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Thermal Conversion Between Diastereomeric 1,4-Dipolar Cycloadducts

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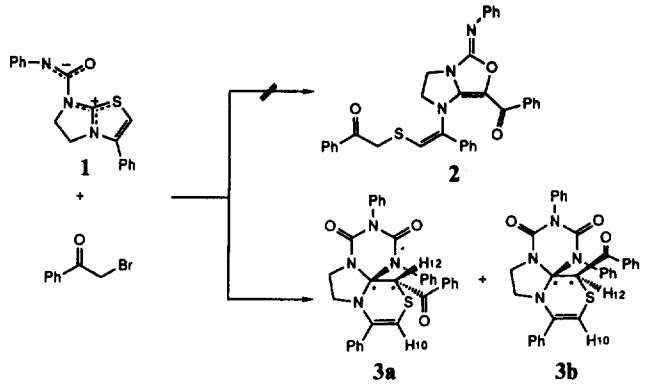
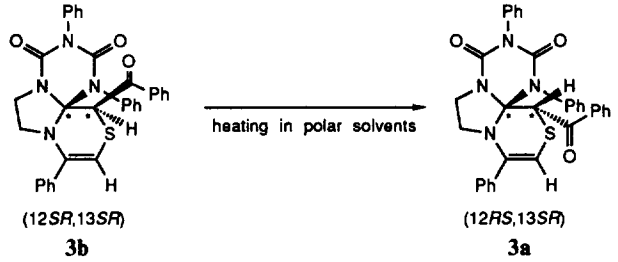
Thermal conversion between diastereomers formed *via* 1,4-dipolar cycloaddition was identified by ^{1}H-NMR spectroscopic study depending on temperature and reaction time. Hereupon the formed product by kinetic control was converted to the thermodynamically controlled product. Various diastereomeric 1,4-dipolar cycloadducts were synthesized by the reacting of 5,6-dihydro-3-phenyl-7-[*N*-phenyl(carbamoyl)]imidazo[2,1-*b*]thiazolium-betaine with a series of *para*-substituted phenacyl bromides and the substituent effects were investigated.

Introduction

N-Bridged thiazolium-betaines show the strong nucleopilicity and basicity based on the presence of the carbanion. These betaines, which are highly reactive organic compounds, can be used for the synthesis of complicated heterocyclic compounds *via* ring transformation and 1,4-dipolar cycloaddition reactions.



Scheme 1.



Scheme 2.

In our previous work, the reaction of 5,6-dihydro-3-phenyl-7-[*N*-phenyl(carbamoyl)]imidazo[2,1-*b*]thiazolium-betaine (**1**)[1,2] with phenacyl bromide had given the diastereomeric 1,4-dipolar cycloadducts (**3a** and **3b**) instead of the ring transformation compound (**2**) (Scheme 1).[3] These cycloadduct, (12*RS*, 13*SR*)- and (12*SR*, 13*SR*)-12-benzoyl-2,4-dioxo-1,3,9-triphenyl-6,7-dihydro-12*H*-thiazino[3',4'; 2,3]imidazo[1,2-*a*][1,3,5]triazines (**3a** and **3b**), had been characterized as the diastereomers having different spatial arrangements at *C*-12.

We report here on the thermal conversion between the diastereomeric cycloadducts and the substituent effects of *para*-substituted phenacyl bromides as the alkylating agents.

Results and Discussion

When the reaction mixture of **1** and phenacyl bromide was refluxed in acetone, thermal conversion occurred between the diastereomeric cycloadducts (**3a** and **3b**) was detected (Scheme 2).

As the reaction was progressed, the amount of **3a** in the reaction mixture was increased in proportion with the decreasing **3b**. After being refluxed for long time, **3b** was completely converted into **3a**. This phenomenon suggests that **3a** and **3b** should be the thermodynamically and kinetically controlled products, respectively. In case of **3b** isolated as a solid, the same result was detected, too.

This conversion was clearly proven by ^{1}H-NMR (in $CDCl_3$) study depending on temperature and time as shown Figure 1. Spectra were recorded with a gradual increase of temperature. No reaction was observed until the temperature of probe reached at 65℃. After 10 min, at this temperature two additional doublets by W-coupling (J=1.6 Hz) between *H*-10 and *H*-12 of **3a** appeared at δ 5.60 and δ 4.78, respectively. As the reaction was proceeded, the singlets of **3b** at

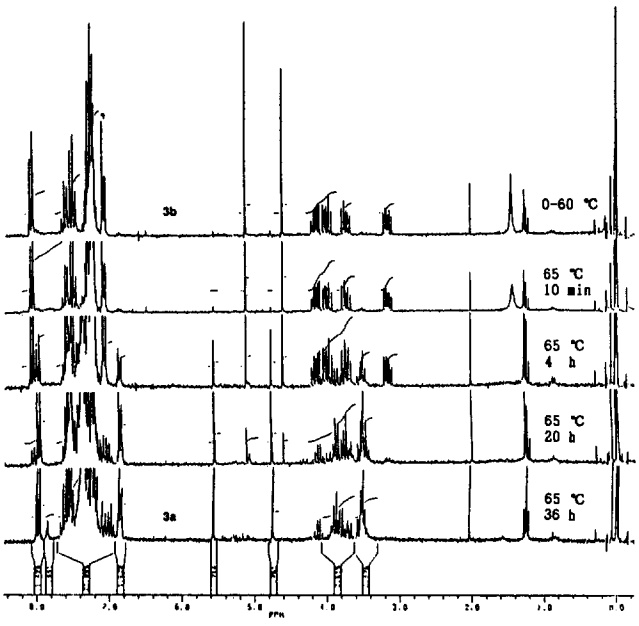
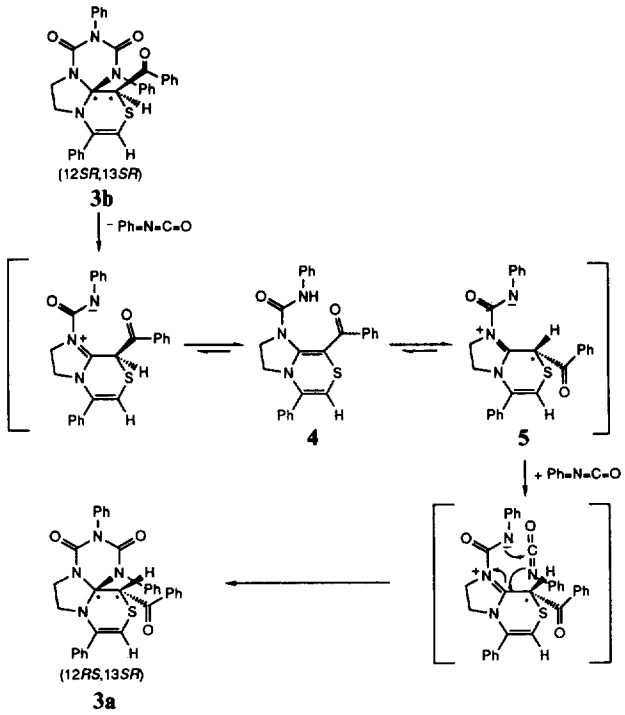


Figure 1. ^{1}H-NMR spectra (in $CDCl_3$) for the conversion of **3b** into **3a** depending on temperature and time.



Scheme 3.

δ 4.62 (*H*-12, methine) and δ 5.11 (*H*-10, vinylic) started decreasing while the two doublets of **3a** at δ 4.78 (*H*-10, vinylic) and δ 5.60 (*H*-12, methine) continued to grow. At the end of 36 h there appeared only protons corresponding to **3a**. The conversion ratio of **3b** to **3a** depends on the reaction temperature and time. Also solvents polarities attribute to conversion rate, that is, more polar solvents give faster conversion than less polar ones. In the procedure of the polar cycloaddition reaction with isocyanates reaction is often occurred in kinetically controlled process. However, in the case

(C-6), 37.4 (C-12); MS m/e 589 (M+H) ion, 135 ($MeOC_6H_4 \equiv O^+$), 119 (C_6H_5-N=C=O); Anal. Calcd for $C_{33}H_{28}N_4O_4S$: C, 69.37; H, 4.79; N, 9.52. Found: C, 69.25; H, 4.84; N, 9.33.

Isomer **6b**: pale yellow solid, yield 0.32 g (36.2%); mp. 173.0-173.5℃ (decomp.); IR (KBr) 1725, 1690 (*vs.* C=O), 1600 (s, ArC=C) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.12-3.23, 3.71-3.79, 3.98-4.07, 4.09-4.22 (m, 4H, NCH_2CH_2N), 3.85 (s, 3H, OMe), 4.58 (s, 1H, CH), 5.09 (s, 1H, =CH) 6.93-8.23 (m, 19H, ArH); ^{13}C-NMR ($CDCl_3$) δ 192.9 (COPh), 151.3 (C-4), 149.1 (C-2), 97.3 (C-10), 83.7 (C-13), 55.6 (OMe), 50.1 (C-12), 49.7 (C-7), 42.5 (C-6); MS m/e 589 (M+H) ion, 135 ($MeOC_6H_4C \equiv O^+$), 119 (C_6H_5-N=C=O); Anal. Calcd for $C_{33}H_{28}N_4O_4S$: C, 69.37; H, 4.79; N, 9.52. Found: C, 69.26; H, 4.84; N, 9.43.

(12*RS*, 13*SR*)- and (12*SR*, 13*SR*)-12-(4′-Phenylbenzoyl)-2,4-dioxo-1,3,9-triphenyl-6,7-dihydro-12*H*-thiazino[3′,4′; 2,3]imidazo[1,2-*a*][1,3,5]triazines (7a and 7b). 4′-Phenylphenacyl bromide (0.41 g) as a alkylating agent was used.

Isomer **7a**: yellow powder, yield 0.20 g (12.0%); mp. 178.0-179.0℃ (decomp.); IR (KBr) 1710, 1670 (*vs.* C=O), 1580 (m, ArC=C) cm^{-1}; ^{1}H-NMR ($CDCl_3$+DMSO-d_6) δ 3.23-3.60, 3.83-4.02 (m, 4H, NCH_2CH_2N), 5.04 (d, $J_{10,12}$=1.5 Hz, 1H, =CH), 6.34 (d, $J_{12,10}$=1.5 Hz, 1H, CH), 6.86-8.51 (m, 24H, ArH); ^{13}C-NMR ($CDCl_3$+DMSO-d_6) δ 188.4 (COPh), 150.9 (C-4), 148.7 (C-2), 87.2 (C-10), 82.8 (C-13), 49.3 (C-7), 42.7 (C-6), 39.4 (C-12); MS m/e 635 (M+H) ion.

Isomer **7b**: yellow powder, yield 0.31 g (32.6%); mp. 174.0-174.5℃ (decomp.); IR (KBr) 1715, 1670 (*vs.* C=O), 1580 (m, ArC=C) cm^{-1}; ^{1}H-NMR ($CDCl_3$+DMSO-d_6) δ 2.54-2.56, 3.24-3.32 (m, 2H, NCH_2), 3.89-4.07 (m, 2H, NCH_2), 5.14 (s, 1H, CH), 5.28 (s, 1H, =CH), 7.04-8.38 (m, 24H, ArH); ^{13}C-NMR ($CDCl_3$+DMSO-d_6) δ 194.6 (COPh), 150.8 (C-4), 148.3 (C-2), 95.9 (C-10), 83.3 (C-13), 49.6 (C-12), 42.2 (C-7), 39.8 (C-6); MS m/e 635 (M+H) ion.

(12*RS*, 13*SR*)- and (12*SR*, 13*SR*)-12-(4′-Fluorobenzoyl)-2,4-dioxo-1,3,9-triphenyl-6,7-dihydro-12*H*-thiazino[3′,4′; 2,3]imidazo[1,2-*a*][1,3,5]triazines (8a and 8b). 4′-Fluorophenacyl bromide (0.26 g) as a alkylating agent was used.

Isomer **8a**: yellow powder, yield 0.25 g (28.9%); mp. 162.5-163.5℃ (decomp.); IR (KBr) 1720, 1680 (*vs.* C=O), 1595 (m, ArC=C) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.48-3.57, 3.72-3.92 (m, 4H, NCH_2CH_2N), 4.74 (d, $J_{10,12}$=1.5 Hz, 1H, =CH), 5.49 (d, $J_{12,10}$=1.5 Hz, 1H, CH), 6.82-7.82 (m, 19H, ArH); ^{13}C-NMR ($CDCl_3$) δ 187.1 (COPh), 151.4 (C-4), 149.6 (C-2), 86.6 (C-10), 83.5 (C-13), 50.1 (C-7), 43.5 (C-6), 40.9 (C-12); MS m/e 577 (M+H) ion.

Isomer **8b**: yellow powder, yield 0.13 g (15.0%); mp. 167.0-168.0℃ (decomp.); IR (KBr) 1715, 1680 (*vs.* C=O), 1590 (s, ArC=C) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.08-3.19, 3.65-3.77 (m, 2H, NCH_2), 3.65-4.18 (m, 2H, NCH_2); 4.51 (s, 1H, CH), 5.05 (s, 1H, =CH), 7.00-8.14 (m, 19H, ArH); ^{13}C-NMR ($CDCl_3$) δ 193.4 (COPh), 151.2 (C-4), 149.0 (C-2), 96.8 (C-10), 83.8 (C-13), 50.3 (C-12), 49.9 (C-7), 42.5 (C-6); MS m/e 577 (M+H) ion.

(12*RS*, 13*SR*)- and (12*SR*, 13*SR*)-12-(4′-Bromobenzoyl)-2,4-dioxo-1,3,9-triphenyl-6,7-dihydro-12*H*-thiazino[3′,4′; 2,3]imidazo[1,2-*a*][1,3,5]triazines (9a and 9b). 4′-Bromophenacyl bromide (0.42 g) as a alkylating agent was used.

Isomer **9a**: yellow powder, yield 0.42 g (43.9%); mp. 163.5-164.5℃ (decomp.); IR (KBr) 1725, 1685 (*vs.* C=O), 1595 (m, ArC=C) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.45-3.55, 3.77-3.90 (m, 4H, NCH_2CH_2N), 4.72 (d, $J_{10,12}$=1.5 Hz, 1H, =CH), 5.49 (d, $J_{12,10}$=1.5 Hz, 1H, CH), 6.82-7.86 (m, 19H, ArH); ^{13}C-NMR ($CDCl_3$) δ 187.4 (COPh), 151.4 (C-4), 149.6 (C-2), 86.4 (C-10), 83.5 (C-13), 50.2 (C-7), 42.0 (C-6), 40.9 (C-12); MS m/e 637 (M+H) ion.

Isomer **9b**: yellow powder, yield 0.17 g (17.8%); mp. 154.5-155.0℃ (decomp.); IR (KBr) 1725, 1685 (*vs.* C=O), 1600 (s, ArC=C) cm^{-1}; ^{1}H-NMR ($CDCl_3$+DMSO-d_6) δ 3.08-3.20, 3.65-3.77 (m, 2H, NCH_2), 3.92-4.18 (m, 2H, NCH_2); 4.49 (s, 1H, CH), 5.05 (s, 1H, =CH), 6.99-8.16 (m, 19H, ArH); ^{13}C-NMR ($CDCl_3$+DMSO-d_6) δ 194.3 (COPh), 150.6 (C-4), 147.9 (C-2), 95.5 (C-10), 83.1 (C-13), 49.4 (C-12), 42.0 (C-7), 39.6 (C-6); MS m/e 637 (M+H) ion.

(12*RS*, 13*SR*)- and (12*SR*, 13*SR*)-12-(4′-Chlorobenzoyl)-2,4-dioxo-1,3,9-triphenyl-6,7-dihydro-12*H*-thiazino[3′,4′; 2,3]imidazo[1,2-*a*][1,3,5]triazines (10a and 10b). 4′-Chlorophenacyl bromide (0.42 g) as a alkylating agent was used.

Isomer **10a**: yellow powder, yield 0.38 g (42.7%); mp. 156.5-157.5℃ (decomp.); IR (KBr) 1715, 1670 (*vs.* C=O), 1590 (m, ArC=C) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.46-3.57, 3.71-3.94 (m, 4H, NCH_2CH_2N), 4.73 (d, $J_{10,12}$=1.5 Hz, 1H, =CH), 5.50 (d, $J_{12,10}$=1.5 Hz, 1H, CH), 6.82-7.94 (m, 19H, ArH); ^{13}C-NMR ($CDCl_3$) δ 187.2 (COPh), 151.4 (C-4), 149.6 (C-2), 87.5 (C-10), 83.5 (C-13), 50.1 (C-7), 43.2 (C-6), 40.9 (C-12); MS m/e 593 (M+H) ion.

Isomer **10b**: yellow powder, yield 0.08 g (9.0%); mp. 145.5-146.5℃ (decomp.); IR (KBr) 1720, 1670 (*vs.* C=O), 1590 (m, ArC=C) cm^{-1}; ^{1}H-NMR ($CDCl_3$+DMSO-d_6) δ 3.10-3.16, 3.68-3.76 (m, 2H, NCH_2), 3.95-4.14 (m, 2H, NCH_2); 4.49 (s, 1H, CH), 5.05 (s, 1H, =CH), 6.99-8.16 (m, 19H, ArH); ^{13}C-NMR ($CDCl_3$+DMSO-d_6) δ 194.1 (COPh), 150.8 (C-4), 148.2 (C-2), 96.0 (C-10), 83.3 (C-13), 49.2 (C-12), 42.2 (C-7), 39.8 (C-6); MS m/e 593 (M+H) ion.

(12*RS*, 13*SR*)-12-(4′-Nitrobenzoyl)-2,4-dioxo-1,3,9-triphenyl-6,7-dihydro-12*H*-thiazino[3′,4′; 2,3]imidazo[1,2-*a*][1,3,5]triazines (11). 4′-Nitrophenacyl bromide (0.37 g) as a alkylating agent was used. Orange powder, yield 0.43 g (47.5%); mp. 168.5-169.5℃ (decomp.); IR (KBr) 1715, 1675 (*vs.* C=O), 1590 (m, ArC=C) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.46-3.58, 3.79-3.93 (m, 4H, NCH_2CH_2N), 4.71 (d, $J_{10,12}$=1.3 Hz, 1H, =CH), 5.54 (d, $J_{12,10}$=1.3 Hz, 1H, CH), 6.82-8.37 (m, 19H, ArH); ^{13}C-NMR ($CDCl_3$) δ 185.8 (COPh), 151.4 (C-4), 150.4 (C-2), 85.7 (C-10), 83.3 (C-13), 50.1 (C-7), 43.6 (C-6), 41.6 (C-12); MS m/e 604 (M+H) ion.

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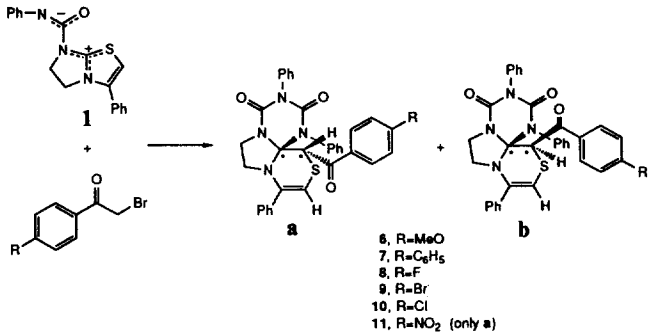

Scheme 4.

Table 1. Formation Ratio of the Thermodynamically Controlled Products to the Kinetically Controlled Products Depending on the Substituents

R	Formation ration
MeO	**6a** / **6b** : 1.0 / 2.7
C_6H_5	**7a** / **7b** : 1.0 / 1.6
H	**3a** / **3b** : 1.1 / 1.0
F	**8a** / **8b** : 1.9 / 1.0
Br	**9a** / **9b** : 2.5 / 1.0
Cl	**10a** / **10b** : 4.8 / 1.0
NO_2	**11** (only **a**)

of lower reactive isocyanates, heating is required, which tends to establish thermodynamically controlled equilibria.[4]

The conversion mechanism is shown in Scheme 3. The structure of **3b**, a kinetically controlled product, seems to be unstable in making observation of its molecular model. It shows steric hindrance between functional groups. This steric hindrance tends to be released by heating in polar solvents. At first phenyl isocyanate is easily dissociated, then the configuration of chiral carbon of thiazine ring is converted into that of the thermally stable structure (**5**) *via* epimerization. Simultaneous 1,4-dipolar cycloaddition reaction[5-9] to form six-membered ring, a thiazine ring takes place to give the thermally stable product (**3a**). On the MS spectrum of **3b**, a fragment of m/e 119 (Ph-N=C=O) indicates that phenyl isocyanate is easily fallen apart under termal condition.

A series of *para*-substituted phenacyl bromides containing electron-donating or electron-withdrawing substituents were used as the alkylating agents in our experiments (Scheme 4).

1 was synthesized from 5,6-dihydro-3-phenylimidazo[2,1-*b*] thiazole[10-13] and phenyl isocyanate in acetone at room temperature. The reaction mixture of **1** with various substituted-phenacyl bromides was refluxed for 1 h in acetone, and the diastereomeric cycloadducts formed were separated by column chromatography. When the substituent *R* of *para*-substituted phenacyl bromide was methoxy or phenyl group having electron donating property, a kinetically controlled product was predominantly obtained over a thermodynamically controlled one. But when *R* was fluoro, bromo, chloro, or nitro group with electron withdrawing tendence, a thermodynamically controlled product was obtained in large quantity. This trend appears remarkably in case that *R* is a strong electron-donating or electron-withdrawing group. In particular the nitro group shows a strong tendence to give thoroughly the thermodynamically controlled product.

The formation ratio of the thermodynamically controlled products (**3a**, **6a-10a**, **11**) to the kinetically controlled products (**3b**, **6b-10b**) was listed at Table 1.

Experimental

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and were uncorrected. IR spectra were recorded on a Perkin-Elmer Model 267 spectrometer using potassium bromide pellet. The following descriptive abbreviations were used; s=strong, m=medium, and, w=weak. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on the AM-200-SY Brucker and 300 MHz Gemini Varian NMR spectrometers. Chemical shift values from tetramethylenesilane were reported on the δ scale. Ms spectra were determined on a GC-MASS 5985B and a HP 5988A mass spectrometer coupled with HP 1090M HPLC. Elemental analyses were determined with a Perkin-Elmer Model 240C elemental analyzer.

1,2-Diamino ethane and phenyl isocyanate were used without purification. But *para*-substitutedphenacyl bromides were purified by recrystallization wtih ethyl alcohol. Kieselgel 60 (70-230 mesh ASTM, MERCK) was used for column chromatography.

5,6-Dihydro-3-phenyl-7-[*N*-phenyl(carbamoyl)]imidazo[2,1-*b*]thiazolium-betaine (1). 5,6-Dihydro-3-phenylimidazo[2,1-*b*]thiazole (2.02 g, 10.0 mmol) was dissolved in acetone (50 m*l*). To this solution phenyl isocyanate (1.19 g, 10.0 mmol) was slowly added at room temperature with constant stirring. During the dropping, white solid was formed and reaction mixture was stirred for 30 min. Then the precipitate was collected by filtration and dried to give the betaine compound. Yield 2.62 g (81.5%); mp. 196.0-197.0 ℃; IR (KBr) 1640 (*vs.* C=O), 1580 (s ArC=C) cm^{-1}; ^{1}H-NMR (CF_3CO_2D) δ 5.01 (s, 4H, NCH_2CH_2N), 7.18 (s, 1H, =CH), 7.47 (s, 5H, ArH), 7.68 (s, 5H, ArH).

General procedure for the preparation of diastereomeric 1,4-dipolar cycloadducts. 5,6-Dihydro-3-phenyl-7-[*N*-phenyl(carbamoyl)]imidazo[2,1-*b*]thiazolium-betaine (**1**, 1.01 g, 3.15 mmol) was dissolved in acetone (300 m*l*) by heating. To this solution *para*-substitutedphenacyl bromide (1.50 mmol) was slowly added. The reaction mixture was refluxed for 1 h with constant stirring. In a few min hydrobromide salt (mp. >250℃) was precipitated. After 1 h, the white salt was filtered off, and filtrate was concentrated, chromatographed on silica-gel column (hexane/ethyl acetate=3 : 2) to give the 1,4-dipolar cycloadducts.

(12*RS*, 13*SR*)- and (12*SR*, 13*SR*)-12-(4′-Methoxybenzoyl)-2,4-dioxo-1,3,9-triphenyl-6,7-dihydro-12*H*-thiazino[3′,4′; 2,3]imidazo[1,2-*a*][1,3,5]triazines (6a and 6b). 4′-Methoxyphenacyl bromide (0.34 g) as a alkylating agent was used.

Isomer **6a**: bright yellow powder, yield 0.12 g (13.6%); mp. 172.0-172.5℃ (decomp.); IR (KBr) 1725, 1680 (*vs.* C=O), 1600 (s, ArC=C) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.47-3.60, 3.68-3.95 (m, 4H, NCH_2CH_2N), 3.89 (s, 3H, OCH_3), 4.76 (d, $J_{10,12}$=1.7 Hz, 1H, =CH), 5.53 (d, $J_{12,10}$=1.7 Hz, 1H, CH), 6.83-8.01 (m, 19H, ArH); ^{13}C-NMR ($CDCl_3$) δ 185.0 (COPh), 148.7 (C-4), 146.8 (C-2), 84.3 (C-10), 80.6 (C-13), 52.8 (OMe), 47.2 (C-7), 40.5

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A Theoretical Study on the Chemisorption Effects in SERS

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With the chemisorption theory based on the charge-transfer model, we evaluate the enhancement ratios in surface enhanced Raman scattering. The extended Hückel (EH) calculation and fragment molecular orbiatal (FMO) analysis have been applied to a system composed of a pyridine molecule adsorbed on a silver cluster. The calculation shows that the enhancement ratios due to the resonant metal-to-molecule charge-transfer are assessed about 1-170.

Introduction

The surface enhanced Raman scattering (SERS) phenomena due to interaction between metal surface and adsorbate molecule have been studied since the discovery of Fleishman.[1] It is now widely accepted that two separate mechanisms must be involved in the origin of SERS.[2-4] The electrodynamic mechanism shows that the enhancement results from the surface plasmon resonances. The enhancement ratios of up to 10^4 can be explained by this mechanism.[5] However, it was also realized that certain types of molecules display enhancement ratios still grater by factors of 10 to 10^3. These are molecules such as pyridine or piperidine having a lone pair of electrons available for bonding with surface. The charge-transfer mechanism due to chemisorption was proposed by Adrian, Lippitsch and Lombardi. We focus on the effect of chemisorption in this work. The chemisorption theory has experienced an evolution. Adrian[6] emphasized on Franck-Condon overlap integral, but ignored Herzberg-Teller term.[7] Lippitsch[8] included vibronic coupling of the molecular ground electronic state with states of the metal in attempt to complement Adrian's theory. Lombardi[9] applied the Herzberg-Teller conditions to a metal-molecule system. Lombardi's theory provides plausible explanations about the intensity profile of experiments and the enhancement of nontotally symmetric mode. The goal of this work is evaluation of enhancement ratio of chemisorption origin on the basis of Lombardi's theory. To evaluate the enhancement ratio, the transition moment between states of metal and molecule, and the energy level of metal are calculated, using the vibronic coupling constants between metal and molecule, and Franck-Condon overlap integral as variables.

Method

We model pyridine-silver system as a typical case of SERS.

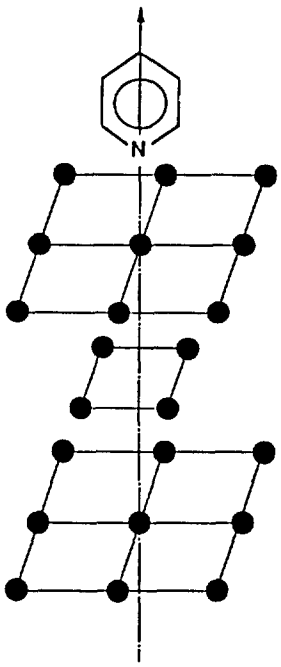

Figure 1. Pyridine-silver cluster model. The Ag_{22} cluster and pyridine have D_{4h} and C_{2v} symmetry respectively. In head-on adsorption configuration, combined system has C_{2v} symmetry.

The silver surface is represented by a cluster of three layers of 22-atoms. The cluster has been proved as a reasonable model for the calculation and for the representation of surface.[10] The geometry is given in Figure 1. The Ag-Ag distance is taken as 2.89 Å,[11] which is the nearest neighbour distance in bulk silver. We take the Ag-N distance to be 2.302 Å,[12] which is found in an Ag complex, The EH parameters[13] used in the calculation are collected in Table 1. The parameters for Ag are taken from the calculation of Hoff-