On the Reaction of (Vinylimino)phosphorane and Related Compounds. 22.[1] Syntheses and Structural Studies of Methanocycloundeca[*b*]pyrrole Ring Systems[2]

Nobuhiro Kanomata, Ken-ichi Kamae, Yukio Iino, and Makoto Nitta*

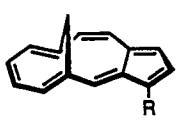
Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 169, Japan

Received February 7, 1992

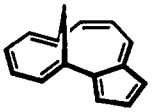
Novel 2-phenyl-6,11- and 2-phenyl-4,9-methanocycloundeca[*b*]pyrroles (**15a** and **16a**) were synthesized in moderate yields by the reaction of 3,8-methano[11]annulenone (**3**), a 10π-electron vinylogue of tropone, with [(1-phenylvinyl)imino]triphenylphosphorane (**8a**) and subsequent dehydrogenation. Similarly, the reaction of the annulenone **3** with (inden-3-ylimino)tributylphosphorane (**8c**) and subsequent aromatization afforded 7,12- and 9,14-methano-15*H*-cycloundeca[*b*]indeno[2,3-*d*]pyrroles (**15c** and **16c**), which also have methanocycloundeca[*b*]pyrrole ring systems. Preparation of 2-phenyl-5,10-methanocycloundeca[*b*]pyrrole (**17**), an isomer of both **15a** and **16a**, was also accomplished in low yield by the reaction of 4,9-methano[11]annulenone (**5**) with an excess of [(1-phenylvinyl)imino]tributylphosphorane (**8d**). The reactivity of annulenone **5** with (vinylimino)phosphoranes was found to be quite low as compared to the higher reactivity of annulenone **3** and tropone. Compounds **15a,c**, **16a,c**, and **17** are the first nitrogen analogues of cyclopentacycloundecene ring systems which have vinylogous structures of 1-azaazulene. Structures of the products obtained were examined by ^{1}H NMR spectra and UV spectra. The ^{1}H NMR spectra clarified that the compounds **15a,c**, **16a,c**, and **17** are aromatic molecules having a diatropic 14π-electron system, and 5,10-methano derivative **17** has a more diatropic nature than the compounds **15a,c** and **16a,c**. The UV spectra of **15a,c**, **16a,c**, and **17** exhibited increased cyclic conjugation of the aromatic perimeter according to a bathochromic shift of the longest absorption maxima as compared to the corresponding 1-azaazulene derivatives.

Bridged annulenes with nonplanar cyclic conjugation have caused chemists to consider the relationship between molecular strain and aromaticity in these compounds. The aromatic character of 1,6-[3] and 1,5-methano[10]annulenes[4] has been studied extensively by using chemical and spectroscopic methods. As for methano-bridged aromatics having a 14π-electron system, Prinzbach et al. reported on a series of 5,10-methanocyclopentacycloundecenes (**1**)[5] as vinylogous compounds of azulene and showed that compound **1** has similar properties to azulene. Although the synthesis of aza analogues of 1,6-methano[10]annulene has been reported,[6,7] no nitrogen analogues of **1** have appeared.

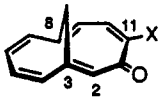
We have demonstrated the synthetic utility of vinylimino)phosphoranes for the preparation of various kinds of heterocycles.[8-11] (Vinylimino)phosphoranes react with tropone and its derivatives to afford the 1-azaazulene ring system.[11] As an application to methano-bridged aromatics, we recently reported the synthesis of methanocyclodeca-[*b*]cyclohepta[*d*]pyrrole[1] by the reaction of (phosphoranylideneamino)-1,6-methano[10]annulene with 2-chlorotropone. On the basis of those studies, we noted that methano[11]annulenones can serve as possible precursors of 1-azaazulene vinylogues, which are nitrogen analogues of **1** and unknown 4,9-methanocyclopentacycloundecene (**2**). Vogel et al. justified viewing 3,8- and 4,9-methano-[11]annulenones (**3** and **5**) as vinylogous compounds of



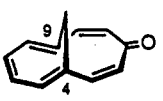
1a: R = H;
1b: R = CO_2Et



2



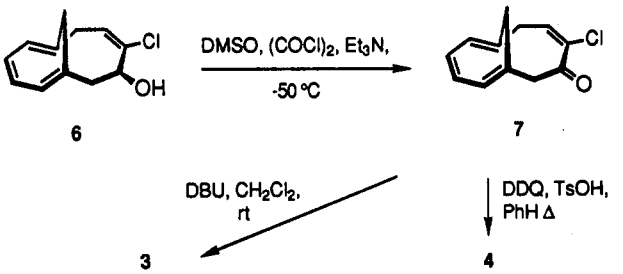
3: X = H
4: X = Cl



5

tropone based on their spectroscopic properties and bas-

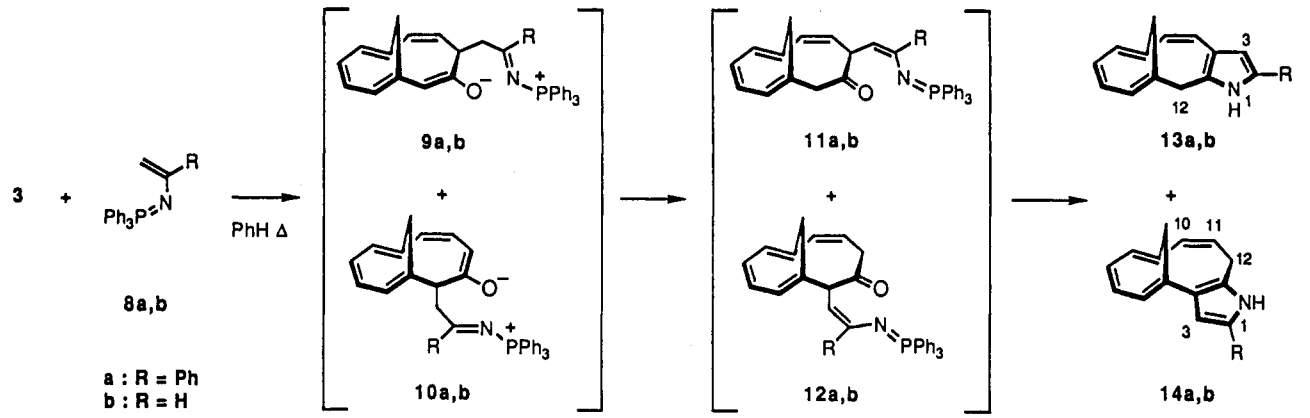
Scheme I



(1) Part 21; Nitta, M.; Kawaji, H.; Kanomata, N. *Tetrahedron Lett.* **1992**, *33*, 251.
(2) Preliminary accounts of paper has appeared: Nitta, M.; Kanomata, N.; Tada, M. *Tetrahedron Lett.* **1990**, *31*, 1291.
(3) (a) Vogel, E.; Roth, H. D. *Angew. Chem.* **1964**, *76*, 145. (b) Cremer, D.; Dick, B. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 865 and references therein.
(4) (a) Masamune, S.; Brooks, D. W. *Tetrahedron Lett.* **1977**, 3239. (b) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. *J. Am. Chem. Soc.* **1981**, *103*, 5216. (c) Scott, L. T.; Sumpter, C. A.; Oda, M.; Erden, I. *Tetrahedron Lett.* **1989**, *30*, 305.
(5) (a) Prinzbach, H.; Knothe, L. *Pure Appl. Chem.* **1986**, *58*, 25. (b) Beck, A.; Hunkler, D.; Prinzbach, H. *Tetrahedron Lett.* **1983**, *24*, 2151. (c) Beck, A.; Knothe, L.; Hunkler, D.; Prinzbach, H. *Tetrahedron Lett.* **1984**, *25*, 1785.
(6) Schäfer-Ridder, M.; Wagner, A.; Schwamborn, M.; Schreiner, H.; Devrout, E.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 853 and references therein.
(7) Tückmantel, W.; Andree, G.; Seidel, A.; Schmickler, H.; Lex, J.; Kraka, E.; Haug, M.; Cremer, D.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 592 and references therein.
(8) Iino, Y.; Nitta, M. *J. Synth. Org. Chem. Jpn.* **1990**, *48*, 681.
(9) (a) Kobayashi, T.; Nitta, M. *Chem. Lett.* **1986**, 1549. (b) Kobayashi, T.; Iino, Y.; Nitta, M. *J. Chem. Soc. Jpn.* (*Nippon Kagaku Kaishi*) **1987**, 1237. (c) Iino, Y.; Nitta, M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2235. (d) Kanomata, N.; Nitta, M. *Tetrahedron Lett.* **1988**, *29*, 5957; *J. Chem. Soc., Perkin Trans. 1* **1990**, 1119. (e) Nitta, M.; Soeda, H.; Iino, Y. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 932. (f) Nitta, M.; Iino, Y. *J. Chem. Soc. Perkin Trans 1* **1990**, 435. (g) Nitta, M.; Ohnuma, M.; Iino, Y. *Ibid.* **1991**, 1115. (h) Kanomata, N.; Kawaji, H.; Nitta, M. *J. Org. Chem.* **1992**, *57*, 618.
(10) (a) Iino, Y.; Kobayashi, T.; Nitta, M. *Heterocycles* **1986**, *24*, 2437. (b) Iino, Y.; Hara, E.; Nitta, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1913.
(11) (a) Niita, M.; Kobayashi, T. *Chem. Lett.* **1986**, 463. (b) Nitta, M.; Iino, Y.; Hara, E.; Kobayashi, T. *J. Chem. Soc., Perkin Trans. 1* **1989**, *51*. (c) Nitta, M.; Iino, Y.; Kamata, K. *Heterocycles* **1989**, *29*, 1655.

0022-3263/92/1957-5313$03.00/0

Scheme II



icities.[12] Little is known, however, about the chemical reactivities of methano[11]annulenones **3** and **5**, especially with nucleophiles. In this paper, we report simple syntheses for, and the spectroscopic properties of, novel nitrogen analogues of **1** and **2** having the vinylogous structures of 1-azaazulene, 6,11-, 4,9-, and 5,10-methanocycloundeca[*b*]pyrrole ring systems.

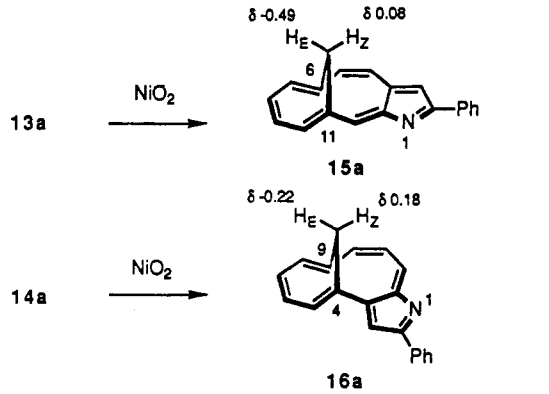
Results and Discussion

Synthesis of 1-Azaazulene Vinylogues. Our synthetic strategy for the preparation of 6,11- and 4,9-methanocycloundeca[*b*]pyrrole ring systems involved the reaction of 3,8-methano[11]annulenone (**3**)[12] or its 11-chloro derivative **4**[13] with [(1-phenylvinyl)imino]triphenylphosphorane (**8a**),[9a] (vinylimino)triphenylphosphorane (**8b**),[9b] and/or (inden-3-ylimino)tributylphosphorane (**8c**).[9g,11c]

Preparation of the annulenones **3** and **4** is outlined in Scheme I. Compound **3** was prepared from 4-chlorobicyclo[5.4.1]dodeca-4,7,9,11-tetraen-3-ol (**6**)[13] via Swern oxidation[14] giving the corresponding ketone **7** (80% yield) and subsequent dehydrochlorination by DBU (88% yield). Compound **4** was derived from ketone **7** by dehydrogenation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (71% yield). Vogel and co-workers reported the synthesis of annulenone **3** from chloro[11]annulenone **4**, which was prepared by the direct oxidation of alcohol **6** with manganese dioxide (25–30% yield).[12,13] The methods we employed here were quite convenient and significantly improved the yields of annulenones **3** and **4**.

The reaction of **3** with 1.5 molar equiv of **8a** in anhydrous benzene was carried out under reflux for 24 h to give the pyrrole derivatives **13a** and **14a** in 42% and 37% yields, respectively. Similarly, the reaction of **3** with 2.0 molar equiv of **8b** in anhydrous toluene gave unsubstituted **13b** and **14b** in 5% and 4% yields, respectively (Scheme II). Structural assignments for the new compounds were obtained by spectral analysis. In the ^{1}H NMR spectra of **13a** and **14a**, the methylene protons of H-12 of **13a** appear at δ 4.11 as a singlet, while those of **14a** appear at δ 3.42 and δ 4.48, both of which are coupled with the olefinic protons of H-11 and H-10. The chemical shifts and coupling patterns of these compounds are in good agreement with the proposed structures of **13a** and **14a**. The structural assignments for **13b** and **14b** were based on the spectral similarity to **13a** and **14a**, respectively. The postulated pathways in the reactions are also shown in Scheme II.[9b] Enamine-type alkylation of the iminophosphoranes **8a,b** on C-11 and C-2 of **3** gives intermediates **9a,b** and **10a,b** respectively. Hydrogen transfer in **9a,b** and **10a,b** regenerates the (vinylimino)phosphorane moieties (**11a,b** and **12a,b**). These intermediates then undergo an intramolecular aza-Wittig reaction followed by hydrogen shifts which generates the pyrrole rings in **13a,b** and **14a,b**. The dehydrogenation reaction of **13a** and **14a** with nickel peroxide[15] was completed within 30 min at room temperature, giving 2-phenyl-6,11-methanocycloundeca[*b*]pyrrole (**15a**) and 2-phenyl-4,9-methanocycloundeca[*b*]pyrrole (**16a**) as green solids (70% and 16% yields, respectively, Scheme III). Compound **16a** is the first example of a nitrogen analogue of 4,9-methanocyclopentacycloundecene **2**. The structures of compounds **15a** and **16a** were supported by their ^{1}H and ^{13}C NMR spectra (vide infra) and mass spectra. Attempts to prepare the parent methanocycloundeca[*b*]pyrroles were also carried out. The dehydrogenation of **13b** and **14b** with nickel peroxide, manganese dioxide, or DDQ, however, gave tarry materials, and the expected product was not obtained.

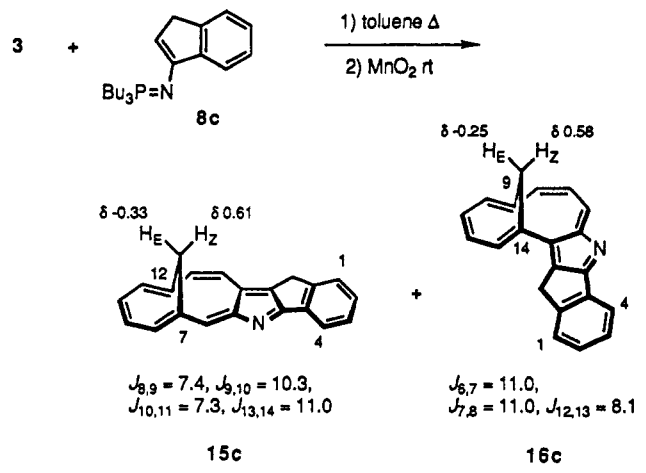
Scheme III



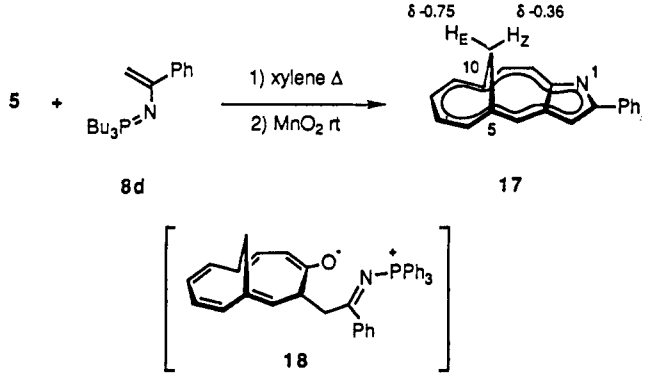
Annulenone **3** was allowed to react with (inden-3-ylimino)tributylphosphorane (**8c**), (prepared in situ from 3-azidoindene and tributylphosphine[11c]), after which time the reaction mixture was chromatographed to remove tributylphosphine oxide. The fractions were concentrated and the expected 5,6-dihydro-7,12- and 5,6-dihydro-9,14-methano-15*H*-cycloundeca[*b*]indeno[2,3-*d*]pyrroles were subsequently dehydrogenated with manganese dioxide[16] to afford 7,12- and 9,14-methano-15*H*-cycloundeca[*b*]-indeno[2,3-*d*]pyrroles (**15c** and **16c**, 6% and 31% yields, respectively, Scheme IV). ^{1}H NMR and mass spectra

(12) Vogel, E. 23rd International Congress of Pure and Applied Chemistry, 1971, *1*, 275.
(13) Reisdorff, J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* 1972, *11*, 218.
(14) Mancuso, A. J.; Swern, D. *Synthesis* 1981, *165*.
(15) Nakagawa, K.; Konaka, R.; Nakata, T. *J. Org. Chem.* 1962, *27*, 1597.
(16) King, R. B.; Stone, F. G. A. *Inorganic Synthesis*; McGraw-Hill: New York, 1963; Vol. VII, pp 194.

Scheme IV



Scheme V



Scheme VI

supported the indeno-annulated structures, **15c** and **16c**. The reacton of 2-chlorotropone with (vinylimino)-phosphoranes **8a** and **8b** afforded 1-azaazulenes **22** and **21**, respectively, in a single step (Figure 2).[11b] The vinylogous compound 11-chloro-3,8-methano[11]annulenone (**4**) seemed to be a good precursor for **15** and **16**, but products such as **15a** or **16a** were not obtained by the reaction of **4** with **8a**. This can be ascribed to the probable instability of the expected **15a** or **16a** under the reaction conditions.

Initial preparation of 5,10-methanocycloundeca[*b*]-pyrrole **17** was attempted through the reaction of 4,9-methano[11]annulenone (**5**) with iminotriphenyl-phosphorane **8a**. Monitoring the reaction by TLC, however, indicated that annulenone **5** is less reactive than annulenone **3**. Even in refluxing xylene the expected products were not obtained. The reaction of **5** with excess [(1-phenylvinyl)imino]tributylphosphorane **8d** was carried out in refluxing xylene (48 h) and afforded a mixture which included the expected dihydrogenated derivative of 2-phenyl-5,10-methanocycloundeca[*b*]pyrrole (**17**). Although purification of the dihydroannulene at this stage was unsuccessful, treatment of the mixture with manganese dioxide gave the desired compound **17** (3% yield, Scheme V). The formation of compound **17** can be explained using a pathway which is similar to those for compounds **15a** and **16a** (Scheme II). Structure **17** as deduced from examination of the ^{1}H NMR (vide infra) spectrum. Other spectral data are consistent with the proposed structure.

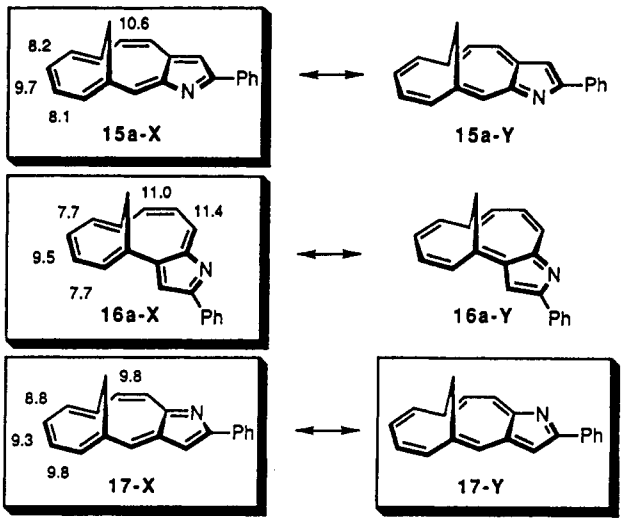


Figure 1. Structures and coupling constants (Hz) of cycloundeca[*b*]pyrrole derivatives.

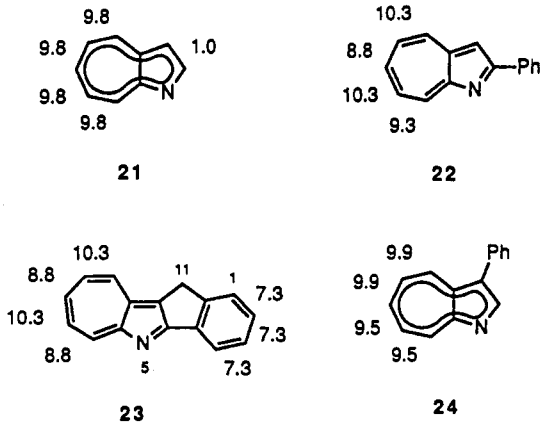


Figure 2. Coupling constants (Hz) of 1-azaazulene and its derivatives.

Reactivity of 3,8- and 4,9-Methano[11]annulenones. It is interesting that annulenones **3** and **5** have different reactivities toward iminophosphoranes. The higher reactivity of **3** can be understood by comparing the thermodynamic stabilities of **3** and **5**. There is a well-known tendency for double bond localization in methanol[11]-annulene systems to favor cycloheptatriene moieties predominantly and to avoid 1,6-dimethylenecyclohepta-2,4-diene moieties.[12,17] A typical example is the prototropic isomerization in hydroxymethano[11]annulenone (a 10π-electorn vinylogue of tropolone). Valence tautomerization favors structure **20** over **19** (Scheme VI).[13] This observation suggests that 4,9-methano[11]annulenone **5** is more stable than 3,8-methano[11]annulenone **3** and that intermediates **9a** and **10a** (Scheme II) should be more stable than intermediate **18** (Scheme V). The calculated heats of formation by the semiempirical method (AM1) also support the greater thermodynamic stability of annulenone **5** (51.1 kcal/mol) over annulenone **3** (53.4 kcal/mol).[18] Therefore, annulenone **3** (the source of **9a** and **10a**) should be more reactive than annulenone **5** (the source of **18**).

Spectroscopic Properties of Methanocycloundeca-[*b*]pyrroles. The ^{1}H NMR spectra of methanocycloundeca[*b*]pyrrole derivatives **15a,c**, **16a,c**, and **17** are noteworthy since the chemical shifts of bridged-annulene

(17) Paquette, L. A.; Berk, H. C.; Ley, S. V. *J. Org. Chem.* **1975**, *40*, 902 and references therein.
(18) Nitta, M.; Akaogi, A. Unpublished results.

systems are quite useful in determining such structural properties as diatropicity and bond alternation. Unambiguous proton assignment was successfully made by analyzing ^1H and 2D ^1H NMR spectra. The chemical shifts of the bridge protons and selected coupling constants of peripheral protons are listed also in Schemes III–V and Figure 1. The chemical shifts of the methylene protons of **15–17** were found in the shielding region (δ –0.75 to 0.61), and the peripheral protons appear in the aromatic region (δ 7.09–9.11). Furthermore, the large geminal coupling constants of the methylene protons ($J_{E,Z}$ = 10.8–11.4 Hz) support the absence of norcaradiene structure for **15–17**. These findings indicate that compounds **15–17** all exist as diatropic molecules having 14π-electron systems.

The chemical shifts of the bridge protons reflect the degree of ring current in methano-bridged aromatics.[19] Their average values of **15a** (δ_{av} = –0.21), **16a** (δ_{av} = –0.02), and **17** (δ_{av} = –0.56) suggest that the degree of diatropic ring current decreases in the order **17** > **15a** > **16a**. The lower diatropicity in **16a** may be ascribed to the increase of strain in the near-planar conformation due to fusion of the five-membered ring next to the bridgehead carbon.[20] Vicinal coupling constants of aromatic perimeter protons suggest bond alternation in **15a** [$J_{8,9}$ (9.7 Hz) > $J_{7,8}$ (8.1 Hz) ≈ $J_{9,10}$ (8.2 Hz)] and **16a** [$J_{6,7}$ (9.5 Hz) > $J_{5,6}$ = $J_{7,8}$ (7.7 Hz)] (Figure 1). On the other hand, the ^1H NMR spectrum exhibits no significant bond alternation in compound **17**. The vicinal coupling constants of $J_{6,7}$ (9.8 Hz), $J_{7,8}$ (9.3 Hz), and $J_{8,9}$ (8.8 Hz) in compound **17** are within 1.0 Hz, and $J_{11,12}$ (9.8 Hz) is smaller than $J_{4,5}$ of **15a** (10.6 Hz) (Figure 1). The vicinal coupling constants in **15c** [$J_{9,10}$ (10.3 Hz) > $J_{8,9}$ (7.4 Hz) ≈ $J_{10,11}$ (7.3 Hz)] (Scheme IV) suggest remarkable bond alternation also in this structure. The position of the signals for the bridge protons of compounds **15c** (δ_{av} = 0.14) and **16c** (δ_{av} = 0.17) (Scheme III) suggests slight decreases in ring current as compared with **15a** and **16a**. In the case of compound **16c**, however, the spectral complexity prevented us from detailed analysis.

The preference for cycloheptatriene moieties[12,17] in methanoannulene systems (vide supra) seems applicable for structural assignments in compounds **15–17**. According to their NMR spectra, canonical structures of **15a-X** and **16a-X** containing the cycloheptatriene element seem to be more preferable to the canonical structures of **15a-Y** and **16a-Y** having the dimethylenecycloheptadiene element (Figure 1). However, compound **17** was found to favor both canonical structures **17-X** and **17-Y**. Thus, there must be other factors which favor the contribution of the canonical stucture **17-Y** in compound **17**.

To investigate the bond alternation in annulated pyrrole ring systems, we reexamined the ^1H NMR spectra of a series of 1-azaazulenes such as cyclohepta[*b*]pyrrole (**21**),[11b,21] 2-phenylcyclohepta[*b*]pyrrole (**22**),[11a,b] cyclohepta[*b*]indeno[2,3-*d*]pyrrole (**23**),[11c] and 3-phenylcyclohepta[*b*]pyrrole (**24**)[22] (see the Experimental Section). The vicinal coupling constants in **21–24** are shown in Figure 2. The coupling constants on the seven-membered ring in **21** (in $CDCl_3$) are the same (J = 9.8 Hz), and support a delocalized structure. This observation is consistent with the previous observation of the ^1H NMR spectral data of **21** measured in methanol-d_4 solution.[21] However, ^1H NMR spectra of **22** and **23** showed that phenyl substitution at the C-2 position or indeno-annulation (having π-system similar to **22**) gives rise to double bond localization in 1-azaazulene systems (Figure 2). Appearance of bond alternation seems to be inherent in 2-phenyl substitution, while the 3-phenyl derivative **24** has a delocalized π-system like the parent compound **21**. Consequently, a phenyl group at the C-2 position seems to conjugate preferably with the C=N double bond rather than the C=C double bond in 1-azaazulene ring systems. Therefore, we conclude that the contribution of the **X** form is predominant for compounds **15a** and **16a**, as they consist of the two preferable moieties, the cycloheptatriene element and PhC=N conjugation. In the case of compound **17**, both canonical structures of **17-X** (cycloheptatriene element) and **17-Y** (PhC=N conjugation) became important in the delocalization of π-system.

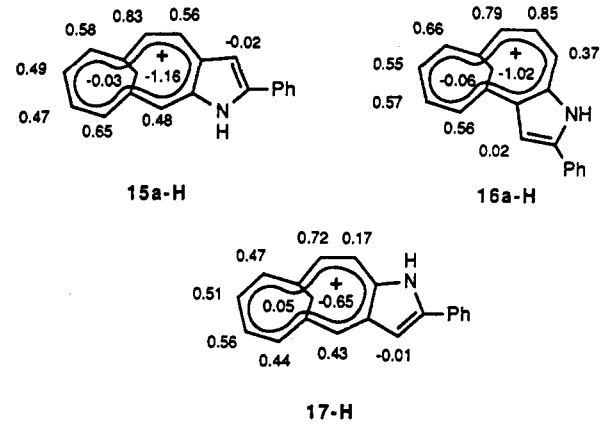


Figure 3. Relative downfield shifts of ^1H NMR spectra for **15a**, **16a**, and **17** in acidic media.

We also studied the ^1H NMR spectra of compounds **15a**, **16a**, and **17** in acidic media (Figure 3). The chemical shifts in $CDCl_3$–CF_3COOH exhibited a downfield shift of the peripheral protons ($\Delta\delta_{av}$ = ca. 0.6) except for the H-3 protons ($\Delta\delta$ = ca. 0). Remarkable upfield shifts for the H_z-13 protons ($\Delta\delta$ = –1.16 for **15a**, $\Delta\delta$ = –1.20 for **16a**, and $\Delta\delta$ = –0.65 for **17**) were also observed. Accordingly, protonation of **15a**, **16a**, **17** occurs at the nitrogen atoms in acidic solution, and the contribution of the canonical structures to the resonance hybrids (Figure 3) seems to be important. The striking similarity of the ^1H NMR spectrum of **15a** to that of **1b**[5a] is seen in the chemical shifts and in the coupling constants of the bridge protons. However, a remarkable difference was observed in the coupling constants of the aromatic protons showing a completely delocalized π-system of annulene **1b** ($J_{7,8}$ = $J_{8,9}$ = $J_{9,10}$ = 8.0 Hz).

Additional support regarding the structural assignments of **15a**, **16a**, and **17** is evident from their ^{13}C NMR and UV spectra. The ^{13}C NMR spectra are also consistent with the presence of aromaticity in these systems. The UV spectral data of compounds **15–17** are summarized in Table I. Compared with **22**[11a,b] [λ_{max} (log ϵ) = 531 nm (3.19, sh)] or **23**[11c] [λ_{max} (log ϵ) = 553 nm (3.03, sh)], compounds **15a,c**, **16a,c**, and **17** exhibit a red-shifted absorption maxima for the longest wavelength absorption. These bathochromic shifts are consistent with extension of conjugation in compounds **15–17**. Furthermore, remarkable hypsochromic shifts are observed in acidic media in accordance with the behavior of 1-azaazulenes, suggesting the vinylogous nature of **15–17**.

Experimental Section

General Methods. General experimental conditions and spectroscopic instrumentation used have been described.[9h]

(19) (a) Vogel, E. *Chem. Soc. Spec. Publ.* **1967**, No. 21, 113. (b) Vogel, E. *Proc. Robert A. Welch Found. Conf. Chem. Res.* **1968**, *12*, 215.
(20) Oda, M. *Pure Appl. Chem.* **1986**, *58*, 7.
(21) Wentrup, C.; Becker, J. *J. Am. Chem. Soc.* **1984**, *106*, 3705.
(22) Yamane, K.; Fujimori, K.; Sin, J.-K.; Nozoe, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1184.

Table I. UV Spectral Data of 15a,c, 16a,c, and 17

compd	solvent	λ_{max}/nm (log ϵ)
15a	EtOH	572 (3.40), 435 (3.93), 352 (4.60), 311 (4.34), 261 (4.16)
	EtOH–CF_3COOH	556 (4.02), 444 (4.09), 359 (4.69), 311 (4.31), 275 (4.05)
15c	EtOH	567 (4.18), 430 (4.00, sh), 358 (4.67), 314 (4.36)
	EtOH–CF_3COOH	566 (4.22), 436 (4.01), 372 (4.69), 317 (4.36)
16a	EtOH	559 (2.67), 460 (3.08, sh), 346 (3.95, sh), 298 (4.17, sh), 264 (4.35)
	EtOH–CF_3COOH	564 (3.87), 461 (3.83), 355 (4.35), 298 (4.23)
16c	EtOH	580 (3.30), 450 (3.26), 398 (3.40, sh), 356 (4.20), 309 (4.05)
	EtOH–CF_3COOH	574 (3.92), 463 (3.59), 360 (4.27), 307 (4.10)
17	EtOH	590 (2.95), 393 (3.86 sh), 361 (4.18), 347 (4.11, sh), 310 (4.16, sh) 296 (4.18)
	EtOH–CF_3COOH	552 (3.61), 399 (3.71), 354 (4.38), 315 (4.26)

4-Chlorobicyclo[5.4.1]dodeca-4,7,9,11-tetraen-3-one (7). To a solution of oxalyl chloride (629 mg, 4.95 mmol) in CH_2Cl_2 (11 mL) was added dropwise DMSO (780 mg, 10.0 mmol) and CH_2Cl_2 (2.3 ml) at −50 °C. After the mixture was stirred for 2 min, a solution of alcohol **6** (938 mg, 4.50 mmol) in DMSO–CH_2Cl_2 (1/1, 5 mL) was added, and the mixture was stirred for 15 min. Triethylamine (2.27 g, 22.5 mmol) was then added, and the reaction mixture was warmed to rt. After the mixture was stirred for several minutes, water (23 mL) was added and the solution was extracted with CH_2Cl_2, washed with saturated NH_4Cl(aq) and water, and then dried. After solvent removal in vacuo, the residue was chromatographed on silica gel. The fractions eluted with hexane–ethyl acetate (10/1) gave the ketone **7** (740 mg, 80%). The compound was used in the next step without further purification.

7: oil; ^1H NMR (60 MHz, $CDCl_3$) δ 1.38 (1 H, d, J = 10.8 Hz), 2.88 (1 H, dt, J = 10.8, 1.1 Hz), 3.04–3.29 (2 H, m), 3.37–3.73 (2 H, m), 5.88–6.24 (3 H, m), 6.44–6.77 (2 H, m); IR ($CHCl_3$) 2997, 1703 cm^{-1}; MS m/z (rel intensity) 208 (15), 206 (M^+, 33), and 128 (100); HRMS m/z 206.0460, calcd for $C_{10}H_{11}ClO$ 206.0498.

3,8-Methano[11]annulenone (3). A solution of the ketone **7** (2.07 g, 10.0 mmol) and DBU (1.67 g, 11.0 mmol) in CH_2Cl_2 (15 mL) was stirred for 30 min at rt. After solvent removal in vacuo, the resulting mixture was chromatographed on silica gel using hexane-ethyl acetate (1/1) to give **3** (1.49 g, 88%).[12]

11-Chloro-3,8-methano[11]annulenone (4). A solution of ketone **7** (1.57 g, 7.61 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (2.25 g, 9.91 mmol) in benzene (10 mL) was heated under reflux for 18 h in the presence of catalytic amount of *p*-toluenesulfonic acid (20 mg). The reaction mixture was filtered through Celite, and the residual solids were washed with benzene. The filtrate was neutralized by aqueous $NaHCO_3$ and extracted with benzene, and the organic layer was dried. After the solvent was removed in vacuo, the residue was filtered to give the product **4** (1.11 g, 71%).[13]

Reaction of 3,8-Methano[11]annulenone (3) with [(1-Phenylvinyl)imino]triphenylphosphorane (8a). A solution of annulenone **3** (85 mg, 0.50 mmol) and **8a** (284 mg, 0.75 mmol) in benzene (5 mL) was heated under reflux for 24 h. After the reaction was completed, the mixture was chromatographed on silica gel with hexane–ethyl acetate (4/1) to remove triphenylphosphine oxide. The fractions eluted were concentrated in vacuo, and the residue was separated by TLC on silica gel using hexane–ether (4/1) as a developer to give **13a** (58 mg, 42%) and **14a** (50 mg, 37%).

13a: slurry oil; ^1H NMR (90 MHz, $CDCl_3$) δ 1.54 (1 H, d, J = 11.0 Hz, H_E-13), 4.11 (2 H, s, H-12), 4.49 (1 H, d, J = 11.0 Hz, H_Z-13), 5.99 (1 H, s, H-3), 5.92–6.18 (3 H, m, H-4,5,10), 6.28 (1 H, d, J = 3.1 Hz, H-7), 6.54 (2 H, m, H-8,9) 7.26–7.56 (5 H, m, Ph), and 8.03 (1 H, broad s, H-1); IR ($CHCl_3$) 3450, 3005, 1604, 1454, 1075 cm^{-1}; MS m/z (rel intensity) 271 (M^+, 79), 270 (100); HRMS m/z 271.1360, calcd for $C_{20}H_{17}N$ 271.1361.

14a: slurry oil; ^1H NMR (90 MHz, $CDCl_3$) δ 0.84 (1 H, d, J = 11.7 Hz, H_E-13), 3.42 (1 H, dd, J = 16.7, 10.1 Hz, H-12) 4.00 (1 H, d, J = 11.7 Hz, H_Z-13), 4.48 (1 H, ddd, J = 16.7, 5.5, 2.4 Hz, H-12), 5.02 (1 H, ddd, J = 10.1, 9.7, 5.5 Hz, H-11), 6.27 (1 H, dd, J = 9.7, 2.4 Hz, H-10), 6.46–7.00 (4 H, m, H-5,6,7,8), 7.00–7.50 (5 H, m, Ph), and 7.94 (1 H, broad s, H-1); IR ($CHCl_3$) 3450, 3001, 1606, 1466, 1264, 907 cm^{-1}; MS m/z (rel intensity) 271 (M^+, 100); HRMS m/z 271.1362, calcd for $C_{20}H_{17}N$ 271.1361.

Reaction of 3 with (Vinylimino)triphenylphosphorane (8b). A solution of annulenone **3** (850 mg, 5.0 mmol) and **8b** (3.30 g, 10.0 mmol) in toluene (20 mL) was refluxed for 4 h. After removal of triphenylphosphine oxide (vide supra), the fractions eluted (benzene eluent) were concentrated in vacuo, and the resulting mixture was separated by MPLC on silica gel (400 mesch) using hexane–ethyl acetate (5/1) as an eluent to give **13b** (50 mg, 5%) and **14b** (39 mg, 4%).

13b: slurry oil; ^1H NMR (90 MHz, $CDCl_3$) δ 1.44 (1 H, d, J = 10.9 Hz), 3.97 (2 H, broad s), 4.37 (1 H, d, J = 10.9 Hz), 5.85–6.05 (5 H, m), 6.43–6.53 (3 H, m), 7.65 (1 H, broad s); IR ($CHCl_3$) 3470, 3010, 1620, 1454, 1400, 1262, 1090, 1044 cm^{-1}; MS m/z (rel intensity) 195 (M^+, 70), 194 (100); HRMS m/z 195.1046, calcd for $C_{14}H_{13}N$ 195.1048.

14b: slurry oil; ^1H NMR (90 MHz, $CDCl_3$) δ 0.75 (1 H, d, J = 11.7 Hz), 3.33 (1 H, dd, J = 16.7, 10.7 Hz), 3.95 (1 H, d, J = 11.7 Hz), 4.44 (1 H, ddd, J = 16.7, 2.9, 2.2 Hz), 4.97 (1 H, td, J = 10.7, 2.9 Hz), 6.10–6.30 (2 H, m), 6.39–6.90 (5 H, m), 7.50 (1 H, broad s); IR ($CHCl_3$) 3575, 3015, 2968, 2935, 1723, 1600, 1467, 1263, 1100, 1028 cm^{-1}; MS m/z (rel intensity) 195 (M^+, 98), 194 (100); HRMS m/z 195.1043, calcd for $C_{14}H_{13}N$ 195.1048.

2-Phenyl-6,11- and 2-Phenyl-4,9-methanocycloundeca-[*b*]pyrroles (15a and 16a). Compound **13a** (58 mg, 0.214 mmol) or **14a** (50 mg, 0.185 mmol) and nickel peroxide (250 mg) in benzene (2 mL) were stirred at rt for 30 min. The reaction mixture was then filtered through Celite. The filtrate was concentrated in vacuo, and the residue was purified by TLC on silica gel using hexane–ethyl acetate (1/2) as a developer to give **15a** (40 mg, 70%) or **16a** (8 mg, 16%). UV spectral data of **15a** and **16a** are summarized in Table I.

15a: green solid; mp 92–96 °C dec; ^1H NMR (400 MHz, $CDCl_3$) δ −0.49 (1 H, d, J = 11.0 Hz, H_E-13), 0.08 (1 H, d, J = 11.0 Hz, H_Z-13), 7.44 (1 H, m, Ph), 7.52 (2 H, m, Ph), 7.55 (1 H, d, J = 8.2 Hz, H-7), 7.60 (1 H, dd, J = 9.7, 8.1 Hz, H-9), 7.62 (1 H, d, J = 10.6 Hz, H-5), 7.69 (1 H, dd, J = 9.7, 8.2 Hz, H-8), 7.82 (1 H, d, J = 8.1 Hz, H-10), 7.96 (1 H, s, H-3), 8.14 (1 H, d, J = 10.6 Hz, H-4), 8.31 (2 H, m, Ph), 9.11 (1 H, s, H-12); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.6, 119.8, 119.8, 121.0, 126.8, 127.87, 127.90, 128.7, 128.9, 129.4, 130.8, 131.7, 132.5, 134.1, 141.6, 142.6, 151.1, 163.4; MS m/z (rel intensity) 269 (M^+, 100); HRMS m/z 269.1201, calcd for $C_{20}H_{15}N$ 269.1204.

16a: green solid; mp 72–77 °C dec; ^1H NMR (400 MHz, $CDCl_3$) δ −0.22 (1 H, d, J = 11.4 Hz, H_E-13), 0.18 (1 H, d, J = 11.4 Hz, H_Z-13), 7.29 (1 H, dd, J = 11.0, 11.4 Hz, H-11), 7.44 (1 H, m, Ph), 7.50 (1 H, dd, J = 9.5, 7.7 Hz, H-7), 7.52 (2 H, m, Ph), 7.60 (1 H, d, J = 7.7 Hz, H-8), 7.68 (1 H, dd, J = 9.5, 7.7 Hz, H-6), 7.83 (1 H, d, J = 11.0 Hz, H-10), 8.02 (1 H, d, J = 7.7 Hz, H-5), 8.12 (1 H, s, H-3), 8.29 (2 H, m, Ph), 8.73 (1 H, d, J = 11.4 Hz, H-12); ^{13}C NMR (100 MHz, $CDCl_3$) 31.0, 110.76, 110.78, 121.2, 124.6, 125.4, 126.9, 127.9, 128.2, 128.7, 131.7, 132.8, 132.9, 141.5, 148.3, 152.5, 163.7, 170.2; MS m/z (rel intensity) 269 (M^+, 100); HRMS m/z 269.1206, calcd for $C_{20}H_{15}N$ 269.1204.

7,12- and 9,14-Methano-15*H*-cycloundeca[*b*]indeno[2,3-*d*]pyrroles (15c and 16c). A solution of 3-azidoindene (157 mg, 1.0 mmol) and tributylphosphine (303 mg, 1.50 mmol) in toluene (4 mL) was stirred at 0 °C for 30 min to generate (inden-3-ylimino)tributylphosphorane in situ. A solution of annulenone **3** (85 mg, 0.5 mmol) in toluene (0.5 mL) was then added, and the reaction mixture was refluxed for 1.5 h. After removal of triphenylphosphine oxide (vide supra), the fractions eluted [hexane–ethyl acetate (2/1) eluent] were concentrated in vacuo, and the residue was treated with manganese dioxide (200 mg) in benzene (40 mL) and stirred at rt for 30 min. The reaction mixture was filtered through Celite, and the filtrate was concentrated in

vacuo. The resulting mixture was separated by TLC on silica gel using 2-propanol–ethyl acetate (1/10) as a developer to give **15c** (8.3 mg, 6%) and **16c** (44 mg, 31%). UV spectral data of **15c** and **16c** are summarized in Table I.

15c: green solid; mp 180 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.33 (1 H, d, J = 11.0 Hz, H_E-16), 0.61 (1 H, d, J = 11.0 Hz, H_Z-16), 3.98 (2 H, s H-15), 7.39 (1 H, d, J = 7.3 Hz, H-11), 7.46 (1 H, m, H-3), 7.47 (1 H, d, J = 7.7 Hz, H-2), 7.52 (1 H, d, J = 11.0 Hz, H-13), 7.57 (1 H, dd, J = 10.3, 7.4 Hz, H-9), 7.61 (1 H, d, J = 7.7 Hz, H-1), 7.62 (1 H, dd, J = 10.3, 7.3 Hz, H-10), 7.67 (1 H, d, J = 7.4 Hz, H-8), 7.76 (1 H, d, J = 11.0 Hz, H-14), 8.17 (1 H, m, H-4) 8.97 (1 H, s, H-6); IR ($CHCl_3$) 2925, 1614, 1596, 1475, 1456, 1331, 1287, 1060 cm^{-1}; MS m/z (rel intensity) 281 (M^+, 100); HRMS m/z 281.1195, calcd for $C_{21}H_{15}N$ 281.1204.

16c: green solid; mp 220 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.25 (1 H, d, J = 11.4 Hz, H_E-16), 0.58 (1 H, d, J = 11.4 Hz, H_Z-16), 3.84 (1 H, d, J = 21.3 Hz, H-15), 4.17 (1 H, d, J = 21.3 Hz, H-15), 7.09 (1 H, t, J = 11.0 Hz, H-7), 7.40–7.44 (4 H, m, H-1, H-2, H-3, and H-10), 7.57 (1 H, m, H-1), 7.62 (1 H, dd, J = 8.8, 8.1 Hz, H-12), 7.68 (1 H, d, J = 11.0 Hz, H-8), 7.70 (1 H, d, J = 8.1 Hz, H-13), 8.14 (1 H, m, H-4), 8.51 (1 H, d, J = 11.0 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 159.8, 151.0, 141.7, 139.2, 136.2, 133.2, 133.0, 132.9, 130.9, 129.9, 128.7, 127.6, 126.2, 125.8, 124.1, 122.8, 122.0, 32.4, 30.4 (one carbon signal is overlapping); IR ($CHCl_3$) 2925, 1696, 1612, 1464, 1300 cm^{-1}; MS m/z (rel intensity) 281 (M^+, 100); HRMS m/z 281.1202, calcd for $C_{21}H_{15}N$ 281.1204.

2-Phenyl-5,10-methanocycloundeca[*b*]pyrrole (17). A solution of annulenone **5** (85 mg, 0.50 mmol) and **8d** (957 mg, 3.0 mmol) was heated in 1,2-dimethylbenzene (5 mL) under reflux for 48 h. After removal of tributylphosphine oxide (vide supra), the fractions eluted (benzene eluent) were concentrated in vacuo to ca. 3 mL and the solution was treated with manganese dioxide (500 mg) and stirred at rt for 50 min. After the reaction mixture was filtered through Celite and was concentrated in vacuo, the residue was separated by TLC on silica gel using hexane–ethyl acetate (1/2) to give **17** (4 mg, 3%). UV spectral data of **17** are summarized in Table I.

17: green solid; mp 89–90 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.75 (1 H, d, J = 10.8 Hz, H_E-13), −0.36 (1 H, d, J = 10.8 Hz, H_Z-13), 7.42 (1 H, m, *p*-Ph), 7.45 (1 H, dd, J = 9.77, 9.28 Hz, H-7), 7.52 (2 H, m, *m*-Ph), 7.61 (1 H, dd, J = 9.28, 8.78 Hz, H-8), 7.82 (1 H, d, J = 9.77 Hz, H-11), 7.85 (1 H, d, J = 8.78 Hz, H-9), 7.86 (1 H, s, H-3), 7.94 (1 H, d, J = 9.77 Hz, H-6), 8.34 (2 H, m, *o*-Ph), 8.88 (1 H, s, H-4), 8.89 (1 H, d, J = 9.77 Hz, H-12), ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 138.7, 137.0, 135.4, 134.3, 133.4, 133.1, 132.5, 129.3, 128.9, 127.8, 110.4, 30.9 (one carbon signal is overlapping); IR ($CHCl_3$) 2934, 1603, 1425, 1253, 1072, 909 cm^{-1}; MS m/z (rel intensity) 269 (M^+, 100); HRMS m/z 269.1204, calcd for $C_{20}H_{15}N$ 269.1204.

^{1}H NMR Spectral Data (400 MHz, $CDCl_3$) of Cyclohepta[*b*]pyrrole (21), 2-Phenylcyclohepta[*b*]pyrrole (22), Cyclohepta[*b*]indeno[2,3-*d*]pyrrole (23), and 3-Phenylcyclohepta[*b*]pyrrole (24).

21: δ 7.41 (1 H, d, J = 1.0 Hz, H-3), 7.64 (1 H, t, J = 9.8 Hz, H-5), 7.75 (1 H, t, J = 9.8 Hz, H-7), 7.89 (1 H, t, J = 9.8 Hz, H-6), 8.59 (1 H, d, J = 9.8 Hz, H-4), 8.77 (1 H, t, J = 9.8 Hz, H-8), 8.78 (1 H, d, J = 1.0 Hz, H-2).

22: δ 7.44 (1 H, tt, J = 7.3, 1.0 Hz, *p*-Ph), 7.51 (2 H, t, J = 7.3 Hz, *m*-Ph), 7.58 (1 H, ddt, J = 10.3, 8.8, 1.0 Hz, H-6), 7.72 (1 H, ddd, J = 10.3, 9.3, 1.0 Hz, H-8), 7.74 (1 H, s, H-3), 7.76 (1 H, ddd, J = 10.3, 8.8, 1.5 Hz, H-7), 8.32 (2 H, J = 7.3 Hz, *o*-Ph), 8.48 (1 H, dd, J = 10.3, 1.0 Hz, H-5), 8.66 (1 H, ddd, J = 9.3, 1.5, 1.0 Hz, H-9).

23: δ 3.88 (2 H, s H-11), 7.41 (1 H, td, J = 7.3, 1.5 Hz, H-2), 7.45 (1 H, td, J = 7.3, 1.5 Hz, H-3), 7.57 (1 H, dd, J = 7.3, 1.5 Hz, H-1), 7.63 (1 H, ddt, J = 10.3, 8.8, 1.1 Hz, H-8), 7.68 (1 H, ddt, J = 10.3, 8.8, 1.5, 0.5 Hz, H-8), 7.49 (1 H, dddd, J = 10.3, 8.8, 1.5, 0.5 Hz, H-9), 8.16 (1 H, dd, J = 7.3, 1.5 Hz, H-4), 8.33 (1 H, dd, J = 10.3, 1.1 Hz, H-10), 8.61 (1 H, ddd, J = 8.8, 1.5, 1.1 Hz, H-6).

24: δ 7.40 (1 H, tt, J = 7.3, 1.1 Hz, *p*-Ph), 7.53 (2 H, dd, J = 7.7, 7.3 Hz, *m*-Ph), 7.62 (2 H, dd, J = 7.7, 1.1 Hz, *o*-Ph), 7.66 (1 H, t, J = 9.9 Hz, H-6), 7.77 (1 H, t, J = 9.5 Hz, H-8), 7.92 (1 H, t, J = 9.5 Hz, H-8), 8.76 (1 H, d, J = 9.9 Hz, H-5), 8.78 (1 H, d, J = 9.5 Hz, H-9), 8.90 (1 H, s, H-2).

Acknowledgment. This work was financially supported by a Grant-in-Aid for Fundamental Science from the Ministry of Education, Science and Culture and by a Waseda University Grant for Special Research Projects.

Supplementary Material Available: ^{1}H and/or ^{13}C NMR spectra of **15a,c**, **16a,c**, and **17** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.