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SYNTHESES AND PROPERTIES OF α- OR β-METHYL SUBSTITUTED BISDEHYDROAZA[14]-, AZA[16]-, AND AZA[18]ANNULENE

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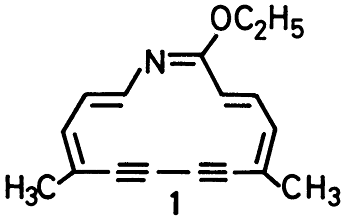
14-Ethoxy-2,5,10-trimethyl-, 14-ethoxy-2-ethyl-5,10-dimethyl-6,8-bisdehydroaza[14]annulene, 2-ethoxy-3,6,11-trimethyl-, 2-ethoxy-6,11,16-trimethyl-7,9-bisdehydroaza[16]annulene, and 18-ethoxy-2,7,12-trimethyl-8,10-bisdehydroaza[18]annulene were prepared. It was found that the molecular skeletons of these α- or β-methylated azaannulenes are less planar than those of α- or β-methyl unsubstituted ones.

Very recently, we have reported the synthesis of the diatropic aza[14]- (**1**)[1] and aza[18]annulene (**2**),[2] and the paratropic aza[16]annulene (**3**),[2] and showed that these azaannulenes proved to keep the conformations indicated between -60 to 60 °C, suggesting the rather high skeletal rigidity of **1**–**3**.[3]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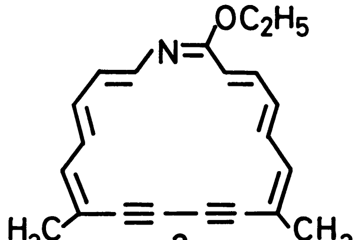
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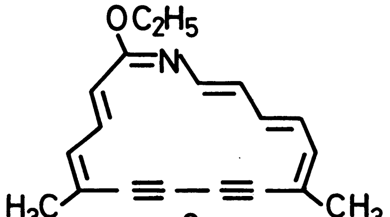
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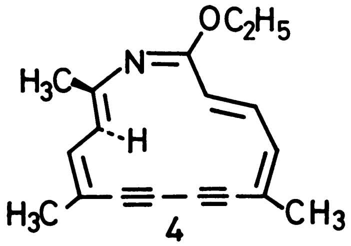
This result as well as a prediction from molecular models led us to expect that these azaannulenes **1**–**3** might set α-alkyl substituent inside the ring. In order to investigate this possibility, it was decided to prepare α-alkyl derivatives of **1**–**3**. However, all the azaannulenes **4**–**8** obtained do not have α- or β-alkyl group inside the rings properly, by an analysis of their ^{1}H NMR spectra.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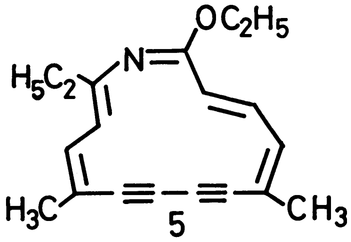
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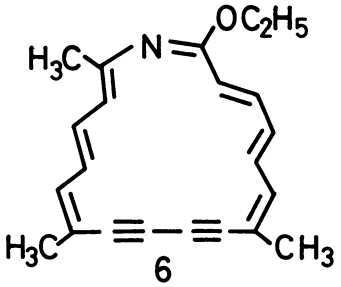
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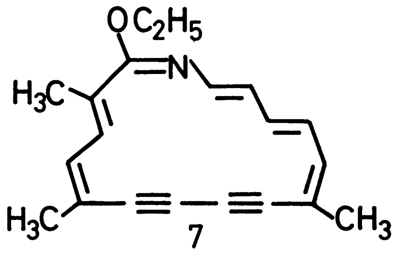
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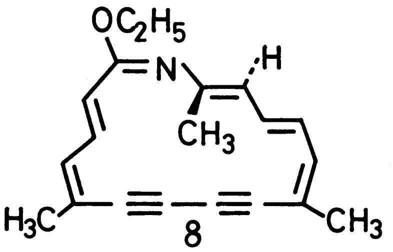
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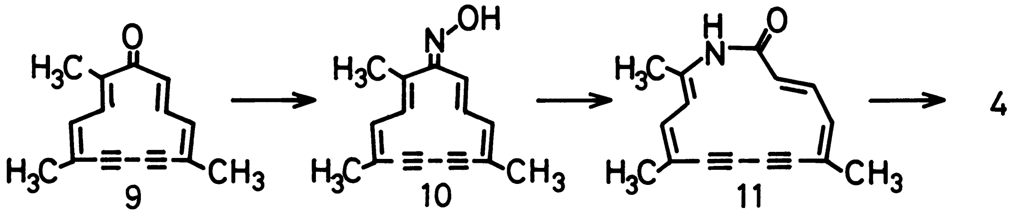
The preparation of the azaannulenes 4–8 was carried out by the same procedure as reported.[1,2]


9 → 10 → 11 → 4

Treatment of the trimethylbisdehydro[13]annulenone (9)[4] with a large excess of hydroxylamine hydrochloride afforded only the isomer 10 (orange needles, mp 164–165 °C (dec), 88%)[5] of the desired oxime. The Beckmann rearrangement of 10 with phosphorus pentachloride led to the lactam 11 (dark red cubes, mp 186–188 °C (dec), 13%), which was converted to the aza[14]annulene (4) (red liquid, 38%) by the reaction of a large excess of triethyloxonium tetrafluoroborate. Similarly, the aza[14]annulene (5) (red liquid), aza[18]annulene (6) (dark brown needles, mp 106–108 °C), aza[16]annulene (7) (brown needles, mp 114–115 °C), and aza[16]annulene (8) (dark red liquid) were prepared by three steps, starting from the corresponding ethyldimethyl[13]-,[6] trimethyl[17]-,[7] trimethyl[15]-,[8] and an another trimethyl-[15]annulenone,[8] respectively.

The ^{1}H NMR spectra of the α-methylated 4 and α-ethylated 5 are shown in Fig. 1, with that of the α-methyl unsubstituted aza[14]annulene (1). The assignment of the spectra was made on the basis of multiplicities and coupling constants, and rigorously follows from decoupling experiments where necessary. Comparison of the chemical shift differences between the olefinic inner and outer protons or the chemical shifts of $\mathrm{OC\underline{H}_2CH_3}$ and $\mathrm{CH_3}$ protons indicates that the diatropicity of

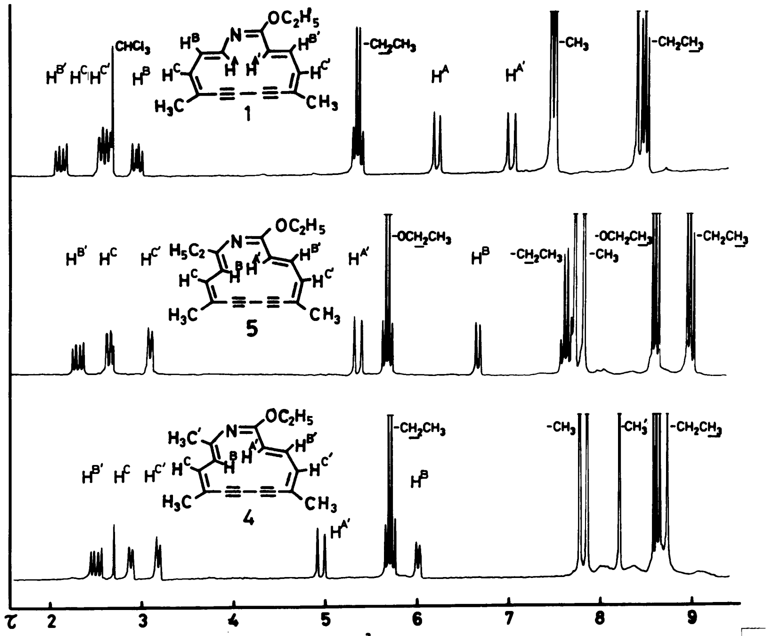


Fig. 1. The 200 MHz ^{1}H NMR spectra of the azaannulenes 1, 4, and 5 in CDCl$_3$.

these azaannulenes decreases in the order of 1 > 5 > 4, demonstrating that the perturbation caused by the α-alkyl substitution for the aza[14]annulene (1) greatly reduces the planarity of the molecular skeleton and it is larger in the α-methyl substitution than in the α-ethyl one. In agreement with this, the ^{1}H NMR spectra of the trimethylaza[14]annulene (4) showed a greater temperature-dependency between -60 to 60°C than those of the ethyldimethylaza[14]annulene (5), particularly in the resonances of CH_3' and H^B protons. It suggests that the CH_3'$-C=CH^B$ moiety of 4 deviates from a molecular plane as depicted. This also permits the safe conclusion that both of 4 and 5 do not set their α-alkyl groups inside the rings properly.

The almost similar observation is made from comparison of the ^{1}H NMR spectra of the aza[18]- (2) and α-methylated aza[18]-annulene (6), illustrated in Fig. 2. Comparison of the chemical shift differences between the olefinic inner and outer protons or the chemical shifts of $-OC\underline{H}_2CH_3$ and CH_3 protons indicates that the diatropicity of 6 is much smaller than that of 2, albeit 6 being diatropic. This again suggests that the perturbation caused by α-methyl substitution for the aza[18]annulene 2 changes the configuration and reduces the planarity of the molecular skeleton. It also indicates that the α-methyl group of 6 is not located inside the ring properly.

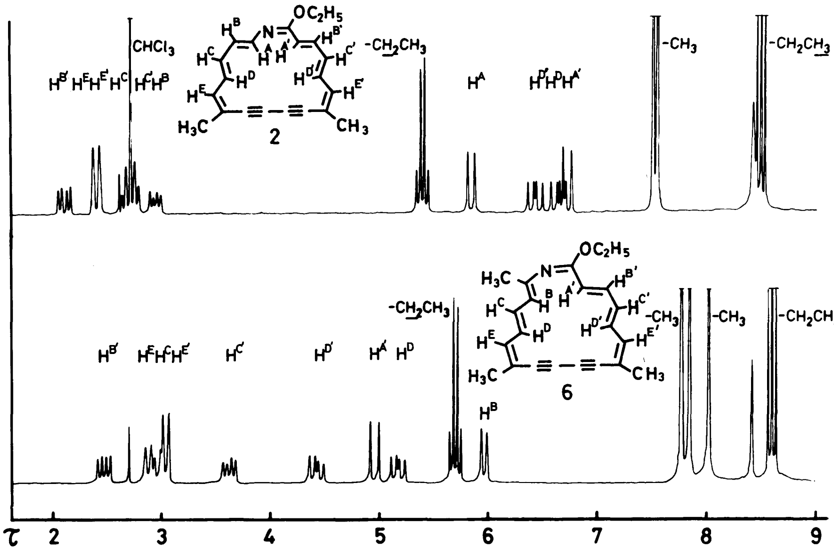


Fig. 2. The 200 MHz ^{1}H NMR spectra of the aza[18]annulenes 2 and 6 in $CDCl_3$.

The ^{1}H NMR spectra of the trimethylaza[16]annulenes (7) and (8) are shown in Fig. 3, altogether with that of the dimethylaza[16]annulene (3). Comparison of the chemical shift differences between the olefinic inner and outer protons indicates that the paratropicity of these azaannulenes decreases in the order of 3 > 7 > 8, suggesting the α-methyl substitution for the aza[16]annulene again greatly reduces the planarity of the molecular skeleton. This also indicates that the trimethylaza[16]annulene (8) does not set the α-methyl group inside the ring properly. The extreme unstability of 7 and 8, as compared with 3, might be due to low planarity of their molecular skeletons.

The results obtained from this study clearly show that the conformations indicated for 1, 2, and 3 are most appropriate for a conjugation of π-electrons in these bisdehydroaza[14]-, -aza[18]-, and -aza[16]annulenes, respectively, and these azaannulenes do not set their α-alkyl groups inside the rings properly.

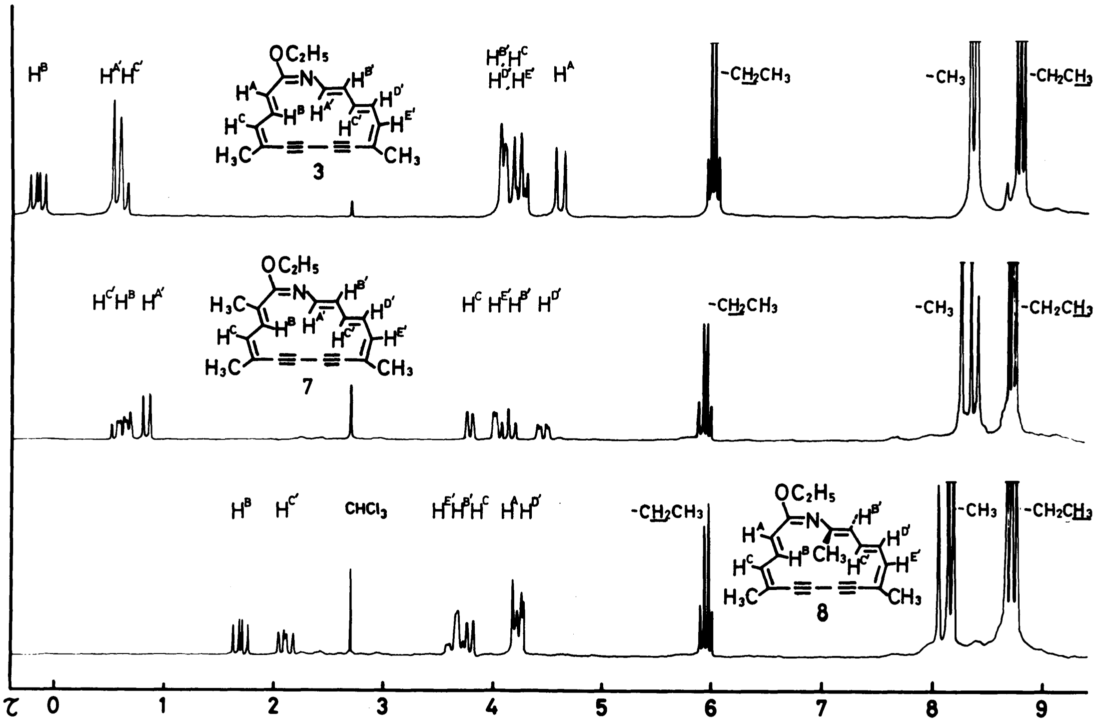


Fig. 3. The 200 MHz ^{1}H NMR spectra of the aza[16]annulenes **3**, **7**, and **8** in CDCl$_3$.

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