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N,*N*-Dialkyl-*N*′-Chlorosulfonyl Chloroformamidines in Heterocyclic Synthesis. Part VII* 4-Dialkylamino[1,2,3,5] Benzoxathiadiazepine Dioxides and 4-Dialkylamino [2,1,3,5]Benzothiatriazepine Dioxides

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N,*N*-dialkyl-*N*′-chlorosulfonyl chloroformamidines **1** reacted with 2-aminophenols **2** to give 4-dialkylamino[1,2,3,5] benzoxathiadiazepine dioxides **3**, which are examples of a new ring system. Reaction of **1** with 1,2-diaminobenzenes **7** afforded 4-dialkylamino[2,1,3,5]benzothiatriazepine dioxides **8** and **9**, which are new derivatives of a rare ring system. Some *N*-alkyl and *N*-acyl derivatives of **3** and **8** were prepared to demonstrate the potential of these compounds as novel scaffolds for synthetic and medicinal chemistry.

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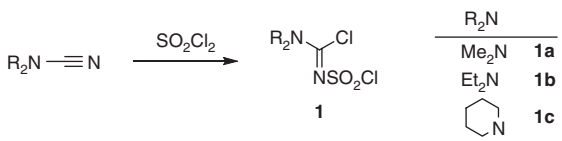
Introduction

We have previously remarked upon the facility with which readily available[1,2] *N*,*N*-dialkyl *N*′-chlorosulfonyl chloroformamidines **1** react with 1,2- and 1,3-bidentate nucleophiles to generate uncommon or previously unknown five-[3] or six-membered[4–8] heterocyclic ring systems, respectively. While the novelty of these products had much to commend them as candidates for biological testing, further evaluation was constrained by a lack of reactive sites where a diversity of substituents could be readily introduced. In order to overcome this limitation as well as to examine the feasibility of creating seven-membered heterocyclic rings, the potential for 2-aminophenols and 1,2-diaminobenzenes to condense with the dichloro compound **1**, was examined.

Results and Discussion

The dichlorides **1a**–**c** were readily prepared[1,2] from sulfuryl chloride and the corresponding dialkyl cyanamide (Scheme 1).

Reaction of **1** with 2-aminophenols **2** in DMPU (dimethylpropylene urea, 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone) in the presence of Hünig's base (*N*,*N*-diisopropylethylamine) provided 4-dialkylamino[1,2,3,5] benzoxathiadiazepine dioxides **3** (Scheme 2, Table 1), examples of a new ring system.



Scheme 1.

The [1,2,3,5]benzoxathiadiazepines **3** were precipitated from the DMPU-based reaction mixture in high purity by the addition of ethyl acetate and water and acidification to pH 3.

The derivatives of the new [1,2,3,5]benzoxathiadiazepine ring system described above were stable, colourless, crystalline solids unaffected by recrystallization from alcohols.

Confirmation of the ring structure of [1,2,3,5]benzoxathiadiazepines **3** was provided by X-ray crystallographic studies of *N*-acylated and *N*-alkylated derivatives (see below). Ring formation to produce compounds **3** proceeds so that the amino group of **2** bonds with the amidine carbon atom of **1** and the hydroxy group reacts with the sulfamoyl chloride moiety. This mode of reaction confirms[3–8] the greater electrophilicity of the amidinyl chloride moiety, relative to the sulfamoyl chloride group, in dichlorides **1**.

The possible regioisomeric products **4** (Scheme 2) were not isolated. Upon chromatographic purification of the residue from evaporation of the mother liquor from isolation of **3b**, the only clearly identifiable component was 2-piperidin-1-ylbenzoxazole,[9,10] produced in low yield.

The new heterocycle **3** contains an NH moiety and thus has the potential for introduction of various substituents. The nucleophilic nature of the nitrogen atoms of the oxathiadiazepine ring was confirmed by acylation and alkylation of **3b** and **3d**.

The reactions of **3b** and **3d** with acetic anhydride and the reaction of **3b** with benzoyl chloride all occurred selectively at N5 to give the acylated products **5a**–**c** (Scheme 3, Table 2).

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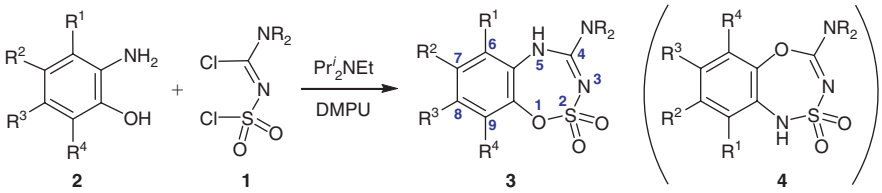
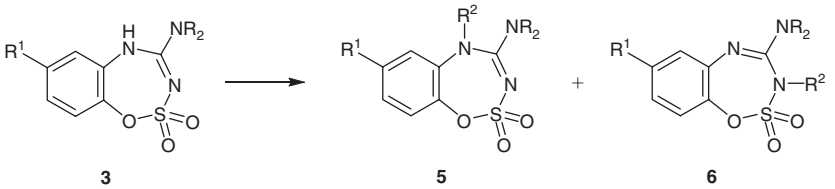


Scheme 2.

Table 1. Synthesis of the 4-dialkylamino[1,2,3,5]benzoxathiadiazepine dioxides 3

R_2N	R^1	R^2	R^3	R^4	Product	Yield [%]
Me_2N (**1a**)	H	H	H	H (**2a**)	**3a**	48
 (**1c**)	H	H	H	H (**2a**)	**3b**	69
 (**1c**)	Me	H	H	H (**2b**)	**3c**	23
Me_2N (**1a**)	H	Me	H	H (**2c**)	**3d**	53
 (**1c**)	H	Me	H	H (**2c**)	**3e**	24
Me_2N (**1a**)	H	H	Me	H (**2d**)	**3f**	71
Et_2N (**1b**)	H	H	Me	H (**2d**)	**3g**	53
Me_2N (**1a**)	H	Cl	H	Cl (**2e**)	**3h**	31
Et_2N (**1b**)	H	Cl	H	Cl (**2e**)	**3i**	48
Et_2N (**1b**)	H	Tetrahydrobenzo	fused	H (**2f**)	**3j**	54



Scheme 3.

Table 2. Synthesis of the [1,2,3,5]benzoxathiadiazepine dioxides 5 and 6

R_2N	R^1	R^2	Method	Product	Yield [%]
	H	$COCH_3$	$(CH_3CO)_2O$, py, 120°C	**5a**	77
Me_2N	CH_3	$COCH_3$	$(CH_3CO)_2O$, py, 120°C	**5b**	77
	H	COPh	PhCOCl, py, room temp.	**5c**	50
	H	4-$ClC_6H_4CH_2$	4-$ClC_6H_4CH_2Br$, cat. Bu^n_4NBr, K_2CO_3, CH_3CN, room temp.	**5d** + **6d**	32 + 49

The structural assignments for **5a**–**c** were based on X-ray crystallographic analysis of the benzoylated product **5c** (Fig. 1).

Alkylation of **3b** with 4-chlorobenzyl bromide was not selective and a mixture of benzylated products **5d** and **6d** was obtained (Scheme 3, Table 2). The structure of compound **6d** was confirmed by X-ray crystallography (Fig. 1).

Having constructed the 2,1,3,5-benzothiatriazepine ring from dichlorides **1** and 2-aminophenols **2**, we envisaged an analogous reaction with 1,2-diaminobenzenes **7**. Indeed, such a reaction gave 4-dialkylamino[2,1,3,5]benzothiatriazepine 2,2-dioxides **8** and, on occasion when $R^2 \neq H$, the isomeric compounds **9** as a minor product (Scheme 4, Table 3). These compounds are new derivatives of a rare[11,12] ring system.

Usually, the 2,1,3,5-benzothiatriazepines **8** were precipitated from the reaction mixture in high purity by our favoured ethyl acetate/water (pH 3) workup method.

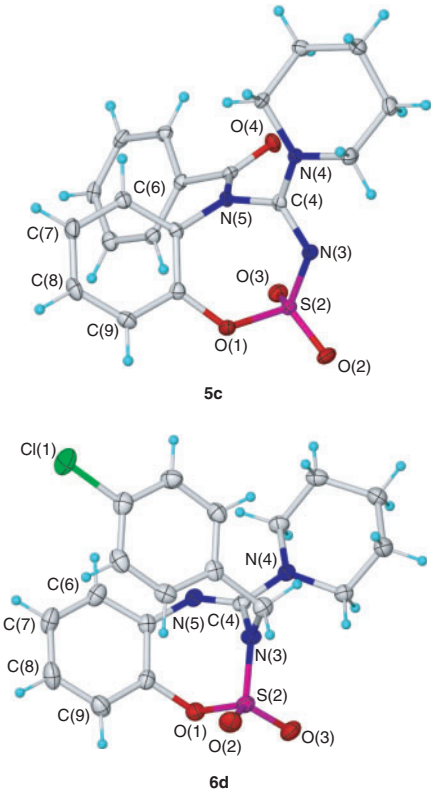


Fig. 1. *ORTEP* diagrams of **5c** (above) and **6d** (below). For **6d**, only one of two crystallographically independent, but virtually identical, molecules is shown.

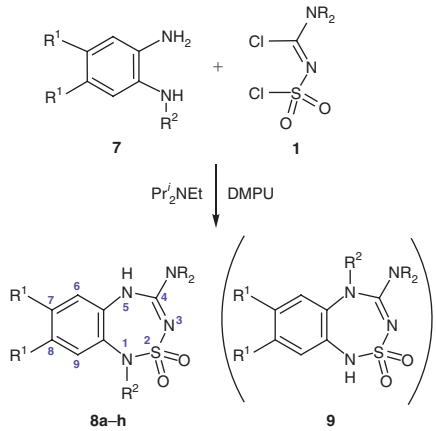
The derivatives of the uncommon heterocyclic system described above were all stable, colourless, crystalline solids unaffected by recrystallization from alcohols. Compound **9h** was more soluble and more mobile during TLC than the major isomer **8h**.

Spectroscopic studies alone did not allow us to distinguish between the two isomeric structures **8** and **9**; therefore structural assignments for compounds listed in Table 3 were based upon X-ray crystallographic analyses of compounds **8g** and **8h** (Fig. 2).

Interestingly, in both crystal structures of **8g** and **8h**·H_2O, a single tautomeric form is clearly evident, with the hydrogen atom residing on the (diaminobenzene-derived) nitrogen atom, N5, rather than N3 (Fig. 2). The thiatriazepine heterocycle exists in a pseudo boat conformation, for which there are two enantiomorphic configurations (A and B, Fig. 3). In the solid state, **8g** crystallizes in the non-centrosymmetric space group $P2_12_12_1$ and the crystal analyzed contained only one configuration (A), whereas **8h**·H_2O has both configurations A and B due to the inversion symmetry present in the centrosymmetric space group $P2_1/c$.

The new heterocyclic products **8** (and **9**) contain either one or two NH moieties in the newly formed thiatriazepine ring and thus have the desired potential for introduction of various substituents. The nucleophilic nature of the nitrogen atoms of the thiatriazepine ring was confirmed by acylation and alkylation of **8a** and **8h**.

Acylation of 1-methyl thiatriazepine **8h** with acetic anhydride or benzoyl chloride occurred preferentially at N3 (Scheme 5, Table 4) to afford the 3-acetyl and 3-benzoyl derivatives **10a** and **10b**, respectively. The structural assignments were confirmed



Scheme 4.

Table 3. Synthesis of the 4-dialkylamino[2,1,3,5]benzothiatriazepine 2,2-dioxides 8 and 9

R_2N	R^1	R^2	Product	Yield [%]
Me_2N (**1a**)	H	H (**7a**)	**8a**	55
N (**1c**)	H	H (**7a**)	**8b**	33
Me_2N (**1a**)	Cl	H (**7b**)	**8c**	66
Et_2N (**1b**)	Cl	H (**7b**)	**8d**	14
Me_2N (**1a**)	Me	H (**7c**)	**8e**	52
Et_2N (**1b**)	Me	H (**7c**)	**8f**	52
Me_2N (**1a**)	H	4-$ClC_6H_4CH_2$ (**7d**)	**8g**	48
N (**1c**)	H	Me (**7e**)	**8h** + **9h**	43 + 2

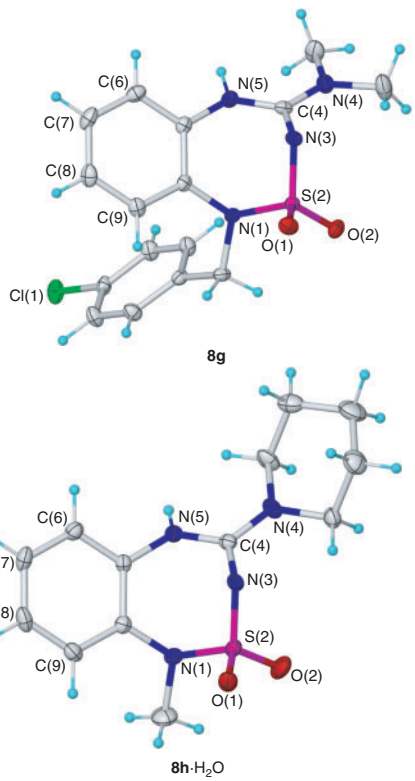


Fig. 2. *ORTEP* diagrams of **8g** (above) and **8h**·H_2O (below). For **8h**·H_2O, the lattice water molecule is not shown.

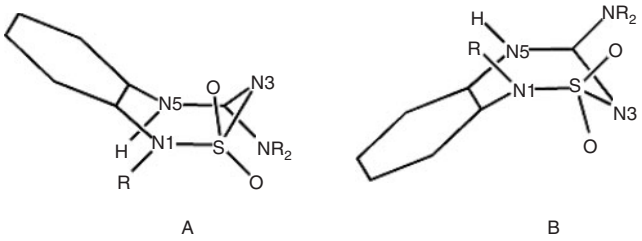
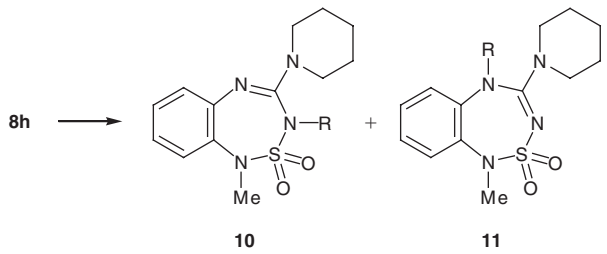


Fig. 3. Enantiomorphic forms of the thiatriazepine ring found in the solid state.



Scheme 5.

Table 4. Synthesis of the [2,1,3,5]benzothiatriazepine 2,2-dioxides 10 and 11

R	Method	Product	Yield [%]
$COCH_3$	$(CH_3CO)_2O$, py, 90°C	**10a**	64
COPh	PhCOCl, py, room temp.	**10b**	38
4-$ClC_6H_4CH_2$	4-$ClC_6H_4CH_2Br$, cat. Bu^n_4NBr, K_2CO_3, CH_3CN, room temp.	**10c** + **11c**	70 + 18

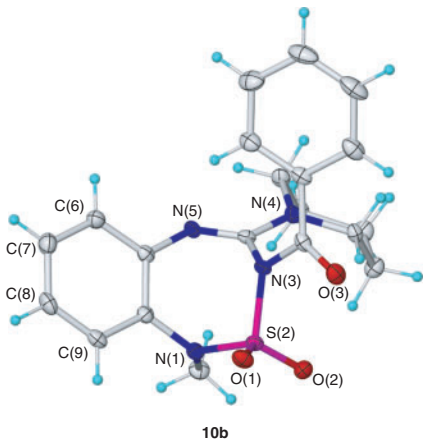
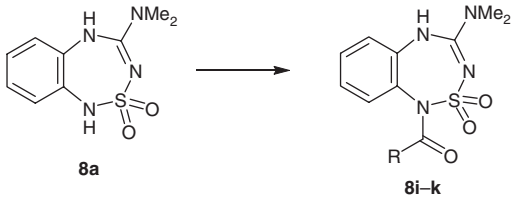


Fig. 4. *ORTEP* diagram of **10b**.

by X-ray crystallography of the benzoyl derivative **10b** (Fig. 4).

Alkylation of **8h** with 4-chlorobenzyl bromide also proceeded predominantly at N3 to give **10c** as the major product, but also occurred at N5, to afford **11c** as a minor product (Scheme 5, Table 4).



Scheme 6.

Table 5. Synthesis of the acylated [2,1,3,5]benzothiatriazepine 2,2-dioxides 8i–k

R	Method	Product	Yield [%]
CH_3	$(CH_3CO)_2O$, py, room temp.	**8i**	69
Ph	PhCOCl, py, room temp.	**8j**	49
4-$CH_3C_6H_4NH$	4-$CH_3C_6H_4NCO$, cat. NEt_3, CH_2Cl_2, room temp.	**8k**	76

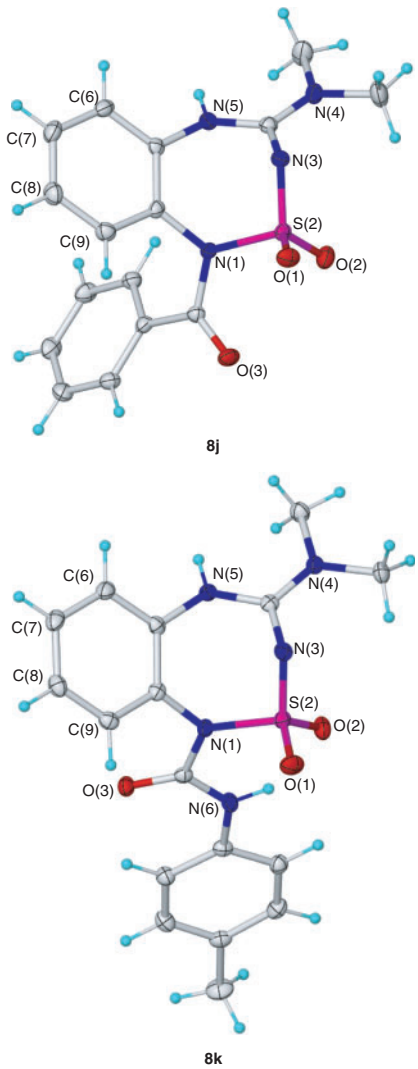


Fig. 5. *ORTEP* diagrams of **8j** (top) and **8k** (bottom). In **8j**, the lattice MeCN has been omitted for clarity and only one conformation of the disordered methyl group is shown.

Evidence to support the structural assignments of **10c** and **11c** was obtained from ^{1}H NMR experiments. During a 500 MHz gradient-selected nuclear overhauser effect correlation spectroscopy (NOESY) two-dimensional ^{1}H NMR experiment with

11c, we observed a relatively strong NOE between the resonance attributed to the benzylic methylene group and the resonance of the *ortho*-hydrogen (relative to N5) of the benzo moiety.

Two striking similarities were observed in the one-dimensional ^{1}H NMR spectrum of **10c** and that of the analogous N3-benzylated benzoxathiadiazepine **6d** (Scheme 3, Table 2, Fig. 1), the structure of which was determined by X-ray crystallography. The splitting pattern for the signals due to the aromatic hydrogen atoms in the ^{1}H NMR spectrum of **10c** was almost identical to that for **6d**, and the chemical shift of δ4.11 for the benzylic methylene group in **10c** was very similar to that for the corresponding signal (δ4.21) in the spectrum of **6d**. The benzylic methylene resonance for **10c** was significantly upfield from the corresponding signal for the isomeric N5-benzylated compound **5d** (δ4.72), which was very similar to that for **11c** (δ4.66) and other N5-benzylated derivatives (see below).

The reactions of **8a** with acetic anhydride, benzoyl chloride, and *p*-tolyl isocyanate all occurred selectively at N1 to give the acylated products **8i**–**k** shown in Scheme 6 and Table 5.

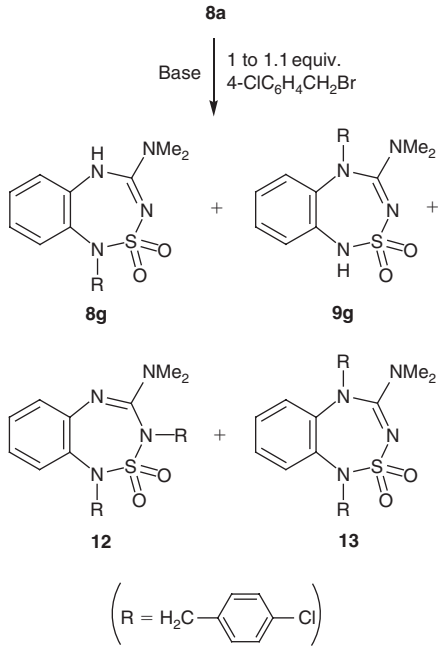
The structural assignments were based on X-ray crystallographic analyses of the benzoylated product **8j** and the isocyanate adduct **8k** (Fig. 5). A single tautomeric form is also clearly evident, with the hydrogen atom residing on the (diaminobenzene-derived) nitrogen atom N5, rather than on N3. As with **8g** (above), **8k** crystallizes in a non-centrosymmetric space group $P2_12_12_1$ and has only the one enantiomorph (A in Fig. 3) present in the crystal.

Alkylation of **8a** with 1 to 1.1 molar equivalents of 4-chlorobenzyl bromide under basic conditions was not selective and mixtures of mono- and di-alkylated products were obtained with a variety of reaction conditions (Scheme 7, Table 6). Aqueous sodium hydroxide, dichloromethane, and a phase transfer catalyst resulted in predominant formation of the 1,3-bis(4-chlorobenzyl) product **12** along with minor proportions of the 1,5-bis(4-chlorobenzyl) product **13** and the N1 monosubstituted derivative **8g**. Potassium carbonate in *N*,*N*-dimethylformamide (DMF) afforded a similar product mixture, with an additional product, the N5-monosubstituted derivative **9g**, being isolated in very low yield. Formation of an N-anion with 1.1 molar equivalents of sodium hydride in tetrahydrofuran (THF)/DMF, followed by addition of 4-chlorobenzyl bromide, resulted in the N1-monosubstituted derivative **8g** being the major product, along with a significant proportion of the 1,3-bis-substituted product **12**, and minor proportions of **9g** and **13**.

These results suggest that initial alkylation probably occurs at N1 and that the resulting compound **8g** is more susceptible to alkylation than the starting material **8a**.

The structural assignments for **9g**, **12**, and **13** were made on the basis of their ^{1}H NMR spectra and insights gained from other alkylation experiments. The benzylic methylene group of **9g** resonated at δ4.71. If the compound had the isomeric structure with N3 substitution, this resonance would have been expected further upfield, as for **10c** (δ4.11). Assignment of 1,3-bis substitution for compound **12** and 1,5-bis substitution for compound **13** was made on the basis of the benzylic methylene resonances at δ4.68 and 4.12 for **12**, and at δ4.68 and 4.43 for **13**.

Successful construction of the [1,2,3,5]benzoxathiadiazepine and [2,1,3,5]benzothiatriazepine rings from 2-aminophenols and 1,2-diaminobenzenes, respectively, encouraged us to investigate the analogous reaction with 2-aminothiophenols. However, reaction of **1a** with 2-aminothiophenol (Hünig's base/DMPU) afforded a complex mixture of products. The only compound obtained from chromatographic purification was the known 2-(*N*,*N*-dimethylamino)benzothiazole.[10]



Scheme 7.

Table 6. Alkylation products from the [2,1,3,5]benzothiatriazepine 2,2-dioxide 8a

Method	Yield of product [%]			
	8g	**9g**	**12**	**13**
NaOH, cat. Bu^n_4NBr, CH_2Cl_2, H_2O, room temp.	4	—	41	2
K_2CO_3, cat. Bu^n_4NBr, DMF, room temp.	8	4	36	2
NaH, THF/DMF (2:1), room temp.	31	5	23	3

Conclusions

The dichloro compounds **1**, readily available 1,3-dielectrophiles, have been shown to react with 2-aminophenols to afford dioxo derivatives of the hitherto unreported [1,2,3,5]benzoxathiadiazepine ring system. Similar reaction of dichlorides **1** with 1,2-diaminobenzenes provides a convenient pathway to the rare [2,1,3,5]benzothiatriazepine dioxides. Convenient alkylation and acylation reactions of representative derivatives of both of the ring systems demonstrated the potential of these compounds as novel scaffolds for synthetic and medicinal chemistry.

Experimental

Methods and Materials

General experimental conditions have been described previously.[4,6] *N*,*N*-Dialkyl-*N*′-chlorosulfonyl chloroformamidines **1a**, **1b**, and **1c** were prepared by literature

procedures[1,2] and used as crude products. Other materials were obtained from commercial sources.

General Synthesis Procedure for 4-Dialkylamino-2,2-dioxo-2λ^6-[1,2,3,5]benzoxathiadiazepines ***3a–j***

N,*N*-Diisopropylethylamine (13 mmol) was added to an ice-water cooled, stirred mixture of the 2-aminophenol **2** (5 mmol), the dichloro compound **1** (6.5 mmol), and DMPU (4 mL). The resulting mixture was stirred at room temperature for at least 4 h. Ethyl acetate (15 mL) was added, followed by water (30 mL) and acidification to pH 3 with concentrated hydrochloric acid. The mixture was stirred vigorously at room temperature for at least 1 h. The precipitate was collected by filtration and washed sequentially with water, ethyl acetate, and diethyl ether.

The following compounds were prepared by the above procedure.

4-Dimethylamino-2,2-dioxo-2λ^6-[1,2,3,5]benzoxathiadiazepine ***3a***

Precipitated as a light beige solid in 48% yield. A sample was recrystallized from ethyl acetate to give off-white crystals, mp 231–232°C. (Found: C 44.8, H 4.5, N 17.6; $M^{+\bullet}$ 241.0511. $C_9H_{11}N_3O_3S$ requires C 44.8, H 4.6, N 17.4%; $M^{+\bullet}$ 241.0516). δ_H ([D$_6$]DMSO) 9.84 (1H, s, NH), 7.33–7.25 (3H, m, ArH), 7.24–7.18 (1H, m, ArH), 3.16 (6H, s, NMe_2). δ_C ([D$_6$]DMSO) 152.6, 144.1, 130.8, 127.4, 126.6, 124.7, 122.9, 38.9. *m/z* (EI) 241 (14%, $M^{+\bullet}$), 161 (39), 134 (26), 71 (100).

2,2-Dioxo-4-piperidin-1-yl-2λ^6-[1,2,3,5]benzoxathiadiazepine ***3b***

Precipitated as a pale beige solid in 69% yield. A sample was recrystallized from ethanol to give off-white crystals, mp 226.5–228.5°C. (Found: C 51.1, H 5.4, N 15.1; $M^{+\bullet}$ 281.0828. $C_{12}H_{15}N_3O_3S$ requires C 51.2, H 5.4, N 14.9%; $M^{+\bullet}$ 281.0829). δ_H ([D$_6$]DMSO) 9.99 (1H, s, NH), 7.31–7.16 (4H, m, ArH), 3.68 (4H, br, 2 × NCH_2), 1.61 (6H, br, 3 × CH_2). δ_C ([D$_6$]DMSO) 151.2, 144.3, 130.7, 127.5, 126.6, 124.7, 122.9, 47.5, 25.9, 23.8. *m/z* (EI) 281 (5%, $M^{+\bullet}$), 201 (30), 134 (34), 111 (37), 84 (100).

The organic phase of the mother liquor was washed four times with water, dried, and evaporated. The residue was chromatographed over silica gel (0–3% methanol in dichloromethane) to afford 2-piperidin-1-ylbenzoxazole[9,10] (1%).

2,2-Dioxo-6-methyl-4-piperidin-1-yl-2λ^6-[1,2,3,5]benzoxathiadiazepine ***3c***

Precipitated as a cream solid in 23% yield. A sample was recrystallized from ethanol to give colourless crystals, mp 264–265°C. (Found: C 52.7, H 6.0, N 14.4; $M^{+\bullet}$ 295.0985. $C_{13}H_{17}N_3O_3S$ requires C 52.9, H 5.8, N 14.2%; $M^{+\bullet}$ 295.0985). δ_H ([D$_6$]DMSO) 9.51 (1H, s, NH), 7.27–7.17 (2H, m, ArH), 7.11–7.06 (1H, m, ArH), 3.67 (4H, m, 2 × NCH_2), 2.32 (3H, s, CH_3), 1.62 (6H, m, 3 × CH_2). δ_C ([D$_6$]DMSO) 151.8, 146.2, 134.6, 129.3, 128.4, 128.0, 120.5, 47.6, 25.9, 23.9, 17.8. *m/z* (EI) 295 (23%, $M^{+\bullet}$), 215 (80), 186 (39), 148 (85), 111 (82), 84 (100).

4-Dimethylamino-2,2-dioxo-7-methyl-2λ^6-[1,2,3,5]benzoxathiadiazepine ***3d***

Precipitated as a beige solid in 53% yield. A sample was recrystallized from ethanol to give off-white crystals, mp 231–232°C. (Found: C 47.0, H 5.2, N 16.6; $M^{+\bullet}$ 255.0676. $C_{10}H_{13}N_3O_3S$ requires C 47.1, H 5.1, N 16.5%; $M^{+\bullet}$ 255.0672). δ_H ([D$_6$]DMSO) 9.73 (1H, s, NH), 7.11 (1H, m, ArH), 7.08 (2H, m, ArH), 3.15 (6H, s, NMe_2), 2.29 (3H, s, $ArCH_3$). δ_C ([D$_6$]DMSO) 152.5, 141.9, 136.0, 130.4, 127.8, 124.8, 122.6, 38.9, 20.8. *m/z* (EI) 255 (48%, $M^{+\bullet}$), 175 (100).

2,2-Dioxo-4-piperidin-1-yl-7-methyl-2λ^6-[1,2,3,5]benzoxathiadiazepine ***3e***

Precipitated as a beige solid in 24% yield. A sample was recrystallized from ethanol to give off-white crystals, mp 261.5–262°C. (Found: C 52.8, H 6.0, N 14.4; $M^{+\bullet}$ 295.0983. $C_{13}H_{17}N_3O_3S$ requires C 52.9, H 5.8, N 14.2%; $M^{+\bullet}$ 295.0985). δ_H ([D$_6$]DMSO) 9.88 (1H, s, NH), 7.11–7.06 (3H, m, ArH), 3.67 (4H, br, 2 × NCH_2), 2.29 (3H, s, $ArCH_3$), 1.59 (6H, br, 3 × CH_2). δ_C ([D$_6$]DMSO) 151.2, 142.1, 136.1, 130.3, 127.9, 124.9, 122.5, 47.5, 25.9, 23.8, 20.7. *m/z* (EI) 295 (27%, $M^{+\bullet}$), 215 (95), 148 (86), 111 (95), 84 (100).

4-Dimethylamino-2,2-dioxo-8-methyl-2λ^6-[1,2,3,5]benzoxathiadiazepine ***3f***

Precipitated as a brilliant white solid in 71% yield. A sample was recrystallized from ethanol to give colourless crystals, mp 269–270°C. (Found: C 47.0, H 5.2, N 16.7; $M^{+\bullet}$ 255.0672. $C_{10}H_{13}N_3O_3S$ requires C 47.1, H 5.1, N 16.5%; $M^{+\bullet}$ 255.0672). δ_H ([D$_6$]DMSO) 9.77 (1H, s, NH), 7.17 (1H, d, *J* 8, ArH), 7.09 (1H, d, *J* 8, ArH), 7.03 (1H, s, ArH), 3.15 (6H, s, NMe_2), 2.30 (3H, s, $ArCH_3$). δ_C ([D$_6$]DMSO) 152.7, 143.9, 137.3, 128.1, 127.1, 124.4, 123.1, 38.8, 20.7. *m/z* (EI) 255 (22%, $M^{+\bullet}$), 175 (77), 148 (48), 93 (46), 71 (100).

4-Diethylamino-2,2-dioxo-8-methyl-2λ^6-[1,2,3,5]benzoxathiadiazepine ***3g***

Precipitated as a white solid in 53% yield. A sample was recrystallized from ethanol to give colourless crystals, mp 209–210°C. (Found: C 50.8, H 6.2, N 15.0; $M^{+\bullet}$ 283.0980. $C_{12}H_{17}N_3O_3S$ requires C 50.9, H 6.1, N 14.8%; $M^{+\bullet}$ 283.0985). δ_H ([D$_6$]DMSO) 9.72 (1H, s, NH), 7.17 (1H, d, *J* 8, ArH), 7.10 (1H, d, *J* 8, ArH), 7.04 (1H, s, ArH), 3.54 (4H, q, *J* 7, 2 × NCH_2), 2.30 (3H, s, $ArCH_3$), 1.18 (6H, t, *J* 7, 2 × CH_3). δ_C ([D$_6$]DMSO) 151.9, 144.2, 137.5, 128.3, 127.1, 124.6, 123.1, 43.7, 20.7, 13.6. *m/z* (EI) 283 (52%, $M^{+\bullet}$), 203 (70), 148 (91), 99 (100).

7,9-Dichloro-4-dimethylamino-2,2-dioxo-2λ^6-[1,2,3,5]benzoxathiadiazepine ***3h***

Precipitated as a fawn solid in 31% yield. A sample was recrystallized from ethanol to give off-white crystals, mp 263.5–264°C. (Found: C 34.9, H 3.2, N 13.7; $M^{+\bullet}$ 308.9727. $C_9H_9Cl_2N_3O_3S$ requires C 34.9, H 2.9, N 13.6%; $M^{+\bullet}$ 308.9736). δ_H ([D$_6$]DMSO) 10.01 (1H, s, NH), 7.65 (1H, d, *J* 2.3, ArH), 7.41 (1H, d, *J* 2.3, ArH), 3.18 (6H, s, NMe_2). δ_C ([D$_6$]DMSO) 152.1, 139.7, 133.4, 130.0, 128.2, 127.1, 123.5, 39.1. *m/z* (EI) 309/311/313 (21/14/3%, $M^{+\bullet}$), 229/231/233 (90/77/16), 202/204/206 (61/36/5), 112 (61), 71 (100).

7,9-Dichloro-4-diethylamino-2,2-dioxo-2λ^6-[1,2,3,5]benzoxathiadiazepine ***3i***

Precipitated as a beige solid in 48% yield. A sample was recrystallized from ethanol to give pale grey crystals, mp 262.5–263°C. (Found: C 39.1, H 4.1, N 12.5; $M^{+\bullet}$ 337.0040. $C_{11}H_{13}Cl_2N_3O_3S$ requires C 39.1, H 3.9, N 12.4%; $M^{+\bullet}$ 337.0049). δ_H ([D$_6$]DMSO) 9.98 (1H, s, NH), 7.67 (1H,

d, *J* 2.4, ArH), 7.41 (1H, d, *J* 2.4, ArH), 3.56 (4H, q, *J* 7, 2 × NCH_2), 1.19 (6H, t, *J* 7, 2 × CH_3). δ_C ([D_6]DMSO) 151.3, 140.2, 133.5, 130.0, 128.2, 127.3, 123.8, 44.1, 13.5. *m/z* (EI) 337/339/341 (14/10/2%, $M^{+\bullet}$), 257/259/261 (64/48/7), 202/204/206 (64/46/8), 72 (100).

4-Diethylamino-2,2-dioxo-2λ⁶-[5,6,7,8] tetrahydronaphthaleno[2,3-f][1,2,3,5] oxathiadiazepine ***3j***

Precipitated as a beige solid in 54% yield. A sample was recrystallized from ethanol to give off-white crystals, mp 235.5–236°C. (Found: C 55.4, H 6.7, N 13.1; $M^{+\bullet}$ 323.1302. $C_{15}H_{21}N_3O_3S$ requires C 55.7, H 6.5, N 13.0%; $M^{+\bullet}$ 323.1298). δ_H ([D_6]DMSO) 9.64 (1H, s, NH), 6.97 (1H, s, ArH), 6.90 (1H, s, ArH), 3.53 (4H, q, *J* 7, 2 × NCH_2), 2.69 (4H, m, 2 × CH_2Ar), 1.71 (4H, m, CH_2CH_2), 1.17 (6H, t, *J* 7, 2 × CH_3). δ_C ([D_6]DMSO) 151.8, 142.1, 136.3, 135.0, 128.1, 124.6, 122.4, 43.7, 28.6, 22.8, 22.7, 13.6. *m/z* (EI) 323 (25%, $M^{+\bullet}$), 243 (93), 99 (100).

5-Acetyl-4-piperidin-1-yl-2,2-dioxo-2λ⁶-[1,2,3,5]benzoxathiadiazepine ***5a***

A stirred mixture of compound **3b** (281 mg, 1.0 mmol), acetic anhydride (1 mL), and pyridine (4 drops) was heated at 120°C for 15 min. The mixture was cooled and diluted with water (10 mL) and allowed to stand at room temperature for 1 h. The precipitate was collected and washed with water followed by ether. Recrystallization from ethanol (charcoal) gave the *title compound* (250 mg, 77%) as colourless crystals, mp 165–166°C. (Found: C 52.0, H 5.2, N 13.2; $M^{+\bullet}$ 323.0935. $C_{14}H_{17}N_3O_4S$ requires C 52.0, H 5.3, N 13.0%; $M^{+\bullet}$ 323.0934). δ_H (200 MHz) 7.53–7.43 (1H, m, ArH), 7.34–7.24 (3H, m, ArH), 3.97–3.70 (2H, m, CH_2N), 3.68–3.60 (2H, m, CH_2N), 2.01 (3H, s, CH_3CO), 1.97–1.50 (6H, m, $CH_2CH_2CH_2$). δ_C (50 MHz) 169.1, 151.9, 147.4, 131.6, 129.4, 127.5, 126.3, 122.4, 48.8, 47.9, 25.9, 24.9, 23.6, 22.2. *m/z* (EI) 323 (11%, $M^{+\bullet}$), 281 (65), 84 (100).

5-Acetyl-4-dimethylamino-2,2-dioxo-7-methyl-2λ⁶-[1,2,3,5]benzoxathiadiazepine ***5b***

A stirred mixture of compound **3d** (256 mg, 1.0 mmol), acetic anhydride (1 mL), and pyridine (0.5 mL) was heated at 120°C for 30 min. The mixture was cooled and allowed to stand at room temperature for 1 h. The precipitate was collected and washed with water followed by ether. Recrystallization from ethanol (charcoal) gave the *title compound* (229 mg, 77%) as colourless crystals, mp 208.5–209°C. (Found: C 48.6, H 5.1, N 14.3; $M^{+\bullet}$ 297.0773. $C_{12}H_{15}N_3O_4S$ requires C 48.5, H 5.1, N 14.1%; $M^{+\bullet}$ 297.0778). δ_H ([D_6]DMSO, 500 MHz, 50°C) 7.59 (1H, br s, ArH), 7.36 (1H, d, *J* 8.3, ArH), 7.24 (1H, d, *J* 8.3, ArH), 3.26 (3H, s, NCH_3), 3.16 (3H, s, NCH_3), 2.35 (3H, s, $ArCH_3$), 1.97 (3H, br s, CH_3CO). δ_C ([D_6]DMSO, 125.75 MHz, 50°C, NMe_2 signals obscured by solvent at 20°C) 168.4, 152.8, 144.1, 136.4, 131.8, 130.5, 127.4, 121.0, 38.8, 38.6, 21.7, 19.9. *m/z* (EI) 297 (10%, $M^{+\bullet}$), 255 (100).

5-Benzoyl-4-piperidin-1-yl-2,2-dioxo-2λ⁶-[1,2,3,5]benzoxathiadiazepine ***5c***

Benzoyl chloride (0.8 mL) was added slowly to a stirred solution of compound **3b** (281 mg, 1 mmol) in pyridine (1.5 mL). The resulting solution was stirred at room temperature for 90 min. Water (20 mL) was cautiously added and the mixture was extracted with dichloromethane (20 mL). The extract was washed thrice with water, dried, and evaporated. The residue was triturated with cyclohexane/*n*-hexane (1:1) to give a pale yellow solid, which was chromatographed over silica gel (0–1% methanol in dichloromethane), followed by recrystallization from ethanol (charcoal) to give the *title compound* (193 mg, 50%) as colourless crystals, mp 194–195°C. (Found: C 59.2, H 5.0, N 11.0; $M^{+\bullet}$ 385.1087. $C_{19}H_{19}N_3O_4S$ requires C 59.2, H 5.0, N 10.9%; $M^{+\bullet}$ 385.1091). δ_H 7.79–7.71 (2H, m, ArH), 7.55–7.35 (5H, m, ArH), 7.32–7.18 (2H, m, ArH), 3.81 (1H, br, CHN), 3.56 (1H, br, CHN), 3.22 (2H, br, CH_2N), 1.46 (6H, br, $CH_2CH_2CH_2$). δ_C 168.1, 151.6, 146.8, 132.5, 132.3, 131.0, 129.8, 129.3, 128.6, 128.4, 126.3, 122.5, 48.9, 48.0, 25.6, 24.4, 23.4. *m/z* (EI) 385 (38%, $M^{+\bullet}$), 280 (24), 105 (100).

3-(4-Chlorobenzyl)-4-piperidin-1-yl-2,2-dioxo-2λ⁶-[1,2,3,5]benzoxathiadiazepine ***6d*** *and 5-(4-Chlorobenzyl)-4-piperidin-1-yl-2,2-dioxo-2λ⁶-[1,2,3,5]benzoxathiadiazepine* ***5d***

A mixture of compound **3b** (141 mg, 0.5 mmol), potassium carbonate (76 mg, 0.55 mmol), 4-chlorobenzyl bromide (113 mg, 0.55 mmol), tetrabutylammonium bromide (18 mg, 0.055 mmol), and acetonitrile (4 mL) was stirred at room temperature overnight. The solvent was removed under vacuum and the residue extracted with ethyl acetate (10 mL). The extract was washed with water (3 × 5 mL), dried, and evaporated. The residue was chromatographed over silica gel (0–1% methanol in dichloromethane) to give two fractions. (i) The *title compound* **6d** (100 mg, 49%). Recrystallized from methanol; colourless crystals, mp 86.5–87.5°C. (Found: C 56.1, H 5.0, N 10.2; $M^{+\bullet}$ 405.0909. $C_{19}H_{20}ClN_3O_3S$ requires C 56.2, H 5.0, N 10.4%; $M^{+\bullet}$ 405.0908). δ_H 7.23 (1H, d, *J* 8, ArH), 7.17 (1H, t, *J* 7.8, ArH), 7.14 (2H, d, *J* 8.3, ArH), 7.05 (1H, t, *J* 7.4, ArH), 6.93 (2H, d, *J* 8.3, ArH), 6.85 (1H, d, *J* 7.7, ArH), 4.21 (2H, s, CH_2Ar), 3.49 (4H, br, 2 × NCH_2), 1.9–1.1 (6H, br, 3 × CH_2). δ_C 146.5, 140.8, 134.7, 132.3, 130.5, 128.7, 127.9, 125.5, 124.1, 122.0, 54.8, 47.1, 25.5, 24.2. *m/z* (EI) 405/407 (58/18%, $M^{+\bullet}$), 280 (22), 258 (62), 125 (100). (ii) The *title compound* **5d** (64 mg, 32%). Recrystallized from dichloromethane/methanol; colourless crystals, mp 274–275°C. (Found: C 56.3, H 5.0, N 10.4; $M^{+\bullet}$ 405.0920. $C_{19}H_{20}ClN_3O_3S$ requires C 56.2, H 5.0, N 10.4%; $M^{+\bullet}$ 405.0908). δ_H ($CDCl_3$, 200 MHz) 7.24–7.09 (8H, m, ArH), 4.72 (2H, s, CH_2Ar), 3.59 (4H, br m, 2 × NCH_2), 1.73 (6H, br s, 3 × CH_2). δ_C ($CDCl_3$ + 3 drops CD_3OD, 100 MHz) 156.6, 147.2, 134.4, 133.7, 132.5, 130.0, 129.7, 128.7, 126.7, 126.2, 123.0, 57.9, 49.7, 25.5, 23.9. *m/z* (EI) 405/407 (9/4%, $M^{+\bullet}$), 325 (4), 280 (8), 258 (20), 125 (100).

*1-*N*-(4-Chlorobenzyl)-1,2-diaminobenzene* ***7d***

Prepared by modification of literature procedures.[13,14] Thus, a mixture of 2-nitrochlorobenzene (3.15 g, 20 mmol) and 4-chlorobenzylamine (7.08 g, 50 mmol) was heated at 100°C for 19 h. Upon cooling, the mixture solidified. The solid was pulverized and washed twice with 10% aqueous citric acid solution, and then washed copiously with water. The resulting solid was dried to give *N*-(4-chlorobenzyl)-2-nitroaniline (3.82 g, 73%) as a bright orange solid, mp 109–111°C (lit.[14] 110°C). δ_H 8.41 (1H, br, NH), 8.20 (1H, dd, *J* 8.6, 1.3, ArH), 7.41–7.25 (5H, m, ArH), 6.75 (1H, d, *J* 8.6, ArH), 6.68 (1H, m, ArH), 4.53 (2H, s, CH_2). A stirred mixture of *N*-(4-chlorobenzyl)-2-nitroaniline (1.30 g, 4.98 mmol), iron powder (1.38 g, 24.7 mmol), ammonium chloride (0.13 g), ethanol (34 mL), and water (17 mL) was

heated at 90–100°C for 40 min. The mixture was cooled and filtered, and the collected solids were washed with ethyl acetate. The filtrates were combined and concentrated. The residue was extracted with dichloromethane and the extract was washed with brine, dried, and evaporated. The residue was chromatographed over silica gel. Elution with dichloromethane afforded the *title compound* (1.04 g, 90%) as a fawn solid, which was used without further purification. δ_H 7.35–7.25 (4H, m, ArH), 6.84–6.72 (3H, m, ArH), 6.65 (1H, d, *J* 7.6, ArH), 4.31 (2H, s, CH_2) 3.94 (3H, br, NH_2 + NH). *m/z* (ES^-) 231/233 (10/4%, M − H), 125/127 (36/12), 106 (100).

General Synthesis Procedure for 4-Dialkylamino-2,2-dioxo-2λ⁶-[2,1,3,5]benzothiatriazepines ***8a–h*** *and* ***9h***

N,*N*-Diisopropylethylamine (13 mmol) was added to an ice-water cooled, stirred mixture of the 1,2-diaminobenzene **7** (5 mmol), the dichloro compound **1** (6.5 mmol), and DMPU (4 mL). The mixture was stirred at room temperature for at least 4 h. Ethyl acetate (15 mL) was added, followed by water (30 mL), and the mixture stirred vigorously for a few minutes. The whole was acidified to pH 3 with concentrated hydrochloric acid and the resulting mixture stirred vigorously at room temperature for at least 1 h. The precipitate was collected by filtration and washed sequentially with water, ethyl acetate, and diethyl ether.

The following compounds were prepared by the above procedure.

4-Dimethylamino-2,2-dioxo-2λ⁶-[2,1,3,5]benzothiatriazepine ***8a***

Precipitated as a white solid in 55% yield. A sample was recrystallized from methanol to give colourless crystals, mp 239–240°C. (Found: C 45.3, H 5.0, N 23.5; $M^{+\bullet}$ 240.0673. $C_9H_{12}N_4O_2S$ requires C 45.0, H 5.0, N 23.3%; $M^{+\bullet}$ 240.0675). δ_H ([D_6]DMSO) 9.25 (1H, s, NH), 8.96 (1H, s, NH), 7.16–7.06 (3H, m, ArH), 7.01 (1H, dd, *J* 7.5, 1.8, ArH), 3.09 (6H, s, NMe_2). δ_C ([D_6]DMSO) 152.7, 133.7, 132.2, 126.2, 124.8, 124.0, 123.7, 38.7. *m/z* (EI) 240 (100%, $M^{+\bullet}$).

2,2-Dioxo-4-piperidin-1-yl-2λ⁶-[2,1,3,5]benzothiatriazepine ***8b***

Precipitated as an off-white solid in 33% yield. A sample was recrystallized from ethanol to give colourless crystals, mp 233.5–234.5°C. (Found: C 51.6, H 5.8, N 20.1; $M^{+\bullet}$ 280.0980. $C_{12}H_{16}N_4O_2S$ requires C 51.4, H 5.8, N 20.0%; $M^{+\bullet}$ 280.0988). δ_H ([D_6]DMSO) 9.41 (1H, s, NH), 8.99 (1H, s, NH), 7.15–7.05 (3H, m, ArH), 7.03–6.99 (1H, m, ArH), 3.59 (4H, m, 2 × NCH_2), 1.65–1.50 (6H, m, 3 × CH_2). δ_C ([D_6]DMSO) 151.7, 133.8, 132.0, 126.3, 124.7, 123.9, 123.6, 47.3, 25.9, 24.1. *m/z* (EI) 280 (36%, $M^{+\bullet}$), 216 (16), 201 (14), 133 (100).

7,8-Dichloro-4-dimethylamino-2,2-dioxo-2λ⁶-[2,1,3,5]benzothiatriazepine ***8c***

Precipitated as an off-white solid in 66% yield. A sample was recrystallized from methanol/DMF (1:1) to give small, white, woolly needles, mp 265–267°C (dec.). (Found: C 35.0, H 3.3, N 18.2; $M^{+\bullet}$ 307.9894. $C_9H_{10}Cl_2N_4O_2S$ requires C 35.0, H 3.3, N 18.1%; $M^{+\bullet}$ 307.9896). δ_H ([D_6]DMSO) 9.34 (1H, s, NH), 9.31 (1H, s, NH), 7.47 (1H, s, ArH), 7.16 (1H, s, ArH), 3.09 (6H, s, NMe_2). δ_C ([D_6]DMSO) 151.9, 133.1, 131.3, 126.9, 125.4, 124.6, 123.2, 38.4. *m/z* (EI) 308/310/312 (90/62/13%, $M^{+\bullet}$), 244/246/248 (78/50/9), 229/231/233 (73/47/8), 201/203/205 (100/64/10).

7,8-Dichloro-4-diethylamino-2,2-dioxo-2λ⁶-[2,1,3,5]benzothiatriazepine ***8d***

Precipitated as a light grey solid in 14% yield. A sample was recrystallized from ethanol (charcoal) to give white crystals, mp 232–233°C. (Found: C 39.4, H 4.2, N 16.5; $M^{+\bullet}$ 336.0202. $C_{11}H_{14}Cl_2N_4O_2S$ requires C 39.2, H 4.2, N 16.6%; $M^{+\bullet}$ 336.0209). δ_H ([D_6]DMSO) 9.32 (1H, s, NH), 9.25 (1H, s, NH), 7.47 (1H, s, ArH), 7.20 (1H, s, ArH), 3.50 (4H, q, *J* 7, 2 × NCH_2), 1.16 (6H, t, *J* 7, 2 × CH_3). δ_C ([D_6]DMSO) 151.6, 134.3, 132.0, 127.9, 126.0, 125.6, 123.9, 43.5, 13.7. *m/z* (EI) 336/338/340 (38/25/6%, $M^{+\bullet}$), 272/274/276 (10/6/1), 257/259/261 (12/8/1), 243/245/247 (22/14/3), 228/230/232 (14/9/3), 214/216/218 (15/10/2), 201/203/205 (80/50/8), 72 (100).

7,8-Dimethyl-4-dimethylamino-2,2-dioxo-2λ⁶-[2,1,3,5]benzothiatriazepine ***8e***

Precipitated as an off-white solid in 52% yield. A sample was recrystallized from methanol to give colourless crystals, mp 247–249°C (dec.). (Found: C 49.2, H 6.0, N 21.1; $M^{+\bullet}$ 268.0991. $C_{11}H_{16}N_4O_2S$ requires C 49.2, H 6.0, N 20.9%; $M^{+\bullet}$ 268.0988). δ_H ([D_6]DMSO) 9.11 (1H, s, NH), 8.75 (1H, s, NH), 6.91 (1H, s, ArH), 6.77 (1H, s, ArH), 3.06 (6H, s, NMe_2), 2.143 (3H, s, CH_3), 2.137 (3H, s, CH_3). δ_C ([D_6]DMSO) 152.5, 134.2, 132.8, 131.1, 129.8, 124.74, 124.68, 38.6, 19.2, 19.1. *m/z* (EI) 268 (100%, $M^{+\bullet}$).

4-Diethylamino-7,8-dimethyl-2,2-dioxo-2λ⁶-[2,1,3,5]benzothiatriazepine ***8f***

Precipitated as a beige solid in 52% yield after addition of diethyl ether (5 mL). A sample was recrystallized from ethyl acetate to give colourless crystals, mp 226–228.5°C. (Found: C 52.7, H 7.1, N 19.2; $M^{+\bullet}$ 296.1297. $C_{13}H_{20}N_4O_2S$ requires C 52.7, H 6.8, N 18.9%; $M^{+\bullet}$ 296.1301). δ_H ([D_6]DMSO) 9.09 (1H, s, NH), 8.70 (1H, s, NH), 6.92 (1H, s, ArH), 6.80 (1H, s, ArH), 3.48 (4H, q, *J* 7, 2 × NCH_2), 2.16 (3H, s, CH_3), 2.15 (3H, s, CH_3), 1.15 (6H, t, *J* 7, 2 × CH_3). δ_C ([D_6]DMSO) 151.6, 134.5, 132.8, 131.6, 130.1, 124.89, 124.85, 43.2, 19.2, 19.1, 13.8. *m/z* (EI) 296 (97%, $M^{+\bullet}$), 232 (31), 217 (34), 203 (54), 188 (28), 174 (26), 161 (100).

1-(4-Chlorobenzyl)-4-dimethylamino-2,2-dioxo-2λ⁶-[2,1,3,5]benzothiatriazepine ***8g***

Precipitated as a brilliant white solid in 48% yield. A sample was recrystallized from ethanol to give colourless prisms, mp 205–207°C. (Found: C 52.9, H 4.8, N 15.5; $M^{+\bullet}$ 364.0751. $C_{16}H_{17}ClN_4O_2S$ requires C 52.7, H 4.7, N 15.4%; $M^{+\bullet}$ 364.0755). δ_H 7.46 (1H, br, NH), 7.19–6.99 (7H, m, ArH), 6.92 (1H, m, ArH), 4.70 (2H, s, CH_2), 2.93 (6H, s, NMe_2). δ_C 150.7, 135.3, 134.8, 133.4, 131.4, 130.3, 128.2, 127.8, 127.5, 125.4, 121.8, 54.5, 38.7. *m/z* (EI) 364/366 (93/57%, $M^{+\bullet}$), 71 (100).

2,2-Dioxo-1-methyl-4-piperidin-1-yl-2λ⁶-[2,1,3,5]benzothiatriazepine ***8h*** *and 2,2-Dioxo-5-methyl-4-piperidin-1-yl-2λ⁶-[2,1,3,5]benzothiatriazepine* ***9h***

No precipitate was obtained initially. The aqueous layer was replaced with fresh water and the resulting mixture stirred vigorously for a further hour, and left to stand overnight. The resultant crystals were collected and washed with water and

ethyl acetate to afford the *title compound* **8h** (43%) as light grey crystals, mp 127–130°C. (Found: C 50.2, H 6.5, N 18.2; $M^{+\bullet}$ 294.1145. $C_{13}H_{18}N_4O_2S.H_2O$ requires C 50.0, H 6.5, N 17.9%; $M^{+\bullet}$ 294.1145). δ_H 8.66 (1H, br, NH), 7.22–7.03 (4H, m, ArH), 3.56 (4H, m, 2 × NCH_2), 3.18 (3H, s, NCH_3), 1.56 (6H, m, 3 CH_2). δ_C ([D_6]DMSO) 152.3, 138.5, 133.3, 126.9, 125.3, 124.1, 122.5, 47.3, 35.2, 25.9, 23.9. *m/z* (EI) 294 (56%, $M^{+\bullet}$), 230 (42), 215 (86), 147 (100). The organic phase of the mother liquor was washed with brine, dried, and evaporated. The residue was chromatographed over silica gel. Elution with 0–5% methanol in dichloromethane, followed by recrystallization from chloroform afforded the *title compound* **9h** (2%) as white crystals, mp 173.5–174.5°C. (Found: C 52.4, H 6.1, N 19.1; $M^{+\bullet}$ 294.1142. $C_{13}H_{18}N_4O_2S$ requires C 53.0, H 6.2, N 19.0%; $M^{+\bullet}$ 294.1145). δ_H 7.31–7.26 (1H, m, ArH), 7.21–7.15 (3H, m, ArH), 6.50 (1H, br, NH), 3.53 (4H, m, 2 × NCH_2), 3.30 (3H, s, NCH_3), 1.69 (6H, m, 3 CH_2). δ_C 158.0, 137.3, 135.4, 129.0, 126.3, 126.1, 124.5, 49.3, 43.1, 25.6, 24.1. *m/z* (EI) 294 (5%, $M^{+\bullet}$), 215 (90), 186 (100).

3-Acetyl-4-piperidin-1-yl-2,2-dioxo-1-methyl-2λ⁶-[2,1,3,5]benzothiatriazepine ***10a***

A stirred mixture of compound **8h** (235 mg, 0.8 mmol), acetic anhydride (1 mL), and pyridine (4 drops) was heated at 90°C for 4 h. More pyridine (0.2 mL) was added and the mixture heated at 90°C for a further 3 h. The mixture was cooled, allowed to stand at room temperature overnight, and then diluted with diethyl ether (4 mL) and water (4 mL) and stirred vigorously for 10 min. The white precipitate was collected and washed with water followed by ether to give the *title compound* (171 mg, 64%) as a white solid. A sample was recrystallized from methanol to give colourless crystals, mp 219–221°C. (Found: C 53.2, H 6.1, N 16.6; $M^{+\bullet}$ 336.1244. $C_{15}H_{20}N_4O_3S$ requires C 53.5, H 6.0, N 16.7%; $M^{+\bullet}$ 336.1251). δ_H (500 MHz) 7.51–7.45 (1H, m, ArH), 7.31 (1H, dd, *J* 8, 0.7, ArH), 7.23–7.17 (2H, m, ArH), 3.96–3.90 (1H, m, CHN), 3.75–3.57 (3H, m, CHN, CH_2N), 3.38 (3H, s, NMe), 1.96–1.84 (1H, m, CH), 1.92 (3H, s, CH_3CO), 1.77–1.52 (5H, m, CH_2CH_2CH). δ_C (125 MHz) 169.1, 151.0, 140.8, 131.7, 131.1, 128.9, 125.2, 121.8, 48.5, 47.7, 35.4, 26.0, 24.9, 23.8, 22.2. *m/z* (EI) 336 (17%, $M^{+\bullet}$), 294 (28), 230 (34), 215 (36), 147 (100).

3-Benzoyl-4-piperidin-1-yl-2,2-dioxo-1-methyl-2λ⁶-[2,1,3,5]benzothiatriazepine ***10b***

Benzoyl chloride (0.8 mL) was added slowly to a stirred solution of compound **8h** (295 mg, 1 mmol) in pyridine (1.5 mL). The resulting solution was stirred at room temperature for 45 min. Water (20 mL) was added cautiously and the mixture was extracted with dichloromethane (20 mL). The extract was washed twice with water, dried, and evaporated. The residue was triturated with cyclohexane/*n*-hexane (1:1) to give a white solid, which was chromatographed over silica gel (0–1% methanol in dichloromethane) to give the *title compound* (150 mg, 38%). A sample was recrystallized from dichloromethane/methanol to give colourless crystals, mp 144–145°C. (Found: C 60.4, H 5.6, N 14.1; $M^{+\bullet}$ 398.1404. $C_{20}H_{22}N_4O_3S$ requires C 60.3, H 5.6, N 14.1%; $M^{+\bullet}$ 398.1407). δ_H 7.54–7.48 (3H, m, ArH), 7.46–7.41 (2H, m, ArH), 7.40–7.34 (2H, m, ArH), 7.27 (1H, d, *J* 8.8, ArH), 7.16 (1H, t, *J* 7.5, ArH), 3.66 (4H, br, 2 × CH_2N), 3.21 (3H, s, NMe), 1.52 (6H, br, $CH_2CH_2CH_2$). δ_C 168.5, 144.8, 144.4, 132.9, 131.0, 130.4, 129.0, 128.3, 128.2, 124.7, 124.2, 47.2, 39.0, 25.6, 24.1. *m/z* (EI) 398 (22%, $M^{+\bullet}$), 293 (10), 105 (100).

3-(4-Chlorobenzyl)-4-piperidin-1-yl-2,2-dioxo-1-methyl-2λ⁶-[2,1,3,5]benzothiatriazepine ***10c*** *and 5-(4-Chlorobenzyl)-4-piperidin-1-yl-2,2-dioxo-1-methyl-2λ⁶-[2,1,3,5]benzothiatriazepine* ***11c***

A mixture of compound **8h** (294 mg, 1.0 mmol), potassium carbonate (152 mg, 1.1 mmol), 4-chlorobenzyl bromide (226 mg, 1.1 mmol), tetrabutylammonium bromide (35 mg, 0.11 mmol), and acetonitrile (2 mL) was stirred at room temperature for 20 h. The mixture was partitioned between dichloromethane (12 mL) and water (6 mL). The aqueous phase was extracted with dichloromethane (10 mL). The extracts were combined, washed with brine, dried, and evaporated. The residual gum was chromatographed over silica gel (0–2% methanol in dichloromethane) to give two fractions. (i) The *title compound* **10c** (293 mg, 70%) as a viscous, colourless gum. (Found: C 57.1, H 5.4, N 13.4; $M^{+\bullet}$ 418.1223. $C_{20}H_{23}ClN_4O_2S$ requires C 57.3, H 5.5, N 13.4%; $M^{+\bullet}$ 418.1225). δ_H 7.30 (1H, d, *J* 7.8, ArH), 7.17 (1H, t, *J* 7.6, ArH), 7.10 (2H, d, *J* 8.2, ArH), 7.06 (1H, t, *J* 7.6, ArH), 6.90 (2H, d, *J* 8.2, ArH), 6.83 (1H, d, *J* 7.8, ArH), 4.11 (2H, s, CH_2Ar), 3.47 (4H, br m, 2 × NCH_2), 3.22 (3H, s, NCH_3), 1.64–1.34 (6H, br m, 3 × CH_2). δ_C 147.0, 144.5, 134.1, 133.1, 131.5, 130.4, 128.4, 128.1, 125.6, 124.8, 123.6, 53.3, 46.9, 37.2, 25.7, 24.3. *m/z* (EI) 418/420 (34/12%, $M^{+\bullet}$), 293 (17), 270 (44), 229 (76), 200 (60), 125 (100). (ii) The *title compound* **11c** (77 mg, 18%). A sample was recrystallized from ethanol to give colourless crystals, mp 226–227°C. (Found: C 57.4, H 5.6, N 13.2; $M^{+\bullet}$ 418.1219. $C_{20}H_{23}ClN_4O_2S$ requires C 57.3, H 5.5, N 13.4%; $M^{+\bullet}$ 418.1225). δ_H 7.27–7.19 (2H, m, ArH), 7.16–7.10 (3H, m, ArH), 7.07 (1H, d, *J* 8, ArH), 7.02 (2H, d, *J* 8, ArH), 4.66 (2H, br s, CH_2Ar), 3.61 (4H, br s, 2 × NCH_2), 2.86 (3H, s, NCH_3), 1.71 (6H, br s, 3 × CH_2). δ_C 157.2, 141.4, 136.0, 134.1, 133.1, 130.4, 129.2, 128.1, 126.2, 125.6, 122.2, 58.0, 49.6, 34.2, 25.7, 24.1. *m/z* (EI) 418 (2%, $M^{+\bullet}$), 340 (3), 293 (5), 270 (6), 235/237 (49/14), 229 (6), 200 (30), 125 (100).

1-Acetyl-4-dimethylamino-2,2-dioxo-2λ⁶-[2,1,3,5]benzothiatriazepine ***8i***

Acetic anhydride (0.1 mL) was added to a stirred mixture of compound **8a** (240 mg, 1 mmol) in pyridine (2 mL). The resultant mixture was stirred at room temperature for 19 h. More acetic anhydride (0.1 mL) was added and the mixture stirred for a further 4 h. The mixture was evaporated and the residue stirred vigorously in a mixture of diethyl ether (4 mL) and water (4 mL). The resultant white solid was collected and washed with water followed by ether and dried to give the *title compound* (194 mg, 69%). A sample was recrystallized from methanol; colourless crystals, mp 238–240°C. (Found: C 46.9, H 5.1, N 19.8; $M^{+\bullet}$ 282.0781. $C_{11}H_{14}N_4O_3S$ requires C 46.8, H 5.0, N 19.9%; $M^{+\bullet}$ 282.0781). δ_H ([D_6]DMSO) 10.00 (1H, s, NH), 7.39–7.19 (4H, m, ArH), 3.18 (6H, s, NMe_2), 2.30 (3H, s, CH_3CO). δ_C ([D_6]DMSO) 170.7, 153.9, 135.2, 132.9, 130.5, 128.5, 126.7, 124.8, 39.0, 25.2. *m/z* (EI) 282 (11%, $M^{+\bullet}$), 240 (100).

1-Benzoyl-4-dimethylamino-2,2-dioxo-2λ⁶-[2,1,3,5]benzothiatriazepine ***8j***

Benzoyl chloride (1.6 mL) was added slowly to a stirred solution of compound **8a** (240 mg, 1 mmol) in pyridine (3 mL). The solution was stirred at room temperature for 45 min. Water (20 mL) was cautiously added and the mixture was extracted twice with dichloromethane. The extracts were combined, washed with saturated, aqueous sodium bicarbonate solution, followed by water, dried, and evaporated. The residue was chromatographed

over silica gel (2–3% methanol in dichloromethane) to give the *title compound* (164 mg, 49%) as a white solid, mp 265–266°C. (Found: C 55.8, H 4.7, N 16.3; $M^{+\bullet}$ 344.0939. $C_{16}H_{16}N_4O_3S$ requires C 55.8, H 4.7, N 16.3%; $M^{+\bullet}$ 344.0938). δ_H ([D_6]DMSO) 10.46 (1H, s, NH), 7.41–7.19 (7H, m, ArH), 7.11–7.01 (1H, m, ArH), 6.99–6.91 (1H, m, ArH), 3.27 (6H, s, NMe_2). δ_C ([D_6]DMSO) 169.7, 154.6, 135.7, 135.0, 134.3, 131.9, 129.7, 129.0, 128.53, 128.47, 127.1, 124.8 (NMe_2 signal obscured by solvent resonances). δ_C (CD_3OD + 3 drops $CDCl_3$) 172.0, 156.4, 136.3, 135.8, 135.4, 132.9, 130.7, 130.1, 129.8, 129.2, 128.3, 125.3, 39.4. *m/z* (EI) 344 (9%, $M^{+\bullet}$), 105 (100). Recrystallization from acetonitrile provided solvated crystals suitable for X-ray crystallographic analysis.

4-Dimethylamino-2,2-dioxo-2λ^6-[2,1,3,5] benzothiatriazepine-1-carboxylic Acid p-*Tolylamide* ***8k***

A mixture of compound **8a** (240 mg, 1 mmol), *p*-tolyl isocyanate (0.14 mL, 1.1 mmol), triethylamine (2 drops), and dichloromethane (3 mL) was stirred at room temperature for 2 days. More *p*-tolyl isocyanate (0.1 mL) and triethylamine (1 drop) were added and the mixture was stirred at room temperature for 7 days. The mixture was partitioned between chloroform and water. The aqueous phase was extracted with chloroform. The organic phases were combined, washed with saturated, aqueous sodium chloride solution, dried, and evaporated. The residue was recrystallized from methanol to give the *title compound* (284 mg, 76%) as colourless crystals, mp 205–206°C. (Found: C 54.8, H 5.1, N 18.8; $M^{+\bullet}$ 373.1201. $C_{17}H_{19}N_5O_3S$ requires C 54.7, H 5.1, N 18.8%; $M^{+\bullet}$ 373.1203). δ_H 9.74 (1H, s, NH), 8.09 (1H, s, NH), 7.45–7.37 (3H, m, ArH), 7.28–7.23 (1H, m, ArH), 7.19–7.13 (3H, m, ArH), 6.81 (1H, d, *J* 7.6, ArH), 2.99 (6H, s, NMe_2), 2.34 (3H, s, CH_3). δ_C 152.2, 152.0, 135.4, 134.8, 134.2, 130.4, 129.6, 128.8, 126.3, 123.3, 120.6, 38.8, 20.8. *m/z* (EI) 373 (2%, $M^{+\bullet}$), 240 (42), 133 (100).

1-(4-Chlorobenzyl)-4-dimethylamino-2,2-dioxo-2λ^6-[2,1,3,5]benzothiatriazepine ***8g***, *5-(4-Chlorobenzyl)-4-dimethylamino-2,2-dioxo-2λ^6-[2,1,3,5]benzothiatriazepine* ***9g***, *1,3-Bis(4-Chlorobenzyl)-4-dimethylamino-2,2-dioxo-2λ^6-[2,1,3,5]benzothiatriazepine* ***12***, *and 1,5-Bis(4-Chlorobenzyl)-4-dimethylamino-2,2-dioxo-2λ^6-[2,1,3,5]benzothiatriazepine* ***13***

Method A

A solution of 4-chlorobenzyl bromide (113 mg, 0.55 mmol) in dichloromethane (1.5 mL) was added to a stirred solution of compound **8a** (120 mg, 0.5 mmol) and sodium hydroxide (30 mg) in water (0.8 mL). Tetrabutylammonium bromide (18 mg, 0.055 mmol) was added and the mixture was stirred vigorously at room temperature for 21 h. The mixture was partitioned between ethyl acetate (10 mL) and water (5 mL) and filtered. The organic phase of the filtrate was washed with water, followed by brine, dried, and evaporated. The residue was chromatographed over silica gel (0–10% methanol in dichloromethane) to give three fractions. (i) The *title compound* **12** (100 mg, 41%) as a colourless solid. A sample was recrystallized from methanol, mp 151–153°C. (Found: C 56.2, H 4.8, N 11.3; $M^{+\bullet}$ 488.0814. $C_{23}H_{22}Cl_2N_4O_2S$ requires C 56.4, H 4.5, N 11.5%; $M^{+\bullet}$ 488.0835). δ_H 7.20–7.09 (6H, m, ArH), 7.06–7.02 (2H, m, ArH), 7.00–6.94 (1H, m, ArH), 6.94–6.90 (2H, m, ArH), 6.85–6.81 (1H, m, ArH), 4.68 (2H, s, CH_2), 4.12 (2H, br s, CH_2), 2.95 (6H, s, NMe_2). δ_C 148.1, 134.6, 134.4, 133.7, 132.9, 130.4, 129.6, 129.0, 128.9, 128.61, 128.57, 127.7, 124.92, 123.9, 54.2, 53.7, 38.4. *m/z* (EI) 488/490/492 (100/88/17%, $M^{+\bullet}$). (ii) The *title compound* **13** (5 mg, 2%) as a colourless gum. δ_H 7.25–7.21 (2H, m, ArH), 7.19–7.12 (5H, m, ArH), 7.11–7.02 (5H, m, ArH), 4.68 (2H, s, CH_2), 4.43 (2H, br s, CH_2), 3.11 (6H, s, NMe_2). *m/z* ($APCI^+$) 511/513 (22/17%, $[M + Na]^{+\bullet}$), 489/491/493 (100/75/16%, $[M + H]^{+\bullet}$). (iii) The *title compound* **8g** (8 mg, 4%).

Method B

A mixture of compound **8a** (120 mg, 0.5 mmol), potassium carbonate (76 mg, 0.55 mmol), 4-chlorobenzyl bromide (113 mg, 0.55 mmol), tetrabutylammonium bromide (18 mg, 0.055 mmol), and DMF (3 mL) was stirred at room temperature for 26 h. The mixture was partitioned between ethyl acetate (10 mL) and water (5 mL). The organic layer was washed four times with water, followed by brine, dried, and evaporated. The residual was chromatographed over silica gel as for Method A above, to afford four fractions. (i) The *title compound* **12** (88 mg, 36%); (ii) the *title compound* **13** (5 mg, 2%); (iii) the *title compound* **9g** (7 mg, 4%), recrystallized from methanol to give white crystals, mp 176–177°C. (Found: $M^{+\bullet}$ 364.0752. $C_{16}H_{17}ClN_4O_2S$ requires $M^{+\bullet}$ 364.0755). δ_H 7.23–7.13 (7H, m, ArH), 7.02–6.99 (1H, m, ArH), 5.94 (1H, br, NH), 4.71 (2H, s, CH_2), 3.14 (6H, s, NMe_2). δ_C 157.9, 136.2, 135.7, 134.4, 133.1, 130.3, 129.2, 128.6, 126.7, 126.3, 124.9, 58.1, 40.0. *m/z* (EI) 364/366 (1/0.5%, $M^{+\bullet}$), 285/287 (32/9), 160 (100). (iv) The *title compound* **8g** (15 mg, 8%).

Method C

A suspension of compound **8a** (240 mg, 1.0 mmol) in THF (4 mL) and DMF (1 mL) was added to a stirred suspension of sodium hydride (60% dispersion in oil, 44 mg, 1.1 mmol) in THF (2 mL) under a nitrogen atmosphere. After the evolution of hydrogen gas had ceased, 4-chlorobenzyl bromide (210 mg, 1.0 mmol) in THF (2 mL) was added and the mixture stirred at room temperature for 21 h. A little water was added carefully and the mixture was neutralized with dilute hydrochloric acid. The whole was extracted twice with ethyl acetate. The extracts were combined and washed with water (twice) followed by brine, dried, and evaporated. The residual gum was chromatographed over silica gel (0–2% methanol in dichloromethane), to afford four fractions. (i) The *title compound* **12** (110 mg, 23%); (ii) the *title compound* **13** (11 mg, 3%); (iii) the *title compound* **9g** (19 mg, 5%); and (iv) the *title compound* **8g** (111 mg, 31%).

X-Ray Crystallography

Single crystals suitable for X-ray analysis were covered in viscous oil and mounted on a glass fibre. Data ($2\theta_{max}$ 55°) were collected at 123(1) K using a Nonius KAPPA CCD system and $Mo_{K\alpha}$ (λ 0.71073 Å) radiation. After integration and scaling, datasets (N_{total}) were merged to N unique reflections (R_{int} as quoted) with N_{obs} considered 'observed' with $I > 2\sigma(I)$. The structures were solved using conventional methods and refined by full matrix least-squares using the *SHELX-97* software,[15] in conjunction with the X-Seed interface.[16] Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were placed in calculated positions. Data were corrected for absorption using SORTAV.[17] Crystals of **6d** have two independent molecules in the unit cell. Both molecules are essentially identical, differing only in the relative rotation of the pendant piperidinyl ring. For structures **8g** and **8k**, the Flack parameter

Table 7. Crystal data and structure refinement for 5c, 6d, 8g, 8h·H_2O, 10b, 8j·CH_3CN, 8k

Parameter	**5c**	**6d**	**8g**	**8h**·H_2O	**10b**	**8j**·CH_3CN	**8k**
CCDC no.	689976	689978	689972	689973	689975	689977	689974
Empirical formula	$C_{19}H_{19}N_3O_4S$	$C_{19}H_{20}ClN_3O_3S$	$C_{16}H_{17}ClN_4O_2S$	$C_{13}H_{20}N_4O_3S$	$C_{20}H_{22}N_4O_3S$	$C_{18}H_{19}N_5O_3S$	$C_{17}H_{19}N_5O_3S$
Formula weight	385.43	405.89	364.85	312.39	398.48	385.44	373.43
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$
Unit cell dimensions							
a [Å]	7.6876(2)	12.3829(2)	9.8031(1)	14.0989(3)	8.6610(2)	15.9516(2)	9.3433(1)
b [Å]	9.4110(2)	11.4067(2)	10.5363(2)	8.4442(2)	9.2395(2)	9.5977(2)	11.8069(2)
c [Å]	12.9256(3)	27.5308(5)	16.8086(3)	12.9662(2)	12.5758(3)	13.0875(2)	15.3081(3)
α [°]	74.287(2)	90	90	90	105.442(1)	90	90
β [°]	81.542(1)	101.990(1)	90	102.338(1)	100.620(1)	112.998(1)	90
γ [°]	78.001(1)	90	90	90	91.258(1)	90	90
Volume [$Å^3$]	876.43(4)	3803.83(11)	1736.19(5)	1508.02(5)	950.73(4)	1844.42(5)	1688.72(5)
Z	2	8	4	4	2	4	4
ρ (calc.) [$Mg\,m^{-3}$]	1.461	1.418	1.396	1.376	1.392	1.388	1.469
μ [mm^{-1}]	0.217	0.336	0.357	0.231	0.200	0.205	0.221
Crystal size [mm]	0.25 × 0.13 × 0.10	0.25 × 0.25 × 0.25	0.38 × 0.38 × 0.38	0.25 × 0.18 × 0.15	0.25 × 0.25 × 0.25	0.33 × 0.20 × 0.15	0.33 × 0.13 × 0.10
Theta range [°]	1.64 to 27.50	1.51 to 27.50	2.28 to 27.50	1.48 to 27.50	1.71 to 27.50	1.39 to 27.50	2.18 to 27.50
N_{total}	13015	42108	21546	15114	11715	17443	16008
N (R_{int})	4012 (0.052)	8732 (0.070)	3987 (0.042)	3456 (0.048)	4275 (0.050)	4232 (0.042)	3878 (0.056)
N_{obs} [$I > 2\sigma(I)$]	3161	5537	3531	2485	3488	3134	3399
R indices [$I > 2\sigma(I)$]							
R_1	0.0446	0.0463	0.0310	0.0448	0.0427	0.0416	0.0355
wR_2	0.1061	0.1080	0.0695	0.1039	0.1088	0.1020	0.0828
R indices (all data)							
R_1	0.0619	0.0924	0.0411	0.0746	0.0559	0.0656	0.0460
wR_2	0.1147	0.1249	0.0743	0.1192	0.1175	0.1150	0.0875
x_{abs}			−0.01(5)				−0.01(7)
GoF (on F^2)	1.034	1.013	1.053	1.055	1.043	1.039	1.051

x_{abs} was refined (see Table 7). CCDC 689972–689978 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.CCDC.cam.ac.uk/data_request/cif.

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