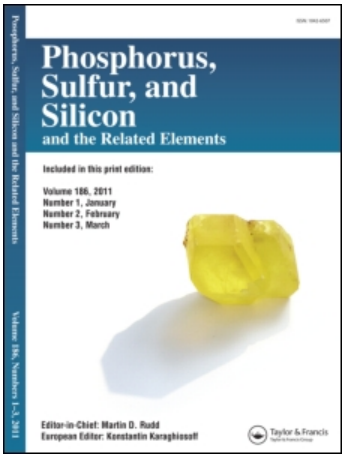

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TAUTOMERISM OF 2-MERCAPTO-8*H*-CYCLOHEPTA[*d*]THIAZOL-8-ONE

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TAUTOMERISM OF 2-MERCAPTO-8*H*-CYCLOHEPTA[*d*]THIAZOL-8-ONE

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The UV, ^{1}H NMR, and ^{13}C NMR spectra of 2-mercapto-8*H*-cyclohepta[*d*]thiazol-8-one (**2**) are extremely near to those of 3-methyl-8-oxo-3,8-dihydrocyclohepta[*d*]thiazoline-2-thione (**6**). These results proved that the thiazoline form **2a** predominates in the tautomeric equilibrium of **2**.

Key words: 2-Mercapto-8*H*-cyclohepta[*d*]thiazol-8-one, 8-oxo-3,8-dihydrocyclohepta[*d*]thiazoline-2-thione, tautomerism, UV spectra, ^{1}H NMR spectra, ^{13}C NMR spectra.

INTRODUCTION

It has been proposed[1] that 2-mercapto-8*H*-cyclohepta[*d*]thiazol-8-one (**2**) exists in tautomeric thiazoline form **2a**. Namely, the UV spectrum of the compound **2** is different from that of 2-methylthio-8*H*-cyclohepta[*d*]thiazol-8-one (**3**). However, another isomeric 3-methyl-8-oxo-3,8-dihydrocyclohepta[*d*]thiazoline-2-thione (**6**) is unknown up to date.

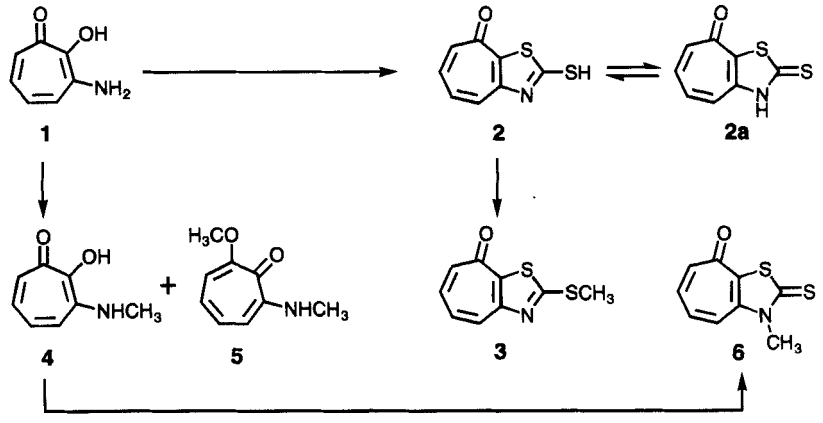
In this paper, we prepared *N*-methyl-substituted isomer **6** and proved that the tautomerism of the parent compound **2** lies in the thiazoline form **2a** by the UV, ^{1}H NMR, and ^{13}C NMR measurements.

RESULTS AND DISCUSSION

Synthesis of 3-Methyl-8-oxo-3,8-dihydrocyclohepta[d]thiazoline-2-thione (6)

2-Mercapto-8*H*-cyclohepta[*d*]thiazol-8-one (**2**)[1] was prepared by the reaction of 3-aminotropolone (**1**) with carbon disulfide. The treatment of the compound **2** with methyl iodide gave 2-methylthio-8*H*-cyclohepta[*d*]thiazol-8-one (**3**) but did not give *N*-methyl isomer **6**.[1] The methylation of the compound **2** with dimethyl sulfate or methyl fluorosulfate also afforded the *S*-methyl derivative **3** as a sole product.

Then, 3-aminotropolone (**1**)[2–4] was treated with methyl fluorosulfonate to afford 3-methylaminotropolone (**4**)[5] and 7-methylamino-2-methoxytropone (**5**). A methanolic solution of the compound **4** and carbon disulfide was refluxed for 3 h to afford 3-methyl-8-oxo-3,8-dihydrocyclohepta[*d*]thiazoline-2-thione (**6**) in 83% yield. Its structure was confirmed by IR and ^{1}H NMR spectra as well as elemental analysis.



SCHEME I

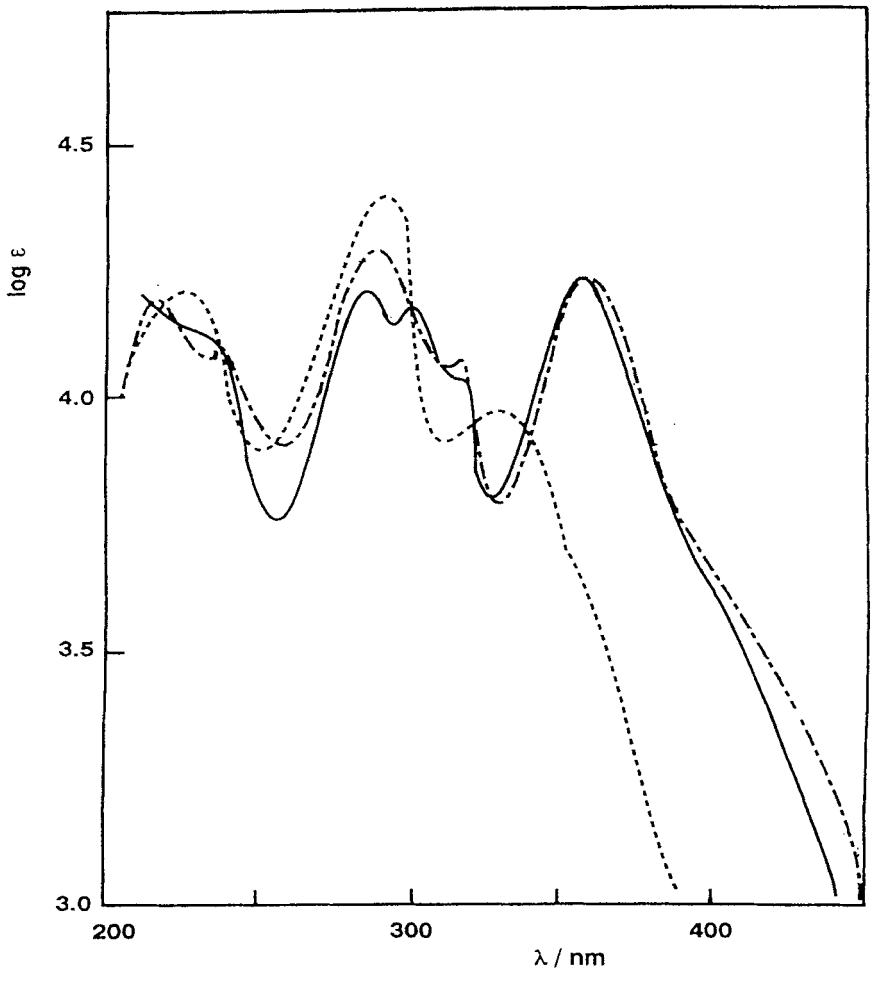


FIGURE 1 The UV spectra of compounds **2** (——), **3** (- - - - -), and **6** (– · – · –).

Tautomerism of 2-Mercapto-8H-cyclohepta[d]thiazol-8-one (**2**)

It was proposed that hydrogen bonding ability and self-association make to shift the tautomeric equilibrium of 2-mercaptothiazoles to thiazoline-2-thiones.[6] In the chemistry of 2-mercapto-8*H*-cyclohepta[*d*]thiazol-8-one (**2**), it was reported that its UV spectrum is different from that of the 2-methylthio derivative **3**, as shown in Figure 1.[1] These results might provide an evidence for tautomeric predominance of the compound **2a** over another tautomer **2**. However, the fixed *N*-methyl derivative of compound **2** was unknown so far.

Now, we newly prepared *N*-methyl isomer **6**, as described above, and measured its UV spectrum. When the UV spectrum of the *N*-methyl isomer **6** is drawn in Figure 1, its spectrum is very similar to that of the parent compound **2**. Consequently, it is doubtless that 2-mercapto-8*H*-cyclo-hepta[*d*]thiazol-8-one (**2**) exists as 8-oxo-3,8-dihydrocyclohepta[*d*]thiazoline-2-thione (**2a**).

The ^{1}H and ^{13}C NMR spectral data of 2-mercapto-, *S*-methyl-, and *N*-methyl derivatives, **2**, **3**, and **6**, are shown in Figure 2. The spectral assignments were done by ^{1}H-^{1}H and ^{1}H-^{13}C COSY measurements. The ^{1}H and ^{13}C NMR spectral data of the parent compound **2** are nearer to those of the N-methyl isomer **6** than those of the *S*-methyl isomer **3**.

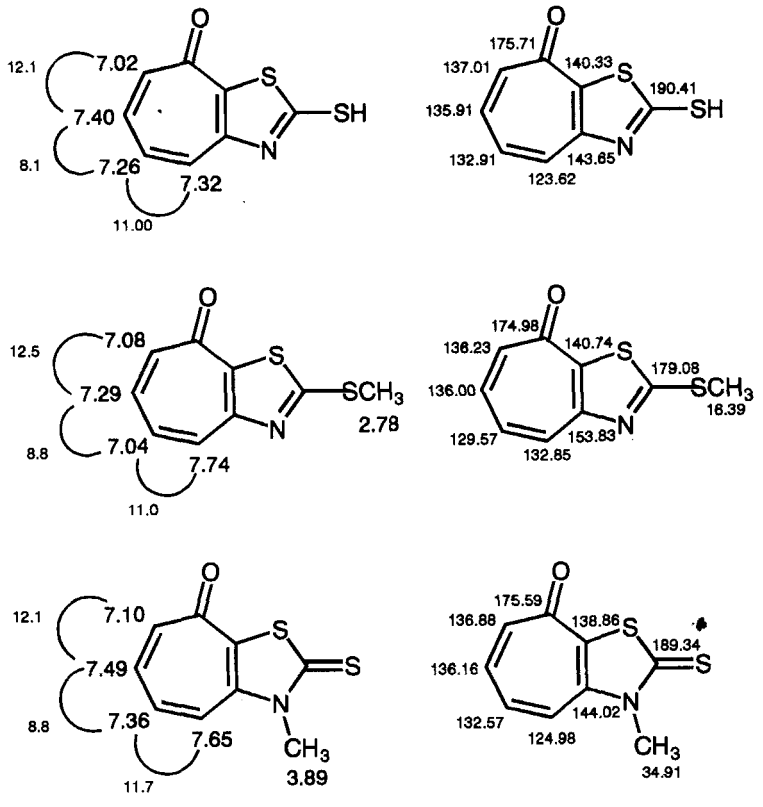


FIGURE 2 The ^{1}H and ^{13}C NMR spectra of compounds **2**, **3**, and **6**.

Particularly, the δ_c values at the 2- and 3a-positions of the compounds **2** and **6** are very similar each other. These 2- and 3a-carbon atoms exist at the both side of the nitrogen atom. Thus, the ^1H and ^{13}C NMR spectral data also support the thiazoline form **2a**.

In conclusion, it was revealed by the UV, ^1H NMR, and ^{13}C NMR spectral data of the fixed *S*- and *N*-methyl isomers that 2-mercapto-8*H*-cyclohepta[*d*]thiazol-8-one (**2**) exists predominantly as the thiazoline form **2a**.

EXPERIMENTAL

The melting points were determined with a Yanagimoto MP-S2 micromelting point apparatus and are uncorrected. The IR spectra were taken on a JASCO A-102 spectrophotometer, the UV spectra on a Hitachi 2000 spectrophotometer. The ^1H and ^{13}C NMR spectra were measured on a JEOL JNM-GX400 spectrometer (400 MHz) and partly on a JEOL JNM-PMXSI60 spectrometer (60 MHz). The mass spectra were obtained with a JEOL JMS-DX300 spectrometer.

2-Mercapto- (**2**) *and 2-Methylthio-8H-cyclohepta[d]thiazol-8-one* (**3**)

These compounds were obtained according to the methods described in the literature.[1]

2: Mp 295°C (dec) [lit,[1] 255–300°C (dec)]; IR (KBr): ν_{max} 1616 cm^{-1} (C=O); UV (CH_3OH): λ_{max} 227 sh (log ε 4.13), 284 (4.20), 297 (4.17), 356 nm (4.22); ^1H NMR (DMSO-d_6): δ 7.02 (1H, d, J = 12.1 Hz, 7-H), 7.26 (1H, dd, J = 11.0, 8.1 Hz, 5-H), 7.32 (1H, dd, J = 11.0, 1.5 Hz, 4-H), 7.40 (1H, dd, J = 12.1, 8.1 Hz, 6-H); ^{13}C NMR (DMSO-d_6): δ 123.62 (4-C), 132.91 (5-C), 135.91 (6-C), 137.01 (7-C),140.33 (8a-C), 143.65 (3a-C), 175.71 (8-C), 190.41 (2-C).

3: Mp 113–114°C (lit,[1] 112–113°C); IR ($CHCl_3$): ν_{max} 1628 cm^{-1} (C=O); UV (CH_3OH):λ_{max} 227 (log ε 4.20), 285 sh (4.36), 291 (4.37), 329 nm (3.94); ^1H NMR ($CDCl_3$): δ 2.78 (3H, s, CH_3), 7.04 (1H, dd, J = 11.0, 8.8 Hz, 5-H), 7.08 (1H, d, J = 12.5 Hz, 7-H), 7.29 (1H, dd, J = 12.5, 8.8 Hz, 6-H), 7.74 (1H, d, J = 11.0 Hz, 4-H); ^{13}C NMR ($CDCl_3$): δ 16.39 (CH_3), 129.57 (5-C), 132.85 (4-C), 136.00 (6-C), 136.23 (7-C), 140.74 (8a-C), 153.83 (3a-C), 174.98 (8-C), 179.08 (2-C); MS: m/z (%) 209 (M^+, 100), 181 (32), 166 (5), 148 (55), 135 (13), 108 (27).

Reaction of 3-Aminotropolone (**1**) *with Methyl Fluorosulfonate*

To a solution of 3-aminotropolone (**1**) (247 mg, 1.8 mmol) in dichloromethane (1.0 ml) was added methyl fluorosulfonate (1.0 ml). The mixture was allowed to stand for 12 h at room temperature. The resulting mixture was diluted with water, treated with 1M sodium hydroxide solution (5 ml), and extracted with chloroform. The evaporation residue was chromatographed on a Wakogel B-10 plate (30 × 30 cm) with ethyl acetate-hexane (1:1) to give 3-methylaminotropolone (**4**) and 7-methylamino-2-methoxytropone (**5**).

4: Yield 108 mg (36%); yellow plates (from ethanol); mp 113–114°C (lit,[5] 113.5–115°C).

5: Yield 7 mg (2%); oil; ^1H NMR ($CDCl_3$, 60 MHz): δ 3.05 (3H, s, NCH_3), 3.95 (3H, s, OCH_3), 6.4–7.4 (4H, m); MS: m/z (%) 165 (M^+, 100), 137 (63), 122 (21). Found: M^+, 165.0801. Calcd for $C_9H_{11}NO_2$: M, 165.0790.

Preparation of 3-Methyl-8-oxo-3,8-dihydrocyclohepta[d]thiazoline-2-thione (**6**)

To a solution of 3-methylaminotropolone (**4**) (108 mg) in methanol (70 ml) containing potassium hydroxide (2.13 g) was added carbon disulfide (3.6 ml). The resulting mixture was refluxed for 3 h. The reaction mixture was concentrated and acidified with 4M hydrochloric acid to give 3-methyl-8-oxo-3,8-dihydrocyclohepta[*d*]thiazoline-2-thione (**6**).

6: Yield 125 mg (83%); yellow crystals (from chloroform); mp 260–261°C; IR (KBr): ν_{max} 1627 cm^{-1} (C=O); UV (CH_3OH): λ_{max} 212 (log ε 4.17), 241 sh (4.04), 285 (4.27), 297 sh (4.19), 312 (4.07), 357 nm (4.21); ^1H NMR (DMSO-d_6): δ 3.89 (3H, s, CH_3), 7.10 (1H, d, J = 12.1 Hz, 7-H), 7.36 (1H, dd, J = 11.7, 8.8 Hz, 5-H), 7.49 (1H, dd, J = 12.1, 8.8 Hz, 6-H), 7.65 (1H, d, J = 11.7 Hz, 4-H); ^{13}C NMR (DMSO-d_6): δ 34.91 (CH_3), 124.98 (4-C), 132.57 (5-C), 136.16 (6-C), 136.88 (7-C), 138.86 (8a-C), 144.02 (3a-C), 175.59 (8-C), 189.34 (2-C); MS: m/z (%) 209 (M^+, 100), 181 (32), 148 (37), 136 (18). Found: C, 51.31; H, 3.28; N, 6.68%. Calcd for $C_9H_7NOS_2$: C, 51.65; H, 3.37; N, 6.69%.

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