On the reaction of (vinylimino)phosphoranes and related compounds.[1] Novel synthesis and properties of [*n*](2,4)pyridinophanes and [*n*](2,4)quinolinophanes (*n* = 9–7)

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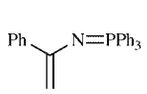
A short, new synthesis of [*n*](2,4)pyridinophanes **13a**–**c** (*n* = 9–7) and **14a**–**c** (*n* = 9–7), as well as **15a** (*n* = 9) and **16a** (*n* = 9) consists of the reaction of 3-aminocyclohex-2-enone and several β-amino enones with cycloalk-2-enones in an enamine-alkylation process, subsequent condensation of the amino group with a carbonyl function, and dehydrogenation of the product in the presence of a dehydrogenating agent (10% Pd/C). Cyclohexenone-annulated [*n*](2,4)pyridinophanes **13a**–**c**, which have a quinoline skeleton, were converted conveniently to a series of [*n*](2,4)quinolinophanes **26a**–**c** (*n* = 9–7), including the known [8](2,4)quinolinophane **26b**. ^{1}H NMR spectroscopy at various temperatures clarified the dynamic behavior of the heptamethylene chain of [7](2,4)pyridinophanes **13c**, **14c**, and [7](2,4)quinolinophane **26c**. The energy barriers ($\Delta G^{\ddagger}_c$) for bridge flipping are 11.3 kcal mol^{-1} (T_c −10 °C) for **13c**, 11.7 kcal mol^{-1} (T_c 0 °C) for **14c**, and 12.2 kcal mol^{-1} (T_c −5 °C) for **26c**. The heptamethylene chain of **26c** does not flex easily as compared with that of **13c** and **14c**. The deformation of the pyridine ring of **13a**–**c** and **26a**–**c** is also suggested by the red shifts of the UV spectra and by the ^{1}H NMR spectra. The base strength of **26a**–**c** seems to be almost independent of the size of the methylene bridge, although pK_a-values of the protonated form of **26a**–**c** become slightly larger when the methylene bridge becomes shorter.

Introduction

The remarkable chemical and physical properties of strained cyclophanes continue to fascinate many chemists.[2–5] Recent studies of these strained molecules have been focused on the challenging synthesis of [5]paracyclophane,[3] the spectroscopic characterization of [4]paracyclophane,[3,6] and more sophisticated molecular orbital calculations.[7] In the field of heterocyclic [*n*]paracyclophanes,[8,9] the smallest known member is [6](2,5)-pyridinophane.[8] In the [*n*]metacyclophane series, [5]metacyclophane is an isolable compound [3,10] and a [4]metacyclophane was also intercepted as a Diels–Alder adduct.[3,11] Although there have been many studies of metacyclophanes, little is known of small-bridged heterophanes. The metapyridinophanes thus far obtained are 3-halogeno-substituted [6](2,4)pyridinophanes,[12] [*n*](2,4)pyridinophanes (*n* = 9 and 7),[13] [*n*](2,6)pyridinophanes (*n* = 12 and 10–6),[14] [*n*](3,5)pyridinophanes (*n* = 9 and 7),[15] 3-chloro-substituted [*n*](2,4)quinolinophanes (*n* = 10, 8, and 6), and [*n*](2,4)quinolinophanes (*n* = 10 and 8).[16,17]



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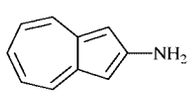

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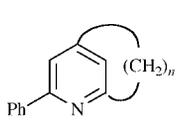

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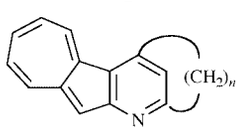

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Previously, we have reported the convenient preparation of [*n*](2,4)pyridinophanes (*n* = 9–6) **3**[18] and azuleno-annulated [*n*](2,4)pyridinophanes **4** (*n* = 9–6)[19] and studied their static and dynamic behavior. The synthetic reaction consists of an enamine-alkylation process of (vinylimino)phosphorane **1** and 2-aminoazulene **2**, respectively, with cycloalk-2-enones, subsequent condensation of the nitrogen moiety with the carbonyl function, and dehydrogenation in the presence of 10% Pd/C or DDQ. The utility of (vinylimino)phosphoranes **1** as useful building blocks for the synthesis of aza-heterocycles has been demonstrated convincingly.[20] Although (vinylimino)phosphoranes are considered to be equivalents of primary enamines, which are generally unstable and undergo rapid conversion into their imine tautomers as well as polymerization,[21] β-amino enones are stable and widely available.[22] According to the literature, Michael-type addition of β-amino enones onto α,β-unsaturated ketones and subsequent condensation gives dihydropyridines.[23] Thus, we applied the reaction to provide a new simple methodology for constructing [*n*](2,4)pyridinophane derivatives **13**–**16**. A series of cyclohexenone-annulated [*n*](2,4)pyridinophanes **13a**–**c** were conveniently converted to a series of [*n*](2,4)quinolinophanes **26a**–**c** (*n* = 9–7) including the known [8](2,4)quinolinophane **26b**. The static and dynamic behavior of the [*n*](2,4)pyridinophanes and [*n*](2,4)quinolinophanes were also studied. We describe herein the results in detail.

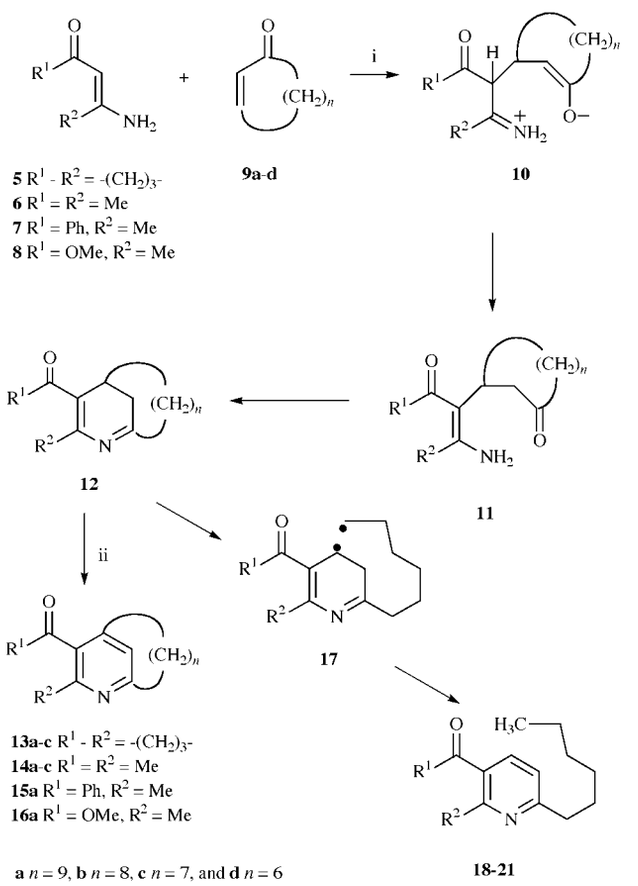
Results and discussion

(a) Synthesis of [*n*](2,4)pyridinophane derivatives and [*n*](2,4)quinolinophanes

The thermal reaction of β-amino enones **5** and **6** with cycloalk-2-enones **9a**–**c** (*n* = 9–7) was examined in *m*-xylene or toluene in the presence of a catalytic amount of a dehydrogenating agent (10% Pd/C) under reflux to give [*n*](2,4)pyridinophanes **13a**–**c** (*n* = 9–7) and **14a**–**c** (*n* = 9–7), respectively (Scheme 1). The reaction conditions and the yields of the products are summarized in Table 1 (runs 1–4 and 6–8). The reaction of **9d** (*n* = 6) with **5** and **6** afforded only 2-hexyl-substituted pyridines **18**

Table 1 Results for the reaction of β-amino enones **5**–**8** with cycloalk-2-enones **9a**–**d**

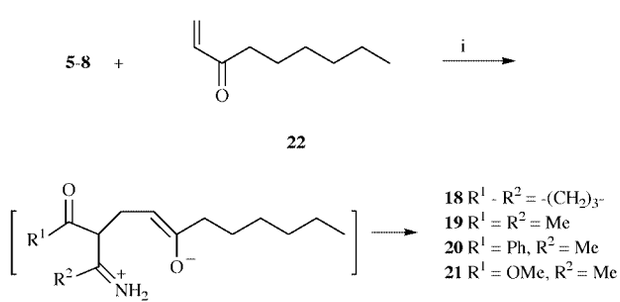
Run	β-Amino enone	Cycloalk-2-enone	*n*	Molar ratio of **5**–**8**:**9**	Solvent	Reaction time (*t*/h)	Product (yield/%)	
1	**5**	**9a**	9	1:1	Xylene	40	**13a** (31)	
2	**5**	**9a**	9	1:2	Toluene	96	**13a** (71)	
3	**5**	**9b**	8	1:2	Toluene	96	**13b** (60)	
4	**5**	**9c**	7	1:2	Toluene	96	**13c** (46)	
5	**5**	**9d**	6	1:2	Toluene	96		**18** (7)
6	**6**	**9a**	9	1.5:1	Xylene	46	**14a** (28)	
7	**6**	**9b**	8	1.5:1	Xylene	48	**14b** (22)	
8	**6**	**9c**	7	1.5:1	Xylene	24	**14c** (26)	
9	**6**	**9d**	6	1.5:1	Xylene	48		**19** (8)
10	**7**	**9a**	9	1:1	Toluene	72	**15a** (34)	
11	**7**	**9d**	6	1:1	Toluene	72		**20** (6)
12	**8**	**6a**	9	1:1	Toluene	72	**16a** (39)	
13	**8**	**9d**	6	1:1	Toluene	72		**21** (5)



Scheme 1 *Reagents and conditions*: i, heat; ii, 10% Pd/C.

(run 5) and **19** (run 9). The formation of [*n*](2,4)pyridinophane derivatives seems to be general, and the reaction of β-amino enones **7** and **8** with **9a** afforded [*n*](2,4)pyridinophanes **15a** (*n* = 9) and **16a** (*n* = 9), respectively (runs 10 and 12). However, attempted reaction of **9d** (*n* = 6) with β-amino enones **7** and **8** resulted also in the formation of 2-hexyl-substituted pyridines **20** and **21**, respectively (runs 11 and 13). The postulated reaction pathways for the formation of [*n*](2,4)pyridinophanes **13a**–**c**, **14a**–**c**, **15a**, and **16a**, and 2-hexyl-substituted pyridines **18**–**21** are shown in Scheme 1. Enamine-alkylation of **5**–**8** to the β-carbon atom of **9a**–**c** gives zwitterions **10**. The following tautomerization in **10** regenerates the β-amino enone moiety in **11**. The enamine intermediates **11** undergo an intramolecular condensation to produce dihydropyridines **12**. Dehydrogenation of dihydropyridines **12** by 10% Pd/C results in the formation of [*n*](2,4)pyridinophanes **13**–**16**. In the case of the constrained **12** (*n* = 6), allylic bond cleavage probably occurs to give diradicals **17**, which undergo aromatization to give 2-hexyl-substituted pyridines **18**–**21**, albeit in low yield. The intermediates **12** (*n* = 6), which have a hexamethylene bridge, seem to be resistant to dehydrogenation in the presence of 10% Pd/C. This fact indicates a high degree of ring strain in the hexamethylene bridge.

Structures of compounds **13a**–**c**, **14a**–**c**, **15a**, and **16a** were deduced from their spectral data and elemental analyses or HRMS data. All the ^{1}H NMR spectra of the compounds correlate well with each other and are in good accord with the proposed structures (Table 2). Structures of 2-hexyl-substituted pyridines **18**–**21** are deduced from their spectral data and HRMS data, and they are further confirmed by independent syntheses. In a similar fashion to the pyridinophane syntheses, thermal reaction of β-amino enones **5**–**8** with non-1-en-3-one **22** in the presence of a dehydrogenating agent (10% Pd/C) afforded 2-hexyl-substituted pyridines **18**–**21**, respectively (Scheme 2). Their spectral data are in good accord with those



Scheme 2 *Conditions*: i, heat.

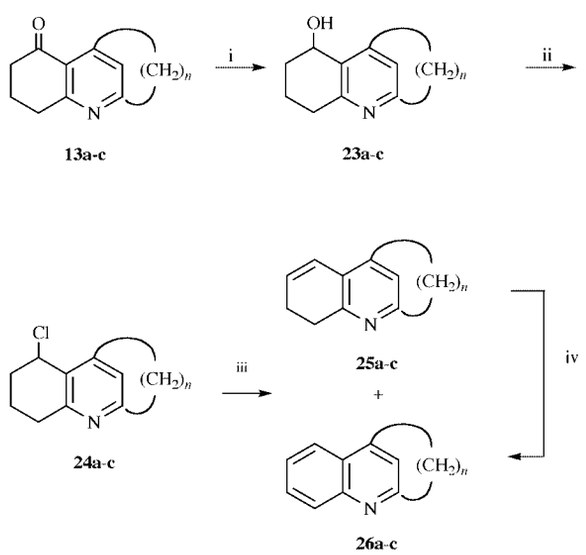
of an authentic specimen; thus, the structures of 2-hexyl-substituted pyridines **18**–**21** are assessed.

The [*n*](2,4)pyridinophanes **13a**–**c** (*n* = 9–7) seemed to be good precursors for the preparation of a series of [*n*](2,4)quinolinophanes **26a**–**c** (*n* = 9–7). Although 3-chloro-substituted [*n*](2,4)-quinolinophanes (*n* = 10, 8, and 6) are known,[16,17] unsubstituted [*n*](2,4)quinolinophane incorporating the smallest chain so far reported has been [8](2,4)quinolinophane.[16,17] Thus, the syntheses and properties of a series of compounds **26a**–**c** are interesting. Reduction of pyridinophanes **13a**–**c** with $NaBH_4$ produced alcohol derivatives **23a**–**c** in good yields (Scheme 3). On treatment with $SOCl_2$, alcohol derivatives **23a**–**c** were converted into chlorides **24a**–**c**, respectively. The dehydrochlorination of chlorides **24a**–**c** with ^{t}BuOK in THF afforded mixtures of [*n*](2,4)-quinolinophanes **26a**–**c** and their dihydrogenated derivatives **25a**–**c**. The mixtures were hardly separable; thus, they were subsequently dehydrogenated with activated MnO_2 to give pure [*n*](2,4)-quinolinophanes **26a**–**c**. Compound **26b** was known, and the structure was assigned on the basis of comparison of the spectral data with those reported in the literature.[16,17] The structures of new compounds

Table 2 ^{1}H NMR spectral data of [*n*](2,4)pyridinophanes **13a–c**, **14a–d**, **15a**, **16a**, and [*n*](2,4)quinolinophanes **26a–c**

Compound	Pyridine	Benzylic		Remaining methylene bridge
	δ H-3	δ H-*n*′	δ H-1′	
13a	7.12	3.14 (2H, t, *J* 6.3)	3.16 (2H, t, *J* 6.3)	0.85–0.93 (2H, m), 0.95–1.00 (2H, m), 1.07–1.18 (6H, m), 1.59–1.83 (4H, m), 2.14 (2H, tt, *J* 6.5 and 6.6), 2.66 (2H, t, *J* 6.6), 2.86 (2H, t, *J* 6.5)
13b	7.16	3.12 (2H, t, *J* 6.3)	3.17 (2H, t, *J* 6.1)	0.70–0.80 (4H, m), 1.12–1.14 (2H, m), 1.23–1.26 (2H, m), 1.59–1.67 (4H, m), 2.13 (2H, quint, *J* 6.5), 2.67 (2H, t, *J* 6.6), 2.80 (2H, t, *J* 6.2)
13c	7.33	3.10 (2H, t, *J* 6.2)	3.20 (2H, br s)	−0.22 (2H, br s), 1.35–1.55 (6H, m), 1.56–1.72 (2H, m), 2.13 (2H, q, *J* 6.5), 2.67 (2H, t, *J* 6.6), 2.84 (2H, t, *J* 6.1)
14a	7.08	2.61 (2H, dd, *J* 6.3 and 6.6)	2.86 (2H, dd, *J* 6.3 and 6.6)	0.82–0.97 (4H, m), 1.11–1.25 (6H, m), 1.63–1.72 (2H, m), 1.74–1.84 (2H, m), 2.47 (3H, s), 2.52 (3H, s)
14b	7.10	2.57 (2H, t, *J* 5.9)	2.78 (2H, dd, *J* 5.9 and 6.3)	0.67–0.77 (4H, m), 1.21–1.27 (4H, m), 1.48–1.63 (4H, m), 2.47 (3H, s), 2.53 (3H, s)
14c	6.90	2.58 (2H, br t, *J* 6.0)	2.78 (2H, t, *J* 5.9 and 6.0)	−0.20 (2H, br s), 1.2–1.7 (8H, m), 2.46 (3H, s), 2.54 (3H, s)
15a	7.17	2.49 (2H, dd, *J* 6.4 and 6.2)	2.92 (2H, t, *J* 6.4)	0.91–1.04 (4H, m), 1.14–1.25 (6H, m), 1.52–1.58 (2H, m), 1.81–1.87 (2H, m), 2.34 (3H, s), 7.47 (2H, dd, *J* 7.7 and 7.3), 7.61 (1H, tt, *J* 7.3 and 1.5), 7.82 (2H, dd, *J* 7.7 and 1.5)
16a	7.30	2.71 (2H, dd, *J* 6.4 and 6.2)	2.85 (2H, t, *J* 6.4)	0.83–0.94 (4H, m), 1.11–1.20 (6H, m), 1.64–1.70 (2H, m), 1.74–1.80 (2H, m), 2.54 (3H, s), 3.91 (3H, s)
26a[a]	7.36	3.04 (2H, t, *J* 6.4)	3.17 (2H, dd, *J* 6.4 and 6.6)	0.81–0.95 (4H, m), 1.03–1.24 (6H, m), 1.84–1.92 (4H, m), 7.49 (1H, dd, *J* 8.1 and 7.2), 7.67 (1H, dd, *J* 8.2 and 7.1), 7.99 (1H, d, *J* 8.2), 8.07 (1H, d, *J* 8.4)
26b[a]	7.38	2.99 (2H, dd, *J* 6.4 and 6.5)	3.11 (2H, dd, *J* 6.0 and 6.2)	0.60–0.66 (2H, m), 0.80–0.85 (2H, m), 1.10–1.26 (4H, m), 1.66–1.74 (4H, m), 7.48 (1H, dd, *J* 7.9 and 7.3), 7.67 (1H, dd, *J* 8.1 and 7.2), 7.97 (1H, d, *J* 8.2), 8.06 (1H, d, *J* 8.4)
26c[a]	7.45	2.87 (2H, t, *J* 5.9)	2.98–3.16 (2H, m)	−0.46 (2H, br s), 1.27–1.70 (8H, m), 7.37 (1H, ddd, *J* 8.3, 6.8 and 1.5), 7.55 (1H, ddd, *J* 8.3, 6.8 and 1.5), 7.86 (1H, dd, *J* 8.6 and 1.5), 7.93 (1H, d, *J* 8.3 and 1.0)

[a] Average chemical shifts of protons on the benzene ring of [*n*](2,4)quinolinophanes: **26a** (δ_{av} = 7.81), **26b** (δ_{av} = 7.80), and **26c** (δ_{av} = 7.68).



Scheme 3 *Reagents and conditions*: i, $NaBH_4$, EtOH; ii, $SOCl_2$, $CHCl_3$; iii, ^{t}BuOK, THF; iv, MnO_2, PhH.

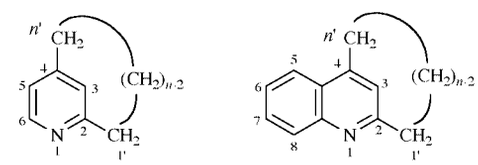


Fig. 1 Numbering of **13**–**16** and **26** in a convenient manner (non-systematic).

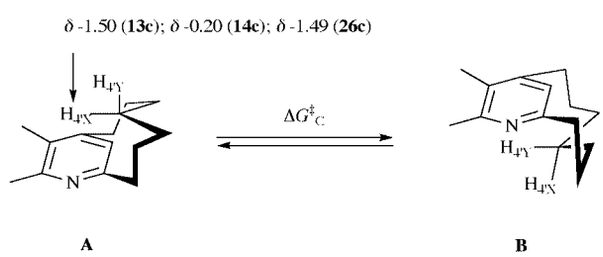


Fig. 2 The flipping of the heptamethylene bridge of **13c**, **14c**, and **26c**.

26a,**c** were deduced from their spectral data and elemental analyses. All the ^{1}H NMR spectra of **26a–c** correlated well with each other and were in good accord with the proposed structures (Table 2).

(b) Conformational change of [7](2,4)pyridinophanes and [7](2,4)quinolinophanes

The ^{1}H NMR spectral data of **13a–c**, **14a–c**, and **26a–c** are listed in Table 2 (see the convenient, but non-systematic, numbering of the methylene illustrated in Fig. 1). Since no [*n*](2,4)pyridinophanes substituted with an electron-withdrawing carbonyl group and no [*n*](2,4)quinolinophanes ($n = 9$ and 7) have been reported, the dynamic behavior of **13a–c**, **14a–c**, and **26a–c** is interesting. A characteristic feature of these compounds is the equivalence of the geminal protons at the 'benzylic' positions, H-1′ and H-*n*′ (Fig. 1). These protons appear as two triplets, a triplet and a broad singlet, two doublets of doublets, and a doublet of doublets and a triplet. This splitting pattern is indicative of a rapid flipping of the methylene bridge of **13a–c**, **14a–c**, **15a**, **16a**, and **26a–c**. Generally, the four 'benzylic' protons of [6](2,4)pyridinophanes exhibited different chemical shifts, suggesting that the bridge flipping of the hexamethylene chain is slow at room temperature.[18,19] The ^{1}H NMR spectra of **13c** were recorded at various temperatures. At 24 °C, the proton signals of H-4′x and H-4′y appear as a mean value at δ −0.22 because of a rapid flipping of the heptamethylene chain (Fig. 2). The signal disappears at −10 °C, and the signal of H-4′x in conformer **A** [or H-4′y in **B**] reappears at δ −1.50 with 1H intensity with a clear coupling pattern at −50 °C. The counterpart was expected to appear at δ 1.16, but it was hidden behind the signals of other aliphatic protons. These observations suggest that each of the geminal protons is located in a different environment and the flipping of the

Table 3 Energy barriers ($\Delta G^{\ddagger}_{c}$ kcal mol^{-1}) of the bridge flipping of [7](2,4)pyridinophanes **13c**, **14c**, **26c**, **3**, and **4**

Compd.	T_c/°C	$\Delta G^{\ddagger}_{c}$/kcal mol^{-1}
13c[a]	−10	11.3
14c[a]	0	11.7
26c[a]	−5	12.2
3[b]	20	12–13
4[c]	−30	10.8

[a] This work. [b] Ref. 18. [c] Ref. 19.

Table 4 UV spectral data of [*n*](2,4)pyridinophanes **13a**–**c** and [*n*](2,4)-quinolinophanes **26a**–**c**

Compound	*n*	λ_{max}(EtOH)/nm (log ε/dm^3 mol^{-1} cm^{-1})
13a	9	208 (4.19), 247 (3.85), 287 (3.67)
13b	8	210 (4.23), 247 (3.89), 287 (3.65)
13c	7	215 (4.18), 249 (3.85), 292 (3.50)
26a	9	230 (4.57), 280 (3.60), 305 (3.50), 318 (3.50)
26b	8	229 (4.59), 278 (3.61), 306 (3.44), 3.19 (3.43)
26c	7	231 (4.58), 283 (3.59), 309 (3.39), 323 (3.36)

heptamethylene chain is frozen on the NMR time-scale. Thus, the coalescence-temperature method[24] could estimate that the energy barrier ($\Delta G^{\ddagger}_{c}$) of the conformational change between **A** and **B** of **13c** is 11.3 kcal mol^{-1}† (T_c −10 °C). The energy barriers of conformational change between **A** and **B** for **14c** and **26c** were also estimated similarly (Fig. 2). The kinetic parameters of the bridge flipping for **13c**, **14c**, **26c** and related compounds are summarized in Table 3. The similar values of $\Delta G^{\ddagger}_{c}$ for **13c** and **14c** suggest that the substituent effect is similar, and these values seem to be slightly smaller than that of **3** (n = 7). The $\Delta G^{\ddagger}_{c}$-value of the quinolinophane **26c** was estimated for the first time, and it was larger than those of **13c**, **14c**, and **4**, but similar to that of **3** (n = 7).

(c) Deformation of [*n*](2,4)pyridinophanes and [*n*](2,4)quinolinophanes

The ^{1}H NMR chemical shifts of aromatic protons are helpful in evaluating the distortion of the pyridine ring of pyridinophanes and quinolinophanes. The H-3 signals in **13a**–**c** and **26a**–**c** shift downfield as the methylene bridge becomes shorter. This feature is attributable to steric compression between H-3 and the methylene bridge.[18,19,25] In contrast, it is remarkable that the corresponding signal of **14c** appears at higher field than that of **14b**. This fact is suggestive of a reduced ring current in the strained pyridine ring of **14c** rather than steric compression. It is remarkable that in the average chemical shifts (δ_{av}) of the protons on the fused benzene ring of quinolinophane **26a**–**c** (Table 2), a subtle high-field shift is observed as the methylene bridge becomes shorter, probably because of the reduced ring current.

The deformation of the aromatic ring of cyclophanes and heterophanes is also evaluated by the red-shift of the UV spectra.[18,19,26] The UV spectra of the series of pyridinophanes **13a**–**c** and quinolinophanes **26a**–**c** are summarized in Table 4. The ring strain of **13a**–**c** and **26a**–**c** is reflected in the red-shift as the value of [*n*] decreases. The longest absorption maxima of **13c** (n = 7) and **26c** (n = 7) are shifted in exactly 5 nm to longer wavelength than those of the corresponding compounds **13a** (n = 9) and **26a** (n = 9), both of which have a planar aromatic ring. Therefore, compound **26c** was suggested to contain the most deformed quinoline ring in the known [*n*](2,4)quinolinophanes.[16,17]

† 1 cal = 4.184 J.

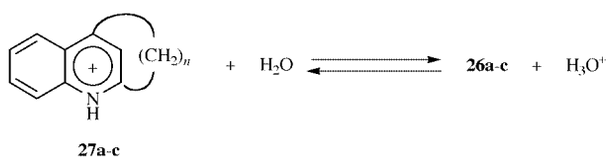
Table 5 pK_a-Values of [*n*](2,4)quinolinophanes **26a**–**c** and reference compounds

n	**26**[a] (Charge density)[b]	**28**[c]	**4**[d]	**29**[d]
		6.72		6.63
9	6.39 (0.14)		6.46	
8	6.44 (0.14)		6.50	
7	6.54 (0.14)		6.47	
6			6.64	

[a] This work. [b] Charge density on the nitrogen atom of **26a**–**c** calculated by AM1 method. [c] Ref. 27. [d] Ref.19.

(d) Basicity of [*n*](2,4)quinolinophanes

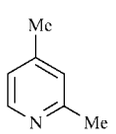
The basicity of amines is determined by the availability of the lone-pair electron on the nitrogen (Scheme 4). Previously, we



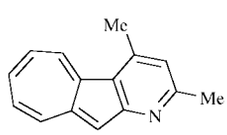
27a-c

Scheme 4

have studied the correlation between the base strength and deformation of the aromatic ring of a series of azuleno-annulated [*n*](2,4)pyridinophanes **4** (n = 9–6).[19] Thus, it was found that the base strength was independent of the size of the methylene bridge, suggesting that the energy difference between the protonated and nonprotonated forms was almost the same for **4** (n = 9–6). Only a few studies of the correlation between the base strength and deformation of the pyridine ring have appeared.[17] The basicities of **26a**–**c** [that is, the acidities (pK_a) of their conjugate acids] were determined, and the results, along with those of **4**, 2,4-dimethylpyridine **28**[27] and the azuleno-annulated pyridine **29**,[19] are summarized (Table 5). The pK_a-values of compound **4** (n = 9–6) are smaller than that of compound **29**. Similarly, the pK_a-values of **26a**–**c** are smaller than



28



29

that of compound **28**, but larger than those of 2-methylpyridine (pK_a = 5.92) and 2-methylquinoline (pK_a = 5.60).[27] The results suggest that the deformation of the pyridine (quinoline) ring does not significantly affect the basicity. This feature is suggested by the similar charge densities on the nitrogen atom of compounds **26a**–**c** (Table 5),[28] and the energy difference between the protonated and nonprotonated forms becomes slightly larger as the methylene chain becomes shorter.

In summary, this work shows for the first time that easily accessible β-amino enones react with cycloalk-2-enones in an enamine-alkylation process followed by condensation and dehydrogenation to give various [*n*](2,4)pyridinophanes derivatives (n = 9–7). The methodology is also applicable to the preparation of [*n*](2,4)quinolinophanes (n = 9–7).

Experimental

IR spectra were recorded on a Perkin-Elmer FT-IR1640 spectrometer. UV spectra were recorded on a Shimadzu UV-3101 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on Hitachi R-90H, JEOL JNM-EX270, JEOL GSX-400, and JEOL JMN-LA500 spectrometers using $CDCl_3$ as solvent, and the chemical shifts are given relative to internal $SiMe_4$ standard:

J-values are given in Hz. The mass spectral and high-resolution mass spectral studies were run on a JEOL Automass 150 and a JEOL JMS-SX102A spectrometer, respectively. Mps were recorded on a Yamato MP-21 apparatus and are uncorrected. (*E*)-Cyclododec-2-enone **9a**, *E*–*Z* mixtures of cycloundec-2-enone **9b** and of cyclodec-2-enone **9c**, and (*Z*)-cyclonon-2-enone **9d** were prepared as described previously.[18,29] β-Amino enones **5**–**8** were prepared by the usual method.[22] Xylene refers to the *m*-isomer.

General synthetic procedure for [*n*](2,4)pyridinophanes 13–16

A solution of cycloalk-2-enone **9a**–**d** (1 or 2 mmol), a β-amino enone **5**–**8** (1 mmol), 0.4 nm molecular sieves (100 mg), and 10% Pd/C (10 mg) in anhydrous xylene or toluene (2 cm^3) was refluxed for the period indicated in Table 1. After the reaction was complete, the mixture was filtered through Celite. The filtrate was concentrated *in vacuo*, and the resulting residue was separated by TLC on silica gel (hexane–AcOEt 1:1) to give [*n*](2,4)pyridinophanes **13a**–**c**, **14a**–**c**, **15a**, and **16a**, as well as pyridines **18**, **19**, **20**, and **21**. The reaction conditions and the yields of the products are summarized in Table 1.

For 13a. Mp 52–53 °C (from AcOEt); δ_C(22.5 MHz) 21.8, 25.0, 25.3 (2C), 25.7 (2C), 26.3, 26.7, 33.9, 34.2, 37.1, 40.6, 124.8, 126.0, 153.7, 164.1, 164.8, 199.1; $\nu_{max}(CHCl_3)/cm^{-1}$ 1685, 1679, 1588; *m*/*z* (rel. int.) 271 (M^+, 100%) (Found: C, 79.9; H, 9.5; N, 5.3; M^+, 271.1909. $C_{18}H_{25}NO$ requires C, 79.66; H, 9.28; N, 5.16%; *M*, 271.1938).

For 13b. Oil; δ_C (22.5 MHz) 21.7, 23.2, 24.1, 25.5, 27.2 (2C), 27.5, 33.7, 34.4, 38.4, 40.6, 123.9, 125.5, 154.0, 164.4, 165.0, 199.1; $\nu_{max}(CHCl_3)/cm^{-1}$ 1680, 1678, 1582; *m*/*z* (rel. int.) 257 (M^+, 100%) (Found: M^+, 257.1797. $C_{17}H_{23}NO$ requires *M*, 257.1781).

For 13c. Oil; δ_C (22.5 MHz) 22.1, 27.7, 28.9, 29.1, 29.3, 29.7, 33.3, 36.2, 39.5, 40.9, 123.8, 126.6, 155.6, 164.7, 165.2, 199.1; $\nu_{max}(CHCl_3)/cm^{-1}$ 1700, 1675, 1582; *m*/*z* (rel. int.) 243 (M^+, 80%), 200 (100) (Found: M^+, 243.1648. $C_{16}H_{21}NO$ requires *M*, 243.1624).

For 14a. Oil; δ_C (22.5 MHz) 22.6, 24.8, 25.2 (2C), 25.3 (2C), 25.5, 25.9, 31.8, 32.4, 37.2, 121.7, 135.2, 145.9, 151.8, 160.8, 206.0; $\nu_{max}(CHCl_3)/cm^{-1}$ 1696, 1589; *m*/*z* (rel. int.) 259 (M^+, 48%), 176 (100) (Found: C, 78.8; H, 10.1; N, 5.2; M^+, 259.1924. $C_{17}H_{25}NO$ requires C, 78.72; H, 9.71; N, 5.40%; *M*, 259.1938).

For 14b. Yellow prisms; mp 37–40 °C (from EtOH); δ_C (22.5 MHz) 22.5, 23.4, 23.7, 26.5 (2C), 27.8, 28.3, 32.7, 32.9, 38.0, 122.5, 134.5, 146.5, 152.5, 160.7, 205.7; $\nu_{max}(CHCl_3)/cm^{-1}$ 1696, 1590; *m*/*z* (rel. int.) 245 (M^+, 37%), 202 (100) (Found: C, 78.6; H, 9.7; N, 5.5; M^+, 245.1808. $C_{16}H_{23}NO$ requires C, 78.32; H, 9.45; N, 5.71%; *M*, 245.1781).

For 14c. Oil; δ_C (22.5 MHz) 22.3 (2C), 23.1, 27.2, 27.9, 28.0, 28.9, 33.0, 39.3, 123.4, 134.0, 147.3, 152.7, 161.0, 206.1; $\nu_{max}(CHCl_3)/cm^{-1}$ 1694, 1590; *m*/*z* (rel. int.) 231 (M^+, 34%), 148 (100) (Found: M^+, 231.1642. $C_{15}H_{21}NO$ requires *M*, 231.1624).

For 15a. Colorless prisms; mp 90–91 °C (from AcOEt); δ_C (100.4 MHz) 23.0, 24.9, 25.0, 25.2, 25.3, 25.5, 25.7, 25.8, 32.2, 37.1, 121.9, 128.9 (2C), 129.4 (2C), 132.4, 133.9, 137.1, 148.0, 153.7, 161.2, 198.7; $\nu_{max}(CHCl_3)/cm^{-1}$ 1665, 1591; *m*/*z* (rel. int.) 321 (M^+, 100%) (Found: C, 82.2; H, 8.7; N, 4.4. $C_{22}H_{27}NO$ requires C, 82.20; H, 8.47; N, 4.36%).

For 16a. Colorless prisms; mp 53–54 °C (from AcOEt); δ_C (100.4 MHz) 23.0, 24.8, 24.9, 25.1, 25.3, 25.4, 25.7, 25.8, 32.3, 37.1, 52.1, 122.2, 126.5, 148.2, 154.9, 161.5, 169.6; $\nu_{max}(CHCl_3)/cm^{-1}$ 1724, 1594, 1558; *m*/*z* (rel. int.) 275 (M^+ 97%), 218 (100) (Found: C, 74.3; H, 9.3; N, 5.2; M^+, 275.1890. $C_{22}H_{27}NO$ requires C, 74.14; H, 9.15; N, 5.09%; *M*, 275.1887).

For 18. Oil δ_H (400 MHz) 0.86–0.91 (3H, m), 1.28–1.42 (6H, m), 1.67–1.76 (2H, m), 2.19 (2H, quintet, *J* 6.4), 2.67 (2H, t, *J* 6.6), 2.81 (2H, t, *J* 7.9), 3.12 (2H, t, *J* 6.2), 7.13 (1H, d, *J* 8.1), 8.18 (1H, d, *J* 8.1); δ_C (100.4 MHz) 14.0, 21.9, 22.5, 29.1, 29.7, 31.6, 32.6, 38.5, 38.9, 121.3, 125.9, 135.2, 163.3, 167.5, 197.9; $\nu_{max}(CHCl_3)/cm^{-1}$ 1682, 1587; *m*/*z* (rel. int.) 231 (M^+, 32%), 174 (100) (Found: M^+, 231.1632. $C_{15}H_{21}NO$ requires *M*, 231.1624).

For 19. Oil; δ_H (500 MHz) 0.86–0.90 (3H, m), 1.29–1.40 (6H, m), 1.67–1.74 (2H, m), 2.57 (3H, s), 2.74 (3H, s), 2.79 (2H, t, *J* 8.0), 7.06 (1H, d, *J* 8.0), 7.89 (1H, d, *J* 8.0); $\nu_{max}(CHCl_3)/cm^{-1}$ 1685, 1586; *m*/*z* (rel. int.) 219 (M^+, 10%), 149 (100) (Found: M^+, 219.1607. $C_{14}H_{21}NO$ requires *M*, 219.1624).

For 20. Oil; δ_H (500 MHz) 0.90 (3H, t, *J* 7.1), 1.30–1.45 (6H, m), 1.72–1.78 (2H, m), 2.53 (3H, s), 2.82 (2H, t, *J* 7.9), 7.06 (1H, d, *J* 7.9), 7.48 (2H, dd, *J* 8.1, 7.6), 7.55 (1H, d, *J* 7.6, 1.7), 7.61 (1H, tt, *J* 7.6, 1.3), 7.77 (2H, dd, *J* 8.1, 1.3); δ_C (125 MHz) 14.1, 22.6, 23.5, 29.2, 29.9, 31.7, 38.7, 119.0, 128.6, 130.0, 131.1, 133.4, 136.8, 137.5, 156.4, 164.1, 197.4; $\nu_{max}(CHCl_3)/cm^{-1}$ 1663, 1587; *m*/*z* (rel. int.) 281 (M^+, 14%), 238 (100) (Found: M^+, 281.1761. $C_{19}H_{23}NO$ requires *M*, 281.1781).

For 21. Oil; δ_H (500 MHz) 0.87–0.89 (3H, m), 1.26–1.39 (6H, m), 1.68–1.74 (2H, m), 2.78 (2H, t, *J* 7.8), 2.81 (3H, s), 3.90 (3H, s), 7.04 (1H, d, *J* 8.0), 8.10 (1H, d, *J* 8.0); δ_C (125 MHz) 14.1, 22.6, 24.9, 29.1, 29.7, 31.7, 38.6, 52.0, 119.7, 122.5, 138.7, 159.5, 165.6, 167.2; $\nu_{max}(CHCl_3)/cm^{-1}$ 1727, 1591; *m*/*z* (rel. int.) 235 (M^+, 8%), 192 (100) (Found: M^+, 235.1593. $C_{14}H_{21}NO_2$ requires *M*, 235.1573).

Independent general synthesis of 2-hexyl-substituted pyridines 18–21

A solution of non-1-en-3-one **22** (1 mmol), a β-amino enone **5**–**8** (1.2 mmol), 10% Pd/C (10 mg), and 0.4 nm molecular sieves (100 mg) in toluene was heated under reflux for 48 h until the reaction was complete. After the solvent had been removed *in vacuo*, the residue was purified by TLC on silica gel using the following developer (for **18**: hexane–AcOEt 2:1; for **19**, **20**, and **21**: hexane–AcOEt 5:1) to give the products **18** (27%), **19** (32%), **20** (27%), and **21** (41%). The spectral data were identical with those of the authentic specimen (*vide supra*).

General synthetic procedure for 2,4-polymethylene-substituted 5-hydroxy-5,6,7,8-tetrahydroquinolines 23a–c

To a stirred solution of $NaBH_4$ (75 mg, 2.03 mmol) in anhydrous EtOH (5 cm^3) was added a solution of a ketone **13a**–**c** (1.0 mmol) in anhydrous EtOH (5 cm^3), and the mixture was stirred at rt for 18 h. To the reaction mixture was added aq. 0.1 M NaOH (20 cm^3), and the new mixture was extracted with CH_2Cl_2, washed with H_2O, and dried over Na_2SO_4. After evaporation of the CH_2Cl_2, the resulting orange oil was crystallized (AcOEt) to give the products **23a** (99%), **23b** (99%), and **23c** (99%) as colorless prisms.

For 23a. Mp 104–105 °C (from AcOEt); δ_H (90 MHz) 0.7–1.5 (8H, m), 1.6–2.2 (12H, m), 2.6–3.1 (4H, m), 5.29 (1H, br s), 7.09 (1H, s); δ_C (22.5 MHz) 17.2, 24.8, 25.1, 25.3, 25.5, 25.7, 25.8, 25.9, 30.6, 31.8, 32.8, 36.8, 63.7, 122.3, 128.7, 150.7, 156.5, 160.1 (Found: C, 79.3; H, 10.2; N, 5.0; M^+, 273.2088. $C_{18}H_{27}NO$ requires C, 79.07; H, 9.95; N, 5.12%; *M*, 273.2094).

For 23b. Mp 156–157 °C (from AcOEt); δ_H (90 MHz) 0.5–1.0 (4H, m), 1.1–2.2 (12H, m), 2.60–3.20 (6H, m), 4.98 (1H,

br s), 7.09 (1H, s) (Found: C, 78.55; H, 9.65; N, 5.16; M^+, 259.1922. $C_{17}H_{25}NO$ requires C, 78.72; H, 9.71; N, 5.40%; *M*, 259.1938).

For 23c. Mp 157–158 °C (from AcOEt); δ_H (90 MHz) −0.1–0.8 (1H, br s), 1.2–2.3 (13H, m), 2.50–3.20 (6H, m), 5.0 (1H, br s), 7.27 (1H, s) (Found: C, 78.4; H, 9.8; N, 5.6; M^+, 245.1776. $C_{16}H_{23}NO$ requires C, 78.32; H, 9.45; N, 5.71%; *M*, 245.1781).

General synthetic procedure for 2,4-polymethylene-substituted 5-chloro-5,6,7,8-tetrahydroquinolines 24a–c

To a stirred solution of alcohol **23a–c** (0.24 mmol) in anhydrous $CHCl_3$ (5 cm^3) was added $SOCl_2$ (0.05 cm^3) dropwise, and the mixture was refluxed for 2 h under nitrogen atmosphere. To the reaction mixture was added water, and the new mixture was neutralized with saturated aq. $NaHCO_3$, extracted with CH_2Cl_2, and the extract dried over Na_2SO_4. After evaporation of the CH_2Cl_2, the resulting residue was purified by TLC on silica gel (hexane–AcOEt 1:1) to give **24a** (86%), **24b** (68%), and **24c** (93%).

For 24a. Yellow oil; δ_H (90 MHz) 0.7–1.9 (16H, m), 2.6–3.2 (6H, m), 5.33 (1H, br s), 7.01 (1H, s); $\nu_{max}(CHCl_3)/cm^{-1}$ 2920, 1599; *m*/*z* (rel. int.) 293 (M^+, 9%), 149 (100) (Found: M^+, 291.1786. $C_{18}H_{26}ClN$ requires *M*, 291.1756).

For 24b. Yellow oil; δ_H (90 MHz) 0.3–3.1 (22H, m), 5.39 (1H, br s), 7.09 (1H, s); $\nu_{max}(CHCl_3)/cm^{-1}$ 2940, 1590; *m*/*z* (rel. int.) 279 (M^+, 8%), 242 (100) (Found: M^+, 277.1581. $C_{17}H_{24}ClN$ requires *M*, 277.1599).

For 24c. Yellow oil; δ_H (90 MHz) −0.7–0.4 (2 H, br s), 1.3–2.5 (12H, m), 2.6–3.1 (6H, m), 5.46 (1H, br), 7.27 (1H, s); $\nu_{max}(CHCl_3)/cm^{-1}$ 2930, 1590; *m*/*z* (rel. int.) 265 (M^+, 3%), 228 (100) (Found: M^+, 263.1415. $C_{16}H_{22}ClN$ requires *M*, 263.1443).

General synthetic procedure for [*n*](2,4)quinolinophanes 26a–c

A solution of a chloride **24a–c** (0.21 mmol) and ᵗBuOK (0.62 mmol) in anhydrous THF (3 cm^3) was refluxed for 18 h under nitrogen atmosphere. To the reaction mixture was added water (20 cm^3), the mixture was extracted with diethyl ether, and the extract was dried over $MgSO_4$. After evaporation of the ether, the residue was separated by TLC on silica gel (hexane–AcOEt 1:1) to give a mixture of dihydroquinolinophane **25a–c** and quinolinophane **26a–c**.

To a solution of the mixture in PhH (2 cm^3) was added MnO_2 (100 mg), and the mixture was stirred at rt for 3 h. The reaction mixture was filtered through Celite, and the filtrate was concentrated to give quinolinophanes **26a** (44%), **26b** (61%), and **26c** (52%).

For 26a. Yellow needles; mp 59–62 °C (from AcOEt); δ_C (100.4 MHz) 24.3, 25.5, 25.6, 26.2, 26.4, 26.5, 31.2, 38.2, 123.5, 125.3, 126.3, 128.9, 129.5, 146.9, 148.4, 162.0 (two carbons overlap in the spectra); $\nu_{max}(CHCl_3)/cm^{-1}$ 2950, 2860, 1602; *m*/*z* (rel. int.) 253 (M^+, 54%), 170 (100) (Found: M^+, 253.1805. $C_{18}H_{23}N$ requires *M*, 253.1832).

For 26b. Yellow needles; mp 64–65 °C (from AcOEt) (lit.,[16] 64–66 °C); δ_C (100.4 MHz) 23.0, 23.9, 25.3, 26.9, 27.2, 27.9, 31.5, 38.8, 122.8, 123.4, 125.2, 125.8, 129.0, 129.3, 147.4, 148.6, 162.3; $\nu_{max}(CHCl_3)/cm^{-1}$ 2928, 2864, 1603; *m*/*z* (rel. int.) 239 (M^+, 57%), 196 (100) (Found: M^+, 239.1650. Calc. for $C_{17}H_{21}N$: *M*, 239.1675).

For 26c. Yellow needles; mp 43–46 °C (from AcOEt); δ_C (100.4 MHz) 27.5, 29.0, 29.3, 35.6, 40.5, 123.3, 123.7, 125.2, 126.0, 129.3, 148.5, 149.2, 162.7 (three carbons overlap in the spectra); $\nu_{max}(CHCl_3)/cm^{-1}$ 2928, 2864, 1603; *m*/*z* (rel. int.) 225 (M^+, 68%), 157 (100) (Found: C, 85.0, H, 8.8; N, 6.1. $C_{16}H_{19}N$ requires C, 85.29; H, 8.50; N, 6.22%).

Determination of pK_a of [*n*](2,4)quinolinophanes 26a–c

Buffer solutions of slightly different acidities (pH 4–8) were prepared by mixing a citric acid solution (0.1 M) in 20% aq. MeCN (1:4 by volume) and a solution of Na_2HPO_4 (0.2 M) in 20% aq. MeCN, in various portions. For the preparation of sample solutions, 1 cm^3 portions of the stock solution, prepared by dissolving 1 mg of a quinolinophane **26a–c** in MeCN (10 cm^3), were diluted to 10 cm^3 with the buffer solution. The UV-vis spectrum was recorded for each quinolinophane **26a–c** in 10 different solutions of buffers. Immediately after recording the spectrum, the pH of each sample solution was determined on a pH meter calibrated with standard buffers. The observed absorbance at the specific absorption wavelength of each phase **26a–c** was plotted against pH to give a classical titration curve, whose midpoint was taken as the pK_a-value.

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