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ORIGINAL PAPER

Reactions of 1,3-benzothiazines and 1,4-benzothiazepines with dimethyl acetylenedicarboxylate

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Abstract Substituted 2*H*-1,3-benzothiazines and 2,3-dihydro-1,4-benzothiazepines react with dimethyl acetylenedicarboxylate in aqueous methanol to give new, unexpected condensed-skeleton heterocycles. The structures of the new compounds were determined by ^{1}H and ^{13}C nuclear magnetic resonance (NMR), two-dimensional (2D) heteronuclear multiple-bond correlation (HMBC), infrared (IR), and for one derivative also by X-ray analysis.

Keywords Sulfur and nitrogen heterocycles · Dimethyl acetylenedicarboxylate · NMR spectroscopy · X-ray structure determination

Professor Gábor Bernáth died on 1 October 2009.

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Introduction

Following the pioneering discovery by Diels and Alder [1], the reactions of dimethyl acetylenedicarboxylate (DMAD) with heterocyclic compounds have been the subject of a great number of publications [2, 3]. A majority of the reactions have been carried out on heteroaromatic systems such as pyridines, quinolines, isoquinolines, thiazoles, imidazoles, phenanthridines, quinoxalines, pyridazines, and their substituted derivatives [2–11]. DMAD is known to react with imines to give a variety of products, depending on the nature of the imine and the reaction conditions. The reaction is highly solvent dependent, and the addition depends on the polarity of the solvent applied.

We earlier reported that cycloaddition of 6,7-dimethoxy-2*H*-1,3-benzothiazine with DMAD in an aprotic solvent such as diethyl ether led to a 1:2 adduct, 2,3-dimethoxy-pyrido[1,2-*c*][1,3]benzothiazine-8,9,10,11-tetracarboxylic acid tetramethyl ester [12]. However, the reaction of 6,7-dimethoxy-2*H*-1,3-benzothiazine with DMAD in refluxing aqueous methanol yielded not the expected product, but (±)-2,3,10,11-tetramethoxy-6*H*,8*H*,13a*H*-[1,3]benzothiazino[4,3-*b*][1,3]benzothiazine (5,13-dithiaxylopinine) and 6,7-dimethoxy-3-methoxycarbonyl-2*H*-benzo[*b*]thiopyran [13]. As a continuation of our investigations on the reactions of sulfur- and nitrogen-containing condensed-skeleton heterocycles including different cycloadditions [12–15], in the present paper we report on the reactions of 1,3-benzothiazines (**1a**–**1c**, **1e**, **1f**) [16, 17] and

1,4-benzothiazepines (**1d**, **1g**) [18] with DMAD in aqueous methanol.

Results and discussion

Chemistry

In recent years, there has been considerable interest in investigations of the reactivity of nitrogen-containing heterocycles with DMAD, and with DMAD in a multicomponent reaction [19–24]. As a consequence, it appeared worthwhile to study the reactions of 4-alkyl- and 4-aralkyl-6,7-dimethoxy-2*H*-1,3-benzothiazine (**1a**–**1c**) and 5-methyl-7,8-dimethoxy-2,3-dihydro-1,4-benzothiazepine (**1d**), because these molecules are capable of reacting as cyclic imines or as secondary enamines (Scheme 1). When **1a**–**1d** were reacted with DMAD in methanol, only one product was formed.

Elemental analysis clearly revealed that the products were formed by the addition of one molecule of DMAD to one molecule of benzothiazine or benzothiazepine, with elimination of one molecule of methanol. Several structures can be presumed for such a product. In the reactions of benzothiazines **1a**–**1c** and benzothiazepine **1d**, there are possibilities for the formation of various isomers of **4**–**7** which would behave very similar spectroscopically (Scheme 1). Likely isomeric products would be **4**, **5** if the reaction took place through the enamine tautomer of **1a**–**1d**, and **6**, **7** if it involved participation of the imine form (Scheme 1).

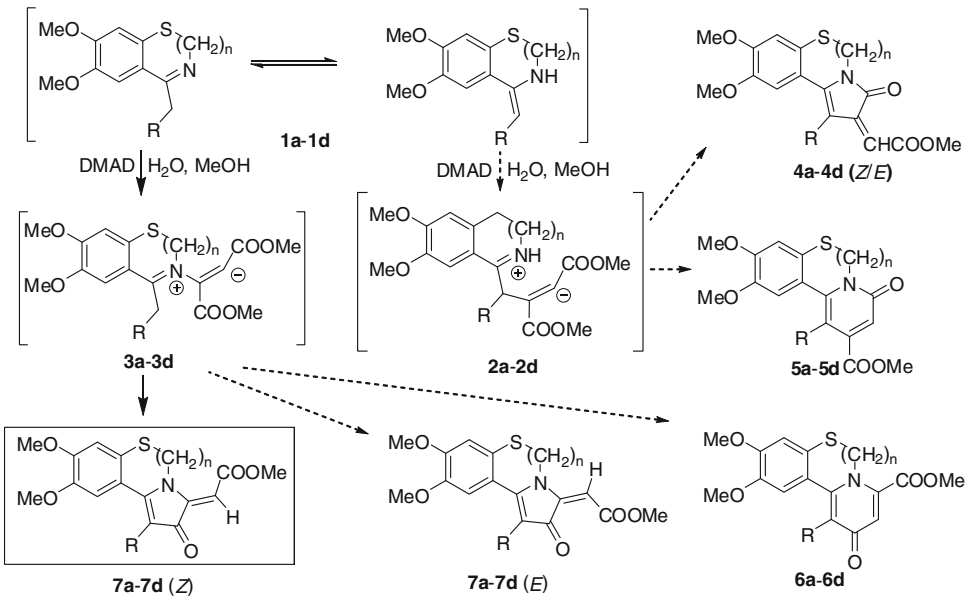
The structures of the reaction products were proved by NMR spectroscopy and by X-ray crystallography as discussed below. In these reactions, the heterocyclic compounds **1a**–**1d** reacted as imines, most probably via intermediates **3a**–**3d** [25]; thus pyrrolo-1,3-benzothiazines **7a**–**7c** (*Z* form) and 1,4-benzothiazepine **7d** (*Z* form) were formed in good yields (Scheme 1).

Similarly as for **1a**–**1d**, in the reactions of aryl-substituted 1,3-benzothiazines (**1e**, **1f**) or 1,3-benzothiazepine (**1g**) with DMAD, several structures come into consideration as possible products (e.g., **9**, **10**, **13**, **14**) (Scheme 2). In these cases, 4-aryl-2*H*-1,3-benzothiazines (**1e**, **1f**) or 2,3-dihydro-7,8-dimethoxy-5-phenyl-1,4-benzothiazepine (**1g**) reacted with DMAD in aqueous methanol to furnish only one product. Oxazolo-1,3-thiazines **14e**, **14f** (*Z* form) and oxazolo-1,4-thiazepine **14g** (*Z* form) were obtained in good yields (Scheme 2).

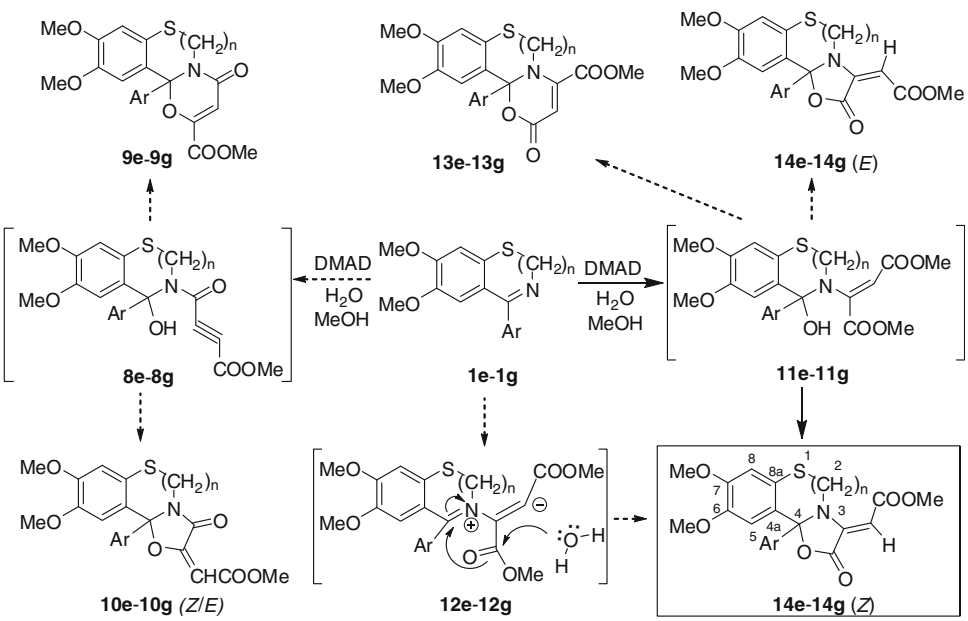
As concerns the possible reaction mechanism, the above results clearly indicate that in these reactions the initial addition product is the corresponding zwitterion [26] **12** formed from the benzothiazine or benzothiazepine and DMAD, which can be trapped very effectively with water to form **11**, and lead by ring closure to **14e**–**14g**. Alternatively, for similar structures, another possible route has been proposed via the related intermediate **12** [9].

To summarize, the cycloadditions of substituted 2*H*-1,3-benzothiazines (**1a**–**1c**, **1e**, **1f**) and 2,3-dihydro-1,4-benzothiazepines (**1d**, **1g**) with dimethyl acetylenedicarboxylate in aqueous methanol provided new, unexpected condensed-skeleton pyrrolo- and oxazolothiazine and thiazepine (**7a**–**7d** and **14e**–**14g**) heterocycles.

Scheme 1



Scheme 2



Structure

The spectral data (IR, ^{1}H, and ^{13}C NMR) unambiguously confirm the structures. Only the following remarks are necessary. As far as structures **4**–**7** are concerned, because of the mesomerism the carbonyl carbon in the enamino-carbonyl (types **4** and **7**) and pyridone (types **5** and **6**) derivatives displays irregular IR frequencies and ^{13}C NMR chemical shifts. Hence, it is not possible to differentiate between the potential structural isomers merely on the basis of routine spectral data. Accordingly, to reach a decision on the structures, C,H-correlations via long-range couplings (HMBC) [26, 27] were used.

The ^{13}C NMR line at 166.7 ppm for product **c** must be assigned to the ester carbonyl, as proven by the C,H-shift correlation in the HMBC spectrum with the signal of the methoxy hydrogens at 3.78 ppm. The other carbonyl line at 187.6 ppm correlates with the ^{1}H NMR signal of the C-methyl hydrogens (2.07 ppm) and the heterocyclic (**6**) =CH– or exocyclic (**7**) hydrogen (6.03 ppm). This suggests structure **6** or **7**. To choose between them, however, is not possible simply from routine IR and NMR spectral data. The 187.6 ppm ^{13}C NMR shift lies on the borderline characteristic of amides (165–186 ppm) and ketones (186–210 ppm) [28]. Therefore, the crystal structure was determined by X-ray crystallography for one (**b**) of these compounds (**a**–**d**). The results proved structure **7b** (Fig. 1). The very similar spectral data of the analogous products **a** and **c** and the thiazepine homolog confirmed identical constitutions, i.e., structures **7a**–**7d**.

The molecules formed from **1e**–**1g** have very high IR carbonyl frequencies (1,798–1,804 cm^{-1}). Conjugated

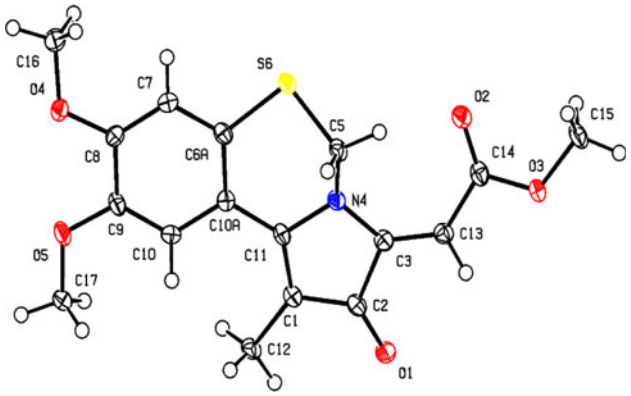


Fig. 1 Ortep plot of **7b** with atomic labeling

esters and δ-lactones cannot have such an IR band [30]. Consequently, only the γ-lactam or γ-lactone structures (**10** and **14**) are in accordance with the spectral data. Similarly as for **4**–**7**, we applied the HMBC method (for product **f**) to decide between structures **10** and **14**. The line of the sp^2 carbon in ring C is at 150.5 ppm. This signal also gives cross-peaks with both methylene hydrogens, the latter further yielding cross-peaks with the C-4 and C-8a lines at 94.9 and 124.6 ppm, respectively. Consequently, the former carbon must be bonded to N-3. Structure **14f** follows unambiguously. Structure **10** can be excluded on the basis of the chemical shift of the carbon in question. The -I effect of the attached oxygen in **10** should cause a significantly higher downfield shift of the line of this C atom. The analogous structures of **14e**–**14g**, similarly as in the case of **7a**–**7d**, are obvious from their very similar spectral parameters.

All of the new compounds synthesized (**7a–7d**, **14e–14g**) contain a carbomethoxymethylidene side-chain (=CHCOOMe). Thus, the geometric isomerism must be clarified. The chemical evidence suggests the preference of the *Z* form because of the unfavorable interaction between the ring carbonyl (ketone or lactone) and the ester oxygens in the side-chain. In accordance, the X-ray measurements on **7b** supplied proof of this steric structure, and the analogous structure follows from the very similar NMR spectra of **7a**, **7c**, and **7d**. For **14f**, we carried out DIFFNOE measurements, which provided indirect proof of the *Z* form for this compound too.

The quasi-equatorial methylene-H in **14f** is coplanar and close to the ester carbonyl, the anisotropy causing the irregular downfield shift of its signal (to 6.32 ppm). The unambiguous assignment of this signal was confirmed by the DIFFNOE measurements, demonstrating the close-lying position of the axial counterpart to the aryl group. Due to the diaxial and near orientation of the methylene-H in question and the aryl ring, irradiation (at 4.75 ppm) resulted in an intensity enhancement for the *ortho*-hydrogens in the Ar substituent.

The drastic differences in the C-4 chemical shifts for structures **7a–7d** (158–176 ppm) and **14e–14g** (87–96 ppm) are in accordance with the change in the hybrid state of this carbon from sp^2 to sp^3 (the numbering of rings A and B in **1a–1c**, **1e**, **1f** is also used for **1d**, **1g** in the text and the experimental part, cf. Scheme 2).

Due to the molecular symmetry ($\mathbf{C}_s$) of **7a–7c**, the 2-methylene hydrogens are chemically equivalent (they give a ^{1}H NMR singlet), while the nonplanar structure of the thiazepine ring in **7d** and **14g** is revealed in the non-equivalence of these hydrogens, with an AB-type spectrum. The hydrogens of both methylene groups in **14e**, **14f** are also nonequivalent because of the presence of a chiral center (C-4) in these molecules.

It is noteworthy that the anisotropy of the phenyl substituent [29] in **7c** causes upfield shifts of the H-5 and 6-methoxy signals. This effect is more pronounced in **14e**, **14f** than in **14g**, in which H-5 and the phenyl ring are more distant from one another in the preferred conformation.

Experimental

General

The IR spectra were recorded in KBr pellets with a Bruker IFS 55 FT spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or dimethyl sulfoxide (DMSO)-d_6 solution in 5 mm tubes at room temperature (RT) on a Bruker WM-250 spectrometer at 250 (^{1}H) and 63 (^{13}C) MHz, with the deuterium signal of the solvent as the lock and tetramethylsilane (TMS) as internal reference. Distortionless enhancement by polarization transfer (DEPT) spectra were run in a standard manner, using only the $\theta = 135°$ pulse to separate the CH/CH_3 and CH_2 lines phased "up" and "down," respectively. The 2D HMBC spectra were obtained on a Bruker DRX 500 spectrometer by using the standard Bruker pulse programs. Results of elemental analyses agreed favorably with calculated values. 1,3-Benzothiazines (**1a–1c**, **1e**, **1f**) [16, 17] and 1,4-benzothiazepines (**1d**, **1g**) [18] were prepared by literature methods.

*General procedure for preparation of pyrrolinobenzothiazine derivatives **7a–7d***

Compound **1a–1d** (2.5 mmol) was dissolved in aqueous methanol (25 cm^3 methanol and 2 cm^3 water), and a solution of DMAD (2.5 mmol) in 10 cm^3 methanol was added dropwise with stirring during 1 h. The mixture was allowed to stand at room temperature for 3 h. The methanol solution was evaporated, and the residue was crystallized from methanol/acetone to yield colorless crystals.

Methyl (Z)-(8,9-dimethoxy-2-oxo-5H-pyrrolo[1,2-c][1,3]-benzothiazin-3(2H)-ylidene)acetate (**7a**, $C_{16}H_{15}NO_5S$)
M.p.: 206–207 °C (from methanol); yield 76%; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.09$ (s, H-5), 6.83 (s, H-8), 6.07 (s, =CH– heteroring), 5.72 (s, =CH–), 5.52 (s, CH_2), 3.95 (s, OMe pos. 7), 3.92 (s, OMe pos. 6), 3.79 (s, OMe ester group) ppm; ^{13}C NMR (80 MHz, $CDCl_3$): $\delta = 185.4$ (C=O ketone), 166.4 (C=O ester), 164.3 (C-4), 152.9 (C-7), 148.1 (C-6), 142.4 (quaternary C in heteroring), 129.2 (C-8a), 116.6 (C-4a), 111.3 (C-8*), 110.5 (C-5*), 99.0 (=CH– exocyclic group), 96.7 (=CH– exocyclic group), 56.2 (OMe pos. 7), 56.1 (OMe pos. 6), 52.0 (OMe ester), 44.5 (C-2) ppm (*interchangeable assignments); IR (KBr): $\bar{\nu} = 1{,}684$ (C=O ester and C=O ketone; overlapping signals) cm^{-1}.

Methyl (Z)-(8,9-dimethoxy-1-methyl-2-oxo-5H-pyrrolo-[1,2-c][1,3]benzothiazin-3(2H)-ylidene)acetate
(**7b**, $C_{17}H_{17}NO_5S$)
M.p.: 210–211 °C (from methanol); yield 68%; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.25$ (s, H-5), 6.91 (s, H-8), 6.03 (s, =CH–), 5.49 (s, CH_2), 3.95 (s, OMe pos. 7), 3.93 (s, OMe pos. 6), 3.78 (s, OMe ester group), 2.07 (s, Me) ppm; ^{13}C NMR (80 MHz, $CDCl_3$): $\delta = 187.6$ (C=O ketone), 166.7 (C=O ester), 158.2 (C-4), 151.3 (C-7), 147.6 (C-6), 140.3 (quaternary C in heteroring), 129.6 (C-8a), 118.8 (C-4a), 112.9 (C-8*), 111.4 (C-5*), 106.2 (=C-R), 97.50 (=CH– exocyclic group), 56.2 (OMe pos. 7), 56.1 (OMe pos. 6), 52.0 (OMe ester), 45.2 (C-2), 8.7 (CCH_3) ppm (*interchangeable assignments); IR (KBr): $\bar{\nu} = 1{,}700$ (C=O ester), 1,669 (C=O ketone) cm^{-1}.

Methyl (Z)-(8,9-dimethoxy-1-phenyl-2-oxo-5H-pyrrolo-[1,2-c][1,3]benzothiazin-3(2H)-ylidene)acetate (**7c**, $C_{22}H_{19}NO_5S$)

M.p.: 226–228 °C (from methanol); yield 71%; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.40–7.20 (5H, m, Ph), 6.85 (s, H-5*), 6.82 (s, H-8*), 6.14 (s, =CH–), 5.56 (s, CH_2), 3.91 (s, OMe pos. 7), 3.80 (s, OMe pos. 6), 3.23 (s, OMe ester group) ppm (*interchangeable assignments); ^{13}C NMR (80 MHz, $CDCl_3$): δ = 185.2 (C=O ketone), 166.5 (C=O ester), 158.1 (C-4), 151.7 (C-7), 146.9 (C-6), 140.3 (quaternary C in heteroring), 131.3 (C4′, phenyl), 130.1 (C-2′,6′, phenyl), 129.7 (C-8a), 128.6 (C-3′,5′, phenyl), 127.3 (C-1′, phenyl), 117.2 (C-4a), 113.8 (C-8*), 111.8 (=C-R), 111.0 (C-5*), 98.5 (=CH– exocyclic group), 56.0 (OMe pos. 7), 54.9 (OMe pos. 6), 52.0 (OMe ester), 45.0 (C-2) ppm (*interchangeable assignments); IR (KBr): $\bar{\nu}$ = 1,701 (C=O ester), 1,675 (C=O ketone) cm^{-1}.

Methyl (Z)-(5,6-dihydro-9,10-dimethoxy-2-oxopyrrolo-[1,2-d][1,4]benzothiazepin-3(2H)-ylidene)acetate (**7d**, $C_{17}H_{17}NO_5S$)

M.p.: 190–191 °C (from methanol/acetone); yield 74%; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.28 (s, H-5), 7.15 (s, H-8), 6.04 (s, =CH– heteroring), 5.48 (s, =CH–), 4.16 (triplet-like signal, CH_2), 3.95 (s, OMe pos. 7), 3.92 (s, OMe pos. 6), 3.78 (s, OMe ester group), 3.43 (triplet-like signal, CH_2) ppm; ^{13}C NMR (80 MHz, $CDCl_3$): δ = 186.8 (C=O ketone), 175.4 (C-4), 166.1 (C=O ester), 151.6 (C-7), 149.4 (C-6), 142.8 (quaternary C in heteroring), 127.2 (C-8a), 123.9 (C-4a), 118.0 (C-5*), 112.6 (C-8*), 99.9 (=CH-), 98.6 (=CH-), 56.1 (OMe pos. 6 and 7, overlapping signals), 51.8 (OMe ester), 45.1 (NCH_2), 36.6 (SCH_2) ppm (*interchangeable assignments); IR (KBr): $\bar{\nu}$ = 1,712 (C=O ester), 1,682 (C=O ketone) cm^{-1}.

*General procedure for preparation of oxazolidinobenzothiazine derivatives **14e–14g***

Compound **1e–1g** (2.5 mmol) was dissolved in aqueous methanol (25 cm^3 methanol and 2 cm^3 water), and DMAD (2.5 mmol) was added. The solution was stirred under reflux for 5 min and then left to stand for 3 h. The precipitated dark-red crystals were filtered off and washed with methanol.

Methyl (Z)-[10b-(2-chlorophenyl)-8,9-dimethoxy-2-oxo-5H,10bH-oxazolo[3,2-c][1,3]benzothiazin-3(2H)-ylidene]-acetate (**14e**, $C_{21}H_{18}ClNO_6S$)

M.p.: 159–160 °C (from methanol); yield 66%; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.50 (dd, H-3′, 2-chlorophenyl), 7.35 (t, H-4′, 2-chlorophenyl), 7.20 (t, H-5′, 2-chlorophenyl), 7.10 (d, H-6′, 2-chlorophenyl), 6.83 (s, H-8), 6.59 (s, H-5), 6.55 (d, J = 13.5 Hz, CH_2, 1H), 5.81 (s, =CH–), 4.65 (d, J = 13.5 Hz, CH_2, 1H), 3.89 (s, OMe pos. 7), 3.79 (s, OMe pos. 6), 3.73 (s, OMe ester group) ppm; ^{13}C NMR (80 MHz, $CDCl_3$): δ = 166.6 (C=O ester), 164.7 (C=O lactone), 150.4 (quaternary C in heteroring), 150.3 (C-7), 147.0 (C-6), 134.0 (C-6′, 2-chlorophenyl), 133.7 (C-2′, 2-chlorophenyl), 133.6 (C-1′, 2-chlorophenyl), 132.8 (C-5′, 2-chlorophenyl), 132.6 (C-4′, 2-chlorophenyl), 131.5 (C-3′, 2-chlorophenyl), 124.3 (C-8a), 122.5 (C-4a), 112.5 (C-8*), 108.8 (C-5*), 96.0 (C-4), 91.1 (=CH-), 56.0 (OMe, pos. 7), 55.9 (OMe, pos. 6), 51.5 (OMe ester), 43.6 (C-2) ppm (*interchangeable assignments); IR (KBr): $\bar{\nu}$ = 1,798 (C=O lactone), 1,694 (C=O ester), 1,645 (C=C) cm^{-1}.

Methyl (Z)-[8,9-dimethoxy-10b-(4-nitrophenyl)-2-oxo-5H,10bH-oxazolo[3,2-c][1,3]benzothiazin-3(2H)-ylidene]-acetate (**14f**, $C_{21}H_{18}N_2O_8S$)

M.p.: 176–177 °C (from methanol); yield 69%; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.26 (d, J = 9 Hz, H-2′,6′, 4-nitrophenyl), 7.54 (d, H-3′,5′, 4-nitrophenyl), 6.72 (s, H-8), 6.65 (s, H-5), 6.32 (d, J = 13.5 Hz, CH_2, 1H), 5.86 (s, =CH–), 4.75 (d, J = 13.5 Hz, CH_2, 1H), 3.90 (s, OMe pos. 7), 3.78 (s, OMe pos. 6), 3.74 (s, OMe ester group) ppm; ^{13}C NMR (80 MHz, $CDCl_3$): δ = 166.2 (C=O ester), 164.1 (C=O lactone), 150.5 (quaternary C in heteroring), 148.7 (C-7), 147.5 (C-6), 144.8 (C-4′, 4-nitrophenyl), 134.3 (C-1′, 4-nitrophenyl), 128.8 (C-2′,6′, 4-nitrophenyl), 124.6 (C-8a), 123.7 (C-3′,5′, 4-nitrophenyl), 121.7 (C-4a), 112.0 (C-8*), 109.4 (C-5*), 94.9 (C-4), 93.2 (=CH-), 56.0 (OMe pos. 6 and 7, overlapping signals), 51.7 (OMe ester), 44.3 (C-2) ppm (*interchangeable assignments); IR (KBr): $\bar{\nu}$ = 1,804 (C=O lactone), 1,692 (C=O ester), 1,649 (C=C) cm^{-1}.

Methyl (Z)-(5,6-dihydro-9,10-dimethoxy-2-oxo-11b-phenyl-10bH-oxazolo[3,2-d][1,4]benzothiazepin-3(2H)-ylidene)-acetate (**14g**, $C_{21}H_{21}NO_6S$)

M.p.: 143–144 °C (from methanol); yield 72%; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.40 (m, H-3′,4′,5′, phenyl), 7.20 (d, H-2′,6′, phenyl), 7.07 (s, H-8*), 7.05 (s, H-5*), 5.57 (s, =CH–), 5.20 (m, NCH_2, 1H), 3.91 (s, OMe pos. 7), 3.82 (s, OMe pos. 6), 3.68 (s, OMe ester group), 3.65 (m, NCH_2, 1H), 3.30 (s, SCH_2, 1H), 2.85 (s, SCH_2, 1H) ppm (*overlapping signals); ^{13}C NMR (80 MHz, $CDCl_3$): δ = 166.6 (C=O ester), 164.4 (C=O lactone), 148.7 (quaternary C in heteroring and C-7, overlapping signals), 148.2 (C-6), 138.1 (C-1′, phenyl), 135.7 (C-4a), 128.6 (C-3′,5′, phenyl), 128.1 (C-2′,6′, phenyl), 124.7 (C-8a), 124.3 (C-8a), 117.0 (C-5**), 112.5 (C-8**), 100.8 (=CH–), 87.2 (C-4), 56.0 (OMe pos. 6 and 7, overlapping signals), 51.1 (OMe ester), 49.5 (NCH_2), 33.0 (SCH_2) ppm (**interchangeable assignments); IR (KBr): $\bar{\nu}$ = 1,799 (C=O lactone), 1,703 (C=O ester), 1,646 (C=C) cm^{-1}.

X-ray analysis of ***7b*** *(Fig. 1)*

The data were collected on a Rigaku Rapid Series diffractometer equipped with a Cu X-ray tube and a graphite crystal monochromator. Triclinic space group $P\text{-}1$ (No. 2) with $a = 8.6461(3)$ Å, $b = 8.7105(2)$ Å, $c = 10.4572(3)$ Å, $\alpha = 100.777(2)°$, $\beta = 91.619(2)°$, $\gamma = 93.212(2)°$, $V = 771.84(4)$ Å^3, $Z = 2$, $d_{calc} = 1.495$ g cm^{-3}, $\mu = 2.125$ mm^{-1}. A total of 13,384 reflections were collected, of which 2,700 were unique ($R_{int} = 0.057$), and corrected for absorption. The structure was solved by using the SHELX97 and SHELXL97 programs. The resulting structural parameters were refined to convergence of $R1 = 0.0404$ for 2,531 independent reflections with $I > 2\sigma(I)$, using full-matrix least-squares techniques and a structural model which incorporated anisotropic vibrational parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. CCDC 736565 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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References

1. Diels O, Alder K, Nienborg N, Schmalbeck O (1931) Ann Chem 490:243
2. Acheson RM, Elmore NF (1978) Adv Heterocycl Chem 23:263
3. Acheson RM (1982) J Heterocycl Chem 19(supplement):59
4. Djaidi D, Bishop R, Craig DC, Scudder ML (1999) J Chem Soc Perkin Trans 1:1859
5. Lin Q, Ball GE, Bishop R (1997) Tetrahedron 53:10899
6. Lin Q, Djaidi D, Bishop R, Craig DC, Scudder ML (1998) Aust J Chem 51:799
7. Yamamoto H, Kobayashi T, Nitta M (1998) Heterocycles 48:1903
8. Kawasaki T, Tang C-Y, Koizumi E, Nakanishi N, Sakamoto M (1998) Heterocycles 48:975
9. Heaney F, Kelly BM, Bourke S, Rooney O, Cunningham D, McArdle P (1999) J Chem Soc Perkin Trans 1:143
10. Nair V, Speekanth AR, Biju AT, Rath NP (2003) Tetrahedron Lett 44:729
11. Nair V, Deviprija S, Suresh E (2008) Tetrahedron 64:3567
12. Fodor L, Szabó J, Bernáth G, Sohár P (1982) Heterocycles 19:488
13. Fodor L, Bernáth G, Sohár P, Gröschl D, Meier H (2006) Monatsh Chem 137:231
14. Fodor L, MacLean DB (1987) Can J Chem 65:18
15. Csomós P, Fodor L, Bernáth G, Sinkkonen J, Salminen J, Wiinamäki K, Pihlaja K (2008) Tetrahedron 64:1002
16. Szabó J, Fodor L, Szűcs E, Bernáth G, Sohár P (1984) Pharmazie 39:426
17. Szabó J, Fodor L, Varga I, Vinkler E, Sohár P (1977) Acta Chim Acad Sci Hung 93:403
18. Szabó J, Bernáth G, Katócs A, Fodor L, Sohár P (1987) Can J Chem 65:175
19. Nair V, Menon RS, Sreekumar V (2005) Pure Appl Chem 77:1191
20. Nair V, Menon RS, Shrekanth AR, Abhilash N, Biju AT (2006) Acc Chem Res 39:520
21. Vedensky VY, Ivanov YV, Kysil V, Williams C, Tkachenko S, Kiselyov A, Khvat AV, Ivachtchenko AV (2005) Tetrahedron Lett 46:3953
22. Yadav JS, Reddy BVS, Yadav NN, Gupta MK (2008) Tetrahedron Lett 49:2815
23. Terzidis MA, Stephanidou-Stephanatou J, Tsoleridis CA (2009) Tetrahedron Lett 50:1196
24. Yavari I, Piltan M, Moradi L (2009) Tetrahedron Lett 50:2067
25. Huisigen R (1969) In: Castle R (ed) Topics in heterocyclic chemistry, chapter 8. Wiley, New York, p 223
26. Bax A, Morris G (1981) J Magn Res 42:501
27. Kessler H, Griesinger C, Zarboch J, Loosi H (1984) J Magn Res 57:331
28. Sohár P (1983) Nuclear magnetic resonance spectroscopy, vol 2. CRC Press, Boca Raton, p 180
29. Sohár P (1983) Nuclear magnetic resonance spectroscopy, vol 1. CRC Press, Boca Raton, pp 35–38
30. Holly S, Sohár P (1995) In: Láng L, Prichard WH (eds) Theoretical and technical introduction to the series absorption spectra in the infrared region. Akadémiai Kiadó, Budapest, pp 100–102