ment with the present work.

In this work, fully Rb^+-exchanged zeolite X was not successfully prepared. Seventy-one Rb^+ ions and 21 Na^+ ions are distributed in the seven different crystallographic sites; four and a half Rb^+ ions and seven Na^+ ions at site I, nine Rb^+ ions at site I', 18 Rb^+ ions at site II, two and a half Rb^+ ions and 14 Na^+ ions at site II', 32 Rb^+ ions at site III, and five Rb^+ ions at site III'.

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Supplementary Material Available. Tables of calculated and observed structure factors with esd's (5 pages). Ordering information is given on any current masthead page.

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Tautomeric and *Ab Initio* Studies of 5-Thioxo-3*H*,4*H*-1,3,4-thiadiazolidin-2-one

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The oxidation product bis(2-oxo-3*H*-1,3,4-thiadiazolidinyl)-5,5-disulfide (5b) was obtained from an attempted synthesis of 5-thioxo-3*H*,4*H*-1,3,4-thiadiazolidin-2-one (**1**). Spectroscopic results indicate that the most stable tautomeric form of **1** is the lactam-thiol form (**1b**). The computed total energies and relative energies at the MP4 level also showed that the most stable tautomer is **1b**.

Introduction

In light of the biological and analytical interest in 3*H*-1,3,4-thiadiazolines, we recently reported the synthesis and tautomeric behaviour of 5-amino-3*H*-1,3,4-thiadiazoline-2-thione[1] and 5-amino-3*H*-1,3,4-thiadiazolin-2-one.[2,3] 5-Amino-3*H*-1,3,4-thiadiazoline-2-thione and 5-aroylamino-3*H*-1,3,4-thiadiazoline-2-thiones can exist in two-tautomeric forms a thione form, and a thiol form. It was established that 5-amino-3*H*-1,3,4-thiadiazoline-3-thione and 5-aroylamino-3*H*-1,3,4-thiadiazoline-2-thiones exist in their thione form on the basis of ^1H NMR, ^{13}C NMR and IR spectral data.[1] Similarly, a stable tautomeric structure for 5-amino-3*H*-1,3,4-thiadiazolin-2-one and 5-aroylamino-3*H*-1,3,4-thiadiazolin-2-ones was proven to be the lactam form.[2] As an extension of these studies, we report our synthetic and tautomeric results for 5-thioxo-3*H*,4*H*-1,3,4-thiadiazolidin-2-one (**1**) on the basis of experimental spectral data and theoretical calculations.

5-Thioxo-3*H*,4*H*-1,3,4-thiadiazolidin-2-one is not a known compound. However, 3*H*,4*H*-1,3,4-thiadiazolidine-2,5-dione

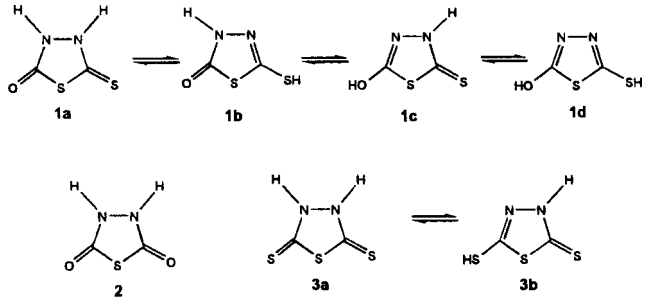


Figure 1.

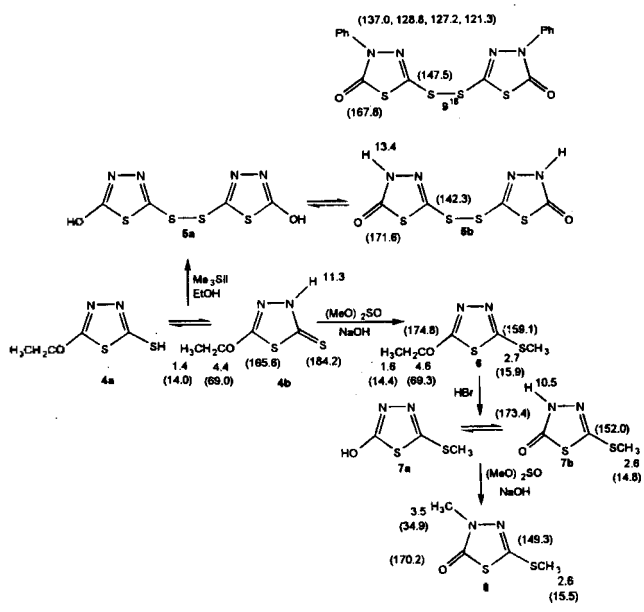
(**2**)[4,5] and 3*H*,4*H*-1,3,4-thiadiazolidine-2,5-di-thione (**3**)[6,7] are recognized as analogues of compound **1**. The most stable tautomeric forms of compounds **2** and **3** have been reported to be the lactam-lactam form[4,5] and the thione-thiol form,[6,7] respectively, even though the only differences between the two compounds are the ketone (oxygen, **2**) and thione (sulfur, **3**) functional groups. Compound **1** is a hybrid structure of compounds **2** and **3**, which prompted us to examine its structural characteristics.

Resulte and Discussion

5-Thioxo-3*H*-1,3,4-thiadiazolidin-2-one (**1**) can theoretically exist in four tautomeric forms, **1a-d** (Figure 1). The synthesis of **1** was attempted *via* hydrolysis of 5-ethoxy-3*H*-1,3,4-thiadiazoline-2-thione (**4**) as shown in Scheme 1. The preparation of **4** followed a literature method.[8] The deethylation reaction was adapted from the demethylation reaction of 2-methoxy-4*H*-1,3,4-thiadiazolin-5-one by hydroiodic acid.[9] However, bis(2-oxo-3*H*-1,3,4-thiadiazolidinyl)5,5-disulfide (**5**) was afforded instead of compound **1**. Various methods of deethylation were carried out: trimethylsilyl iodide,[10-13] HCl,[14] HBr and HI, all under an atmosphere of nitrogen. **5** has been reported as being synthesized in a photolytic reaction yielding dark brown crystals. Supporting evidence for **5** in the literature source[15] (the molecular ion peak of its mass spectrum and IR spectroscopy) is insufficient in our view. Our yields of **5**, the only product, were wide-ranging. The melting point of **5** was lower than the literature value, and our product was a colourless solid. We present spectroscopic data and elemental analytical data in support of its structure.

^{13}C NMR spectroscopy is a powerful tool for distinguishing between thione and thiol functional groups, using the large difference in their chemical shift. The difference in chemical shift between lactam and lactim is much less than in the case of thione-thiol. However, it is ambiguous to identify a stable structural form only by absolute chemical shifts, and substituent effects should also be carefully considered. Either a lactam or lactim standard compound is required for chemical shift comparisons. For this purpose, derivatives of **1** were prepared as shown in Scheme 1.

The structure of compound **4** was identified by a comparison of melting points.[8] **4** can exist as an equilibrium between two tautomers: a thione and thiol. Since the ring carbon chemical shifts of **4** are 184.2 and 165.6 ppm, this is clear evidence that the stable form is a thione form, **4b**.



Scheme 1. Syntheses of derivatives of 5-thioxo-3*H*,4*H*-1,3,4-thiadizolidin-2-one.

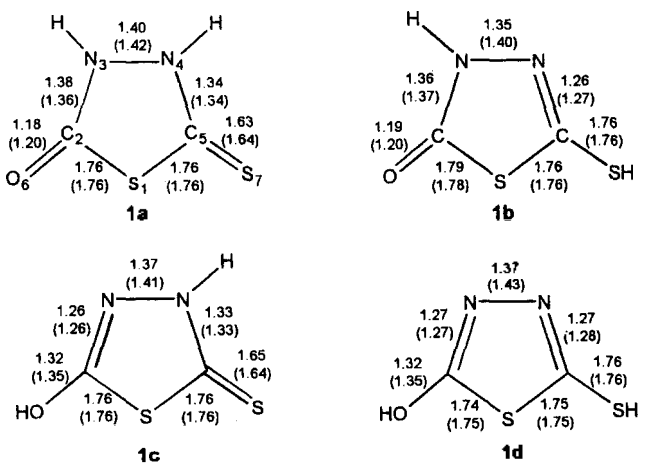
Direct alkylations of **4** in a basic medium (NaOH and TEA) gives regioselective S-alkylation affording **6**, as does **3** and its derivatives.[7]

The dealkylation[9,14] of **6** by hydrobromic acid was accomplished regioselectively at the O-alkyl substituent giving **7**. The disappearance of the ^{1}H NMR ethyl signal and consequent appearance of the NH signal (10.5 ppm) served as supporting evidence for the deethylation of **6** to give **7**. Like **4**, the structure of **7** can also be represented as a lactam-lactim equilibrium (**7a**, **7b**). To determine the stable tautomeric form of **7** by ^{13}C NMR, a standard lactam form (**8**) was synthesized. Regioselective N-alkylation of **7** was undertaken in a similar manner to those of 5-amino-3*H*-1,3,4,-thiadiazolin-2-one[14] and 5-amino-2H-1,2,4-thiadiazolin-3-one.[16,17] ^{1}H NMR, IR and elemental analysis were in support of our structure for **8** (Scheme 1). In the IR spectrum of **8**, the lactam group appeared as a strong diagnostic band at 1680 cm^{-1}. ^{1}H NMR spectroscopy indicated the presence of the N-Me and the S-Me groups at 3.5 ppm and 2.6 ppm, respectively. ^{13}C NMR helped to confirm the structure of **8**. The lactam, thiol, N-Me and S-Me carbon signals appeared at 170.2, 149.3, 34.9 and 15.5 ppm, respectively. Furthermore, its elemental analysis was satisfactory. The ring position ^{13}C chemical shifts of **7** and **8** are similar, when substituent effects are taken into consideration. If **7** existed as a lactim form (**7a**), the chemical shift of the C-O carbon would be more upfield than for lactim **6** (174.8 ppm). This implies that the stable tautomer of **7** is lactam form **7b**. In addition, the appearance of a strong IR band at 1650 cm^{-1} of a lactam carbonyl group supports structure **7b**.

The structure of **5** can be represented as two tautomers: lactam (**5a**) and lactim (**5b**). Its structure was identified as bis(2-oxo-3*H*-1,3,4-thiadiazolidinyl)5,5-disulfide (**5b**) by ^{1}H, ^{13}C NMR and IR spectroscopies. The disappearance of the ethyl signal in the ^{1}H NMR and consequent appearance of NH (13.4 ppm) served as supporting evidence for the

deethylation of **4** to give **5b**, under our conditions. The lactam carbonyl group appeared in the IR spectrum at 1700 cm^{-1}. The lactam and C-S carbon signals appeared at 171.6 and 142.3 ppm, respectively. It is reasonable to interpret the signal at 171.6 ppm as that of a lactam by comparing the chemical shifts of lactams **7**, **8** and **9**.[18] From these results we postulate that the stable tautomeric form of **1** is the lactam-thiol form, **1b**. Because thiols are easily oxidized to disulfides, we suspect that **1b** was oxidized as soon as it formed, by an oxygen contaminant of the nitrogen atmosphere used to give **5a**.

We also conducted ab initio calculations on the tautomers of 5-thioxo-3*H*,4*H*-1,3,4-thiadiazolidin-2-one (**1a-1d**) with the GAUSSIAN 94 package[19] on a Cray Y-MP C916 supercomputer. Molecular geometries were optimized at the Hartree-Fock (HF) level with standard 3-21G* and 6-31G* basis sets.[20] Fourth-order Moller-Pleset perturbation (MP4) calculations were carried out at the HF optimized geometries to obtain improved energy comparisons. The optimized geometries of the four tautomers are shown in Scheme 2. The numbers in parentheses are bond distance values at the HF/3-21G* level. The optimized bond distances at both the 6-31G* and 3-21G* levels are very close to each other, with the exception of the N(3)-N(4) distance. The N(3)-N(4) distance at the 6-31G* level was computed to be 0.04 Å shorter on average than at the 3-21G* level. Significant changes in the optimized geometries of four tautomers (**1a-1d**) also occur in the C-O and C-S bond distances. The C=O bond distance of 1.19 Å in **1b** increases by 0.13 Å in the C-O single bond distance of 1.32 Å in the 1c tautomer. This is in good agreement with other ab initio calculations on pyrimidine bases.[2,21,22] The C(5)-S(7) distance of 1.76 Å in **1b** is shortened to 1.63 Å in 1a on account of the double bond. The computed total energies and relative energies at the MP4 level are summarized in Table 1. The most stable tautomer is **1b** at both 6-31G* and 3-21G* levels, which corresponds to our experimental result. The stability ordering for these tautomers is computed to be **1b>1a>1c>1d**, with the two different level calculations.



Scheme 2. Optimized bond distances (in Å) for **1a-1d** at the HF/6-31G* and HF/3-21G* levels. The values in parentheses are the HF/3-21G* level.

Experimental

All melting points were determined on an electrically heated Thomas-Hoover capillary melting point apparatus and were uncorrected. The ir spectra were measured on a Jasco Report-100 spectrophotometer. The ^1H and ^{13}C nmr spectra were recorded on either a 80 MHz Bruker AC-80 or a 300 MHz Bruker AM-300 using tetramethylsilane as the internal standard. Elemental analyses were carreied out on a Elementar Analysensyateme GmbH Vario EL, at the Basic Science Research Institute, Seoul Korea. The progress of the reaction and the purity of all compounds were checked by thin layer chromatography on precoated glass plates with silicagel 60 F-254 as the absorbent (purchased from Whatman cat. no. 4861110). Most of the commercially available starting materials and solvents were purchased from Aldrich Chemical Company, Milwaukee, WI.

Potassium ethylxanthate was prepared with the yield of more than 80% by the procedure described in the literature.[8,9] **The synthesis of ethyl thiocarbazinate** was also followed the Ruffenacht's method.[8,9]

5-Ethoxy-3*H*-1,3,4-thiadiazoline-2-thione (4b). Ethyl thiocarbazinate (11.6 g, 0.1 mol) was dissolved in CS_2 (6.5 mL, 0.11 mol). KOH (0.86 g, 18 mmol) in 20 mL of methyl alcohol was added to the above solution and it was refluxed for 6 hours. The reaction mixture was cooled to room temperature and distilled off the solvent under the reduced pressure. The resulting residue was dispersed in 20 mL water and acidified with c-HCl (9 mL). **4** was collected (8.0 g, 51%) and recrystallized from benzene to obtain the analytical sample (7.1 g, 45%).; mp 128-130 °C (lit.[8] 129-130 °C); Rf, 0.48 (hexane : ethyl acetate=7 : 3 v/v); ^1H NMR ($CDCl_3$, δ, ppm): 13.7 (b, 1H, NH), 4.4 (q, 2H, CH_2), 1.4 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$, δ, ppm): 184.2 (C=S), 165.6 (C-O), 69.0 (CH_2), 14.0 (CH_3); ir (KBr, ν, cm^{-1}); 3100 (NH), 2850 (CH), 1560 (C=N), 1350. Anal. Calcd. for $C_4H_6N_2OS_2$: C, 29.62; H, 3.73; N, 17.27. Found: C, 29.75, H, 3.58, N, 16.56.

Bis(2-oxo-3*H*-1,3,4-thiadiazolidinyl)5-5'-disulfide (5b). **4b** (0.5 g, 6.2 mmol) was dissolved in 10 mL of dioxane and $(CH_3)_3SiI$ (0.76 mL, 9.3 mmol) was added. It was heated at 60 °C for 30 hours. After distillated off solvent white solide, 5 was isolated (0.76 g, 82.5 %). mp 217-220 °C (lit.[15] 280 °C); ^1H NMR (DMSO-d_6, δ, ppm): 13.4 (2H, b, 2NH); ^{13}C NMR (DMSO-d_6, δ, ppm): 171.6 (C=O), 147.8 (C-S); ir (KBr, ν, cm^{-1}); 3150 (NH), 3050, 1700 (C=

Table 1. Relative energies (in kcal/mol) and total energies (in a.u.) for **1a-1d** tautomers

	1a	1b	1c	1d
MP4//HF/6-31G*[a]	2.49(−1056.72246)	0.00(−1056.72643)[b]	9.16(−1056.71184)	13.32(−1056.70520)
MP4//HF/3-21G*	0.31(−1051.31562)	0.00(−1051.31612)	11.01(−1051.29857)	11.77(−1051.29736)

[a]MP4//HF/6-31G* represents a MP4 single point calculation at the HF optimized geometry with 6-31G* basis set. [b]The values in parentheses are total energies.

O), 1670. Mass m/z; 266 (M^+). Anal. Calcd. for $C_4H_2N_4O_2S_4$: C, 18.05; H, 0.75; N, 21.05. Found: C, 18.65, H, 0.85, N, 21.28.

2-Ethoxy-5-methylthio-1,3,4-thiadiazole (6). **4b** (1 g, 6.2 mmol) was dissolved in 20 mL THF and NaOH (0.42 g, 8.7 mmol) was added during the course of 30 minutes. After addition of dimethylsulfate (0.9 mL, 9.5 mmol) it was refluxed for 3 hours. The salt was filtered off. Ether was added and washed with water. The solvent was distilled off under the reduced pressure to obtain the liquid product **5** (1.03 g, 95%). To afford an analytical sample, the liquid product was distilled (0.87 g, 80%). bp 100-102 °C/2.5 torr; Rf, 0.54 (hexane : ethyl acetate = 7 : 3 v/v); ^{1}H NMR ($CDCl_3$, δ, ppm): 4.6 (q, 2H, OCH_2), 2.7 (s, 3H, SCH_3) 1.4 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$, δ, ppm): 174.8 (C-O), 159.1 (C-S), 69.3 (OCH_2), 15.9 (SCH_3) 14.4 (CH_3); ir (KBr, v, cm $^{-1}$); 2900 (CH), 1500 (C=N), 1280 (C-O).

2-Methylthio-4*H*-1,3,4-thiadiazolin-2-one (7b). **6** (2 g, 12 mmol) was dissolved in 30 mL dioxane and HBr (0.32 mL, 24 mmol) was added. The reaction mixture was refluxed for 8 hours. After the reflux the solvent was distilled off under the reduced pressure. The reaction residue was dissolved in ether and washed with water. The ether was distilled off under the reduced pressure to collect the solid product (1.35 g, 80%). To afford the analytical sample the product was recrystallized from hexane and benzene (1 : 1 v/v) (1.2 g, 73%); mp 90-92 °C; Rf, 0.57 (hexane : ethyl acetate=7 : 3 v/v); ^{1}H NMR ($CDCl_3$, δ, ppm): 10.8 (b, 1H, NH), 2.6 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, δ, ppm): 173.4 (C=O), 152.0 (C-S), 14.8 (CH_3); ir (KBr, v, cm $^{-1}$); 3180 (CH), 2900 (CH), 1650 (C=O), 1520 (C=N). Anal. Calcd. for $C_3H_4N_2OS_2$: C, 24.35; H, 2.72; N, 18.93; S, 43.33. Found: C, 24.41, H, 2.77, N, 18.67 ; S, 42.45.

2-Methylthio-4-methyl-1,3,4-thiadiazolin-2-one (8). **7** (0.3 g, 2 mmol) was dissolved in 30 mL dioxane and KOH (0.17 g, 3 mmol) was added. The reaction mixture was stirred for one hour and dimethyl sulfate (1.3 mL, 3 mmol) was added. The reaction mixture was heated at 60 °C for 2 hours. Reaction mixture was cooled to room temperature and the white salt was filtered off. Solvent was distilled off under the reduced pressure and residue was dispersed in water to collect the solide product (0.26 g, 79%). To afford the analytical sample the product was recrystallized from hexane (0.2 g, 61%); mp 68 °C; Rf, 0.7 (hexane : ethyl acetate=7 : 3 v/v); ^{1}H NMR ($CDCl_3$, δ, ppm): 3.5 (s, 3H, NCH_3), 2.6 (s, 3H, SCH_3); ^{13}C NMR ($CDCl_3$, δ, ppm): 170.2 (C=O), 149.3 (C-S), 34.9 (NCH_3), 15.5 (CH_3); ir (KBr, v, cm $^{-1}$); 2950 (CH), 1680 (C=O), 1660, 1500 (C=N). Anal. Calcd. for $C_4H_6N_2OS_2$: C, 29.66; H, 3.73; N, 17.29; S, 39.59. Found: C, 29.68, H, 3.76, N, 12.33; S, 39.67.

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