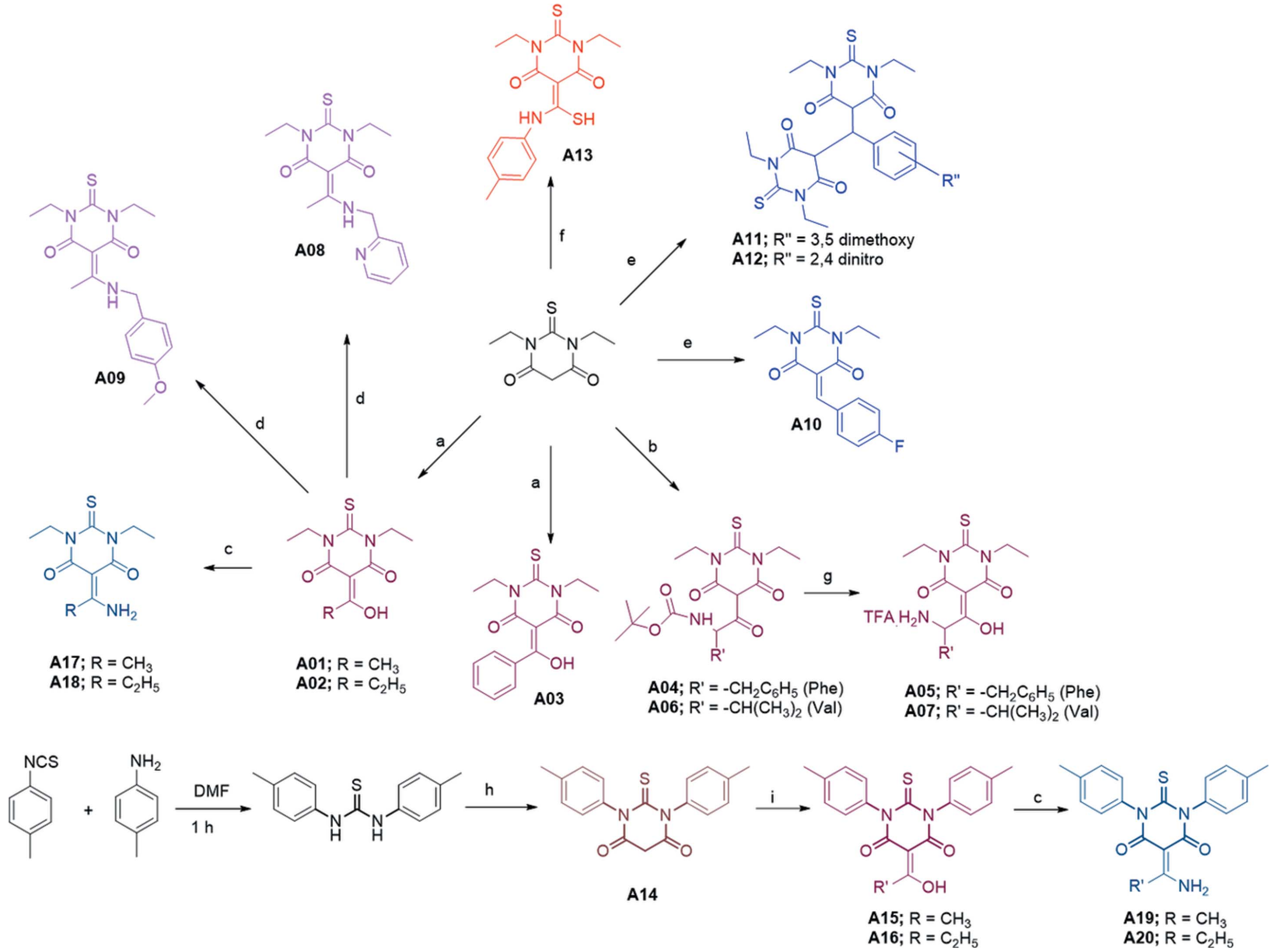

Figure 2

Conditions: (**a**) anhydride/NaHCO$_3$/H$_2$O, overnight; (**b**) *tert*-butyloxycarbonyl-protected amino acids (Boc–amino acid), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), 1-hydroxybenzotriazole (HOBt), 4-dimethylaminopyridine (DMAP), dichloromethane (DCM), 16 h; (**c**) NH$_4$Cl/EtOH, overnight; (**d**) amine/conc. HCl/EtOH, overnight; (**e**) aldehyde/EtOH, 10 min; (**f**) 1-isothiocyanato-4-methylbenzene, *N*,*N*-diisopropylethylamine (DIEA), DCM, overnight; (**g**) trifluoroacetic acid (TFA), 1 h; (**h**) malonic acid and acetyl chloride, 40 °C, 12 h; (**i**) acetic acid/propionic acid, few drops conc. H$_2$SO$_4$, reflux 1 h.

2.4. Theoretical calculations

The above crystal structures were used as the starting points for the calculations which were performed using the DFT-B3LYP/6-311++(d,p) method implemented in *GAUSSIAN09* (Frisch *et al.*, 2009) without solvent correction. Vibration analysis showed that the optimized structure indeed represents a minimum on the potential energy surface (no negative eigenvalues). A four-membered ring transition state was calculated (Gonzalez & Schlegel, 1989, 1990).

3. Results and discussion

All the derivatives (Fig. 2) were synthesized earlier by our group (Sharma *et al.*, 2018) and well characterized by a variety of spectroscopic techniques which will be discussed in the subsequent sections.

3.1. Synthesis and characterization

All the derivatives were synthesized earlier by our group (Sharma *et al.*, 2018) and were characterized by NMR and UV spectrometry (Fig. 3) in a variety solvents. Some of the derivatives (**A01**, **A02**, **A03**, **A04**, **A06**, **A10**, **A12**, **A13**, **A14** and **A17**) were evaluated using IR spectroscopy and different absorption stretching frequencies were compared to the reported literature (Larkin, 2017). The stretching frequencies of C═S in all spectra were found in the range 1108–1357 cm^{-1}, which is in agreement with a C═S group attached to a tertiary nitrogen (Pretsch *et al.*, 2000). In **A12**, the stretching frequency at 1377 cm^{-1} indicated the presence of a nitro group (NO_2). The presence of stretching frequencies at 1680/825 and 1613/838 cm^{-1} in **A01** and **A17**, respectively, indicates the presence of 'substituted alkene'. A broad signal around 1541 cm^{-1} indicates the enol '–OH' group. A distinct signal at 3295 cm^{-1} in **A17** further indicates the presence of primary amine, clearly supporting the enamine formation.

In **A01**, the C-5 proton in acetylated 1,3-diethyl-2-thiobarbituric acid (DETBA) showed a signal at 17.72 ppm (singlet), which reflects the presence of OH, hence indicating that the enol form is more stable than the keto form. The enolization of the carbonyl group was also in excellent agreement with the observed signal at 96.7 ppm for C-5 in the ^{13}C NMR spectrum. Furthermore, the NMR spectra for **A17**, **A18**, **A19** and **A20** revealed a shift of the peaks during the conversion from enol to enamine. Of note, we detected an interesting feature in all the enamine derivatives where the 'NH_2' proton showed two distinct peaks, one around 9.7 ppm and another at 11 ppm, clearly indicating different chemical environments of the two protons in '–NH_2'.

Given the non-aromaticity of TBA, they absorb UV on the thin-layer chromatography (TLC) plate and during the HPLC, UV absorption of a few derivatives was also studied using acetonitrile (ACN), ethanol and dichloromethane (DCM) as solvent. 1,3-Diethyl-2-thiobarbituric acid (DETBA) showed a λ_{max} absorption at 285 nm. **A01** showed absorption at a maximum (λ_{max}) of 316 nm, whereas **A04** and **A12** showed absorptions at 322 and 289 nm, respectively. However, similar results were obtained for **A12** in the case of ethanol as solvent, but in case of DCM as solvent, λ_{max} was observed at 305 nm. Also the derivative with an aryl substitution on 'N', *i.e.* **A14**, absorbed at 286 nm. However, with further substitution at C-5 in **A14** affording **A16**, λ_{max} shifts to 318 nm. A comparison of **A01** and **A17** revealed UV absorption changes from 316 to 320 nm as the conversion from the keto to the enamine form occurred.

In the case of **A04**, the λ_{max} absorption was at 322 nm and absorption shifted slightly to 308 nm after Boc removal in

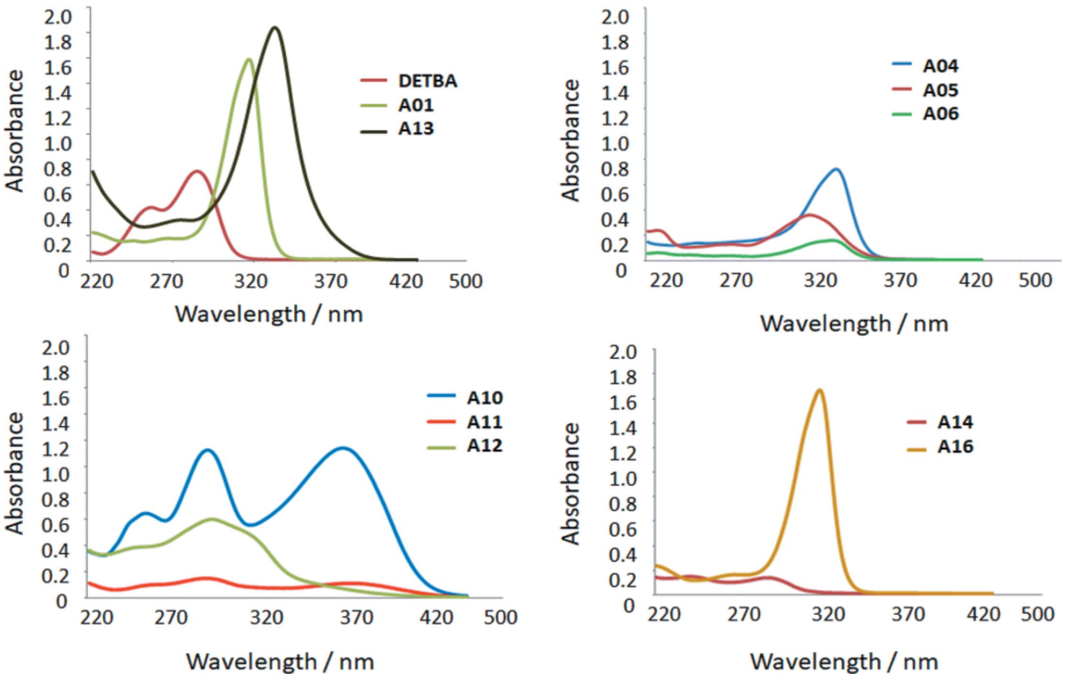

Figure 3
UV spectra of some TBA derivatives.

Table 2
RMSD (r.m.s. deviation) values of fitted atoms of $P_{\rm DETBA}$ and dihedral angles (°) $P_{\rm DETBA}$–$P_{\rm ENOL}$, $P_{\rm DETBA}$–$P_{\rm ENAMINE}$ and $P_{\rm DETBA}$–$P_{\rm THIOAMIDE}$ observed in **A01**, **A02**, **A06**, **A13**, **A17** and **A18**.

Compound	RMSD of fitted atoms of $P_{\rm DETBA}$[a]	Dihedral angle [$P_{\rm DETBA}$–$P_{\rm ENOL}$[b]/$P_{\rm ENAMINE}$[c]/$P_{\rm THIOAMIDE}$[d]]
A01	0.0187	6.3 (1)
A02	0.0270	7.3 (2)
A06	0.0117	8.7 (2)
A13	0.0171	0.2 (2)
A17	0.0544, 0.0465	7.9 (2), 5.3 (2)
A18	0.0245	5.6 (2)

Notes: (*a*) Atoms used to define $P_{\rm DETBA}$: (**A01**) C3–C6–C7–C8–N1–N2; (**A02**) C4–C5–C9–N2–C8–N1; (**A06**) C8–C3–C6–N2–N1–C7; (**A13**) C3–C4–C11–C14–N1–N3; (**A17**) C3–C9–C10–C8–N3–N2; (**A18**) C3–C9–C10–C11–N1–N2. (*b*) Atoms used to define $P_{\rm ENOL}$: (**A01**) C9–C10–O3; (**A02**) C1–C2–C3–O3; (**A06**) C9–C10–O3. (*c*) Atoms used to define $P_{\rm ENAMINE}$: (**A17**) C6–C7–C8–N1; (**A18**) C6–C7–C8–N3. (*d*) Atoms used to define $P_{\rm THIOAMIDE}$: (**A13**) C5–N2–S2.

A05. A06 showed the $\lambda_{\rm max}$ absorption at 320 nm, a value that did not differ greatly from that of **A04**. UV–Vis absorption was also studied for the Knoevenagel reaction (**A10** and **A11**). Two $\lambda_{\rm max}$ absorption peaks – one caused by DETBA and the other by the respective aldehyde – were detected. For **A10**, the $\lambda_{\rm max}$ absorption peaks were at 287 and 361 nm, whereas for **A11**, they were at 284 and 366 nm. The reaction of DETBA with *p*-tolyl isothiocyanate resulted in **A13**, which has a thioamide bond, which showed a shift from 285 (in case of DETBA) to 333 nm. Furthermore, **A14** showed two UV–Vis absorption peaks at 241 and 286 nm, which were caused by the presence of 'tolyl', as well as a 'thiobarbituric ring'.

3.2. Crystal structure descriptions of A01, A02, A06, A13, A17 and A18

Colourless X-ray-quality crystals of **A01**, **A02**, **A06**, **A13**, **A17** and **A18** were obtained by hot recrystallization from ethanol.

Molecules in the asymmetric unit of these derivatives are shown in Fig. 4. Each molecule consists of a DETBA ring with either an enol (in **A01**, **A02** and **A06**), enamine (in **A17** and **A18**) or thioamide (in **A13**) moiety. The DETBA ring, together with the various moieties, were identified as approximately planar, which best describes the molecular conformations of **A01**, **A02**, **A06**, **A13**, **A17** and **A18**. In Table 2, the DETBA, enol, enamine and thioamide planes are denoted as $P_{\rm DETBA}$, $P_{\rm ENOL}$, $P_{\rm ENAMINE}$ and $P_{\rm THIOAMIDE}$, respectively, whilst the dihedral angles between the corresponding planes are designated as $P_{\rm DETBA}$–$P_{\rm ENOL}$, $P_{\rm DETBA}$–$P_{\rm ENAMINE}$ or $P_{\rm DETBA}$–$P_{\rm THIOAMIDE}$. R.m.s. deviations (RMSDs, usually measured in Ångström) of the fitted atoms of DETBA, along with the dihedral angles between the various planes, are listed in Table 2. The six-membered DETBA ring did not appear to be completely planar in any of the compounds, since the RMSD values of the fitted atoms of the DETBA rings were all greater than zero. The RMSD of $P_{\rm DETBA}$ increased as the carbon chain on the enol in **A01** (0.0187) extended to **A02** (0.0270). Interestingly, the presence of a bulky Boc–Val group on the enol in **A06** significantly improved the planarity of $P_{\rm DETBA}$ over that observed in **A01**. However, the $P_{\rm DETBA}$–$P_{\rm ENOL}$ dihedral angle appeared to increase with the carbon chain length and steric demand of the enol moiety. Compound **A17** is an enamine form of **A01** and showed RMSD values (0.0465–0.544) higher than those of all the enol counterparts,

Table 4
Selected hydrogen bonds observed in **A01**, **A02**, **A06**, **A13**, **A17** and **A18**.

D—H···A	D—H	H···A	D···A	D—H···A
A01				
C10—H10A···S1$^{\rm i}$	0.98	2.88	3.8316 (14)	163
O3—H3···O2	0.84	1.71	2.4756 (13)	150
A02				
C2—H2A···O2$^{\rm i}$	0.99	2.56	3.384 (2)	140
C6—H6A···O1$^{\rm ii}$	0.99	2.57	3.440 (2)	146
C11—H11B···O2$^{\rm iii}$	0.99	2.56	3.539 (2)	170
O3—H3···O2	0.84	1.67	2.4395 (17)	151
A06				
C11—H11···N2$^{\rm i}$	1.00	2.63	3.613 (3)	166
C18—H18A···S1$^{\rm ii}$	0.98	2.85	3.760 (2)	154
N3—H3···S1$^{\rm i}$	0.83 (1)	2.87 (1)	3.6957 (17)	172 (2)
O2—H2H···O3	0.86 (1)	1.59 (1)	2.3723 (19)	150 (1)
O3—H1H···O2	0.86 (1)	1.56 (1)	2.3723 (19)	155 (1)
A13				
N2—H2A···O1	0.88	1.79	2.5671 (15)	147
O2—H2···S2	0.84	1.99	2.7802 (10)	157
A17				
C6—H6A···O3$^{\rm i}$	0.98	2.43	3.3103 (17)	149
N1—H1E···O3$^{\rm i}$	0.88	1.99	2.8540 (15)	168
N4—H4D···O1	0.88	2.07	2.9473 (15)	172
A18				
C1—H1A···S1$^{\rm i}$	0.98	2.80	3.661 (2)	147
C7—H7A···O1$^{\rm ii}$	0.99	2.54	3.505 (2)	166
N3—H3B···O2$^{\rm iii}$	0.88	2.24	2.999 (2)	145

Symmetry codes for **A01**: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; for **A02**: (i) $-x, y + \frac{1}{2}, -z + 1$; (ii) $-x + 1, y - \frac{1}{2}, -z + 1$; (iii) $-x + 1, y + \frac{1}{2}, -z + 1$; for **A06**: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + \frac{3}{2}, -y + 2, z - \frac{1}{2}$; for **A17**: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; for **A18**: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 2$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x, y - \frac{1}{2}, -z + \frac{3}{2}$.

Table 3
Selected bond lengths (Å) observed in **A01**, **A02**, **A06**, **A17** and **A18**.

Bond parameter	**A01**	**A02**	**A06**	**A17**	**A18**
$C_{\rm carbonyl}$—$O_{\rm carbonyl}$[a]	1.247 (2)	1.257 (2)	1.250 (2)	1.239 (2) 1.237 (2)	1.242 (2)
$C_{\rm carbonyl}$—$C_{\rm ethylene}$[b]	1.435 (2)	1.430 (3)	1.404 (2)	1.434 (2) 1.437 (2)	1.436 (3)
$C_{\rm ethylene}$—$C_{\rm enol/enamine}$[c]	1.398 (2)	1.406 (3)	1.394 (2)	1.425 (2) 1.425 (2)	1.430 (3)
$C_{\rm enol/enamine}$—$O_{\rm enol}$/$N_{\rm enamine}$[d]	1.309 (2)	1.301 (2)	1.260 (2)	1.308 (2) 1.312 (2)	1.314 (2)

Notes: (*a*) **A01** = C6—O2; **A02** = C4—O2; **A06** = C2—O6; **A17** = C10—O2 and C19—O4; **A18** = C10—O1; (*b*) **A01** = C6—C7; **A02** = C4—C5; **A06** = C6—C7; **A17** = C10—C8 and C19—C18; **A18** = C10—C9; (*c*) **A01** = C7—C8; **A02** = C5—C3; **A06** = C7—C9; **A17** = C8—C7 and C18—C17; **A18** = C9—C8; (*d*) **A01** = C9—O3; **A02** = C3—O3; **A06** = C9—O3; **A17** = C7—N1 and C17—N4; **A18** = C8—N3.

with $P_{\rm DETBA}$–$P_{\rm ENAMINE}$ dihedral angles ranging between 5.2 (2) and 7.9 (2)°. In contrast to enol derivatives **A01** and **A02**, extending the carbon chain of the enamine forms of **A01** and **A02** led to a decrease in the RMSD of the DETBA ring from 0.0465–0.0544 (in **A17**) to 0.0245 (in **A18**). Exchanging the enamine for a thioamide moiety in **A13** resulted in the smallest dihedral angle [$P_{\rm DETBA}$–$P_{\rm THIOAMIDE}$ = 0.2 (2)°] observed in this series, with a $P_{\rm DETBA}$ RMSD that was intermediate between that of the enol derivatives (Table 2).

The bond lengths and angles are comparable to those of related compounds (Coe *et al.*, 1999; Asiri *et al.*, 2009; Galán *et al.*, 2012; Bourhill *et al.*, 1994); the bond parameters of interest in compounds **A01**, **A02**, **A06**, **A17** and **A18** are summarized in Table 3. Compounds **A01** and **A02** displayed enolic properties, evidenced by a shorter $\rm C_{carbonyl}{-}O_{carbonyl}$ [1.247 (2)–1.257 (2) Å] bond length than $\rm C_{enol}{-}O_{enol}$ [1.309 (2)–1.301 (2) Å], which were comparable with that of enamine forms **A17** and **A18**. Furthermore, $\rm C_{ethylene}{-}C_{enol}$ [1.398 (2)–1.406 (3) Å] appeared to be shorter than $\rm C_{carbonyl}{-}C_{ethylene}$ [1.435 (2)–1.430 (3) Å]. In compound **A06**, the $\rm C_{carbonyl}{-}C_{ethylene}$ [1.404 (2) Å] and $\rm C_{enol}{-}O_{enol}$ [1.260 (2) Å] bonds were significantly shorter than in **A01** and **A02**. This observation reveals electron delocalization between a carbonyl group of the DETBA ring and the enol moiety, which is unique to **A06**.

Hydrogen-bonding patterns in the crystal packing of **A01**, **A02**, **A06**, **A13**, **A17** and **A18** are shown in Fig. 5, while the hydrogen-bond parameters are listed in Table 4. Intramolecular O—H⋯O hydrogen bonds with graph-set notation $R_2^2(6)$ were observed in enol derivatives **A01**, **A02** and **A06**. Nonclassical intermolecular C—H⋯S hydrogen bonds link neighbouring molecules to form chains of a one-dimensional supramolecular structure that extend along the crystallographic *c* axis. In **A02**, intermolecular C—H⋯O hydrogen bonds join adjacent molecules to form a two-dimensional honeycomb-like supramolecular network extending along the crystallographic *ab* axis. The N—H⋯S hydrogen bonds link neighbouring molecules of **A06** to form chains that extend along the crystallographic *b* axis. These chains were further joined *via* C—H⋯O hydrogen bonds along the crystallographic *a* axis, forming a two-dimensional corrugated sheet-like supramolecular structure. A combination of intermolecular N—H⋯O and C—H⋯O hydrogen bonds (in **A17**) forms six-membered rings with graph-set notation $R_2^1(6)$ and

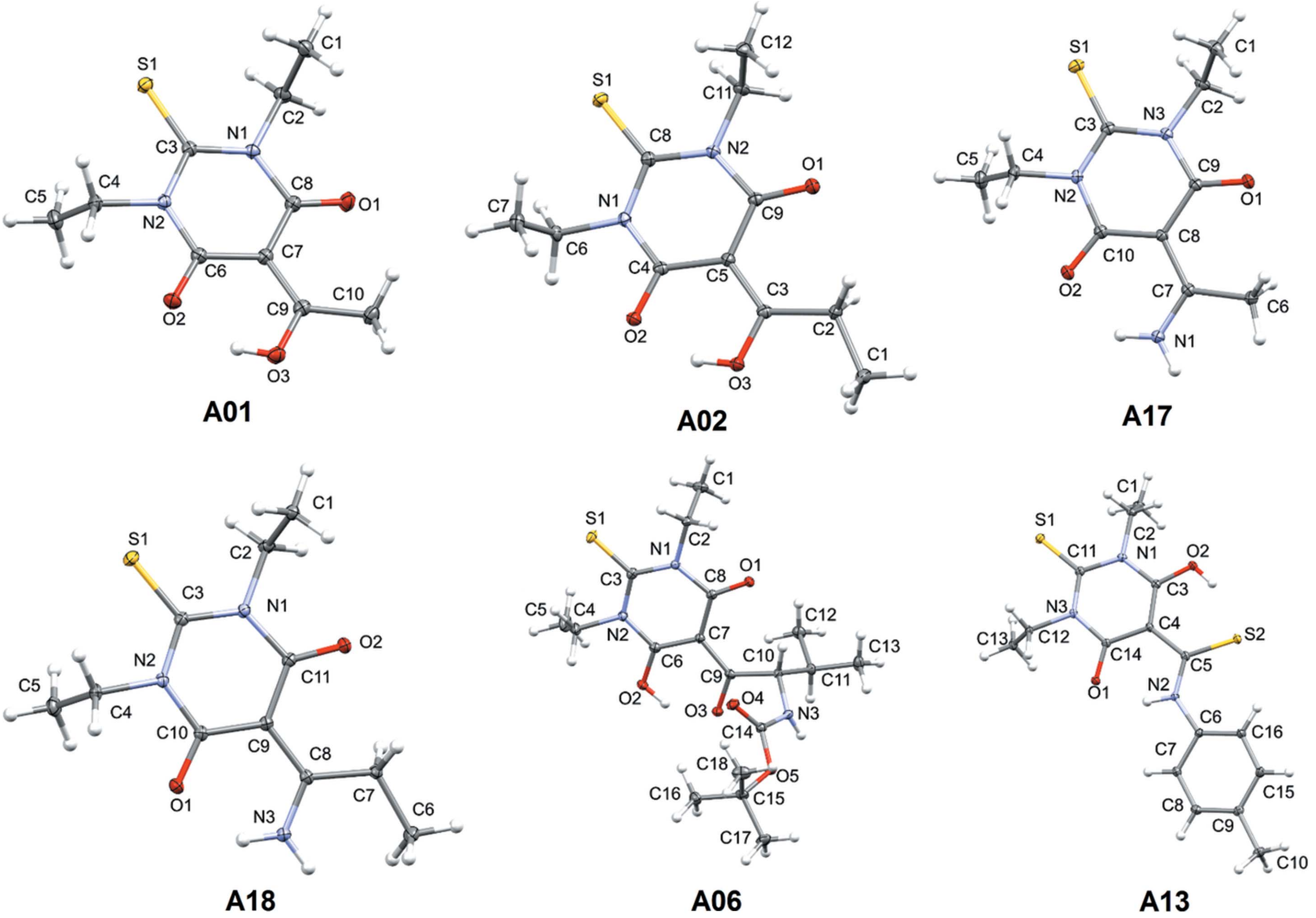

Figure 4
The molecular structures of compounds **A01**, **A02**, **A06**, **A13**, **A17** and **A18**, drawn with displacement ellipsoids at the 50% probability level. One of the two molecules of compound **A17** has been omitted for clarity.

result in a single-stranded helical supramolecular structure that elongates along the crystallographic *b* axis. On the other hand, N—H···O hydrogen bonds link neighbouring molecules to form chains that extend along the crystallographic *b* axis. Then C—H···O hydrogen bonds join the chains along the crystallographic *a* axis to form a two-dimensional sheet-like supramolecular architecture.

3.3. Theoretical calculations

A density functional theory (DFT) geometry optimization with the *GAUSSIAN09* program package (Frisch *et al.*, 2009), employing the B3LYP [Becke three parameters Lee–Yang–Parr exchange correlation functional, which combines the hybrid exchange functional of Becke (1988) with the gradient-correlation functional of Lee, Yang and Parr (Lee *et al.*, 1988)]

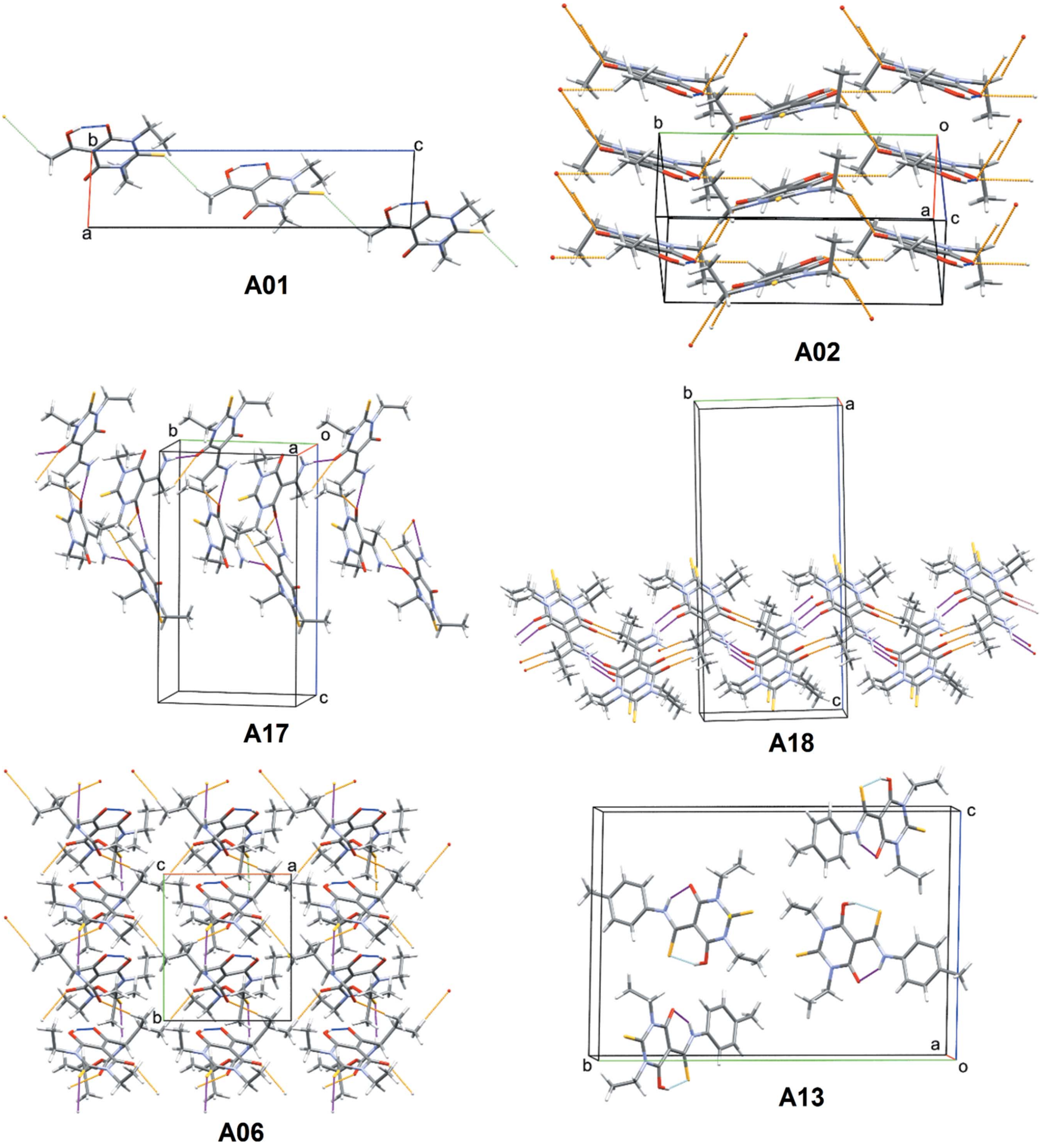

Figure 5
Hydrogen-bonding patterns observed in the crystal packing of compounds **A01**, **A02**, **A06**, **A13**, **A17** and **A18**. Intramolecular O—H···O, N—H···O and O—H···S hydrogen bonds are represented as dashed blue, purple and light-blue bonds, respectively. Intermolecular C—H···O, C—H···S, N—H···O and N—H···S hydrogen bonds are shown as dashed orange, light-green, magenta and pink bonds, respectively.

Table 5
Total energy and frontier orbital energy [B3LYP/6-311++G(d,p)] for **A01** in Hartrees.

	DFT (keto form)	DFT (enol form)
$E_{\text{total}}{}^{a}$	−1123.12965976	−1123.15077113
E_{HOMO}	−0.24121	−0.23291
E_{LUMO}	−0.09332	−0.09290
ΔE^{b}	0.14789	0.14001

Notes: (*a*) 1 Hartree = 4.35974417 × 10–18 J = 27.2113845 eV; (*b*) $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$.

Table 6
Calculated reaction profile using DFT [B3LYP/6-311++G(d,p)].

	Relative Energies (kcal mol^{-1})
Keto form	0
Transition state	43.51
Enol form	−11.54

using the 6-311G++(d,p) basis set was performed in the gas phase. No solvent corrections were made with these calculations, as gas-phase calculations frequently correspond quite well with crystal structures (Honarparvar *et al.*, 2013). The starting geometries for **A01**, **A04**, **A13**, **A17** and **A18** were taken from the X-ray-refined data. The optimized-geometry results in the free molecule state were compared to those in the crystalline state. No negative vibrational modes were obtained. The DFT calculated structure and geometric parameters (bond lengths and angles) were in agreement with each other. All optimized structures had a *C*1 point group.

The optimized geometry of **A01** indicates electron delocalization between atoms C16—C17—C19—O28. The C19—O28 bond length was 1.31 Å, which is slightly longer than that of the carbonyl (C═O, usually 1.22 Å), and the H3—O3 group formed a strong intramolecular hydrogen bond with atom O2. However, **A04**, with a similar structure, showed delocalization of electrons in the TBA ring, unlike that found in **A01**, but also the presence of strong intramolecular hydrogen bonding. **A13** showed the presence of two intramolecular hydrogen bonds caused by the presence of a thioamide bond. **A17** and **A18** showed the presence of intermolecular hydrogen bonding, in addition to intramolecular hydrogen bonding.

3.3.1. Frontier orbital energy analysis and molecular total energies.

Molecular total energy and frontier orbital energy levels were calculated using DFT (Table 5), as discussed previously by our group (Sharma *et al.*, 2017).

The crystal structure of **A01** (enol form) was used for DFT calculations. The energy gap between the HOMO and LUMO was calculated by the B3LYP method using the 6-311G++(d,p) basis set. The title compound (in enol form) showed an energy gap (ΔE = 0.14001 Hartree = 3.78 eV) for HOMO – LUMO (Fig. 6). This energy gap affords the theoretical absorption at $\lambda_{\max}$ = 326 nm. The keto form was optimized using *GaussView05* (Dennington *et al.*, 2009), and the results were compared with those of the enol form (Table 5). The keto form showed an energy gap (ΔE = 0.14789 Hartree = 3.99 eV; $\lambda_{\max}$ = 308 nm) for HOMO – LUMO (HOMO is the highest occupied molecular orbital and LUMO is the lowest unoccupied molecular orbital) that was greater than that of enol form. HOMO and LUMO are important factors that affect bioactivity, chemical reactivity, and electron affinity and ionization potential (Clare, 1994, 1995; Zhang & Musgrave, 2007). Thus, a study of the frontier orbital energy can provide useful information about the biological and chemical reaction mechanism.

3.4. Transition state calculations

A transition state is broadly considered as the first order saddle point on the Potential Energy Surface (PES) of a molecular system. The vibrational spectrum of a transition state is characterized by one imaginary frequency (implying a negative force constant), which means that in one direction in the nuclear configuration space the energy has a maximum,

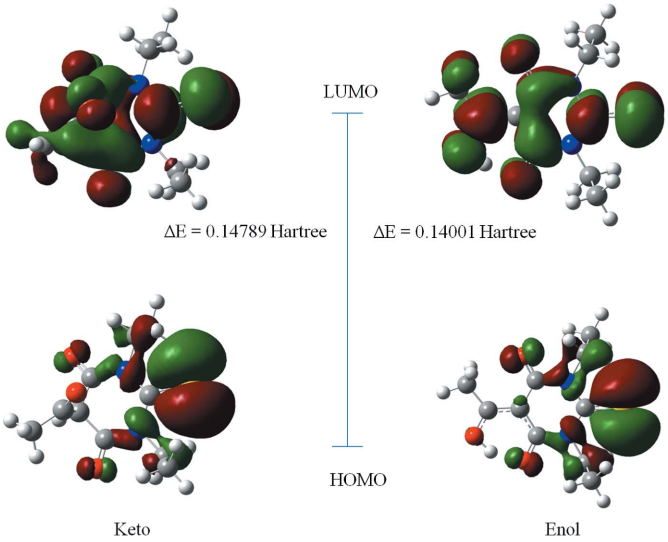

Figure 6
Frontier molecular orbitals of **A01** [B3LYP/6-311++G(d,p)].

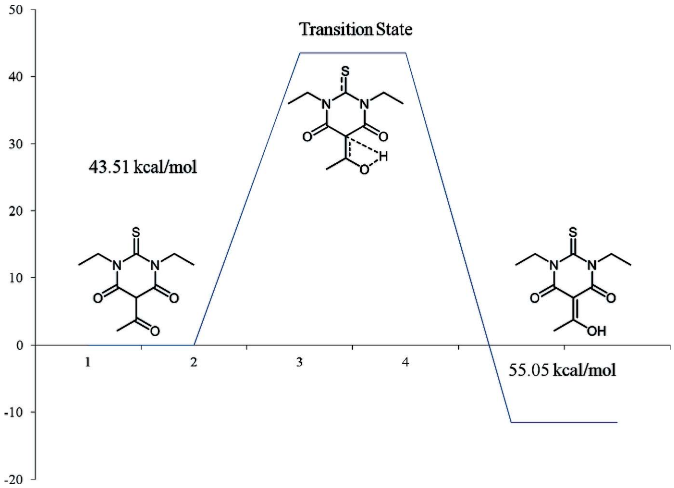

Figure 7
Transition state for the keto–enol form of **A01**.

while in all other orthogonal directions the energy is a minimum (Lewars, 2003). In order to verify this, **A01** (keto form) was optimized using *GAUSSIAN09*, followed by frequency calculations at the same computational level as that used for the enol form (**A01**). The energies calculated are listed in Table 6 and shown schematically in Fig. 7.

The calculated energy confirms that the reaction (Fig. 7) is more favourable in a forward direction, *i.e.* the enol form. In order to convert the keto form to the enol, an energy barrier of 55.05 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}) needs to be overcome (Table 6); this value is much higher than the inherent energy limit of 15–20 kcal mol^{-1} at room temperature (Kruger, 2002; Singh *et al.*, 2012).

The theoretical results thus suggest that if the product (enol) forms, it will not interconvert at room temperature. This notion was also confirmed by the NMR spectra (only the enol form was observed). A similar observation was made for all similar derivatives.

4. Conclusion

We have demonstrated the successful characterization of synthesized TBA derivatives by various spectroscopic techniques. UV spectroscopy explained the absorptivity for the TBA derivatives at different wavelengths depending on the structure. The $\lambda_{\max}$ for the TBA derivatives did not reveal any significant shift with change of solvent. Intramolecular hydrogen bonding is observed in all cases (**A01**, **A02**, **A06**, **A13**, **A17** and **A18**) and intermolecular hydrogen bonding is also observed for **A17**. In **A13**, the presence of two intramolecular hydrogen bonds was observed. Acylation with simple carboxylic acid derivatives afforded the enamine, as shown by ^{1}H NMR spectroscopy and X-ray crystallography. The preference of the enol over the keto form was confirmed using the *GAUSSIAN09* program package. To convert the keto form to the enol form, an energy barrier of 55.05 kcal mol^{-1} needs to be overcome, as confirmed by transition-state calculations. These studies provide an insight into the field of materials science, since TBA derivatives possess good NLO properties and corrosion inhibition properties. These results also support the application of TBA derivatives in the design of engineering materials due to their possessing both hydrogen-bond donors and acceptors.

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supporting information

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Crystal structure, spectroscopic studies and theoretical studies of thiobarbituric acid derivatives: understanding the hydrogen-bonding patterns

Anamika Sharma, Sizwe J. Zamisa, Sikabwe Noki, Zainab Almarhoon, Ayman El-Faham, Beatriz G. de la Torre and Fernando Albericio

Computing details

For all structures, data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT-Plus* (Bruker, 2008); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 2008); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015b); molecular graphics: *ORTEP-3* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

5-Acetyl-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (A01)

Crystal data

$C_{10}H_{14}N_2O_3S$
$M_r = 242.29$
Monoclinic, $P2_1/n$
$a = 4.6212\ (1)$ Å
$b = 12.5742\ (4)$ Å
$c = 19.3936\ (6)$ Å
$\beta = 92.869\ (1)°$
$V = 1125.51\ (6)$ Å^3
$Z = 4$
$F(000) = 512$
$D_x = 1.430$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8036 reflections
$\theta = 2.7–28.3°$
$\mu = 0.28$ mm^{-1}
$T = 100$ K
Rod, colourless
0.29 × 0.23 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2012)
$T_{min} = 0.911$, $T_{max} = 0.978$
14896 measured reflections
2704 independent reflections
2309 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 28.3°$, $\theta_{min} = 1.9°$
$h = -5\rightarrow6$
$k = -16\rightarrow15$
$l = -25\rightarrow24$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.085$
$S = 1.05$
2704 reflections
146 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 0.5533P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. School of Chemsitry and Physics University of KwaZulu-Natal Private Bag X 54001 Durban 4000

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
C1	0.7202 (3)	0.48420 (11)	0.60194 (7)	0.0266 (3)
H1A	0.8478	0.4238	0.6134	0.040*
H1B	0.5607	0.4853	0.6334	0.040*
H1C	0.6415	0.4771	0.5543	0.040*
C2	0.8914 (3)	0.58714 (10)	0.60935 (7)	0.0210 (3)
H2A	0.9735	0.5935	0.6573	0.025*
H2B	1.0545	0.5853	0.5781	0.025*
C3	0.5442 (3)	0.72435 (9)	0.64289 (6)	0.0160 (2)
C4	0.2000 (3)	0.86382 (11)	0.67718 (7)	0.0221 (3)
H4A	0.1216	0.8095	0.7082	0.027*
H4B	0.0344	0.9021	0.6543	0.027*
C5	0.3853 (4)	0.94198 (11)	0.71960 (8)	0.0302 (3)
H5A	0.2676	0.9758	0.7541	0.045*
H5B	0.5475	0.9041	0.7430	0.045*
H5C	0.4603	0.9965	0.6891	0.045*
C6	0.3421 (3)	0.85049 (10)	0.55737 (6)	0.0174 (2)
C7	0.5078 (3)	0.80209 (9)	0.50516 (6)	0.0170 (2)
C8	0.7076 (3)	0.71693 (10)	0.52324 (6)	0.0183 (2)
C9	0.4614 (3)	0.83582 (10)	0.43682 (7)	0.0191 (2)
C10	0.6033 (3)	0.79100 (11)	0.37626 (7)	0.0251 (3)
H10A	0.4933	0.8115	0.3338	0.038*
H10B	0.6090	0.7133	0.3799	0.038*
H10C	0.8013	0.8186	0.3751	0.038*
N1	0.7069 (2)	0.68092 (8)	0.59257 (5)	0.0165 (2)
N2	0.3693 (2)	0.81041 (8)	0.62405 (5)	0.0167 (2)
O1	0.8729 (2)	0.67545 (8)	0.48428 (5)	0.0281 (2)
O2	0.1740 (2)	0.92637 (7)	0.54481 (5)	0.0236 (2)
O3	0.2780 (2)	0.91243 (8)	0.42115 (5)	0.0240 (2)
H3	0.2035	0.9341	0.4572	0.036*
S1	0.55504 (7)	0.67705 (2)	0.72282 (2)	0.02091 (10)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0310 (7)	0.0206 (6)	0.0278 (7)	0.0059 (5)	−0.0021 (5)	−0.0034 (5)
C2	0.0181 (6)	0.0226 (6)	0.0219 (6)	0.0061 (5)	−0.0021 (5)	0.0006 (5)
C3	0.0139 (5)	0.0162 (5)	0.0179 (6)	−0.0027 (4)	−0.0008 (4)	−0.0016 (4)
C4	0.0217 (6)	0.0239 (6)	0.0213 (6)	0.0049 (5)	0.0070 (5)	−0.0015 (5)

C5	0.0407 (9)	0.0231 (7)	0.0272 (7)	0.0010 (6)	0.0064 (6)	−0.0074 (5)
C6	0.0152 (6)	0.0182 (5)	0.0188 (6)	−0.0015 (4)	−0.0010 (4)	−0.0007 (4)
C7	0.0153 (6)	0.0188 (6)	0.0167 (6)	−0.0015 (4)	0.0000 (4)	−0.0001 (4)
C8	0.0165 (6)	0.0204 (6)	0.0178 (6)	−0.0007 (4)	0.0004 (4)	−0.0002 (5)
C9	0.0162 (6)	0.0214 (6)	0.0194 (6)	−0.0033 (4)	−0.0008 (4)	0.0009 (5)
C10	0.0277 (7)	0.0304 (7)	0.0170 (6)	0.0007 (5)	0.0007 (5)	0.0005 (5)
N1	0.0150 (5)	0.0175 (5)	0.0170 (5)	0.0019 (4)	−0.0004 (4)	0.0003 (4)
N2	0.0162 (5)	0.0175 (5)	0.0164 (5)	0.0014 (4)	0.0017 (4)	−0.0009 (4)
O1	0.0285 (5)	0.0351 (6)	0.0214 (5)	0.0119 (4)	0.0075 (4)	0.0014 (4)
O2	0.0239 (5)	0.0232 (5)	0.0235 (5)	0.0076 (4)	−0.0008 (4)	0.0018 (4)
O3	0.0247 (5)	0.0271 (5)	0.0200 (5)	0.0036 (4)	−0.0008 (4)	0.0028 (4)
S1	0.02501 (18)	0.02170 (17)	0.01597 (16)	−0.00059 (11)	0.00046 (11)	0.00196 (11)

Geometric parameters (Å, º)

C1—C2	1.5202 (19)	C5—H5B	0.9800
C1—H1A	0.9800	C5—H5C	0.9800
C1—H1B	0.9800	C6—O2	1.2469 (15)
C1—H1C	0.9800	C6—N2	1.3877 (16)
C2—N1	1.4818 (15)	C6—C7	1.4350 (17)
C2—H2A	0.9900	C7—C9	1.3979 (17)
C2—H2B	0.9900	C7—C8	1.4457 (17)
C3—N1	1.3746 (16)	C8—O1	1.2184 (16)
C3—N2	1.3887 (15)	C8—N1	1.4188 (16)
C3—S1	1.6588 (12)	C9—O3	1.3089 (15)
C4—N2	1.4849 (15)	C9—C10	1.4847 (18)
C4—C5	1.518 (2)	C10—H10A	0.9800
C4—H4A	0.9900	C10—H10B	0.9800
C4—H4B	0.9900	C10—H10C	0.9800
C5—H5A	0.9800	O3—H3	0.8400

C2—C1—H1A	109.5	H5B—C5—H5C	109.5
C2—C1—H1B	109.5	O2—C6—N2	119.10 (11)
H1A—C1—H1B	109.5	O2—C6—C7	122.41 (11)
C2—C1—H1C	109.5	N2—C6—C7	118.49 (11)
H1A—C1—H1C	109.5	C9—C7—C6	118.59 (11)
H1B—C1—H1C	109.5	C9—C7—C8	121.36 (11)
N1—C2—C1	111.45 (10)	C6—C7—C8	119.99 (11)
N1—C2—H2A	109.3	O1—C8—N1	118.83 (11)
C1—C2—H2A	109.3	O1—C8—C7	125.41 (12)
N1—C2—H2B	109.3	N1—C8—C7	115.75 (11)
C1—C2—H2B	109.3	O3—C9—C7	120.68 (12)
H2A—C2—H2B	108.0	O3—C9—C10	113.72 (11)
N1—C3—N2	117.05 (10)	C7—C9—C10	125.59 (12)
N1—C3—S1	121.94 (9)	C9—C10—H10A	109.5
N2—C3—S1	121.01 (9)	C9—C10—H10B	109.5
N2—C4—C5	111.49 (11)	H10A—C10—H10B	109.5
N2—C4—H4A	109.3	C9—C10—H10C	109.5

C5—C4—H4A	109.3	H10A—C10—H10C	109.5
N2—C4—H4B	109.3	H10B—C10—H10C	109.5
C5—C4—H4B	109.3	C3—N1—C8	124.98 (10)
H4A—C4—H4B	108.0	C3—N1—C2	119.30 (10)
C4—C5—H5A	109.5	C8—N1—C2	115.70 (10)
C4—C5—H5B	109.5	C6—N2—C3	123.53 (10)
H5A—C5—H5B	109.5	C6—N2—C4	117.14 (10)
C4—C5—H5C	109.5	C3—N2—C4	119.33 (10)
H5A—C5—H5C	109.5	C9—O3—H3	109.5

O2—C6—C7—C9	−5.16 (18)	O1—C8—N1—C3	176.16 (12)
N2—C6—C7—C9	174.28 (11)	C7—C8—N1—C3	−3.50 (17)
O2—C6—C7—C8	177.67 (11)	O1—C8—N1—C2	−5.83 (17)
N2—C6—C7—C8	−2.89 (17)	C7—C8—N1—C2	174.51 (10)
C9—C7—C8—O1	8.3 (2)	C1—C2—N1—C3	84.75 (14)
C6—C7—C8—O1	−174.57 (12)	C1—C2—N1—C8	−93.38 (13)
C9—C7—C8—N1	−172.03 (11)	O2—C6—N2—C3	178.14 (11)
C6—C7—C8—N1	5.06 (17)	C7—C6—N2—C3	−1.32 (17)
C6—C7—C9—O3	2.29 (18)	O2—C6—N2—C4	−1.88 (17)
C8—C7—C9—O3	179.42 (11)	C7—C6—N2—C4	178.66 (11)
C6—C7—C9—C10	−177.00 (12)	N1—C3—N2—C6	2.99 (17)
C8—C7—C9—C10	0.13 (19)	S1—C3—N2—C6	−177.18 (9)
N2—C3—N1—C8	−0.42 (17)	N1—C3—N2—C4	−176.99 (10)
S1—C3—N1—C8	179.74 (9)	S1—C3—N2—C4	2.84 (15)
N2—C3—N1—C2	−178.36 (10)	C5—C4—N2—C6	−98.68 (13)
S1—C3—N1—C2	1.80 (15)	C5—C4—N2—C3	81.30 (14)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5*B*···S1	0.98	2.88	3.4223 (15)	116
C10—H10*A*···S1^{i}	0.98	2.88	3.8316 (14)	163
O3—H3···O2	0.84	1.71	2.4756 (13)	150
O3—H3···O2^{ii}	0.84	2.47	3.0073 (13)	122

Symmetry codes: (i) $x-1/2, -y+3/2, z-1/2$; (ii) $-x, -y+2, -z+1$.

1,3-Diethyl-5-propionyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (A02)

Crystal data

$C_{11}H_{16}N_2O_3S$	$F(000) = 272$
$M_r = 256.32$	$D_x = 1.409$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 4.9140$ (1) Å	Cell parameters from 7194 reflections
$b = 12.9450$ (3) Å	$\theta = 2.7–27.5°$
$c = 9.7630$ (3) Å	$\mu = 0.27$ mm^{-1}
$\beta = 103.474$ (1)°	$T = 100$ K
$V = 603.95$ (3) Å^3	Block, colourless
$Z = 2$	0.19 × 0.14 × 0.07 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2012)
$T_{\mathrm{min}} = 0.940$, $T_{\mathrm{max}} = 0.991$

8623 measured reflections
8623 independent reflections
8469 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.000$
$\theta_{\mathrm{max}} = 27.5°$, $\theta_{\mathrm{min}} = 2.2°$
$h = -6 \rightarrow 6$
$k = -16 \rightarrow 16$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.070$
$S = 1.09$
8623 reflections
158 parameters
1 restraint
Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 0.0526P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\mathrm{max}} < 0.001$
$\Delta\rho_{\mathrm{max}} = 0.21$ e Å^{-3}
$\Delta\rho_{\mathrm{min}} = -0.26$ e Å^{-3}
Absolute structure: Flack *x* determined using 1252 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: 0.034 (16)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.3177 (3)	0.72567 (12)	0.49804 (17)	0.0214 (4)
O2	0.1016 (3)	0.37732 (11)	0.38393 (16)	0.0186 (3)
C5	0.1988 (4)	0.54922 (16)	0.4577 (2)	0.0146 (4)
N2	0.4821 (4)	0.64360 (14)	0.32802 (19)	0.0155 (4)
C1	−0.1348 (5)	0.58442 (19)	0.7760 (3)	0.0281 (6)
H1A	−0.030796	0.526690	0.828470	0.042*
H1B	−0.324936	0.561794	0.730933	0.042*
H1C	−0.143850	0.641443	0.840824	0.042*
C2	0.0123 (4)	0.62058 (18)	0.6641 (2)	0.0191 (5)
H2A	−0.093981	0.679108	0.612254	0.023*
H2B	0.200516	0.646446	0.711133	0.023*
C3	0.0435 (4)	0.53884 (15)	0.5607 (2)	0.0159 (4)
C4	0.2242 (4)	0.46125 (17)	0.3735 (2)	0.0155 (4)
N1	0.3909 (3)	0.46756 (14)	0.27790 (19)	0.0157 (4)
C6	0.4312 (4)	0.37043 (16)	0.2038 (2)	0.0176 (5)
H6A	0.434322	0.311261	0.268416	0.021*
H6B	0.614315	0.372912	0.178006	0.021*
C7	0.2017 (4)	0.35365 (19)	0.0718 (2)	0.0234 (5)
H7A	0.020823	0.347983	0.097378	0.035*
H7B	0.238772	0.289922	0.025153	0.035*

H7C	0.197113	0.412224	0.007745	0.035*
C8	0.5062 (4)	0.55963 (19)	0.2455 (2)	0.0160 (4)
C9	0.3308 (4)	0.64530 (17)	0.4348 (2)	0.0158 (4)
O3	−0.0832 (3)	0.45221 (11)	0.57302 (17)	0.0198 (3)
H3	−0.053435	0.409823	0.513011	0.030*
C11	0.6030 (4)	0.74399 (18)	0.2997 (2)	0.0198 (5)
H11A	0.771894	0.731567	0.263124	0.024*
H11B	0.660559	0.783241	0.388804	0.024*
C12	0.3955 (5)	0.80712 (19)	0.1941 (3)	0.0261 (5)
H12A	0.334132	0.767587	0.106781	0.039*
H12B	0.484358	0.871449	0.174372	0.039*
H12C	0.233420	0.823310	0.232739	0.039*
S1	0.66844 (10)	0.56606 (5)	0.11383 (6)	0.02182 (15)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0278 (8)	0.0164 (8)	0.0221 (8)	−0.0033 (6)	0.0104 (7)	−0.0031 (6)
O2	0.0214 (7)	0.0139 (7)	0.0221 (8)	−0.0018 (6)	0.0085 (6)	0.0006 (6)
C5	0.0156 (8)	0.0131 (12)	0.0152 (9)	0.0000 (8)	0.0036 (7)	0.0004 (8)
N2	0.0164 (8)	0.0136 (9)	0.0172 (10)	−0.0022 (7)	0.0053 (7)	−0.0004 (7)
C1	0.0436 (13)	0.0212 (14)	0.0252 (12)	0.0035 (10)	0.0193 (11)	0.0023 (9)
C2	0.0241 (10)	0.0177 (11)	0.0176 (11)	0.0017 (9)	0.0090 (9)	−0.0006 (8)
C3	0.0150 (9)	0.0154 (11)	0.0166 (10)	0.0025 (8)	0.0022 (8)	0.0027 (8)
C4	0.0133 (9)	0.0162 (10)	0.0164 (10)	0.0025 (8)	0.0020 (8)	0.0035 (8)
N1	0.0180 (9)	0.0138 (9)	0.0161 (9)	0.0020 (7)	0.0056 (7)	−0.0005 (7)
C6	0.0198 (10)	0.0127 (11)	0.0217 (11)	0.0033 (8)	0.0080 (9)	−0.0015 (8)
C7	0.0252 (11)	0.0235 (13)	0.0217 (12)	0.0033 (9)	0.0056 (9)	−0.0043 (10)
C8	0.0135 (8)	0.0163 (10)	0.0178 (10)	0.0018 (9)	0.0027 (8)	0.0007 (9)
C9	0.0150 (9)	0.0166 (11)	0.0152 (11)	0.0012 (8)	0.0021 (8)	0.0015 (9)
O3	0.0249 (8)	0.0143 (8)	0.0234 (9)	−0.0015 (6)	0.0122 (7)	−0.0008 (6)
C11	0.0228 (10)	0.0165 (11)	0.0218 (12)	−0.0057 (8)	0.0089 (9)	0.0003 (9)
C12	0.0334 (12)	0.0172 (12)	0.0320 (14)	0.0044 (10)	0.0163 (11)	0.0074 (10)
S1	0.0268 (3)	0.0199 (3)	0.0233 (3)	0.0010 (2)	0.0151 (2)	0.0016 (2)

Geometric parameters (Å, º)

O1—C9	1.219 (3)	N1—C8	1.388 (3)
O2—C4	1.258 (3)	N1—C6	1.487 (3)
C5—C3	1.403 (3)	C6—C7	1.517 (3)
C5—C4	1.427 (3)	C6—H6A	0.9900
C5—C9	1.444 (3)	C6—H6B	0.9900
N2—C8	1.375 (3)	C7—H7A	0.9800
N2—C9	1.415 (3)	C7—H7B	0.9800
N2—C11	1.481 (3)	C7—H7C	0.9800
C1—C2	1.518 (3)	C8—S1	1.665 (2)
C1—H1A	0.9800	O3—H3	0.8400
C1—H1B	0.9800	C11—C12	1.510 (3)

C1—H1C	0.9800	C11—H11A	0.9900
C2—C3	1.495 (3)	C11—H11B	0.9900
C2—H2A	0.9900	C12—H12A	0.9800
C2—H2B	0.9900	C12—H12B	0.9800
C3—O3	1.302 (2)	C12—H12C	0.9800
C4—N1	1.380 (3)		

C3—C5—C4	118.13 (18)	C7—C6—H6A	109.2
C3—C5—C9	122.15 (18)	N1—C6—H6B	109.2
C4—C5—C9	119.72 (18)	C7—C6—H6B	109.2
C8—N2—C9	125.18 (18)	H6A—C6—H6B	107.9
C8—N2—C11	119.42 (17)	C6—C7—H7A	109.5
C9—N2—C11	115.24 (18)	C6—C7—H7B	109.5
C2—C1—H1A	109.5	H7A—C7—H7B	109.5
C2—C1—H1B	109.5	C6—C7—H7C	109.5
H1A—C1—H1B	109.5	H7A—C7—H7C	109.5
C2—C1—H1C	109.5	H7B—C7—H7C	109.5
H1A—C1—H1C	109.5	N2—C8—N1	116.74 (17)
H1B—C1—H1C	109.5	N2—C8—S1	122.36 (17)
C3—C2—C1	114.14 (19)	N1—C8—S1	120.90 (17)
C3—C2—H2A	108.7	O1—C9—N2	119.02 (19)
C1—C2—H2A	108.7	O1—C9—C5	125.34 (19)
C3—C2—H2B	108.7	N2—C9—C5	115.63 (18)
C1—C2—H2B	108.7	C3—O3—H3	109.5
H2A—C2—H2B	107.6	N2—C11—C12	111.45 (17)
O3—C3—C5	120.04 (19)	N2—C11—H11A	109.3
O3—C3—C2	114.87 (18)	C12—C11—H11A	109.3
C5—C3—C2	125.08 (18)	N2—C11—H11B	109.3
O2—C4—N1	118.5 (2)	C12—C11—H11B	109.3
O2—C4—C5	122.33 (19)	H11A—C11—H11B	108.0
N1—C4—C5	119.19 (18)	C11—C12—H12A	109.5
C4—N1—C8	122.91 (18)	C11—C12—H12B	109.5
C4—N1—C6	116.51 (17)	H12A—C12—H12B	109.5
C8—N1—C6	120.51 (17)	C11—C12—H12C	109.5
N1—C6—C7	112.16 (17)	H12A—C12—H12C	109.5
N1—C6—H6A	109.2	H12B—C12—H12C	109.5

C4—C5—C3—O3	−3.1 (3)	C11—N2—C8—N1	179.47 (16)
C9—C5—C3—O3	176.66 (18)	C9—N2—C8—S1	175.37 (14)
C4—C5—C3—C2	175.57 (18)	C11—N2—C8—S1	0.2 (3)
C9—C5—C3—C2	−4.6 (3)	C4—N1—C8—N2	9.3 (3)
C1—C2—C3—O3	6.4 (3)	C6—N1—C8—N2	−173.90 (16)
C1—C2—C3—C5	−172.34 (19)	C4—N1—C8—S1	−171.45 (15)
C3—C5—C4—O2	3.6 (3)	C6—N1—C8—S1	5.3 (3)
C9—C5—C4—O2	−176.22 (18)	C8—N2—C9—O1	−177.70 (19)
C3—C5—C4—N1	−175.80 (18)	C11—N2—C9—O1	−2.4 (3)
C9—C5—C4—N1	4.4 (3)	C8—N2—C9—C5	1.3 (3)
O2—C4—N1—C8	171.61 (18)	C11—N2—C9—C5	176.63 (16)

C5—C4—N1—C8	−9.0 (3)	C3—C5—C9—O1	−1.6 (3)
O2—C4—N1—C6	−5.3 (3)	C4—C5—C9—O1	178.24 (19)
C5—C4—N1—C6	174.09 (16)	C3—C5—C9—N2	179.51 (18)
C4—N1—C6—C7	87.0 (2)	C4—C5—C9—N2	−0.7 (3)
C8—N1—C6—C7	−90.0 (2)	C8—N2—C11—C12	88.9 (2)
C9—N2—C8—N1	−5.4 (3)	C9—N2—C11—C12	−86.7 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*A*···O2^{i}	0.99	2.57	3.385 (3)	140
C6—H6*A*···O1^{ii}	0.99	2.57	3.440 (3)	146
C11—H11*B*···O2^{iii}	0.99	2.56	3.541 (3)	170
O3—H3···O2	0.84	1.67	2.440 (2)	151

Symmetry codes: (i) $-x, y+1/2, -z+1$; (ii) $-x+1, y-1/2, -z+1$; (iii) $-x+1, y+1/2, -z+1$.

tert-Butyl [1-(1,3-diethyl-4,6-dioxo-2-thioxohexahydropyrimidin-5-yl)-3-methyl-1-oxobutan-2-yl)carbamate (A06)

Crystal data

$C_{18}H_{29}N_3O_5S$
$M_r = 399.50$
Orthorhombic, $P2_12_12_1$
$a = 8.3816$ (12) Å
$b = 9.6258$ (14) Å
$c = 24.297$ (3) Å
$V = 1960.3$ (5) Å^3
$Z = 4$
$F(000) = 856$
$D_x = 1.354$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9709 reflections
$\theta = 2.3$–27.6°
$\mu = 0.20$ mm^{-1}
$T = 100$ K
Block, colourless
0.33 × 0.25 × 0.21 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2012)
$T_{min} = 0.925$, $T_{max} = 0.968$
15360 measured reflections
15360 independent reflections
14556 reflections with $I > 2\sigma(I)$
$R_{int} = 0.000$
$\theta_{max} = 27.7°$, $\theta_{min} = 2.3°$
$h = -10 \rightarrow 8$
$k = -12 \rightarrow 12$
$l = -31 \rightarrow 28$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.070$
$S = 1.04$
15360 reflections
264 parameters
5 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0272P)^2 + 0.5031P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Absolute structure: Flack *x* determined using 1707 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: 0.001 (2)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.2383 (3)	0.8543 (3)	0.93914 (10)	0.0272 (6)	
H1A	0.176111	0.780871	0.921212	0.041*	
H1B	0.165661	0.921401	0.956221	0.041*	
H1C	0.306906	0.813187	0.967456	0.041*	
C2	0.3395 (3)	0.9267 (2)	0.89713 (9)	0.0179 (5)	
H2A	0.269559	0.974270	0.870259	0.021*	
H2B	0.405263	0.998194	0.915642	0.021*	
C8	0.3789 (3)	0.7723 (2)	0.81999 (9)	0.0147 (5)	
C9	0.4471 (3)	0.6340 (2)	0.73724 (9)	0.0157 (5)	
C10	0.2971 (2)	0.6640 (2)	0.70544 (9)	0.0154 (5)	
H10	0.244444	0.748873	0.720766	0.018*	
C15	0.6228 (3)	0.8459 (2)	0.56077 (10)	0.0204 (5)	
C14	0.4478 (3)	0.7825 (2)	0.63569 (9)	0.0170 (5)	
C17	0.6270 (3)	0.7970 (3)	0.50255 (10)	0.0302 (6)	
H17A	0.528464	0.824740	0.483854	0.045*	
H17B	0.636686	0.695525	0.501853	0.045*	
H17C	0.718745	0.838476	0.483697	0.045*	
C3	0.5935 (3)	0.8077 (2)	0.88664 (9)	0.0172 (5)	
C6	0.6383 (3)	0.6611 (2)	0.80864 (9)	0.0170 (5)	
N2	0.6884 (2)	0.72189 (19)	0.85597 (8)	0.0165 (4)	
C4	0.8554 (3)	0.6961 (3)	0.87195 (10)	0.0249 (6)	
H4A	0.894512	0.774890	0.894399	0.030*	
H4B	0.922293	0.690459	0.838428	0.030*	
C5	0.8721 (3)	0.5651 (3)	0.90395 (12)	0.0366 (7)	
H5A	0.839680	0.486213	0.881032	0.055*	
H5B	0.804131	0.569445	0.936715	0.055*	
H5C	0.983622	0.553283	0.915187	0.055*	
C11	0.1811 (3)	0.5412 (2)	0.70810 (10)	0.0190 (5)	
H11	0.228993	0.463815	0.686188	0.023*	
C12	0.1553 (3)	0.4880 (3)	0.76531 (10)	0.0252 (6)	
H12A	0.079967	0.410248	0.764402	0.038*	
H12B	0.111986	0.562602	0.788342	0.038*	
H12C	0.257240	0.456467	0.780629	0.038*	
C13	0.0255 (3)	0.5789 (3)	0.68128 (11)	0.0294 (6)	
H13A	0.045063	0.607953	0.643222	0.044*	
H13B	−0.024473	0.655239	0.701633	0.044*	
H13C	−0.045504	0.498008	0.681496	0.044*	
C18	0.5949 (3)	0.9999 (2)	0.56391 (12)	0.0336 (7)	
H18A	0.676742	1.048385	0.542446	0.050*	

H18B	0.600427	1.030111	0.602386	0.050*	
H18C	0.489215	1.021770	0.548949	0.050*	
C16	0.7711 (3)	0.8032 (3)	0.59051 (11)	0.0279 (6)	
H16A	0.782223	0.701934	0.588917	0.042*	
H16B	0.764416	0.832903	0.629021	0.042*	
H16C	0.863932	0.846781	0.573080	0.042*	
N1	0.4442 (2)	0.83019 (18)	0.86787 (7)	0.0140 (4)	
C7	0.4840 (3)	0.6877 (2)	0.78880 (9)	0.0139 (5)	
N3	0.3372 (2)	0.6871 (2)	0.64868 (8)	0.0170 (4)	
O1	0.24103 (17)	0.79625 (16)	0.80922 (6)	0.0184 (4)	
O2	0.73574 (18)	0.58447 (17)	0.78407 (7)	0.0210 (4)	
O3	0.54486 (19)	0.55537 (17)	0.71284 (7)	0.0203 (4)	
O4	0.50057 (18)	0.86552 (17)	0.66745 (6)	0.0223 (4)	
O5	0.48618 (18)	0.77041 (17)	0.58289 (6)	0.0192 (4)	
S1	0.66106 (8)	0.88046 (6)	0.94304 (3)	0.02442 (16)	
H3	0.327 (3)	0.624 (2)	0.6266 (9)	0.027 (7)*	
H2	0.695 (3)	0.563 (5)	0.7528 (9)	0.03 (2)*	0.50 (7)
H3A	0.627 (3)	0.549 (5)	0.7338 (10)	0.03 (2)*	0.50 (7)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0309 (14)	0.0277 (13)	0.0229 (13)	0.0047 (12)	0.0080 (12)	−0.0008 (12)
C2	0.0224 (12)	0.0172 (11)	0.0141 (12)	0.0049 (11)	0.0003 (10)	−0.0028 (9)
C8	0.0179 (12)	0.0122 (10)	0.0141 (11)	−0.0019 (10)	0.0012 (10)	0.0018 (9)
C9	0.0157 (12)	0.0134 (11)	0.0179 (12)	−0.0023 (11)	0.0042 (9)	0.0013 (10)
C10	0.0150 (12)	0.0169 (12)	0.0142 (11)	−0.0007 (9)	−0.0004 (9)	−0.0017 (10)
C15	0.0230 (12)	0.0185 (11)	0.0196 (12)	−0.0056 (10)	0.0075 (11)	0.0014 (10)
C14	0.0179 (12)	0.0176 (11)	0.0155 (12)	0.0025 (11)	−0.0008 (10)	0.0002 (10)
C17	0.0366 (16)	0.0328 (15)	0.0211 (13)	−0.0102 (13)	0.0074 (12)	−0.0023 (12)
C3	0.0217 (13)	0.0130 (11)	0.0168 (12)	−0.0013 (10)	−0.0012 (10)	0.0031 (10)
C6	0.0191 (12)	0.0148 (11)	0.0172 (12)	−0.0009 (10)	0.0021 (10)	0.0014 (9)
N2	0.0139 (10)	0.0171 (9)	0.0186 (10)	0.0012 (8)	−0.0026 (8)	−0.0002 (9)
C4	0.0152 (12)	0.0308 (14)	0.0286 (14)	0.0040 (12)	−0.0070 (11)	−0.0051 (12)
C5	0.0322 (15)	0.0345 (15)	0.0430 (18)	0.0137 (13)	−0.0141 (14)	−0.0005 (14)
C11	0.0184 (12)	0.0192 (12)	0.0192 (13)	−0.0032 (10)	0.0012 (10)	−0.0004 (10)
C12	0.0254 (13)	0.0251 (13)	0.0251 (14)	−0.0051 (12)	0.0032 (11)	0.0050 (11)
C13	0.0205 (13)	0.0364 (15)	0.0314 (15)	−0.0089 (12)	−0.0048 (11)	0.0080 (13)
C18	0.0482 (17)	0.0222 (13)	0.0304 (16)	−0.0015 (13)	0.0112 (14)	0.0046 (12)
C16	0.0215 (13)	0.0319 (15)	0.0303 (15)	−0.0054 (12)	0.0054 (11)	−0.0049 (13)
N1	0.0149 (10)	0.0143 (9)	0.0128 (9)	0.0016 (8)	−0.0001 (8)	−0.0001 (8)
C7	0.0128 (11)	0.0143 (11)	0.0145 (11)	−0.0008 (9)	0.0008 (9)	0.0017 (9)
N3	0.0203 (10)	0.0178 (10)	0.0129 (10)	−0.0044 (9)	−0.0010 (9)	−0.0026 (9)
O1	0.0139 (8)	0.0234 (9)	0.0180 (9)	0.0036 (7)	−0.0011 (7)	−0.0028 (7)
O2	0.0167 (8)	0.0258 (10)	0.0205 (10)	0.0058 (7)	0.0008 (8)	−0.0050 (8)
O3	0.0172 (9)	0.0247 (9)	0.0190 (9)	0.0048 (8)	−0.0003 (8)	−0.0065 (7)
O4	0.0264 (9)	0.0207 (8)	0.0199 (9)	−0.0064 (8)	0.0019 (7)	−0.0045 (8)
O5	0.0211 (9)	0.0230 (9)	0.0134 (8)	−0.0070 (7)	0.0028 (7)	−0.0002 (7)

S1	0.0295 (3)	0.0236 (3)	0.0201 (3)	0.0030 (3)	−0.0098 (3)	−0.0048 (3)

Geometric parameters (Å, º)

C1—C2	1.499 (3)	C6—O2	1.252 (3)
C1—H1A	0.9800	C6—N2	1.357 (3)
C1—H1B	0.9800	C6—C7	1.404 (3)
C1—H1C	0.9800	N2—C4	1.474 (3)
C2—N1	1.462 (3)	C4—C5	1.488 (3)
C2—H2A	0.9900	C4—H4A	0.9900
C2—H2B	0.9900	C4—H4B	0.9900
C8—O1	1.207 (3)	C5—H5A	0.9800
C8—N1	1.401 (3)	C5—H5B	0.9800
C8—C7	1.419 (3)	C5—H5C	0.9800
C9—O3	1.263 (3)	C11—C12	1.497 (3)
C9—C7	1.390 (3)	C11—C13	1.502 (3)
C9—C10	1.504 (3)	C11—H11	1.0000
C10—N3	1.437 (3)	C12—H12A	0.9800
C10—C11	1.532 (3)	C12—H12B	0.9800
C10—H10	1.0000	C12—H12C	0.9800
C15—O5	1.459 (3)	C13—H13A	0.9800
C15—C17	1.491 (3)	C13—H13B	0.9800
C15—C16	1.496 (3)	C13—H13C	0.9800
C15—C18	1.503 (3)	C18—H18A	0.9800
C14—O4	1.196 (3)	C18—H18B	0.9800
C14—O5	1.328 (3)	C18—H18C	0.9800
C14—N3	1.343 (3)	C16—H16A	0.9800
C17—H17A	0.9800	C16—H16B	0.9800
C17—H17B	0.9800	C16—H16C	0.9800
C17—H17C	0.9800	N3—H3	0.816 (18)
C3—N1	1.349 (3)	O2—H2	0.860 (3)
C3—N2	1.368 (3)	O3—H3A	0.860 (3)
C3—S1	1.640 (2)		
C2—C1—H1A	109.5	N2—C4—H4B	109.3
C2—C1—H1B	109.5	C5—C4—H4B	109.3
H1A—C1—H1B	109.5	H4A—C4—H4B	107.9
C2—C1—H1C	109.5	C4—C5—H5A	109.5
H1A—C1—H1C	109.5	C4—C5—H5B	109.5
H1B—C1—H1C	109.5	H5A—C5—H5B	109.5
N1—C2—C1	112.05 (19)	C4—C5—H5C	109.5
N1—C2—H2A	109.2	H5A—C5—H5C	109.5
C1—C2—H2A	109.2	H5B—C5—H5C	109.5
N1—C2—H2B	109.2	C12—C11—C13	111.1 (2)
C1—C2—H2B	109.2	C12—C11—C10	113.2 (2)
H2A—C2—H2B	107.9	C13—C11—C10	110.26 (19)
O1—C8—N1	118.5 (2)	C12—C11—H11	107.3
O1—C8—C7	126.0 (2)	C13—C11—H11	107.3

N1—C8—C7	115.43 (19)	C10—C11—H11	107.3
O3—C9—C7	120.1 (2)	C11—C12—H12A	109.5
O3—C9—C10	114.61 (19)	C11—C12—H12B	109.5
C7—C9—C10	125.3 (2)	H12A—C12—H12B	109.5
N3—C10—C9	109.09 (18)	C11—C12—H12C	109.5
N3—C10—C11	107.94 (19)	H12A—C12—H12C	109.5
C9—C10—C11	111.15 (18)	H12B—C12—H12C	109.5
N3—C10—H10	109.5	C11—C13—H13A	109.5
C9—C10—H10	109.5	C11—C13—H13B	109.5
C11—C10—H10	109.5	H13A—C13—H13B	109.5
O5—C15—C17	102.17 (18)	C11—C13—H13C	109.5
O5—C15—C16	109.71 (18)	H13A—C13—H13C	109.5
C17—C15—C16	110.6 (2)	H13B—C13—H13C	109.5
O5—C15—C18	110.53 (19)	C15—C18—H18A	109.5
C17—C15—C18	111.3 (2)	C15—C18—H18B	109.5
C16—C15—C18	112.1 (2)	H18A—C18—H18B	109.5
O4—C14—O5	126.3 (2)	C15—C18—H18C	109.5
O4—C14—N3	124.1 (2)	H18A—C18—H18C	109.5
O5—C14—N3	109.6 (2)	H18B—C18—H18C	109.5
C15—C17—H17A	109.5	C15—C16—H16A	109.5
C15—C17—H17B	109.5	C15—C16—H16B	109.5
H17A—C17—H17B	109.5	H16A—C16—H16B	109.5
C15—C17—H17C	109.5	C15—C16—H16C	109.5
H17A—C17—H17C	109.5	H16A—C16—H16C	109.5
H17B—C17—H17C	109.5	H16B—C16—H16C	109.5
N1—C3—N2	116.87 (19)	C3—N1—C8	125.37 (18)
N1—C3—S1	122.31 (17)	C3—N1—C2	119.59 (19)
N2—C3—S1	120.81 (17)	C8—N1—C2	114.98 (17)
O2—C6—N2	117.1 (2)	C9—C7—C6	116.5 (2)
O2—C6—C7	123.0 (2)	C9—C7—C8	123.8 (2)
N2—C6—C7	119.8 (2)	C6—C7—C8	119.6 (2)
C6—N2—C3	122.84 (19)	C14—N3—C10	119.53 (19)
C6—N2—C4	116.39 (19)	C14—N3—H3	115.5 (18)
C3—N2—C4	120.72 (19)	C10—N3—H3	119.3 (18)
N2—C4—C5	111.7 (2)	C6—O2—H2	107.6 (4)
N2—C4—H4A	109.3	C9—O3—H3A	106.6 (4)
C5—C4—H4A	109.3	C14—O5—C15	120.17 (18)

O3—C9—C10—N3	−41.3 (3)	C7—C8—N1—C2	174.93 (18)
C7—C9—C10—N3	137.3 (2)	C1—C2—N1—C3	−92.5 (2)
O3—C9—C10—C11	77.6 (2)	C1—C2—N1—C8	90.1 (2)
C7—C9—C10—C11	−103.8 (3)	O3—C9—C7—C6	6.1 (3)
O2—C6—N2—C3	−180.0 (2)	C10—C9—C7—C6	−172.4 (2)
C7—C6—N2—C3	1.2 (3)	O3—C9—C7—C8	−177.47 (19)
O2—C6—N2—C4	2.8 (3)	C10—C9—C7—C8	4.0 (3)
C7—C6—N2—C4	−176.0 (2)	O2—C6—C7—C9	−5.4 (3)
N1—C3—N2—C6	0.2 (3)	N2—C6—C7—C9	173.3 (2)
S1—C3—N2—C6	−179.03 (17)	O2—C6—C7—C8	178.0 (2)

N1—C3—N2—C4	177.34 (19)	N2—C6—C7—C8	−3.3 (3)
S1—C3—N2—C4	−1.9 (3)	O1—C8—C7—C9	8.4 (4)
C6—N2—C4—C5	−86.0 (3)	N1—C8—C7—C9	−172.6 (2)
C3—N2—C4—C5	96.7 (3)	O1—C8—C7—C6	−175.3 (2)
N3—C10—C11—C12	168.4 (2)	N1—C8—C7—C6	3.7 (3)
C9—C10—C11—C12	48.8 (3)	O4—C14—N3—C10	−11.4 (3)
N3—C10—C11—C13	−66.4 (2)	O5—C14—N3—C10	169.31 (19)
C9—C10—C11—C13	174.0 (2)	C9—C10—N3—C14	−53.7 (3)
N2—C3—N1—C8	0.4 (3)	C11—C10—N3—C14	−174.61 (19)
S1—C3—N1—C8	179.63 (17)	O4—C14—O5—C15	11.1 (3)
N2—C3—N1—C2	−176.76 (18)	N3—C14—O5—C15	−169.58 (18)
S1—C3—N1—C2	2.5 (3)	C17—C15—O5—C14	177.0 (2)
O1—C8—N1—C3	176.7 (2)	C16—C15—O5—C14	59.7 (3)
C7—C8—N1—C3	−2.3 (3)	C18—C15—O5—C14	−64.4 (3)
O1—C8—N1—C2	−6.0 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10···O1	1.00	2.20	2.863 (3)	123
C11—H11···N2^{i}	1.00	2.64	3.615 (3)	166
C18—H18*A*···S1^{ii}	0.98	2.86	3.760 (3)	154
C18—H18*B*···O4	0.98	2.39	2.937 (3)	115
C16—H16*B*···O4	0.98	2.42	3.000 (3)	117
N3—H3···S1^{i}	0.82 (2)	2.89 (2)	3.698 (2)	170 (2)
O2—H2···O3	0.86 (1)	1.59 (1)	2.374 (2)	150 (1)
O3—H3*A*···O2	0.86 (1)	1.56 (1)	2.374 (2)	156 (1)

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+3/2; (ii) −*x*+3/2, −*y*+2, *z*−1/2.

1,3-Diethyl-4,6-dioxo-2-thioxo-<i.N-(p-tolyl)hexahydropyrimidine-5-carbothioamide (A13)

Crystal data

$C_{16}H_{19}N_3O_2S_2$
M_r = 349.46
Monoclinic, $P2_1/c$
a = 4.8156 (2) Å
b = 21.7395 (7) Å
c = 15.1912 (5) Å
β = 95.656 (1)°
V = 1582.61 (10) Å^3
Z = 4
F(000) = 736
D_x = 1.467 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 9954 reflections
θ = 2.3–28.6°
μ = 0.35 mm^{-1}
T = 100 K
Rod, yellow
0.19 × 0.12 × 0.11 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
φ and *ω* scans
Absorption correction: multi-scan (SADABS; Bruker, 2012)
T_{min} = 0.925, T_{max} = 0.976
25387 measured reflections
4036 independent reflections
3430 reflections with *I* > 2*σ*(*I*)
R_{int} = 0.027
θ_{max} = 28.7°, θ_{min} = 1.9°
h = −6→6
k = −28→29
l = −16→20

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.031$	$w = 1/[\sigma^2(F_o^2) + (0.0319P)^2 + 0.9919P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.078$	$(\Delta/\sigma)_{max} = 0.003$
$S = 1.04$	$\Delta\rho_{max} = 0.38$ e Å^{-3}
4036 reflections	$\Delta\rho_{min} = -0.25$ e Å^{-3}
212 parameters	
0 restraints	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	y	z	U_{iso}*/U_{eq}
C1	0.6364 (3)	0.05024 (7)	1.11011 (9)	0.0200 (3)
H1A	0.444617	0.059313	1.122381	0.030*
H1B	0.738110	0.031661	1.162536	0.030*
H1C	0.633537	0.021547	1.060273	0.030*
C2	0.7801 (3)	0.10933 (6)	1.08713 (9)	0.0165 (3)
H2B	0.802275	0.136248	1.139925	0.020*
H2C	0.968596	0.099599	1.070263	0.020*
C3	0.4240 (3)	0.18473 (6)	1.03472 (8)	0.0130 (2)
C4	0.2647 (3)	0.21854 (6)	0.96914 (8)	0.0122 (2)
C5	0.0575 (3)	0.26444 (6)	0.99080 (8)	0.0124 (2)
C6	−0.2913 (3)	0.33867 (6)	0.91476 (8)	0.0132 (3)
C7	−0.4266 (3)	0.34618 (6)	0.82949 (9)	0.0153 (3)
H7	−0.379058	0.320332	0.782841	0.018*
C8	−0.6294 (3)	0.39103 (6)	0.81270 (9)	0.0166 (3)
H8	−0.719285	0.395317	0.754494	0.020*
C9	−0.7045 (3)	0.43003 (6)	0.87935 (9)	0.0159 (3)
C10	−0.9212 (3)	0.47956 (7)	0.86014 (10)	0.0200 (3)
H10A	−1.107692	0.461102	0.855538	0.030*
H10B	−0.891626	0.499911	0.804258	0.030*
H10C	−0.904996	0.509862	0.908134	0.030*
C11	0.6700 (3)	0.12958 (6)	0.92701 (9)	0.0132 (2)
C12	0.5668 (3)	0.15332 (6)	0.76841 (8)	0.0148 (3)
H12A	0.767628	0.145225	0.764691	0.018*
H12B	0.516924	0.191291	0.734493	0.018*
C13	0.3974 (3)	0.09994 (7)	0.72690 (9)	0.0184 (3)
H13A	0.453484	0.061833	0.758223	0.028*
H13B	0.431028	0.096098	0.664552	0.028*
H13C	0.198559	0.107472	0.731147	0.028*
C14	0.3072 (3)	0.20499 (6)	0.87829 (8)	0.0124 (2)
C15	−0.5709 (3)	0.42136 (6)	0.96368 (9)	0.0187 (3)

H15	−0.621330	0.446804	1.010404	0.022*
C16	−0.3657 (3)	0.37673 (6)	0.98239 (9)	0.0183 (3)
H16	−0.277263	0.372309	1.040768	0.022*
N1	0.6200 (2)	0.14275 (5)	1.01321 (7)	0.0132 (2)
N2	−0.0813 (2)	0.29283 (5)	0.92183 (7)	0.0134 (2)
H2A	−0.032193	0.280534	0.870382	0.016*
N3	0.5180 (2)	0.16309 (5)	0.86255 (7)	0.0125 (2)
O1	0.1706 (2)	0.22802 (4)	0.81289 (6)	0.0156 (2)
O2	0.4004 (2)	0.18827 (4)	1.11873 (6)	0.0158 (2)
H2	0.282227	0.215350	1.127983	0.024*
S1	0.90026 (7)	0.07630 (2)	0.90407 (2)	0.01698 (9)
S2	−0.00427 (8)	0.27972 (2)	1.09736 (2)	0.01633 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0230 (8)	0.0181 (7)	0.0185 (7)	0.0025 (6)	0.0010 (6)	0.0038 (5)
C2	0.0157 (7)	0.0187 (7)	0.0143 (6)	0.0026 (5)	−0.0029 (5)	0.0022 (5)
C3	0.0126 (6)	0.0126 (6)	0.0137 (6)	−0.0027 (5)	0.0009 (5)	0.0000 (5)
C4	0.0134 (6)	0.0123 (6)	0.0108 (5)	−0.0010 (5)	0.0011 (5)	−0.0007 (4)
C5	0.0133 (6)	0.0116 (6)	0.0125 (6)	−0.0027 (5)	0.0015 (5)	−0.0009 (4)
C6	0.0134 (6)	0.0121 (6)	0.0143 (6)	0.0003 (5)	0.0023 (5)	0.0002 (5)
C7	0.0170 (7)	0.0159 (6)	0.0129 (6)	−0.0007 (5)	0.0016 (5)	−0.0012 (5)
C8	0.0167 (7)	0.0172 (6)	0.0151 (6)	−0.0008 (5)	−0.0015 (5)	0.0009 (5)
C9	0.0133 (6)	0.0145 (6)	0.0201 (6)	−0.0016 (5)	0.0027 (5)	0.0025 (5)
C10	0.0165 (7)	0.0179 (7)	0.0252 (7)	0.0027 (5)	0.0008 (6)	0.0020 (5)
C11	0.0120 (6)	0.0121 (6)	0.0155 (6)	−0.0027 (5)	0.0018 (5)	0.0005 (5)
C12	0.0162 (7)	0.0174 (6)	0.0116 (6)	0.0011 (5)	0.0053 (5)	−0.0003 (5)
C13	0.0204 (7)	0.0205 (7)	0.0146 (6)	−0.0005 (5)	0.0034 (5)	−0.0048 (5)
C14	0.0123 (6)	0.0113 (6)	0.0134 (6)	−0.0024 (5)	0.0011 (5)	−0.0009 (4)
C15	0.0227 (7)	0.0169 (7)	0.0171 (6)	0.0048 (6)	0.0046 (5)	−0.0014 (5)
C16	0.0235 (7)	0.0183 (7)	0.0130 (6)	0.0042 (6)	0.0005 (5)	−0.0007 (5)
N1	0.0132 (6)	0.0134 (5)	0.0128 (5)	0.0002 (4)	−0.0004 (4)	0.0009 (4)
N2	0.0161 (6)	0.0138 (5)	0.0105 (5)	0.0025 (4)	0.0019 (4)	−0.0006 (4)
N3	0.0130 (6)	0.0133 (5)	0.0115 (5)	−0.0003 (4)	0.0023 (4)	−0.0005 (4)
O1	0.0188 (5)	0.0169 (5)	0.0109 (4)	0.0030 (4)	0.0004 (4)	0.0003 (3)
O2	0.0181 (5)	0.0188 (5)	0.0105 (4)	0.0032 (4)	0.0011 (4)	0.0006 (4)
S1	0.01535 (17)	0.01646 (17)	0.01953 (17)	0.00346 (12)	0.00381 (13)	0.00027 (12)
S2	0.02104 (18)	0.01790 (17)	0.01023 (15)	0.00360 (13)	0.00249 (12)	−0.00065 (12)

Geometric parameters (Å, º)

C1—C2	1.516 (2)	C9—C10	1.5078 (19)
C1—H1A	0.9800	C10—H10A	0.9800
C1—H1B	0.9800	C10—H10B	0.9800
C1—H1C	0.9800	C10—H10C	0.9800
C2—N1	1.4876 (16)	C11—N3	1.3726 (16)
C2—H2B	0.9900	C11—N1	1.3846 (17)

C2—H2C	0.9900	C11—S1	1.6639 (14)
C3—O2	1.2947 (16)	C12—N3	1.4874 (16)
C3—N1	1.3752 (17)	C12—C13	1.5192 (19)
C3—C4	1.4038 (17)	C12—H12A	0.9900
C4—C14	1.4453 (17)	C12—H12B	0.9900
C4—C5	1.4711 (18)	C13—H13A	0.9800
C5—N2	1.3370 (16)	C13—H13B	0.9800
C5—S2	1.7071 (13)	C13—H13C	0.9800
C6—C16	1.3931 (18)	C14—O1	1.2415 (16)
C6—C7	1.4011 (18)	C14—N3	1.4019 (17)
C6—N2	1.4164 (17)	C15—C16	1.3942 (19)
C7—C8	1.3855 (19)	C15—H15	0.9500
C7—H7	0.9500	C16—H16	0.9500
C8—C9	1.395 (2)	N2—H2A	0.8800
C8—H8	0.9500	O2—H2	0.8400
C9—C15	1.3885 (19)		

C2—C1—H1A	109.5	H10A—C10—H10C	109.5
C2—C1—H1B	109.5	H10B—C10—H10C	109.5
H1A—C1—H1B	109.5	N3—C11—N1	115.75 (11)
C2—C1—H1C	109.5	N3—C11—S1	122.66 (10)
H1A—C1—H1C	109.5	N1—C11—S1	121.58 (10)
H1B—C1—H1C	109.5	N3—C12—C13	112.27 (11)
N1—C2—C1	111.91 (11)	N3—C12—H12A	109.2
N1—C2—H2B	109.2	C13—C12—H12A	109.2
C1—C2—H2B	109.2	N3—C12—H12B	109.2
N1—C2—H2C	109.2	C13—C12—H12B	109.2
C1—C2—H2C	109.2	H12A—C12—H12B	107.9
H2B—C2—H2C	107.9	C12—C13—H13A	109.5
O2—C3—N1	113.75 (11)	C12—C13—H13B	109.5
O2—C3—C4	124.99 (12)	H13A—C13—H13B	109.5
N1—C3—C4	121.24 (12)	C12—C13—H13C	109.5
C3—C4—C14	116.88 (12)	H13A—C13—H13C	109.5
C3—C4—C5	122.11 (12)	H13B—C13—H13C	109.5
C14—C4—C5	120.98 (11)	O1—C14—N3	117.45 (11)
N2—C5—C4	115.81 (11)	O1—C14—C4	124.63 (12)
N2—C5—S2	122.21 (10)	N3—C14—C4	117.92 (11)
C4—C5—S2	121.98 (9)	C9—C15—C16	122.49 (13)
C16—C6—C7	118.85 (12)	C9—C15—H15	118.8
C16—C6—N2	126.56 (12)	C16—C15—H15	118.8
C7—C6—N2	114.56 (11)	C6—C16—C15	119.45 (12)
C8—C7—C6	120.49 (12)	C6—C16—H16	120.3
C8—C7—H7	119.8	C15—C16—H16	120.3
C6—C7—H7	119.8	C3—N1—C11	123.34 (11)
C7—C8—C9	121.49 (12)	C3—N1—C2	117.49 (11)
C7—C8—H8	119.3	C11—N1—C2	119.16 (11)
C9—C8—H8	119.3	C5—N2—C6	133.01 (11)
C15—C9—C8	117.22 (13)	C5—N2—H2A	113.5

C15—C9—C10	121.62 (13)	C6—N2—H2A	113.5
C8—C9—C10	121.16 (12)	C11—N3—C14	124.58 (11)
C9—C10—H10A	109.5	C11—N3—C12	119.10 (11)
C9—C10—H10B	109.5	C14—N3—C12	116.26 (10)
H10A—C10—H10B	109.5	C3—O2—H2	109.5
C9—C10—H10C	109.5		

O2—C3—C4—C14	−175.61 (12)	C4—C3—N1—C11	−1.66 (19)
N1—C3—C4—C14	2.86 (19)	O2—C3—N1—C2	−1.73 (17)
O2—C3—C4—C5	2.6 (2)	C4—C3—N1—C2	179.63 (12)
N1—C3—C4—C5	−178.90 (12)	N3—C11—N1—C3	2.49 (18)
C3—C4—C5—N2	−179.38 (12)	S1—C11—N1—C3	−177.43 (10)
C14—C4—C5—N2	−1.21 (18)	N3—C11—N1—C2	−178.82 (11)
C3—C4—C5—S2	−0.13 (18)	S1—C11—N1—C2	1.26 (17)
C14—C4—C5—S2	178.04 (10)	C1—C2—N1—C3	89.70 (14)
C16—C6—C7—C8	0.5 (2)	C1—C2—N1—C11	−89.06 (15)
N2—C6—C7—C8	−177.64 (12)	C4—C5—N2—C6	−179.88 (13)
C6—C7—C8—C9	0.2 (2)	S2—C5—N2—C6	0.9 (2)
C7—C8—C9—C15	−1.1 (2)	C16—C6—N2—C5	15.8 (2)
C7—C8—C9—C10	178.74 (13)	C7—C6—N2—C5	−166.23 (14)
C3—C4—C14—O1	175.27 (12)	N1—C11—N3—C14	−5.00 (18)
C5—C4—C14—O1	−3.0 (2)	S1—C11—N3—C14	174.92 (10)
C3—C4—C14—N3	−4.98 (18)	N1—C11—N3—C12	177.82 (11)
C5—C4—C14—N3	176.76 (11)	S1—C11—N3—C12	−2.26 (17)
C8—C9—C15—C16	1.3 (2)	O1—C14—N3—C11	−173.84 (12)
C10—C9—C15—C16	−178.54 (14)	C4—C14—N3—C11	6.40 (18)
C7—C6—C16—C15	−0.3 (2)	O1—C14—N3—C12	3.41 (17)
N2—C6—C16—C15	177.58 (13)	C4—C14—N3—C12	−176.35 (11)
C9—C15—C16—C6	−0.6 (2)	C13—C12—N3—C11	85.26 (15)
O2—C3—N1—C11	176.97 (12)	C13—C12—N3—C14	−92.15 (14)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7···O2$^{\text{i}}$	0.95	2.62	3.3136 (16)	130
C13—H13*A*···S1	0.98	2.95	3.4766 (15)	115
C16—H16···S2	0.95	2.51	3.1509 (14)	125
N2—H2*A*···O1	0.88	1.79	2.5671 (15)	147
O2—H2···S2	0.84	1.99	2.7802 (10)	157

Symmetry code: (i) *x*−1, −*y*+1/2, *z*−1/2.

5-(1-Aminoethylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (A17)

Crystal data

$C_{10}H_{15}N_3O_2S$
M_r = 241.31
Monoclinic, $P2_1/c$
a = 12.8983 (4) Å

b = 9.8458 (3) Å
c = 18.2217 (6) Å
β = 98.250 (2)°
V = 2290.10 (13) Å^3

$Z = 8$
$F(000) = 1024$
$D_x = 1.400$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9096 reflections

$\theta = 1.7–28.4°$
$\mu = 0.27$ mm^{-1}
$T = 100$ K
Block, colourless
0.19 × 0.13 × 0.09 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2012)
$T_{\min} = 0.941$, $T_{\max} = 0.985$

14727 measured reflections
5036 independent reflections
4323 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.024$
$\theta_{\max} = 27.2°$, $\theta_{\min} = 2.3°$
$h = -16 \rightarrow 16$
$k = -12 \rightarrow 12$
$l = -23 \rightarrow 22$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.088$
$S = 1.03$
5036 reflections
291 parameters
3 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 0.8588P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	y	z	$U_{\text{iso}}*/U_{\text{eq}}$
C6	0.61243 (11)	0.27480 (14)	0.36078 (8)	0.0203 (3)
H6A	0.6519	0.2775	0.3187	0.030*
H6B	0.6093	0.3662	0.3816	0.030*
H6C	0.5412	0.2422	0.3440	0.030*
C7	0.66566 (10)	0.18105 (13)	0.41878 (7)	0.0150 (3)
C10	0.68959 (10)	0.07191 (13)	0.54211 (7)	0.0149 (3)
C4	0.72421 (11)	−0.01292 (14)	0.66991 (8)	0.0191 (3)
H4A	0.7107	0.0230	0.7184	0.023*
H4B	0.7971	0.0108	0.6640	0.023*
C5	0.71329 (12)	−0.16651 (15)	0.67012 (9)	0.0248 (3)
H5A	0.7629	−0.2047	0.7106	0.037*
H5B	0.6417	−0.1909	0.6772	0.037*
H5C	0.7282	−0.2031	0.6227	0.037*
C3	0.55336 (10)	0.09224 (13)	0.62285 (7)	0.0156 (3)
C9	0.53259 (10)	0.21474 (13)	0.50361 (7)	0.0155 (3)
C2	0.38748 (10)	0.20954 (14)	0.57743 (8)	0.0178 (3)

H2A	0.3550	0.1377	0.6046	0.021*
H2B	0.3450	0.2196	0.5280	0.021*
C1	0.38662 (11)	0.34275 (15)	0.61955 (9)	0.0234 (3)
H1A	0.3143	0.3670	0.6246	0.035*
H1B	0.4275	0.3326	0.6689	0.035*
H1C	0.4175	0.4145	0.5923	0.035*
C20	0.15999 (10)	0.69458 (13)	0.29638 (7)	0.0147 (3)
C13	0.00875 (10)	0.80458 (13)	0.33995 (8)	0.0164 (3)
C14	−0.00593 (10)	0.80558 (14)	0.47372 (8)	0.0191 (3)
H14A	−0.0333	0.8988	0.4643	0.023*
H14B	0.0466	0.8081	0.5190	0.023*
C15	−0.09521 (11)	0.71255 (17)	0.48682 (9)	0.0278 (3)
H15A	−0.1269	0.7459	0.5292	0.042*
H15B	−0.1481	0.7112	0.4425	0.042*
H15C	−0.0683	0.6204	0.4973	0.042*
C17	0.27977 (10)	0.55276 (13)	0.38352 (8)	0.0157 (3)
C16	0.34694 (11)	0.51622 (15)	0.32607 (8)	0.0206 (3)
H16A	0.4017	0.4528	0.3474	0.031*
H16B	0.3794	0.5985	0.3095	0.031*
H16C	0.3037	0.4733	0.2837	0.031*
C19	0.13125 (10)	0.67181 (13)	0.42765 (7)	0.0149 (3)
C12	0.02386 (11)	0.79835 (15)	0.20565 (8)	0.0209 (3)
H12A	−0.0535	0.8050	0.1995	0.025*
H12B	0.0422	0.7236	0.1735	0.025*
C11	0.06788 (13)	0.93049 (16)	0.18012 (9)	0.0276 (3)
H11A	0.0390	0.9473	0.1282	0.041*
H11B	0.0486	1.0054	0.2109	0.041*
H11C	0.1444	0.9240	0.1848	0.041*
C8	0.62892 (10)	0.15566 (13)	0.48761 (7)	0.0146 (3)
N2	0.65158 (8)	0.05361 (11)	0.61006 (6)	0.0152 (2)
N3	0.49530 (8)	0.16758 (11)	0.56810 (6)	0.0150 (2)
N1	0.74982 (9)	0.12103 (12)	0.40227 (6)	0.0173 (2)
H1D	0.7846	0.0640	0.4339	0.021*
H1E	0.7716	0.1377	0.3596	0.021*
N5	0.06334 (8)	0.76423 (11)	0.28415 (6)	0.0157 (2)
N6	0.04578 (8)	0.76099 (11)	0.41021 (6)	0.0154 (2)
C18	0.19109 (10)	0.64012 (13)	0.36918 (7)	0.0145 (3)
N4	0.30665 (9)	0.49831 (12)	0.44921 (7)	0.0197 (3)
H4C	0.2697	0.5156	0.4852	0.024*
H4D	0.3616	0.4445	0.4573	0.024*
O1	0.47924 (7)	0.29948 (10)	0.46500 (5)	0.0213 (2)
O2	0.77401 (7)	0.01732 (10)	0.53471 (5)	0.0197 (2)
O3	0.20935 (7)	0.68444 (10)	0.24372 (5)	0.0187 (2)
O4	0.15024 (7)	0.62872 (10)	0.49193 (5)	0.0192 (2)
S1	0.50759 (3)	0.05125 (4)	0.70094 (2)	0.02191 (10)
S2	−0.09755 (3)	0.90311 (4)	0.32209 (2)	0.02713 (11)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C6	0.0229 (7)	0.0194 (7)	0.0191 (7)	0.0044 (6)	0.0048 (5)	0.0033 (5)
C7	0.0151 (6)	0.0133 (6)	0.0162 (6)	−0.0016 (5)	0.0008 (5)	−0.0027 (5)
C10	0.0147 (6)	0.0127 (6)	0.0168 (7)	−0.0016 (5)	0.0009 (5)	−0.0017 (5)
C4	0.0177 (7)	0.0214 (7)	0.0165 (7)	0.0002 (5)	−0.0030 (5)	0.0030 (5)
C5	0.0236 (7)	0.0215 (7)	0.0280 (8)	0.0024 (6)	−0.0004 (6)	0.0059 (6)
C3	0.0176 (6)	0.0138 (6)	0.0151 (6)	−0.0024 (5)	0.0014 (5)	−0.0035 (5)
C9	0.0154 (6)	0.0152 (6)	0.0155 (6)	−0.0002 (5)	0.0010 (5)	−0.0030 (5)
C2	0.0128 (6)	0.0205 (7)	0.0203 (7)	0.0007 (5)	0.0031 (5)	−0.0041 (5)
C1	0.0180 (7)	0.0243 (7)	0.0278 (8)	0.0030 (6)	0.0028 (6)	−0.0085 (6)
C20	0.0137 (6)	0.0114 (6)	0.0186 (6)	−0.0022 (5)	0.0014 (5)	−0.0028 (5)
C13	0.0145 (6)	0.0131 (6)	0.0209 (7)	0.0002 (5)	0.0005 (5)	−0.0020 (5)
C14	0.0174 (6)	0.0205 (7)	0.0202 (7)	0.0027 (5)	0.0050 (5)	−0.0058 (5)
C15	0.0203 (7)	0.0337 (8)	0.0313 (8)	−0.0015 (6)	0.0098 (6)	−0.0033 (7)
C17	0.0139 (6)	0.0129 (6)	0.0201 (7)	−0.0017 (5)	0.0013 (5)	−0.0022 (5)
C16	0.0170 (7)	0.0216 (7)	0.0238 (8)	0.0052 (5)	0.0050 (5)	−0.0003 (6)
C19	0.0126 (6)	0.0129 (6)	0.0190 (7)	−0.0012 (5)	0.0012 (5)	−0.0012 (5)
C12	0.0205 (7)	0.0234 (7)	0.0171 (7)	0.0026 (6)	−0.0032 (5)	−0.0001 (6)
C11	0.0313 (8)	0.0261 (8)	0.0238 (8)	0.0019 (6)	−0.0017 (6)	0.0066 (6)
C8	0.0143 (6)	0.0135 (6)	0.0159 (6)	0.0002 (5)	0.0019 (5)	−0.0011 (5)
N2	0.0148 (5)	0.0154 (5)	0.0146 (6)	0.0007 (4)	0.0000 (4)	0.0010 (4)
N3	0.0134 (5)	0.0153 (5)	0.0165 (6)	0.0008 (4)	0.0028 (4)	−0.0019 (4)
N1	0.0169 (6)	0.0184 (6)	0.0171 (6)	0.0029 (4)	0.0046 (4)	0.0009 (5)
N5	0.0153 (5)	0.0150 (5)	0.0163 (6)	0.0016 (4)	0.0001 (4)	0.0001 (4)
N6	0.0133 (5)	0.0144 (5)	0.0184 (6)	0.0015 (4)	0.0021 (4)	−0.0029 (4)
C18	0.0132 (6)	0.0131 (6)	0.0171 (6)	−0.0004 (5)	0.0022 (5)	−0.0018 (5)
N4	0.0169 (6)	0.0214 (6)	0.0205 (6)	0.0064 (5)	0.0020 (5)	0.0019 (5)
O1	0.0192 (5)	0.0241 (5)	0.0209 (5)	0.0093 (4)	0.0035 (4)	0.0046 (4)
O2	0.0156 (4)	0.0216 (5)	0.0217 (5)	0.0056 (4)	0.0023 (4)	0.0026 (4)
O3	0.0189 (5)	0.0208 (5)	0.0171 (5)	0.0006 (4)	0.0050 (4)	0.0005 (4)
O4	0.0193 (5)	0.0221 (5)	0.0165 (5)	0.0034 (4)	0.0036 (4)	0.0019 (4)
S1	0.02434 (19)	0.02587 (19)	0.01656 (18)	−0.00022 (14)	0.00644 (14)	0.00183 (14)
S2	0.02287 (19)	0.0292 (2)	0.0281 (2)	0.01446 (15)	−0.00076 (15)	−0.00179 (16)

Geometric parameters (Å, º)

C6—C7	1.4940 (18)	C20—C18	1.4338 (19)
C6—H6A	0.9800	C13—N6	1.3695 (18)
C6—H6B	0.9800	C13—N5	1.3758 (17)
C6—H6C	0.9800	C13—S2	1.6729 (13)
C7—N1	1.3083 (17)	C14—N6	1.4828 (16)
C7—C8	1.4251 (18)	C14—C15	1.517 (2)
C10—O2	1.2390 (16)	C14—H14A	0.9900
C10—N2	1.4071 (17)	C14—H14B	0.9900
C10—C8	1.4337 (18)	C15—H15A	0.9800
C4—N2	1.4842 (17)	C15—H15B	0.9800

C4—C5	1.519 (2)	C15—H15C	0.9800
C4—H4A	0.9900	C17—N4	1.3120 (18)
C4—H4B	0.9900	C17—C18	1.4250 (18)
C5—H5A	0.9800	C17—C16	1.4953 (18)
C5—H5B	0.9800	C16—H16A	0.9800
C5—H5C	0.9800	C16—H16B	0.9800
C3—N2	1.3743 (17)	C16—H16C	0.9800
C3—N3	1.3754 (18)	C19—O4	1.2367 (16)
C3—S1	1.6667 (14)	C19—N6	1.4095 (16)
C9—O1	1.2352 (16)	C19—C18	1.4367 (17)
C9—N3	1.4107 (17)	C12—N5	1.4864 (17)
C9—C8	1.4390 (18)	C12—C11	1.519 (2)
C2—N3	1.4838 (16)	C12—H12A	0.9900
C2—C1	1.5204 (19)	C12—H12B	0.9900
C2—H2A	0.9900	C11—H11A	0.9800
C2—H2B	0.9900	C11—H11B	0.9800
C1—H1A	0.9800	C11—H11C	0.9800
C1—H1B	0.9800	N1—H1D	0.8800
C1—H1C	0.9800	N1—H1E	0.8800
C20—O3	1.2294 (16)	N4—H4C	0.8800
C20—N5	1.4123 (16)	N4—H4D	0.8800

C7—C6—H6A	109.5	C14—C15—H15A	109.5
C7—C6—H6B	109.5	C14—C15—H15B	109.5
H6A—C6—H6B	109.5	H15A—C15—H15B	109.5
C7—C6—H6C	109.5	C14—C15—H15C	109.5
H6A—C6—H6C	109.5	H15A—C15—H15C	109.5
H6B—C6—H6C	109.5	H15B—C15—H15C	109.5
N1—C7—C8	120.98 (12)	N4—C17—C18	120.92 (12)
N1—C7—C6	115.39 (12)	N4—C17—C16	115.89 (12)
C8—C7—C6	123.62 (12)	C18—C17—C16	123.19 (12)
O2—C10—N2	117.57 (12)	C17—C16—H16A	109.5
O2—C10—C8	125.10 (12)	C17—C16—H16B	109.5
N2—C10—C8	117.30 (11)	H16A—C16—H16B	109.5
N2—C4—C5	113.10 (11)	C17—C16—H16C	109.5
N2—C4—H4A	109.0	H16A—C16—H16C	109.5
C5—C4—H4A	109.0	H16B—C16—H16C	109.5
N2—C4—H4B	109.0	O4—C19—N6	118.00 (12)
C5—C4—H4B	109.0	O4—C19—C18	124.98 (12)
H4A—C4—H4B	107.8	N6—C19—C18	117.01 (11)
C4—C5—H5A	109.5	N5—C12—C11	113.38 (12)
C4—C5—H5B	109.5	N5—C12—H12A	108.9
H5A—C5—H5B	109.5	C11—C12—H12A	108.9
C4—C5—H5C	109.5	N5—C12—H12B	108.9
H5A—C5—H5C	109.5	C11—C12—H12B	108.9
H5B—C5—H5C	109.5	H12A—C12—H12B	107.7
N2—C3—N3	116.45 (11)	C12—C11—H11A	109.5
N2—C3—S1	121.73 (10)	C12—C11—H11B	109.5

N3—C3—S1	121.81 (10)	H11A—C11—H11B	109.5
O1—C9—N3	117.90 (12)	C12—C11—H11C	109.5
O1—C9—C8	125.76 (13)	H11A—C11—H11C	109.5
N3—C9—C8	116.31 (11)	H11B—C11—H11C	109.5
N3—C2—C1	111.89 (11)	C7—C8—C10	119.54 (11)
N3—C2—H2A	109.2	C7—C8—C9	120.88 (12)
C1—C2—H2A	109.2	C10—C8—C9	119.57 (12)
N3—C2—H2B	109.2	C3—N2—C10	124.04 (11)
C1—C2—H2B	109.2	C3—N2—C4	119.84 (11)
H2A—C2—H2B	107.9	C10—N2—C4	116.12 (11)
C2—C1—H1A	109.5	C3—N3—C9	124.50 (11)
C2—C1—H1B	109.5	C3—N3—C2	119.26 (11)
H1A—C1—H1B	109.5	C9—N3—C2	116.17 (11)
C2—C1—H1C	109.5	C7—N1—H1D	120.0
H1A—C1—H1C	109.5	C7—N1—H1E	120.0
H1B—C1—H1C	109.5	H1D—N1—H1E	120.0
O3—C20—N5	117.43 (12)	C13—N5—C20	123.88 (11)
O3—C20—C18	125.76 (12)	C13—N5—C12	120.33 (11)
N5—C20—C18	116.81 (11)	C20—N5—C12	115.74 (11)
N6—C13—N5	116.97 (11)	C13—N6—C19	124.23 (11)
N6—C13—S2	121.99 (10)	C13—N6—C14	120.08 (11)
N5—C13—S2	121.04 (10)	C19—N6—C14	115.67 (11)
N6—C14—C15	112.37 (11)	C17—C18—C20	120.40 (12)
N6—C14—H14A	109.1	C17—C18—C19	119.85 (12)
C15—C14—H14A	109.1	C20—C18—C19	119.74 (11)
N6—C14—H14B	109.1	C17—N4—H4C	120.0
C15—C14—H14B	109.1	C17—N4—H4D	120.0
H14A—C14—H14B	107.9	H4C—N4—H4D	120.0

N1—C7—C8—C10	5.16 (19)	N6—C13—N5—C20	−7.27 (18)
C6—C7—C8—C10	−175.35 (12)	S2—C13—N5—C20	172.41 (10)
N1—C7—C8—C9	−175.84 (12)	N6—C13—N5—C12	175.36 (11)
C6—C7—C8—C9	3.6 (2)	S2—C13—N5—C12	−4.96 (17)
O2—C10—C8—C7	−0.1 (2)	O3—C20—N5—C13	−167.99 (12)
N2—C10—C8—C7	177.99 (11)	C18—C20—N5—C13	12.88 (18)
O2—C10—C8—C9	−179.13 (12)	O3—C20—N5—C12	9.49 (17)
N2—C10—C8—C9	−1.02 (18)	C18—C20—N5—C12	−169.64 (11)
O1—C9—C8—C7	−7.1 (2)	C11—C12—N5—C13	92.32 (15)
N3—C9—C8—C7	170.88 (11)	C11—C12—N5—C20	−85.25 (15)
O1—C9—C8—C10	171.89 (13)	N5—C13—N6—C19	−4.06 (18)
N3—C9—C8—C10	−10.12 (18)	S2—C13—N6—C19	176.25 (10)
N3—C3—N2—C10	−8.11 (18)	N5—C13—N6—C14	177.13 (11)
S1—C3—N2—C10	172.50 (10)	S2—C13—N6—C14	−2.55 (17)
N3—C3—N2—C4	172.44 (11)	O4—C19—N6—C13	−172.51 (12)
S1—C3—N2—C4	−6.95 (17)	C18—C19—N6—C13	8.68 (18)
O2—C10—N2—C3	−170.97 (12)	O4—C19—N6—C14	6.34 (17)
C8—C10—N2—C3	10.78 (19)	C18—C19—N6—C14	−172.46 (11)
O2—C10—N2—C4	8.51 (17)	C15—C14—N6—C13	88.19 (15)

C8—C10—N2—C4	−169.74 (11)	C15—C14—N6—C19	−90.71 (14)
C5—C4—N2—C3	89.41 (15)	N4—C17—C18—C20	−177.45 (12)
C5—C4—N2—C10	−90.08 (14)	C16—C17—C18—C20	2.01 (19)
N2—C3—N3—C9	−4.72 (18)	N4—C17—C18—C19	1.37 (19)
S1—C3—N3—C9	174.67 (10)	C16—C17—C18—C19	−179.17 (12)
N2—C3—N3—C2	178.38 (11)	O3—C20—C18—C17	−7.7 (2)
S1—C3—N3—C2	−2.23 (17)	N5—C20—C18—C17	171.32 (11)
O1—C9—N3—C3	−168.30 (12)	O3—C20—C18—C19	173.46 (12)
C8—C9—N3—C3	13.55 (18)	N5—C20—C18—C19	−7.50 (18)
O1—C9—N3—C2	8.69 (17)	O4—C19—C18—C17	0.0 (2)
C8—C9—N3—C2	−169.46 (11)	N6—C19—C18—C17	178.75 (11)
C1—C2—N3—C3	87.13 (15)	O4—C19—C18—C20	178.86 (12)
C1—C2—N3—C9	−90.02 (14)	N6—C19—C18—C20	−2.43 (18)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6*A*···O3^{i}	0.98	2.43	3.3103 (17)	149
N1—H1*D*···O2	0.88	1.92	2.5977 (15)	133
N1—H1*E*···O3^{i}	0.88	1.99	2.8540 (15)	168
N4—H4*C*···O4	0.88	1.92	2.6029 (15)	133
N4—H4*D*···O1	0.88	2.07	2.9473 (15)	172

Symmetry code: (i) −*x*+1, *y*−1/2, −*z*+1/2.

5-(1-Aminopropylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (A18)

Crystal data

$C_{11}H_{17}N_3O_2S$	D_x = 1.383 Mg m^{-3}
M_r = 255.33	Mo *Kα* radiation, λ = 0.71073 Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 5433 reflections
a = 4.9625 (3) Å	θ = 2.6–27.3°
b = 10.6358 (7) Å	μ = 0.26 mm^{-1}
c = 23.2402 (15) Å	*T* = 100 K
V = 1226.62 (14) Å^3	Rod, orange
Z = 4	0.25 × 0.11 × 0.09 mm
F(000) = 544	

Data collection

Bruker APEXII CCD diffractometer	10534 measured reflections
Radiation source: sealed tube	10534 independent reflections
Graphite monochromator	9991 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.000
Absorption correction: multi-scan (SADABS; Bruker, 2012)	θ_{max} = 27.5°, θ_{min} = 1.8°
T_{min} = 0.924, T_{max} = 0.988	*h* = −6→6
	k = −13→13
	l = −30→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.076$
$S = 1.03$
10534 reflections
154 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0273P)^2 + 0.4988P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Absolute structure: Flack *x* determined using 1038 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: −0.02 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.6440 (6)	0.8030 (2)	0.90953 (10)	0.0193 (5)
H1A	0.614519	0.878231	0.933081	0.029*
H1B	0.830720	0.774705	0.913955	0.029*
H1C	0.609323	0.823020	0.869034	0.029*
C2	0.4537 (5)	0.6994 (2)	0.92894 (10)	0.0176 (6)
H2A	0.486896	0.680627	0.970053	0.021*
H2B	0.265388	0.728966	0.925109	0.021*
C3	0.6710 (5)	0.4948 (2)	0.91284 (9)	0.0165 (5)
C4	0.8881 (5)	0.2876 (2)	0.89628 (11)	0.0187 (6)
H4A	1.043489	0.326064	0.916389	0.022*
H4B	0.956508	0.245498	0.861222	0.022*
C5	0.7578 (6)	0.1907 (3)	0.93530 (11)	0.0259 (7)
H5A	0.890515	0.126206	0.945486	0.039*
H5B	0.692791	0.231900	0.970376	0.039*
H5C	0.605865	0.151385	0.915244	0.039*
C6	−0.1787 (6)	0.4847 (2)	0.68889 (11)	0.0237 (6)
H6A	−0.297294	0.553048	0.676335	0.035*
H6B	−0.056686	0.461776	0.657430	0.035*
H6C	−0.287702	0.411508	0.699611	0.035*
C7	−0.0142 (5)	0.5278 (2)	0.74073 (10)	0.0159 (5)
H7A	0.089865	0.603344	0.729509	0.019*
H7B	−0.140542	0.553209	0.771579	0.019*
C8	0.1772 (5)	0.4330 (2)	0.76485 (10)	0.0147 (5)
C9	0.3485 (5)	0.4573 (2)	0.81314 (10)	0.0135 (5)
C10	0.5338 (5)	0.3619 (2)	0.83171 (10)	0.0150 (5)
C11	0.3302 (5)	0.5736 (2)	0.84439 (10)	0.0145 (5)
N1	0.4895 (4)	0.58329 (19)	0.89474 (8)	0.0146 (5)
N2	0.6952 (4)	0.38770 (18)	0.87954 (8)	0.0147 (5)

O1	0.5626 (4)	0.25808 (16)	0.80789 (7)	0.0204 (4)
O2	0.1876 (4)	0.66376 (16)	0.83154 (7)	0.0205 (4)
N3	0.1851 (5)	0.32251 (19)	0.73951 (8)	0.0185 (5)
H3A	0.295382	0.263996	0.752250	0.022*
H3B	0.080206	0.307096	0.709809	0.022*
S1	0.85678 (15)	0.51436 (6)	0.97179 (3)	0.02579 (18)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0194 (14)	0.0181 (13)	0.0205 (13)	0.0008 (12)	−0.0006 (12)	−0.0028 (10)
C2	0.0162 (13)	0.0207 (14)	0.0158 (12)	0.0013 (11)	0.0010 (10)	−0.0055 (11)
C3	0.0150 (12)	0.0178 (13)	0.0168 (12)	−0.0028 (12)	0.0009 (9)	0.0027 (10)
C4	0.0165 (14)	0.0193 (14)	0.0203 (13)	0.0043 (11)	−0.0024 (11)	0.0031 (10)
C5	0.0295 (17)	0.0211 (14)	0.0269 (15)	−0.0008 (12)	−0.0015 (12)	0.0086 (12)
C6	0.0252 (15)	0.0207 (14)	0.0251 (13)	0.0009 (13)	−0.0074 (11)	−0.0006 (12)
C7	0.0141 (12)	0.0152 (13)	0.0183 (12)	0.0005 (11)	−0.0011 (10)	0.0013 (10)
C8	0.0140 (13)	0.0143 (12)	0.0157 (12)	−0.0003 (11)	0.0036 (10)	0.0026 (10)
C9	0.0126 (12)	0.0140 (12)	0.0138 (11)	−0.0001 (10)	0.0018 (10)	0.0008 (9)
C10	0.0135 (13)	0.0168 (13)	0.0149 (12)	−0.0017 (10)	0.0022 (10)	0.0027 (10)
C11	0.0120 (13)	0.0170 (12)	0.0143 (12)	−0.0022 (11)	0.0007 (10)	0.0019 (10)
N1	0.0142 (11)	0.0155 (11)	0.0141 (11)	0.0002 (9)	−0.0003 (9)	−0.0005 (9)
N2	0.0134 (11)	0.0133 (10)	0.0173 (10)	0.0001 (9)	−0.0014 (9)	0.0025 (8)
O1	0.0221 (11)	0.0159 (10)	0.0232 (10)	0.0044 (8)	−0.0022 (8)	−0.0034 (8)
O2	0.0219 (11)	0.0170 (9)	0.0226 (9)	0.0058 (8)	−0.0049 (8)	−0.0016 (7)
N3	0.0225 (13)	0.0158 (11)	0.0173 (10)	0.0022 (10)	−0.0053 (9)	−0.0017 (9)
S1	0.0308 (4)	0.0239 (4)	0.0227 (3)	−0.0017 (3)	−0.0131 (3)	0.0009 (3)

Geometric parameters (Å, º)

C1—C2	1.520 (4)	C6—C7	1.526 (3)
C1—H1A	0.9800	C6—H6A	0.9800
C1—H1B	0.9800	C6—H6B	0.9800
C1—H1C	0.9800	C6—H6C	0.9800
C2—N1	1.480 (3)	C7—C8	1.494 (3)
C2—H2A	0.9900	C7—H7A	0.9900
C2—H2B	0.9900	C7—H7B	0.9900
C3—N1	1.369 (3)	C8—N3	1.315 (3)
C3—N2	1.383 (3)	C8—C9	1.432 (3)
C3—S1	1.664 (2)	C9—C10	1.436 (3)
C4—N2	1.483 (3)	C9—C11	1.437 (3)
C4—C5	1.518 (3)	C10—O1	1.243 (3)
C4—H4A	0.9900	C10—N2	1.398 (3)
C4—H4B	0.9900	C11—O2	1.228 (3)
C5—H5A	0.9800	C11—N1	1.416 (3)
C5—H5B	0.9800	N3—H3A	0.8800
C5—H5C	0.9800	N3—H3B	0.8800

C2—C1—H1A	109.5	C7—C6—H6C	109.5
C2—C1—H1B	109.5	H6A—C6—H6C	109.5
H1A—C1—H1B	109.5	H6B—C6—H6C	109.5
C2—C1—H1C	109.5	C8—C7—C6	115.7 (2)
H1A—C1—H1C	109.5	C8—C7—H7A	108.4
H1B—C1—H1C	109.5	C6—C7—H7A	108.4
N1—C2—C1	111.8 (2)	C8—C7—H7B	108.4
N1—C2—H2A	109.3	C6—C7—H7B	108.4
C1—C2—H2A	109.3	H7A—C7—H7B	107.4
N1—C2—H2B	109.3	N3—C8—C9	119.7 (2)
C1—C2—H2B	109.3	N3—C8—C7	117.0 (2)
H2A—C2—H2B	107.9	C9—C8—C7	123.3 (2)
N1—C3—N2	116.8 (2)	C8—C9—C10	119.2 (2)
N1—C3—S1	122.12 (18)	C8—C9—C11	121.0 (2)
N2—C3—S1	121.03 (19)	C10—C9—C11	119.8 (2)
N2—C4—C5	111.7 (2)	O1—C10—N2	117.6 (2)
N2—C4—H4A	109.3	O1—C10—C9	124.6 (2)
C5—C4—H4A	109.3	N2—C10—C9	117.8 (2)
N2—C4—H4B	109.3	O2—C11—N1	117.8 (2)
C5—C4—H4B	109.3	O2—C11—C9	125.8 (2)
H4A—C4—H4B	107.9	N1—C11—C9	116.4 (2)
C4—C5—H5A	109.5	C3—N1—C11	124.9 (2)
C4—C5—H5B	109.5	C3—N1—C2	119.2 (2)
H5A—C5—H5B	109.5	C11—N1—C2	115.9 (2)
C4—C5—H5C	109.5	C3—N2—C10	123.9 (2)
H5A—C5—H5C	109.5	C3—N2—C4	120.0 (2)
H5B—C5—H5C	109.5	C10—N2—C4	115.9 (2)
C7—C6—H6A	109.5	C8—N3—H3A	120.0
C7—C6—H6B	109.5	C8—N3—H3B	120.0
H6A—C6—H6B	109.5	H3A—N3—H3B	120.0

C6—C7—C8—N3	−0.2 (3)	S1—C3—N1—C2	−0.8 (3)
C6—C7—C8—C9	179.6 (2)	O2—C11—N1—C3	−175.6 (2)
N3—C8—C9—C10	2.3 (4)	C9—C11—N1—C3	5.1 (3)
C7—C8—C9—C10	−177.5 (2)	O2—C11—N1—C2	3.7 (3)
N3—C8—C9—C11	−175.3 (2)	C9—C11—N1—C2	−175.6 (2)
C7—C8—C9—C11	4.9 (4)	C1—C2—N1—C3	90.0 (3)
C8—C9—C10—O1	1.7 (4)	C1—C2—N1—C11	−89.4 (3)
C11—C9—C10—O1	179.4 (2)	N1—C3—N2—C10	−4.6 (3)
C8—C9—C10—N2	−179.0 (2)	S1—C3—N2—C10	175.80 (18)
C11—C9—C10—N2	−1.3 (3)	N1—C3—N2—C4	179.9 (2)
C8—C9—C11—O2	−5.3 (4)	S1—C3—N2—C4	0.3 (3)
C10—C9—C11—O2	177.1 (2)	O1—C10—N2—C3	−174.9 (2)
C8—C9—C11—N1	174.0 (2)	C9—C10—N2—C3	5.7 (3)
C10—C9—C11—N1	−3.7 (3)	O1—C10—N2—C4	0.8 (3)
N2—C3—N1—C11	−1.1 (3)	C9—C10—N2—C4	−178.6 (2)
S1—C3—N1—C11	178.49 (19)	C5—C4—N2—C3	90.3 (3)
N2—C3—N1—C2	179.6 (2)	C5—C4—N2—C10	−85.6 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*A*···S1^{i}	0.98	2.80	3.662 (3)	147
C7—H7*A*···O1^{ii}	0.99	2.54	3.507 (3)	166
N3—H3*A*···O1	0.88	1.85	2.550 (3)	135
N3—H3*B*···O2^{iii}	0.88	2.24	3.000 (3)	145

Symmetry codes: (i) $x-1/2, -y+3/2, -z+2$; (ii) $-x+1, y+1/2, -z+3/2$; (iii) $-x, y-1/2, -z+3/2$.