Reversible Bond Switch with Participation of Hypervalent Sulfurane in a Thiadiazole Ring System and Its Kinetic Study in a Protonated System

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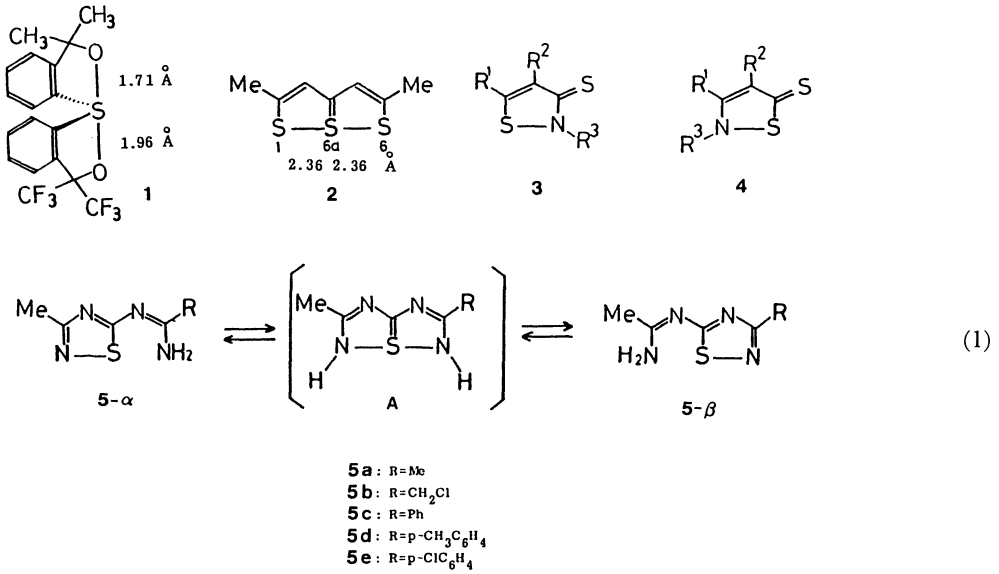
The existence of ring transformation equilibrium (bond switch) in 5-(1-aminoethylideneamino)-3-methyl-1,2,4-thiadiazole (**5a**) was confirmed by nitrogen-15 labeling experiment. Kinetic studies were carried out under neutral or acidic conditions. Kinetic parameters of the intramolecular equilibration of the monoprotonated **5a** (**5a**-H^+) were obtained by line shape analyses of the ^1H NMR, i.e., $\Delta G^{\ddagger}_{273}$=14.8±0.2, $\Delta H^{\ddagger}$=11.6±1.0 kcal·mol^{-1} $\Delta S^{\ddagger}$=−12±3 eu, k_{273}=9 s^{-1}. Position of protonation was determined at the nitrogen of the ethylideneamino part of the amidino group. It was concluded that the central sulfur atom moves back and forth in the range of 0.38 Å nine times a second at 0 °C, that is, bond switching.

Labile and polarizable nature of three-center four-electron bond in hypervalent molecules has been amply demonstrated by X-ray analyses of organic molecules of main group elements and sulfuranes are typical examples among them. Sulfurane **1** was synthesized by Martin,[1a] and two S-O bond lengths are longer than usual covalent bond and differ by 0.25 Å. The S-S bond length in 1,6,6a-trithiapentalene system (**2**) lies close to 2.36 Å but fluctuates within the range of 0.4 Å according to substituents.[2] The lability of bond length is one of the characteristics of hypervalent bond. The apparent bond switch in the 1,3-dipolar cycloaddition of five-membered sulfur containing heterocycles with activated acetylenes and so on have been considered to proceed through unsymmetrical trithiapentalene type intermediates.[3] Large difference of reactivity with activated acetylenes was noticed between isoelectronic 3(2*H*)- and 5(2*H*)-isothiazolethiones (**3** and **4**), that is, the latter was much more reactive than the former, because the central sulfur atom could participate in the 1,3-dipolar cycloaddition.[3f] Reid and co-workers reported the bond switch in the trithiapentalene-tungsten complexes.[4]

We have communicated a facile bond switch in some 1,2,4-thiadiazol-5(4*H*)-imine system by methylation or protonation,[5] and simplified the system in order to observe reversible bond switch via symmetrical sulfurane as an intermediate. In this system the sulfur-nitrogen bond was switched by prototropy, and the facility of the equilibration would suggest that the stability of the intermediate **A** reduced the activation energy (Eq. 1).[6] This type of equilibration does not take place at all when an oxygen is substituted for the sulfur.

In this paper the observed phenomenon was confirmed to be bond switching by introducing ^{15}N to the amidino group and kinetic studies on equilibration were carried out under neutral and acidic conditions.[7]



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5a: R=Me
5b: R=CH_2Cl
5c: R=Ph
5d: R=p-$CH_3C_6H_4$
5e: R=p-ClC_6H_4

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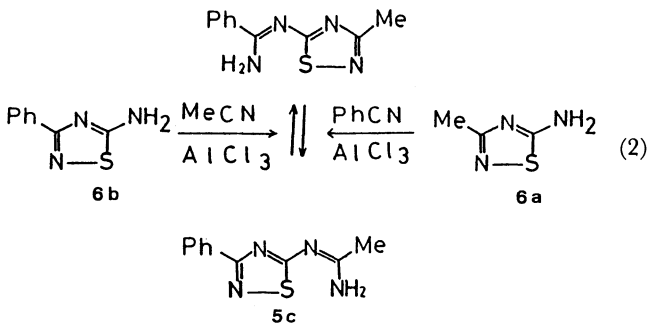
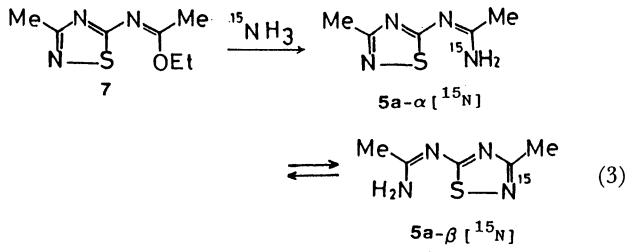
Results and Discussion

Confirmation of Bond Switch by ^{15}N Labeling Experiment and Estimation of the Rate under Neutral Conditions. As described before 5-(1-substituted 1-aminomethyleneamino)-3-methyl-1,2,4-thiadiazole (**5**α) was considered to be in equilibrium with the bond-switched **5**β. The conclusion was drawn by the following facts: (i) in the ^1H NMR spectra of unsymmetrical **5b** and so on signals due to the methyl and the substituent (R) appeared as a pair, respectively, but those of symmetrical **5a** (R=Me) showed only two peaks due to two different methyl groups; (ii) relative intensity of the methyl corresponded exactly to that of the other substituent (R). In order to present an unambiguous evidence for bond switch, **5c** was synthesized also from 5-amino-3-phenyl-1,2,4-thiadiazole (**6b**)[8] and acetonitrile in the presence of aluminum trichloride to give an identical compound with previously prepared one from 5-amino-3-methyl-1,2,4-thiadiazole (**6a**) and benzonitrile[6] (Eq. 2). Further



(2)

conclusive evidence came from the ^{15}N labeling experiment. Thus an imidate **7** was prepared from **6a** and triethyl orthoacetate in 95% yield. The imidate **7** was converted with ammonia at room temperature to give **5a**, which was identical with the compound synthesized previously. This method was mild and efficient thus it was applied to the synthesis of ^{15}N labeled **5a** in 60% yield using $^{15}NH_3$ (in situ prepared from [^{15}N]ammonium chloride (^{15}N 99% enriched) and 1 equiv of potassium hydroxide). In the proton



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decoupled ^{15}N NMR spectrum of **5a**[^{15}N] two peaks with almost equal height were observed. The chemical shifts of these nitrogens were obtained from that of nitromethane as an external reference and were calculated into the values from liquid ammonia.[9a] The peak at δ 104.1 was observed as a triplet (J_{NH}=91 Hz) in nondecoupled conditions, thus it is assigned to the nitrogen of the amino group in the amidino group. It is reasonable that the other peak at δ 240.7 (singlet in nondecoupled conditions) is assigned to the N(2) of the thiadiazole ring by comparison with reported chemical shift data.[9b] Off-resonance ^{15}N NMR spectrum of **5a**[^{15}N] is shown in Fig. 1. Therefore bond switch was evidently confirmed to take place.

It is interesting that ^{15}N NMR chemical shift of the amino nitrogen is in somewhat lower field than usual and that of the N(2) of the thiadiazole is in higher field.[9b] This tendency can be understood by contribution of intramolecular electron shift from the electron-rich amidino group into the electron-deficient five-membered thiadiazole ring.[9c] The explanation can also be applied to the electronic effects of the subsituents on the equilibrium ratio (β/α), that is, 2.14 in **5b** (R=CH_2Cl), 5.99 in **5d** (R=p-MeC_6H_4), 14.5 in **5c** (R=C_6H_5), and ca. 50 in **5e** (R=p-ClC_6H_4) (all values in $CDCl_3$ at 34 °C). Thus β-forms are further stabilized in polar solvents (**5b**: 2.14 in $CDCl_3$, 6.46 in CD_3CN). Measurements of the equilibrium ratios of **5b** in several solvents at various temperatures were carried out to give thermodynamic parameters of the bond switch. The results are shown in Table 1. It was found that ΔS was about zero and ΔH was almost responsible for the equilibrium ratio.

The rather large difference between the equilibrium ratio in $CDCl_3$ and CD_3OD (2.9 and 10.7 at −26 °C) was tried to use for the determination of the rate of the equilibration. Thus, to a $CDCl_3$ solution of **5b** (β/α=3) at −50 °C precooled CD_3OD (−50 °C) was added and ^1H NMR spectrum of the mixture was measured quickly at that temperature. In the first measurement which was done during 2—3 min after mixing, the ratio (β/α) was determined to be ca. 7 and in

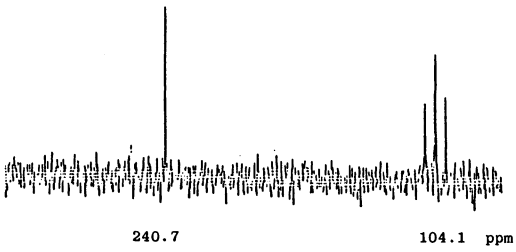


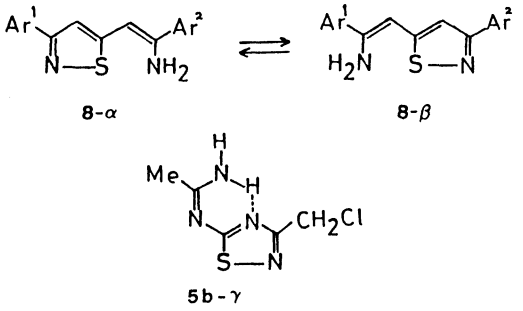
Fig. 1. Off-resonance ^{15}N NMR of **5a**[^{15}N] in neutral solution ($CDCl_3$).

Table 1. Solvent Effect on the Thermodynamic Parameters between **5b**α and **5b**β

Solvent	Polarity E_T	β/α (34 °C)	ΔG_{307} kcal mol^{-1}	ΔH kcal mol^{-1}	ΔS eu
$CDCl_3$	39.1	2.14	−0.48	−0.75	−0.9
CD_2Cl_2	41.1	3.28	−0.72	−0.77	−0.2
CD_3CN	46.0	6.46	−1.14	−1.02	+0.4
CD_3OD	55.5	6.53	−1.15	−1.28	−0.4

the next measurement (4—5 min after mixing) a new equilibrium ratio (β/α=8) was observed. Therefore it was concluded that the exchange process between α- and β-forms was fairly fast even at −50 °C. Although the ratios thus obtained contain large experimental error, the rate of equilibration ($\alpha \rightarrow \beta$) was roughly estimated to be ca. 10^{-2} s^{-1} at −50 °C by reversible first order approximations and $\Delta G^{\ddagger}_{223}$ was estimated to be about 14—15 kcal mol^{-1}(1 cal=4.184 J). Therefore the coalescence method was employed to determine the rate. A solution of **5b** in *o*-dichlorobenzene and DMSO-d_6 was heated until 170 °C in an NMR probe, but coalescence between two signals of the methyl (or chloromethyl) group was not observed. Free energy of activation ($\Delta G^{\ddagger}_{443}$) of the bond switch is calculated to be over 23 kcal mol^{-1} at 170 °C.

Accurate and detailed kinetic studies were carried out for a similar system **8** under neutral conditions



and kinetic parameters were obtained as $\Delta H^{\ddagger}$=12.2 kcal mol^{-1}, $\Delta S^{\ddagger}$=−41 eu, and $\Delta G^{\ddagger}$=24.4 kcal mol^{-1} (R^1=R^2=*p*-ClC_6H_4) (Eq. 4).[10a] The large negative value of activation entropy is characteristic and a much larger value is expected for **5**, because **5b-γ** is hydrogen-bonded intramolecularly in the ground state.[10b] Detailed discussion on the mechanism of the bond switch under neutral conditions was carried out for **8**.

Bond Switch under Acidic Conditions. When an acid was added to a solution of **5**, rate of bond switching was greatly accelerated and only one methyl signal could be observed at room temperature. Figure 2 shows that downfield shift of the methyl protons in **5a** takes place according to the amount of trifluoroacetic acid (TFA). Good linear relationship was observed until the added acid reached to one equiv to **5a**. When it exceeded one equiv, chemical shift of the methyl signal became constant even with large excess of TFA (6 equiv) or trifluoromethanesulfonic acid (13 equiv), indicating that only monoprotonation occurred and di- or polyprotonation did not. pK_a of **5a** was measured to be 4.87±0.02 by potentiometry, therefore the acidity of TFA (pK_a 0.23)[11] is high enough to protonate **5** stoichiometrically. The position of protonation will be discussed in a later section.

In order to determine the rate of equilibration under acidic conditions ^{1}H NMR of **5b** was measured in $CDCl_3$-DMSO-d_6 at low temperatures. By lowering the temperature two pairs of two singlets appeared again when a limited amount of TFA was added (Table 2). The fact that the signal split into two pairs indicates the bond switch between monoprotonated species [(**5b**-α-H^++**5b**-α)⇄(**5b**-β-H^++**5b**-β)] was to be observed. But in excess of TFA it was impossible to observe split because β/α ratio became large (> 15) according to the amount of TFA. Therefore in order to observe this exchange equilibration between protonated α- and β-forms, ^{1}H NMR of **5a** was measured. In the case of **5a**, protonated forms (**5a**-α-H^+⇄**5a**-β-H^+) are identical before and after the bond switch, therefore only two singlets were observed. After comparison of the experimental spectra with computer simulated ones,[12] the obtained rate constants were applied to the Eyring equation. In every case the spectra used to obtain one rate constant were measured at six to eight temperatures and the statistical errors of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were rendered very small by deliberate experiments. The activation free energy ($\Delta G^{\ddagger}$) and the rate were calculated from $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, and the $\Delta G^{\ddagger}$ was consistent with the value calculated from coalescence temperature (T_c) within 0.2 kcal mol^{-1}. In Table 3-A the effect of concentration of TFA is shown while that of **5a** is kept almost constant. Solubility of **5a** was much larger in CD_3OD and CD_3CN in comparison

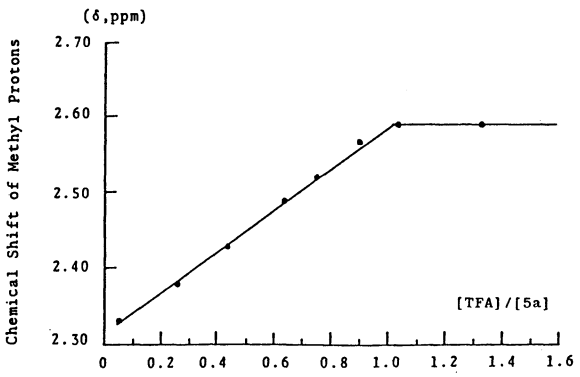


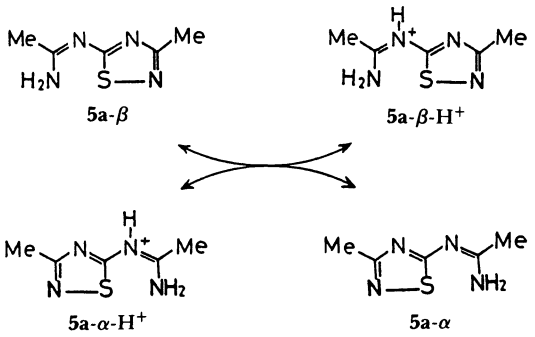
Fig. 2. Relation of chemical shift of methyl protons in **5a** and the amount of added TFA (CD_2Cl_2). [**5a**]=0.3—0.4 M.

Table 2. Low Temperature ^{1}H NMR Data of **5b** in the Presence of TFA[a,b]

TFA (equiv)	Temp °C	δ/ppm β	δ/ppm α	β/α
0	9	2.17, 4.61	2.49, 4.23	6
0.06	9	2.18, 4.63	2.48, 4.25	8
0.13	−17	2.21, 4.66	2.51, 4.27	9
0.31	−47	2.31, 4.73	2.51, 4.28	15
0.68	−47	2.48, 4.78		
1.02	−47	2.59, 4.78		
3.26	−47	2.59, 4.83		

a) $CDCl_3$-DMSO-d_6 as a solvent. b) The upfield signals are due to the methyl group and the downfield ones are assigned to methylene protons of the chloromethyl group.

with CD_2Cl_2 and so on, and in addition split widths ($\Delta\nu$) in polar solvents were larger than those in non-polar ones, therefore only CD_3OD and CD_3CN were used in the presence of more than one equiv of TFA. A remarkable point in Table 3-A was that the kinetic parameters in 1.23 equiv of TFA were considerably different from those in other cases. For example, free energy of activation ($\Delta G^{\ddagger}_{273}$) became larger from 13.5 (0.66 equiv) to 14.7 (1.23 equiv) kcal mol^{-1}, hence the rate (k_{273}) decreased considerably. So the effect of concentration of **5a** was studied with less than one equiv of TFA (Table 3-B) and it was clear that $\Delta G^{\ddagger}$ and the rate were dependent on the concentration. These facts imply that intermolecular process (ex. **5a**-α+**5a**-β-$H^+ \rightleftarrows$**5a**-α-H^++**5a**-β) played an important role for the bond switching in the presence of less than one equiv of TFA (Eq. 5). This intermolecular process cannot take part in the bond switching in the presence of more than one equiv of TFA. In fact both effects of concentration of **5a** and the ratio of the acid were not observed (Table 3-C). That is, $\Delta G^{\ddagger}_{273}$ was almost constant although split width ($\Delta\nu$) and coalescence temperature (T_c) changed with polarity of the solvent system. Evidently intramolecular reversible bond switching was observed under these conditions. Even when trifluoromethanesulfonic acid was used instead of TFA almost no change of kinetic parameters was observed. Therefore, the possibility that the equilibration proceeded through small amount of diprotonated intermediates can be ruled out. In CD_3CN different values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained probably due to the effect of solvation but $\Delta G^{\ddagger}$ was nealy equal to that in CD_3OD.



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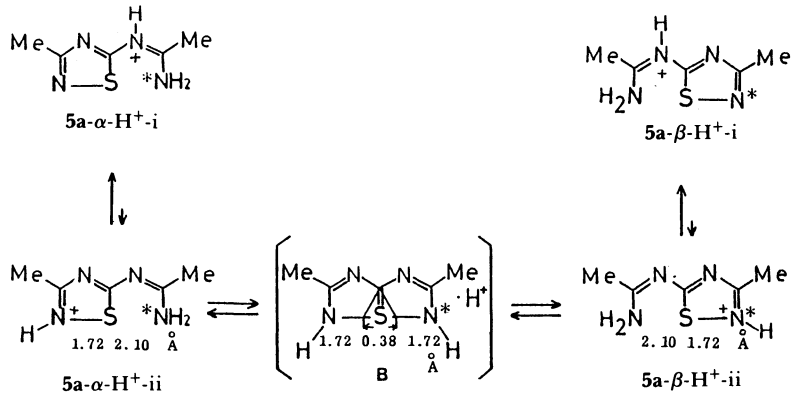
Position of Protonation and Mechanism of Bond Switching. There can be several types of monopro-



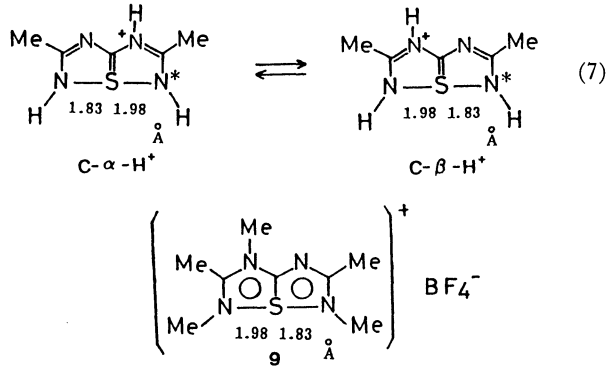
(6)

Table 3. Kinetic Parameters of the Ring Transformation of **5a**

	Run	Solv.	[5a]	[Acid][a)]/[5a]	$\Delta\nu$ Hz	T_c °C	$\Delta G^{\ddagger}_{273}$ kcal mol^{-1}	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ eu	k_{273} s^{-1}
A	1	CD_2Cl_2	0.35	0.05	15.7	−29	13.5	4.3±0.4	−34±2	90
	2		0.29	0.28	10.1	−40	13.9	2.2±0.4	−43±2	43
	3	CD_3OD	0.43	0.06	16.9	−10	13.8	8.4±0.6	−20±2	55
	4		0.39	0.13	15.9	−13	13.6	8.7±1.2	−18±5	79
	5		0.39	0.48	11.3	−21	13.7	6.8±0.4	−25±2	63
	6		0.41	0.66	9.1	−25	13.5	7.8±1.1	−21±5	91
	7		0.39	1.23	4.4	−4	14.7	11.2±1.0	−13±4	11
B	8	CD_2Cl_2	0.08	0.21	11.8	−13	14.2	4.7±0.8	−35±3	27
	9	CD_3OD	0.71	0.13	15.9	−16	13.5	8.9±1.3	−17±5	91
	10		0.15	0.13	16.7	+13	14.4	8.7±1.0	−21±4	18
C	11	CD_3OD	0.37	1.9	4.7	−4	14.6	11.3±1.5	−12±6	11
	12		0.10	3.5	6.1	+6	14.9	11.7±0.9	−12±3	7
	13		0.43	6.5	3.7	−7	14.7	11.1±0.4	−13±2	10
	14		0.11	6.5	5.6	−1	14.7	11.8±1.0	−11±4	9
	15[a)]		0.11	12.8	9.5	+21	15.1	11.9±1.1	−12±4	5
	16	CD_3CN	0.09	6.0	11.9	+3	14.4	15.1±0.3	+3±1	19

a) TFA was used throughout Run 1 to 14 (60 MHz), 16 (90 MHz) and trifluoromethanesulfonic acid was used for Run 15 (90 MHz).

tonated species, we conclude the structure of monoprotonated species observed in solution is **5a**-α-H^+-i (≡**5a**-β-H^+-i) among them. ^{15}N NMR peaks in the presence of 1.42 equiv of TFA at −20 °C ($CDCl_3$-CD_3CN=3 : 1) appeared at δ 129.3 and 242.5 under complete proton decoupled conditions and the latter was observed as a singlet and the former as a triplet (J_{NH}=92 Hz) under nondecoupled conditions, respectively. This indicates that the protonation took place at the nitrogen of the amino group in the amidino group which is *not* labeled by ^{15}N. Basicity of both N(2) and N(4) of the thiadiazole ring is very much smaller than that of **5**,[13] thus monoprotonation at those cannot be the case. Thus the possibility of Eq. 7



(7)

can be ruled out. But it is unlikely that **5a**-α-H^+-i is an appropriate precursor of the bond switch because of the much lowered nucleophilicity of the amidino group than **5a**. In contrast, **5a**-α-H^+-ii should be the precursor in the point that S-N bond in the thiadiazole ring is weakened by protonation at N(2) and the sulfur atom becomes highly susceptible to nucleophilic attack by the amino group. Kinetic data for the bond switching in Eq. 6 (Table 3-C) are summarized as $\Delta G^{\ddagger}_{273}$=14.8±0.2, $\Delta H^{\ddagger}$=11.6±1.0 kcal mol^{-1}, $\Delta S^{\ddagger}$=−12±3 eu, k_{273}=9 s^{-1}. The equilibrium ratio of (**5a**-α-H^+-i/**5a**-α-H^+-ii) is very difficult to estimate. It is not so unreasonable to assume that the ratio can be estimated by the difference between pK_a values in **5a** (4.87) and isothiazole (−0.51)[14] or 5-amino-3-phenyl-1,2,4-thiadiazole (1.4).[15] Thus the equilibrium ratio is estimated to be in the range of $10^{4.9-1.4}$ to $10^{4.9-(-0.5)}$. Then the real rate of the ring transformation should be in the range of $9\times10^{3.5}$ to $9\times10^{5.4}$ s^{-1} at 0 °C and the activation free energy ($\Delta G^{\ddagger}_{273}$) from **5a**-α-$H^+$-ii to **5a**-β-$H^+$-ii is calculated to be from 8.0 to 10.3 kcal mol^{-1}. Such a low barrier of the bond switch can be attributed to the stability of the intermediate thiapentalenium salt **B** and also to the essential weakness of the hypervalent N-S^{IV}-N bond.

Total N-S^{IV}-N bond length of the intermediate (or transition state) **B** can be estimated based on the structure of thiapentalenium salt **9**, which was synthesized by us and the structure was determined by X-ray diffraction.[5,16] The N-S bond length in **5a**-α-H^+-ii can be estimated by the data for an isothiazolium salt to be 1.72 Å[17] then S-N bond length becomes 2.10 Å. It can be visualized that the central sulfur atom moves back and forth as a pendulum in the range of 0.38 Å nine times a second at 0 °C, that is, bond switching. This can be regarded as a model of reversible S_N2 reaction at the central sulfur (Eq. 6) and really is the first experimental evidence to show the presence of double minimum in energy in trithiapentalene analogous system, i.e., so called no-bond resonance compound.

Experimental

IR spectra were recorded on Hitachi EPI-G2 spectrometer. ^1H NMR spectra were obtained with Hitachi R-20B or R-24B spectrometer, and kinetic measurements were done mainly with JEOL FX-60 spectrometer. Partial measurement of kinetics in ^1H NMR and all work for ^{15}N NMR were carried out with JEOL FX-90Q and Hitachi R-90H spectrometer. All melting points were uncorrected.

Alternative Synthesis of 5-(1-Aminoethylideneamino)-3-phenyl-1,2,4-thiadiazole (5c). A mixture of 5-amino-3-phenyl-1,2,4-thiadiazole (**6b**) (480 mg, 2.7 mmol), anhydrous aluminum trichloride (414 mg, 3.1 mmol), and acetonitrile (0.18 ml, 3.5 mmol) was heated at 100 °C for 1 h, and it was poured into ca. 20 ml of aq HCl (0.5 M; 1 M=1 mol dm^{-3}) and the product was extracted with chloroform (50 ml×3). After drying ($MgSO_4$) and evaporation of the solvent, the residue was subjected to dry column chromatography to give 18% yield of **5c**, which was identical with the previously prepared compound from 5-amino-3-methyl-1,2,4-thiadiazole (**6a**) and benzonitrile by mp (148.0—148.7 °C), NMR and IR spectroscopy.[6]

5-(1-[^{15}N]Aminoethylideneamino)-3-methyl-1,2,4-thiadiazole (5a[^{15}N]). A mixture of 5-amino-3-methyl-1,2,4-thiadiazole (1.96 g, 17.0 mmol) and triethyl orthoacetate (8.01 g, 49.4 mmol) was heated at 110 °C for 16 h. After removal of the excess orthoacetate, the residue was distilled under reduced pressure to give 5-(1-ethoxyethylideneamino)-3-methyl-1,2,4-thiadiazole (**7**) as colorless liquid. Yield 3.00 g (95%); bp 70—71 °C/1 mmHg (1 mmHg≈133.322 Pa); ^1H NMR (CCl_4) δ=1.31 (t, 3 H, J=7 Hz), 2.11 (s, 3 H), 2.40 (s, 3 H), 4.20 (q, 2 H, J=7 Hz).

Aqueous ammonia (28%) (1.5 ml, 22.5 mmol) was added to a solution of **7** (1.02 g, 5.51 mmol) in 10 ml of ethanol at 0 °C, and the mixture was stirred for 3 h. After the solvent was evaporated the residue was recrystallized from benzene-hexane to give 701 mg (82%) of **5a**, which was identical with the previously synthesized compound by mp (109.5—111.5 °C), NMR and IR spectroscopy.[6]

To a solution of ammonium chloride (^{15}N 99% enriched, 105 mg, 1.93 mmol) in 5 ml of methanol a solution of potassium hydroxide (85%, 130 mg, 1.97 mmol) in 2 ml of methanol was added at 0 °C, and then **7** (346 mg, 1.87 mmol) was added to the mixture. After it was stirred for 5 h at room temperature, the solvent was evaporated and the residue was recrystallized from benzene-hexane to give 176 mg (60%) of **5a**[^{15}N]. Mp 108—110.5 °C. ^1H NMR ($CDCl_3$) δ=2.19 (s, 3H), 2.50 (s, 3H), 6.5 (bm, 2H). ^{15}N NMR ($CDCl_3$) δ=104.1 (t, J=91 Hz), 240.7 (s).

The Measurement of Bond Switching Equilibrium between 5b-α and 5b-β. About 10 to 15 mg of **5b** was dissolved in several solvents in an NMR sample tube (concen-

trations were kept almost the same (ca. 0.2 M)). The sample tube was cooled and the equilibrium ratio of the α- and β-isomers was measured from the peak area of both signals of the methyl protons and that of the methylene protons of the chloromethyl group. Integral ratios were measured four to six times for each condition and the average ratio was obtained. Thermodynamic parameters were calculated using the average ratios at five to six temperatures between 34 and −26 °C.

Low-Temperature ^{1}H NMR Measurement of 5b in the Presence of TFA. 34—38 mg of **5b** in $CDCl_3$ (510—600 mg) and DMSO-d_6 (199—234 mg) in the presence of the various amounts of TFA (0.06—3.26 equiv) were cooled to 9, −17, and −47 °C in an NMR tube and ^{1}H NMR were measured. Separation of peaks of methyl and chloromethyl groups could not be observed in the presence of more than 0.68 equiv of TFA.

Low-Temperature ^{1}H NMR Measurement of 5a in the Presence of TFA and Trifluoromethanesulfonic Acid. The chemical shift difference of the separated signals of the two methyl groups became constant at low temperatures (ca. −50—−60 °C) for each run in CD_3OD and CD_3CN and this constant value was employed as the line separation width without exchange ($\Delta\nu$). Computer calculation of all data were carried out using DNMR-3 program with Hitac 8700/8800 or Hitac M-200H computer in the University of Tokyo. The rate of exchange was determined by superimposing the simulated spectra on the observed ones.

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