Synthesis and structural characteristics of novel 5*H*-thiazolo[2,3-*d*][1,5]benzothiazepine derivatives

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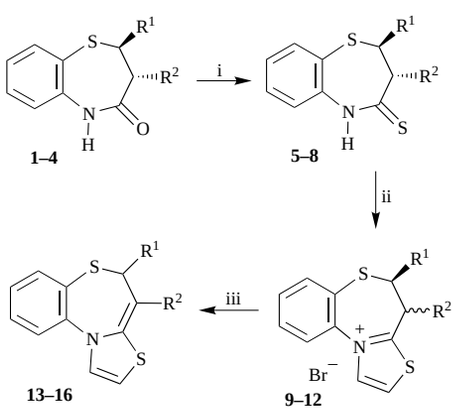
The 5*H*-thiazolo[2,3-*d*][1,5]benzothiazepines 13–16 have been synthesized by condensation of the 1,5-benzothiazepine-2-thiones 5–8 and α-bromoacetaldehyde diethyl acetal followed by treatment with alkali. The structure and stereochemistry of the adducts obtained has been established on the basis of spectroscopic data. For compounds 15 and 16 the presence in solution of two conformers has been postulated. An X-ray crystallographic structural study of thiazolobenzothiazepine 15 reveals that only one conformer is present in the solid state, stabilized by the presence of a short S · · · O contact (2.59 Å).

There are numerous studies directed towards the development of syntheses of new annelated 1,5-benzothiazepine derivatives, owing to their remarkable pharmacological activity on the CNS.[1] In connection with our interest in the chemistry of annelated benzodiazepines[2] and benzothiazepines,[3] with particular reference to the stereochemical features of the new tricyclic systems obtained, in the present paper we report the synthesis and the stereochemistry both in solution and in the solid state of new thiazolo[2,3-*d*][1,5]benzothiazepines. To our knowledge, thiazolo-1,5-benzothiazepine derivatives have not been previously synthesized and the only example reported in the literature concerns the fusion of the thiazolidine nucleus to the benzothiazepin-2-one system.[4] The added heterocycle could influence the conformational properties of the thiazepine nucleus and be of interest in checking the importance of conformational mobility in interactions with a suitable receptor and therefore in biological activity.

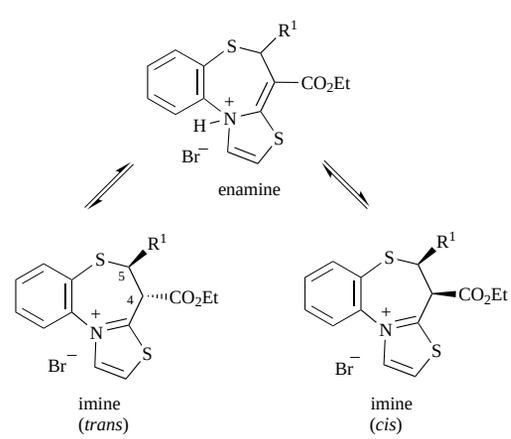
Results and discussion

The 5*H*-thiazolo[2,3-*d*][1,5]benzothiazepines **13–16** were obtained through the procedure reported in Scheme 1. The 1,5-benzothiazepin-4-one derivatives **1–4**, prepared using methods previously described,[5] were transformed into the corresponding 1,5-benzothiazepine-4-thiones **5–8** by treatment with Lawesson's reagent[6] in refluxing toluene. Successively, α-bromoacetaldehyde diethyl acetal was added to a solution of each of compounds **5–8** in butan-2-one–water. The resulting mixtures were heated under reflux for various periods of time to afford the thiazolo[2,3-*d*][1,5]benzothiazepinium bromides **9–12** which upon treatment with sodium hydroxide in 50% methanol–water, furnished the derivatives **13–16**. When a 2-phenyl group was present in the thione precursor, a secondary 2-styrylbenzothiazole was obtained through a thiazepine ring contraction and H_2S elimination according to Kaupp.[7]



	R^1	R^2
1, 5, 9, 13	Me	H
2, 6, 10, 14	Ph	H
3, 7, 11, 15	Me	CO_2Et
4, 8, 12, 16	Ph	CO_2Et

Scheme 1 *Reagents and conditions*: i, Lawesson's reagent, toluene, reflux; ii, $BrCH_2CH(OEt)_2$, butan-2-one–water, reflux; iii, NaOH 3 M in 50% methanol–water, room temperature



Scheme 2 Tautomerism of thiazolo[2,3-*d*][1,5]benzothiazepinium bromides **11** and **12**

1H NMR spectra of the thiazolobenzothiazepinium bromides **9–12** showed two doublets between 8.25 and 9.03 ppm attributable to protons of the thiazole nucleus shifted to such low fields by the presence of a positive charge on the nitrogen atom (Table 1). It is interesting to note that when an ethoxycarbonyl group is present on the benzothiazepine nucleus (**11** and **12**) the **1**H NMR spectra contain two sets of signals due to the coexistence of two imine derivatives which differ because of the disposition of the ethoxycarbonyl group with respect to the substituent at C-5: in the *trans* form the 4-ethoxycarbonyl group is equatorial, and axial in the *cis* epimer. The *cis* and *trans* forms are interconverted *via* the enamine tautomer, which has not been detected (Scheme 2). The *cis* and *trans* isomers have been

Table 1 ^{1}H NMR data for compounds **9**–**12**

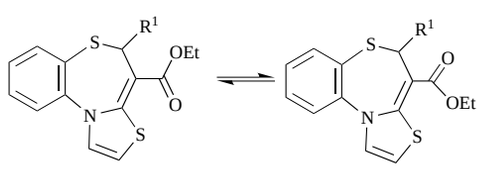
			11[b]		**12**[b]	
	9[a]	**10**[a]	*trans*	*cis*	*trans*	*cis*
H-1	8.56d $J_{1,2}$ 3.8	8.59d $J_{1,2}$ 4.0	8.85d $J_{1,2}$ 3.8	8.93d $J_{1,2}$ 3.9	8.90d $J_{1,2}$ 3.6	9.03d $J_{1,2}$ 4.0
H-2	8.25d	8.25d	8.70d	8.60d	8.76d	8.66d
H-4$_{ax}$	4.00m	4.17dd $J_{4ax,4eq}$ −12.2 $J_{4ax,5}$ 5.0	3.97m	4.66d $J_{4,5}$ 6.3	4.47d $J_{4,5}$ 12.1	4.96d $J_{4,5}$ 7.4
H-4$_{eq}$	2.66m	3.31dd $J_{4eq,5}$ 11.6				
H-5	4.00m	5.11dd	3.97m	4.52m *J* 6.7	4.89d	5.57d
5-CH_3	1.39d *J* 6.6		1.58d *J* 6.6	1.32d *J* 6.7		
C*H*$_3$CH$_2$			1.32t *J* 7.1	1.32t *J* 7.1	0.77t *J* 7.0	1.20t *J* 7.1
CH$_3$C*H*$_2$			4.28m *J* 7.1	4.32q *J* 7.1	3.94q *J* 7.0	4.02m
ArH	7.64–7.85 4H m	7.23–7.86 9H m	7.54–8.21 4H m	7.62–8.21 4H m	7.06–8.37 9H m	7.15–8.24 9H m

[a] In CD_3OD solution. [b] In $CDCl_3$ solution.

characterized by means of H-4 and H-5 signals and the relative coupling constants: for the *trans* form of **12**, the H-4 and H-5 signals appear as two doublets at 4.47 and 4.89 ppm (J = 12.1 Hz) upfield relative to the corresponding doublets at 4.96 and 5.57 ppm (J = 7.4 Hz) for the *cis* epimer. Assignment of the ^{13}C NMR resonances of **11** and **12** has been difficult owing to the considerable overlapping of the signals of the two forms, in particular in the aromatic zone; consequently, we report only the resonances of the carbons that have been unambiguously assigned on the basis of HETCOR spectra (Table 2).

The treatment of **9**–**12** with an alkaline medium provided 5*H*-thiazolo[2,3-*d*][1,5]benzothiazepines **13**–**16** (Scheme 1). However, since compounds **13**, **14** are relatively unstable in the air and at room temperature their formation has been evidenced only by ^{1}H NMR spectroscopy: addition of NaOD to a suspension of the bromides **9** and **10** in $CDCl_3$ gave rise to ^{1}H NMR signals consistent with the presence of the thiazolobenzothiazepines **13** and **14**; in particular, the signals of the thiazole nucleus were shifted upfield (between 6.0 and 7.0 ppm) with respect to those (between 8.0 and 9.0 ppm) of the corresponding bromides **9** and **10**; further, all other resonance patterns agreed with the proposed structure (Table 3).

The thiazolo[2,3-*d*][1,5]benzothiazepines **15** and **16** showed unexpected behaviour: the spectral data indicate the presence, in solution, of two conformers **I** and **II** in which the ethoxycarbonyl group is arranged differently. The distribution of the two conformers **I** and **II** (Scheme 3) was determined by ^{1}H NMR



I **II**

15 R^1 = Me
16 R^1 = Ph

Scheme 3

spectroscopy. Spectra recorded immediately after dissolution show that only the type **I** rotamer is present, being stable at low temperature (−20 °C), independent of the nature of the solvent and having similar characteristics to the isomer present in the solid state (*vide infra*). With an increase in the temperature, the signals of the conformer **II** gradually increased reaching at

Table 2 Selected ^{13}C NMR data for compounds **11** and **12** in $CDCl_3$

	11		**12**	
	trans	*cis*	*trans*	*cis*
C-1	127.34	128.26	127.76	128.58
C-2	136.42	135.43	137.03	136.30
C-3a	167.84	166.91	167.75	167.12
C-4	52.78	51.48	53.14	52.66
C-5	51.26	50.45	61.61	61.27
5-CH_3	16.01	18.41		
*C*H$_3$CH$_2$	14.17	14.25	13.11	13.77
CH$_3$*C*H$_2$	63.53	62.88	62.99	62.99
*C*O$_2$Et	167.13	166.83	165.96	166.80

25 °C an equilibrium state in which the relative ratios of **I** *vs*. **II** were, to a small degree, influenced by the solvent: that is 42 : 58 in CCl_4, 53 : 47 in $CDCl_3$ and 56 : 44 in [$^2H_6$]-DMSO. These values remained practically unchanged even at higher temperatures (up to 120 °C). The spectroscopic changes described may result from a difference in the spatial disposition of the ethoxycarbonyl group in the two conformers. Thus, if it is assumed that in conformers **I** a short intramolecular S···O contact is present due to charge delocalization from the heterocycle into the carbonyl group, the corresponding effect induced in type **II** derivatives may be less. This would explain the different chemical shift and coupling constant values for H-1 and H-2 of the thiazole ring in type **I** and type **II** derivatives (Table 3). Moreover, the downfield shift of H-5 in conformers **II** can be accounted for by the presence of an intramolecular hydrogen bond between the carbonyl group and H-5, which stabilizes type **II** forms. Furthermore, this proton is long-range coupled, through the sulfur atom, with H-2 only in type **II** derivatives (Table 3), since in conformers **I** delocalization of the sulfur lone pair into the carbonyl group prevents this coupling.

Complete assignments of the ^{1}H and ^{13}C NMR resonances of the two conformers of compounds **15** and **16** have been performed through interactive interpretation of COSY and HETCOR spectra (Table 4).

In order to gain more insight into the structural characteristics of such compounds, a single crystal of **15** was subjected to X-ray analysis, the ORTEP diagram of which is shown in Fig. 1. Some selected bond lengths and bond angles are reported in Table 5, while crystallographic details are given in the Experimental section. This crystallographic structural determination reveals that only conformer **I** is present in the solid state, stabilized by the presence of a short S(1)···O(1) contact. As can be

Table 3 ^{1}H NMR data for compounds **13**–**16** in $CDCl_3$

			15		**16**	
	13	**14**	**I**	**II**	**I**	**II**
H-1	6.85d $J_{1,2}$ 7.7	7.01d $J_{1,2}$ 6.9	6.84d $J_{1,2}$ 4.7	7.05d $J_{1,2}$ 8.0	6.95d $J_{1,2}$ 4.7	7.02d $J_{1,2}$ 8.0
H-2	5.93d	6.03d	6.41d	6.20dd $J_{2,5}$ 1.1	6.50d	5.89dd $J_{2,5}$ 1.1
H-4	5.19d $J_{4,5}$ 4.4	4.72d $J_{4,5}$ 4.6				
H-5	3.72dq J 7.1	5.44d	4.60q J 6.9	4.82dq J 6.9	5.90s	6.08d
5-CH_3	1.45d		1.05d	1.60d		
CH_3CH_2			1.30t J 7.1	1.35t J 7.1	1.12t J 7.1	1.21t J 7.1
CH_3CH_2			4.23m	4.20m	4.12m	4.10m
ArH	6.75–7.14 4H m	6.83–7.35 9H m	7.22–7.60 4H m	7.07–7.45 4H m	6.90–7.18 9H m	7.02–7.28 9H m

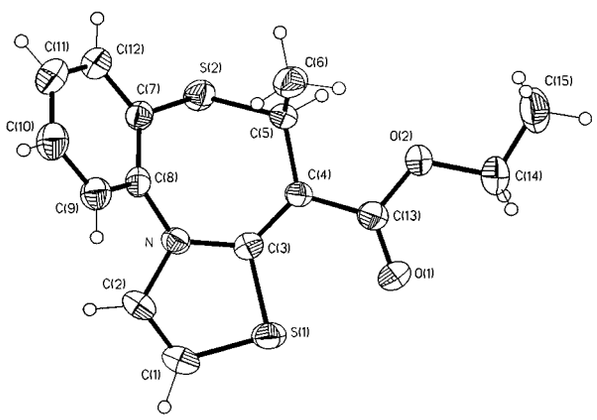


Fig. 1 A perspective view of the molecular structure with crystallographic numbering scheme for 4-ethoxycarbonyl-5-methyl-5*H*-thiazolo[2,3-*d*][1,5]benzothiazepine **15**

seen in Fig. 1 and by 'puckering' coordinates[8] and asymmetry parameters,[9] the thiazepine nucleus assumes a distorted envelope conformation, rather unusual for analogous systems which generally adopt a distorted boat conformation.[10] The S(2) atom and the methyl group at C(5), as can be seen from molecular space filling, are in opposite directions so minimizing the steric hindrance. In this disposition the methyl group is situated in front of the benzene fused ring and interacts with its π-electronic cloud as demonstrated from the intramolecular distances involving C(6) [C(6)···C(8), 3.429(4) Å and C(6)···C(7), 3.020(4) Å]. This result offers an explanation for the upfield chemical shift observed in the ^{1}H NMR spectrum of **15**, for the 5-methyl in conformer **I** form with respect to that in conformer **II** (Table 3).

Bond distances and angles of the seven-membered ring are in good agreement with those reported in the Crystallographic Structural Database (CSD) for other benzothiazepines.[11]

The N–C(3)–C(4)–C(5) fragment deviates slightly from planarity [−8.7(5)°] making possible a wide π-electronic delocalization that extends its influence from the thiazole system to the ethoxycarbonyl group.

The thiazole ring is nearly planar and is not far from being co-planar with the ester fragment. The nitrogen atom deviates −0.082(2) Å from the best mean plane calculated through C(2), C(3), C(8), thus testifying to a sp^2 hybridization and its lone pair delocalization, also confirmed by bond distances N–C(2) 1.405(3) Å and N–C(3) 1.397(3) Å. Although the S–C bond lengths appear to be different [S(1)–C(1) 1.728(3) Å and S(1)–C(3) 1.763(3) Å], they bear out a partial double-bond character that is more marked in the former. Such a difference

Table 4 ^{13}C NMR data for compounds **15** and **16** in $CDCl_3$

	15		**16**	
	I	**II**	**I**	**II**
C-1	130.60	128.82	130.65	131.77
C-2	106.95	112.54	107.24	115.77
C-3a	158.56	156.01	157.28	156.65
C-4	105.46	97.89	93.40	99.43
C-5	40.65	39.55	50.55	49.77
C-6a	130.21	126.66	130.08	126.60
C-7	136.18	121.18	135.96	121.25
C-8	126.03	123.80	127.06	124.18
C-9	128.87	125.66	128.59	125.87
C-10	125.79	111.39	125.48	111.66
C-10a	145.49	140.45	145.50	140.49
CH_3CH_2	14.51	14.65	14.39	14.44
CH_3CH_2	59.86	60.60	59.99	60.79
CO_2Et	166.74	166.29	166.93	166.62
CH_3-5	24.44	24.77		
C-1′			142.83	143.30
C-2′,6′			127.14	127.87
C-3′,5′			127.28	127.99
C-4′			126.98	126.47

arises from the asymmetric partial delocalization of the out-of-plane S lone pair with high p character with the two adjacent carbon atoms. This difference suggests that the way S(1)–C(1)=C(2)–N–C(3)=C(4)–C(13)=O(1) used to make the π-electron delocalization occur from the heterocycle into the carbonyl group is more efficient. The C(1)–S(1)–C(3) bond angle of 91.5(1)° is comparable to that reported for thiazole systems.[12]

The intramolecular S(1)···O(1) distance 2.590(2) Å is markedly shorter than the sum of van der Waals radii of the two atoms (3.25 Å) and is an intermediate value in the large range of S···O distances (from 2.178 Å up to 3.25 Å, vdW value) observed in >1000 organosulfur compounds reported in the CSD.[11] The observed value cannot be justified only by the electrostatic interactions due to the π delocalization which generates a charge separation between the sulfur atom and the carbonyl oxygen [+0.5003 on S(1), −0.371 on O(1)].[13] Although there are several *ab initio* and semiempirical reports[14] about this interaction also found in other chalcogen atoms (Se, Te),[15] no conclusive interpretation and rationalization has been made: synthesis, structural characterizations and semiempirical calculations on model systems properly substituted are in progress and will be reported in a forthcoming publication.

The molecular packing is mainly determined by the normal van der Waals interactions and from a weak intermolecular hydrogen bonding involving H(2) of the thiazole ring and the O(1) of the carbonyl group thus determining along the *a* axis parallel rows of molecules in a zig-zag disposition (Fig. 2).

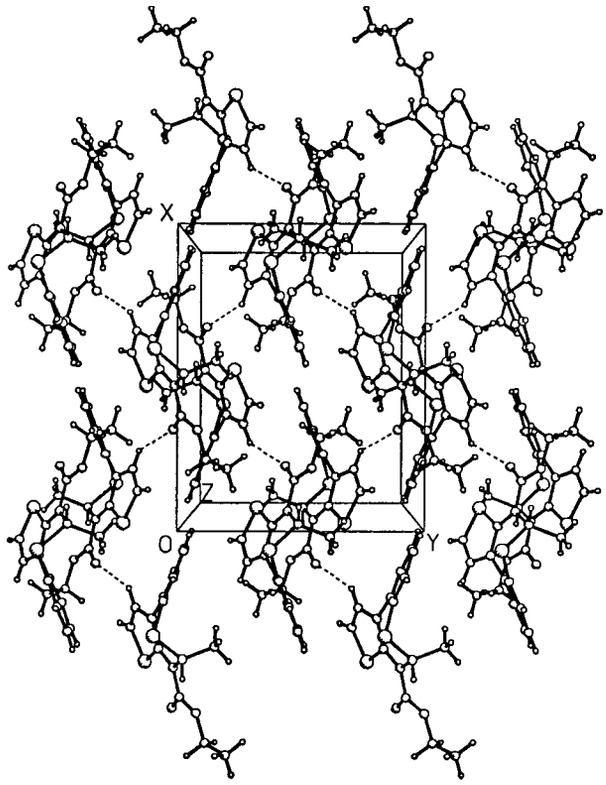


Fig. 2 Molecular packing for **15** viewed down the *c* axis

Experimental

Mps were determined on a Kofler hot-stage apparatus and are uncorrected. Elemental analyses (C, H, N) were carried out on a C. Erba Model 1106 Elemental Analyzer. Merck silica gel 60 F_{254} plates were used for analytical TLC. Mass spectra were recorded in a Hewlett-Packard Model 5995 GC–MS. ^{1}H and ^{13}C NMR spectra were measured with a Varian-Gemini-300 instrument; chemical shifts are expressed in δ (ppm) and coupling constants (*J*) in Hz. The *cis*–*trans* tautomer ratios were obtained by integration of the ^{1}H NMR spectra. COSY, COSY-LR, HETCOR and HETCOR-LR experiments were carried out by using the standard spectrometer software package.

General procedure for the thiazolo[2,3-*d*][1,5]benzothiazepinium bromides 9–12

To a stirred solution of the appropriate 1,5-benzothiazepine-4-thione derivative **5**–**8** (0.001 mol) in butan-2-one (20 ml) a solution of α-bromoacetaldehyde diethyl acetal (0.001 mol) in the same solvent (5 ml) and water (0.1 ml) were added dropwise. After the reaction mixture had been refluxed for the appropriate time (as indicated in each case), it was cooled and stored overnight at room temperature. The precipitated product was filtered off and crystallized from methanol.

4,5-Dihydro-5-methylthiazolo[2,3-*d*][1,5]benzothiazepinium bromide 9. Reaction time 2 h, mp 245–247 °C, yield 44%; *m/z* 313 (M, 5%), 233 (23), 232 (28), 231 (72), 230 (71), 200 (67), 186 (100), 174 (14) and 69 (44) (Found: C, 45.64; H, 3.66; N, 4.57. Calc. for $C_{12}H_{12}BrNS_2$: C, 45.86; H, 3.85; N, 4.46%); δ_C(CD_3OD) 24.46 (CH_3), 36.78 (C-4), 52.00 (C-5), 124.89 (C-2), 127.60 (C-6a), 127.05, 137.49, 132.77, 133.22 (Ar-CH), 138.51 (C-1), 141.27 (C-10a) and 174.00 (C-3a).

4,5-Dihydro-5-phenylthiazolo[2,3-*d*][1,5]benzothiazepinium bromide 10. Reaction time 1.5 h, mp 231–234 °C, yield 55%; *m/z* 375 (M, 3%), 238 (10), 237 (43), 236 (100) and 69 (6) (Found: C, 54.29; H, 3.88; N, 3.51. Calc. for $C_{17}H_{14}BrNS_2$: C, 54.40; H, 3.76; N, 3.73%); δ_C(CD_3OD) 36.47 (C-4), 59.17 (C-5), 125.25 (C-2), 128.05 (C-6a), 126.51, 127.41, 128.34, 129.15, 132.96, 133.53, 138.17 (Ar-CH), 138.67 (C-1), 141.23 (C-10a), 143.59 (C-1′) and 172.86 (C-3a).

Table 5 Selected bond lengths (Å) and angles (°) and torsion angles (°) for the crystal structure of compound **15**[a]

S(1)–C(1)	1.728(3)	C(4)–C(13)	1.444(4)
S(1)–C(3)	1.763(3)	C(5)–C(6)	1.517(4)
C(1)–C(2)	1.320(4)	C(5)–S(2)	1.834(3)
C(2)–N	1.405(3)	S(2)–C(7)	1.753(3)
N–C(3)	1.397(3)	C(13)–O(1)	1.220(3)
N–C(8)	1.436(3)	C(13)–O(2)	1.357(3)
C(3)–C(4)	1.367(3)	O(2)–C(14)	1.447(3)
C(4)–C(5)	1.513(3)	C(14)–C(15)	1.452(4)
C(1)–S(1)–C(3)	91.5(1)	C(3)–C(4)–C(5)	125.5(2)
S(1)–C(1)–C(2)	112.7(2)	C(4)–C(5)–S(2)	112.3(2)
C(1)–C(2)–N	113.8(3)	C(6)–C(5)–S(2)	113.3(2)
C(2)–N–C(8)	116.8(2)	C(5)–S(2)–C(7)	98.3(1)
C(2)–N–C(3)	113.7(2)	C(4)–C(13)–O(2)	111.8(2)
C(3)–N–C(8)	128.6(2)	C(4)–C(13)–O(1)	126.4(3)
S(1)–C(3)–N	108.3(2)	C(13)–O(2)–C(14)	116.8(2)
N–C(3)–C(4)	129.2(2)	O(2)–C(14)–C(15)	107.3(3)
C(3)–C(4)–C(13)	117.1(2)		
S(1)–C(3)–C(4)–C(13)	−6.2(4)	C(4)–C(5)–S(2)–C(7)	80.5(2)
C(3)–C(4)–C(13)–O(1)	3.6(4)	C(5)–S(2)–C(7)–C(8)	−57.4(2)
C(3)–N–C(8)–C(7)	54.1(4)	S(2)–C(7)–C(8)–N	−10.4(4)
C(3)–C(4)–C(5)–S(2)	−37.5(3)		

[a] For the numbering scheme of atoms, see Fig. 1.

4,5-Dihydro-4-ethoxycarbonyl-5-methylthiazolo[2,3-*d*][1,5]-benzothiazepinium bromide 11. Reaction time 45 min, mp 187–190 °C, yield 68% (Found: C, 47.01; H, 4.29; N, 3.74. Calc. for $C_{15}H_{16}BrNO_2S_2$: C, 46.76; H, 4.19; N, 3.64%).

4,5-Dihydro-4-ethoxycarbonyl-5-phenylthiazolo[2,3-*d*][1,5]-benzothiazepinium bromide 12. Reaction time 30 min, mp 189–191 °C, yield 64% (Found: C, 53.79; H, 4.18; N, 3.22. Calc. for $C_{20}H_{18}BrNO_2S_2$: C, 53.69; H, 4.06; N, 3.13%).

General procedure for the thiazolo[2,3-*d*][1,5]benzothiazepines 15–16

The thiazolo[2,3-*d*][1,5]benzothiazepinium bromides **11**–**12** were dissolved in 50% methanol–water and treated with an excess of 3 M aqueous sodium hydroxide to give the free bases **15**–**16** as white solids. The crude products were collected and crystallized from diethyl ether.

4-Ethoxycarbonyl-5-methyl-5*H*-thiazolo[2,3-*d*][1,5]benzothiazepine 15. Mp 118–121 °C, yield 88%, *m/z* 305 (M, 2%), 274 (18), 273 (100), 259 (37), 245 (37), 244 (50), 231 (17), 230 (23), 228 (38), 214 (23), 200 (20), 186 (12), 173 (10), 115 (13) and 69 (12) (Found: C, 59.24; H, 4.88; N, 4.52. Calc. for $C_{15}H_{15}NO_2S_2$: C, 59.01; H, 4.96; N, 4.59%).

4-Ethoxycarbonyl-5-phenyl-5*H*-thiazolo[2,3-*d*][1,5]benzothiazepine 16. Mp 104–106 °C, yield 74%, *m/z* 367 (M, 3%), 337 (8), 336 (25), 335 (100), 307 (24), 306 (23), 291 (8), 290 (31), 262 (17), 260 (26), 109 (8) and 77 (5) (Found: C, 65.41; H, 4.72; N, 3.66. Calc. for $C_{20}H_{17}NO_2S_2$: C, 65.38; H, 4.67; N, 3.81%).

Crystal structure of compound 15

Crystals were grown from diethyl ether.

Crystal data. $C_{15}H_{15}NO_2S_2$, $M = 305.4$. Orthorhombic, $a = 12.747(2)$, $b = 10.043(1)$, $c = 22.613(3)$ Å, $V = 2894.9(7)$ Å^3 (by least-squares refinement on setting angles for 35 strong reflections in the range $13 < 2\theta < 30°$, $\lambda = 0.710\,73$ Å), space group *Pbca*, $Z = 8$, $D_x = 1.401$ g cm^{-3}, μ(MoKα) = 0.368 mm^{-1}, $F(000) = 1280$, $T = 293$ K. Crystal dimensions 0.20 × 0.31 × 0.27 mm.

Data collection and processing. Siemens R3m/V four-circle diffractometer using graphite-monochromated MoKα ($\lambda = 0.710\,73$ Å) radiation. Crystal and electronic stability was confirmed by the constancy of three check reflections monitored every 197 reflections. 2607 Reflections measured ($3 < 2\theta < 49°$, $0 < h < 15$, $0 < k < 12$, $-1 < l < 27$), 2418 unique

[merging $R = 1.48\%$ after absorption correction (max., min. transmission factors = 0.75, 0.73)], giving 1329 with $I > 2\sigma(I)$.

Structure analysis and refinement. The structure was solved by direct methods with SIR92 program;[16] subsequent calculations were mainly carried out using the SHELXTL *Plus*[17] and SHELXL93[18] programs. All the H atoms were added at calculated positions and included in the structure factor calculations with a common thermal parameter ($U = 0.07$ Å^2). The structure was refined by full-matrix least squares on F^2, with all non-H atoms refined anisotropically. The final R_1 value was 0.0355 and wR_2 0.0679. The weighing scheme used in the last refinement cycle was $w = 1/[\sigma^2(F_o^2) + 0.0333P^2]$, where $P = (F_o^2 + 2F_c^2)/3$, Goodness-of-fit = 0.795. Final difference map had extreme features of ± 0.17 e Å^{-3}, $(\Delta/\sigma)_{max} = 0.001$. Atomic scattering factors from International Tables for Crystallography.[19] Tables of atomic coordinates, anisotropic thermal parameters and hydrogen position have been deposited at the Cambridge Crystallographic Data Centre and are available on request.† Any such request should be accompanied by a full bibliographic reference for this work together with the deposition number 207/118.

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† For details of the deposition scheme, see Instructions for Authors (1997), *J. Chem Soc., Perkin Trans. 1*, 1997, Issue 1.

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