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Novel synthesis, static and dynamic properties, and structural characteristics of 5-cyano[*n*](2,4)pyridinophane-6-ones (*n* = 9–6) and their chemical transformations

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A novel synthesis of 5-cyano[*n*](2,4)pyridinophane-6-ones **12a–d** (*n* = 9, 8, 7, and 6) consists of allowing cyanoacetatoamide to react with cycloalk-2-enones. Their static and dynamic properties as well as structural characteristics are studied on the basis of their spectroscopic properties, cyclic voltammetry, and theoretical calculations. The ^{1}H and ^{13}C NMR spectra at various temperatures have clarified the dynamic behavior of the methylene chains for [7](2,4)- and [6](2,4)pyridinophane-6-one derivatives **12c** and **12d**. The energy barrier ($\Delta G^{\ddagger}$) of the bridge flipping of **12c** is estimated to be 12.0 kcal mol^{-1} ($T_c = 0$ °C). On the other hand, compound **12d** undergoes pseudorotation (conformational change of the methylene chain) at room temperature, and does not undergo bridge flipping even at 150 °C in DMSO-d_6. The energy barrier ($\Delta G^{\ddagger}$) of the pseudorotation of the methylene chain of **12d** is found to be 10.5 kcal mol^{-1} ($T_c = -25$ °C), and thus, two stable conformers of the hexamethylene bridge of **12d** are determined as predicted by theoretical calculations. Deformation of the pyridone ring of **12d** is also determined by X-ray crystallographic analysis. Furthermore, chemical transformations of **12a–c** leading to 5-carbamoyl[*n*](2,4)pyridinophanes **15a–c** are also accomplished successfully in moderate to good yields.

Introduction

The past years have been rather fruitful in the field of small paracyclophane chemistry.[1] Since the discovery of [6]paracyclophane in 1974,[2] the continuous search for more highly strained members of this family resulted in the synthesis of [5]paracyclophane in 1985,[3] and the spectroscopic characterization of [4]paracyclophane.[4] In the field of heterocyclic [*n*]paracyclophanes,[5,6] the smallest known member is [6](2,5)pyridinophane (parapyridinophane) **1** (Fig. 1).[5] In the [*n*]metacyclophane series, the known members thus far synthesized are 3-halogeno[6](2,4)pyridinophanes,[7] [*n*](2,6)pridinophane (*n* = 12 and *n* = 10–6) **2**,[8] [*n*](3,5)pyridinophanes (*n* = 9 and 7) **3**,[9] and 3-chloro-substituted [6](2,4)quinolinophane.[10,11] Previously, we have also worked on convenient preparations of a series of [*n*](2,4)pyridinophanes (*n* = 9–6) **4**,[12] azuleno-annulated [*n*](2,4)pyridinophanes (*n* = 9–6),[13] [*n*](2,4)quinolinophanes (*n* = 9–7),[14] and dimethyluracil-annulated [*n*](2,4)pyridinophanes (*n* = 9–6),[15] and studied their static and dynamic behaviors. The synthesis consists of an enamine alkylation process of vinyliminophosphoranes,[12,16] 2-aminoazulenes,[13] β-amino enones,[14] and 6-amino-1,3-dimethyluracil[15] with cycloalk-2-enones, respectively, and subsequent condensation of the nitrogen moiety with the carbonyl function and dehydrogenation. Thus, a few easy reaction steps enable the synthesis of novel and highly interesting types of condensed heterocycles, which are difficult to obtain by other synthetic means.[16] The only known cyclophane derived from pyridone is the large-membered system of [26](2,6)pyridinophan-4-one **5**,[17] and a Dewar isomer of [5](2,5)pyridinophane-6-one.[18] In this context, as well as to pursue our interest in synthesizing several [*n*](2,4)pyridinophanes, we have now studied a new facile synthesis, static and dynamic properties, and the structural characteristics of novel 5-cyano[*n*](2,4)pyridinophane-6-ones **12a–d** (*n* = 9, 8, 7, and 6). Their chemical transformation toward 5-carbamoyl[*n*](2,4)pyridinophanes (*n* = 9, 8, and 7) **15a–c**, except **12d**, which is not obtained in a sufficient amount, are studied as well. The synthesis is based on the chemistry of 2-pyridone synthesis using cyanoacetamide and α,β-unsaturated carbonyl compounds.[19] We report herein the results in detail.

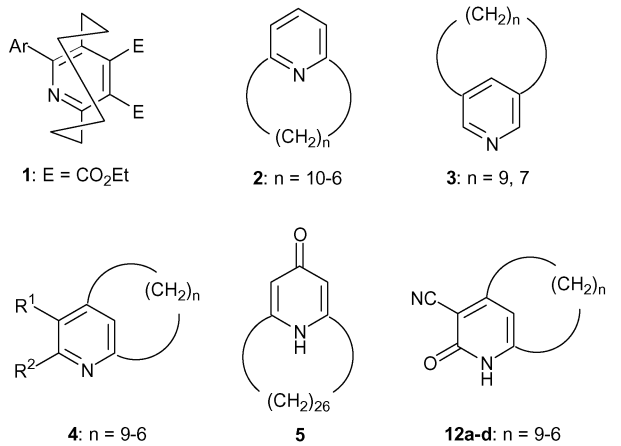

Fig. 1

Results and discussion

Synthesis

Addition of the cycloalk-2-enone **7a–d** (*n* = 9–6) to equivalent amounts of ^{t}BuOK and cyanoacetamide **6** in DMSO (room temperature, nitrogen atmosphere) and stirring the mixture in a flask fitted with an N_2 balloon for 0.5–1 h resulted in the Michael addition. Upon completion of this process (monitoring by TLC), further ^{t}BuOK (3 molar equivalent amounts) was added to the mixture, and the N_2 balloon was displaced by an O_2 balloon, and the mixture was stirred at room temperature for another 2 h. Then the mixture was poured into water, neutralized with 4% HCl, and extracted with CH_2Cl_2 to result in the formation of 5-cyano[*n*](2,4)pyridinophane-6-ones [**12a** (*n* = 9): 71%; **12d** (*n* = 8): 63%; **12c** (*n* = 7): 11%; **12d** (*n* = 6): 5%]. A mechanistic pathway for the pyridinophane forming process is outlined in Scheme 1. The initial Michael adducts

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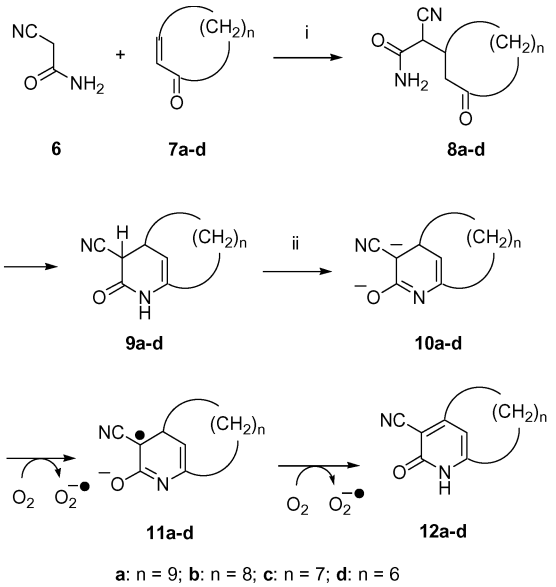


Scheme 1 *Reagents and conditions*: (i) ^{t}BuOK, DMSO, rt, under N_2; (ii) ^{t}BuOK, rt, under O_2.

8a–d undergo base-induced cyclization to dihydropyridinophane **9a–d**, which gives a dianion of the type **10a–d** in the presence of ^{t}BuOK. Single electron transfer from **10a–d** to an O_2 yields radical anion **11a–d**, aromatization of which may involve either H atom transfer to an O_2 or further single electron transfer process, or combination with O_2, followed by elimination, results in the formation of 5-cyano[*n*](2,4)pyridinophane-6-ones **12a–d**. This general mechanistic aspect is supported by several pieces of chemical evidence.[19]

The structures of the compounds were deduced from their spectral data and elemental analyses. The ^{1}H NMR spectral data of **12a–d** are summarized in Table 1 (see the convenient, but not systematic, numbering of the methylene illustrated in Fig. 2). A characteristic feature of **12a,b** is the equivalence of the geminal hydrogens at the 'benzylic' positions H1′ and H*n*′ (Fig. 2), where the signals appear as a couple of triplets. For compound **12c**, these signals overlap and appear as multiplets. This feature is indicative of a rapid flipping of the methylene chain of **12a–c** at room temperature; and spectral properties similar to this feature were also observed for [*n*](2,4)pyridinophane derivatives ($n = 9$–7), which undergo rapid bridge-flipping.[12–14] In contrast, the four benzylic hydrogens of **12d** exhibited different chemical shifts at room temperature (Table 1), suggesting that the flipping of the constrained hexamethylene chain is frozen in the NMR time scale at room temperature (*vide infra*). The UV-Vis spectra of pyridinophane **12a–d** are summarized in Table 2. The spectra of **12a–d** are similar, but the longest absorption maxima are shifted very slightly to longer wavelengths as the methylene chain becomes shorter.[12–15] The redox potentials of **12a–d** were measured by cyclic voltammetry (CV) in CH_3CN. The redox waves are irreversible under the conditions of CV measurement; the peak potentials of **12a–d** are summarized in Table 4 together with the energy levels of the HOMO and LUMO predicted by AM1 calculation (MOPAC Ver 6.12). In the $E1_{ox}$ of **12a–d**, the value shifted to less positive as the methylene chain becomes shorter, suggesting the HOMO of **12a–d** becomes higher as the methylene chain becomes shorter. In contrast, the value of $E1_{red}$ for **12a–d** shifted to more negative as the methylene chain becomes shorter, suggesting the LUMO of **12a–d** becomes higher as the methylene chain becomes shorter. For **12a–d**, the $E1_{ox}$ and $E1_{red}$ correlate well with the corresponding energy levels of the HOMO and LUMO, respectively, reflecting the highest HOMO and LUMO of **12d**. Furthermore, the small differences in the HOMO–LUMO gap (Δ in Table 3) for **12a–d** reflect the similarity of their UV-Vis spectra (Table 2).

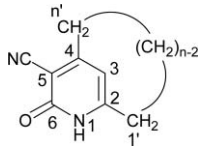


Fig. 2 Numbering of the methylene bridge of **12a–d**.

Table 2 UV-Vis spectral data of **12a–d**

Compd	λ_{max} (EtOH)/nm (log [ε/dm^{3}mol^{-1}cm^{-1}])		
12a	222 (4.31)		335 (3.87)
12b	221 (4.30)		335 (3.96)
12c	222 (4.12)	245 (3.12)	336 (3.88)
12d	223 (4.13)	256 (3.47)	336 (3.90)

Dynamic behavior

Since no cyclophane involving the 2-pyridone ring has been reported, study of the dynamic behavior of **12a–d** is interesting. A characteristic feature of **12a–c**, the equivalence of the geminal hydrogens at the 'benzylic' positions H1′ and Hn′ (Fig. 2), is indicative of a rapid flipping of the methylene chain of **12a–c**

Table 1 ^{1}H NMR spectral data of [*n*](2,4)pyridinophane-6-ones **12a–d**[a]

	Pyridone	Benzylic	Remaining methylene bridge
Compd	δ H3	δ H1′ and δ H*n*′	δ
12a[b]	6.38	2.77 (2H, t, *J* 6.3, H1′), 2.81 (2H, t, *J* 6.4, H9′)	0.96–1.13 (4H, m), 1.17–1.37 (6H, m), 1.76–1.92 (4H, m), 13.38 (1H, bs)
12b[b]	6.39	2.69 (2H, t, *J* 5.9, H1′), 2.75 (2H, t, *J* 5.9, H8′)	0.82–1.00 (4H, m), 1.24–1.46 (4H, m), 1.62–1.80 (4H, m), 13.39 (1H, bs)
12c[b]	6.58	2.66–2.90 (4H, m, H1′, H7′)	−0.05–0.89 (2H, m), 1.35–1.88 (8H, m), 13.32 (1H, bs)
12d[c]	6.35	2.69 (1H, dt, *J* 13.6, 5.6, H1′), 2.76 (1H, dt, *J* 13.0, 6.7, H6′), 2.77 (1H, dt, *J* 13.6, 6.9, H1′), 2.88 (1H, dt, *J* 13.0, 6.5, H6′)	0.58 (1H, broad s, H4′x), 0.94 (1H, broad s, H3′x), 1.19–1.29 (1H, m, H3′y), 1.37–1.47 (1H, m, H4′y), 1.50–1.60 (1H, m, H2′), 1.62–1.73 (1H, m, H5′), 1.84–1.98 (2H, m, H2′, H5′), 12.87 (1H, broad s, H1)
12d-A[d,e]	6.34	2.50 (1H, m, H1′), 2.58 (1H, m, H6′), 2.74 (1H, m, H1′), 2.98 (1H, m, H6′)	−0.74 (1H, m, H4′x), 0.77 (1H, m, H3′y), 0.96 (1H, m, H2′), 1.63 (2H, m, H4′y, H5′), 2.02 (1H, m, H2′), 2.07 (2H, m, H3′x, H5′), 13.59 (1H, broad s, H1)
12d-B[d,e]	6.40	2.36 (1H, m, H1′), 2.44 (1H, m, H6′), 2.98 (1H, m, H6′), 3.13 (1H, m, H1′)	−0.74 (1H, m, H3′x), 0.90 (2H, m, H4′y, H5′), 1.63 (2H, m, H2′, H3′y), 2.02 (1H, m, H5′), 2.07 (2H, m, H2′, H4′x), 13.76 (1H, broad s, H1)

[a] Convenient but not systematic numbering of the methylene chain is illustrated in Fig. 2. [b] Recorded on a 400 MHz spectrometer in $CDCl_3$. [c] Recorded on a 500 MHz spectrometer in $CDCl_3$. [d] Recorded on a 500 MHz spectrometer in CD_2Cl_2. [e] Recorded at −95 °C.

Table 3 Redox potentials and the energy levels of HOMO and LUMO of **12a–d**

Compd.	Redox potential[a]/V		Energy level/eV		
	$E1_{ox}$	$E1_{red}$	HOMO	LUMO	Δ^b
12a	+1.49	−1.03	−9.023	−0.806	8.217
12b	+1.48	−1.06	−9.014	−0.798	8.216
12c	+1.48	−1.21	−8.993	−0.790	8.203
12d	+1.36	−1.33	−8.945	−0.749	8.196

[a] V *vs* $Ag/AgNO_3$; peak potential. [b] Calculated HOMO–LUMO energy gap.

at room temperature. In contrast, the four benzylic hydrogens of **12d** exhibited different chemical shifts at room temperature (Table 1), suggesting that the flipping of the hexamethylene chain is frozen on the NMR time scale (*vide supra*). Concerning **12c**, the proton signal of H4′x and H4′y appears as a mean value at δ 0.37 because of a rapid flipping of the heptamethylene chain at room temperature (Fig. 3). The signal at δ 0.37 disappeared at 0 °C, and the signal of H4′x for conformer **12c-A** [H4′y for conformer **12c-B**] reappeared at δ −0.83 as of ^{1}H intensity at −90 °C. The counterpart (the signal of H4′x for **12c-B** [H4′y for **12c-A**] apeared at δ 1.35. Furthermore, all benzylic protons (H1′ and H7′) appeared as for the independent signals (δ 2.40, 2.49, 2.80, and 3.00). These observations suggest that each geminal proton is located in a different environment and the flipping of the heptamethylene chain is frozen at −90 °C on the NMR time scale. Then, the coalescence temperature method could estimate that the energy barrier ($\Delta G_c^{\ddagger}$) of the bridge flipping between **12c-A** and **12c-B** is 12.0 kcal mol^{-1} ($T_c = 0$ °C).

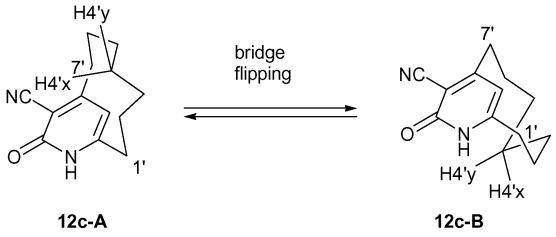


Fig. 3

Regarding the assignment of the hydrogens and the carbons for the hexamethylene chain of **12d** at room temperature (Tables 1 and 4), four geminal hydrogens at the benzylic positions (H1′ and H6′) appear as two pairs of signals (δ 2.69 and δ 2.77; δ 2.76 and δ 2.88: assigned by ^{1}H–^{1}H COSY spectrum) at lower field than the remaining bridge protons (H2′–H5′), because of the anisotropy effect of the 2-pyridone ring. ^{1}H–^{13}C heteronuclear multiple bond connectivity (HMBC) spectrum elucidated that the pair of signals at δ 2.76 and δ 2.88 correlate with the carbon atom of the cyano group (δ 97.1), so this pair of signals was assigned to the protons H6′ and the other pair of signals at δ 2.69 and δ 2.77 was assigned to protons H1′. The remaining bridge hydrogens were assigned by ^{1}H–^{1}H COSY spectrum. In analogy with the previous studies of 6-phenyl[6](2,4)pyridinophane,[12] the signals for one of H3′ (δ 0.94) and one of H4′ (δ 0.58) were assigned to H3′x and H4′x for **A** and **B** [H3′y and H4′y for **C** and **D**], respectively, because of the anisotropy effect of the 2-pyridone ring. The carbons of the hexamethylene chain were assigned by the ^{1}H–^{13}C COSY spectrum. Similarly, the signals of the hydrogens and the carbons for conformers **A** and **B** [**C** and **D**] at −95 °C were assigned as summarized in Tables 1 and 4. Thus, ^{1}H NMR spectroscopy was conducted at various temperatures to clarify the dynamic behavior of **12d**. In DMSO-d_6, at an increase in the temperature around 150 °C **12d** exhibited no change in the spectrum. This feature indicates that **12d** does not undergo a bridge flipping of the hexamethylene chain even at 150 °C (270 MHz in DMSO-d_6). In addition, the conformation of **12d** is not fixed in either conformer **A** or **B** [**C** or **D**] (Table 1 and Fig. 4) at room temperature, and a rapid equilibrium between **A** and **B** [**C** and **D**] would exist due to the pseudorotation (conformational change of the hexamethylene chain). Two proton signals (in CD_2Cl_2, Table 1) at δ 0.58 (δ_{av} of H4′x for **A** and **B** [δ_{av} of H4′y for **C** and **D**]) and δ 0.94 (δ_{av} of H3′x for **A** and **B** [δ_{av} of H3′y for **C** and **D**]) disappeared at −25 °C, and reappeared at δ −0.74 (H4′x for **A** [H4′y for **C**] and H3′x for **B** [H3′y for **D**]) at −95 °C. The signals of the counterparts appear at δ 2.07 (H4′x for **B** [H4′y for **D**] and H3′x for **A** [H3′y for **C**]). According to the intensity of the protons H3′ for conformers **A** [**C**] and **B** [**D**], these comformers exist in the ratio of 58:42 at −95 °C. Thus, the conformer **A** [**C**] is slightly more stable than the conformer **B** [**D**]. At this temperature the pseudorotation also stopped. Furthermore, the AM1 calculation suggests that **12d** exists as two stable conformers **A** [**C**] and **B** [**D**], and the calculated heat of formations (ΔH_f°) are listed in Fig. 4, suggesting the conformer **A** [**C**] is more stable than the conformer **B** [**D**]. Thus, the experimental result is in accordance with the theoretical predictions. Consequently, the energy barrier ($\Delta G_c^{\ddagger}$) for the pseudorotation (conformational change) between

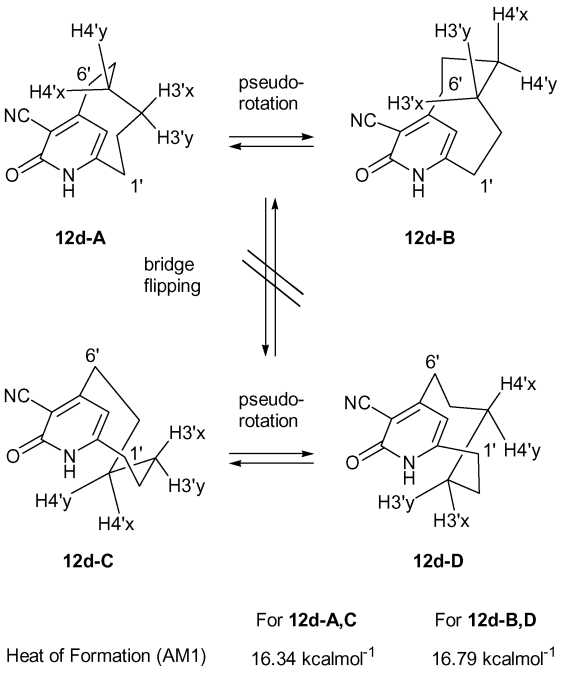


Fig. 4

Table 4 ^{13}C NMR spectral data (δ) of **12d** in CD_2Cl_2 at various temperatures[a]

Compd.	Temp/°C	C3	C1′	C2′	C3′	C4′	C5′	C6′	Remaining signals
12d	27	114.8	33.8	31.4	28.2	27.2	31.3	34.4	97.1, 115.6, 155.5, 164.8, 166.3
12d-A	−95	113.6	34.7	31.2	29.4	23.8	29.7	31.2	97.6, 115.5, 153.8, 164.4, 166.8
12d-B	−95	115.2	30.5	29.9	24.5	29.3	32.0	36.3	92.5, 115.3, 157.1, 164.3, 164.7

[a] Recorded on a 125.8 MHz spectrometer.

A and **B** [**C** and **D**] was estimated to be 10.5 kcal mol^{-1}, and the free energy difference (ΔG) between **A** and **B** [**C** and **D**] was estimated to be 0.11 kcal mol^{-1}, which is smaller than the calculated values (Fig. 4). Regarding $\Delta G_c^{\ddagger}$ values of the bridge flipping of **12c** (12.0 kcal mol^{-1}, $T_c = 0$ °C) and pseudorotation of **12d** (10.5 kcal mol^{-1}, $T_c = -30$ °C), these values are not much different from those of the corresponding value of 6-phenyl[7](2,4)pyridinophane (bridge flipping: 12–13 kcal mol^{-1}, $T_c = +20$ °C) and 6-phenyl[6](2,4)pyridinophane (pseudorotation: 9.8 kcal mol^{-1}; $T_c = -30$ °C).[12] Consequently, it is clarified that the flexibility of 5-cyano[6](2,4)pyridinophane-6-ones **12c,d** seems to be similar to that of the corresponding 6-phenyl[*n*](2,4)pyridinophane having the same value of *n*.[12]

Structural characteristics of 12d

We performed the structure determination of **12d** at −180 °C. The X-ray crystal analysis revealed that **12d** exhibits two structures (**I** and **II**) in the solid state. ORTEP drawings of structures **I** and **II** are shown in Fig. 5. The selected bond lengths and angles of **12d** are listed in Table 5. The bond lengths and angles of **12d-I** and **12d-II** resemble each other. The most remarkable feature in the structure of **12d** is the deformation of the 2-pyridone ring from planarity, which is represented by the deviation angles of the *para* carbons (α_1 and α_2) from the base plane of the boat-shaped 2-pyridone ring and those of the benzylic carbons (β_1 and β_2) from the bow of the 2-pyridone ring as shown in Fig. 6. The α_1 value is derived from the mean value of the torsion angle of C1–N1–C5–C4 and N1–C5–C4–C3 (C11–N3–C15–C14 and N3–C15–C14–C13). The α_2 value is derived from the mean value of the torsion angle of C3–C2–C1–N1 and C4–C3–C2–C1 (C13–C12–C11–N3 and C14–C13–C12–C11). The β_1 value is derived from the mean value of the torsion angle of C6–C1–C3–N1 and C6–C1–C3–C4 (C16–C11–C13–N3 and C16–C11–C13–C14). The β_2 value is derived from the mean value of the torsion angle of C7–C3–C1–C4 and C7–C3–C1–N1 (C17–C13–C11–C14 and C17–C13–C11–N3). The deformation angles of **12d** are listed in Table 6. The bent angles of C2 (C12) (α_2) are larger than those of C5 (C15) (α_1). In addition, the deviation angles (β_1 and β_2) of the benzylic carbons are larger than the bent angles of C5 (C15) and C2 (C12) (α_1 and α_2). The feature suggests that the strains of pyridinophane-6-one having a short methylene bridge cause a substantial deformation of the benzylic carbons C6 (C16) and C7 (C17).

Table 5 Selected bond lengths and bond angles of **12d** obtained by X-ray structure analysis

12d	Bond length/Å						Bond angle/degree						
I	N1–C1	C1–C2	C2–C3	C3–C4	C4–C5	C5–N1	N1–C1–C2	C1–C2–C3	C2–C3–C4	C3–C4–C5	C4–C5–N1	C5–N1–C1
	1.357	1.364	1.406	1.387	1.436	1.386	120.0	117.9	118.7	120.9	114.8	123.4
II	N3–C11	C11–C12	C12–C13	C13–C14	C14–C15	C15–N3	N3–C11–C12	C11–C12–C13	C12–C13–C14	C13–C14–C15	C14–C15–N3	C15–N3–C11
	1.366	1.367	1.397	1.387	1.452	1.384	119.7	118.6	118.7	120.9	114.6	123.6

Chemical transformation

Even though the 2-pyridone ring of the [6](2,4)pyridinophane-6-one is deformed from planarity, spectroscopic data indicate that it has still an aromatic character. Thus, chemical transformations of **12a–c** except **12d**, which was not obtained in a sufficient amount, were examined in order to find the stability or lability depending on the size of the methylene chain. The transformations of **12a–c** followed the approach outlined in Scheme 2.[20] Upon treatment with $POCl_3$ at 50–60 °C under nitrogen atmosphene for 2 h,[20] pyridinophanes **12a–c** gave **13a** (99%), **13b** (88%), and **13c** (77%), respectively. The structures of the reaction products as the 6-chloro-5-cyano[*n*](2,4)pyridinophane ($n = 9$, 8, and 7) were derived from the spectral data, HRMS data, and elemental analyses. The four benzylic protons (*cf.* Fig. 2) and the protons of the methylene bridge of **13a–c** are diagnostic in determining **13a–c** as the [*n*](2,4)pyridiniphane derivatives, which undergo a rapid flipping of the methylene bridge. The disappearance of the carbonyl stretching frequencies of the 2-pyridone ring of **12a–c** can be recognized for **13a–c**. Although Pd/C and hydrazine are known to be reagents for hydrogenation of chloropyridine to pyridine,[21] compound **13a** was reduced to **14a** in modest yield (51% isolated yield). On the other hand, phosphinic acid and sodium hypophosphite (NaH_2PO_2) are known to be effective reagents for the transfer

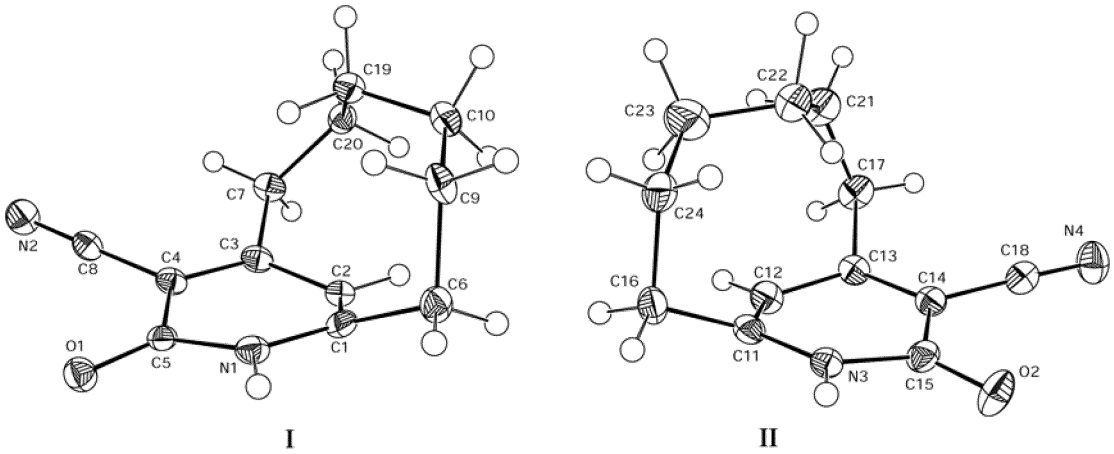


Fig. 5 ORTEP drawing of **12d**.

Table 6 Deformation angles (α_1, α_2, β_1, and β_2/degree) of **12d**

Compd.		α_1	α_2	β_1	β_2
12d	**I**	10.5	18.1	39.7	33.7
	II	6.4	18.3	40.4	37.3

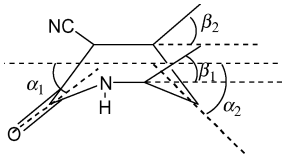
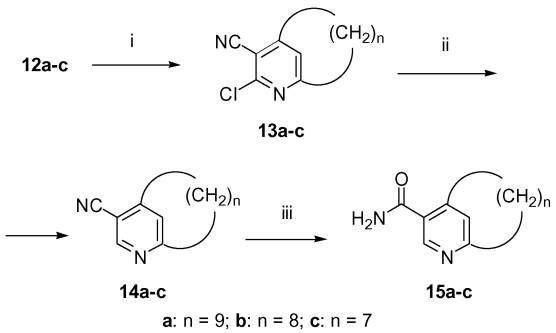


Fig. 6 Deformation angles of **12d**.

hydrogenation of certain functional groups in the presence of an appropriate catalyst.[22] In this way, we carried out the reduction of **13a** with NaH_2PO_2, Na_2CO_3, and 10% Pd/C in THF–H_2O, and **14a** was obtained in 98% isolated yield.[23] In a similar fashion, compounds **13b,c** were also converted to **14b** (81%) and **14c** (91%) in good yields, respectively. The hydrolysis of **14a–c** with KOH in ^{t}BuOH allowed the clean disappearance of the cyano group and appearance of the carbamoyl group to give 5-carbamoyl[*n*](2,4)pyridinophanes **15a** (73%), **15b** (73%), and **15c** (52%). The structures of new compounds **14a–c** and reported compounds **15a–c**[24] are deduced from the inspection of the NMR, IR, HRMS, and elemental analyses. The benzylic protons and the protons of the methylene chain of **14a–c** and **15a–c** exhibiting a similar feature to those of **12a–c** and **13a–c** are diagnostic in determining them as [*n*](2,4)pyridinophane derivatives, which undergo a rapid flipping of the methylene chain.



Scheme 2 *Reagents and conditions*: (i), $POCl_3$, 50–60 °C, 2 h; (ii), $N_2H_4{\cdot}H_2O$, 10% Pd/C or 10% Pd/C, Na_2CO_3, $NaH_2PO_4{\cdot}H_2O$, THF–H_2O, 60 °C, 25 h; (iii), KOH, Bu^{t}OH, heat, 2 h.

Conclusion

A synthesis of [*n*](2,4)pyridinophane-6-ones **12a–d** (n = 9–6), the first example of small-bridged cyclophanes having a 2-pyridone ring, is conveniently accomplished. Their redox potentials are recorded to be parallel to the calculated energy levels of HOMO and LUMO. The similarity of the UV-Vis spectra of the compounds seems also to be consistent with the redox potentials and the theoretical calculation. The dynamic behaviors of **12c** (n = 7) and **12d** (n = 6) are also studied, suggesting their similarity to the simple [*n*](2,4)pyridinophanes (n = 7 and 6), respectively. The structural characteristics of **12d** (n = 6) are studied by X-ray crystallographic analysis, suggesting an appreciable deformation of the 2-pyridone ring. The chemical transformations of **12a–c** (n = 9–7) to several [*n*](2,4)pyridinophanes **13a–c**, **14a–c** and **15a–c** are successfully demonstrated.

Experimental

General

General experimental conditions and spectroscopic instrumentation used have been described previously.[13] *trans*-Cyclododec-2-enone **9a**, *cis–trans* mixtures of cycloundec-2-enone **9b** and of cyclodec-2-econe **9c**, and *cis*-cyclonon-2-enone **9d** were prepared as described previously.[12]

General synthetic procedure for 5-cyano[*n*](2,4)pyridinophane-6-ones (12a–d)

To a stirred solution of **6** (168 mg, 2 mmol) and ^{t}BuOK (224 mg, 2 mmol) in dry DMSO (4 mL) in a flask fitted with an N_2 balloon was added each of **7a–d** (364 mg, 2 mmol) and the mixture was stirred at room temperature for 15 min under nitrogen atmosphere. To the mixture was added ^{t}BuOK (672 mg, 6 mmol) and the N_2 balloon was displaced with an O_2 balloon, the mixture was stirred at room temperature for 2 h. To the reaction mixture was added water (4 mL) and then 4% HCl (20 mL) slowly, the mixture was extracted with CH_2Cl_2 and the extract was dried over Na_2SO_4. After evaporation of the CH_2Cl_2, the resulting mixture was separated by flash column chromatography (SiO_2–CH_2Cl_2). The fractions were concentrated and the contaminated dimethyl sulfone was removed by distillation under reduced pressure. The resulting residue was recrystallized from EtOH to give **12a** (71%), **12b** (63%), **12c** (11%), and **12d** (5%).

12a: mp 217–218 °C (from EtOH); δ_C (100.4 MHz, $CDCl_3$) 24.3, 24.6, 24.9, 25.3, 25.6, 25.7 (2C), 32.6, 34.5, 100.1, 109.3, 115.2, 154.5, 164.1, 164.8; ν_{max} (KBr)/cm^{-1} 2221, 1648; *m/z* (EI, rel. int.) 244 (M^+, 41), 161 (100%) (Found: $M^+ + 1$, 245.1565.

$C_{15}H_{20}N_2O$ requires M + 1, 245.1577) (Found: C, 73.45; H, 8.24; N, 11.63. $C_{15}H_{20}N_2O$ requires C, 73.74; H, 8.25; N, 11.46%).

12b: mp 212–213 °C (from EtOH); δ_C (100.4 MHz, $CDCl_3$) 23.6, 23.7, 26.6, 26.8, 27.3, 27.9, 34.0, 35.5, 99.0, 110.5, 115.2, 154.5, 164.5, 165.4; ν_{max} (KBr)/cm^{-1} 2223, 1639; *m/z* (EI, rel. int.) 230 (M^+, 94), 148 (100%) (Found: M^+, 230.1425. $C_{14}H_{18}N_2O$ requires M, 230.1420) (Found: C, 72.70; H, 7.80; N, 11.88. $C_{14}H_{18}N_2O$ requires C, 73.01; H, 7.88; N, 12.16%).

12c: mp 215–216 °C (from EtOH); δ_C (100.4 MHz, $CDCl_3$) 27.7, 28.9, 29.0, 29.2, 29.3, 35.3, 36.8, 98.1, 111.3, 115.2, 154.8, 164.5, 165.7; ν_{max} (KBr)/cm^{-1} 2220, 1648; *m/z* (EI, rel. int.) 216 (M^+, 100), 161 (56%) (Found: M^+, 216.1274. $C_{13}H_{16}N_2O$ requires M, 216.1264) (Found: C, 71.94; H, 7.53; N; 12.67. $C_{13}H_{16}N_2O$ requires C, 72.19; H, 7.46; N, 12.95%).

12d: mp 188–189 °C (from EtOH); δ_C (100.4 MHz, $CDCl_3$) 26.9, 27.9, 31.1, 33.4, 34.0, 96.9, 114.5, 115.3, 155.2, 164.5, 165.7; ν_{max} (KBr)/cm^{-1} 2217, 1655; *m/z* (EI, rel. int.) 202 (M^+, 82), 148 (100%) (Found: M^+, 202.1112. $C_{12}H_{14}N_2O$ requires M, 202.1107).

General synthetic procedure for 6-chloro-5-cyano[*n*](2,4)-pyridinophanes (13a–c)

A solution of each **12a–c** (1.41 mmol) in $POCl_3$ (5 mL) was heated at 50–60 °C for 2 h under nitrogen atmosphere. The solution was cooled to room temperature and excess $POCl_3$ was removed under reduced pressure. To the residue was added aqueous $NaHCO_3$ to neutralize the solution. The mixture was extracted with CH_2Cl_2 and the extract was dried over Na_2SO_4. After evaporation of the CH_2Cl_2, the residue was purified by column chromatography on SiO_2. The fractions eluted with CH_2Cl_2 were concentrated, and crystallized from EtOH to give **13a** (99%), **13b** (88%), and **13c** (79%).

13a: mp 84–85 °C (from EtOH); δ_H (270 MHz, $CDCl_3$) 0.78–1.01 (4H, m), 1.03–1.33 (6H, m), 1.77–1.91 (4H, m), 2.92 (2H, t, *J* 6.4), 2.93 (2H, t, *J* 6.4), 7.29 (1H, s); δ_C (67.5 MHz, $CDCl_3$) 24.7, 24.8, 25.1, 25.3, 25.4, 25.5, 25.6, 33.8, 37.1, 107.8, 114.1, 123.1, 152.4, 157.7, 165.9; ν_{max} (KBr)/cm^{-1} 2259, 1594; *m/z* (EI, rel. int.) 264 (M^+ + 2, 15), 262 (M^+, 44), 179 (100%) (Found: M^+, 262.1212. $C_{15}H_{19}N_2Cl$ requires M, 262.1239) (Found: C, 68.3; H, 7.57; N, 10.63. $C_{15}H_{19}N_2Cl$ requires C, 68.56; H, 7.29; N, 10.66%).

13b: mp 67–68 °C (from EtOH); δ_H (400 MHz, $CDCl_3$) 0.59–0.74 (4H, m), 1.25–1.35 (4H, m), 1.54–1.72 (4H, m), 2.80–2.90 (4H, m), 7.30 (1H, s); δ_C (100.4 MHz, $CDCl_3$) 23.3, 23.5, 26.4, 26.5, 27.6, 27.9, 34.9, 38.5, 106.9, 114.2, 123.7, 153.0, 158.2, 165.8; ν_{max} (KBr)/cm^{-1} 2250, 1594; *m/z* (EI, rel. int.) 250 (M^+ + 2, 22), 248 (M^+, 62), 166 (100%) (Found: M^+, 248.1064. $C_{14}H_{17}N_2Cl$ requires M, 248.1082) (Found: C, 67.40; H, 7.12; N, 11.30. $C_{14}H_{17}N_2Cl$ requires C, 67.60; H, 6.89; N, 11.26%).

13c: mp 89–90 °C (from EtOH); δ_H (400 MHz, $CDCl_3$) −0.60–0.50 (2H, m), 1.20–1.80 (8H, m), 1.54–1.72 (4H, m), 2.88 (2H, t, *J* 6.0), 2.80–3.10 (2H, b), 7.49 (1H, s); δ_C (100.4 MHz, $CDCl_3$) 27.6, 28.5 (two carbons overlapping), 29.1, 29.3, 36.1, 39.5, 106.1, 114.2, 124.5, 152.7, 158.3, 166.0; ν_{max} (KBr)/cm^{-1} 2245, 1598; *m/z* (EI, rel. int.) 236 (M^+ + 2, 34), 234 (M^+, 100%) (Found: M^+, 234.0931. $C_{13}H_{15}N_2Cl$ requires M, 234.0926) (Found: C, 66.65; H, 6.66; N, 11.98. $C_{13}H_{15}N_2Cl$ requires C, 66.52; H, 6.44; N, 11.93%).

General synthetic procedure for 5-cyano[*n*](2,4)pyridinophanes (14a–c)

Method A: A solution of **13a** (50 mg, 0.19 mmol), hydrazine hydrate (1 mL), and 10% Pd/C (10 mg) in EtOH (5 mL) was heated at 50–60 °C for 2.5 h. The reaction mixture was filtered through Celite, and the filtrate was extracted with benzene, and the extract was dried over Na_2SO_4 and concentrated. The resulting residue was purified by TLC on SiO_2 (hexane–AcOEt 5 : 1) to give **14a** (22 mg, 51%).

Method B: To a stirred mixture of each **13a–c** (0.55 mmol), Na_2CO_3 (175 mg 1.65 mmol), and 10% Pd/C (20 mg) in THF (2 mL), was added a solution of $NaH_2PO_2{\cdot}H_2O$ (175 mg 1.65 mmol) in H_2O (1 mL) dropwise, and the mixture was heated at 60 °C for 25 h. The reaction mixture was filtered through Celite, and the filtrate was neutralized with aqueous $NaHCO_3$ solution, extracted with ether and the extract was dried over $MgSO_4$. After evaporation of the ether, the resulting residue was crystallized from EtOH to give **14a** (98%), **14b** (81%), and **14c** (92%).

14a: mp 63–64 °C (from EtOH); δ_H (400 MHz, $CDCl_3$) 0.77–0.94 (4H, m), 1.03–1.12 (2H, m), 1.12–1.28 (4H,m), 1.86–1.90 (4H, m), 2.86–2.99 (4H, m), 7.35 (1H, s), 8.74 (1H, s); δ_C (100.4 MHz, $CDCl_3$) 24.6, 24.9, 25.1, 25.3, 25.4 (two carbons overlapping), 25.8, 33.4, 37.3, 107.6, 116.4, 124.7, 152.8, 154.1, 165.9; ν_{max} (KBr)/cm^{-1} 2256, 1594; *m/z* (EI, rel. int.) 228 (M^+, 58), 145 (100%) (Found: C, 78.65; H, 8.69; N, 12.0. $C_{15}H_{20}N_2$ requires C, 78.90; H, 8.83; N, 12.27%).

14b: pale yellow oil; δ_H (400 MHz, $CDCl_3$) 0.50–0.75 (4H, m), 1.23–1.36 (4H, m), 1.54–1.70 (4H, m), 2.82–2.90 (4H, m), 7.36 (1H, s), 8.74 (1H, s); δ_C (100.4 MHz, $CDCl_3$) 23.2, 23.5, 26.4, 26.4, 27.7, 28.0, 34.3, 38.8, 106.7, 116.2, 124.8, 153.3, 154.5, 165.7; ν_{max} (KBr)/cm^{-1} 2228, 1596; *m/z* (EI, rel. int.) 214 (M^+, 72), 171 (100%) (Found: M^+, 214.1509. $C_{14}H_{18}N_2$ requires M, 214.1471).

14c: orange oil; δ_H (400 MHz, $CDCl_3$) −1.0–0.5 (2H, br m), 1.30–1.40 (4H, br s), 1.40–1.70 (4H, br s), 2.86 (4H, br s), 7.50 (1H, s), 8.61 (1H, s); δ_C (100.4 MHz, $CDCl_3$) 27.3, 28.5 (two carbons overlapping), 29.1, 29.3, 35.5, 39.8, 105.8, 116.2, 125.6, 152.9, 154.7, 165.9; ν_{max} (KBr)/cm^{-1} 2245, 1596; *m/z* (EI, rel. int.) 200 (M^+, 100%) (Found: M^+, 200.1297. $C_{13}H_{16}N_2$ requires M, 200.1315).

General synthetic procedure for 5-carbamoyl[*n*](2,4)-pyridinophanes (15a–c)

A mixture of each **14a–c** (0.54 mmol) and KOH (1.0 g) in ^{t}BuOH (5 mL) was heated under reflux for 2 h. After the mixture was cooled to rt, the mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4. After evaporation of the CH_2Cl_2, the resulting residue was crystallized from EtOH to give **15a** (73%), **15b** (73%), and **15c** (52%).

15a: mp 189–191 °C (from EtOH); δ_H (400 MHz, DMSO-d_6) 0.66–0.94 (4H, br d), 0.94–1.16 (6H, br s), 1.57–1.78 (4H, br s), 2.79 (2H, t, *J* 6.2), 2.87 (2H, t, *J* 6.2), 7.38 (1H, s), 7.42 (1H, br s), 7,90 (1H, br s), 8.47 (1H, s); δ_C (100.4 MHz, DMSO-d_6) 24.3, 24.4, 24.9, 25.0, 25.3, 25.4, 25.9, 31.2, 36.3, 125.6, 130.0, 147.6, 148.4, 161.6, 169.0; ν_{max} ($CHCl_3$)/cm^{-1} 1678, 1594; *m/z* (EI, rel. int.) 246 (M^+, 69), 163 (100%) (Found: M^+, 246.1708. $C_{15}H_{20}N_2O$ requires M, 2461734) (Found: C, 72.92; H, 8.79; N, 11.12. $C_{15}H_{22}N_2O$ requires C, 73.13; H, 9.00; N, 11.37%).

15b: mp 184–186 °C (from EtOH); δ_H (400 MHz, $CDCl_3$) 0.41 (4H, br s), 1.10–1.30 (4H, br s), 1.50–1.75 (4H, br s), 2,82 (2H, t, *J* 6.0), 2.92 (2H, t, *J* 6.0), 5.90–6.30 (2H, br s), 7.31 (1H, s), 8.64 (1H, s); δ_C (100.4 MHz, $CDCl_3$) 23.3, 23.4, 26.2, 26.5, 27.7, 28.3, 32.9, 38.0, 126.0, 127.8, 148.2, 150.8, 163.6, 169.5; ν_{max} ($CHCl_3$)/cm^{-1} 1676, 1592; *m/z* (EI, rel. int.) 232 (100%) (Found: M^+, 232.1570. $C_{14}H_{20}N_2O$ requires M, 232.1577) (Found: C, 72.32; H, 8.68; N, 12.08. $C_{14}H_{20}N_2O$ requires C, 72.38; H, 8.68; N, 12.06%).

15c: mp 185–187 °C (from EtOH); δ_H (400 MHz, $CDCl_3$) −0.60–0.30 (2H, br s), 1.30–1.50 (4H, br s), 1.50–1.70 (4H, br s), 2,87 (2H, t, *J* 6.0), 2.90–3.10 (2H, br s), 5.70–6.10 (2H, br d), 7.50 (1H, s), 8.58 (1H, s); δ_C (100.4 MHz, $CDCl_3$) 27.4, 28.6, 29.1, 29.7, 34.6, 39.5, 126.8, 127.2, 148.0, 151.3, 163.9, 169.3; ν_{max} ($CHCl_3$)/cm^{-1} 1678, 1592; *m/z* (EI, rel. int.) 218 (100%) (Found: C, 71.59; H, 8.29; N, 12.49. $C_{13}H_{18}N_2O$ requires C, 71.53; H, 8.31; N, 12.83%).

Cyclic voltammetry of 12a–d

The oxidation-reduction potentials of **12a–d** were determined using a CV-27 voltammetry controller (BAS Co). A three-electrode cell was used, consisting of Pt working and counter electrodes and a reference $Ag/AgNO_3$ electrode. Nitrogen was bubbled through an acetonitrile solution (4 mL) of **12a–d** (0.5 mmol dm^{-3}) and Bu_4NClO_4 (0.1 mol dm^{-3}) to deaerate it. The measurements were made at a scan rate of 0.1 V s^{-1} and the voltammograms were recorded on a WX-1000-UM-019 (Graphtec Co) X–Y recorder. Immediately after the measurements, ferrocene (0.1 mmol) ($E_{1/2} = +0.083$) was added as the internal standard, and the observed peak potential was corrected with reference to this standard. The compounds **12a–d** exhibited an oxidation wave and a reduction wave, respectively, and they are summarized in Table 3.

X-Ray structure determination of 12d

Colorless prisms, $C_{12}H_{14}N_2O$, $M = 202.26$, orthorhombic, space group *Pbca*, $a = 9.6984(2)$, $b = 16.5958(3)$, $c = 25.4450(6)$ Å, $V = 4095.4(1)$ Å^3, $Z = 16$, $D_c = 1.312$ g cm^{-3}, crystal dimensions 0.50 × 0.20 × 0.20 mm. Data were measured on a Rigaku RAXIS-RAPID radiation diffractometer with graphite monochromated Mo-Kα radiation. A total of 35879 reflections were collected, using the ω–2θ scan technique to a maximum 2θ value of 55.0°. The structure was solved by direct methods and refined by a full-matrix least-squares method using SIR92 structure analysis software,[25] with 299 variables and 2208 observed reflections [$I > 3.00\sigma(I)$]. The non-hydrogen atoms were refined anisotropically. The weighting scheme $w = [\sigma_c^2(F_0) + 0.0050 \times F_0^2]^{-1}$ gave satisfactory agreement analysis. The final R and Rw values were 0.056 and 0.098. The maximum peak and minimum peak in the final difference map were 0.85 and −0.33 e$^-$ Å^{-3}.

CCDC reference number 253407. See http://www.rsc.org/suppdata/ob/b4/b416013d/ for crystallographic data in .cif or other electronic format.

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