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STEREOISOMERIZATION OF 1,4-DIHYDROARSININE-TETRACARBOXYLIC ACID DIIMIDES UNDER NON-ACIDIC CONDITION FROM *cis*- TO *trans*-FORMS

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Abstract – Stereoisomerization of *cis*-1,4-dihydro-1,4-dimethyl-1,4-diarsininetetracarboxylic acid diimides, which were prepared from *cis*-1,4-dihydro-1,4-diarsininetetracarboxylic acid dianhydride with *n*-dodecylamine or aniline, to *trans*-isomers in $CDCl_3$ proceeded at room temperature and quantitatively by repeated concentration and dissolution process in various solvents such as $CHCl_3$, toluene, and ethyl acetate. Two stereoisomers were isolated respectively as single crystals, of which structures were determined by X-ray crystallography.

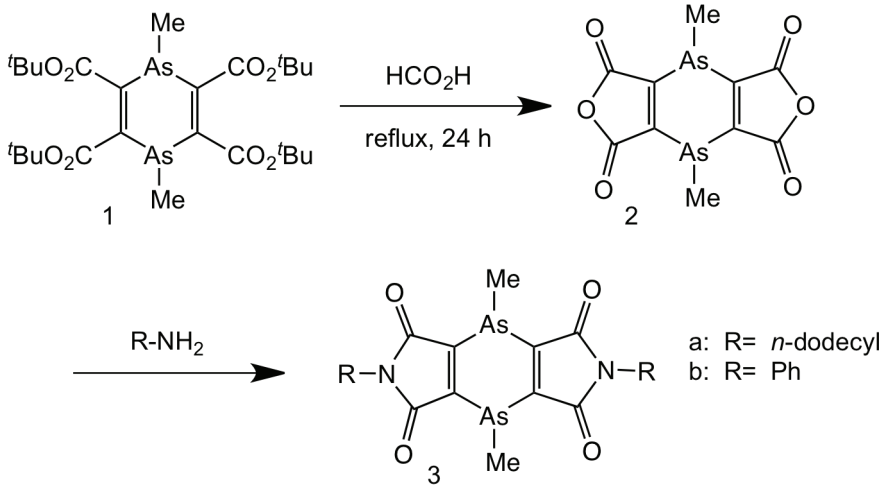
INTRODUCTION

Arsines have been reported to be ligands superior to phosphines in a number of transition metal-catalyzed organic reactions due to their poorer σ-donor ability.[1] In the case of heavier elements like arsine, the angles are close to 90°, which suggests the substitution via p orbitals with little s character and the increased s character of the lone pair rather than using sp^3 hybridized orbitals. As well known for NH_3, the heavier hydride AsH_3 also invert via a trigonal D_{3h} planar transition structure. Inversion barriers calculated for NH_3 and AsH_3 are 6.0 and 39.2 kcal mol^{-1}, respectively.[2] As is apparent from these barriers,

the pyramidal D_{3v} structures of the heavier hydrides are rigid in contrast to NH_3 which exhibits rapid umbrella inversion motion at room temperature. For example, half-life for racemization of (+)- and (-)-ethylmethylphenylarsine is calculated to ca. 740 h at 200 ˚C from the kinetic data, 41.8±0.5 kcal mol^{-1}.[3] Although cyclic (4p-2p)π conjugation contributes to the lowering of the inversion barrier such as arsindole, the free energy of activation is still high, 34.6 kcal mol^{-1} at 151 ˚C.[4] This is related to the inert-pair effect: the heavier atoms can preserve the ns^2np^2 valence configuration in the pyramidal C_{3v} structures with bond angles of ca. 90˚. Although racemization at an arsenic center is observed by acid-catalyzed inversion[5] and in cationic metal complexes,[6] it has been accepted that free tertiary arsine are configurationally stable under the non-acidic conditions employed. The inversion barrier for the trivalent arsine center is generally high enough to keep the stereochemical structure at room temperature.

We have synthesized 1,4-dihydro-1,4-diarsinines, 1,4-diarsa-1,4-cyclohexadienes, as cyclic ditopic organoarsenic ligands by radical reaction of pentamethylcyclopentaarsine (*cyclo*-$(MeAs)_5$) and acetylene derivatives.[7] Their stability toward air and moisture was great enough to allow its handling in air. The 1,4-dihydro-1,4-diarsinines are mainly obtained as *cis*-isomers. The structures of *cis*-1,4-dihydro-1,4-diarsinines were suitable for ligands of a dinuclear complex because direction of two coordination sites is parallel.[8] The ^1H NMR spectrum of crude 1,4-dihydro-1,4-diarsinines before recrystallization indicated a coexistence of a stereoisomer as a miner product, which is *trans*-isomers. However, no isomerization and racemization behaviors were observed.

We also reported that the reaction of *cis*-1,4-dihydro-1,4-diarsininetetracarboxylic acid dianhydride (***cis*-2**), which was prepared from *cis*-1,4-dihydro-1,4-dimethyl-2,3,5,6-tetrakis(*t*-butoxycarbonyl)-1,4-diarsinine (***cis*-1**), with aniline at moderate temperature produced the corresponding *cis*-1,4-dihydro-1,4-diarsininetetracarboxylic acid diimides. Here, we found that stereoisomerization of *cis*-1,4-dihydro-1,4-dimethyl-1,4-diarsininetetracarboxylic acid diimides to



Scheme 1. Synthesis of *cis*-1,4-dihydro-1,4-dimethyl-1,4-diarsininetetracarboxylic acid diimides (**3**) from 1,4-dihydro-1,4-dimethyl-2,3,5,6-tetrakis(*t*-butoxycarbonyl)-1,4-diarsinine (**1**)

corresponding *trans*-isomers quantitatively proceeded by repeated concentration in $CHCl_3$ under no-acidic condition. We study crystal and optical properties of both the *cis*- and *trans*-isomers.

RESULTS AND DISCUSSION

cis-1,4-Dihydro-1,4-diarsinine-2,3,5,6-tetracarboxylic acid dianhydride (***cis*-2**) was quantitatively formed from *cis*-1,4-dihydro-1,4-dimethyl-2,3,5,6-tetrakis(*t*-butoxycarbonyl)-1,4-diarsinine (***cis*-1**) treated with formic acid as a Brønsted acid.[9] After the removal of formic acid under reduced pressure and extracted with $CHCl_3$, the solvent was removed to yield a yellow solid. Although ***cis*-1** contained no *trans*-isomer according to ^{1}H NMR analysis, the product afforded one sharp resonance for As-Me at 1.81 ppm and one minor resonance at 1.67 ppm. Since the peak assigned to the methyl groups on the arsenic atom for ***trans*-1** shifted to an upfield compared with that for ***cis*-1**, which may be due to increase the electron density of the methyl groups on the arsenic atom, the later resonance might due to a ***trans*-2**. The

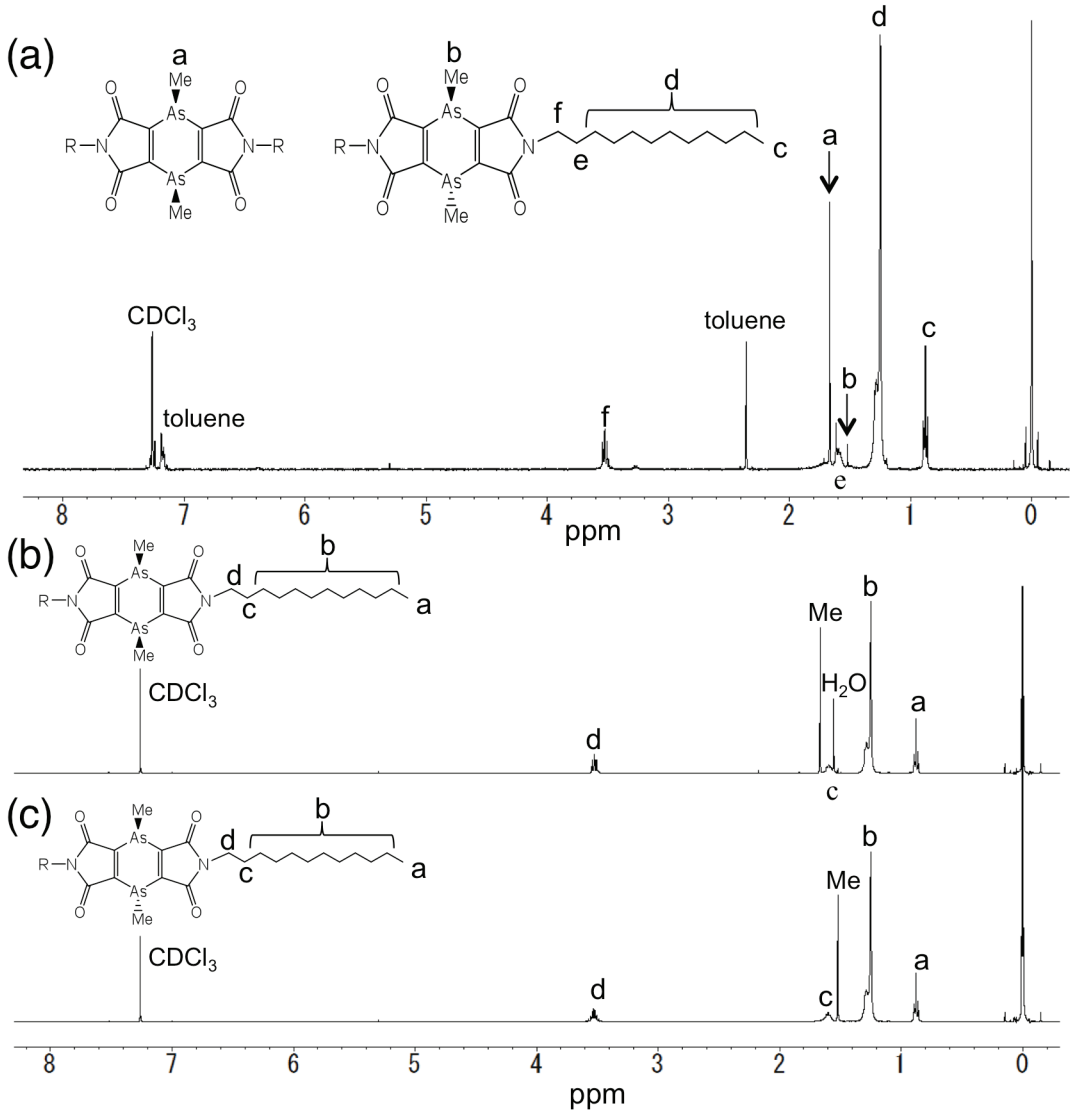


Figure 1. ^{1}H NMR spectra of the reaction mixture of ***cis*-2** with *n*-dodecylamine (a), isolated ***cis*-3a** (b) and ***trans*-3a** (c) in $CDCl_3$

integrated area for these peaks suggests that the sample contains 5 mol% of the *trans*-isomer. When isolated ***cis*-2** was dissolved in toluene and reflux for 24 h, increase of the peak corresponding to the *trans*-isomer was not observed. This result suggests that no isomerization proceeded under heating condition. Formic acid may contribute for the stereoisomerization.

Imidation reaction of ***cis*-2** with *n*-dodecylamine and aniline was studied. After the reaction with *n*-dodecylamine for 6 h in toluene under reflux, the solvent was removed under reduced pressure. The ^{1}H NMR and FT-IR analysis of the residue showed quantitative conversion to an imide structure. The ^{1}H NMR analysis shows one sharp resonance for As-Me at 1.67 ppm and one minor resonance at 1.52 ppm were observed. The later resonance might due to the *trans*-isomer of ***cis*-3a**. The integrated area for these peaks suggests that the sample contains 12 mol% of the *trans*-isomer. In the case of using aniline, ^{1}H NMR analysis of the residue after the reaction for 6 h shows no ***cis*-3b** but other peaks corresponding to the amic acid. The degree of the imidation is 40%. After the reaction for 24 h, the imidation was completely occurred. The ^{1}H NMR analysis shows one sharp resonance for As-Me at 1.79 ppm and one minor resonance at 1.65 ppm were observed. The later resonance might due to the *trans*-isomer of ***cis*-3b**. The integrated area for these peaks suggests that the sample contains 11 mol% of the *trans*-isomer. These results suggest that stereoisomerization from the *cis*-isomers to the *trans*-isomers occurred during the imidation.

Repeating recrystallization for the products from *n*-dodecylamine and aniline gave pure *cis*-isomers as yellow crystals in 66% and 45% and (***cis*-3a** and ***cis*-3b**), respectively. The structures of both the crystals were established by ^{1}H and ^{13}C NMR, MASS spectrometry, and elemental analysis. Although preparation of single crystals of ***cis*-3a** suitable for X-ray crystallography was failed, the stereochemical structure of ***cis*-3b** was determined by X-ray crystallography. The X-ray crystallography shows that the six-membered ring for ***cis*-3b** was a boat form and one methyl group on the arsenic atom is in an equatorial position as shown in Figure 2.

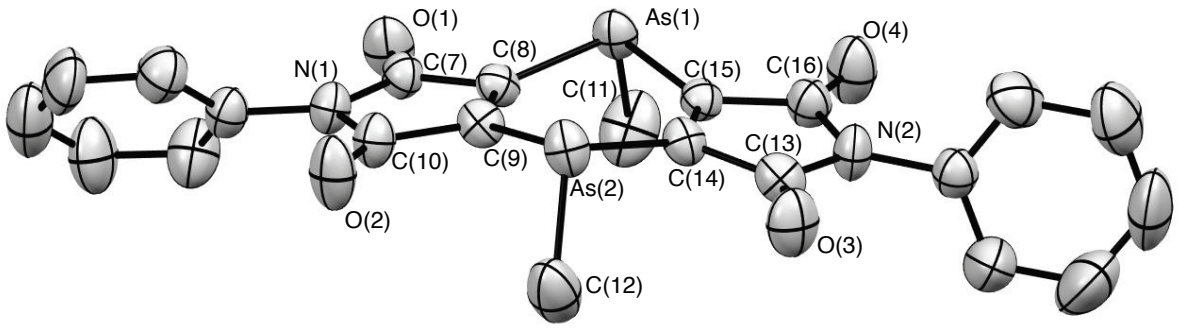


Figure 2. ORTEP diagrams of ***cis*-3b** with thermal ellipsoids shown at the 50% probability level

The solvent was removed from the pale yellow filtrates of ***cis*-3a** after the recrystallization, and the residue was recrystallized from CH_2Cl_2 and methanol for the further purification. After the recrystallization process was repeated for 7 times, a yellow single crystal was obtained in 7% yield. The ^{1}H NMR analysis of the crystals shows no resonance for As-Me of ***cis*-3a** at 1.79 ppm and only the resonance at 1.65 ppm, suggesting ***trans*-3a** was isolated. The structure of ***trans*-3a** was confirmed by ^{13}C NMR, MASS spectrometry, and elemental analysis. The stereochemical structure of ***trans*-3a** was determined by X-ray crystallography. The X-ray crystallography shows that the six-membered ring for ***trans*-3a** was a chair form and was a nearly flat as shown in Figure 3.

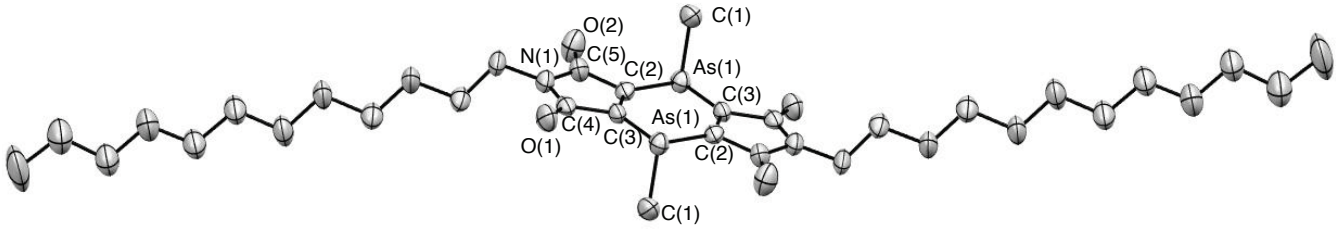


Figure 3. ORTEP diagrams of ***trans*-3a** with thermal ellipsoids shown at the 50% probability level

After ***cis*-3a** was dissolved in $CDCl_3$ for measuring ^{1}H NMR analysis, the solvent was immediately removed under reduced pressure at room temperature. The residue was again dissolved in $CDCl_3$ and carried out ^{1}H NMR analysis. We found that one minor resonance at 1.52 ppm corresponding to the *trans*-isomer appeared in addition to one sharp resonance for As-Me at 1.67 ppm. Therefor, we studied this unique *cis-trans* isomerization behavior by repeating the concentration and dissolution process. Figure 4 shows a plot of molar ratios of ***trans*-3a** estimated by ^{1}H NMR analysis against the cycle numbers of concentration and dissolution process at room temperature. Repeating this concentration and dissolution process increased the molar ratios of ***trans*-3a** and quantitative transformation to the *trans*-form proceeded after repeating the cycles for 13 times. The same experiment was performed using ***cis*-3b** and results were also shown in Figure 4. We found that transformation to the *trans*-form also proceeded, the molar ratio of the *trans*-form reached 95% after repeating the cycles for 13 times and no increase the molar ratio was observed even further repeating the cycles. To elucidate solvent effect, 1 mg of **3a** including 30 mol% *trans*-form was dissolved in 1 mL of solvents, i.e., chloroform, toluene, ethyl acetate, and acetone, and the solvents were removed under reduced pressure at room temperature. The molar ratios of the *trans*-form of the residues from chloroform, toluene, ethyl acetate, and acetone increased to 39, 43, 45, and 40 mol%, respectively. These results reveal that the stereoisomerization from the *cis*-isomers to the *trans*-isomers is independent on the solvents.

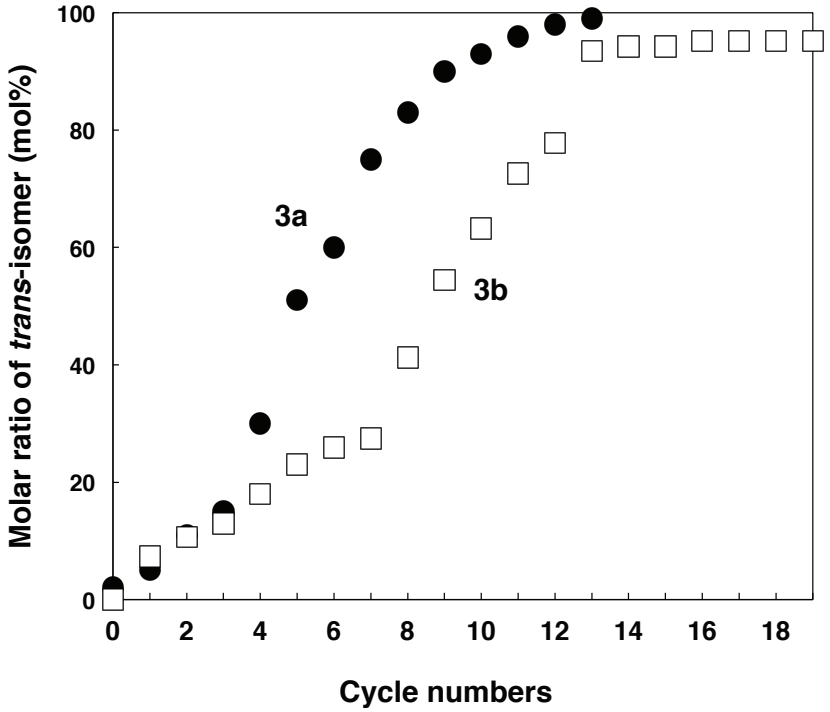


Figure 4. Plots of molar ratios of ***trans*-3a** and ***trans*-3b** determined from ^{1}H NMR analysis against the cycle numbers of dissolution in $CDCl_3$ and concentration

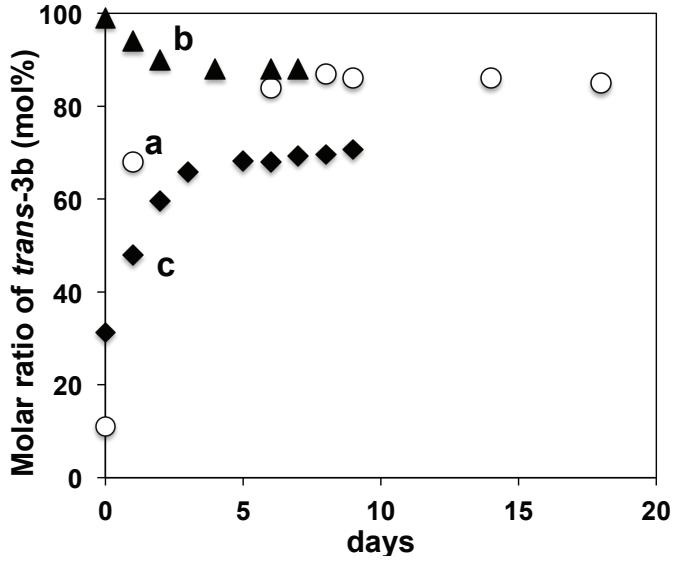


Figure 5. Plots of molar ratios of ***trans*-3a** determined from ^{1}H NMR analysis after (a) ***cis*-3a** and (b) ***trans*-3a** were dissolved in $CDCl_3$, and (c) ***cis*-3a** in acetone-d_6 incubated at room temperature

Although ***cis*-3a** contained minor amounts of the *trans*-isomer according to ^{1}H NMR analysis immediately after dissolving in $CDCl_3$, significant large intensity of the resonance at 1.52 ppm corresponding to the *trans*-isomer were observed in addition to the resonance for As-Me at 1.67 ppm after keeping the solution at room temperature for 4 days. After 8 days incubation, stereoisomerization of ***cis*-3a** to the *trans*-isomer reached at 86 mol% as shown in Figure 5. When ***trans*-3a** was dissolved in

$CDCl_3$ for measuring ^1H NMR analysis, no *cis*-isomer was observed immediately after dissolving in $CDCl_3$. After keeping the solution at room temperature for 4 days, the sharp resonance at 1.67 ppm corresponding to the *cis*-isomer were observed in addition to one sharp resonance for As-Me at 1.52 ppm. After 8 days incubation, stereoisomerization of ***trans*-3a** to the *cis*-isomer also reached at the same ratio of that of starting from the *cis*-isomer as shown in Figure 5. These observations suggest that *cis*, *trans*-isomerization of ***cis*-3a** and ***trans*-3a** proceeded at room temperature in solution. When ***cis*-3a** was dissolved in acetone-d_6 for measuring ^1H NMR analysis, stereoisomerization of ***cis*-3a** to the *trans*-isomer also proceed as the case in $CDCl_3$ and reached at 64 mol%. The present *cis*, *trans*-isomerization may proceed through thermodynamic control. On the other hand, repeating the concentration and dissolution process as shown in Figure 4 may involve some kinetic control process.

After the reaction of ***cis*-2** with aniline for 6 h in toluene under reflux, the solvent was removed under reduced pressure. After the product was repeated the cycle numbers of concentration and dissolution process for several times, the obtained yellow residue was recrystallized from CH_2Cl_2 / MeOH to yield a yellow crystal in 48% yield. The ^1H NMR analysis of the crystals shows no resonance for As-Me of ***cis*-3b** at 1.79 ppm and only the resonance at 1.65 ppm, suggesting ***trans*-3b** was isolated. The structure of ***trans*-3b** was confirmed by ^{13}C NMR, MASS spectrometry, and elemental analysis. The stereochemical structure of ***trans*-3b** was determined by X-ray crystallography. The X-ray crystallography suggests the six-membered ring for ***trans*-3b** was a chair form and was a nearly flat as shown in Figure 6.

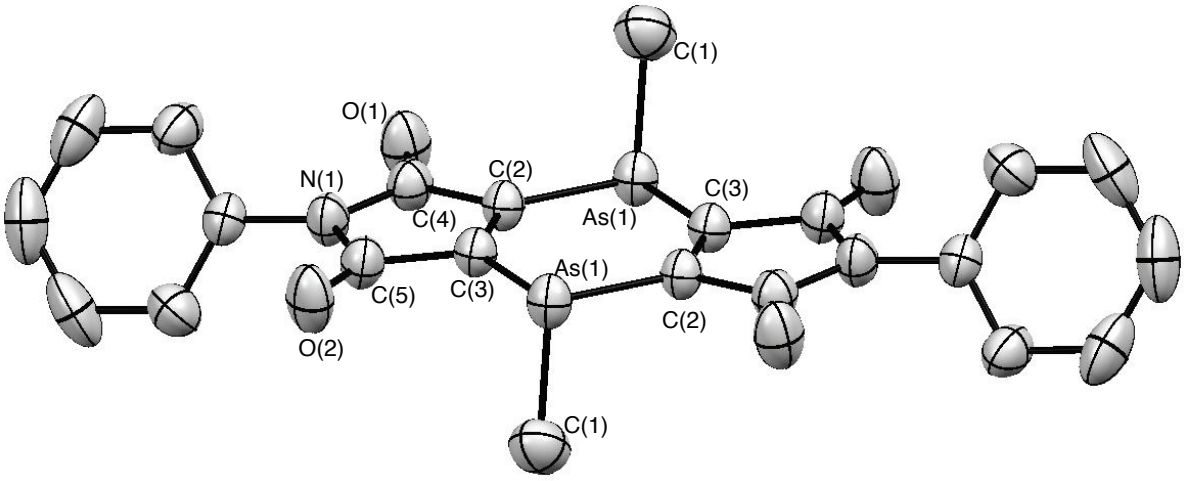


Figure 6. ORTEP diagram of ***trans*-3b** with thermal ellipsoids shown at the 50% probability level

A selection of bond lengths and angles for the three crystals is summarized in Table 1. The interior angles at around the arsenic atoms of the six-membered rings in ***cis*-3b** and ***trans*-3b** are 94.2(3)° and 94.26(8)°, respectively, suggesting both the lone pairs on the arsenic atoms have the *s* character. Although a usual bond angle at the sp^2 hybridized carbon is 120°, the As-C=C bond angles extended to over 130°. The

As-As distance in the six-membered rings for ***trans*-3b** (3.9684(3) Å) was longer than that for ***cis*-3b** (3.894(2) Å). Dihedral angles of the six-membered rings of ***cis*-3b** and ***trans*-3b** are 12.99° and 5.24°, respectively. These results indicate that the six-membered ring for the *trans*-isomer is flatter than that of the *cis*-isomer. The As-As distance and dihedral angle in the six-membered ring for ***trans*-3a** are 3.9701(6) Å and 3.37°, respectively. These values are very close to those for ***trans*-3b**.

Table 1. Selected Distances (Å) and Angle (deg) of the frame of ***trans*-3b**, ***cis*-3b**, and ***trans*-3a**

	***trans*-3a**		***cis*-3b**		***trans*-3b**	
α [°]	C(2)As(1)C(3)-C(2)C(3)C(2)C(3)	3.37	C(8)As(1)C(15)-C(8)C(9)C(14)C(15)	12.99	C(2)As(1)C(3)-C(2)C(3)C(2)C(3)	5.24
β [°]			C(9)As(2)C(14)-C(8)C(9)C(14)C(15)	14.72		
C-As-C [°]	C(2)-As(1)-C(3)	94.5(1)	C(15)-As(1)-C(8)	94.2(3)	C(2)-As(1)-C(3)	94.26(8)
			C(9)-As(2)-C(14)	93.9(3)		
As-C=C [°]	As(1)-C(2)-C(3)	133.1(3)	As(1)-C(8)-C(9)	131.7(5)	As(1)-C(2)-C(3)	132.0(2)
	As(1)-C(3)-C(2)	132.3(3)	As(1)-C(15)-C(14)	131.6(5)	As(1)-C(3)-C(2)	133.3(2)
			As(2)-C(9)-C(8)	131.5(5)		
			As(2)-C(14)-C(15)	131.0(6)		
As-As [Å]	As(1)-As(1)	3.9701(6)	As(1)-As(2)	3.894(2)	As(1)-As(1)	3.9686(3)
As-C [Å]	As(1)-C(2)	1.936(3)	As(1)-C(8)	1.927(6)	As(1)-C(2)	1.935(3)
	As(1)-C(3)	1.931(4)	As(1)-C(15)	1.928(7)	As(1)-C(3)	1.939(2)
			As(2)-C(9)	1.941(7)		
			As(2)-C(14)	1.928(8)		
C=C [Å]	C(2)-C(3)	1.346(5)	C(8)-C(9)	1.325(9)	C(2)-C(3)	1.337(3)
			C(15)-C(14)	1.35(1)		

The UV-vis absorption spectra of ***cis*-3a** and ***trans*-3a** in CH_2Cl_2 showed long-wavelength absorption maxima due to intramoleular charge-transfer bands at 340 nm (3295 M^{-1} cm^{-1}) and 370 nm (802 M^{-1} cm^{-1}), respectively (Figure 7). The UV-vis absorption spectra also show π- π* transition at 286 nm (7398 M^{-1}

cm^{-1}) and 292 nm (2614 M^{-1} cm^{-1}), respectively. The conjugation system of the nearly flat six-membered ring of ***trans*-3a** affected the longer absorption wavelength. The UV-vis absorption spectra of ***cis*-1** and ***trans*-1** in CH_2Cl_2 showed long-wavelength absorption maxima at 272 nm (11000 M^{-1} cm^{-1}) and 300 nm (5200 M^{-1} cm^{-1}), respectively, derived from intramolecular charge-transfer.[7b] The π- π* transitions for ***cis*-3a** and ***trans*-3a** are similar as those of ***cis*-1** and ***trans*-1**.

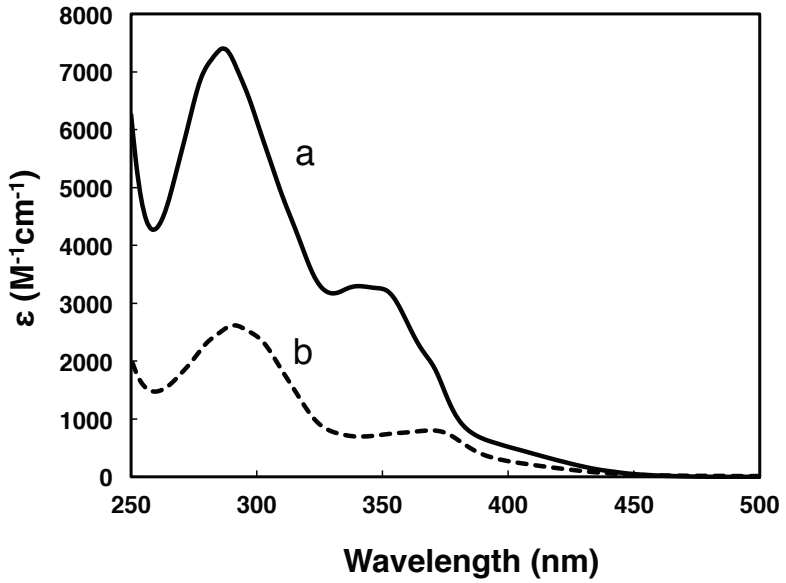


Figure 7. UV-vis absorption spectra of (a) ***cis*-3a** and (b) ***trans*-3a** in CH_2Cl_2

To elucidate the thermodynamical stability for *cis*-, *trans*- and transition-state forms of 1,4-dihydro-1,4-dimethyl-1,4-diarsininetetracarboxylic acid diimides, DFT calculations of *N*,*N*'-dimethyl-1,4-dihydro-1,4-diarsininetetracarboxylic acid diimide (**3c**) were carried out at B3LYP/6-31G** level using the Gaussian 09 program package (Figure 8).[10] The relative energy of the transition state is 31.57 kcal mol^{-1} higher than that of the *cis*-form. Inversion barrier is comparable to the tertiary arsine derivatives previously reported.[2-4] This value suggests inversion of the compound from the *cis*-isomer to the *trans*-isomer via the transition state hardly proceeds under room temperature. The relative energy of the *trans*-form is 0.77 kcal mol^{-1} higher than that of the *cis*-form, suggesting that the *cis*-form is thermodynamically stable than the *trans*-form. Based on the DFT calculations, the present *cis*, *trans*-isomerization is unexpected and the mechanism is still unknown.

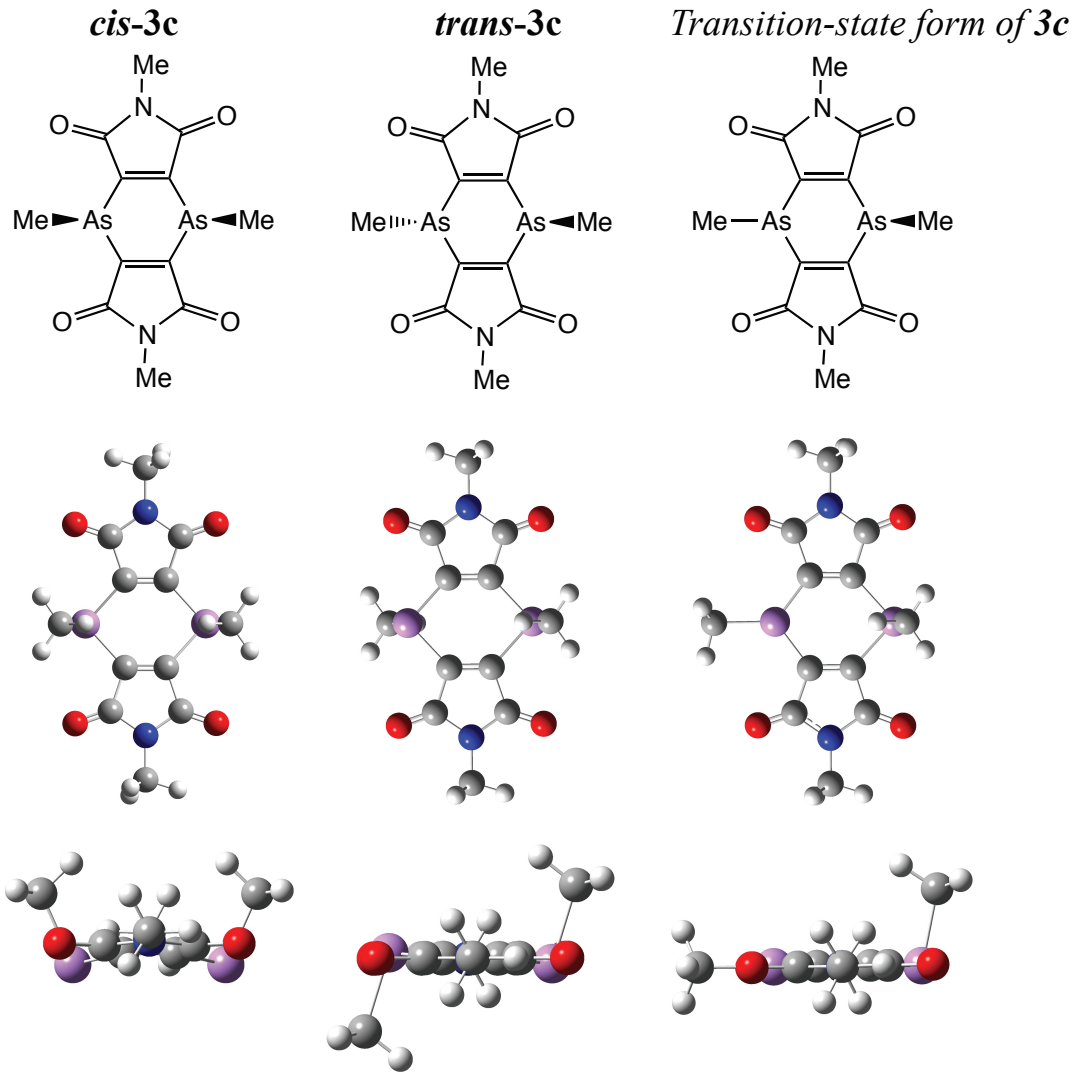


Figure 8. Chemical (top) and the optimized structures of top (middle) and side (bottom) views of ***cis*-3c**, ***trans*-3c**, and the transition-state form of **3c**

CONCLUSION

It has been accepted that tertiary arsine centers are configurationally stable under the non-acidic conditions employed, because inversion barrier for trivalent arsine centers is high enough to keep the stereochemical structures at room temperature. In this study, we found that racemization *cis*, *trans*-isomerization of 1,4-dihydro-1,4-dimethyl-1,4-diarsininetetracarboxylic acid diimides (**3**) proceeded in solution even at room temperature. DFT calculations using neutral *N*,*N*'-dimethyl-1,4-dihydro-1,4-diarsininetetracarboxylic acid diimide (**3c**) suggest inversion of the compound from the *cis*-isomer to *trans*-isomer hardly proceed under room temperature. Although the mechanism of the present unique *cis*, *trans*-isomerization is still unknown, both the *cis* and *trans*-forms are regarded as unique and rigid building blocks, which will produce well-defined crystal structures and polymeric structures such as macrocycles, networks or cages by supramolecular self-assembly with metal ions.

EXPERIMENTAL

Materials. Unless otherwise noted, all reagents and chemicals were purchased from commercial sources and used without further purification. 1,4-Dihydro-1,4-diarsininetetracarboxylic acid dianhydride (**2**) was prepared as described in the literature.[9]

Equipment. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL EX400 spectrometer, and samples were analyzed in $CDCl_3$ using tetramethylsilane as an internal standard. UV-vis spectra were obtained on a SHIMADZU UV-3600 spectrophotometer, and samples were analyzed in CH_2Cl_2 at room temperature. Elemental analysis was performed at the Microanalytical Center of Kyoto University. High-resolution mass spectra (HR MS) were obtained on a JEOL JMS-SX102A spectrometer. All procedures were performed under nitrogen or argon atmosphere.

***N*,*N*'-Bis-*n*-dodecyl-*cis*-1,4-dihydro-1,4-diarsininetetracarboxylic acid diimide (*cis*-3a).** 1,4-Dihydro-1,4-diarsininetetracarboxylic acid dianhydride (**2**) (101 mg, 0.272 mmol) and *n*-dodecylamine (101 mg, 0.554 mmol) was dissolved in toluene (2 mL) and heated at 120 ˚C for 6 h. After the solvent and unreacted aniline were removed under reduced pressure, the residue was dissolved in CH_2Cl_2 and was added MeOH to crystallized a yellow crystal. Yield was 66%. ^{1}H NMR ($CDCl_3$): δ 3.53 (t, J = 7.2 Hz, 2H); 1.67 (s, 3H); 1.60 (br, 2H); 1.25 (br, 18H); 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 169.86; 149.35; 38.68; 31.92; 29.62; 29.56; 29.48; 29.35; 29.11; 28.55; 26.79; 22.69; 14.13; 10.80. FT-IR(KBr): 1759 cm^{-1}, 1698 cm^{-1} (C=O). FAB-HR-MS, *m/z*: calcd, 707.2705 $[M+H]^+$; found, 707.2750. Anal. Calcd for $C_{34}H_{56}As_2N_2O_4$: C, 57.79; H, 7.99; N, 3.96. Found: C, 57.80; H, 8.15; N, 3.81.

***N*,*N*'-Bis-*n*-dodecyl-*trans*-1,4-dihydro-1,4-diarsininetetracarboxylic acid diimide (*trans*-3a).** The solvent of the pale yellow filtrate of recrystallization of ***cis*-3b** was removed, and the residue was recrystallized from CH_2Cl_2 and MeOH to give a pale yellow crystal. After the recrystallization process was repeated for 7 times, a yellow crystal was obtained. Yield was 7%. ^{1}H NMR ($CDCl_3$): δ 3.53 (m, 2H); 1.52 (s, 3H); 1.60 (br, 2H); 1.25 (br, 18H); 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 170.46; 152.95; 38.72; 31.92; 29.63; 29.56; 29.47; 29.35; 29.10; 28.54; 26.80; 22.69; 14.13; 11.17. FT-IR(KBr): 1762 cm^{-1}, 1704 cm^{-1} (C=O). FAB-HR-MS; *m/z* calcd for $[M+H]^+$ 707.2752; found 707.2745. Anal. Calcd for $C_{34}H_{56}As_2N_2O_4$: C, 57.79; H, 7.99; N, 3.96. Found: C, 58.03; H, 8.18; N, 3.77.

***N*,*N*'-Diphenyl-*cis*-1,4-dihydro-1,4-diarsininetetracarboxylic acid diimide (*cis*-3b).** 1,4-Dihydro-1,4-diarsininetetracarboxylic acid dianhydride (**2**) (372 mg, 1.00 mmol) and aniline (274 mg, 2.73 mmol) was dissolved in toluene (15 mL) and refluxed for 24 h. After the solvent was removed under reduced pressure, the residue was dissolved in CH_2Cl_2 and was added MeOH to crystallized a yellow crystal, which was dissolved in CH_2Cl_2 and added MeOH to recrystallize again to yield. Yield: 45%. ^{1}H NMR ($CDCl_3$) δ: 7.51-7.37 (m, 5H); 1.79 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 168.53; 149.90; 131.41; 129.21; 127.99; 125.63; 10,87. FT-IR(KBr): 1759 cm^{-1}, 1700 cm^{-1} (C=O), 1382 cm^{-1} (CN). HR FAB-MS: *m/z*

calcd for $[M]^+$ 521.9542; found 521.9545. Anal. Calcd for $C_{22}H_{16}As_2N_2O_4$: C, 50.60; H, 3.09. Found: C, 50.43; H, 2.93.

***N*,*N*'-Diphenyl-*trans*-1,4-dihydro-1,4-diarsininetetracarboxylic acid diimide (*trans*-3b).** 1,4-Dihydro-1,4-diarsininetetracarboxylic acid dianhydride (**2**) (85.2 mg, 0.229 mmol) and aniline (42.6 mg, 0.458 mmol) was dissolved in toluene (2.5 mL) and refluxed for 24 h. After the solvent was removed under reduced pressure, the residue was recrystallized from CH_2Cl_2 / MeOH to give a yellow crystal, which was dissolved in CH_2Cl_2 and evaporated for several time. Then the obtained yellow crystal was recrystallized from CH_2Cl_2 / MeOH to yield a yellow crystal. Yield was 48.6%. ^{1}H NMR ($CDCl_3$) δ: 7.52-7.37 (m, 5H); 1.65 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 169.12; 153.44; 131.43; 129.21; 128.02; 125.63; 11.24. HR EI-MS: *m*/*z* calcd for $[M+H]^+$ 522.9620; found 522.9630. Anal. Calcd for $C_{22}H_{16}As_2N_2O_4$: C, 50.60; H, 3.09; N, 5.36. Found: C, 50.59; H, 3.17; N, 5.47.

X-Ray crystal structure analysis. The single crystal was mounted on glass fibres with epoxy resin. Intensity data were collected at room temperature on a Rigaku RAXIS RAPID II imaging plate area detector with graphite monochromated Mo-Ka radiation. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. The data were collected at room temperature to a maximum 2q value of 55.0°. Data were processed by the PROCESS-AUTO[11] program package. An empirical or numerical absorption correction[12] was applied. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction[13] was applied. The structure was solved by heavy-atom Patterson methods[14] and expanded using Fourier techniques.[15] Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on observed reflections and variable parameters. In the case of the crystalline product recrystallized from acetone, the final cycle of full-matrix least-squares refinement on F was based on observed reflections and variable parameters. All calculations were performed using the CrystalStructure[16,17] crystallographic software package. Crystal data and more information on X-ray data collection are summarized in Table 2. Deposition numbers CCDC-1536581, 1536582, and 1536580 for ***trans*-3a**, ***cis*-3b**, and ***trans*-3b**, respectively. Free copies of the data can be obtained via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 2. Crystallographic data and refinement parameters

	***trans*-3a**	***cis*-3b**	***trans*-3b**
Empirical formula	$C_{34}H_{56}As_2N_2O_4$	$C_{22}H_{16}As_2N_2O_4$	$C_{22}H_{16}As_2N_2O_4$
Formula weight	706.67	522.22	522.22
Crystal system	triclinic	orthorhombic	monoclinic
Space group	*P*-1	$Pca2_1$	$P2_1/c$
a (Å)	5.5599(3)	8.8198(3)	9.3943(3)
b (Å)	7.0989(3)	9.1398(4)	9.1874(3)
c (Å)	23.4805(12)	26.7294(8)	12.0057(5)
α (deg)	87.8497(14)	90	90
β (deg)	82.1052(15)	90	91.7284(11)
γ (deg)	88.7185(12)	90	90
V ($Å^3$)	917.18(7)	2154.69(13)	1035.73(6)
Z	1	4	2
D_{calc} (g cm^{-3})	1.279	1.610	1.674
μ (mm^{-1})	1.858	3.133	3.259
T (K)	296	296	296
Reflections collected	9082	19858	10086
Independent reflections (R_{int})	4152(0.0358)	4749(0.046)	2350(0.0293)
Observed reflections [$I>2\sigma(I)$]	3012	2939	1920
Parameters	216	287	144
T_{max}/T_{min}	0.629/0.373	0.391/0.301	0.521/0.309
Residual density ($eÅ^{-3}$)	0.81/-0.69	0.63/-0.47	0.475/-0.365
R_1	0.0400	0.0447	0.0255
wR_2	0.1482	0.1171	0.0687
GOF	1.164	1.011	1.002

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