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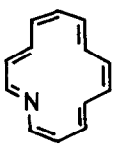
THE SYNTHESIS OF 2-ETHOXY-6,11-DIMETHYL-7,9-BISDEHYDROAZA[14]ANNULENE AND ITS BENZANNELATED DERIVATIVES

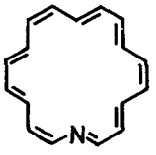
Jūro Ojima,* Tetsuya Nakada, Mitsunobu Nakamura, and Emiko Ejiri
Department of Chemistry, Faculty of Science, Toyama University, Gofuku, Toyama 930, Japan

Summary: Title azaannulenes were synthesized starting from annulenones, and the ^{1}H-NMR spectra are discussed in connection with tropicity of these annulenes.

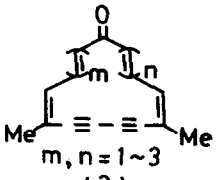
The synthesis of monoazaannulenes, the higher homologues of pyridine, remains one of the stimulating problem in the study of nonbenzenoid aromatic system. Until now, a systematic examination on the property of monocyclic azaannulenes containing [4n]-member has not been made, although the aza[14]- (1)[1] and the aza[18]annulene (2)[2] were prepared by photolysis of tetracyclic azides by Schröder. Some bridged aza[10]annulenes[3] were also prepared starting from appropriate ketones, and this general reaction sequence from ketones to construct molecular skeleton of azaannulene intrigued us.



(1)



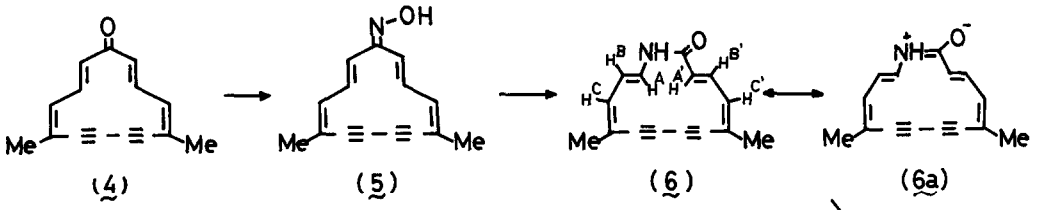
(2)



(3)

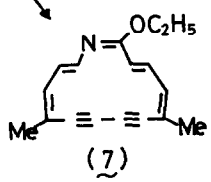
Synthesis of a series of both diatropic and paratropic bisdehydroannulenones, conjugated cyclic ketones, of type (3) has been described previously.[4] Starting from these annulenones, synthesis of a series of monocyclic azaannulenes, in which the number of the double bonds could be increased systematically, would be feasible and a study of their spectral properties appeared to be informative. The synthesis of the bisdehydroaza[14]annulene (7), which, as expected, proved to be diatropic, and its benzannelated derivatives is described in present communication, and that of related bisdehydroaza[16]- and -[18]annulene in the following one.[5]

Treatment of the dimethylbisdehydro[13]annulenone (4)[4a] with a large excess of hydroxylamine hydrochloride in methanol, tetrahydrofuran, and water for 5 h at 40°C afforded the oxime (5) (orange cubes, mp 144–146°C (dec), 90%).[6] The Beckmann rearrangement of (5) with phosphorus pentachloride in tetrahydrofuran for 1.5 h at room temperature led to the lactam (6) (orange needles, mp 196–198°C (dec), 56%, ^{1}H-NMR τ(200 MHz, $CDCl_3$: 1.19 (broad d, J=11 Hz, NH), 2.44



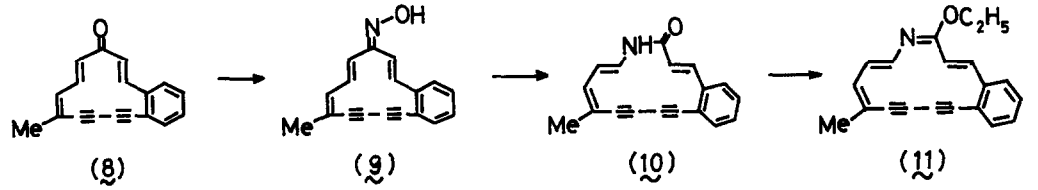
(4) (5) (6) (6a)

(dd, 16, 7, $H^{B'}$), 3.17 (d, 7, $H^{C'}$), 3.27 (d, 7, H^{C}), 3.82 (dd, 14, 11, H^{A}), 3.98 (dd, 14, 7, H^{B}), 4.36 (d, 16, $H^{A'}$), 7.76 (s, Me), and 7.85 (s, Me)). The compound (6) reacted with a large excess of triethyloxonium fluoroborate in dichloromethane for 7 h at room temperature with the formation of the iminoether, the desired 2-ethoxy-6,11-dimethyl-7,9-bisdehydroaza[14]annulene (7) (red needles, mp 103–104°C, 24%).



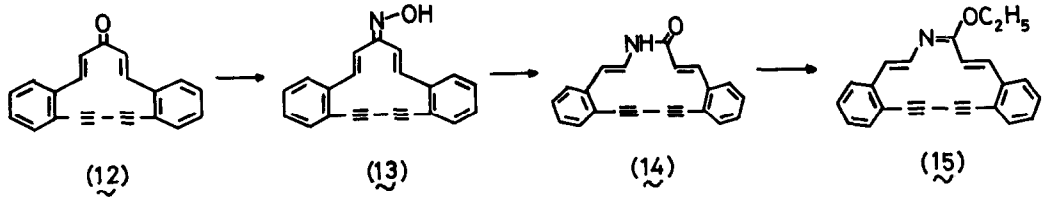
(7)

This three-step sequence was then applied for synthesis of the benzannelated azaannulenes (11) and (15) as described for the conversion of (4) to (7).



(8) (9) (10) (11)

The reaction of the monobenzo[13]annulenone (8)[7] with hydroxylamine gave the sole isomer (9) (yellow cubes, mp 146–147°C (dec), 44%) of two possible stereoisomeric products, which was converted to the lactam (10) (yellow needles, mp 217–218°C (dec), 40%). The structure of (10) was determined by ^{1}H-NMR spectrum. Since Beckmann rearrangement is considered to proceed usually in *anti*-migration with respect to hydroxyl group,[8] the precursor of the lactam (10), the oxime must have the structure of (9). The reaction of (10) with an excess of oxonium salt gave the desired monobenzazaannulene (11) (yellow needles, mp 163–164°C, 38%).



(12) (13) (14) (15)

The oxime (13) (pale yellow needles, mp 149–150°C (dec), 66%), obtained from the dibenzo[13]annulenone (12)[7] was converted to the lactam (14) (yellow needles, mp 296–298°C (dec), 37%), which has the conformation indicated by inspection of

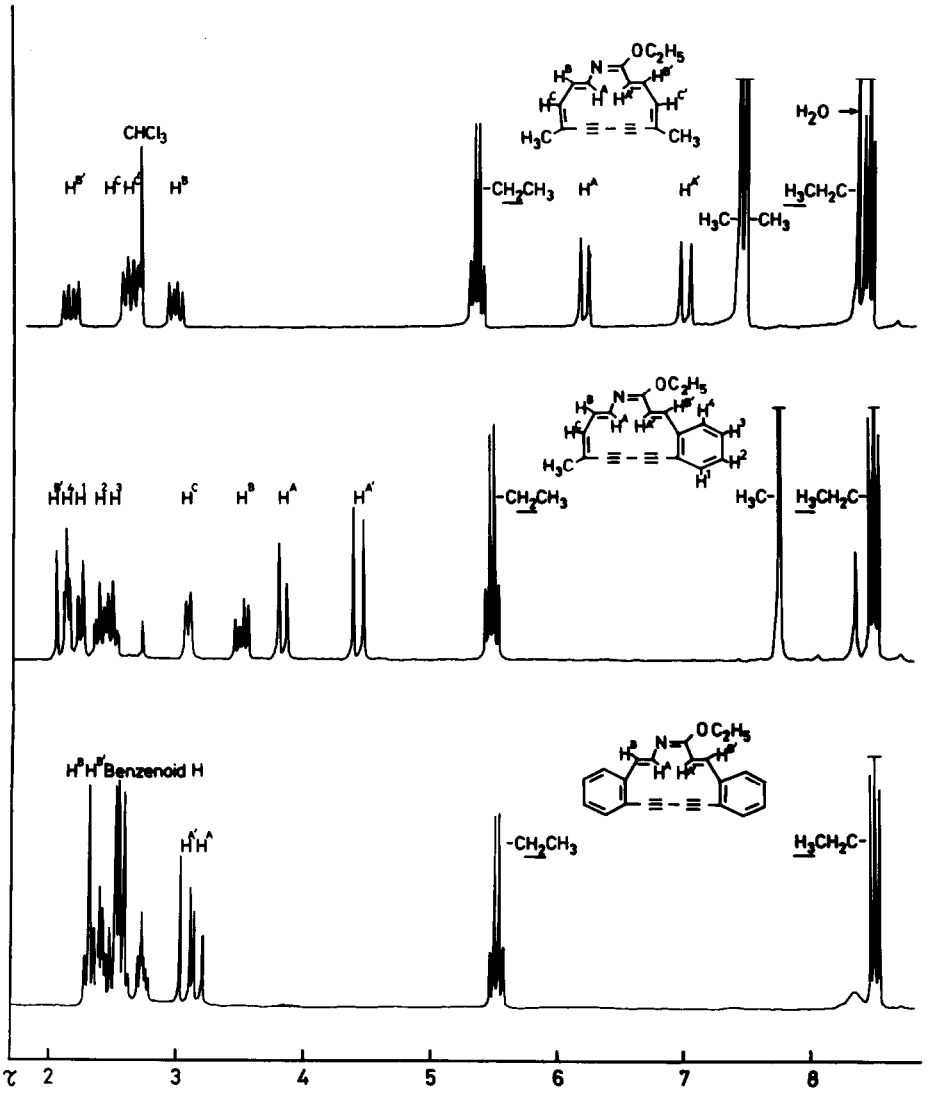


Fig. 1. ^{1}H-NMR spectra of the azaannulenes (7), (11), and (15) in $CDCl_3$ at 200 MHz.

molecular model. The compound (14) experienced almost exclusive O-ethylation to dibenzobisdehydroaza[14]annulene (15) (yellow needles, mp 164–165°C, 59%).

The ^{1}H-NMR spectra of these azaannulenes (7), (11), and (15) are shown in Figure 1. The dimethylbisdehydroaza[14]annulene (7) is clearly diatropic, as expected of a 14π-electron system, since the outer protons of the ring being deshielded and the inner protons shielded. In contrast, the chemical shifts of the protons of benzannelated annulenes suggest (11) to be at most weakly diatropic and (15) atropic, indicating that the skeletons of the benzannelated azaannulenes are less delocalized π-electron systems than that of non-annelated

one, as has been found for carbocyclic system.[9]

It is seen in the ^{1}H-NMR spectrum (text, see above) of the lactam (6) that the outer protons resonate at low field, while the inner protons do at high field, although the outer H^B proton resonance violates the situation. Thus, the fact that the spectrum of (6) is in rather parallel to that of the azaannulene (7), particularly in methyl resonances,[10] suggests that the fourteen-membered lactam (6) can also be considered to be diatropic and (6) might exist in a zwitter ionic form (6a). This finding is also discussed in the following communication.

The observation that despite of the presence of two acetylenic linkages, the dimethylbisdehydroaza[14]annulene (7) is much less diatropic than the aza[14]-annulene (1) (inner protons: τ (10.64–12.57), outer protons: τ (-0.11–2.33)) is presumably due to the less planarity of the former system, caused by steric strain of the molecular skeleton.

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