

SYNTHESIS OF 2-ETHOXY-6,11-DIMETHYL-7,9-BISDEHYDROAZA[16]ANNULENE AND 2-ETHOXY-8,13-DIMETHYL-9,11-BISDEHYDROAZA[18]ANNULENE

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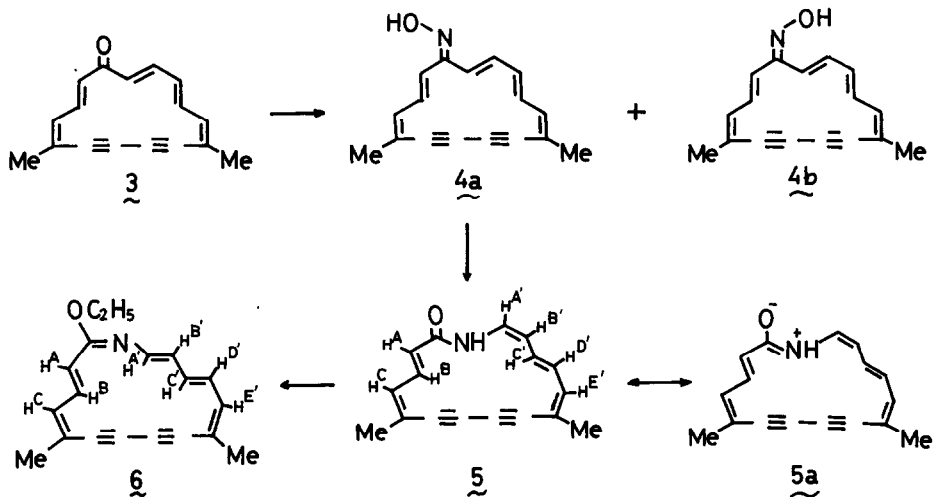
Summary: Title azaannulenes, the paratropic and diatropic vinylogues of pyridine, were synthesized starting from the annulenones.

In the preceding paper, we have described the synthesis of bisdehydroaza[14]-annulene (λ),¹⁾ which proved to be diatropic, and its precursor, the lactam (ζ) also shows the diatropic nature. The reaction sequence of the synthesis of aza[14]annulene (λ) starting from the annulenone appeared to be applicable to preparation of vinylogous bisdehydroaza[16]- and -[18]annulene. These were required in order to discover whether the same alternation of electromagnetic properties between $[4n+2]$ and $[4n]\pi$ -electron systems occurs in these azaannulenes as has already been demonstrated in the carbocyclic annulene series.²⁾ This synthetic objective has been realized in practice.

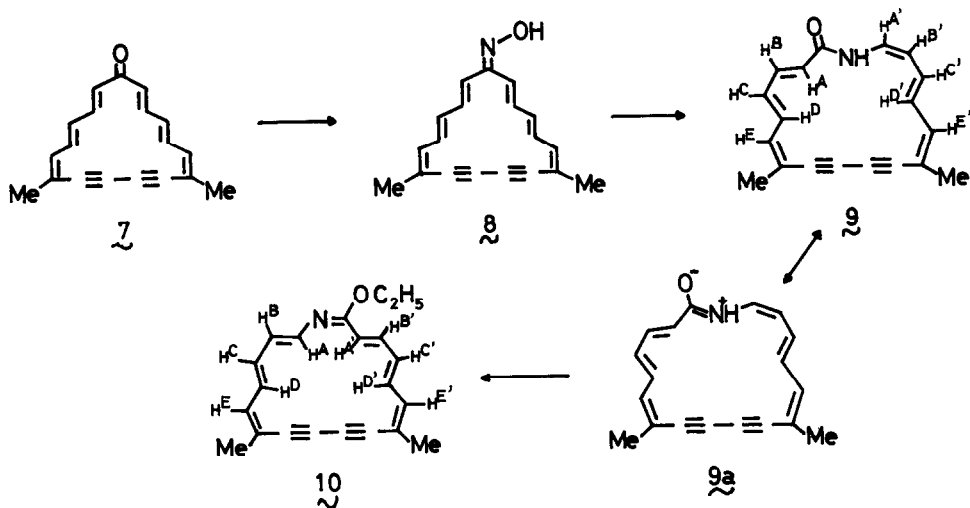


We now describe the synthesis and properties of the title compounds. Among them, 2-ethoxy-6,11-dimethyl-7,9-bisdehydroaza[16]annulene (δ) is the first example of monocyclic azaannulene of pyridine type to show paramagnetic ring current.

Treatment of the bisdehydro[15]annulenone (ζ)³⁾ with a large excess of hydroxylamine hydrochloride in methanol, tetrahydrofuran, and water for 5 h at 40°C gave a mixture of the oximes (λ_a) and (λ_b) (5:2) in a 93% yield, which was separated by crystallization, and only the isomer (λ_a) (orange needles, mp 201-202°C (dec))⁴⁾ was isolated. The Beckmann rearrangement of the mixture with phosphorus pentachloride in tetrahydrofuran for 5 h at room temperature gave the lactam (ξ) (brown needles, mp 138-140°C (dec), 41%), of which structure was determined by its ¹H-NMR spectrum. Since Beckmann rearrangement is considered to proceed usually in *anti*-migration,⁵⁾ the main



isomer of the oxime, the precursor of the lactam (**5**), should have the structure of **4a**. The reaction of **5** with a large excess of triethyloxonium fluoroborate in dichloromethane at room temperature overnight gave the iminoether, the desired 2-ethoxy-6,11-dimethyl-7,9-bisdehydroaza[16]annulene (**6**) (purple needles, mp 115–116°C, 38%).



The dimethylbisdehydroaza[18]annulene (**10**) was obtained analogously. Treatment of the dimethylbisdehydro[17]annulenone (**7**)³ with hydroxylamine gave the oxime (**8**) (orange cubes, mp 196–198°C (dec), 88%), which was led to the lactam (**9**) (brown needles, mp 188–190°C (dec), 43%). **9** reacted with an excess of triethyloxonium fluoroborate in dichloromethane for 2 h at room temperature to give the desired 2-ethoxy-8,13-dimethyl-9,11-bisdehydroaza[18]annulene (**10**) (brown needles, mp 138–140°C, 11%).

Table 1. The $^1\text{H-NMR}$ Chemical Shifts of Azaannulenes (\mathcal{L}), (\mathcal{R}), and ($\mathcal{L}\mathcal{O}$) in CDCl_3 at 200 MHz (τ -Values, Internal Standard Me_4Si)

	H^{A}	$\text{H}^{\text{A}'}$	H^{B}	$\text{H}^{\text{B}'}$	H^{C}	$\text{H}^{\text{C}'}$	H^{D}
(\mathcal{L})	6.25	7.06	2.99	2.19	2.62	2.70	
(\mathcal{R})	4.61	0.56	-0.14	4.27	4.11	0.60	
($\mathcal{L}\mathcal{O}$)	5.85	6.74	2.96	2.14	2.72	2.76	6.65
	$\text{H}^{\text{D}'}$	H^{E}	$\text{H}^{\text{E}'}$	$-\text{CH}_2\text{CH}_3$	$-\text{CH}_2\text{CH}_3$	Me	
(\mathcal{L})				5.40	8.51	7.49, 7.54	
(\mathcal{R})	4.25		4.12	6.00	8.78	8.33, 8.38	
($\mathcal{L}\mathcal{O}$)	6.44	2.44	2.44	5.40	8.50	7.52, 7.56	

The $^1\text{H-NMR}$ chemical shifts of the various protons of the bisdehydroaza[16]-(\mathcal{R}) and -[18]annulene ($\mathcal{L}\mathcal{O}$) are listed in Table 1, altogether with those of the bisdehydroaza[14]annulene (\mathcal{L}). The chemical shifts indicate that the aza[16]-annulene (\mathcal{R}) is paratropic, as expected of a 16π -electron system, the outer protons including ethoxy and methyl protons being shielded and the inner protons deshielded. On the other hand, it is evident that the aza[18]annulene ($\mathcal{L}\mathcal{O}$) is diatropic, the outer protons including ethoxy and methyl protons being deshielded and the inner protons shielded, as has been observed for the aza[14]annulene (\mathcal{L}). This is a reversal of the behavior of the paratropic aza[16]annulene (\mathcal{R}). The alternation of electromagnetic properties between the aza[$4n+2$]annulenes (\mathcal{L}) and ($\mathcal{L}\mathcal{O}$) and the aza[$4n$]annulene (\mathcal{R}) is thereby clearly established.

The chemical shifts of the protons of the lactams (\mathcal{Z}), (\mathcal{S}), and (\mathcal{Q}), the precursors of the azaannulenes (\mathcal{L}), (\mathcal{R}), and ($\mathcal{L}\mathcal{O}$), respectively, are shown in Table 2. As is seen from Table 2, the sixteen-membered lactam (\mathcal{S}) shows the inner proton resonances at low field and the outer proton resonances at high field. On the other hand, the eighteen-membered lactam (\mathcal{Q}) shows the inner

Table 2. The $^1\text{H-NMR}$ Chemical Shifts of Lactams (\mathcal{Z}), (\mathcal{S}), and (\mathcal{Q}) in CDCl_3 at 200 MHz (τ -Values, Internal Standard Me_4Si)

	NH	H^{A}	$\text{H}^{\text{A}'}$	H^{B}	$\text{H}^{\text{B}'}$	H^{C}
(\mathcal{Z})	1.19	3.82	4.36	3.98	2.44	3.27
(\mathcal{S})	-0.69	3.96	3.66	0.26	5.24	3.94
(\mathcal{Q})	4.56	5.84	2.44	2.19	4.32	3.18
	$\text{H}^{\text{C}'}$	H^{D}	$\text{H}^{\text{D}'}$	H^{E}	$\text{H}^{\text{E}'}$	Me
(\mathcal{Z})	3.17					7.76, 7.85
(\mathcal{S})	1.74		2.82		4.19	8.30, 8.32
(\mathcal{Q})	3.25	4.82	5.65	2.79	2.96	7.68, 7.74

proton resonances at high field and the outer proton resonances at low field, albeit the outer $H^{B'}$ proton resonance violates the situation. The similar observation is made for the fourteen-membered lactam (\mathcal{Z}).¹⁾

The simplest test for the nature of the ring current of the compounds listed in Tables 1 and 2 is provided by the chemical shifts of the methyl protons, since the methyl groups must always be external and can readily be recognized. The alternation of the methyl resonances between $[4n+2]$ lactams (\mathcal{Z}) and (\mathcal{Q}) (relatively low field) and $[4n]$ lactam (\mathcal{S}) (relatively high field) confirms the diatropicity of the former and the paratropicity of the latter, albeit the degree of the alternation being not greater than that between aza $[4n+2]$ annulenes (\mathcal{I}) and ($\mathcal{I}\mathcal{Q}$) and aza $[4n]$ annulene (\mathcal{G}). This result suggests us that these lactams, the precursors of the azaannulenes, can be considered to exist in zwitter ionic forms such as ($\mathcal{S}\mathcal{a}$) and ($\mathcal{Q}\mathcal{a}$), as has been demonstrated for the "parent" lactam, 2-pyridone.⁶⁾

In the electronic spectra, taken in tetrahydrofuran, of both the azaannulenes and the lactams, the main maxima of the aza $[14]$ annulene (\mathcal{I}) (317 nm) and the fourteen-membered lactam (\mathcal{Z}) (305 nm) as well as the aza $[18]$ annulene ($\mathcal{I}\mathcal{Q}$) (346 nm) and the eighteen-membered lactam (\mathcal{Q}) (333 nm) are in longer wavelengths than those of the aza $[16]$ annulene (\mathcal{G}) (287 nm) and the sixteen-membered lactam (\mathcal{S}) (292 nm). Clearly, this is due to the occurrence of the same sort of alternation between the maxima of $[4n-2]$ and $[4n]$ systems, as has been observed for monocyclic annulenes and dehydroannulenes [$(4n-2)\pi$ systems absorbing at higher wavelengths than the $(4n)\pi$ systems].⁷⁾

This work was financially supported by grants from the Ministry of Education, Japan (58540306), and the Kûdo Science Foundation.

References and Note

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(Received in Japan 25 September 1984)