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Revised Structures, 1-Methylene-1*H*-[1,4]thiazino[4,3-*a*]-benzimidazole and 10-Methylene-10*H*-imidazo[2,1-*c*][1,4]-benzothiazine Derivatives, for the Cycloadducts Accompanying Rearrangement from Imidazo[2,1-*b*]benzothiazole and Thiazolo[3,2-*a*]benzimidazole Derivatives with Propiolic Esters†

Noritaka Abe,*[a] Hiroyuki Fujii,[a] Akikazu Kakehi[b] and Motoo Shiro[c]

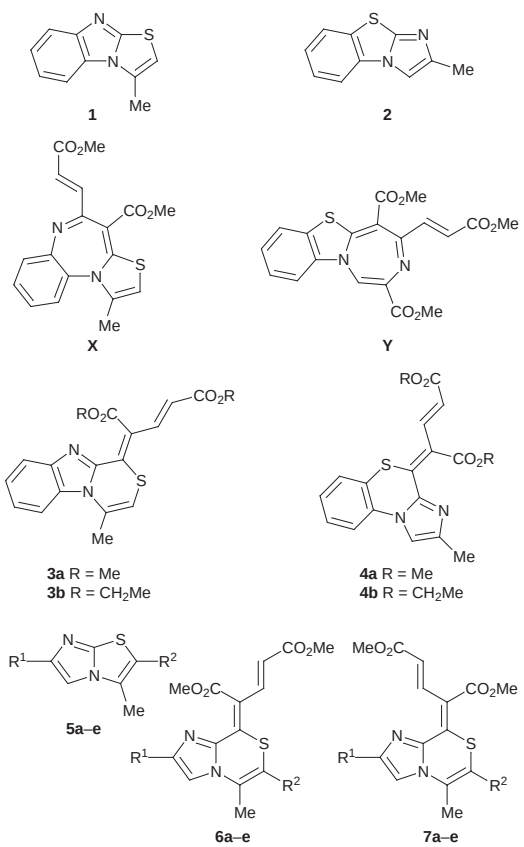
[a] *Department of Chemistry, Faculty of Science, Yamaguchi University, Yamaguchi 753-8512, Japan*
[b] *Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University, Wakasato Nagano 380-8553, Japan*
[c] *Rigaku X-Ray Research Laboratory, Rigaku Corporation, Matsubara-cho, Akisima, Tokyo 196-0003, Japan*

Formerly-proposed structures, thiazolo[3,2-*a*][1,5]benzodiazepine and [1,4]diazepino[7,1-*b*]benzothiazole derivatives, cycloadducts from the reactions of thiazolo[3,2-*a*]benzimidazole and imidazo[2,1-*b*]benzothiazole derivatives with propiolic esters, are revised to methyl 2-[4-methyl-(*E*)-1*H*-[1,4]thiazino[4,3-*a*]benzimidazol-1-ylidene)methoxycarbonylmethyl]-(*E*)-acrylate and methyl [2-methyl-(*E*)-10*H*-imidazo[2,1-*c*][1,4]benzothiazine-10-ylidene)-methoxycarbonylmethyl]-(*E*)-acrylate, respectively, whose structures are deduced by X-ray structure analysis.

Aromatic azapentalenes, such as thiazolo[3,2-*a*]benzimidazoles imidazo[2,1-*b*]benzothiazoles and imidazo[2,1-*b*]-thiazoles, react with acetylenic esters in various features of cycloaddition.[1–3] In the reaction of 2-methylthiazolo-[3,2-*a*]benzimidazole **1** and 2-methylimidazo[2,1-*b*]benzothiazole **2** with methyl propiolate (MP), we proposed the diazepine structures **X** and **Y** as the cycloadducts.[2] When we expanded the reaction to imidazo[2,1-*b*]thiazoles with MP, isomeric mixtures, in which two sets of *trans*-situated vinylic protons existed, were obtained (see below). The formerly proposed reaction mechanism failed to explain the results. In addition, it is considered that the maxima of the longest absorption bands, at $\lambda_{max} = 430$ nm (log $\epsilon = 4.14$) and 398 (log $\epsilon = 4.45$) observed in the electronic spectra of **X** and **Y**, should be too short for thiazolo[3,2-*a*][1,5]benzodiazepine and [1,4]diazepino[7,1-*b*]benzothiazole systems. In view of this uncertainty in the formerly proposed diazepine structures **X** and **Y**, X-ray crystal structure analysis was employed to resolve this problem. We now revise the structures of cycloadducts **X** and **Y** to **3a** and **4a**.

Treatment of 2-methylthiazolo[3,2-*a*]benzimidazole **1** and 2-methylimidazo[2,1-*b*]benzothiazole **2** with MP in refluxing acetonitrile gave **3a** and **4a** in 41 and 81% yield, respectively. Reaction of **1** and **2** with ethyl propiolate gave similar results. The structures of **3a** and **4a** were defined as methyl 2-[(4-methyl-1*H*-[1,4]thiazino[4,3-*a*]benzimidazol-1-ylidene)-methoxycarbonylmethyl]-(*E*)-acrylate and methyl [2-methyl-(*E*)-10*H*-imidazo[2,1-*c*][1,4]benzothiazine-10-ylidene)methoxycarbonylmethyl]-(*E*)-acrylate, respectively, by X-ray crystal structure analysis at −130 °C. ORTEP drawings of **3a** and **4a** are shown in Figs. 1 and 2.

When 3-methyl-6-phenylimidazo[2,1-*b*]thiazole **5a** was treated with an excess of MP, an isomeric mixture (1:2 adduct from elemental analysis), which could not be separated in pure form, was obtained. In its ^{1}H NMR spectrum, two sets of signals of [δ_H 2.36 (Me, s), 3.78, 3.94 (each OMe, s), 5.84, (H-2, s), 5.91 (vinyl-H, d, *J* 16.1 Hz), 7.25–7.40 (*m, p*-phenyl-H, m), 7.47 (H-5, s), 7.79 (*o*-phenyl, d, *J* 8.5 Hz) and 7.67 (vinyl-H, d, *J* 15.8 Hz)] and [δ_H 2.41 (Me, s), 3.86, 3.90, (each OMe, s), 5.97 (H-2, s), 6.18 (vinyl-H, d, *J* 15.9 Hz), 7.25–7.40 (*m,p*-phenyl-H, m), 7.61 (H-5, s), 7.95 (*o*-phenyl, d, *J* 8.5 Hz) and 9.49 (vinyl-H, d, *J* 16.1 Hz)] were seen in a ratio of *ca.* 2.5:1. From comparison with the ^{1}H NMR spectra of **3a** and **4a**, we assigned that the former is **6a** and the latter is **7a**. An anisotropic effect of the imidazole moiety of **7a** would cause the lower field resonation of vinyl proton (δ_H 9.49). Similar treatment of imidazo[2,1-*b*]thiazoles **5b**–**e** with MP gave mixtures of **6b**–**e** and **7b**–**e**. Results are summarized in Table 1.



* To receive any correspondence (*e-mail:* abe@po.cc.yamaguchi-u.ac.jp).

† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

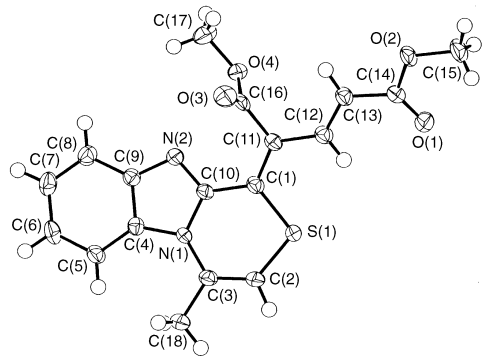


Fig. 1 An ORTEP drawing of **3a** with thermal ellipsoid plot (50% probability)

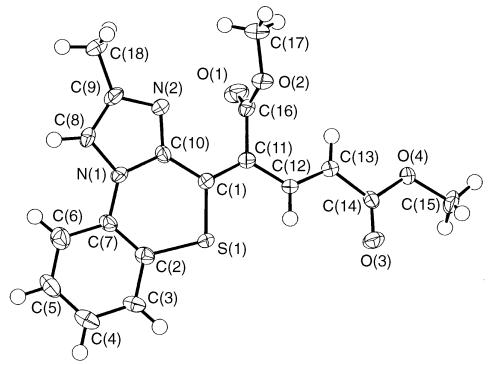


Fig. 2 An ORTEP drawing of **4a** with thermal ellipsoid plot (50% probability)

A plausible mechanism for the described reaction is shown in Scheme 1.

Experimental

Mps were uncorrected. ^{1}H NMR spectra (250 MHz) were recorded on Hitachi R-250H spectrometer using deuteriochloroform as a solvent with tetramethylsilane as an internal standard; *J* values are recorded in Hz. Electronic spectra were taken with Hitachi 220A spectrophotometer and IR spectra were recorded on a Hitachi 270-50 infrared spectrophotometer. Kieselgel 60 was used for column chromatography.

Reaction of 2-*Methyl* 2-*Methylthiazolo*[3,2-a]*benzimidazole* **1** *with Methyl Propiolate. Typical Procedure.*—A solution of **1** (0.565 g, 3.00 mmol) and methyl propiolate (1.26 g, 15.0 mmol) in dry acetonitrile (50 ml) was refluxed for 5 days, then evaporated. The residue was chromatographed with benzene-chloroform (1:1) to give recovered **1** (0.058 g, 10%) and methyl 2-[(4-methyl-1*H*-[1,4] thiazino[4,3-*a*]benzimidazol-1-ylidene)-methoxycarbonylmethyl]-(*E*)-acrylate **3a** (0.440 g, 41%).

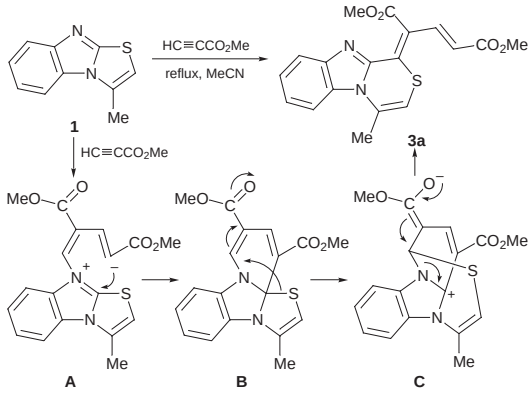
Compound **3a**: orange needles (from cyclohexane–benzene), mp 185–186 °C; δ_H 2.37 (3H, s), 3.79 (3H, s), 3.96 (3H, s), 5.73 (1H, br s), 6.10 (1H, d, *J* 15.3 Hz), 7.25–7.40 (2H, m), 7.70–7.80 (1H, m) and 7.75 (1H, d, *J* 15.3 Hz); ν_{max}(Nujol)/cm^{-1} 1710 (C=O) and 960; λ_{max}(EtOH)/nm (log ϵ) 245 (4.37), 316 (4.19), 360 (4.14) and 430 (4.14); *m/z* (rel. intensity) 356 (M^+, 4),325 (3), 297 (100) and 238 (6) (Found: C, 60.6; H, 4.7; N, 7.7; S, 9.2. Calc. for $C_{18}H_{16}N_2O_4S$: C, 60.7; H, 4.5; N, 7.9; S, 9.0%).

In a similar manner, **2** was reacted with methyl propiolate to give **4a** (81%), and **1** and **2** were reacted with ethyl propiolate to give **3b** (43%) and **4b** (43%).

Compound **4a**: yellow prisms (from ethanol–benzene), mp 189–190 °C; δ_H 2.31 (3H, s), 3.92 (3H, s), 3.80 (3H, s), 6.05 (1H, d, *J* 15.3 Hz), 7.20–7.50 (5H, m) and 8.09 (1H, d, *J* 15.3 Hz); ν_{max}(Nujol)/cm^{-1} 1720 and 1700 (C=O) and 975; λ_{max} ($CHCl_3$) nm (log ϵ) 261 (4.20, sh), 295 (4.21), 320 (4.13), 337 (4.08) and 398 (4.45); *m/z* (rel. intensity) 356 (M^+, 1), 325 (4), 297 (100) and 238 (6) (Found: C, 60.9; H, 4.5; N, 7.9; S, 9.2. Calc. for $C_{18}H_{16}N_2O_4S$: C, 60.7; H, 4.5; N, 7.9; S, 9.0%).

Table 1 Reaction of imidazo[2,1-*b*]thiazoles with methyl propiolate

Substrate	Reaction conditions	Yield(%)	(**6**:**7**)	Recovery of **5**(%)
5a	MeCN, reflux, 20 h	39	(2:1)	54
5a	MeCN, reflux, 3 days	73	(2:1)	5
5b	MeCN, reflux, 3 days	69	(2.5:1)	15
5c	MeCN, reflux, 7 h	68	(3.5:1)	9
5d	MeCN, reflux, 20 h	77	(1.8:1)	10
5e	MeCN, reflux, 13 days	63	(2:1)	30



Scheme 1

Crystal Data.—**3a**: orange prisms, $C_{18}H_{16}N_2O_4S$, $M = 356.40$, monoclinic, space group $P2_1/n$, $a = 14.125(3)$, $b = 8.186(1)$, $c = 14.174(3)$ Å, $\beta = 90.74(1)°$, $V = 1638.7(4)$ Å^3, $Z = 4$, $D_c = 1.445$ g cm^{-3}, crystal dimensions $0.30 \times 0.15 \times 0.10$ mm. Data were measured on a RAXIS-IV radiation diffractometer with graphite-monochromated Mo-Kα radiation at -130 ± 1 °C. A total of 3468 reflections were collected using the $\omega-2\theta$ scan technique to a maximum 2θ value of 55.6°. The structure was solved by direct methods and expanded using Fourier techniquesand refined by a full-matrix least-squares method using TEXSAN structure analysis software, using 3051 observed reflections (227 variables) [$I > 2\sigma(I)$]. The non-hydrogen atoms were refined anisotropically. The weighting scheme $w = 1/\sigma^2(F_o$ gave satisfactory agreement analyses. Final *R* and R_w values are 0.032, 0.047. The maximum peak and minimum peak in final difference map were 0.34 and -0.27 e$^-$ Å^{-3}.

4a: yellow prisms, $C_{18}H_{16}N_2O_4S$, $M = 356.40$, orthorhombic, space group $Pna2_1$, $a = 19.493(2)$, $b = 37.012(2)$, $c = 6.825(1)$ Å, $V = 4924.3(7)$ Å^3, $Z = 12$, $D_c = 1.442$ g cm^{-3}, crystal dimensions $0.30 \times 0.30 \times 0.30$ mm. Data were measured as above. A total 4861 reflections were collected using the $\omega-2\theta$ scan technique to a maximum 2θ value of 50.1°. The structure was solved and refined as above using 4401 observed reflections (676 variables) [$I > 2\sigma(I)$]. The non-hydrogen atoms were refined anisotropically. The weighting scheme $w = 1/\sigma^2(F_o)$ gave satisfactory agreement analyses. Final *R* and R_w values are 0.038, 0.060. The maximum peak and minimum peak in final difference map were 0.54 and -0.33 e$^-$ Å^{-3}.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Cebtre (CCDC). See Instructions for Authors, *J. Chem. Research (S)*, 1998, Issue 1. Any request to the CDDC for this material should quote the full literature citation and the reference number 423/19.

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