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Syntheses and Properties of Two Ethoxytrimethylbisdehydroaza-[16]annulenes and Ethoxytrimethylbisdehydroaza[18]annulene

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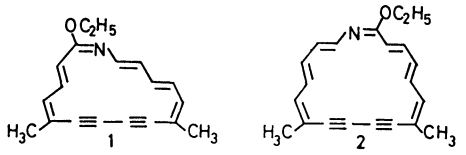
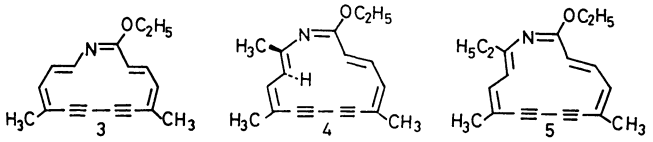
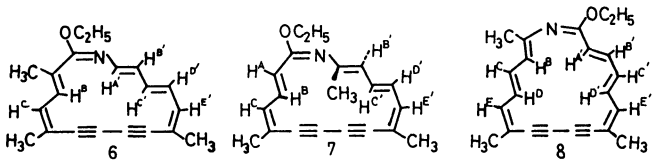
Syntheses of 2-ethoxy-3,6,11-trimethyl-7,9-bisdehydroaza[16]annulene, 2-ethoxy-6,11,16-trimethyl-7,9-bisdehydroaza[16]annulene, and 18-ethoxy-2,7,12-trimethyl-8,10-bisdehydroaza[18]annulene are described. It was found that the molecular skeletons of these α- or β-methylated aza[16]- and -[18]annulene are less planar than those of α- or β-methyl unsubstituted aza[16]- and aza[18]annulene, from examination of their ^{1}H NMR and electronic spectra.

In the previous paper, we have reported the synthesis of the paratropic dimethylbisdehydroaza[16]annulene (**1**) and the diatropic dimethylbisdehydroaza[18]-annulene (**2**).[1] In the preceding paper, we showed that the diatropicity, i.e., the planarity of the aza[14]annulene ring system decreases in the sequence of **3**> **5**>**4** on the basis of the chemical shifts of the olefinic protons. Also, the dimethylaza[14]annulene **3** can not set the α-alkyl group inside the ring and the trimethylaza[14]annulene **4** is a conformationally mobile molecule.[2]

Bearing these results in mind, we were interested in examining the properties of the higher analogs of the trimethylaza[14]annulene (**4**), and we expected that the aza[16]annulene **1** and the aza[18]annulene **2** with a larger π-electron cavity than the aza[14]annulene **3** might have the α-methyl group inside the ring. This paper is concerned with the syntheses and properties of the title compounds **6**—**8**, as well as comparison of the properties of **1** and **2**.[3]

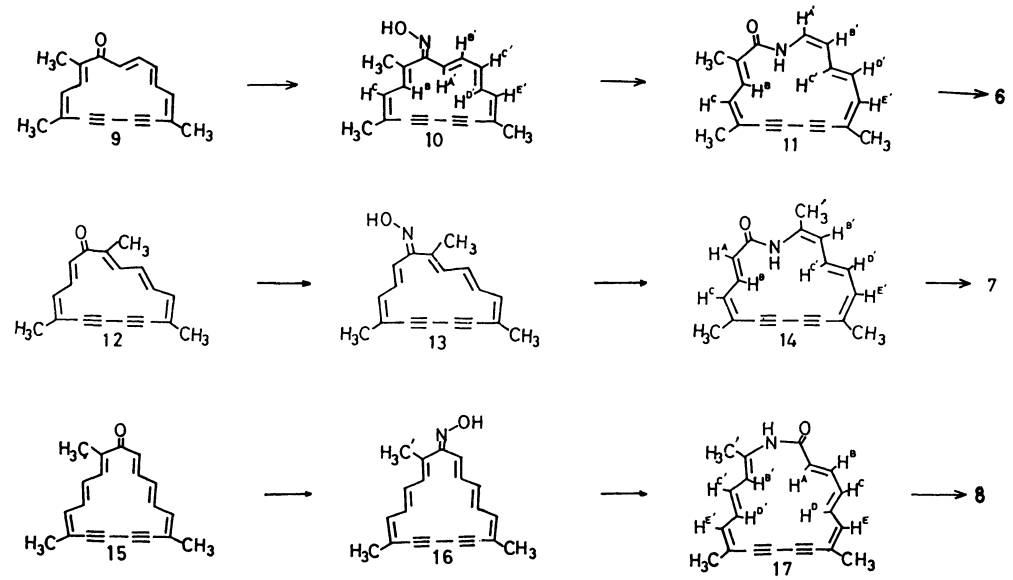






Results and Discussion

Synthesis. Synthesis of the azaannulenes **6**—**8** was carried out by the same procedure as that used for **1** and **2**. Treatment of the trimethylbisdehydro[15]annulenone (**9**)[4] with a large excess of hydroxylamine hydrochloride afforded only the isomer **10**[5] of the desired oxime in 58% yield. The reaction of **10** with phosphorus pentachloride led to the lactam **11** in 45% yield, which was converted to the unstable aza[16]annulene **6** in 0.4% yield by the reaction with triethyloxonium tetrafluoroborate. Similarly, the trimethylbisdehydro[15]annulenone (**12**)[4] was led to the



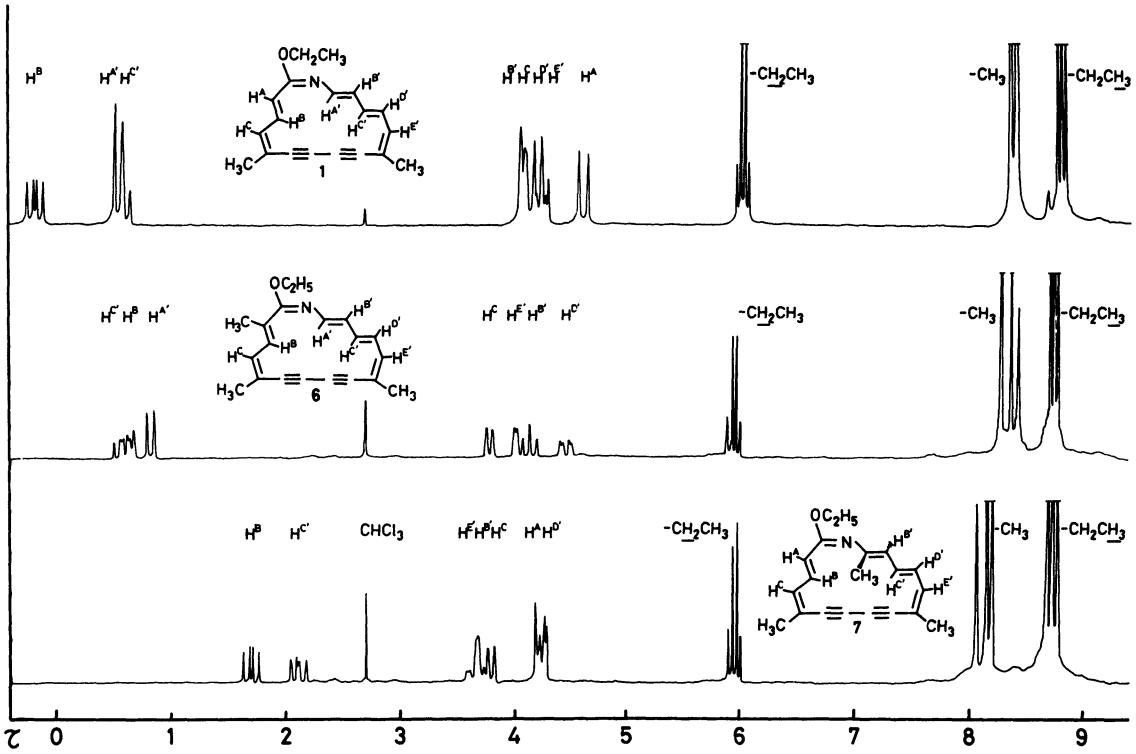


Fig. 1. The 200 MHz ^{1}H NMR spectra of the aza[16]annulenes **1**, **6**, and **7** in $CDCl_3$ (internal standard, TMS).

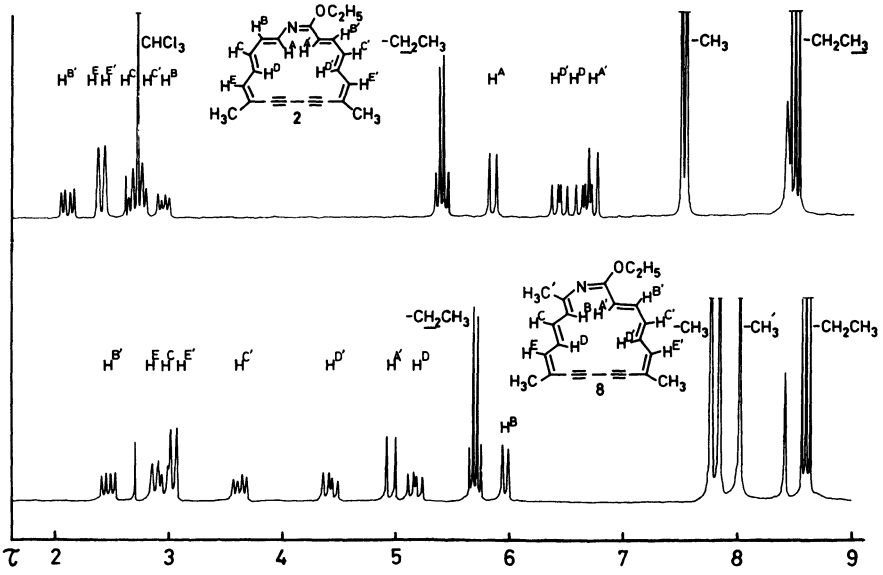


Fig. 2. The 200 MHz ^{1}H NMR spectra of the aza[18]annulenes **2** and **8** in $CDCl_3$ (internal standard, TMS).

oxime **13** (88%) as a sole product, which was converted to the lactam **14** in 47% yield. Lactam **14** gave the unstable aza[16]annulene **7** in 2.6% yield.

The oxime **16** (73%), obtained from the trimethylbisdehydro[17]annulenone (**15**)[6] was led to the lactam **17** in 46% yield, which was converted to the aza[18]annulene **8** as stable crystals in 11% yield.

^{1}H NMR Spectra. The ^{1}H NMR spectra of the trimethylaza[16]annulenes **6** and **7** are shown in Fig. 1, together with that of the dimethylaza[16]annulene **1**. The assignments of the resonances to the individual protons were made on the basis of multiplicities and coupling constants, and rigorously follow from decoupling experiments. Comparison of the chemical shift differences between the olefinic inner and outer protons indicate that the paratropicity of these azaannulenes decreases in the order of **1**>**6**>**7**, suggesting that the α-methyl substitution for the aza[16]annulene **1** greatly reduces the planarity of the molecular skeleton. This also indicates that the

Table 1. ^{1}H NMR Chemical Shifts of Aza[18]annulene **8** (In $CDCl_3$) at 90 MHz and **8'** (CF_3COOD in $CDCl_3$) at 200 MHz, Determined at 21 °C (τ Value: internal standard, Me_4Si)

T°/C	$H^{A'}$	H^B	$H^{B'}$	H^C	$H^{C'}$	H^D	$H^{D'}$	H^E	$H^{E'}$	$CH_{3'}$	CH_3	$-OC\underline{H}_2CH_3$	$-OCH_2C\underline{H}_3$
+60	4.96	5.95	2.54	3.05	3.67	5.16	4.43	2.95	3.10	8.05	7.81, 7.88	5.72	8.63
+25	4.99	5.99	2.51	3.04	3.66	5.20	4.47	2.91	3.08	8.04	7.79, 7.87	5.73	8.62
−30	5.06	6.08	2.44	2.95	3.65	5.29	4.55	2.86	3.02	8.01	7.79, 7.83	5.73	8.59
−60	5.13	6.15	2.44	2.92	3.63	5.35	4.58	2.86	3.02	8.01	7.77, 7.82	5.80	8.59
8'	5.46	5.74	1.84	3.05	3.91	5.25	3.78	2.75	2.92	7.87	7.64, 7.74	5.26	8.37

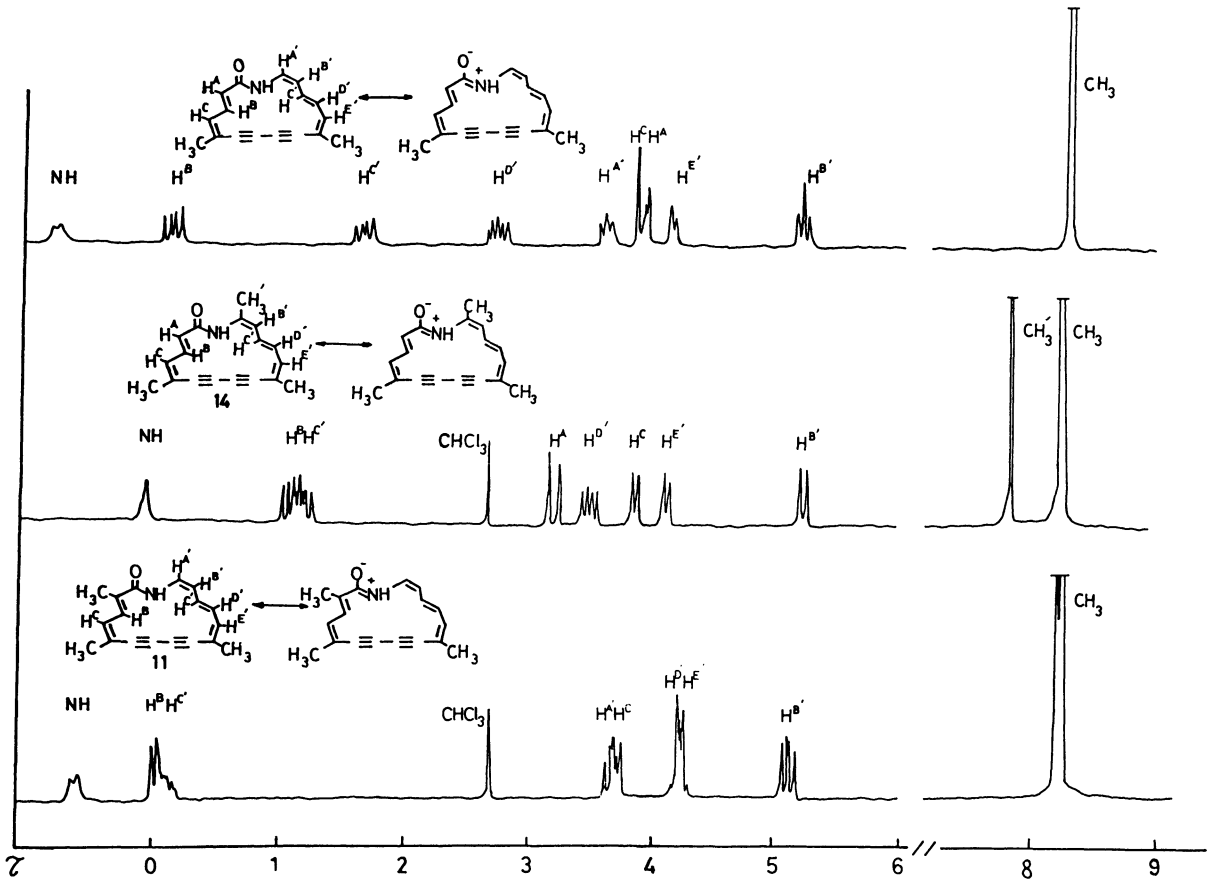


Fig. 3. The 200 MHz ^{1}H NMR spectra of the sixteen-membered lactams in $CDCl_3$ (internal standard, TMS).

trimethylaza[16]annulene **7** does not set the α-methyl group inside the ring properly. The extreme thermal unstability of **6** and **7**, as compared with **1**, might be due to low planarity of their molecular skeletons.

The ^{1}H NMR spectra of the dimethylaza[18]annulene **2** and the trimethylaza[18]annulene **8** are shown in Fig. 2. Comparison of the chemical shift differences of the olefinic inner and outer protons or of the chemical shifts of $-OC\underline{H}_2CH_3$ and CH_3 protons between **8** and **2** indicates that the diatropicity of **8** is smaller than that of **2**. 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 **8** does not locate inside the ring.

Variable-temperature ^{1}H NMR spectra of the trimethylaza[18]annulene **8** were taken at 90 MHz over the range of −60 to 60 °C, and the chemical shifts of the protons are listed in Table 1. As we see from Table 1, the spectra of **8** which is the higher analog of the conformationally mobile trimethylaza[14]annulene **4**,[2] proved to be essentially temperature-independent between these temperatures. Thus, no notable change around the potentially mobile, CH_3-C=CH^B moiety occurred, in contrast to the case of the trimethylaza[14]annulene **4**, indicating that the molecular skeleton of **8** is more rigid and less strained than that of **4**. One possible explanation for this behavior is that in the case of aza[18]annulene **8**, the steric strain caused by α-methyl substitution can be relieved over the whole of a larger molecular skeleton of **8**, as compared with the case of **4**.

The ^{1}H NMR chemical shifts of the deuterated species **8'**, taken in deuteriochloroform solution admixed with a few drops of deuteriotrifluoroacetic acid are

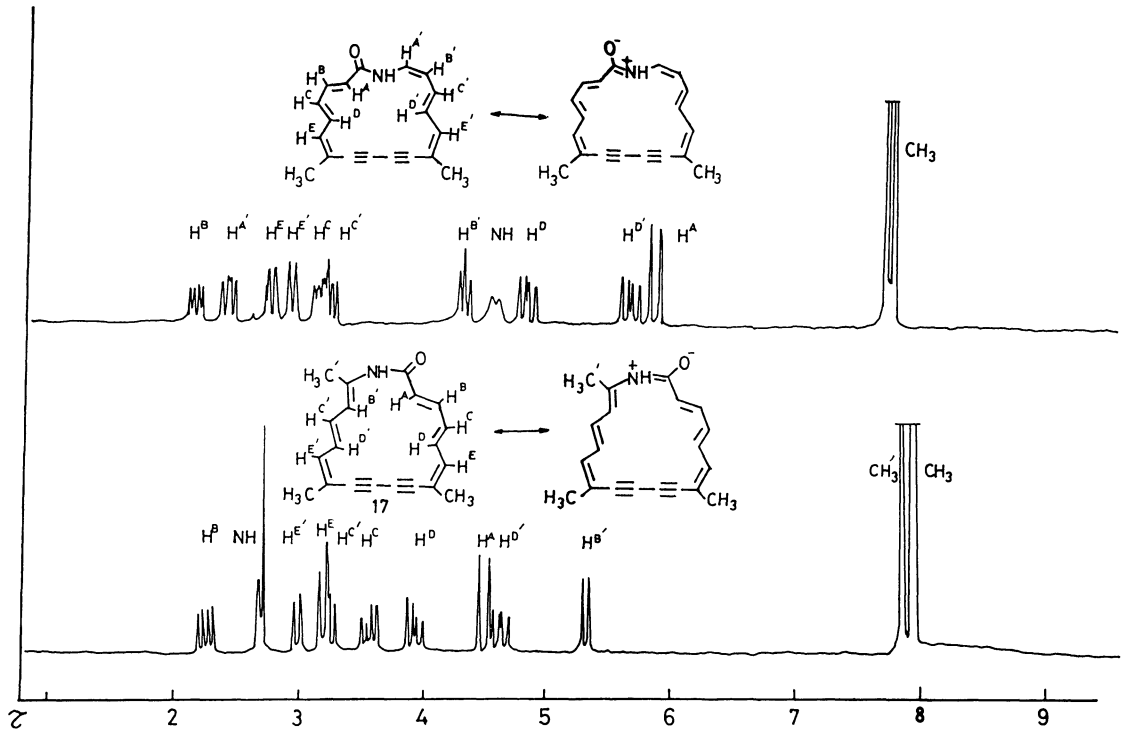


Fig. 4. The 200 MHz ^{1}H NMR spectra of the eighteen-membered lactams in $CDCl_3$ (internal standard, TMS).

also given in Table 1. It is apparent that the resonances of almost all the protons including ethoxyl and methyl protons in **8** shift toward lower field, except the protons nearby the nitrogen atom. This seems to be attributable to diminished π-electron perimeter in azaanulene **8**, arising from withdrawal of electrons by deuteration.

The ^{1}H NMR spectra of the lactams **11** and **14**, which are the precursors of the azaannulenes **6** and **7**, respectively, are shown in Fig. 3, together with that of the dimethylated lactam of the precursor of **1**, and the spectra of the lactam **17** and of the dimethylated lactam of the precursor of **2** are shown in Fig. 4. As can be seen from Fig. 3, the sixteen-membered lactams **11** and **14** as well as the dimethylated one show the inner proton resonances at low field and the outer proton (including methyl protons) resonances at high field. On the other hand, as we see from Fig. 4, the eighteen-membered lactam **17** as well as the dimethylated lactam shows the inner proton resonances at high field and the outer proton (including methyl protons) resonances at low field. Thus, it is noted that the spectra of these lactams are parallel to those of the corresponding azaanulenes with respect to the high-field and low-field shifts due to the olefinic and methyl protons. These results indicate that the sixteen-membered lactams **11** and **14** are paratropic, while the eighteen-membered lactam **17** is diatropic, and these lactams can be considered to exist in zwitter ionic forms, as indicated in Figs. 3 and 4, constructing fully conjugated macrocycles, as has been discussed previously.[1b] Furthermore, from Fig. 3, the chemical shift differences between the olefinic outer and inner protons as well as the chemical shifts of the methyl protons are almost the same in these lactams, indicating that the paratropicity, i.e., the planarity of the molecular skeletons of the sixteen-membered lactams are nearly the same. This fact is in contrast to the cases of the corresponding azaannulene series **1**, **6**, and **7** (Fig. 1), albeit both their lactams and the azaannulenes have the similar conformations each other. This suggests that the lactam ring have a more flexible perimeter for the steric strain, as compared with the azaannulene ring, presumably due to two single bonds on both sides of a nitrogen atom.

As we see from Fig. 4, the diatropicity decreases in the order of the dimethylated lactam>the trimethylated lactam **17** as similarly to the cases of the corresponding azaannulenes between **2** and **8**. This is reasonably attributed to the fact that the configurations both between the lactam **17** and the corresponding dimethylated lactam, and between the azaanulenes **2** and **8** are different.

Electronic Spectra. The electronic absorption spectra, taken in tetrahydrofuran, of the bisdehydroaza[16]annulenes **1**, **6**, and **7**, and of the bisdehydroaza[18]-annulenes **2** and **8** are illustrated in Fig. 5 and 6, respectively. As is seen from both Figs. 5 and 6, the longest wavelength bands shift toward longer wavelengths in the order of **1**>**6**>**7** (Fig. 5), **2**>**8** (Fig. 6), demonstrating the sequence for the degree of extended conjugation of π-electron system in these aza[16]- and

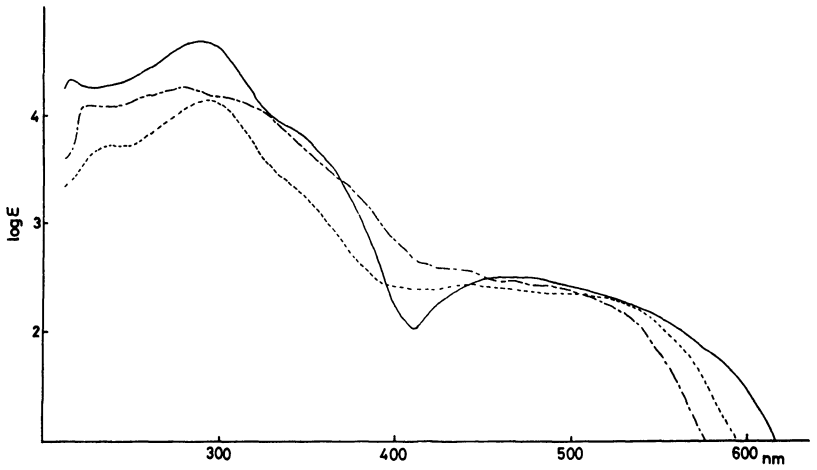


Fig. 5. Electronic spectra of the aza[16]annulenes **1** (——), **6** (------), and **7** (—·—·—) in THF.

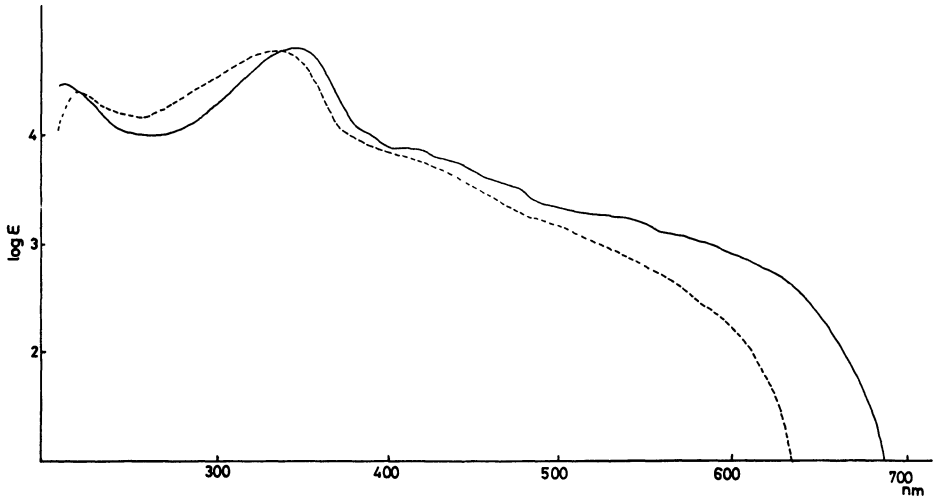


Fig. 6. Elelctronic spectra of the aza[18]annulenes **2** (——) and **8** (------) in THF.

-[18]annulene systems, respectively, as revealed above by examination from ^{1}H NMR spectra.

These results show that the conformations indicated for **1** and **2** are most appropriate for conjugation of π-electrons in these bisdehydroaza[16]- and -[18]annulene systems, respectively.

Experimental

All melting points are uncorrected. IR spectra were measured on Hitachi 260-50 spectrophotometer as KBr disk; only significant maxima are reported. UV spectra were taken on Hitachi 220A spectrophotometer and were recorded in nm, in tetrahydrofuran solution. ε-Values are given in parentheses, the shoulders being denoted by sh. Mass spectra were measured with JEOL JMS-200 spectrometer at 75 eV using a direct inlet system. ^{1}H NMR spectra were taken on JEOL FX-90Q (90 MHz) or Varian XL-200 (200 MHz) spectrometer, and refer to solutions in $CDCl_3$, unless othewise stated, in τ-values with TMS as an internal standard. The coupling constants (*J*) are given in Hz. Alumina (II-III) was used for column chromatography. Preparative TLC was carried out on 20×20 cm silica-gel plates (Merck, 0.5 or 2.0 mm thick). Dichloromethane was distilled over calcium hydride before use. Tetrahydrofuran (THF) was refluxed over potassium hydroxide pellets and distilled before use. Organic extracts with dichloromethane or chloroform were dried over anhyd calcium chloride prior to solvent removal.

1-Hydroxyimino-2,5,10-trimethylcyclopentadeca-2,4,10,12,14-pentaene-6,8-diyne (10). To a stirred soln of the trimethylbisdehydro[15]annulenone (**9**)[4] (1.70 g, 6.8 mmol) in methanol (250 ml) and THF (80 ml) was added a soln of hydroxylamine hydrochloride (19.0 g, 0.273 mol) in water (50 ml) at 38 °C in one portion. After stirring for further 24 h at 38—45 °C, further quantities of hydroxylamine hydrochloride (each 10 g in water (10 ml)) were added after every 24 h. After stirring for a total of 78 h, the soln was poured into aq sodium hydrogencarbonate soln and extracted with chloroform. The combined extracts were washed with aq sodium chloride soln, dried, and evaporated. The residue after solvent removal was chromatographed on alumina (3.7×7.5 cm). The early fractions eluted with hexane–chloroform (1:1) gave the recovered annulenone (**9**) (167 mg). The following fractions eluted with chloroform gave the oxime **10** (1.04 g, 58%) as a solid. Recrystallization from hexane–chloroform afforded orange needles: Mp 192 °C (decomp); MS *m/z* 263 (M^+, 37%)

230 (100); mol wt 263.3; IR 3230 (-OH), 2160 (-C≡C-), 990, and 970 cm^{-1} (trans C=C); UV_{max} 279 (27300), 309 (39200), and 395 nm sh (3400); ^1H NMR (90 MHz, DMSO-d_6) τ=−1.70 (s, 1H, OH, exchangeable with D_2O), 2.67 (dd, 16, 4, 1H, $H^{B'}$), 2.72—3.54 (m, 5H, H^B, H^C, $H^{C'}$, $H^{D'}$, and $H^{E'}$), 3.81 (d, 16.5, 1H, $H^{A'}$), 8.00 (s, 3H, CH_3), 8.02 (s, 3H, CH_3), and 8.08 (s, 3H, CH_3).

Found: C, 82.14; H, 6.45; N, 5.28%. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32%.

3,6,11-Trimethylazacyclohexadeca-3,5,11,13,15-pentaene-7,9-diyn-2-one (11). A soln of phosphorus pentachloride (5.0 g, 24 mmol) in THF (80 ml) was added to an ice-cooled, stirred soln of the oxime **10** (902 mg, 3.4 mmol) in THF (200 ml). The soln was stirred for a further 4 h at 25—28 °C, and then was poured into water. Then an aq sodium hydrogencarbonate soln was added (pH 8). The mixture was extracted with chloroform. The combined extracts were washed with aq sodium chloride soln, and dried. The residue after solvent removal was chromatographed on alumina (3.7×9.0 cm). The fractions eluted with hexane–benzene (3:2) gave the lactam **11** (405 mg, 45%) as a solid. Recrystallization from hexane–benzene afforded purple brown needles: Mp 187—189 °C; MS *m/z* 263 (M^+, 100%); mol wt 263.3; IR 3280 (NH), 2180 (-C≡C-), 1680 (C=O), 1620 (C=C), and 970 cm^{-1} (trans C=C); UV_{max} 265 sh (23500), 293 (38100), 310 sh (29200), 341 sh (9420), and 464 nm (1050); ^1H NMR (200 MHz) τ=−0.65 (d, 11, 1H, NH), −0.05 (d, 11, 1H, H^B), −0.04—0.12 (m, 1H, $H^{C'}$), 3.69 (dd, 11, 9.5, 1H, $H^{A'}$), 3.74 (d, 11.5, 1H, H^C), 4.24 (dd, 15, 11.5, 1H, $H^{D'}$), 4.28 (d, 11, 1H, $H^{E'}$), 5.16 (dd, 11, 9, 1H, $H^{B'}$), 8.25 (s, 3H, CH_3), 8.28 (s, 3H, CH_3), and 8.30 (s, 3H, CH_3), and see Fig. 3.

Found: C, 82.37; H, 6.46; N, 5.21%. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32%.

2-Ethoxy-3,6,11-trimethyl-7,9-bisdehydroaza[16]annulene (6). To a stirred soln of the lactam **11** (581 mg, 2.21 mmol) in dichloromethane (100 ml) was added dropwise a soln of triethyloxonium tetrafluoroborate (4.19 g, 22.1 mmol) in dichloromethane (30 ml) during 30 min at room temp under argon. After stirring for 1.5 h at the same temp, further quantities of the oxonium salt (each 4.19 g in dichloromethane (30 ml)) were added twice every 6 h. After stirring for a total 18 h, the soln was cooled in an ice-bath and an aq potassium carbonate soln was added dropwise (pH 8). The mixture was poured into water and extracted with dichloromethane. The combined extracts were washed with saturated aq sodium chloride soln, and dried. The residue after solvent removal was chromatographed on alumina (3.7×8.0 cm). The initial fractions eluted with 3% ether in hexane gave a dark red liquid, which was further purified by preparative TLC. The fast moving, red band on evaporation afforded the aza[16]annulene **6** (2.4 mg, 0.37%) as an unstable solid. Recrystallization from hexane–benzene afforded brown needles: Mp 114—115 °C; IR 2180 (-C≡C-), 1575 (C=C), and 1260 cm^{-1} (-O-); UV_{max} 237 (5270), 292 (13400), 340 sh (2210), and 455 nm (260), and see Fig. 5; ^1H NMR (200 MHz) τ=0.64 (dd, 16, 12, 1H, $H^{C'}$), 0.70 (d, 10, 1H, H^B), 0.88 (d, 13, 1H, $H^{A'}$), 3.83 (d, 11, 1H, H^C), 4.05 (d, 5.5, 1H, $H^{E'}$), 4.17 (t, 12, 1H, $H^{B'}$), 4.49 (dd, 16, 5, 1H, $H^{D'}$), 5.96 (q, 7, 2H, $-OC\underline{H}_2CH_3$), 8.28 (s, 3H, CH_3), 8.36 (s, 3H, CH_3), 8.43 (s, 3H, CH_3), and 8.74 (t, 7, 3H, $-OCH_2C\underline{H}_3$), and see Fig. 1.

HRMS: Found: 291.1607. Calcd for $C_{20}H_{21}NO$: 291.1620.

1-Hydroxyimino-5,10,15-trimethylcyclopentadeca-2,4,10,12,14-pentaene-6,8-diyne (13). To a stirred soln of the trimethylbisdehydro[15]annulenone (**12**)[4] (1.33 g, 5.34 mmol) in methanol (223 ml) and THF (65 ml) was added in one portion a soln of hydroxylamine hydrochloride (7.42 g, 0.107 mol) in water (8 ml) at room temp. After stirring for 17 h at room temp, a further quantity of hydroxylamine hydrochloride (14.8 g, 0.214 mmol) in water (15 ml) was added to the soln, and stirring was continued for a further 15 h. Then the soln was worked up as in the preparation of **10**. The residue after solvent removal was chromatographed on alumina (3.7×7.5 cm). The fractions eluted with 5% ethanol in chloroform gave the oxime **13** (1.24 g, 88%) as a solid. Recrystallization from hexane–chloroform afforded orange needles: Mp 198—200 °C (decomp); MS *m/z* 263 (M^+, 46%) and 231 (100); mol wt 263.3; IR 3250 (NH), 2150 (-C≡C-), 975, and 960 cm^{-1} (trans C=C); UV_{max} 278 sh (36100), 300 (50600), and 385 nm sh (20300); ^1H NMR (90 MHz, DMSO-d_6) τ=−1.37 (s, 1H, OH, exchangeable with D_2O), 2.79—3.94 (m, 7H, olefinic H), 8.02 (s, 3H, CH_3), 8.07 (s, 3H, CH_3), and 8.13 (s, 3H, CH_3).

Found: C, 82.19; H, 6.40; N, 5.46%. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32%.

6,11,16-Trimethylazacyclohexadeca-3,5,11,13,15-pentaene-7,9-diyn-2-one (14). A soln of phosphorus pentachloride (7.08 g, 34.0 mmol) in THF (210 ml) was added dropwise during 40 min to a soln of the oxime **13** (1.79 g, 6.80 mmol) in THF (210 ml) with stirring at 2—6 °C. After stirring for a further 2 h at the same temp, a further quantity of phosphorus pentachloride (1.42 g) in THF (22 ml) was added and stirring was continued for a further 1 h. Then the mixture was worked up as in the preparation of **11**. The residue after solvent removal was chromatographed on alumina (4.0×8.5 cm). The fractions eluted with 5% chloroform in benzene gave the lactam **14** (853 mg, 47%) as a solid. Recrystallization from hexane–chloroform afforded purple cubes: Mp 202—203 °C; MS *m/z* 263 (M^+, 100%); mol wt 263.3; IR 3300 (NH), 2180 (-C≡C-), 1650 (C=O), 1630, 1615 (C=C), and 970 cm^{-1} (trans C=C); UV_{max} 291 (26800), 342 sh (6380), and 459 nm (1110); ^1H NMR (200 MHz) τ=0.01 (s, 1H, NH), 1.17 (dd, 16.5, 9.0, 1H, H^B), 1.27 (dd, 15.8, 10.6, 1H, $H^{C'}$), 3.26 (d, 16.5, 1H, H^A), 3.56 (dd, 15.9, 8.6, 1H, $H^{D'}$), 3.93 (d, 9.2, 1H, H^C), 4.18 (d, 8.6, 1H, $H^{E'}$), 5.29 (d, 10.8, 1H, $H^{B'}$), 7.89 (s, 3H, CH_3'), 8.27 (s, 3H, CH_3), and 8.29 (s, 3H, CH_3), and see Fig. 3.

Found: C, 82.31; H, 6.51; N, 5.39%. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32%.

The later fractions eluted with 10% ethanol in chloroform gave the recovered oxime **13** (250 mg).

2-Ethoxy-6,11,16-trimethyl-7,9-bisdehydroaza[16]annulene (7). To a stirred soln of the lactam **14** (481 mg, 1.83 mmol) in dichloromethane (200 ml) was added a soln of triethyloxonium tetrafluoroborate (6.92 g, 36.5 mmol) in dichloromethane (60 ml) dropwise during 45 min with stirring at room temp under argon. After stirring for 3 h at the same temp, a further quantity of the oxonium salt (1.73 g) in dichloromethane (15 ml) was added, and stirring was continued for 21 h. Then the mixture was worked up as in the preparation of **6**. The dark red liquid after solvent removal was chromatographed on alumina (3.7×7.0 cm). The early fractions eluted with hexane gave an unstable red liquid, which was further purified by preparative TLC. The fast moving, red band on evaporation afforded the aza[16]-annulene **7** (13.6 mg, 2.6%) as a brown liquid: IR (neat) 2170 (-C≡C-), 1605 (C=C), and 1280 cm^{-1} (-O-); UV_{max} 266 sh (16700), 278 (18600), 304 (14800), 321 sh (11900), and 380

nm sh (1730), and see Fig. 5; ^{1}H NMR (200 MHz) τ=1.74 (dd, 16, 11, 1H, H^B), 2.16 (dd, 15.5, 11.5, 1H, $H^{C'}$), 3.71 (d, 4, 1H, $H^{E'}$), 3.73 (d, 11.5, 1H, $H^{B'}$), 3.82 (d, 11, 1H, H^C), 4.25 (d, 16, 1H, H^A), 4.27 (dd, 11.5, 4, 1H, $H^{D'}$), 5.91 (q, 7, 2H, $-OCH_2CH_3$), 8.07 (s, 3H, CH_3), 8.16 (s, 3H, CH_3), 8.20 (s, 3H, CH_3), and 8.73 (t, 7, 3H, $-OCH_2CH_3$), and see Fig. 1.

HRMS: Found: 291.1598. Calcd for $C_{20}H_{21}NO$: 291.1621.

The later fractions eluted with 5% ethanol in chloroform gave the recovered lactam **14** (76 mg).

1-Hydroxyimino-2,7,12-trimethylcycloheptadeca-2,4,6,12,14,16-hexaene-8,10-diyne (16). A soln of hydroxylamine hydrochloride (6.60 g, 95.0 mmol) in water (10 ml) was added in one portion to a stirred soln of trimethylbisdehydro[17]annulenone (**15**)[6] (657 mg, 2.40 mmol) in methanol (130 ml) and THF (40 ml) at room temp. After stirring for 19 h at 40 °C, a further quantity of hydroxylamine hydrochloride (6.6 g) in water (10 ml) was added and stirring was continued for a further 21 h at the same temp. Then the soln was worked up as in the preparation of **10**. The residue after solvent removal was chromatographed on alumina (4.2×7.5 cm). The fractions eluted with 5% ethanol in chloroform gave the oxime **16** (505 mg, 73%) as a solid. Recrystallization from hexane–chloroform afforded orange needles: Mp 218—220 °C (decomp): MS *m/z* 289 (M^+, 100%); mol wt 289.3; IR 3230, 3140 (-OH), 2170 (-C≡C-), 970, and 950 cm^{-1} (trans C=C); UV_{max} 300 (48800), 307 (48700), 370 sh (9490), and 398 nm sh (7180); ^{1}H NMR (90 MHz, DMSO-d_6) τ=−1.51 (s, 1H, OH, exchangeable with D_2O), 2.70—3.67 (m, 9H, olefinic H), 8.04 (s, 3H, CH_3'), and 8.15 (s, 6H, CH_3).

Found: C, 83.31; H, 6.63; N, 4.82%. Calcd for $C_{20}H_{19}NO$: C, 83.01; H, 6.62; N, 4.84%.

8,13,18-Trimethylazaoctadeca-3,5,7,13,15,17-hexaene-9,11-diyn-2-one (17). A soln of phosphorus pentachloride (2.44 g, 11.7 mmol) in THF (100 ml) was added dropwise during 30 min at −10 °C to a stirred soln of the oxime **16** (484 mg, 1.67 mmol) in THF (100 ml) and stirring was continued for a further 3.5 h at room temp. Then the soln was worked up as in the preparation of **11**. The residue after solvent removal was chromatographed on alumina (3.7× 9.0 cm). The fractions eluted with benzene–chloroform (1:1) gave the lactam **17** (221 mg, 46%) as a solid. Recrystallization from hexane–chloroform afforded dark brown cubes: Mp 202—204 °C (decomp); MS *m/z* 289 (M^+, 100%); mol wt 289.3; IR 3170, 3050 (NH), 2160 (-C≡C-), 1655 (C=O), 1605, 1585 (C=C), and 960 cm^{-1} (trans C=C); UV_{max} 327 (52100) and 403 nm sh (6250); ^{1}H NMR (200 MHz) τ=2.29 (dd, 15.5, 8.5, 1H, H^B), 2.70 (s, 1H, NH), 3.01 (d, 11, 1H, $H^{E'}$), 3.21 (d, 10.5, 1H, H^E), 3.25 (dd, 15, 11, 1H, $H^{C'}$), 3.58 (dd, 15.5, 8.5, 1H, H^C), 3.95 (dd, 15.5, 9.5, 1H, H^D), 4.50 (d, 15.5, 1H, H^A), 4.63 (dd, 15, 10.5, 1H, $H^{D'}$), 5.32 (d, 11, 1H, $H^{B'}$), 7.84 (s, 3H, CH_3'), 7.92 (s, 3H, CH_3), and 7.93 (s, 3H, CH_3), and see Fig. 4.

Found: C, 82.87; H, 6.80; N, 4.90%. Calcd for $C_{20}H_{19}NO$: C, 83.01; H, 6.62; N, 4.84%.

18-Ethoxy-2,7,12-trimethyl-8,10-bisdehydroaza[18]annulene (8). To a stirred soln of triethyloxonium tetrafluoroborate (4.05 g, 21.3 mmol) in dichloromethane (40 ml) was added a soln of the lactam **17** (206 mg, 0.712 mmol) in dichloromethane (35 ml) during 30 min at room temp under argon. After stirring for 17 h, a further quantity of the oxonium salt (2.5 g) in dichloromethane (20 ml) was added to the soln, and stirring was continued for a further 6 h. Then the soln was worked up as in the preparation of **6**. The residue after solvent removal was chromatographed on alumina (3.7×8.0 cm). The early fractions eluted with 2% ether in hexane gave the aza[18]annulene **8** (23.0 mg, 11.2%) as a solid. Recrystallization from hexane–benzene afforded dark brown needles: Mp 106—108 °C; MS *m/z* 317 (M^+, 88%) and 258 (100); mol wt 317.4; IR 2170 (-C≡C-), 1620, 1600, 1560 (C=N, C=C), 1280, 1265, 1055 (-O-), and 960 cm^{-1} (trans C=C); UV_{max} 291 sh (27000), 333 (55500), 412 sh (5660), and 510 nm sh (1270), and see Fig. 6; ^{1}H NMR (200 MHz) τ=2.51 (dd, 15.5, 8, 1H, $H^{B'}$), 2.92 (d, 10, 1H, H^E), 3.04 (dd, 15, 10.5, 1H, H^C), 3.08 (d, 10, 1H, $H^{E'}$), 3.66 (dd, 15, 8, 1H, $H^{C'}$), 4.46 (dd, 15, 10, 1H, $H^{D'}$), 4.99 (d, 15.5, 1H, $H^{A'}$), 5.20 (dd, 15, 10, 1H, H^D), 5.73 (q, 7, 2H, $-OCH_2CH_3$), 5.99 (d, 10.5, 1H, H^B), 7.79 (s, 3H, CH_3), 7.86 (s, 3H, CH_3), 8.04 (s, 3H, CH_3'), and 8.62 (t, 7, 3H, $-OCH_2CH_3$), and see Fig. 2, (200 MHz, CF_3COOD in $CDCl_3$) τ=1.84 (dd, 15.5, 8, 1H, $H^{B'}$), 2.75 (d, 10.5, 1H, H^E), 2.92 (d, 8, 1H, $H^{E'}$), 3.05 (dd, 15.5, 10.5, 1H, H^C), 3.78 (dd, 15.5, 8, 1H, $H^{D'}$), 3.91 (dd, 15.5, 8, 1H, $H^{C'}$), 5.25 (dd, 15.5, 10.5, 1H, H^D), 5.26 (q, 7, 2H, $-OCH_2CH_3$), 5.46 (d, 15.5, 1H, $H^{A'}$), 5.74 (d, 10.5, 1H, H^B), 7.64 (s, 3H, CH_3), 7.74 (s, 3H, CH_3), 7.87 (s, 3H, CH_3'), and 8.37 (t, 7, 3H, $-OCH_2CH_3$).

Found: C, 83.42; H, 7.24; N, 4.57%. Calcd for $C_{22}H_{23}NO$: C, 83.24; H, 7.30; N, 4.41%.

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