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The Synthesis of Macrocyclic Diaza *n*-*n*′-Fulvadiene Derivatives

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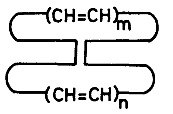
The diaza analogs of 7-13-, 7-15-, 7-17-, 13-13-, 13-15-, 15-15-, and 19-19-fulvadiene derivatives were synthesized through the reaction of 2,4,6-cycloheptatrienone and the corresponding bisdehydroannulenones with hydrazine dihydrochloride. The ^{1}H NMR and electronic spectra of these compounds are discussed in connection with tropicity.

Bicyclic polyenes containing a cyclic cross-conjugated π-electron system of the fulvalenes of type **1** have been extensively investigated.[1] The convenient synthesis of the bisdehydroannulenones of type **2**[2] in satisfactory yield made it possible to prepare the heptafulvalenes[3] and the pentafulvalenes[4,5] using **2** as the starting material.



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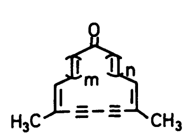

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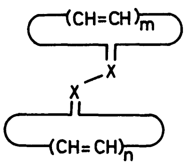
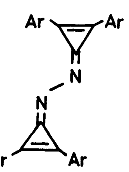


3a : X = CH
3b : X = N



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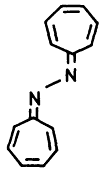

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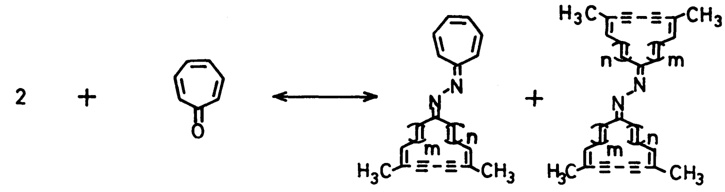
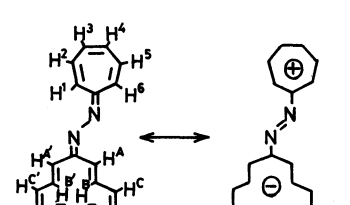
Recently, a number of vinylogous fulvalenes (fulvadienes) of type **3a** have been studied.[6] We were interested in a synthesis of the diaza analogs **3b** of the system; only known examples are the diaza analogs **4**[7] and **5**[8] of the triatriafulvadiene and the heptaheptafulvadiene, respectively, in which both rings are the same.

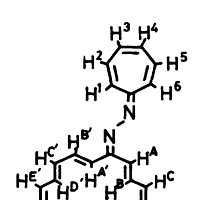
We considered that the diazafulvadienes containing different-membered rings might cause π-electron polarization across the azine group. For example, the diaza 7-13- **9**[9] and 13-15-fulvadiene **13** will be expected to exhibit π-electron polarization from 7- and 15-membered ring to 13-membered rings to form zwitterionic forms **9a** and **13a**, respectively, in which all rings are $[4n+2]\pi$-electron systems and are potentially diatropic. To examine this, preparation of the diazafulvadienes having inner ring protons as marks would be desirable. In this paper, we describe synthesis



6 7 8



9 9a



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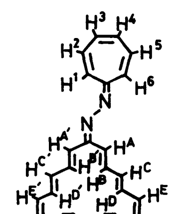

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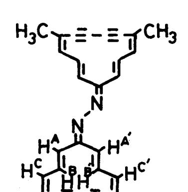

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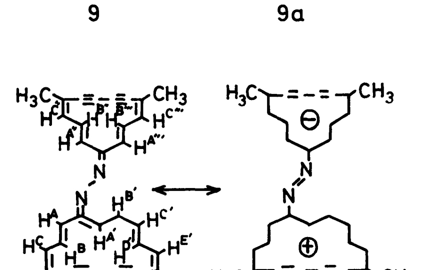
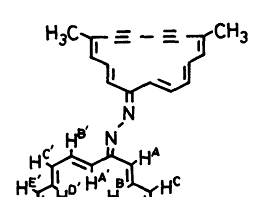


13 13a



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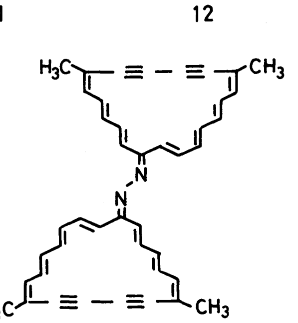

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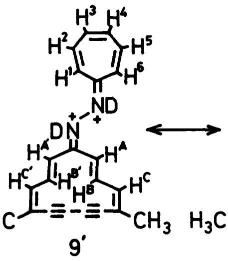
Table 1. Electronic Absorption Maxima of Diazafulvadienes **9**—**15** in Tetrahydrofuran
λ_{max}/nm (ε_{max})

9	**10**	**11**	**12**	**13**	**14**	**15**
276 (32200)	293 (31700)	222 (23400)	255 (33000)	265 (35500)	278 (37000)	231 sh (25000)
442 (28200)	375 (20700)	264 sh (26400)	264 sh (32500)	318 (31300)	323 (31000)	313 (47500)
	444 (26300)	281 sh (52900)	290 (26000)	465 (25300)	466 (22100)	404 sh (26600)
		298 (83700)	420 (28000)			495 (23800)
		306 (85400)				
		422 (7240)				

a) All the spectra showed tailing to ≃600 nm.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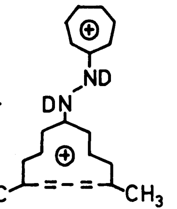
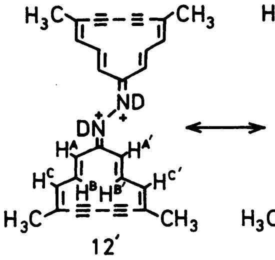

9'a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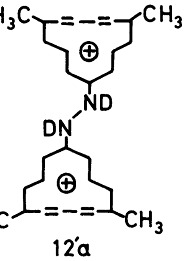
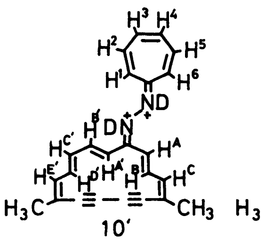

12'a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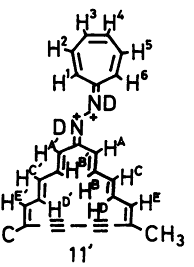
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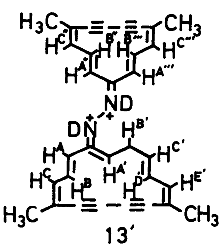
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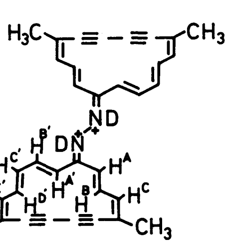
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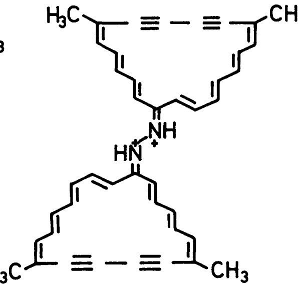
15'

and properties of some of the hepta-derivatives **7** (**9**—**11**) and the large-ring ones **8** (**12**—**15**).

Results and Discussion

Synthesis. The synthesis was accomplished by the reaction of the bisdehydroannulenones **2** with hydrazine dihydrochloride in the presence of 2,4,6-cycloheptatrienone (**6**), usually giving rise to the diaza hepta- **7** and large-ring derivatives **8**. Thus, the reaction of a mixture of the ketone **6** and one of the following annulenones, 5,10-dimethyl-6,8-bisdehydro[13]annuleone,[2a)] 5,10-dimethyl-6,8-bisdehydro[15]annulenone,[2b)] and 7,12-dimethyl-8,10-bisdehydro[17]annulenone[2b)] withhydrazine dihydrochloride in methanol-tetrahydrofuran at room temperature gave the diaza 7-13- **9** (5.0%), 7-15- **10** (3.0%), and 7-17-fulvadiene **11** (6.6%), respectively. In the first two cases, bis-condensation products, the diaza 13-13- **12** (24%) and 15-15-fulvadiene **14** (3.6%) were formed, but rather surprisingly, the diaza 7-7-fulvadiene was not obtained in any above reactions. The diaza analog **13** of 13-15-fulvadiene was obtained (2.9%) by the reaction of a mixture of [13]- and [15]-annulenones with hydrazine dihydrochloride. Compounds **12** and **14** were also prepared by the reaction of [13]- and [15]annulenones with hydrazine, respectively. The diaza 19-19-fulvadiene **15** (1.4%) was obtained by the reaction of 7,12-dimethyl-8,10-bisdehydro[19]annulenone[2b)] with hydrazine in the presence of **6**; however the diaza 7-19-fulvadiene was not detected in the reaction mixture. The diaza 17-17-fulvadiene also was not detected in the reaction mixtures of the [17]annulenone with hydrazine in the presence of **6** or in the absence of **6**. These diazafulvadienes **9**—**15** thus obtained were recrystallized from hexane–benzene or hexane–chloroform to afford

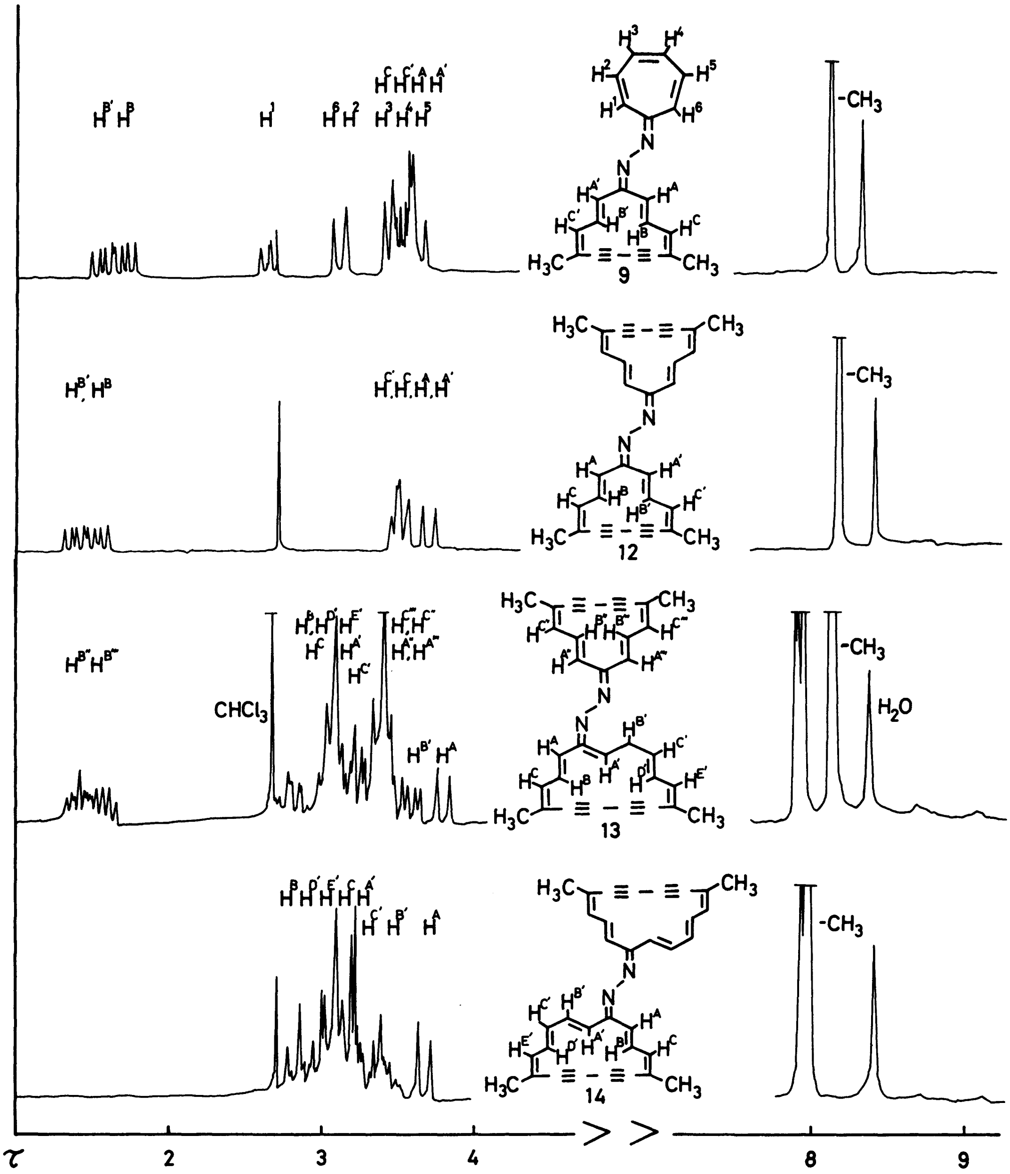

Fig. 1. The 200 MHz ^{1}H NMR spectra of the diazafulvadienes **9**, **12**, **13**, and **14** in CDCl$_3$.

deep colored (dark reddish or dark purple), unstable crystals, which were gradually decomposed at room temperature to diffused light under air.

Electronic Spectra. The electronic absorption maxima (in tetrahydrofuran) of these diazafulvadienes **9**—**15** are listed in Table 1. In two series compounds, hepta-derivatives **9**—**11** and large-ones **12**—**15**, it is clear that the most intensive maxima exhibit an almost regular bathochromic shift as the ring size increases. Thus, the occurrence of the same sort of alternation along with increasing ring size between the maxima of [4*n*—2] and of [4*n*]systems, as has been observed for annulenes and dehydroannulenes [(4*n*—2)π-systems absorbing at longer wavelengths than the (4*n*)π-systems],$^{10)}$ is not observed, suggesting that these diazafulvadienes are atropic, as revealed by examination of ^{1}H NMR spectra (vide infra).

The electronic absorption maxima of these diazafulvadienes **9**—**15** in trifluoroacetic acid (TFA) are listed in Table 2. It is evident that protonation with this acid causes the shift of the maxima to longer wavelength in every case and gives the corresponding protonated (or deuteronated when TFA-d_1 is used) species **9′**—**15′**, in which **9′** was brown in color, **10′** blue, **11′** green, **12′** brown, **13′** reddish purple, **14′** blue, and **15′** brown. Neutralization of the protonated large-ring species **12′**—**15′** with aqueous sodium hydrogencarbonate resulted in regeneration of **12**—**15**, respectively. However, standing the solutions of the protonated hepta-species **9′**—**11′** resulted in a change, and the diazafulvadiene **9**—**11** were not recovered from them on quenching.

^{1}H NMR Spectra. The ^{1}H NMR chemical shifts of olefinic and methyl protons of these diazafulvadienes

Table 2. Electronic Absorption Maxima of Diazafulvadienes **9**—**15** in Trifluoroacetic Acid λ_{max}/nm (Relative extinction coefficient)[a]

9	10	11	12	13	14	15
261 sh (0.66)	258 (0.47)	264 (0.33)	271 (0.78)	258 sh (0.64)	258 (0.37)	275 sh (0.93)
284 (0.85)	367 (0.98)	308 sh (0.58)	289 (0.79)	274 (0.76)	277 sh (0.28)	285 (1.00)
417 (1.00)	378 (1.00)	326 (1.00)	445 (1.00)	293 (0.69)	366 (1.00)	306 (0.93)
526 (0.21)	461 sh (0.14)	358 (0.67)	580 sh (0.19)	346 sh (0.73)	375 sh (0.99)	423 (0.90)
	491 sh (0.20)	437 (0.68)		382 (1.00)	429 (0.36)	447 sh (0.86)
	542 (0.36)	671 (0.03)		593 (0.95)	529 sh (0.20)	464 sh (0.74)
	579 (0.66)			608 sh (0.92)	598 (0.82)	628 (0.56)
					634 sh (0.54)	701 sh (0.47)

a) All the spectra showed tailing to ≃800 nm.

Table 3. ^{1}H NMR Chemical Shifts of Diaazafulvadienes **9**—**14** (in $CDCl_3$) and Deuterated Species **9′**—**14′** (CF_3COOD in $CDCl_3$) at 200 MHz, Determined at 21 °C (τ Value; Standard, Me_4Si)

Compd	H^A	$H^{A'}$	$H^{A''}$	$H^{A'''}$	H^B	$H^{B'}$	$H^{B''}$	$H^{B'''}$	H^C	$H^{C'}$	$H^{C''}$	$H^{C'''}$
9	3.53	3.66			1.73	1.58			3.45	3.46		
9′	3.77	3.79			1.07	0.87			3.67	3.58		
10	3.64	2.74			2.95	3.66			3.20	3.55		
10′	3.06	6.06			4.11	(1.76—2.39)			2.83	(1.76—2.39)		
11	3.46	3.76			2.38	2.42			(3.34 —	— 3.77)		
11′	3.98	3.98			1.44	1.44			3.87[a]	3.93[a]		
12	3.71	3.54			1.54	1.39			3.49	3.50		
12′	3.91	3.77			−0.76	−0.67			3.84	3.85		
13	3.83	(2.72 —			— 3.51)	3.61	(1.45 —	— 1.64)	(2.72 —			— 3.51)
13′	(1.98—2.35)	(3.11 —			— 3.81)	1.28	0.50[b]	0.70[b]	(1.98—2.35)	2.44	(3.11 —	— 3.81)
14	3.70	3.20			2.91	3.50			3.19	3.31		
14′[c]	(2.16—2.96)	(4.82—5.60)			(4.82—5.60)	(2.16—2.96)			(2.16 —	— 2.96)		

Compd	H^D	$H^{D'}$	H^E	$H^{E'}$	H^1	H^6	H^2	H^5	H^3	H^4	CH_3
9					2.59—2.68	(3.10 —	— 3.19)	(3.49 —		— 3.63	8.18
9′					1.50—1.56	(1.98—2.13)	2.24 —	— 2.38	(1.98 —	— 2.13)	8.20
10		2.97		3.15	2.49—2.59	2.86—2.91	3.50 —	— 3.71	3.17 —	— 3.24	7.99, 8.02
10′		4.31		(1.76—2.39)	1.50—1.67	(1.76 —				— 2.39)	7.47, 7.54
11	2.56	2.56	(3.34—3.77)		2.57—2.60	3.16—3.22	(3.34 —			— 3.77)	8.14
11′	1.25	1.25	3.63	3.63	1.69—1.75	(2.04—2.20)	2.32 —	— 2.42	(2.04 —	— 2.20)	8.20
12											8.19, 8.20
12′											8.28
13		(2.72—3.51)		(2.72—3.51)							7.96, 7.99, 8.12, 8.17
13′		(3.11—3.81)		(1.98—2.35)							7.42, 7.67, 8.21
14		3.04		3.15							7.96, 8.01
14′[c]		(4.82—5.60)		(2.16—2.96)							7.64, 7.71

a), b) Assignments may be reversed in each group (see Experimental). c) At 270 MHz.

9—**14** are listed in Table 3, together with those of their deuteronated species **9′**—**14′**, obtained in deuteriochloroform solution admixed with a few drops of TFA-d_1. Individual assignments, some of which are tentative, were made on the basis of multiplicities, coupling constants, and the assumption that protons in a similar environment resonate at similar field, and were clarified by decoupling experiments where necessary. The ^{1}H NMR spectra of only the diaza 7-13- **9**, 13-13- **12**, 13-15- **13**, and 15-15-fulvadiene **14** are illustrated in Fig. 1. As we see from Table 3 and Fig. 1, the downfield and upfield shifts of the olefinic protons as well as the methyl protons are not observed in the spectrum of the diaza 7-13-fulvadiene **9**, as compared with the resonances of the corresponding protons in the spectrum of the diaza 13-13-fulvadiene **12**, which is not expected to polarize since both rings are the same. Similarly, the olefinic and methyl protons of **13** resonate at the almost same field as those of the resonances of the corresponding protons of the diaza 13-13- **12** and 15-15-fulvadiene **14**. These facts show that both **9** and **13** do not exhibit π-electron polarization across the azine group to form polar structures **9a** and **13a**. On the other hand, the spectra of the deuteronated species **9′** and **12′**, which are illustrated in Fig. 2, show the downfield or upfield shifts of olefinic resonances. In the spectrum of **9′**, the proton resonances of the 7-membered ring appear in lower field ($\Delta -0.6$ ppm), and the outer proton resonances of the 13-membered ring in higher field ($\Delta +1$ ppm), as compared with the resonances of the corresponding olefinic protons of **9**. In the spectrum of **12′**, the much larger downfield shift ($\Delta -1.5$ ppm) of the inner proton resonances, as compared with the resonances of the corresponding protons of **12**, is seen. These facts suggest that the 7-membered ring in **9′** is diatropic, while the 13-membered ring in both **9′** and **12′** is paratropic, and the dicationic forms **9a′** and **12a′** contribute to the structures **9′** and **12′** as resonance hybrid to some extent, respectively.

As we can see from Table 3, the upfield and downfield shifts of the proton resonances of the large ring are not seen in the spectrum of the diaza 7-15-fulvadiene **10**, as compared with the resonances of the corresponding protons of the diaza 15-15-fulvadiene **14**.

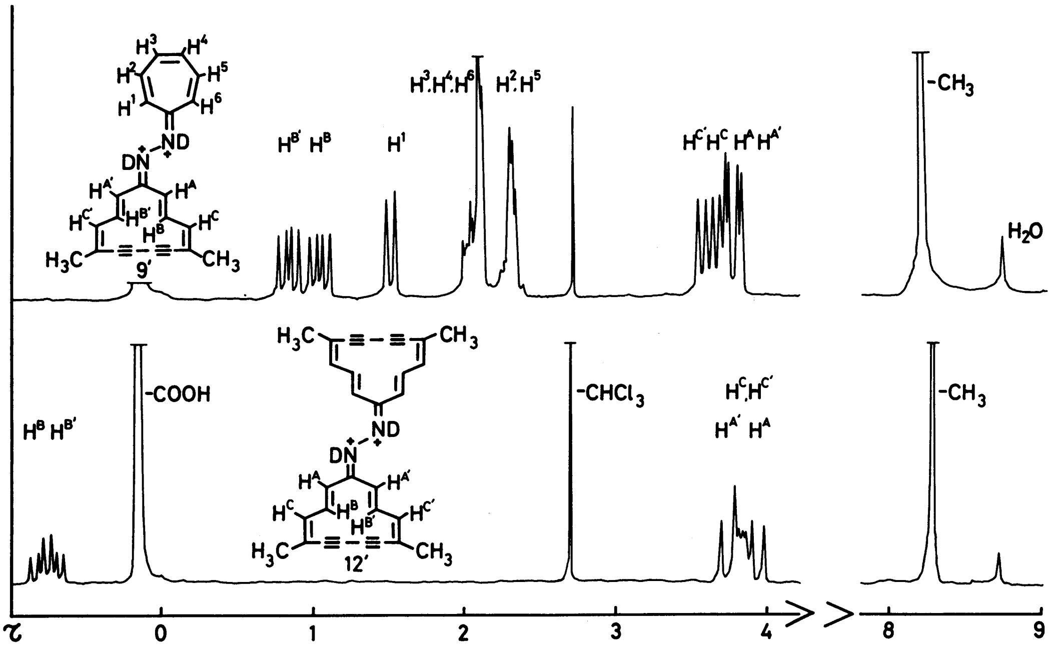

Fig. 2. The 200 MHz ^{1}H NMR spectra of the deuterated species **9′** and **12′**.

Thus, the compound **10** also does not exhibit π-electron polarization. The olefinic protons of both the diaza 7-17- **11** (Table 3) and the diaza 19-19-fulvadiene **15** (see Experimental) resonate in normal region, and these are also polyolefinic molecules. On the other hand, the deuteronated species, **10′**, **11′**, **13′**, and **14′** show that the downfield or upfield shifts of the olefinic proton resonances as well as the methyl proton resonances, as compared with the corresponding proton resonances of the respective diazafulvadienes **10**, **11**, **13**, and **14** (Table 3). In the spectra of the deuteronated species **10′** and **11′**, the protons of the 7-membered ring resonate at low field, indicating that the ring is diatropic. In **10′**, **13′**, **14′**, the inner protons of the 15-membered ring resonate at high field, and the outer and methyl protons at low field, indicating the 15-membered ring in **10′**, **13′**, and **14′** being diatropic. Conversely, the inner protons of the 13- and 17-membered rings in **11′** and **13′** resonate at low field, and the outer and methyl protons at high field, indicating the 13- and 17-membered rings in **11′** and **13′** being paratropic. These results also suggest that the similar dicationic forms as those (**9a′** and **12a′**) depicted for **9′** and **12′**, contribute to the structures of the species **10′**, **11′**, **13′**, and **14′**.

Experimental

Melting points are uncorrected. IR spectra were measured on Hitachi 260-50 spectrophotometer as KBr disk; only significant maxima are reported. Electronic spectra were recorded on Hitachi 220-A spectrophotometer in nm, in tetrahydrofuran solution. Mass spectra were measured with JMS-D 200 spectrometer at 75 eV using a direct inlet system or JMS-D spectrometer equipped with field desorption system. ^{1}H NMR spectra were taken on Varian XL-200 (200 MHz) or JEOL GX-270 (270 MHz) spectrometer, and refer to solution in $CDCl_3$, unless otherwise stated, in τ-values with TMS as an internal standard. The coupling constants (*J*) are given in Hz. The individual assignments were made on the basis of multiplicities and coupling constants, and were further clarified by decoupling experiments where necessary. Alumina (II—III) was used for column chromatography. Progress of most reactions was monitored by TLC using precoated Merck silica-gel plates. Preparative plate chromatography was carried out on 20X20 cm silica-gel plates (Merck, 0.5 or 2 mm thick). Evaporation of solvents was performed under water aspirator pressure, and sodium sulfate was used as drying agent.

1-(2,4,6-Cycloheptatrienylidene)-2-(5,10-dimethyl-2,4,10,12-tridecatetraene-6,8-diynylidene)hydrazine (9) and 1,2-Bis(5,10-dimethyl-2,4,10,12-tridecatetraene-6,8-diynylidene)hydrazine (12). A soln of hydrazine dihydrochloride (170 mg, 1.62 mmol) in water (2 ml) was added in one portion to a stirred soln of 2,4,6-cycloheptatrienone (**6**) (170 mg, 1.60 mmol) and 5,10-dimethyl-6,8-bisdehydro[13]annulenone[2a] (300 mg, 1.44 mmol) in methanol (80 ml) and tetrahydrofuran (THF) (20 ml) at 40 °C, and stirring was continued overnight at the same temperature. After an aqueous 10% sodium hydrogencarbonate soln was added (pH 7—8), the mixture was poured onto water and extracted with chloroform. The combined extracts were washed with brine, and dried. After solvent removal, the residual dark red liquid was chromatographed on alumina (4.0X7.0 cm). The early fractions eluted with hexane–chloroform (3:2) gave a red solid, which was purified by preparative plate chromatography (4 times, benzene–chloroform as eluent). The fast-moving, first band gave the diaza 13-13-fulvadiene **12** (140 mg, 24%). Recrystallization from hexane–tetrahydrofuran afforded purple needles: Mp 189—190 °C (decomp); MS *m/z* 412 (M^+, 16%) and 32 (100); mol wt 412.5; ^{1}H NMR (200 MHz) τ=1.39 (dd, 16, 10, 2H, $H^{B'}$), 1.54 (dd, 17, 10, 2H, H^B), 3.49 (d, 10, 2H, H^C), 3.50 (d, 10, 2H, $H^{C'}$), 3.54 (d, 16, 2H, $H^{A'}$), 3.71 (d, 17, 2H, H^A), 8.19 (s, 6H, CH_3), 8.20 (s, 6H, CH_3), and see Fig. 1; (CF_3COOD in $CDCl_3$, 200 MHz) $\tau=-0.76$ (dd, 16.5, 10, 2H, H^B), −0.67 (dd, 16.5, 10, 2H, $H^{B'}$), 3.77 (d, 16.5, 2H, $H^{A'}$), 3.84 (d, 10, 2H, H^C), 3.85 (d, 10, 2H, $H^{C'}$), 3.91 (d, 16.5, 2H, H^A), 8.28 (s, 12H, CH_3), and see Fig. 2.

Found: C, 87.16; H, 5.95; N, 6.81%. Calcd for $C_{30}H_{24}N_2$: C, 87.34; H, 5.87; N, 6.79%.

The later fractions eluted with hexane–chloroform (2:3) gave a red liquid, which was purified by preparative plate chromatography (4 times, benzene–chloroform as eluent). The fast-moving, second band gave the diaza 7-13-fulvadiene **9** (23 mg, 5.0%). Recrystallization from hexane afforded red cubes: Mp 141—142 °C; MS *m/z* 310 (M^+, 41%) and 190 (100); mol wt 310.3; IR 2170 (–C≡C–) and 975 cm^{-1} (trans C=C); UV: see Tables 1 and 2; ^1H NMR (200 MHz) $\tau=1.58$ (dd, 17, 10, 1H, $H^{B'}$), 1.73 (dd, 17, 10, 1H, H^B), 2.59—2.68 (m, 1H, H^1), 3.10—3.19 (m, 2H, H^2, H^6), 3.45 (d, 10, 1H, H^C), 3.46 (d, 10, 1H, $H^{C'}$), 3.49—3.63 (m, 3H, H^3, H^4, H^5), 3.53 (d, 17, 1H, H^A), 3.66 (d, 17, 1H, $H^{A'}$), 8.18 (s, 6H, CH_3), and see Fig. 1; (CF_3COOD in $CDCl_3$, 200 MHz) $\tau=0.87$ (dd, 16, 10, 1H, $H^{B'}$), 1.07 (dd, 16, 10, 1H, H^B), 1.50—1.56 (m, 1H, H^1), 1.98—2.13 (m, 3H, H^3, H^4, H^6), 2.24—2.38 (m, 2H, H^2, H^5), 3.58 (d, 10, 1H, $H^{C'}$), 3.67 (d, 10, 1H, H^C), 3.77 (d, 16, 1H, H^A), 3.79 (d, 16, 1H, $H^{A'}$), 8.20 (s, 6H, CH_3), and see Fig. 2.

Found: C, 85.30; H, 5.90; N, 9.01%. Calcd for $C_{22}H_{18}N_2$: C, 85.13; H, 5.85; N, 9.03%.

The Diaza 13-13-Fulvadiene 12 from Bisdehydro[13]annulenone. A soln of hydrazine dihydrochloride (50 mg, 0.48 mmol) in water (1 ml) was added in one portion to a stirred soln of bisdehydro[13]annulenone[2a)] (152 mg, 0.73 mmol) in methanol (100 ml) and THF (17 ml) at room temperature and stirring was continued overnight. The mixture was worked up as described above. The residue, after solvent removal, was chromatographed on alumina (3.7×7.5 cm). The fractions eluted with benzene gave the diaza 13-13-fulvadiene **12** (110 mg, 73%).

1-(2,4,6-Cycloheptatrienylidene)-2-(5,10-dimethyl-2,4,10,12,-14-pentadecapentaene-6,8-diynylidene)hydrazine (10) and 1,2-Bis(5,10-dimethyl-2,4,10,12,14-pentadecapentaene-6,8-diynylidene)hydrazine (14). A soln of hydrazine dihydrochloride (260 mg, 2.48 mmol) in water (2 ml) was added in one portion to a stirred soln of the ketone **6** (255 mg, 2.40 mmol) and the bisdehydro[15]annulenone[2b)] (563 mg, 2.40 mmol) in methanol (180 ml) and THF (50 ml) at room temperature and stirring was continued overnight. The mixture was worked up as in the isolation of **9** and **12**. The residual red liquid, after solvent removal, was chromatographed on alumina (3.7×12.5 cm). The fractions eluted with hexane–benzene (1:4—1:9) gave a red solid, which was further purified by preparative plate chromatography (5 times, benzene as eluent). The fast moving, purple band gave the diaza 15-15-fulvadiene **14** (20 mg, 3.6%). Recrystallization from hexane–benzene afforded purple needles: Mp 171—172 °C (decomp); MS (field desorption method) *m/z* 464 (M^+); mol wt 464.6; IR 2170 (–C≡C–) and 975 cm^{-1} (trans C=C); UV: see Tables 1 and 2; ^1H NMR (200 MHz) $\tau=2.91$ (dd, 16, 11, 2H, H^B), 3.04 (dd, 16, 11, 2H, $H^{D'}$), 3.15 (d, 11, 2H, $H^{E'}$), 3.19 (d, 11, 2H, H^C), 3.20 (d, 15.5, 2H, $H^{A'}$), 3.31 (dd, 16, 5, 2H, $H^{C'}$), 3.50 (dd, 15.5, 5, 2H, $H^{B'}$), 3.70 (d, 16, 2H, H^A), 7.96 (s, 6H, CH_3), 8.01 (s, 6H, CH_3), and see Fig. 1; (CF_3COOD in $CDCl_3$, 270 MHz) $\tau=2.16$—2.96 (m, 10H, H^A, $H^{B'}$, H^C, $H^{C'}$, $H^{E'}$), 4.82—5.60 (m, 6H, $H^{A'}$, H^B, $H^{D'}$), 7.64 (s, 6H, CH_3), and 7.71 (s, 6H, CH_3).

Found: C, 87.04; H, 5.86; N, 6.15%. Calcd for $C_{34}H_{28}N_2$: C, 87.89; H, 6.08; N, 6.03%. Attempts to improve the elemental analysis failed.

The following fractions eluted with benzene gave a semisolid, which was further purified by preparative plate chromatography (5 times, benzene as eluent). The fast-moving, second band gave the diaza 7-15-fulvadiene **10** (24 mg, 3.0%). Recrystallization from hexane afforded red cubes: Mp 130—131 °C; MS *m/z* 336 (M^+, 100%); mol wt 336.4; IR 2170 (–C≡C–), 1640 (C=N), and 975 cm^{-1} (trans C=C); UV: see Tables 1 and 2; ^1H NMR (270 MHz) $\tau=2.49$—2.59 (m, 1H, H^1), 2.74 (d, 16, 1H, $H^{A'}$), 2.86—2.91 (m, 1H, H^6), 2.95 (dd, 16, 11, 1H, H^B), 2.97 (dd, 15.5, 10, 1H, $H^{D'}$), 3.15 (d, 10, 1H, $H^{E'}$), 3.17—3.24 (m, 2H, H^3, H^4), 3.20 (d, 11, 1H, H^C), 3.50—3.71 (m, 2H, H^2, H^5), 3.55 (dd, 15.5, 5, 1H, $H^{C'}$), 3.64 (d, 16, 1H, H^A), 3.66 (dd, 16, 5, 1H, $H^{B'}$), 7.99 (s, 3H, CH_3), and 8.02 (s, 3H, CH_3); (CF_3COOD in $CDCl_3$, 200 MHz) $\tau=1.50$—1.67 (m, 1H, H^1), 1.76—2.39 (m, 8H, $H^{B'}$, $H^{C'}$, $H^{E'}$, H^2, H^3, H^4, H^5, H^6), 2.83 (d, 11, 1H, H^C), 3.06 (d, 16, 1H, H^A), 4.11 (dd, 16, 11, 1H, H^B), 4.31 (dd, 16, 11, 1H, $H^{D'}$), 6.06 (d, 16, 1H, $H^{A'}$), 7.47 (s, 3H, CH_3), and 7.54 (s, 3H, CH_3).

Found: C, 85.44; H, 6.07; N, 8.36%. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33%.

The Diaza 15-15-Fulvadiene 14 from Bisdehydro[15]annulenone. A soln of hydrazine dihydrochloride (93 mg, 0.86 mmol) in water (2 ml) was added in one portion to a soln of [15]annulenone[2b)] (413 mg, 1.76 mmol) in methanol (120 ml) and THF (60 ml). After stirring overnight at room temperature, the mixture was worked up as in the isolation of **9** and **12**. The residual dark red liquid, after solvent removal, was chromatographed on alumina (4.2×13 cm). The fractions eluted with hexane–benzene (1:4) gave a red solid, which was further purified by preparative plate chromatography (5 times, benzene–chloroform as eluent). The fast-moving, second red band gave the diaza 15-15-fulvadiene **14** (28 mg, 6.9%).

1-(2,4,6-Cycloheptatrienylidene)-2-(7,12-dimethyl-2,4,6,12,14,16-heptadecahexaene-8,10-diynylidene)hydrazine (11). A soln of hydrazine dihydrochloride (210 mg, 2.00 mmol) in water (2 ml) was added in one portion to a stirred soln of the ketone **6** (215 mg, 2.03 mmol) and bisdehydro[17]-annulenone[2b)] (496 mg, 1.91 mmol) in methanol (200 ml) and THF (80 ml) at room temperature and stirring was continued overnight at the same temperature. Then a further quantity of the ketone **6** (80 mg) in methanol (5 ml) was added and the mixture was stirred for further 8 h. The mixture was worked up as in the isolation of **9** and **12**. The residual red liquid, after solvent removal, was chromatographed on alumina (4.0×12.5 cm). The fractions eluted with benzene–chloroform (4:1—2:3) gave a brown solid, which was further purified by preparative plate chromatography (6 times, chloroform as eluent). The fast moving, second band gave the diaza 7-17-fulvadiene **11** (46 mg, 6.6%). Recrystallization from hexane–chloroform afforded purple needles: Mp 209 °C (decomp); MS *m/z* 362 (M^+, 100%); mol wt 362.4; IR 2190 (–C≡C–), 1620 (C=N), and 1000 cm^{-1} (trans C=C); UV: see Tables 1 and 2; ^1H NMR (200 MHz) $\tau=2.38$ (dd, 15, 11, 1H, H^B), 2.42 (dd, 16, 11, 1H, $H^{B'}$), 2.56 (dd, 16, 11, 2H, H^D, $H^{D'}$), 2.57—2.60 (m, 1H, H^1), 3.16—3.22 (m, 1H, H^6), 3.34—3.77 (m, 8H, H^C, $H^{C'}$, H^E, $H^{E'}$, H^2, H^3, H^4, H^5), 3.46 (d, 15, 1H, H^A), 3.76 (d, 16, 1H, $H^{A'}$), and 8.14 (s, 6H, CH_3); (CF_3COOD in $CDCl_3$, 200 MHz)

τ=1.25 (dd, 15.5, 10, 2H, H^{D}, $H^{D'}$), 1.44 (dd, 15.5, 11, 2H, H^{B}, $H^{B'}$), 1.69—1.75 (m, 1H, H^{1}), 2.04—2.20 (m, 3H, H^{3}, H^{4}, H^{6}), 2.32—2.42 (m, 2H, H^{2}, H^{5}), 3.63 (d, 10, 2H, H^{E}, $H^{E'}$), 3.87 (dd, 15.5, 11, 1H, H^{C} or $H^{C'}$), 3.93 (dd, 15.5, 10, 1H, H^{C} or $H^{C'}$), 3.98 (d, 15.5, 2H, H^{A}, $H^{A'}$), and 8.20 (s, 6H, CH_3).

Found: C, 85.88; H, 6.20; N, 8.04%. Calcd for $C_{26}H_{22}N_2$: C, 86.16; H, 6.12; N, 7.73%.

The Reaction of Bisdehydro[17]annulenone with Hydrazine Dihydrochloride. The reaction of the bisdehydro[17]-annulenone with hydrazine dihydrochloride was carried out under the exactly same conditions as those for the preparation of the diaza 13-13-fulvadiene **12**; however the diaza 17-17-fulvadiene was not obtained.

1,2-Bis(7,12-dimethyl-2,4,6,12,14,16,18-nonadecaheptaene-8,10-diynylidene)hydrazine (15). A soln of hydrazine dihydrochloride (225 mg, 2.14 mmol) in water (3 ml) was added in one portion to a stirred soln of the ketone **6** (230 mg, 2.17 mmol) and bisdehydro[19]annulenone[2b)] (606 mg, 2.11 mmol) in methanol (150 ml) and THF (80 ml), and stirring was continued for 7 h at the room temperature. Then a further quantity of the ketone **6** (50 mg) in methanol (5 ml) was added and the mixture was stirred for further 15 h. Then the mixture was worked up as in the isolation of **9** and **12**. The residual red liquid, after solvent removal, was chromatographed on alumina (4.0×12 cm). The fractions eluted with benzene–chloroform (9:1—3:7) gave a red solid, which was further purified by preparative plate chromatography (5 times, chloroform as eluent). The fast-moving, second band gave the diaza 19-19-fulvadiene **15** (16 mg, 1.4%). Recrystallization from hexane–benzene afforded purple microcrystals: Mp 146—147 °C (decomp); MS (field desorption method) m/z 568 (M^+); mol wt 568.7; IR 2175 (–C≡C–), 995, and 970 cm^{-1} (trans C=C); UV: see Tables 1 and 2; ^{1}H NMR (200 MHz) τ ca. 2.50—3.08 (m, 4H, olefinic H), 3.10—3.76 (m, 20H, olefinic H), 7.82 (s, 3H, CH_3), 7.90 (s, 3H, CH_3), 7.96 (s, 3H, CH_3), and 8.00 (s, 3H, CH_3). In this reaction the diaza 7-19-fulvadiene was not obtained.

1-(5,10-Dimethyl-2,4,10,12-tridecatetraene-6,8-diynylidene)-2-(5,10-dimethyl-2,4,10,12,14-pentadecapentaene-6,8-diynylidene)hydrazine (13). A soln of hydrazine dihydrochloride (220 mg, 2.10 mmol) in water (2 ml) was added in one portion to a stirred soln of bisdehydro[13]annulenone (421 mg, 2.02 mmol) and bisdehydro[15]annulenone (642 mg, 2.74 mmol) in methanol (160 ml) and THF (80 ml) at room temperature and the mixture was stirred for 6 h. After a further quantity of hydrazine dihydrochloride (100 mg) in water (2 ml) was added, stirring was continued for further 19 h at room temperature. Then the mixture was worked up as in the isolation of **9** and **12**. The residual dark red liquid, after solvent removal, was chromatographed on alumina (4.0× 12.5 cm). The early fractions eluted with hexane–benzene (2:3) gave the diaza 13-13-fulvadiene **12** (70 mg, 17%). The following fractions eluted with hexane–benzene (3:7) gave a red solid, which was further purified by preparative plate chromatography (6 times, benzene as eluent). The fast moving, second band gave the diaza 13-15-fulvadiene **13** (26 mg, 2.9%). Recrystallization from hexane–benzene afforded purple plates: Mp 160—161 °C (decomp); MS (field desorption method) m/z 439 (M^+); mol wt 438.5; IR 2160 (–C≡C–) and 980 cm^{-1} (trans C=C); UV: see Tables 1 and 2; ^{1}H NMR (200 MHz) τ=1.45—1.64 (m, 2H, $H^{B''}$, $H^{B'''}$), 2.72—3.51 (m, 10H, $H^{A'}$, $H^{A''}$, $H^{A'''}$, H^{B}, H^{C}, $H^{C'}$, $H^{C''}$, $H^{C'''}$, $H^{D'}$, $H^{E'}$), 3.61 (dd, 16.5, 7, 1H, $H^{B'}$), 3.83 (d, 16.5, 1H, H^{A}), 7.96 (s, 3H, CH_3), 7.99 (s, 3H, CH_3), 8.12 (s, 3H, CH_3), 8.17 (s, 3H, CH_3), and see Fig. 1; (CF_3COOD in $CDCl_3$, 200 MHz) τ=0.50 (dd, 15.5, 11, 1H, $H^{B''}$ or $H^{B'''}$), 0.70 (dd, 15.5, 11, 1H, $H^{B''}$ or $H^{B'''}$), 1.28 (dd, 15, 7, 1H, $H^{B'}$), 1.98—2.35 (m, 3H, H^{A}, H^{C}, $H^{E'}$), 2.44 (dd, 15.5, 7, 1H, $H^{C'}$), 3.11—3.81 (m, 7H, $H^{A'}$, $H^{A''}$, $H^{A'''}$, H^{B}, $H^{C''}$, $H^{C'''}$, $H^{D'}$), 7.42 (s, 3H, CH_3), 7.67 (s, 3H, CH_3), and 8.21 (s, 6H, CH_3).

Found: C, 87.36; H, 6.14; N, 6.65%. Calcd for $C_{32}H_{26}N_2$: C, 87.64; H, 5.98; N, 6.39%.

The later fractions eluted with hexane–benzene (1:4—1:9) gave the diaza 15-15-fulvadiene **14** (29 mg, 3.0%).

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