OXAZEPINES AND THIAZEPINES, 36[1]. DIASTEREOSELECTIVE SULFOXIDATION OF 2,3-DIHYDRO-1,5-BENZOTHIAZEPIN-4(5*H*)-ONES BY DIMETHYLDIOXIRANE*

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Abstract - The highly chemoselective dimethyldioxirane oxidation of 2-substituted 2,3-dihydro-1,5-benzothiazepin-4(5*H*)-one (**1**) allows the synthesis of the corresponding sulfoxides (**2**) or sulfones (**3**) in good yields. The relative stereochemistry of the sulfoxides has been unequivocally determined by X-Ray and NMR methods. The high *trans* diastereoselectivity can be explained on the basis of steric control.

INTRODUCTION

Benzothiazepines are compounds with a wide array of biological activity such that their synthesis has been a subject of intense study.[1,2] A subclass of them, the family of 1,5-benzothiazepin-4-(5*H*)-ones, includes a number of important substances such as thiazesim[3] with antidepressant and diltiazem[4] with antianginal activity. Less has been reported on the 1-oxide and 1,1-dioxide derivatives of 1,5-benzothiazepin. Some of these compounds have been shown to display antibacterial,[5] anticonvulsive and sedative,[6] as well as growth hormone secretagogue[7] activities, and the inhibition of human leukocyte elastase (HLE), [8] HIV-1 reverse transcriptase[9] and angiotensin converting enzyme (ACE).[10] Moreover, a 2-aryl-2,3-dihydro-3-hydroxy-1,5-benzothiazepin-4-(5*H*)-one 1-oxide has been reported as an effective chiral solvating agent in the NMR determination of enantiomeric excess.[11] 1,5-Benzothiazepin-4-(5*H*)-one 1-oxides and 1,1-dioxides have usually been prepared by the oxidation of the parent sulfides and only two examples have been reported where the Schmidt reaction of 1-thiochromanone 1-oxides and 1,1-dioxides was exploited.[12] In the

synthesis of 1,5-benzothiazepin-4-(5*H*)-one 1-oxides sodium periodate[7,9,13] or *m*-chloroperbenzoic acid,[10,14] hydrogen peroxide in formic acid,[15] *tert*-butyl hydroperoxide in the presence of $MoO_2(acac)_2$[16] or Dess-Martin periodinane[8] have been employed as oxidants. 1,5-Benzothiazepin-4-(5*H*)-one 1,1-dioxides have been synthesized either from the sulfides or their sulfoxides upon treatment with *m*-chloroperbenzoic acid at ambient or reflux temperature[7-9,13,17] or hydrogen peroxide in acetic acid.[18]

The oxidation of 2,3-dihydro-1,5-benzothiazepin-4-(5*H*)-ones with substituents in their heterocyclic part may result in diastereomeric sulfoxides. Surprisingly, only in a few case have diastereomeric mixtures and their separation by column chromatography has been mentioned[7-10] and their relative configuration has not been determined at all. The most detailed study has been performed by Breitschuh and Seebach,[16] who isolated and characterized both diastereomers of 2,3-dihydro-2,5-dimethyl-1,5-benzothiazepin-4-(5*H*)-one 1-oxides, but their relative configuration remained undefined.

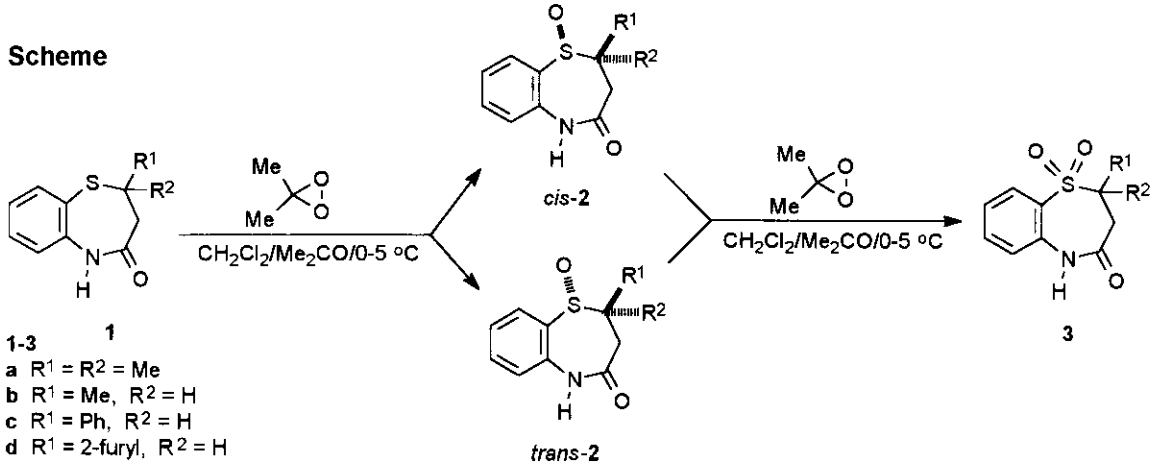
Dioxiranes, especially the isolated dimethyldioxirane (DMD),[19] are highly reactive oxidants which work under mild conditions. Due to its electrophilic character,[20] DMD is the oxygen-transfer reagent of choice for the selective sulfoxidation of sulfides.[20,21] Previously we have also demonstrated the high chemoselectivity of the DMD toward the sulfur atom in the presence of double bond and a sulfoxide moiety for 1-thioaurones and 3-arylidene-1-thiochromanones and -1-thioflavanones as substrates.[22]

In the present paper we report on the synthetic usefulness of DMD in the sulfur oxidation of 2,3-dihydro-1,5-benzothiazepin-4-(5*H*)-ones, as well as the chemoselectivity (sulfide *vs.* sulfoxide attack) and the diastereoselectivity. Of particular interest was to determine the relative configuration of the sulfoxide and thereby assign the preferred attack in the DMD sulfoxidation.

RESULTS AND DISCUSSION

The results of the oxidation of 2,3-dihydro-1,5-benzothiazepin-4-(5*H*)-ones (**1a-d**) by DMD are summarized in Table 1 (Scheme).

Scheme



1-3 **1**
a $R^1 = R^2 = Me$
b $R^1 = Me$, $R^2 = H$
c $R^1 = Ph$, $R^2 = H$
d R^1 = 2-furyl, $R^2 = H$

Table 1. Oxidation of 2-substituted 2,3-dihydro-1,5-benzothiazepin-4(5*H*)-ones 1 by dimethyldioxirane

Entry	Substrate (mmol)	R^1	R^2	DMD (equiv)	Conversion[a] (%)	Product ratio[a] (%) 2 [*trans*:*cis*]	3	Mass balance (%)	Yield (%) 2	3
1	**1a** (2.00)	Me	Me	1.80	90	81 [-]	19	83	66	11
2	**1b** (3.00)	Me	H	1.41	72	96 [77:23]	4	98	71	3
3	**1c** (1.50)	Ph	H	2.08	100	89 [~100:0]	11	71	63	8
4	**1c** (2.13)	Ph	H	3.73	100	0	100	98	0	98
5	**1d** (1.21)	2-furyl	H	2.40	98	92 [~100:0]	8	94	88	6
6	**1d** (2.99)	2-furyl	H	2.85	100	56 [~100:0]	44	93	58	35

[a] Determined by ^{1}H-NMR analysis (200 or 360 MHz). Characteristic signals are as follows: for mixture obtained from **1a**: 2-Me signals, for mixture obtained from **1b**: 2-Me and 3-H signals, for mixture obtained from **1c**: 2-H signals, for mixture obtained from **1d**: 2-H signals..

A low excess of DMD favored formation of sulfoxides (**2a-d**), only a limited amount of the sulfones (**3a-d**) was observed (Table 1, Entries 1,3,5). When the reaction was terminated at lower conversion, the corresponding sulfoxide was obtained nearly exclusively (Table 1, Entry 2). In contrast, higher amounts of DMD gave the corresponding sulfone in excellent yield (Table 1, Entry 4). These results clearly show that DMD is a chemoselective oxidant, which is advantageously applicable for the synthesis of either sulfoxides (**2**) or the sulfones (**3**) by controling its amount.

^{1}H-NMR analysis directly of the reaction mixtures (after solvent evaporation) and also of the isolated sulfoxides (**2**) indicated that a mixture of diastereomers (77:23) was formed in the DMD oxidation of 2,3-dihydro-2-methyl-1,5-benzothiazepin-4-(5*H*)-one (**1b**) while for the sulfoxides (**1c,d**) a sole diastereomer was obtained as (within the detection limit of the ^{1}H-NMR spectroscopy). A similar diastereomeric ratio (2:1) was reported for the 2,3-dihydro-2,5-dimethyl-1,5-benzothiazepin-4-(5*H*)-one 1-oxides when *tert*-butyl hydroperoxide in the presence of $MoO_2(acac)_2$ was used.[16] Moreover, the major product was the more polar sulfoxide just as in our case.

The comparison of the ^{1}H NMR spectra of the isolated pure diastereomers of **2b** was of little help to assign the *cis/trans*[23] configuration of the sulfoxides. As the data in Table 2 show, characteristic shifts are found for the two sulfoxide diastereomers when compared to the parent sulfide. Thus, for one of the diastereomers a marked upfield shift of the 2-methyl group and a smaller downfield shift of the 2-hydrogen atom are apparent, whereas the other diastereomer exhibits a strong downfield shift of

Table 2. Characteristic ^{1}H-NMR data of the diastereomeric sulfoxides (***cis*-2b**) and (***trans*-2b**)

		***cis*-2b**	***trans*-2b**	**3b**
δ(2-Me) (Δδ)[a]	[ppm]	1.19 (-0.24)	1.75 (+0.32)	1.50 (+0.07)
δ(2-H) (Δδ)	[ppm]	4.06 (+0.16)	3.43 (-0.47)	3.84 (-0.06)
δ(3-H(*trans*)) (Δδ)	[ppm]	2.10 (-0.26)	2.33 (-0.03)	2.86 (+0.50)
δ(3-H(*cis*)) (Δδ)	[ppm]	2.68 (0)	2.86 (+0.18)	2.39 (-0.29)
^3J(2H, 3-H(*trans*))	[Hz]	11.0	2.4	6.6
^{3}J(2H, 3-H(*cis*))	[Hz]	6.9	7.8	7.9

[a] Δδ = δ(**2b**) - δ(**1b**)

the 2-methyl group and a strong upfield shift on the 2-hydrogen atom. However, these shift values are insufficient for the unequivocal assignment of the *cis/trans* configuration since they originate from the combined diamagnetic shielding/deshielding effects of both the sulfoxide and the carbonyl functionalities, moreover, the relative spatial position of these groups depends on the conformation of the molecule.

Definitive configurational assignment was provided by X-Ray analysis. Thus, the more polar major diastereomer is the *trans*-sulfoxide (***trans*-2b**), while the less polar minor one the *cis*-sulfoxide (***cis*-2b**), as shown in Figures 1 and 2. This constitutes the first case in which the relative configuration of such heterocyclic sulfoxides was determined unambiguously.

Figure 1. X-Ray crystal structure of ***trans-2b***

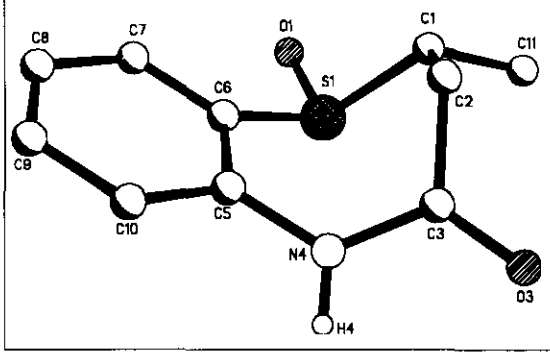
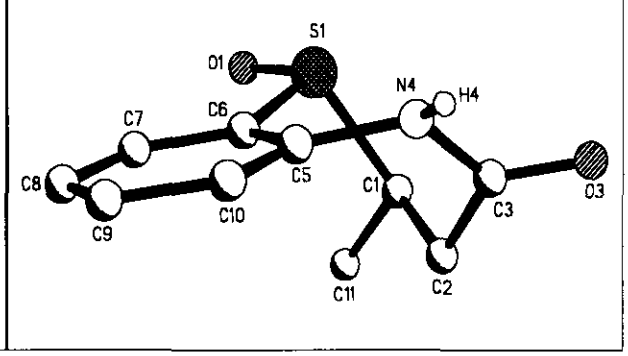
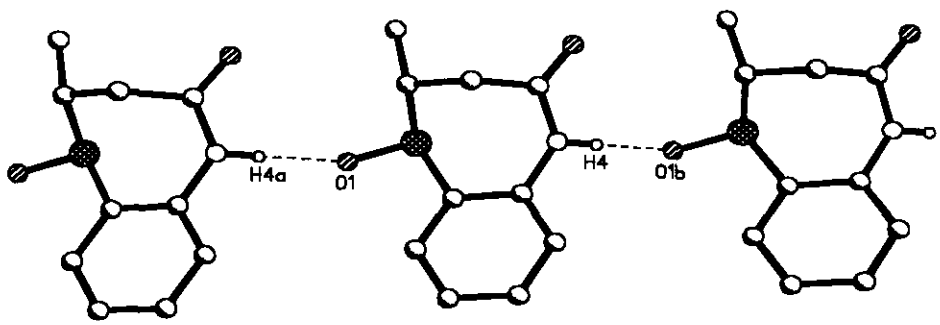


Figure 2. X-Ray crsytal structure of ***cis-2b***



According to the X-Ray structures, both ***cis***- and ***trans*-2b** exist in conformations with the sulfoxide group in the pseudoequatorial position in the crystalline state. PM3 calculations[24] show the same preferred conformations for both diastereomers but the X-Ray structures indicate a more flattened heteroring. The reasons for this distortion are the minimization of transannular dipolar interactions[25] and the hydrogen bonding between the sulfoxide oxygen and the amide hydrogen atoms. This latter interaction is well demonstrated by the X-Ray structures, the distance of the amide hydrogen atom (H4a) and sulfoxide oxygen atom (O1) is 206.4 pm (Figure 3).

Figure 3. Hydrogen bond between the molecules of ***trans*-2b**



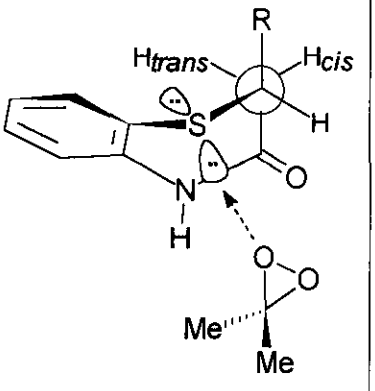
Since the chemical shift values of 2-H, 2-methyl and 3-H protons and the coupling constants of the sulfoxides (**2c**) and (**2d**) are very similar to those of the ***trans*-2b**, the same configuration applies. The results of NOE difference measurements for ***trans*-2d** (Table 3) support this assignment and suggest the same dominating conformation as in the case of ***trans*-2b**.

Table 3. NOE's measured for sulfoxide ***trans*-2d** and sulfones **3b,d**

Compound	Irradiated nuclei	Observed NOE's[a]
***trans*-2d**	3-H(*trans*)	3-H(*cis*) (16), 2-H (1), 4'-H (2)
	3-H(*cis*)	3-H(*trans*) (16), 2-H (6)
	2-H	3-H(*cis*) (3), 4'-H (1), 9-H (0.5)
3b	2-Me	3-H(*trans*) (4), 3-H_{cis} (1.5), 2-H (12), 9-H (2)
	3-H(*trans*)	2-Me (1), 3-H_{cis} (23), 2-H (1)
	3-H(*cis*)	3-H(*trans*) (35), 2-H (6)
	2-H	2-Me (2), 3-H(*trans*)(1), 3-H_{cis} (3)
3d	3-H(*trans*)	3-H(*cis*) (15), 2-H (1), 4'-H (2)
	3-H(*cis*)	3-H(*trans*) (13), 2-H (5)
	2-H	3-H(*cis*) (2), 4'-H (1)

[a] Intensities in %

Figure 4. Preferred attack for the dioxirane oxidation of 1



The NOE measurements also allowed the assignment of the protons in the ^{1}H-NMR spectra of sulfones (**3a-d**). In these derivatives the additional axial S=O bond radically changes the shifts of the 2-H, 2-methyl and 3-H atoms *versus* those of the parent sulfides (Table 2).

The observed high *trans* diastereoselectivity in the formation of sulfoxides (**2**) originates from a steric control during the attack of the DMD in this sulfoxidation. Thus, for the dominating conformer[26] of the 2-substituted-2,3-dihydro-1,5-benzothiazepin-4(5*H*)-ones (**1**), the dioxirane approaches preferably from the sterically much less hindered side, namely opposite to the 2-R group (Figure 4), which leads to the ***trans*-2** diastereomer.

EXPERIMENTAL

General: Dimethyldioxirane (as acetone solution) was prepared as reported[27] and its concentration was determined iodometrically. The 2,3-dihydro-1,5-benzothiazepin-4(5*H*)-ones (**1a-d**) were prepared according to the literature procedure.[28] Mp: Boetius hot-stage, uncorrected values. IR: Perkin-Elmer 16 PC-FT, KBr disc. NMR: Bruker WP 200 SY (200 and 50 MHz for ^{1}H and ^{13}C), Bruker AM 360 (360 MHz), Bruker DRX 500 (500 MHz), $CDCl_3$ as solvent, TMS as internal standard (δ = 0 ppm). MS: VG Trio-2 (EI, 70 eV). Elemental analysis: Carlo Erba 1106 EA. TLC: Kieselgel 60 F_{254} (Merck), ethyl acetate. Column chromatography: Kieselgel 60 (0.063-0.2 mm).

General Procedure of the Oxidation of 2,3-Dihydro-1,5-benzothiazepin-4(5*H*)-ones (1) by DMD: The particular benzothiazepine (**1**) was dissolved in dichloromethane (10 mL CH_2Cl_2/1 mmol substrate) and 0.3 equiv. of DMD was added and the mixture was allowed to stand in refrigerator (0-5° C). Additional batches of a fresh DMD stock solution (0.07-0.11 M in acetone)[27] was added in 12-h intervals and the reaction was monitored by TLC. Equivalents of DMD required to complete the oxidation is given in Table 1. The solvent was removed (20°C, 50 Torr) and the residue was submitted to silica gel chromatography. Ethyl acetate was used as eluent with the only exception of the mixtures obtained from **1d** (Entries 5 and 6, Table 1), for which toluene/ethyl acetate/acetic acid (10:8:1) was used. Further experimental details are given in Table 1, the physical and spectral characteristics of the oxidized products are listed below.

2,3-Dihydro-2,2-dimethyl-1,5-benzothiazepin-4(5*H*)-one 1-oxide (2a): Colorless crystals, mp 201-203 °C (methanol) (lit.[12b]: mp 201-202 °C). IR: 3108, 3040, 2966, 2898, 1680 (amide-I), 1474, 1374, 1074, 1044 (S=O), 768 cm^{-1}. ^{1}H-NMR: 1.20 (s, 3H, 2-Me_{trans}), 1.72 (s, 3H, 2-Me_{cis}), 2.36 (AB q, J = 12.6 Hz, 2H, 3-H), 7.14 (m, 1H, 6-H), 7.50 (m, 2H, 7,8-H), 7.79 (m, 1H, 9-H), 8.59 (br s, 1H, 5-H). *Anal.* Calcd for $C_{11}H_{13}NO_2S$: C, 59.17; H, 5.87; N, 6.27. Found: C, 59.28; H, 5.65; N, 6.11.

2,3-Dihydro-2,2-dimethyl-1,5-benzothiazepin-4(5*H*)-one 1,1-dioxide (3a): Colorless plates, mp 222-223 °C (ethyl acetate-hexane). IR: 3108, 3070, 3046, 2970, 1680 (amide-I), 1592, 1476, 1380, 1306 (SO_2), 1142 (SO_2), 722, 628 cm^{-1}. ^{1}H-NMR: 1.53 (s, 6H, 2-Me_2), 2.48 (s, 2H, 3-H), 7.24 (d, J = 7.9 Hz, 1H, 6-H), 7.35 (m, 1H, 8-H), 7.66 (m, 1H, 7-H), 8.04 (dd, J = 7.9 and 1.4 Hz, 1H, 9-H), 8.80 (br s, 1H, 5-H). *Anal.* Calcd for $C_{11}H_{13}NO_3S$: C, 55.21; H, 5.48; N, 5.85. Found: C, 55.39; H, 5.45; N, 5.71.

***cis*-2,3-Dihydro-2-methyl-1,5-benzothiazepin-4(5*H*)-one 1-oxide (*cis*-2b)**: Colorless crystals, mp 179-181 °C (ethyl acetate-hexane).[29] R_f (ethyl acetate) = 0.28. IR: 3188, 2964, 1684 (amide-I), 1588, 1474, 1370, 1078, 1046 (S=O), 770 cm^{-1}. ^{1}H-NMR: 1.19 (d, J = 6.7 Hz, 3H, 2-Me), 2.10 (dd, J = 12.4 and 11.0 Hz, 1H, 3-H_{trans}), 2.68 (ddd, J = 12.4, 6.9, and 1.4 Hz, 1H, 3-H_{cis}), 4.06 (m, 1H, 2-H), 7.15 (m, 1H, 6-H), 7.49 (m, 2H, 7,8-H), 7.76 (m, 1H, 9-H), 9.12 (d, J = 1.4 Hz, 1H, 5-H). MS: *m/z* (%) 209 (10) [$M^{+\bullet}$], 193 (5) [M-O], 167 (7) [M-C_3H_6], 149 (5), 141 (18) [HOS-C_6H_4-NH_2], 127 (10) [HS-C_6H_4-NH_2], 125 (18), 96 (19), 69 (100) [MeCH=CHCO$^{\oplus}$]. *Anal.* Calcd for $C_{10}H_{11}NO_2S$: C, 57.70; H, 5.30; N, 6.69. Found: C, 57.49; H, 5.23; N, 6.71.

***trans*-2,3-Dihydro-2-methyl-1,5-benzothiazepin-4(5*H*)-one 1-oxide (*trans*-2b)**: Colorless crystals, mp 176-178° C (ethyl acetate-hexane). [29] R_f (ethyl acetate) = 0.22. IR: 3180, 3130, 2970, 2942, 1682 (amide-I), 1588, 1474, 1356, 1076w, 1024 (S=O), 766 cm^{-1}. ^{1}H-NMR: 1.75 (d, J = 7.3 Hz, 3H, 2-Me), 2.33 (ddd, J = 12.5, 2.4, and 1.6 Hz, 1H, 3-H_{trans}), 2.86 (dd, J = 12.5 and 7.8 Hz, 1H, 3-H_{cis}), 3.43 (m, 1H, 2-H), 7.17 (m, 1H, 6-H), 7.50 (m, 2H, 7,8-H), 7.85 (m, 1H, 9-H), 8.87 (d, J = 1.6 Hz, 1H, 5-H). MS: *m/z* (%) 209

(19) [$M^{+\bullet}$], 193 (5) [M-O], 167 (16) [M-C_3H_6], 149 (9), 141 (41) [HOS-C_6H_4-NH_2], 127 (41) [HS-C_6H_4-NH_2], 96 (44), 69 (100) [MeCH=CHCO$^{\oplus}$]. *Anal.* Calcd for $C_{10}H_{11}NO_2S$: C, 57.70; H, 5.30; N, 6.69. Found: C, 57.79; H, 5.58; N, 6.48.

2,3-Dihydro-2-methyl-1,5-benzothiazepin-4(5*H*)-one 1,1-dioxide (3b): Colorless plates, mp 207-210 °C (methanol). IR: 2968, 286, 1684 (amide-I), 1594, 1478, 1376, 1312 (SO_2), 1146 (SO_2), 1122, 744 cm^{-1}. ^{1}H-NMR: 1.50 (d, J = 7.0 Hz, 3H, 2-Me), 2.39 (dd, J = 13.1 and 7.9 Hz, 1H, 3-H_{cis}), 2.86 (dd, J = 13.1 and 6.6 Hz, 1H, 3-H_{trans}), 3.84 (m, 1H, 2-H), 7.23 (d, J = 7.9 Hz, 1H, 6-H), 7.41 (ddd, 1H, 8-H), 7.67 (ddd, 1H, 7-H), 8.06 (dd, J = 7.9 and 1.6 Hz, 1H, 9-H), 8.53 (br s, 1H, 5-H). *Anal.* Calcd for $C_{10}H_{11}NO_3S$: C, 53.32; H, 4.92; N, 6.22. Found: C, 53.51; H, 5.11; N, 6.11.

***trans*-2,3-Dihydro-2-phenyl-1,5-benzothiazepin-4(5*H*)-one 1-oxide (*trans*-2c)**: Colorless crystals, mp 197-200 °C (ethyl acetate) (lit.,[13]: mp 201-202°C (decomp.), lit.,[18]: mp 197-198 °C). IR: 3174, 3056, 2952, 2894, 1668 (amide-I), 1476, 1380, 1072, 1046 (S=O), 766, 704 cm^{-1}. ^{1}H-NMR: 2.87 (ddd, J = 13.2, 1.9, and 1.7 Hz, 1H, 3-H_{trans}), 3.08 (dd, J = 13.2 and 9.4 Hz, 1H, 3-H_{cis}), 4.40 (dd, J = 9.4 and 1.9 Hz, 1H, 2-H), 7.16 (dd, J = 7.9 and 1.7 Hz, 1H, 6-H), 7.43 (m, 3H, 3',4',5'-H), 7.54-7.63 (m, 4H, 7,8,2',6'-H), 7.97 (dd, J = 7.1 and 1.9 Hz, 1H, 9-H), 8.16 (broad s, 1H, 5-H). *Anal.* Calcd for $C_{15}H_{13}NO_2S$: C, 66.40; H, 4.83; N, 5.16. Found: C, 66.61; H, 5.01; N, 5.05.

2,3-Dihydro-2-phenyl-1,5-benzothiazepin-4(5*H*)-one 1,1-dioxide (3c): Colorless crystals, mp 239-241 °C (ethyl acetate-hexane) (lit.,[12b]: mp 236-239 °C, lit.,[18]: mp 239-240 °C). IR: 3282 (NH), 1682 (amide-I), 1478, 1320, 1296 (SO_2), 1148 (SO_2), 1126, 762 cm^{-1}. ^{1}H-NMR: 3.08 (d, J = 7.4 Hz, 2H, 3-H), 4.92 (t, J = 7.4 Hz, 1H, 2-H), 7.28 (m, 1H, 6-H), 7.42 (m, 5H, Ph), 7.44 (m, 1H, 8-H), 7.73 (m, 1H, 7-H), 8.04 (overlapping dd and br s, 2H, 5,9-H). *Anal.* Calcd for $C_{15}H_{13}NO_3S$: C, 62.70; H, 4.56; N, 4.87. Found: C, 62.49; H, 4.52; N, 4.55.

***trans*-2,3-Dihydro-2-furyl-1,5-benzothiazepin-4(5*H*)-one 1-oxide (*trans*-2d)**: Pale brownish crystal powder, mp 163-166 °C (ethyl acetate-hexane) (lit.,[18]: mp 163-164 °C). IR: 3122, 2950, 2890, 1670 (amide-I), 1586, 1474, 1366, 1308, 1182, 1074, 1040 (S=O), 1002, 768 cm^{-1}. ^{1}H-NMR: δ = 2.89 (dd, J = 13.1 and 3.7 Hz, 1H, 3-H_{trans}), 3.05 (dd, J = 13.1 and 8.5 Hz, 1H, 1H, 3-H_{cis}), 4.59 (dd, J = 8.5 and 3.7 Hz, 1H, 2-H), 6.43 (m, 1H, 3'-H), 6.62 (d, J = 3.3 Hz, 4'-H), 7.19 (dd, J = 7.6 and 1.4 Hz, 1H, 6-H), 7.54 (m, 3H, 7,8,5'-H), 7.85 (dd, J = 7.4 and 1.8 Hz, 1H, 9-H), 8.23 (br s, 1H, 5-H). *Anal.* Calcd for $C_{13}H_{11}NO_3S$: C, 59.76; H, 4.24; N, 5.36. Found: C, 59.52; H, 4.13; N, 5.65.

2,3-Dihydro-2-furyl-1,5-benzothiazepin-4(5*H*)-one 1,1-dioxide (3d): Pale brownish crystal powder, mp 215-218 °C (ethyl acetate) (lit.,[18]: mp: 161-162 °C). IR: 3336 (NH), 3120, 2960, 1696 (amide-I), 1592, 1478, 1362, 1321 (SO_2), 1298, 1258, 1240, 1162, 1154 (SO_2), 1116, 766, 760, 735 cm^{-1}. ^{1}H-NMR: 3.00 (dd, J = 13.2 and 6.8 Hz, 1H, 3-H_{cis}), 3.13 (dd, J = 13.2 and 10.4 Hz, 1H, 3-H_{trans}), 5.06 (dd, J = 10.4 and

6.8 Hz, 1H, 2-H), 6.42 (m, 1H, 3'-H), 6.49 (d, J =3.3 Hz, 1H, 4'-H), 7.28 (m, 1H, 6-H), 7.42 (m, 2H, 8,5'-H), 7.71 (m, 1H, 7-H), 7.94 (dd, J = 7.9 and 1.4 Hz, 1H, 9-H), 8.18 (br s, 1H, 5-H). *Anal.* Calcd for $C_{13}H_{11}NO_4S$: C, 56.31; H, 4.00; N, 5.05. Found: C, 56.52; H, 4.20; N, 5.01.

X-Ray Crystallographic Study: Data collection: Data were collected with Mo K_α radiation on a Siemens P4 diffractometer, monochromator: graphite, collection mode: ω-scan. Structure solution: direct phase determination, method of refinement: full-matrix LSQ, hydrogen positions of riding model with fixed isotropic U. Siemens SHELXTL PLUS program was used for structural analysis and refinement. Further data are collected in Table 4.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101397. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 4. Crystallographic data for ***cis*-2b** and ***trans*-2b**

Compound	***cis*-2b**	***trans*-2b**
Empirical formula	$C_{10}H_{11}NO_2S$	$C_{10}H_{11}NO_2S$
Molecular mass	209.27	209.27
Cell constants		
a [pm]	625.51(4)	1166.2(2)
b [pm]	726.91(4)	667.8(1)
c [pm]	1065.96(7)	1301.9(2)
β [deg]	101.871(5)	110.05(1)
V [pm^3]	494.79(5) x 10^6	952.5(3) x 10^6
Z	2	4
d (calcd) [g x cm^{-3}]	1.404	1.459
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
Crystal size [mm]	0.5 x 0.6 x 0.15	0.35 x 0.55 x 0.1
Θ range [deg]	1.75 - 27.5	1.75 - 27.5
Recip. latt. segment	h = -8 → 0, k = -9 → 9, l = -13 → 13	h = -15 → 0, k = 0 → 8, l = -15 → 16
No. of reflections		
measured	2489	2474
unique	2284	2176
$F > 3\sigma(F)$	2267	1823
Lin. abs. coeff. [mm^{-1}]	0.30	0.31
Abs. correction	ψ-scan	ψ-scan
Data-to parameter ratio	17.44	13.92
R, R_W	0.039, 0.042	0.041, 0.042
Weighting scheme	$w = 1/\sigma^2(F)$	$w = 1/\sigma^2(F)$
Largest difference peak and hole	0.73 eÅ^{-3},0.70 eÅ^{-3}	0.33 eÅ^{-3}, 0.46 eÅ^{-3}

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