ARTICLE

OBC
www.rsc.org/obc

An alternative synthesis of 2-(*N*-arylhydrazono)-1-benzothiophen-3-ones

Jalal A. Zahra,[a] Bassam A. Abu Thaher,[b] Mustafa M. El-Abadelah *[a] and Roland Boese[c]

[a] *Chemistry Department, Faculty of Science, University of Jordan, Amman-Jordan. E-mail: mustelab@ju.edu.jo; Fax: 00962 6 534 8932*

[b] *Chemistry Department, Faculty of Science, Islamic University of Gaza, Gaza Strip*

[c] *Institut für Anorganische Chemie, Universität Essen, Universitätstrasse 3-5, D-45117 Essen, Germany*

Received 19th November 2002, Accepted 7th January 2003
First published as an Advance Article on the web 5th February 2003

In the presence of triethylamine, 2-mercaptobenzoic acid readily adds onto acylhydrazonoyl chlorides (**1a**–**c**) (precursors of the reactive nitrile imine 1,3-dipolar species) to afford good yields of the corresponding 2-[(2-oxo-1-arylhydrazonopropan-1-yl)mercapto]benzoic acids (**2a**–**c**). The latter acyclic adducts, in THF in the presence of 1,1′-carbonyldiimidazole, undergo intramolecular cyclization involving the activated carboxy and the enol functionality to deliver the respective 2-(*N*-arylhydrazono)-3-oxobenzothiophenes (**3a**–**c**). In the solid state, the latter compounds adopt the (*Z*)-geometry around the C=N double bond as evidenced by single crystal X-ray structure determination for **3b**.

Introduction

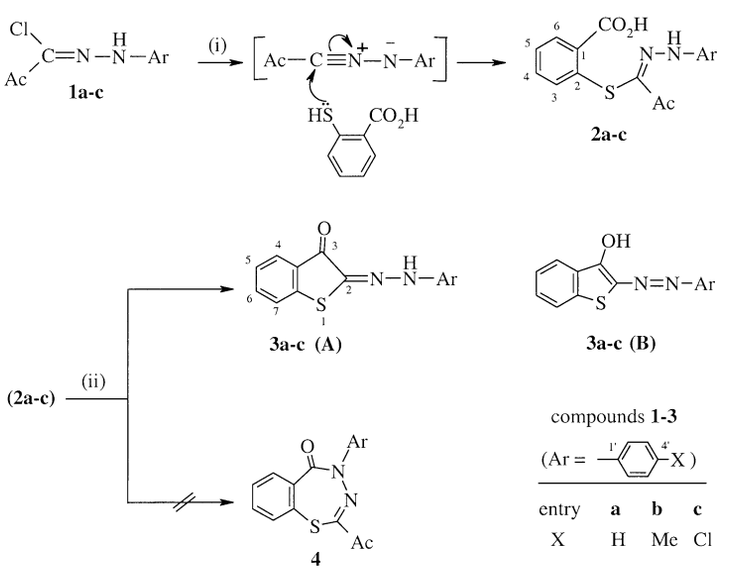
Quite recently, we have reported on the synthesis of some 1,4-dihydro-1,3,4-benzotriazepin-5-ones[1] *via* cyclocondensation of the respective amidrazone precursors, induced by 1,1′-carbonyldiimidazole (CDI). The required amidrazones are readily prepared[1,2] by direct interaction between 2-aminobenzoic acid and the respective nitrile imine (the reactive 1,3-dipolar species, generated *in situ* from their hydrazonoyl chloride precursors in the presence of triethylamine). This versatile two-step route furnishes unequivocally the desired dihydrobenzotriazepinones in good overall yield.

Following this route, we envisaged employing 2-mercaptobenzoic acid (in place of 2-aminobenzoic acid) which would react similarly with hydrazonoyl chlorides (**1a**–**c**) in the presence of triethylamine to give the respective arylthio–acylhydrazone adducts (**2a**–**c**) (Scheme 1). This expectation has been realized in this study. However, CDI-induced cyclocondensation of **2a**–**c** did not yield the expected 1,3,4-benzothiadiazepin-5-ones (**4**). Instead, the main isolable products were identified as 2-arylhydrazono-1-benzothiophen-3-ones (**3a**–**c**) (Scheme 1). Accordingly, the present work deals with this new synthetic route towards benzothiophen-3-one derivatives, and for which a plausible mechanistic pathway is postulated (Scheme 2).

Results and discussion

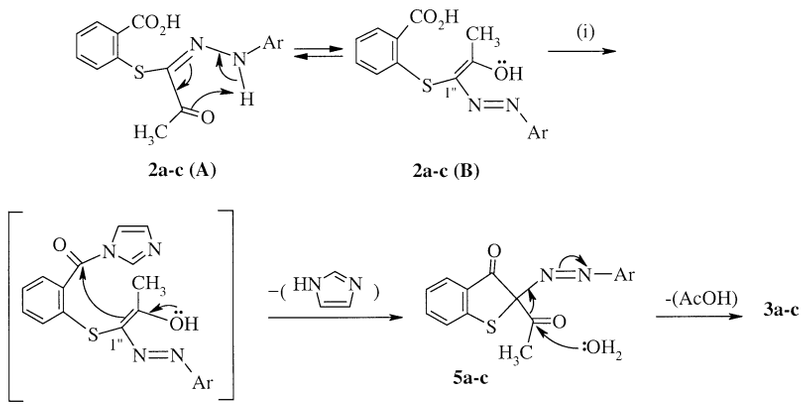
Synthesis

2-Mercaptobenzoic acid, acting as a sulfur nucleophile in a basic medium, adds readily to nitrile imines (the reactive 1,3-dipolar intermediates, generated *in situ* from their hydrazonoyl chloride precursors **1a**–**c** in the presence of triethylamine) to produce the corresponding 2-{[2-oxo-(1-arylhydrazono)-propan-1-yl]mercapto}benzoic acids (**2a**–**c**) (Scheme 1). This mode of nucleophilic addition reaction of various nucleophiles to 1,3-dipoles is well-documented,[3,4] and several adducts related to **2** were obtained from the reaction of thiols with hydrazonoyl chlorides (such as **1**). The required hydrazonoyl chlorides **1a**,[5–7]



Scheme 1 *Reagents and conditions*: (i) aq. MeOH, THF, NEt_3; (ii) THF, CDI.

DOI: 10.1039/b211458p



Scheme 2 *Reagents and conditions*: (i) THF, CDI.

1b[5,6] and **1c**[5–7] were previously characterized, and were made accessible *via* the Japp–Klingemann reaction[5,8,9] involving coupling of the appropriate arenediazonium chloride with 3-chloropentane-2,4-dione in aqueous pyridine.

In a separate step, the acyclic adducts **2** in tetrahydrofuran in the presence of 1,1′-carbonyldiimidazole, undergo facile cyclocondensation to form the respective 2-arylhydrazono-1-benzothiophen-3-ones **3** (Scheme 1) which lack the acetyl group, present in **2**, as evidenced from NMR, MS and single crystal X-ray data (*vide infra*). The formation of **3** from **2** might be explained by assuming that the oxohydrazones **2**(**A**) experience transfer of the N–H proton into the corresponding enol-azo forms **2**(**B**) in solution (Scheme 2). The latter **2**(**B**) undergo intramolecular cyclization involving the activated carboxy and the enol π-system to deliver the respective 2-acetyl-2-arylazo-1-benzothiophen-3-ones (**5**).

Here the nucleophilicity of the enol carbon-1″ in **2**(**B**) appears to be activated by the easily polarized sulfur atom anchored thereat. This might explain the difference regarding the mode of cyclization for the 'sulfur' adducts (**2**/Scheme 1) as compared to their 'nitrogen' analogs.[1] In a subsequent step, the intermediate arylazo compounds **5a**–**c** are converted into the corresponding arylhydrazone derivatives **3a**–**c** *via* loss of the acetyl group. This type of azo- to hydrazone rearrangement process constitutes a unique example of the Japp–Klingemann reaction for which various related azo- to hydrazone conversions were reported in the literature.[8,9] However, no attempt was made to isolate the intermediates **5a**–**c**.

It is worth mentioning that compounds **3a**,**b** were previously prepared[10–13] by the usual coupling reaction of the appropriate arenediazonium salt with 1-benzothiophen-3-one. The two-step reaction described in the present work (Scheme 1) provides an alternative and convenient route towards synthesis of **3**.

Spectral data

The IR, MS, and NMR spectral data and microanalyses of compounds **2a**–**c** and **3a**–**c** conform to the suggested structures, and are given in the Experimental section. Thus, their MS spectra display the correct molecular ions for which the measured high resolution data are in good agreement with the calculated values. ^{1}H-signal assignments are straightforward, and ^{13}C-assignments follow from DEPT and 2D (COSY, HMQC and HMBC) experiments.

Crystal structure determination of 3b †

Crystal data. C_{15} H_{12} N_2 O S, M = 268.33, monoclinic, a = 13.949(5), b = 8.165(3), c = 12.755(5) Å, β = 117.150(7)°, D_{calcd} = 1.379 g cm^{-3}, U = 1292.7(8) Å^3, T = 203(2) K, space group $P2_1/c$, Z = 4, μ(Mo–K$_\alpha$) = 0.242 mm^{-1}, 7070 reflections measured ($2\theta_{max}$ = 48°), 2012 unique [$R_{int}(F^2)$ = 0.1643] which were used in all calculations. The final R_1 was 0.0669 and wR_2 (F^2) = 0.1716 (all data).

Table 1 Selected bond lengths (Å) and angles (°) for **3b**

S(1)–C(1)	1.755(5)	N(1)–N(2)–C(9)	119.2(4)
S(1)–C(7)	1.783(4)	N(1)–C(1)–C(2)	119.1(4)
N(1)–C(1)	1.299(5)	N(1)–C(1)–S(1)	128.1(3)
N(1)–N(2)	1.337(5)	C(2)–C(1)–S(1)	112.8(3)
N(2)–C(9)	1.410(6)	O(1)–C(2)–C(8)	127.4(4)
O(1)–C(2)	1.223(5)	O(1)–C(2)–C(1)	124.3(4)
C(1)–C(2)	1.497(6)	C(8)–C(2)–C(1)	108.2(4)
C(2)–C(8)	1.451(6)	C(8)–C(7)–S(1)	112.8(3)
H(2) ··· O1A	1.875	C(6)–C(7)–S(1)	124.3(4)
N(1)–H(2)	1.077	C(7)–C(8)–C(2)	115.4(4)
C(1)–S(1)–C(7)	90.8(2)	C(3)–C(8)–C(2)	125.8(4)
C(1)–N(1)–N(2)	118.4(4)	N(2)–H(2) ··· O1A	151.1

The molecular structure of **3b** is displayed in Fig. 1, and selected bond lengths and angles are given in Table 1. The crystallographic data revealed that **3b** (and by inference **3a** and **c**) exist, at least in solid state, in the oxo-hydrazone tautomeric form (**A**) rather than the enol-azo tautomer (**B**) shown in Scheme 1.

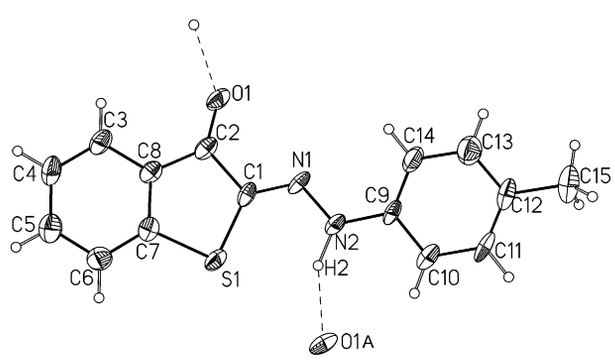
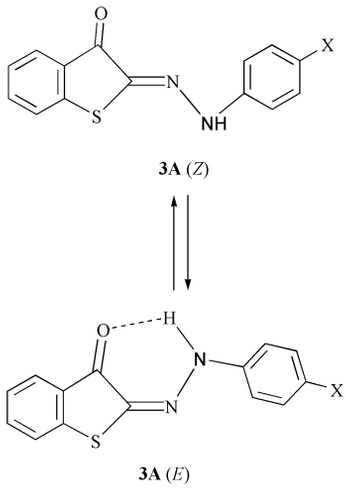


Fig. 1 ORTEP plot (50%) of the molecular structure of **3b**.

Previous spectroscopic studies,[11–13] concluding the predominance of the oxohydrazone tautomer **3**(**A**), are in accord with our X-ray findings. The phenomenon of *Z*–*E* isomerisation of **3**(**A**) (X = H, Me, Br, OMe) in relation to the C=N double bond in solution, was investigated by vibrational, electronic and ^{1}H NMR spectroscopy.[13] In non-polar solvents the compounds exist exclusively in the intramolecular hydrogen-bonded *E*-form **3A**(*E*), while in polar solvents a $Z \rightleftharpoons E$ equilibrium is set up between the two oxohydrazone forms[13] (Chart 1). Of the two possible *Z*–*E* diastereomers, **3b**(**A**) adopts the (*Z*)–geometry in the solid state, which is stabilized by

† CCDC reference number 195385. See http://www.rsc.org/suppdata/ob/b2/b211458p/ for crystallographic files in .cif or other electronic format.



3A (*Z*)

3A (*E*)

Chart 1

intermolecular hydrogen bonding involving the hydrazone N–H and the 3-keto oxygen as evidenced from X-ray data (Fig. 2).

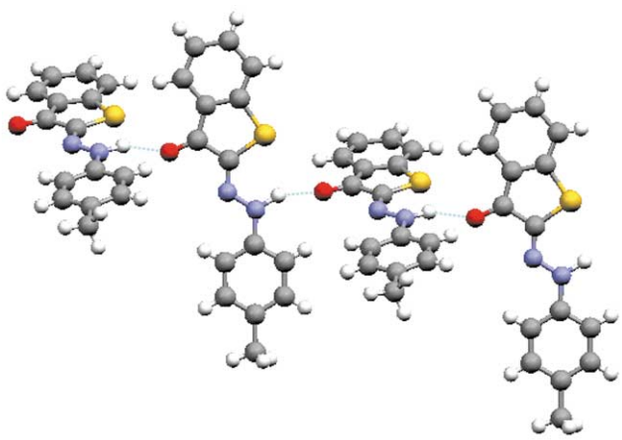


Fig. 2 Intermolecular hydrogen bonding in **3b**.

Conclusion

A new unequivocal synthetic route towards 2-(*N*-arylhydrazono)-1-benzothiophen-3-ones (**3a**–**c**), described in the present work, utilizes readily available and inexpensive reactants (2-mercaptobenzoic acid and acylhydrazonoyl chlorides). This versatile and efficient route involves a two-step reaction that is conveniently conducted at or below room temperature to give the respective 1-benzothiophen-3-one derivatives (**3a**–**c**) in good overall yield and high purity.

Experimental

2-Mercaptobenzoic acid, 3-chloropentane-2,4-dione, and 1,1′-carbonyldiimidazole were purchased from Acros. Melting points (uncorrected) were determined on an electrothermal Mel-Temp. Apparatus. ^{1}H- and ^{13}C-NMR spectra were measured on a Bruker DPX-300 instrument with Me_4Si as internal reference. *J* values are given in Hz. Electron-impact mass spectra were obtained using a Finnigan MAT TSQ-70 spectrometer at 70 eV; ion source temperature = 200 °C. IR spectra were recorded as KBr discs on a Nicolet Impact-400 FTIR spectrophotometer. Microanalyses were preformed at the Microanalytical Laboratory-Inorganic Chemistry Department, Tübingen University, Germany.

1-Arylhydrazono-1-chloropropanones 1a–c

These hydrazonoyl chlorides were prepared *via* direct coupling of the appropriate arenediazonium chloride with 3-chloropentane-2,4-dione in aqueous pyridine, following standard procedures.[5–7]

2-{[2-Oxo-1-(phenylhydrazono)propan-1-yl]mercapto}benzoic acid 2a

A homogeneous solution of 2-mercaptobenzoic acid (3.1 g, 20 mmol) in aqueous methanol (70%, 35 cm^3) and triethylamine (6 cm^3) was added dropwise to a stirred and cooled (0 °C) solution of 1-chloro-1-phenylhydrazonopropanone (**1a**) (3.9 g, 20 mmol) in tetrahydrofuran (50 cm^3). Additional triethylamine (5 cm^3) in tetrahydrofuran (10 cm^3) was then introduced dropwise into the reaction mixture which was further stirred at 0 °C for 20–30 min, and then at room temperature for 8–10 h. The organic solvents were then removed from the reaction mixture *in vacuo*, and the residual aqueous solution was directly acidified with glacial acetic acid (6 cm^3). The resulting crude solid product was collected, dried and recrystallized from hot chloroform–methanol (5 : 1 v/v). Yield 4.8 g (77%); mp 233–234 °C (Found: C, 61.0; H, 4.4; N, 8.8; S, 10.1. $C_{16}H_{14}N_2O_3S$ requires C, 61.1; H, 4.5; N, 8.9; S, 10.2%); ν_{max}(KBr)/cm^{-1} 3450 br, 3243, 1687, 1672, 1601, 1510, 1470, 1422, 1316, 1274, 1232 and 1036; δ_H(300 MHz; DMSO-d_6 Me_4Si): 2.51(3 H, s, COMe), 6.74 (1 H, d, *J* 8, H-3), 7.00 (1 H, t, *J* 7.3, H-4′), 7.19 (1 H, dd, *J* 7.4 and 7.7, H-5), 7.31 (3 H, m, H-3′/H-5′, H-4′), 7.47 (2 H, d, *J* 8, H-2′/H-6′), 7.92 (1 H, dd, *J* 7.7 and 1.2, H-6), 10.96 (1 H, s, NH) and 13.20 (1 H, br s, CO_2H); δ_C(75 MHz; DMSO-d_6; Me_4Si) 26.1(CO*Me*), 115.8(C-2′/C-6′), 123.6 (C-4′), 125.6 (C-5), 127.0 (C-3), 128.9 (C-1), 129.7 (C-3′/C-5′), 131.1 (C=N), 131.9 (C-6), 133.1 (C-4), 137.4 (C-2), 143.2 (C-1′), 168.1 (*C*O_2H) and 193.3 (*C*OMe); *m*/*z* (EI) 314.071575 ($C_{16}H_{14}N_2O_3S$ requires 314.072491), 314 (M$^+$, 46%), 271 (8), 253 (6), 213 (19), 195 (8), 160 (9), 153 (11), 136 (23), 118 (100) and 92 (97).

2-{[2-Oxo-1-[(4-methylphenyl)hydrazono]propan-1-yl}-mercapto]benzoic acid 2b

This compound was prepared from 2-mercaptobenzoic acid (3.1 g, 20 mmol) and 1-chloro-1-[(4-methylphenyl)hydrazono]-propanone (**1b**) (4.2 g, 20 mmol) by following the same procedure and experimental conditions described above for obtaining **2a**. Yield 5.3 g (81%); mp 234–235 °C (Found: C, 62.0; H, 4.8; N, 8.5; S, 9.6. $C_{17}H_{16}N_2O_3S$ requires C, 62.2; H, 4.9; N, 8.5; S, 9.8%); ν_{max}(KBr)/cm^{-1} 3435 br, 3251, 1686, 1672, 1522, 1465, 1428, 1319, 1270, 1235, 1151 and 1032; δ_H(300 MHz; DMSO-d_6; Me_4Si) 2.22 (3 H, s, C(4′)Me), 2.49 (3 H, s, COMe), 6.73 (1 H, d, *J* 8.1, H-3), 7.11 (2 H, d, *J* 8.4, H-3′/H-5′), 7.19 (1 H, dd, *J* 7.6 and 7.7, H-5), 7.33 (1 H, dd, *J* 7.6 and 8.1, H-4), 7.35 (2 H, d, *J* 8.4, H-2′/H-6′), 7.92 (1 H, dd, *J* 7.7 and 1.5, H-6), 10.89 (1 H, s, NH) and 13.25 (1 H, br s, CO_2H); δ_C(75 MHz; DMSO-d_6; Me_4Si) 20.9 (C(4′)*Me*), 26.1 (CO*Me*), 115.9 (C-2′/C-6′), 125.5 (C-5), 127.0 (C-3), 128.9 (C-1), 130.3 (C-3′/C-5′), 130.7 (C-4′), 131.9 (C-6), 132.7 (C = N), 133.1 (C-4), 137.5 (C-2), 140.9 (C-1′), 168.1 (*C*O_2H) and 193.3 (*C*OMe); *m*/*z* (EI) 328.085888 ($C_{17}H_{16}N_2O_3S$ requires 328.088141), 328 (M$^+$, 39%), 285 (3), 267(2), 227 (8), 209 (4), 174 (7), 136 (10), 132 (100) and 106 (65).

(2-{[2-Oxo-1-[(4-chlorophenyl)hydrazono]propan-1-yl}-mercapto)benzoic acid 2c

This compound was prepared from 2-mercaptobenzoic acid (3.1 g, 20 mmol) and 1-chloro-1-[(4-chlorophenyl)hydrazono]-propanone (**1c**) (4.6 g, 20 mmol) by following the same procedure and experimental conditions described above for obtaining **2a**. Yield 5.8 g (83%); mp 236–237 °C (Found: C, 54.9; H, 3.7; Cl, 10.0; N, 7.9; S, 9.0. $C_{16}H_{13}ClN_2O_3S$ requires C, 55.1; H, 3.8; Cl, 10.2; N, 8.0; S, 9.2%); ν_{max}(KBr)/cm^{-1} 3445 br, 3250, 1679, 1595, 1514, 1467, 1316, 1267, 1219 and 1048; δ_H(300 MHz; DMSO-d_6; Me_4Si) 2.50 (3 H, s, COMe), 6.76 (1 H, d, *J* 8.0, H-3), 7.20 (1 H, dd, *J* 7.4 and 7.5, H-5), 7.38 (3 H, m,

H-3′/H-5′, H-4), 7.47 (2 H, d, *J* 8.8, H-2′/H-6′), 7.90 (1 H, d, *J* 7.5, H-6), 11.20 (1 H, s, NH) and 13.28 (1 H, br s, CO_2H); δ_C(75 MHz; DMSO-d_6; Me_4Si) 26.2 (CO*Me*), 117.4 (C-2′/C-6′), 125.7 (C-5), 127.2 (C-4′), 127.4 (C-3), 128.8 (C-1), 129.6 (C-3′/C-5′), 131.8 (C-6), 132.4 (C=N), 133.0 (C-4), 137.0 (C-2), 142.2 (C-1′), 168.3 (*C*O_2 H) and 193.4 (*C*OMe); *m*/*z* (EI) 348.031462 (C_{16} H_{13} Cl N_2 O_3 S requires 348.033516), 348 (M^+, 36%), 271 (8), 305 (2), 287 (2), 247 (8), 229 (5), 194 (11), 152 (100), 126 (61) and 99 (31).

1-Benzothiophene-2,3-dione 2-(*N*-phenylhydrazone) 3a

To a mixture of 1,1′-carbonyldiimidazole (2.0 g, 12.5 mmol) and compound **2a** (3.1 g, 10 mmol) was added dry tetrahydrofuran (50 cm^3), and the resulting solution was stirred at rt for 1–2 h. The solvent was then removed *in vacuo* and the residue was immediately treated with water (40 cm^3) and extracted with chloroform (2 × 40 cm^3). The combined organic extracts were dried (Na_2SO_4), the solvent chloroform was evaporated and the residual solid product was recrystallized from $CHCl_3$–petroleum ether (bp 40–60 °C). Yield 1.9 g (74%); mp 194–195 °C (Lit.[10] 194 °C) (Found: C, 65.9; H,3.9; N, 11.1; S, 12.5. $C_{14}H_{10}N_2OS$ requires C, 66.1; H, 4.0; N, 11.0; S, 12.6%); ν_{max}(KBr)/cm^{-1} 3217, 3180, 1656, 1586, 1488, 1445, 1264, 1223, 1107 and 1062; δ_H(300 MHz; DMSO-d_6; Me_4Si) 6.99 (1 H, m, H-4′), 7.34 (5 H, m, H-2′/H-6′, H-3′/H-5′, H-5), 7.67 (1 H, dd, *J* 6.9 and 7.2, H-6), 7.75 (1 H, d, *J* 6.9, H-7), 7.78 (1 H, d, *J* 6.8, H-4) and 10.89 (1 H, s, NH); δ_C(75 MHz; DMSO-d_6; Me_4Si) 115.3 (C-2′/C-6′), 123.2 (C-4′), 125.7 (C-4), 126.4 (C-7), 126.8 (C-5), 129.8 (C-3′/C5′), 130.5 (C-3a), 131.9 (C=N), 136.2 (C-6), 141.7 (C-7a), 143.8 (C-1′) and 183.8 (C=O); *m*/*z* (EI) 254.052626 (C_{14} H_{10} N_2 O S requires 254.051385), 254 (M^+, 100%), 237 (7), 225 (14), 197 (8), 167 (23), 162 (36), 149 (94), 134 (18) and 121 (16).

1-Benzothiophene-2,3-dione 2-[*N*-(4-methylphenyl)hydrazone] 3b

This compound was prepared from **2b** (3.3 g, 10 mmol) and 1,1′-carbonyldiimidazole (2.0 g, 12.5 mmol) by following the same procedure and experimental conditions described above for **3a**. Yield 2.0 g (75%); mp 198–200 °C (Lit.[12] 198 °C) (Found: C, 67.2; H, 4.4; N, 10.3; S, 11.8. $C_{15}H_{12}N_2OS$ requires C, 67.1; H, 4.5; N, 10.4; S, 11.95%); ν_{max}(KBr)/cm^{-1} 3226, 3183, 1659, 1600, 1498, 1262 and 1098; δ_H(300 MHz; DMSO-d_6; Me_4Si) 2.23 (3 H, s, Me), 7.13 (2 H, d, *J* 8.3, H-3′/H-5′), 7.26 (2 H, d, *J* 8.3, H-2′/H-6′), 7.36 (1 H, dd, *J* 7.8 and 7.1, H-5), 7.67 (1 H, dd, *J* 7.1 and 8.0, H-6), 7.74 (1 H, d, *J* 8.0, H-7), 7.77 (1 H, d, *J* 7.8, H-4) and 10.82 (1 H, s, NH); δ_C(75 MHz; DMSO-d_6; Me_4Si) 20.9 (Me), 115.3 (C-2′/C-6′), 125.6 (C-7), 126.3 (C-4), 126.7 (C-5), 130.3 (C-3′/C-5′), 130.7 (C-3a), 131.3 (C=N), 132.3 (C-1′), 136.0 (C-6), 141.5 (C-4′), 141.6 (C-7a) and 183.6 (C=O); *m*/*z* (EI) 268.068604 (C_{15} H_{12} N_2 O S requires 268.067035), 268 (M^+, 100%), 251 (10), 239 (9), 197 (5), 167 (19), 162 (39), 149 (63), 134 (18), and 121 (10).

1-Benzothiophene-2,3-dione 2-[*N*-(4-chlorophenyl)hydrazone] 3c

This compound was prepared from **2c** (3.5 g, 10 mmol) and 1,1′-carbonyldiimidazole (2.0 g, 12.5 mmol) by following the same procedure and experimental conditions described above for **3a**. Yield 2.4 g (82%); mp 241–243 °C (Found: C, 58.1; H, 3.1; Cl, 12.1; N, 9.6; S, 10.9. $C_{14}H_9ClN_2OS$ requires C, 58.2; H, 3.1; Cl, 12.3; N, 9.7; S, 11.1%); ν_{max}(KBr)/cm^{-1} 3218, 3183, 1659, 1537, 1483, 1262, 1220, 1084 and 1062; δ_H(300 MHz; DMSO-d_6; Me_4Si) 7.37 (5 H, m, H-2′/H-6′, H-3′/H-5′, H-5), 7.68 (1 H, dd, *J* 7.3 and 7.7, H-6), 7.75 (1 H, d, *J* 7.7, H-7), 7.78 (1 H, d, *J* 7.5, H-4) and 10.94 (1 H, s, NH); δ_C(75 MHz; DMSO-d_6; Me_4Si) 116.8 (C-2′/C-6′), 125.7 (C-7), 126.5 (C-4), 126.7 (C-4′), 126.9 (C-5), 129.7 (C-3′/C-5′), 130.4 (C-3a), 132.7 (C=N), 136.3 (C-6), 141.5 (C-4′), 141.6 (C-7a), 142.9 (C-1′) and 183.7 (C=O); *m*/*z* (EI) 288.013677 (C_{14} H_9 Cl N_2 O S requires 288.012413), 288 (M^+, 100%), 271 (7), 259 (6), 225 (5), 197 (6), 177 (3), 162 (66), 149 (6), 134 (26) and 121 (13).

Collection of X-ray diffraction data and the structure analysis of 3b

Orange plate crystals of **3b** were grown by allowing a saturated solution of **3b** in chloroform–methanol (10 : 1, v/v) to evaporate slowly at room temperature over 6–7 days. Crystal dimensions of the thin plate were about 0.27 × 0.24 × 0.05 mm, producing problems with the absorption correction which is apparent in the ADPs (anisotropic displacement parameters) displayed in Fig. 1. The crystal data were collected with a Siemens SMART CCD diffractometer [graphite monochromator] operating in the omega scan mode (0.3°). The data were reduced with the Siemens–Bruker program suite XSCANS,[14] and the structure was solved by the direct method using SHELXTL PLUS programs.[15] All non-hydrogen atoms were refined anisotropically by a full-matrix, least-squares procedure based on F^2 using all unique data. GOF = 0.935, residual electron density between 0.482 and −0.379 e $Å^{-3}$. The hydrogen atoms were located from the difference Fourier electron density synthesis and were then refined isotropically using a 'riding model'.

Acknowledgements

We wish to thank the Advanced Pharmaceutical Industries Co. Ltd., Amman – Jordan for financial support.

References

1 B. A. Abu Thaher, J. A. Zahra and M. M. El-Abadelah, *J. Heterocycl. Chem.*, 2002, **39**, 901.
2 P. Trimarco and C. Lastrucci, *J. Heterocycl. Chem.*, 1976, **13**, 913.
3 (*a*) R. N. Butler and F. L. Scott, *Chem. Ind. (London)*, 1970, 1216; (*b*) H. Ulrich, in *The Chemistry of Imidoyl Halides*, Plenum Press, New York, 1968, Chapter 7, pp. 174–192; (*c*) A. F. Hegarty, J. B. Aylward and F. L. Scott, *J. Chem. Soc. C*, 1967, 2587; (*d*) P. Dalla Corce, P. Del Buttero, E. Licandro and S. Maiorana, *Synthesis*, 1979, 299; (*e*) G. Heubach, *Liebigs Ann. Chem.*, 1980, 1376; (*f*) H. M. Hassaneen, H. A. H. Mousa and N. M. Abed, *Heterocycles*, 1988, **27**, 695; (*g*) T. Benincori and F. Sannicoló, *J. Org. Chem.*, 1988, **53**, 1309.
4 (*a*) V. A. Galishev, V. N. Chistokletov and A. A. Petrov, *Zh. Obshch. Khim.*, 1975, **45**, 1695; (*b*) A. S. Shawali and C. Párkányi, *J. Heterocycl. Chem.*, 1980, **17**, 833.
5 M. M. El-Abadelah, A. Q. Hussein and B. A. Abu Thaher, *Heterocycles*, 1991, **32**, 1879.
6 N. F. Eweiss and A. Osman, *J. Heterocycl. Chem.*, 1980, **17**, 1713.
7 R. Fusco and R. Romani, *Gazz. Chim. Ital.*, 1946, **76**, 419.
8 (*a*) R. R. Phillips, *Org. React.*, 1959, **10**, 143; (*b*) H. C. Yao and P. Resnick, *J. Am. Chem. Soc.*, 1962, **84**, 3514.
9 G. C. Barrett, M. M. El-Abadelah and M. K. Hargreaves, *J. Chem. Soc. C*, 1970, 1986.
10 K. Auwers and K. Müller, *Justus Liebigs Ann. Chem.*, 1911, **381**, 276.
11 C. H. Yoder, R. C. Barth, W. M. Richter and F. A. Snavely, *J. Org. Chem.*, 1972, **25**, 4121.
12 V. A. Bren', M. I. Knyazhanskii, A. É. Lyubarskaya, V. S. Orekhovskii, G. D. Palui, V. P. Rybalkin and Kh. A. Kurdanov, *Izv. Sev. Kavk. Nauchn. Tsentra Vyssh. Shk. Estestv. Nauki*, 1984, 63 (*Chem. Abstr.*, 1985, **103**, 53899b).
13 V. P. Rybalkin, N. I. Makarova, A. É. Lyubarskaya, V. A. Bren' and V. I. Minkin, *Zh. Org. Khim.*, 1990, **26**, 335 (*Chem. Abstr.*, 1990, **113**, 77450f).
14 Bruker AXS SADABS program multiscan V2.03.
15 G. M. Sheldrick, SHELXTL PLUS System of computer programs for the determination of crystal structure from the X-Ray diffraction data, Vers.5.10.DOS/WIN 95/NT.