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[N](3,5)ISOXAZOLOPHANES: DYNAMIC BEHAVIOR AND REACTION WITH ELECTRON-DEFICIENT ACETYLENE LEADING TO [N](2,6)PYRIDINOPHANES

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Abstract--^{1}H NMR spectroscopy at various temperatures clarified the dynamic behavior of the oligomethylene chains for [8](3,5)isoxazolophane (**1**) and unsubstituted and 4-methyl-substituted [9](3,5)-isoxazolophanes (**2a,b**). The energy barriers ($\Delta G_c^{\ddagger}$) for the bridge flipping are 18.6 kcalmol^{-1} (T_c 100 ℃) for **1** and 11.5 kcalmol^{-1} (T_c -10 ℃) for **2a**. Compound (**2b**) does not undergo bridge flipping in temperatures ranging from 25 ℃ to 150 ℃. The energy barriers for the pseudorotation are 11.1-11.2 kcalmol^{-1} (T_c -10 ℃), 9.1 kcalmol^{-1} (T_c -70 ℃), and 8.6 kcalmol^{-1} (T_c -80 ℃) for **1**, **2a**, and **2b**, respectively. The $Mo(CO)_6$-induced reaction of **2a,b** with dimethyl acetylenedicarboxylate afforded [9](2,6)pyridinophane derivatives, *albeit in* low yields.

In the field of heterocyclic [n]paracyclophanes,[1-3] the smallest known member is [6](2,5)pyridinophane.[1] Although cyclophane chemistry has now been extended to include five-membered heterocycles[4] and the dynamic behavior of [8](2,5)heterophanes (**3a-c**)[5-7] and [7](2,4)- or [7](3,5)heterophanes (**4a-c**)[8] has been investigated, the dynamic behavior of [n](3,5)isoxazolophanes has not been studied.[9] In continuation of previous studies of pyridinophanes[1,10-13] as well as (vinylimino)phosphoranes,[14] we have synthesized new [8](3,5)isoxazolophane (**1**) and the known [9](3,5)isoxazolophane (**2a**),[9] which

1: n=8; R=H
2a: n=9; R=H **2b**: n=9; R=Me

3a: X=O
3b: X=S
3c: X=NR

4a: Z=N; X=NH
4b: Z=MeC; X=S
4c: Z=MeC; X=NH

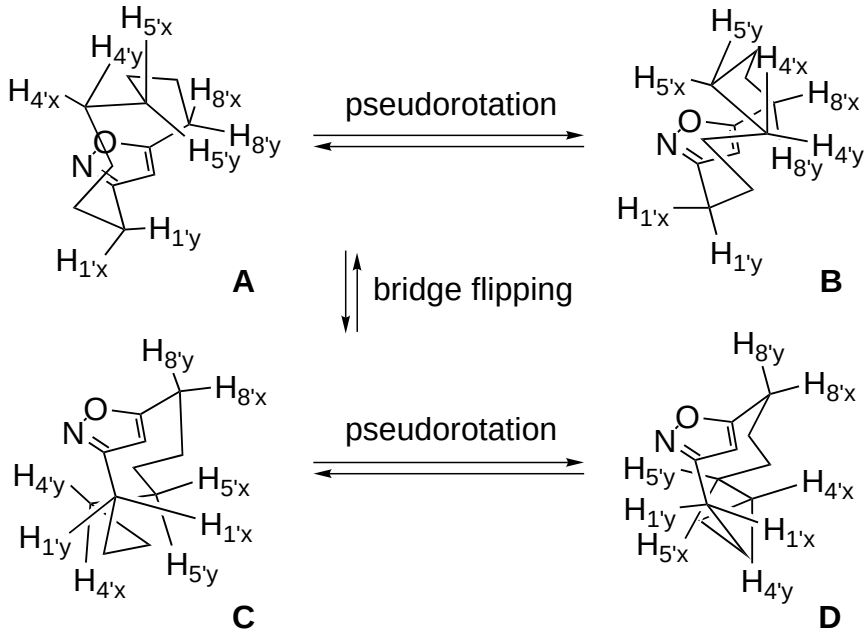
9a: R=H
9b: R=Me

Scheme 1.

was prepared through 2-cyclododecenone oxime or 2-cyclododecynone oxime, by the reaction of 3-chloro-2-cyclododecenone with NaN_3, respectively, (Scheme 1).[13] Thus, we have studied the dynamic behavior of [n](3,5)isoxazolophanes (**1**) and (**2a,b**) for the first time. Furthermore, 3,5-disubstituted isoxazoles and 4,5-polymethylene-substituted isoxazoles were clarified to react with dimethyl acetylenedicarboxylate (DMAD) in the presence of $Mo(CO)_6$ to give substituted pyridines[15] and [n](2,5)pyridinophanes (n = 9-6).[1] In exploration of methodology for synthesizing [n](2,6)pyridinophanes,[13] we studied the $Mo(CO)_6$-induced reaction of **2a,b** with DMAD to give [9](2,6)pyridinophanes, *albeit in* low yield. We report herein the results in detail.

The compounds (**1**) and (**2a**) were prepared as described previously,[13] and 4-methyl-substituted [9](3,5)isoxazolophane (**2b**) is prepared according to the procedure described in the literature.[16] ^{1}H NMR spectral data of **1** and **2a,b** are summarized in Table 1.

The MM2, MNDO, AM1, and PM3 calculations suggest that [8](3,5)isoxazolophane (**1**) exists in two stable conformers **A** [**C**] and **B** [**D**] in Scheme 2.[17,18] The calculated total energy and the heat of formations ($\Delta H_f°$) obtained by several methods are listed in Table 2. Thus, ^{1}H NMR spectroscopy is conducted at various temperatures to clarify the dynamic behavior of **1**. The signals of four methylene protons at "benzylic-type" positions, $H_{1'}$ and $H_{8'}$ (see the convenient numbering shown in



Scheme 2.

Table 1. ^{1}H NMR spectral data of [n](3,5)isoxazolophanes (**1**) and (**2a,b**) at 25 ℃[a]

Compd.	Solvent	δH_4	Benzylic-type $\delta H_{1'}$ and $\delta H_{n'}$	Remaining methylene bridge
1	CD_2Cl_2[b]	6.09	2.49 (1H, ddd, J=13.3, 9.3, 5.2), 2.58 (1H, ddd, J=13.9, 11.7, 4.9), 2.79 (1H, dt, J=13.3, 5.4), 2.85 (1H, dt, J=13.9, 4.4)	-0.02 (1H, br s),[d] 0.45 (1H, br s),[d] 0.85-0.95 (1H, m), 0.97-1.09 (2H, m), 1.18-1.34 (4H, m), 1.41-1.51 (1H, m), 1.81-1.90 (2H, m)
	DMSO-d_6[c]	6.47	2.45-2.55 (1H, m),[d,e] 2.61 (1H, ddd, J=13.8, 10.7, 5.6),[d] 2.67 (1H, dt, J=13.4, 5.3),[d] 2.77 (1H, dt, J=13.8, 4.3)[d]	-0.10 (1H, br s), 0.38 (1H, br s), 0.78-1.47 (8H, m), 1.75-1.92 (2H, m)
2a	CD_2Cl_2[b]	6.04	2.60 (2H, t, J=6.2), 2.72 (2H, t, J=6.2)	0.44 (2H, br s),[d] 1.00-1.10 (4H, m), 1.18-1.21 (2H, m), 1.23-1.29 (2H, m), 1.53-1.60 (2H, m), 1.64 (2H, quint, J=6.2)
2b	CD_2Cl_2[b]	2.02[f]	2.54 (1H, ddd, J=13.5, 12.5, 4.6), 2.66 (1H, ddd, J=14.3, 9.9, 4.3), 2.69 (1H, dt, J=13.5, 4.0), 2.73 (1H, dt, J=14.3, 5.0)	-0.16--0.04 (1H, m),[d] 0.76-0.91 (3H, m), 0.98-1.08 (3H, m), 1.08-1.17 (1H, m), 1.29-1.39 (2H, m), 1.44-1.57 (2H, m), 1.66-1.80 (2H, m)
	DMSO-d_6[c]	2.01[f]	2.42 (1H, ddd, J=13.2, 12.6, 4.5), 2.66 (1H, dt, J=14.3, 5.3), 2.72 (1H, dt, J=13.2, 4.0), 2.74 (1H, ddd, J=14.3, 9.5, 4.9)	-0.28--0.07 (1H, m), 0.65-0.91 (3H, m), 0.92-1.11 (4H, m), 1.19-1.52 (4H, m), 1.60-1.80 (2H, m)

a. J-Values are given in Hz. b. Recorded on 500 MHz spectrometer. c. Recorded on 270 MHz spectrometer. d. Used for $\Delta G_c^{\ddagger}$ determination. e. Overlapping with signals of DMSO-d_6. f. Signal of methyl group.

Scheme 2), appear at different chemical shifts, δ 2.77, δ 2.67, δ 2.61, and δ 2.45-2.55, in DMSO-d_6 (Table 1), suggesting that the bridge flipping of the octamethylene chain is frozen. An increase in temperature to 100 ℃ (T_c) provided clear indication of coalescence of the benzylic-type protons, which reappeared at δ 2.74 ($H_{1'}$ or $H_{8'}$) and 2.63 ($H_{8'}$ or $H_{1'}$) as a couple of triplets at 150 ℃. This feature has

a resemblance to those of **3a-c**.[5] Consequently, the coalescence temperature method[19] estimated that the energy barrier ($\Delta G_c^{\ddagger}$) for the bridge flipping of the octamethylene chain of **1** (**A**, **B** $\rightleftarrows$ **C**, **D** in Scheme 2) is 18.6 kcalmol^{-1} (Table 3). In addition, the conformation of **1** is not fixed in either conformer **A** or **B** [**C** or **D**] at room temperature and a rapid equilibrium between **A** and **B** [**C** and **D**] would exist due to the pseudorotation. Two proton signals (in CD_2Cl_2, Table 1) at δ 0.45 (δ_{av} of $H_{4'x}$ for **A** and **B** or δ_{av} of $H_{5'x}$ for **A** and **B** [δ_{av} of $H_{4'y}$ for **C** and **D** or δ_{av} of $H_{5'y}$ for **C** and **D**]) and δ -0.02 (δ_{av} of $H_{5'x}$ for **A** and **B** or δ_{av} of $H_{4'x}$ of **A** and **B** [δ_{av} of $H_{5'y}$ for **C** and **D** or δ_{av} of $H_{4'y}$ for **C** and **D**]) disappeared at -10 ℃, and reappeared at δ -1.00 ($H_{4'x}$ for **A** or $H_{5'x}$ for **B** [$H_{4'y}$ for **C** or $H_{5'y}$ for **D**]) as of 0.53H intensity and δ -1.22 ($H_{5'x}$ for **B** or $H_{4'x}$ for **A** [$H_{5'y}$ for **D** or $H_{4'y}$ for **C**]) as of 0.47H intensity at -90 ℃. The signals of the counterparts expected to appear at δ 2.09 ($H_{4'x}$ for **B** or $H_{5'x}$ for **A** [$H_{4'y}$ for **D** or $H_{5'y}$ for **C**]) and δ 1.04 ($H_{5'x}$ for **A** or $H_{4'x}$ for **B** [$H_{5'y}$ for **C** or $H_{4'y}$ for **D**]), respectively, are not observed because they are hidden behind the other signals of the aliphatic protons. At this temperature the pseudorotation is stopped. These findings are in accordance with the results found for [8](2,5)thiophenophane, which shows similar phenomena in the dynamic ^{1}H NMR study.[6,7] Consequently, the energy barrier ($\Delta G_c^{\ddagger}$) of the conformational change (pseudorotation) between **A** and **B** [**C** and **D**] was estimated to be 11.1-11.2 kcalmol^{-1}, and the free energy difference (ΔG) between **A** and **B** [**C** and **D**] was estimated to be 0.04 kcalmol^{-1} (Table 3), which seems to support the calculated values (Table 2) and existence of the two stable conformations of **1**.

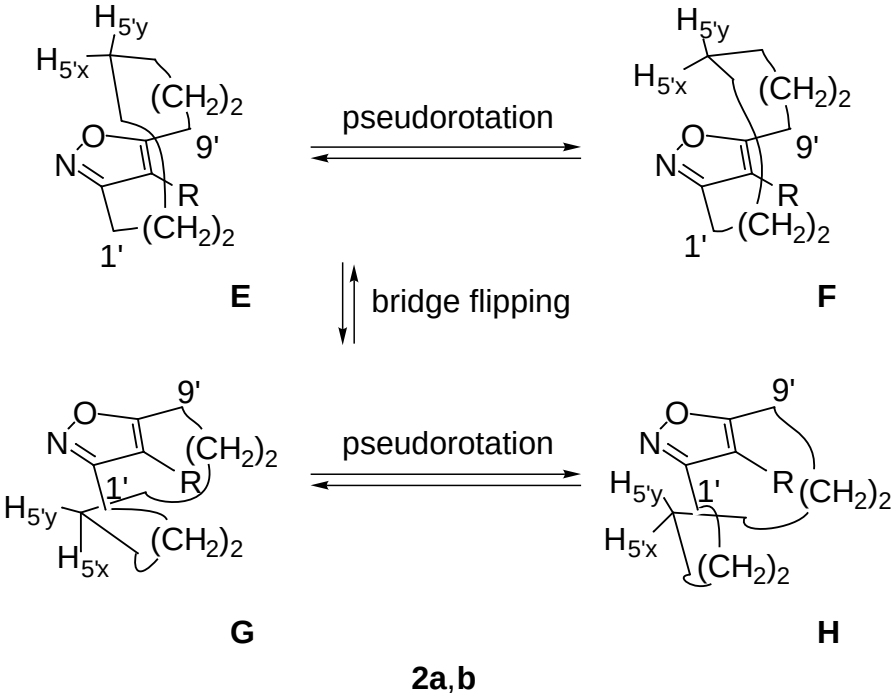
Table 2. Calculated energy (kcalmol^{-1}) for the optimized conformers (**A**) and (**B**) of **1**

Method	Conformer **A**	Conformer **B**
MM2[a]	30.11	30.03
MNDO[b]	-4.88	-4.97
AM1[b]	6.62	6.83
PM3[b]	7.87	7.95

a. Ref. 17; numerical values denote total energy.
b. Ref. 18; numerical values denote heat of formation (ΔH_f°)

Unlike in the case of **1**, stable conformers for **2a** and **2b** are not suggested by calculations.[17,18] A characteristic feature of the ^{1}H NMR of [9](3,5)isoxazolophane (**2a**) is the equivalence of the geminal protons at the "benzylic-type" positions, and these signals appear as a couple of triplets at δ 2.60 and δ 2.72 (Table 1). This is indicative of a rapid bridge flipping of the nonamethylene chain at 25 ℃. The ^{1}H NMR spectra of **2a** at low temperatures clarified that the proton signal appearing at δ 0.44 (δ_{av} of $H_{5'x}$ and $H_{5'y}$) disappeared at -10 ℃ (Tc), and reappeared at δ -0.25 (δav of H5'x for **E** and **F** [δav of H5'y for **G** and **H**]) as of 1H intensity at -40 ℃ (Scheme 3). The signal of the counterpart was expected to appear

at δ 1.13 (δ_{av} of $H_{5'y}$ for **E** and **F** [δ_{av} of $H_{5'x}$ for **G** and **H**]), but it was hidden behind the signals of other aliphatic protons. Consequently, the energy barrier ($\Delta G_c^{\ddagger}$) for the bridge flipping of the nonamethylene chain of **2a** [**E**, **F**$\rightleftarrows$ **G**, **H** in Scheme 3] was estimated to be 11.5 kcalmol^{-1} (Table 3). Furthermore, the proton signals at δ -0.25 at -40 ℃ disappeared again at -70 ℃ and reappeared at δ -0.14 ($H_{5'x}$ for **E** [$H_{5'y}$ for **G**]: appearing lower field) as of 0.14H intensity and δ -0.74 ($H_{5'x}$ for **F** [$H_{5'y}$ for **H**]: appearing higher field) as of 0.86H intensity at -90 ℃. Consequently, the energy barrier ($\Delta G_c^{\ddagger}$) for the conformational change (pseudorotation) between two major conformers for **2a** was estimated to be 9.1 kcalmol^{-1} (Table 3). The conformation around $C_{1'}$-$C_{2'}$-$C_{3'}$-$C_{4'}$ and $C_{6'}$-$C_{7'}$-$C_{8'}$-$C_{9'}$ is obscure even for the two major conformers, **E** and **F** [**G** and **H**]. The energy difference (ΔG) between the two major conformers, **E** and **F** [**G** and **H**], is calculated to be 0.66 kcalmol^{-1} (Table 3). An observation of several minor and broad signals (δ -0.45 and δ -0.29) at -90 ℃ suggests a possibility of the existence of further conformers of **2a**.



Scheme 3.

On the other hand, the four signals of "benzylic-type" protons of 4-methyl[9](3,5)isoxazolophane (**2b**) appear at different chemical shifts (Table 1), suggesting that the bridge flipping of the nonamethylene chain is frozen because of the existence of the methyl group at the 4-position. The signals did not change at temperatures ranging from 25 ℃ to 150 ℃. The ^{1}H NMR spectra of **2b** at low temperatures in CD_2Cl_2 clarified that the proton signal at δ -0.16 - -0.04 (δ_{av} of $H_{5'x}$ for **E** and **F** [δ_{av} of $H_{5'y}$ for **G** and **H**]) at 25 ℃ disappeared at -80 ℃ (T_c), and reappeared at δ -0.12 ($H_{5'x}$ for **E** [$H_{5'y}$ for **G**]: appearing lower field) as of 0.15H intensity and δ -0.83 ($H_{5'x}$ for **F** [$H_{5'y}$ for **H**]: appearing higher field) as of 0.85H intensity at -95 ℃. Consequently, $\Delta G_c^{\ddagger}$ for the conformational change (pseudorotation) of the nonamethylene chain of **2b** (**E**$\rightleftarrows$**F** [**G**$\rightleftarrows$**H**] in Scheme 3) was estimated to be 8.6 kcalmol^{-1}, and energy difference (ΔG) between **E** and **F** [**G** and **H**] was calculated to be 0.61 kcalmol^{-1} (Table 3). An

observation of another minor and broad signal (δ -0.39) at -95 ℃ suggests a possibility of the existence of a further conformer of **2b**. Similarly to the case of **2a**, the conformation around $C_{1'}$-$C_{2'}$-$C_{3'}$-$C_{4'}$ and $C_{6'}$-$C_{7'}$-$C_{8'}$-$C_{9'}$ is obscure even for the two major conformers, **E** and **F** [**G** and **H**], for **2b**.

Regarding $\Delta G_c^{\ddagger}$ values of the bridge flipping and pseudorotation for **1**, **2a,b**, and related compounds summarized in Table 3, the $\Delta G_c^{\ddagger}$ value for the bridge flipping of **1** is smaller than those of the corresponding values of [7](3,5)pyrazolophane (**4a**)[8] and [6](2,4)pyridinophane,[10] but larger than that of 3',6'-dioxo[8](2,5)thiophenophane (16.0 kcalmol^{-1})[6] and [7](2,4)pyridinophane,[10] which is larger than that of the corresponding value of **2a**. Furthermore, there is no large difference between $\Delta G_c^{\ddagger}$ values for the pseudorotation of **1**, as well as **2a,b**, and those of the corresponding values of 3',6'-dioxo[8](2,5)thiophenophane (11.4 kcalmol^{-1})[6] and [6](2,4)pyridinophane.[10] Consequently, it is clarified that [n](3,5)isoxazolophane is less flex than the corresponding [n](2,4)pyridinophane having the same value of n.

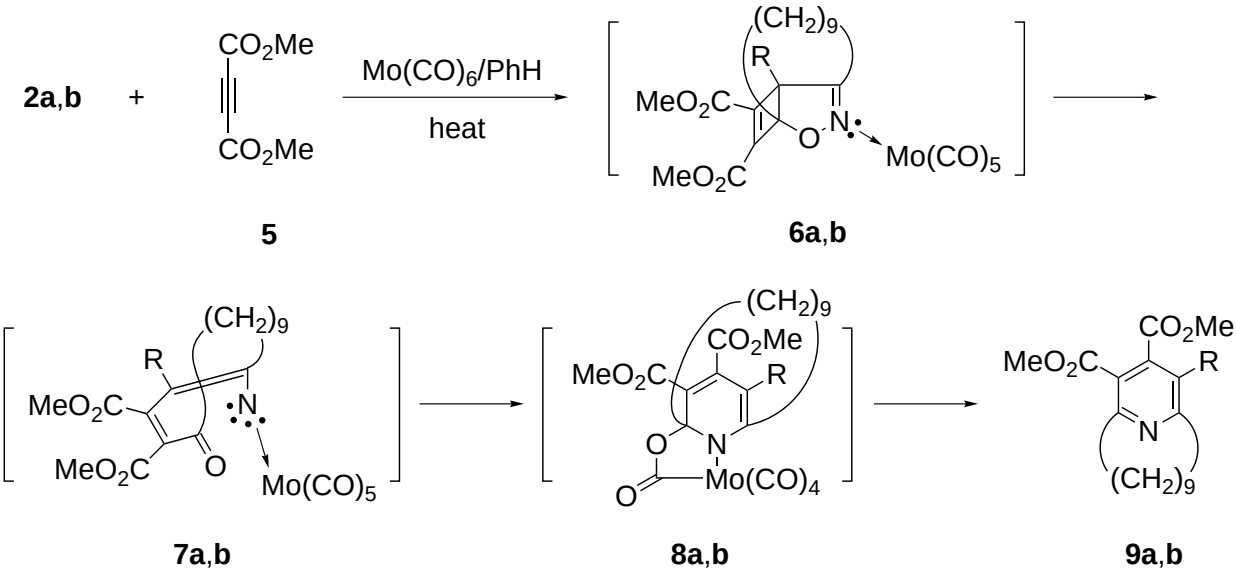
Table 3. Energy barriers ($\Delta G_c^{\ddagger}$ kcalmol^{-1}) for the bridge flipping and the pseudorotation of [n](3,5)isoxazolophanes (**1**), (**2a,b**)

	1	**2a**	**2b**	**4a**[a]	6-phenyl[n](2,4)pyridinophane[b]	
					n=6	n=7
Bridge	18.6	11.5	---	> 23	21-22	12-13
flipping	T_c=100 ℃	T_c=-10 ℃	---		T_c=150 ℃	T_c=20 ℃
Pseudo-	11.1-11.2	9.1	8.6		9.8	---
rotation	T_c=-10 ℃	T_c=-70 ℃	T_c=-80 ℃		T_c=-30 ℃	---
ΔG^c	0.04	0.66	0.61			

a. Ref. 8 b. Ref. 10. c. Energy difference (kcalmol^{-1}) between two major conformers (**A** and **B** of **1**, **E** and **F** of **2a,b**) calculated from their ratio based on ^{1}H NMR spectroscopy.

In connection with the previous studies,[1,15] the $Mo(CO)_6$-induced reaction of [9](3,4)isoxazolophanes (**2a,b**) with DMAD (**5**) was examined. Reaction of **2a** with DMAD (**5**) in the presence of $Mo(CO)_6$ afforded 3,4-bis(methoxycarbonyl)[9](2,6)pyridinophane (**9a**) in 9% yield (Scheme 4). The reaction of **2b** with **5** under similar conditions gave pyridinophane (**9b**) in 9% yield. The postulated reaction pathways for the formation of **9a,b** are also shown in Scheme 4. The formal [2 + 2] cycloaddition occurs to give the intermediate (**6**), which undergoes ring cleavage of the isoxazoline ring to give $Mo(CO)_5$-nitrene

complex (**7**).[15] The intermediate (**7**) then undergoes formal condensation *via* **8** to give the products (**9a,b**). The structures of **9a,b** are deduced from the ^{1}H NMR, ^{13}C NMR, and IR spectral data, as well as MS spectral data. The ^{1}H NMR and/or ^{13}C NMR spectra of **9a,b** show existence of the pyridine ring, and they correlate well with each other, respectively.[13] A characteristic feature is as follows: geminal protons at the benzylic positions, H-1' and H-9' appear at δ 2.92 (2H, t) and δ 2.94 (2H, t) for **9a**, while



Scheme 4.

they appear at δ 2.93 (2H, t) and δ 3.05 (2H, t) for **9b**. These features are indicative of the rapid flipping of the nonamethylene chain of **9a,b** at room temperature.

In summary, dynamic behavior of [8](3,5)- and [9](3,5)isoxazolophanes (**1**) and (**2a,b**) has been studied for the first time. The compounds seem to be less flex than the corresponding [n](2,4)pyridinophane having the same value of n. The $Mo(CO)_6$-induced reaction of **2a,b** with DMAD afforded [9](2,6)pyridinophane derivatives, *albeit in* low yields.

EXPERIMENTAL

IR spectra were recorded on a Horiba FT-710 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA500 and a JNM-EX270 spectrometers using $CDCl_3$ (unless otherwise specified) as a solvent, and the chemical shifts are given relative to internal $SiMe_4$ standard: J-values are given in Hz. MS spectra and HRMS spectra were run on a JEOL Automass 150 and a JEOL JMS-SX102A spectrometers, respectively. The desired [8](3,5)isoxazolophane (**1**)[13] and [9](3,5)isoxazolophanes (**2a,b**)[13,16] were prepared by the procedure reported in the literature. All the reactions were carried out under dry nitrogen

atmosphere.

Reaction of [9](3,5)isoxazolophanes (2a,b) with dimethyl acetylenedicarboxylate (5). A solution of **2a,b** (1 mmol), hexacarbonylmolybdenum (264 mg, 1 mmol), and **5** (284 mg, 2 mmol) in benzene (10 mL) was heated under reflux for 24 h. To the reaction mixture was added hexane (20 mL), and the mixture was filtered through Celite and the filtrate was concentrated *in vacuo*. The resulting residue was separated by TLC on silica gel (hexane-AcOEt : 2/1) to give [9](2,6)pyridinophane derivatives (**9a**) (28 mg, 9%) and (**9b**) (28 mg, 9%).

3,4-Bis(methoxycarbonyl)[9](2,6)pyridinophane (**9a**): colorless oil; ^{1}H NMR (500 MHz) δ 0.97-1.08 (4H, m), 1.22-1.35 (6H, m), 1.85-1.96 (4H, m), 2.92 (2H, t, J=6.1), 2.94 (2H, t, J=6.2), 3.91 (3H, s), 3.93 (3H, s), 7.44 (1H, s); ^{13}C NMR (125.8 MHz) δ 24.3, 24.6, 24.7, 25.1, 25.6, 25.9, 26.0, 34.7, 37.1, 52.7, 52.9, 119.8, 125.9, 135.9, 159.0, 163.4, 165.7, 169.0; IR (film) 2929, 2857, 1739, 1584, 1562, 1444, 1299, 1270, 1221 cm^{-1}; MS (*m/z*) 319 (M^{+}, 100%). HRMS Calcd for $C_{18}H_{25}NO_4$: 319.1783. Found: 319.1764.

3,4-Bis(methoxycarbonyl)-5-methyl[9](2,6)pyridinophane (**9b**): colorless oil; ^{1}H NMR (500 MHz) δ 1.13-1.22 (4H, m), 1.22-1.39 (6H, m), 1.82-1.93 (4H, m), 2.23 (3H, s), 2.93 (2H, t, J=6.2), 3.05 (2H, t, J=6.2), 3.87 (3H, s), 3.90 (3H, s); ^{13}C NMR (125.8 MHz) δ 14.8, 23.7, 24.7, 24.9, 26.0, 26.1, 26.3, 26.7, 34.8, 34.9, 52.5, 52.6, 122.1, 125.2, 141.1, 157.0, 162.4, 167.7, 168.3; IR (film) 2929, 2856, 1738, 1564, 1439, 1410, 1298, 1269, 1216 cm^{-1}; MS (*m/z*) 333 (M^{+}, 94%), 77 (100). HRMS Calcd for $C_{19}H_{27}NO_4$: 333.1940. Found: 333.1930.

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