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Thermal Valence Isomerization of Hemi-Dewar Type Isomers of [6](1,4)Naphthaleno- and [6](1,4)Anthracenophanes

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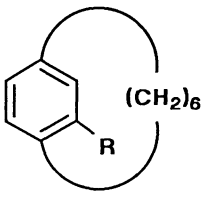
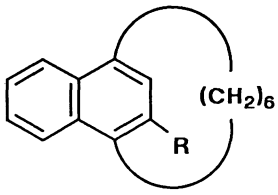
8-Methoxycarbonyl substituted [6](1,4)naphthaleno- and [6](1,4)anthracenophanes were prepared by the thermal valence isomerization of the corresponding hemi-Dewar type valence isomers. The rates of their isomerization were remarkably faster than those of the Dewar isomer of [6]paracyclophanes.

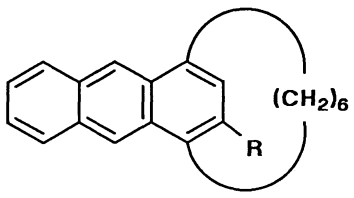
We have developed synthetic methods to prepare [6]paracyclophanes (**1a**, **1b**), the smallest-bridged paracyclophanes that have been isolated, based on the central bond cleavage of the [6.2.2]propellane framework through two different ways; oxidative decarboxylation of the propellanecarboxylic acid or thermal valence isomerization of the propelladienes (**2a**, **2b**).[1] By utilizing the former method, we have succeeded in the synthesis of [6](1,4)naphthalenophane (**3a**) and [6](1,4)anthracenophane (**4a**), which would be the smallest-bridged acenophanes that are stable at ambient temperature.[2] In this communication, we disclose the synthesis of the methoxycarbonyl substituted derivatives **3b** and **4b** by means of the second route, the thermal valence isomerization of the corresponding hemi-Dewar type isomers **5b** and **6b** with benzo- or naphtho[6.2.2]propelladiene skeleton. We also prepared the parent hemi-Dewar naphthalenophane **5a** by photochemical valence isomerization of **3a** and measured the rates of cycloreversion of **5a**, **5b**, and **6b** to **3a**,



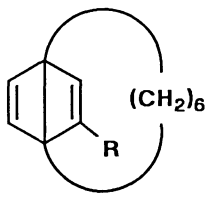
1a, 1b



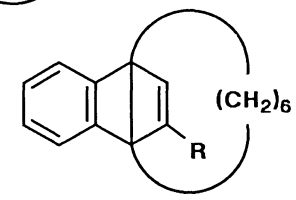
3a, 3b



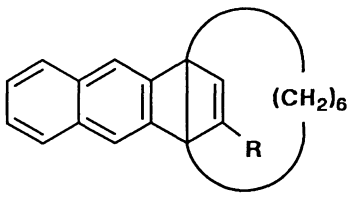
4a, 4b



2a, 2b



5a, 5b



6a, 6b

a R=H ; **b** R=CO_2Me

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3b, and **4b**, respectively. Particularly noteworthy is the rates of isomerization of the hemi-Dewar acenophanes **5a**, **5b**, and **6b** which are remarkably faster than those of the Dewar benzenophanes **2a** and **2b**.

The hemi-Dewar isomers **5b**[3] and **6b**[3] were prepared from the corresponding benzo- and naphthopropellanecarboxylates[2] according to the phenylselenenylation-selenoxide elimination protocol as described previously.[1] The thermal valence isomerization of **5b** and **6b** took place smoothly to give the corresponding acenophanes **3b**[3] and **4b**[3] quantitatively.

As in the case of the parent systems,[2] **3b** and **4b** exhibited temperature dependence in the NMR spectra due to the fluxional behavior of the methylene chain. The ^{1}H NMR chemical shifts of the benzyl protons (Ha, Hb, Hc, and Hd), the central methylene protons (He, Hf, Hg, and Hh), and the aromatic protons (Hi) of the major (**A**) and the minor (**B**) conformers are listed in Table 1. The stereochemical assignment for the conformers is based on the coupling pattern of the benzyl protons (Hb) of **A** (dd, J=5.9, 12.5 Hz) and **B** (ddd, coupling constants undetermined) which are remarkably deshielded (0.9-1.0 ppm) due to the ester group. The chemical shifts of the shielded methylene protons (Hg and Hh) of the major isomer **A** are not much different from those of the hydrocarbons **3a** and **4a**. On the other hand, whereas He of the minor conformer **B** shows downfield shift by about 0.2 ppm, Hf of **B** exhibits upfield shift by ca. 0.3 ppm. The ratios of the major (**A**) and the minor (**B**) conformers are ca. 4:1 in both cases which are similar to that of the benzenophane **2b**.[1] The barrier for the flipping of the bridge was estimated from the coalescence temperature of the aromatic protons (Hi); **3b** $\Delta G_c^{\neq}$(253 K)=13.3 kcal/mol, **4b** $\Delta G_c^{\neq}$(253 K)=12.7 kcal/mol. These values are similar to but slightly smaller than those of the parent hydrocarbons **3a** and **4a**.[2]

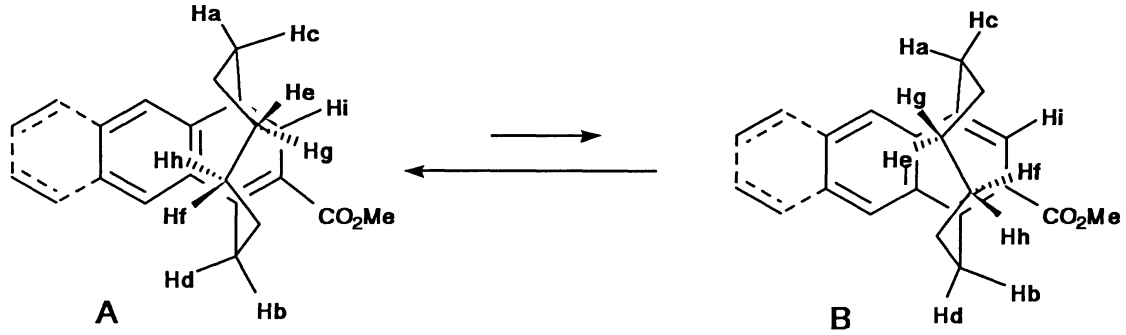

Table 1. ^{1}H NMR Chemical Shifts of **3b** and **4b**[a]

	Naphthalenophane **3b**		Anthracenophane **4b**	
Proton	Conformer A	Conformer B	Conformer A	Conformer B
Ha	3.47 (3.49)	---[b]	3.58 (3.58)	---[b]
Hb	4.01 (3.01)	3.10 (2.27)	4.14 (3.08)	3.24 (2.36)
Hc	2.32 (2.27)	3.02 (3.01)	2.43 (2.36)	---[b]
Hd	2.89 (2.86)	3.56 (3.49)	3.08 (3.00)	3.70 (3.58)
He	1.14 (1.11)	-1.65 (-1.84)	1.20 (1.14)	-1.58 (-1.81)
Hf	0.84 (0.79)	-0.79 (-0.47)	0.78 (0.71)	-0.59 (-0.31)
Hg	-0.57 (-0.47)	---[b]	-0.36 (-0.31)	---[b]
Hh	-1.88 (-1.84)	---[b]	-1.80 (-1.81)	---[b]
Hi	7.89 (7.34)	7.95 (7.41)	7.80 (7.27)	7.86 (7.34)

a) In $CDCl_3$ at -40 °C. The corresponding chemical shifts of **3a** and **4a** are given in parentheses.
b) The signal was concealed in those of the major conformer **A**.

Table 2. Kinetic Data for Thermal Valence Isomerization of **2a**, **2b**, **5a**, **5b**, and **6b**[a)]

Compd	Temp °C	10^6k s^{-1}	k_{rel}	Ea kcal mol^{-1}	$\Delta H^{\neq}$ kcal mol^{-1}	$\Delta S^{\neq}$ cal $deg^{-1}mol^{-1}$
2a[b)]	25.0[c)]	1.07	1.0	21.7±1.0	21.1±1.0	-15.3±3.4
2b[d)]	25.0[c)]	3.34	3.1	24.9±0.3	24.3±0.3	-2.0±1.0
5a	35.9	135±1				
	40.1	220±8				
	44.2	310±5				
	25.0[c)]	43.3	41	19.5±0.3	18.9±0.3	-15.3±1.3
5b	25.0	61.8±0.7	58	23.8±0.5	23.2±0.5	0.0±1.9
	31.5	155±2				
	38.2	339±8				
6b	20.5	253±5				
	25.0	423±8	400	21.8±0.4	21.2±0.4	-2.8±1.5
	29.3	747±2				

a) In cyclohexane. *b*) Ref. 5. *c*) Extrapolated from higher temperatures. *d*) Ref. 1.

In order to determine the rate of isomerization of the parent hydrocarbon system, the hemi-Dewar naphthalenophane **5a**[3)] was prepared by UV-irradiation of **3a** in cyclohexane solution through a Pyrex filter.[4)] The rates of thermal cycloreversion were determined by the spectroscopic method[1)] and are summarized in Table 2 together with the kinetic data for isomerization of **2a**[5)] and **2b**.[1)]

As shown in Table 2, activation entropies for the isomerization of the hydrocarbons **2a** and **5a** are negative while those of the esters **2b**, **5b**, and **6b** are slightly negative or zero. This suggests that transition states for the isomerization of the substrates with the same substituents (R=H or CO_2Me) are similar regardless of their skeleton. The most striking is that the isomerization rates of the hemi-Dewar naphthalenophanes **5a** and **5b** are faster than those of the Dewar benzenophanes **2a** and **2b** by 41 and 19 times, respectively; the activation energies for the isomerization of **5a** and **5b** are less than those of **2a** and **2b** by 1-2 kcal/mol. Moreover, the rate of **6b** is 130 times of that of **2b** and Ea is less by 3 kcal/mol than that of **2b**. Extrapolation from the above data would lead to a rough estimate of Ea for **6a** as small as about 17.5 kcal/mol.[4)]

Taking the reported lengths of the central bond of the derivatives of Dewar benzene[6)] and hemi-Dewar naphthalene[7)] as well as those of cyclobut[*a*]acenaphthylene and its benzo- and naphtho-derivatives[8)] into account, it is reasonable to assume that the central bond lengths of the propellanes **2a**, **2b**, **5a**, **5b**, and **6b** are not much different. Consequently, the rate acceleration of **5a**, **5b**, and **6b** relative to the Dewar benzenophanes **2a** and **2b** would be ascribed to the relative ease to accomodate the bridgehead double bond character developing in the transition state of the isomerization. Indeed, the molecular structure of **4a** detemined by the X-ray analysis revealed that the out-of-plane bending of the bridged aromatic ring of **4a** was larger than that of the [6]paracyclophane deivatives.[2)] It seems likely therefore that the bridgehead double bonds in the acenophanes **3a** and **4a** are not as much involved as 10π and 14π aromatic systems, respectively, as that of the benzenophane does as a 6π system, probably because the acenophanes have already gained aromatic character in the unbridged rings as 6π and 10π systems, respectively. Though we were unable to detect decrease of aromatic character in the acenophanes **3a** and **4a** relative to **2a** by the spectroscopic methods (NMR, UV, and photoelectron spectra),[2)] their unusual reactivities are in line with this notion.[9)]

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References

1) Y. Tobe, K. -I. Ueda, K. Kakiuchi, Y. Odaira, Y. Kai, and N. Kasai, *Tetrahedron,* **42**, 1851 (1986).

2) Y. Tobe, T. Takahashi, T. Ishikawa, M. Yoshimura, M. Suwa, K. Kobiro, K. Kakiuchi, and R. Gleiter, *J. Am. Chem. Soc.,* in press.

3) Selected spectral properties of **3b**, **4b**, **5a**, **5b**, and **6b** follow:

3b ^{13}C NMR ($CDCl_3$, -40 °C) Major conformer **A** δ 168.3, 148.9, 140.0, 138.4, 135.7, 129.6, 127.1, 127.0, 125.7, 125.6, 123.4, 52.4, 36.6, 35.6, 35.1, 31.4, 26.9, 25.1; Minor conformer **B** δ 168.4, 146.6, 140.2, 139.7, 135.5, 132.4, 127.2, 125.4, 124.7, 123.9, 52.5, 36.2, 35.0, 33.2, 33.1, 26.3, 25.9 (one signal missing); UV λ_{max} (cyclohexane) 362 (ε 2780), 317 (4270), 260 (32000) nm.

4b ^{13}C NMR ($CDCl_3$, -40 °C) Major conformer **A** δ 168.3, 150.8, 139.2, 137.9, 134.2, 131.6, 131.0, 128.3, 128.1, 127.9, 126.5, 126.1, 125.5, 124.4, 121.3, 52.4, 36.7, 35.8, 31.1, 27.1, 25.0; Minor conformer **B** δ 168.5, 148.1, 140.1, 138.5, 134.5, 132.0, 130.7, 128.1, 123.3, 121.8, 52.5, 36.3, 35.7, 33.6, 33.1, 26.2, 25.9 (five signals missing); UV λ_{max} (cyclohexane) 407 (ε 2170), 380 (sh, 1730), 356 (sh, 1310), 273 (37000) nm.

5a ^{1}H NMR (C_6D_{12}) δ 7.4 (m, 4H), 6.87 (s, 2H), 2.64 (ddd, J=4.0, 5.9, 15.4 Hz, 2H), 2.50 (ddd, J=4.0, 10.6, 15.4 Hz, 2H), 2.1-1.9 (m, 4H), 1.8-1.7 (m, 2H), 1.6-1.5 (m, 2H); ^{13}C NMR (C_6D_{12}) δ 152.7, 147.2, 127.7, 124.0, 67.7, 28.4, 28.3, 26.9.

5b ^{1}H NMR ($CDCl_3$) δ 7.3-7.1 (m, 4H), 7.12 (s, 1H), 3.71 (s, 3H), 2.49 (ddd, J=4.0, 6.2, 15.4 Hz, 1H), 2.30 (ddd, J=3.6, 6.5, 15.4 Hz, 1H), 2.2-2.1 (m, 2H), 1.7-1.5 (m, 4H), 1.4-1.3 (m, 2H), 1.2-1.1 (m, 2H).

6b ^{1}H NMR (CD_2Cl_2) δ 7.8 (m, 2H), 7.65 (s, 1H), 7.56 (s, 1H), 7.4 (m, 2H), 7.28 (s, 1H), 3.73 (s, 3H), 2.60 (ddd, J=4.1, 5.9, 15.6 Hz, 1H), 2.41 (ddd, J=4.1, 6.1, 16.1 Hz, 1H), 2.3-2.2 (m, 2H), 1.75-1.6 (m, 4H), 1.4-1.3 (m, 2H), 1.2-1.05 (m, 2H).

4) Irradiation of **4a** did not lead to the formation of **6a** but gave a mixture of photodimers. We were unable to detect the formation of **6a** by NMR even through irradiation at low temperature (-50 °C). Details of the photoreaction of **4a** will be reported elsewhere.

5) Y. Tobe, A. Nakayama, K. Kakiuchi, Y. Odaira, Y. Kai, and N. Kasai, *J. Org. Chem.,* **52**, 2639 (1987).

6) G. Bieri, E. Heilbronner, T. Kobayashi, A. Schmelzer, M. J. Goldstein, R. S. Leight, and M. S. Lipton, *Helv. Chim. Acta,* **59**, 2657 (1976), and references cited therein.

7) R. W. Franck, R. Gruska, and J. G. White, *Tetrahedron Lett.,* **1977**, 509.

8) A. C. Hazell and Å. Weigelt, *Acta Crystallogr., Sect. B,* **32**, 306 (1976); A. C. Hazell, *ibid.,* **32**, 2010 (1976); A. C. Hazell and R. G. Hazell, *ibid.,* **33**, 360 (1977).

9) Y. Tobe, T. Takahashi, K. Kobiro, and K. Kakiuchi, *Angew. Chem.,* submitted for publication.

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