Photoisomerization of Sultams Derived from Saccharin; Part 3:[1,2] Dihydro[1]benzothieno[3,2-*b*]pyrrole 4,4-Dioxides from Dihydropyrrolo[1,2-*b*][1,2]benzisothiazole 5,5-Dioxides

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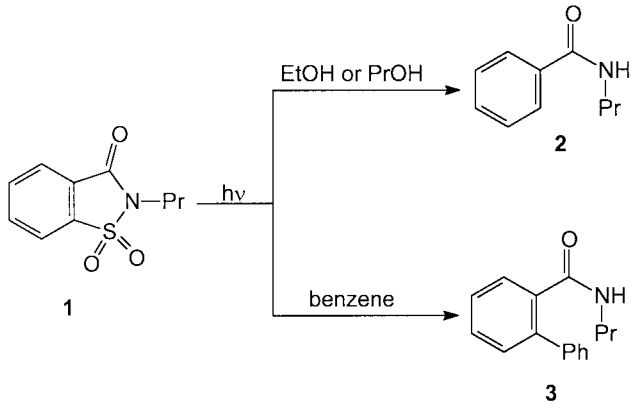
Dedicated to Prof. Howard E. Zimmerman on the occasion of his 75th birthday

Abstract: 1-Substituted 2,3-dihydropyrrolo[1,2-*b*][1,2]benzisothiazole 5,5-dioxides **7a–c,e** undergo a smooth and efficient transformation into the 2,3-dihydro[1]benzothieno[3,2-*b*]pyrrole 4,4-dioxides **8a–c,e** upon irradiation at 254 nm in acetonitrile. The structures of the products have been elucidated by spectroscopic methods and a single crystal X-ray structure determination for **8b**.

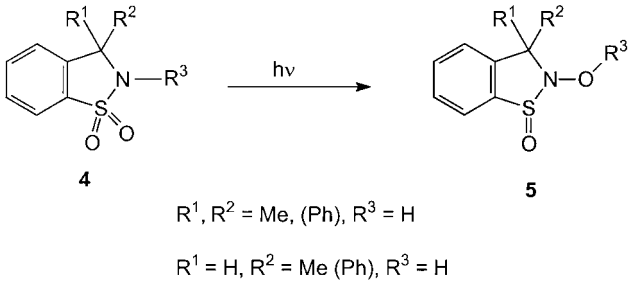
Key words: photoisomerization, sultams, dihydro[1]benzothieno-[3,2-*b*]pyrrole 4,4-dioxides

The photoreactivity of sulfonamides and sultams is dominated by S–N bond homolysis.[3,4] Among five-membered sultams, saccharin derivatives have been irradiated in solution.[1,2,5,6] For example, upon irradiation, 2,3-dihydro-3-oxo-2-propyl-[1,2]benzisothiazole 1,1-dioxide (**1**) in ethanol or propanol undergoes extrusion of sulfur dioxide to form *N*-propylbenzamide (**2**) by hydrogen uptake, while in benzene as solvent *N*-propylbiphenyl-2-carboxamide (**3**) is formed (Scheme 1).[5,6]



Scheme 1

When the 3-oxo group is replaced by either two alkyl (or phenyl) groups or one hydrogen atom and an alkyl (or phenyl) group as in **4**, a net migration of one oxygen atom from sulfur to nitrogen is observed upon irradiation at 254 nm, whereby the electrophilic substituent on the nitrogen atom (H, alkoxymethyl) is attached to this oxygen atom (Scheme 2).[1,2] Product **5** is in fact a sulfine hydroxamic acid derivative, a functional group not accessible in free form by treating hydroxylamines with sulfinyl halides or esters.[7,8]



Scheme 2

We wanted to clarify whether a similar oxygen shift as in the case **4** → **5** would also be possible with [*b*]fused [1,2]benzoisothiazole 5,5-dioxides **7**. Compounds **7a–c**[9] have been obtained by intramolecular condensation of the oxo group with the activated methylene group adjacent to R in the side chain (Scheme 3). It soon became apparent, however, that a similar oxygen shift as outlined above did not take place. We report here the outcome of this photoreaction, which appears to be another type of reaction, being in fact a skeletal rearrangement of **7**.

The amide **7e** was obtained from the carboxylic acid derivative **7d** (R = CO_2H), which was prepared by hydrolyzing the methyl ester **7b** or the ethyl ester **7c** in acetone with added 10% aqueous sodium hydroxide solution at room temperature. Upon neutralization with dilute hydrochloric acid the carboxylic acid **7d** was obtained in good yield and converted into the acid chloride by boiling with excess thionyl chloride. The acid chloride in turn was refluxed with *p*-toluidine in anhydrous benzene to give the amide **7e**. All the new synthesized compounds were unambiguously characterized by both elemental analyses and spectroscopic techniques.

The UV spectrum of the ethyl ester **7c** shall be discussed briefly. In acetonitrile, two distinct structureless bands are observed: A broad band with an onset of absorption at

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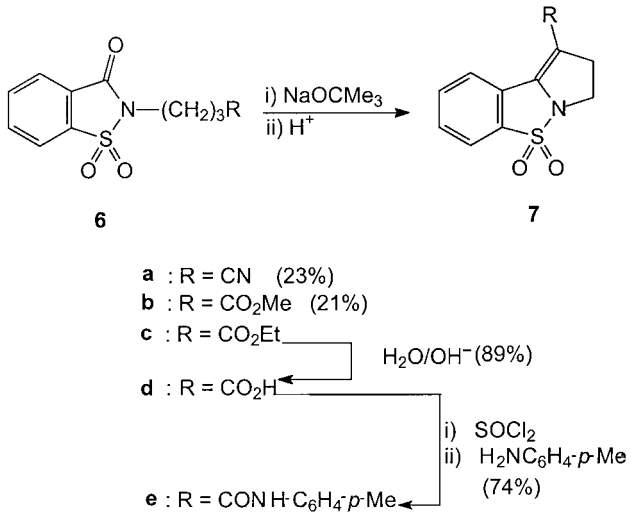


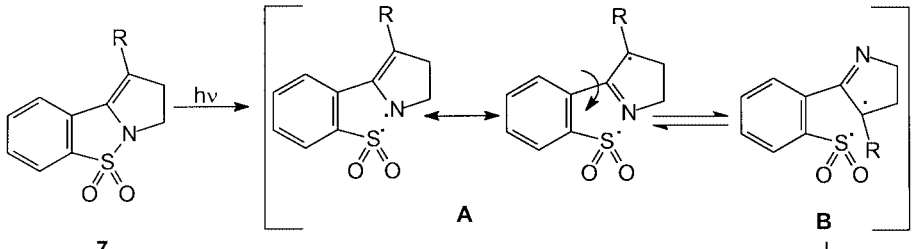
Scheme 3

λ_{max} = 400 nm and λ_{max} = 324 nm (log ε = 4.00), and a second band (λ_{max} = 250 nm, log ε = 3.91). In benzene, the long wavelength band appears at the same wavelength and shows the same intensity as in acetonitrile. Whereas irradiation at the long wavelength absorption using Duran-filtered (λ ≥280 nm) UV light slowly gave a complex mixture of products in low yield, it had been found that selective irradiation into the short wavelength absorption band (254 nm) gave an efficient transformation (see below), which probably involves an higher excited singlet state.

When 1-substituted 2,3-dihydropyrrolo[1,2-*b*][1,2]benzisothiazole 5,5-dioxides **7a**–**c**,**e** are irradiated with the 254 nm emission of the low-pressure mercury lamp in argon-purged acetonitrile (through a quartz jacket retaining the 185 nm emission), a smooth and efficient isomerization into the 2,3-dihydro[1]benzothieno[3,2-*b*]pyrrole 4,4-dioxide derivatives **8a**–**c**,**e** is observed (Scheme 4). The same result was obtained using methanol as the solvent.

This photochemical isomerization of **7a**–**c**,e to **8a**–**c**,**e** could be rationalized through the biradical **A** which is formed via homolytical S–N rupture. This biradical is resonance stabilized and, following rotation around the C–C bond, ring-closure occurs from conformer **B** producing **8a**–**c**,**e** (Scheme 4). No attempts have been made to trap the biradical, since intramolecular combination forming a five-membered ring seemed highly favourable. Practically it has been noticed that the more electron-withdrawing the character of the substituent R, the faster the transformation of **7** into **8**. This observation is in complete agreement with the proposed mechanistic pathway. By monitoring the reaction with thin layer chromatography it was found that for R = CN (**7a**) the shortest time was needed for the appearance of the irradiation product in the reaction medium, and the rate of conversion and the percent yield of the product (based on the consumed starting material) was higher than that of the esters **7c**,**b**, followed by the amide derivative **7e**, which was photolyzed very slowly. The low yield (22% with 63% recovery of **7e**) and the long time of irradiation required for the amide **7e** may be rationalized not only by the low electron-withdrawing effect of the amide group (especially, if the *N*-substituent was aromatic) but also, by the steric influence of the phenyl group which might have hindered the final ring-closure. Moreover, the presence of the *N*-phenyl group may cause a retardation due to absorption of some of the incident UV light.

The structures of **8a**–**c**,**e** may be delineated primarily from the mass spectral and NMR data but are firmly supported by a single crystal X-ray structure determination for compound **8b**[10] (Figures 1 and 2, Table 1).



7, 8	R	Yield (%)
a	CN	91
b	CO_2Me	86
c	CO_2Et	88
e	$CONH\text{-}C_6H_4\text{-}p\text{-}Me$	22

Scheme 4

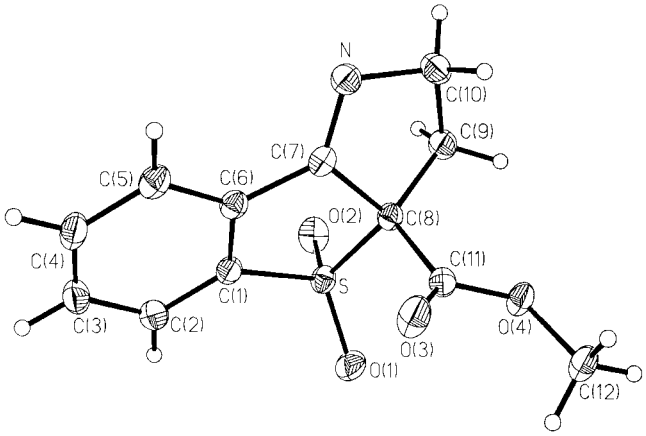


Figure 1 ORTEP-plot of molecular structure of **8b** in the crystal (the crystallographic numbering does not reflect the systematic numbering)

Table 1 Selected Bond Lengths and Angles of Compound **8b** in the Crystal (The Crystallographic Numbering does not Reflect Systematic Numbering)

Bond Lengths (pm)		Bond Angles (°)	
C8–S	181.93 (16)	C9–C8–S	119.27 (0.119)
C8–C7	152.8 (2)	C7–C8–C11	110.72 (0.12)
C8–C9	152.8 (2)	C7–C8–S	102.19 (0.10)
C8–C11	153.24 (2)	C9–C8–C7	100.10 (0.12)
C7–N	126.83 (2)	C6–C7–C8	113.67 (0.13)
C1–S	176.46 (16)	C8–C7–N	115.07 (0.14)
C10–N	148.22 (21)	C9–C10–N	105.69 (012)
		C7–N–C10	107.47 (013)

Due to the formation of a new stereogenic centre (C-3a) in **8**, the A_2X_2 pattern of the CH_2–CH_2 fragment in the nearly planar **7** is changed into a complicated pattern in **8** giving rise to the occurrence of several multiplets, one of which overlaps with the resonances of the diastereotopic ester methylene protons (in **8b**). An attempt to resolve all multiplets has not been made. Thus, the ^{1}H NMR spectrum of **7b** shows two triplets at $\delta = 3.33$ and 3.81 for 2 H at C-2 and 2 H at C-3, respectively. These four protons in the product **8b** are all under different environments, thus a pattern of four multiplets at $\delta = 2.62$, 2.93, 4.33 and 4.65 is obtained. Also, the ^{13}C NMR of **8b** reveals a new sp^3 carbon signal at $\delta = 82.0$ attributable to the new quaternary stereogenic centre (C-3a). The analogous products **8a**,**c**,**e** likewise show a quaternary carbon at $\delta = 70.1$, 82.2, and 83.5, respectively. In the infrared spectra, the carbonyl absorption band in **7b** (being an α,β-unsaturated ester) at 1706 cm^{-1} was shifted by 19.0 cm^{-1} towards higher wavenumber and appeared at 1725 cm^{-1} in **8b** as a typical value for normal esters.

In summary, we have found a remarkably clean light-induced transformation of pyrrolo[1,2-*b*][1,2]benzisothiazole 5,5-dioxides into [1]benzothieno[3,2-*b*]pyrrole 4,4-oxides. The formally related case of formation of 3,4-benzo-2-thia-6-azabicyclo[3,2,0]hepta-3,6-dienes initiated by [2+2] photocycloaddition of electron-rich alkynes to 1,2-benzisothiazoles,[11] has been interpreted in a different way, however.

The NMR spectra were recorded on Bruker WM 300 and DRX 500 spectrometers (300 MHz and 500 MHz, respectively for ^{1}H, 75 and 125 MHz, respectively, for ^{13}C) using TMS as internal standard and the deuterated solvent as lock. IR spectra were obtained by using a Perkin–Elmer 983 spectrophotometer (m: medium intense, s: strong). Electron impact ionisation mass spectrometry (EIMS) was performed on a Varian AMD 604 instrument using 70 eV ionization energy. Melting points (mp) are uncorrected. All the chromatographic separations were performed on 48 × 20 cm glass plates covered with an air-dry layer (1 mm thick) of silica gel (Merck Kieselgel PF_{254}). Reactions were monitored by TLC.

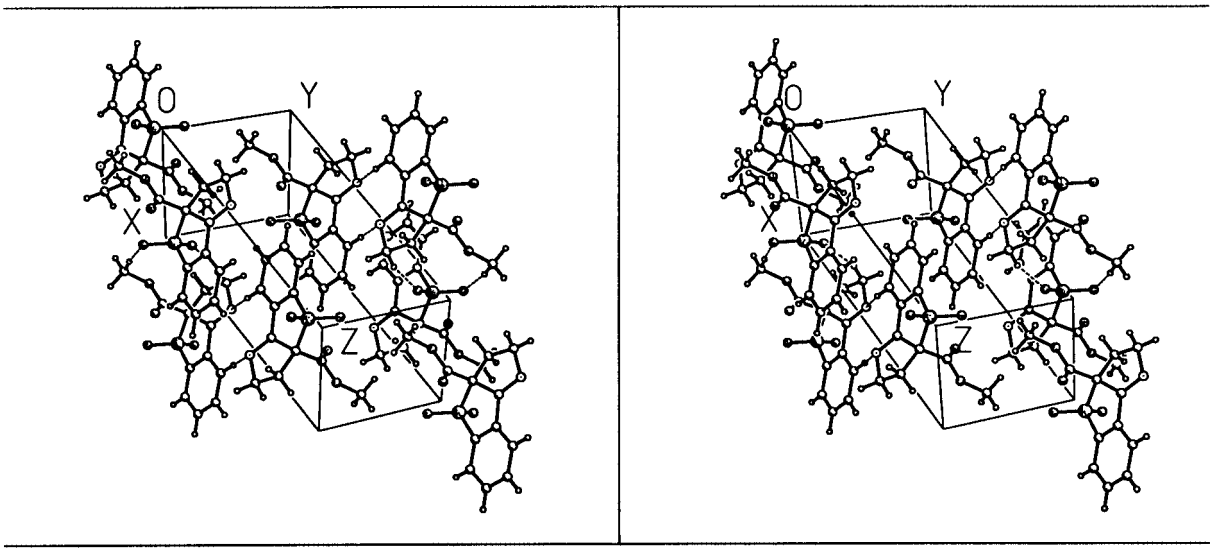


Figure 2 Stereo-view of crystal packing of **8b**

N-Substituted 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxides **6a–c** were prepared following the literature procedure.[9]

2,3-Dihydropyrrolo[1,2-*b*][1,2]benzisothiazole 5,5-Dioxides 7a–c; General Procedure

To a solution of NaO*t*-Bu (0.07mol) in *tert*-butyl alcohol (100 mL) at 110 °C was added powdered **6a–c** (0.035 mol) in one lot. The reaction mixture was kept at 110 °C for 20–25 min, then poured into concd HCl–ice mixture. The resulting solid was filtered, washed with H_2O, and air-dried.

2,3-Dihydropyrrolo[1,2-*b*][1,2]benzisothiazole-1-carbonitrile 5,5-Dioxide (**7a**)

Colorless solid (2.1 g, 23%); mp 227 °C (EtOH) (Lit.[9a] mp 210 °C).

UV (MeCN): λ_{max} (log ε) = 250 (3.67), 280 (3.48), 324 nm (3.65).

^{1}H NMR ($CDCl_3$): δ = 8.13 (m, 1 H, aryl-H), 7.88–7.72 (m, 3 H, aryl-H), 3.94 (t, 2 H, *J* = 8.8 Hz, 3-H_2), 3.32 (t, 2 H, *J* = 8.8 Hz, 2-H_2).

^{13}C NMR ($CDCl_3$): δ = 151.1, 139.9, 134.5, 133.4, 124.9, 123.6, 122.3, 115.2, 83.9, 43.4, 34.8.

Methyl 2,3-Dihydropyrrolo[1,2-*b*][1,2]benzisothiazole-1-carboxylate 5,5-Dioxide (**7b**)

Colorless crystals (0.95 g, 21%); mp 181 °C (MeOH) (Lit.[9a] mp 176 °C).

UV (MeCN): λ_{max} (log ε) = 250 (3.60), 3.24 nm (4.03).

Ethyl 2,3-Dihydropyrrolo[1,2-*b*][1,2]benzisothiazole-1-carboxylate 5,5-Dioxide (**7c**)

Colorless crystals (2.92 g, 54%); mp 153 °C (EtOH) (Lit.[9b,c] mp 152 °C).

UV (MeOH): λ_{max} (log ε) = 250 (3.91), 324 nm (4.00).

2,3-Dihydropyrrolo[1,2-*b*][1,2]benzisothiazole-1-carboxylic Acid 5,5-Dioxide (7d)

A 10% aq NaOH solution (0.5 mL) was added to a solution of 1.00 g (3.80 mmol) of the methyl ester **7b** (or the ethyl ester **7c**) in acetone (5 ml) at 0 °C. Then the mixture was stirred at r.t. for 4 h (TLC-monitoring) and H_2O (50 mL) was added. The resulting clear solution was neutralized with dil. HCl and the precipitate was collected by filtration and washed with H_2O.

Colorless crystals (0.89 g, 89%); mp 227 °C (EtOH).

IR (KBr): ν = 3200s–2800s (br, OH), 1676s (C=O) 1318s, 1177s (SO_2) cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 13.0 (s, 1 H, CO_2H); 8.94 (m, 1 H, aryl-H), 8.10 (m, 1 H, aryl-H), 7.81 (m, 2 H, aryl-H), 3.81 (t, 2 H, *J* = 9.0 Hz, 3-H_2) 3.35 (t, 2 H, *J* = 9.0 Hz, 2-H_2).

^{13}C NMR (DMSO-d_6): δ = 166.1, 146.2, 140.2, 134.1, 133.1, 128.3, 125.3, 122.1, 110.0, 41.3, 34.2.

MS: *m/z* (%) = 251 (M^+, 100), 206 (43), 186 (36), 142 (32), 115 (50), 103 (17), 89 (18), 77 (12).

Anal. Calcd for $C_{11}H_9NO_4S$ (251.1): C, 52.59; H, 3.59; N, 5.58; S, 12.75. Found: C, 52.55; H, 3.53; N, 5.60; S, 12.61.

2,3-Dihydropyrrolo[1,2-*b*][1,2]benzisothiazole-1-[*N*-(4-methyl phenyl)] carboxamide 5,5-Dioxide (7e)

A mixture of **7d** (1.10 g, 4.4 mmol) and excess $SOCl_2$ (5 mL) was refluxed for 4 h at 85–90 °C. Then the unreacted $SOCl_2$ was evaporated in vacuo to give the crude acid chloride as a pale yellow solid which was used directly in the next step. A mixture of the acid chloride (0.86 g, 3.2 mmol) and *p*-toluidine (0.34 g, 3.18 mmol) was refluxed for 4 h (TLC-monitoring) in anhyd benzene (50 mL). The solvent was evaporated completely in vacuo and the residue was washed several times with 10% aq $NaHCO_3$ solution, then with H_2O, and air dried.

Pale yellow crystals (0.81 g, 74%); mp 219–220 °C (EtOH).

UV (MeCN): λ_{max} (log ε) = 250 (4.21) 340 nm (4.29).

IR (KBr): ν = 3337s (NH), 1648s (C=O), 1359s, 1173s (SO_2) cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 9.51 (s, 1 H, NH), 8.92 (m, 1 H, aryl-H), 8.12 (m, 1 H, aryl-H), 7.85 (m,1 H, aryl-H), 7.81 (m, 1 H, aryl-H), 7.60 (m, 2 H, aryl-H), 7.15 (m, 2 H), 3.82 (t, 2 H, *J* = 9.0 Hz, 3-H_2), 3.52 (t, 2 H, *J* = 9.0 Hz, 2-H_2), 2.30 (s,3 H, CH_3).

^{13}C NMR (DMSO-d_6): δ = 162.1, 145.5, 139.3, 136.5, 134.3, 133.3, 132.6, 130.9, 129.2, 125.5, 122.2, 121.5, 114.5, 42.2, 33.0, 20.2.

MS: *m/z* (%) = 340 (M^+, 18), 234 (100), 164 (8), 115 (13).

Anal.Calcd for $C_{18}H_{16}N_2O_3S$ (340.1) C, 63.53; H, 4.71; N, 8.23; S, 9.47. Found: C, 63.20; H, 4.64; N, 8.12; S, 9.23.

Photoconversion of 2,3-Dihydropyrrolo[1,2-*b*]benzisothiazole 5,5-Dioxides 7a–c,e into Dihydro[1]benzothieno[3,2-*b*]pyrrole 4,4-Dioxides 8a–c,e; General Procedure

Samples of **7a–c,e** (1.1 mmol each) in MeCN (80 mL) were irradiated for the time listed using a quartz immersion well in connection with a Hanau TNN 15 low pressure mercury lamp (15W input) with continuous argon purging. After concentration the residue was chromatographed on two silica gel plates with EtOAc–hexane (1:1). The R_f values of the appropriate zones are given below.

2,3-Dihydro[1]benzothieno[3,2-*b*]pyrrole-3a-carbonitrile 4,4-Dioxide (**8a**)

After 3 h irradiation (from zone with R_f 0.25); colorless solid (0.21 g, 91%), mp 184–185 °C.

IR (KBr): ν = 2242m (CN), 1653m (C=N), 1337s, 1131s (SO_2) cm^{-1}.

^{1}H NMR ($CDCl_3$) δ = 8.03 (m, 2 H, aryl-H), 7.85 (m, 2 H, aryl-H), 4.85 (m, 1 H, 2-H), 4.63 (m, 1 H, 2-H), 2.85 (m, 2 H, 3-H_2).

^{13}C NMR($CDCl_3$) δ = 163.6, 146.7, 135.8, 134.3, 129.5, 125.5, 123.5, 112.5, 70.1, 68.2, 32.1.

MS: *m/z* (%) = 232 (M^+, 100), 176 (10), 168 (47), 152 (15), 140 (66), 129 (24), 114 (22), 103 (18), 90 (18), 76 (9).

Anal. Calcd for $C_{11}H_8N_2O_2S$ (232.1): C, 56.89; H, 3.44; N, 12.06; S, 13.79. Found: C, 56.74; H, 3.49; N, 12.18; S, 13.78.

Methyl 2,3-Dihydro-[1]benzothieno[3,2-*b*]pyrrole-3a-carboxylate 4,4-Dioxide (**8b**)

After 6 h of irradiation (from zone with R_f 0.26); colorless solid (0.13g, 86%); mp 170–171 °C (MeOH).

IR (KBr): ν = 1725s (C=O), 1648m (C=N), 1315s, 1153s (SO_2) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.91 (m, 1 H, aryl-H), 7.75 (m, 1 H, aryl-H), 7.65 (m, 2 H, aryl-H), 4.65 (m,1 H, 2-H), 4.33 (m, 1 H, 2-H), 3.75 (s, 3 H, OCH_3), 2.93 (m, 1 H, 3-H), 2.62 (m, 1 H, 3-H).

^{13}C NMR ($CDCl_3$): δ = 168.4, 164.6, 148.4, 134.7, 133.8, 132.6, 124.0, 122.5, 82.0, 67.0, 54.1, 30.0.

MS: *m/z* (%) = 265 (M^+, 23), 250 (10), 234 (16), 206 (42), 201 (57), 186 (29), 164 (28), 142 (28), 115 (100), 102 (12), 89 (20), 77 (11), 59 (35).

Anal.Calcd. for $C_{12}H_{11}NO_4S$ (265.2): C, 54.34; H, 4.15; N, 5.28; S, 12.08. Found: C, 54.15; H, 4.18; N, 5.30; S, 12.10.

Ethyl 2,3-Dihydro-[1]benzothieno[3,2-*b*]pyrrole-3a-carboxylate 4,4-Dioxide (**8c**)

After 5 h of irradiation (from zone at R_f 0.18); colorless solid (0.14 g, 88%); mp 84 °C (EtOH).

IR (KBr): ν = 1725s (C=O), 1648m (C=N), 1515s, 1153s (SO_2) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.95 (m, 1 H, aryl-H), 7.85 (m, 1 H, aryl-H), 7.75 (m, 2 H, aryl-H), 4.65 (m, 1 H, 2-H), 4.25 (m, 3 H, 2-H and OCH_2CH_3 overlap), 2.91 (m, 1 H, 3-H), 2.82 (m, 1 H, 3-H), 1.15 (t, 3 H, *J* = 7.0 Hz).

^{13}C NMR ($CDCl_3$): δ = 168.2, 164.1, 148.0, 134.1, 133.0, 132.0, 124.1, 122.5, 82.2, 67.2, 64.1, 30.2, 14.1.

MS: *m/z* (%) = 279 (M^+, 11), 250 (13), 234 (24), 215 (100), 186 (43), 164 (52), 151 (23), 142 (70), 129 (18), 115 (86), 101 (73), 89 (22), 77 (14).

Anal. Calcd for $C_{13}H_{13}NO_4S$ (279.23): C, 55.91; H, 4.65; N, 5.01; S, 11.46. Found: C, 55.88; H, 4.65; N, 5.00; S, 11.29.

2,3-Dihydro-[1]benzothieno[3,2-*b*]pyrrole-3a-[*N*-(4-methylphenyl)]carboxamide 4,4-dioxide (**8e**)
After 24 h of irradiation (from zone with R_f 0.36) colorless solid (0.06 g, 22%); mp 217–218 °C (EtOH).

IR (KBr): ν = 3303m (NH), 1672m (C=O), 1611m (C=N) 1149s, 1319s cm^{-1} (SO_2).

^1H NMR ($CDCl_3$): δ = 8.65 (s, 1 H, NH), 8.0 (m, 1 H, aryl-H), 7.91 (m, 1 H, aryl-H), 7.75 (m, 2 H, aryl-H), 7.35 (m, 2 H, aryl-H), 7.10 (m, 2 H, aryl-H), 4.82 (m, 1 H, 2-H), 4.55 (m, 1 H, 2-H), 3.04 (m, 1 H, 3-H), 2.65 (m, 1 H, 3-H), 2.41 (s, 3 H, CH_3).

^{13}C NMR ($CDCl_3$): δ = 168.2, 162.1, 148.5, 137.5, 137.2, 136.8, 136.5, 135.4, 133.5, 130.3, 125.5, 123.5, 120.3, 83.5, 68.3, 51.2, 31.5, 21.1.

MS: *m/z* (%) = 340 (M^+, 25), 234 (100), 115 (44), 102 (21), 89 (21).

Anal. Calcd for $C_{18}H_{16}N_2O_3S$ (340.1) C, 63.53; H, 4.71; N, 8.23; S, 9.47. Found: C, 63.21; H, 4.64; N, 8.12; S, 9.23.

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(10) Crystal data and structure refinement: Crystal size 0.55 × 0.24 × 0.18 mm, from MeOH. $C_{12}H_{11}NO_4S$, formula weight 265.28. Triclinic system, *P*–1. Unit cell dimensions: a = 6.923(2), b = 7.126(2), c = 12.471(3) Å; α = 82.67(2), β = 78.60(2), γ = 73.52(2)°; Z = 4, cell volume 576.6(3) $Å^3$, d_C = 1.528 g cm^{-3}, λ = 0.71073 Å (MoK_α), μ = 0.287 mm^{-1}. F(000) = 276, Θ = 2.99–27.00°, limiting indices $-8 \le h \ge 0$, $-9 \le k \ge 8$, $-15 \le l \ge 15$. A Siemens P4RA four-circle diffractometer with graphite monochromator and scintillation counter was used to collect 2728 reflections, 2514 of which were unique (R_{int} = 0.0204). Ψ-Scan, transmission range 0.884−0.794. Refinement method: Full-matrix least-squares on F^2, 2514 data, 165 parameters. Goodness of fit on F^2 1.082, final *R* indices, all data ($I \ge 2\sigma(I)$), *R*1 = 0.0361 (0.0323), *wR*2 = 0.0885 (0.0855). Extinction coefficient: 0.013(3). Residual electron density between –0.367 and 0.445 $eÅ^{-3}$. The programs SHELXS-97 for crystal structure solution and SHELXL-97 for crystal structure refinement by Sheldrick, G. M., University of Göttingen, Germany, 1997 have been used. All crystallographic data have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-152473. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.
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