The Synthesis of Tetrakisdehydrotetraazaannulenes. Tetramethyl[36]-, -[48]annulene, and Their Benzoannelated Derivatives

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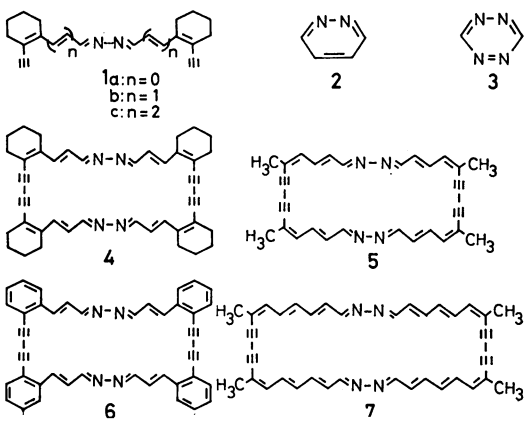
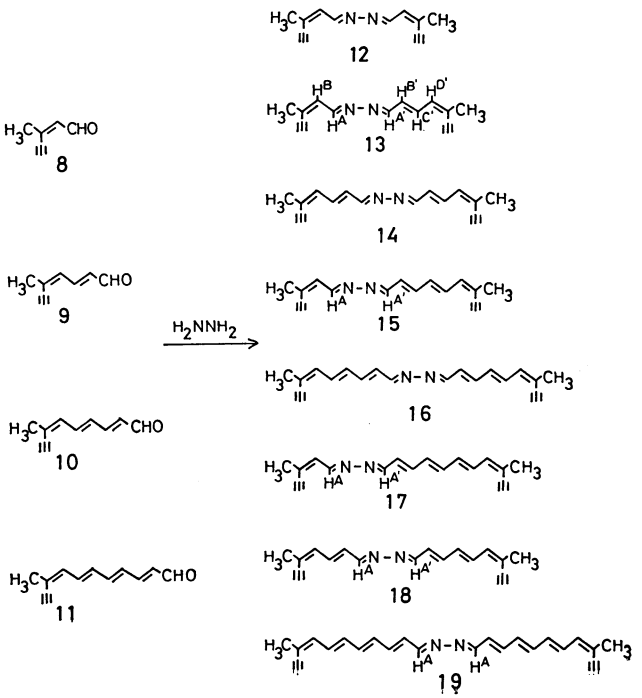
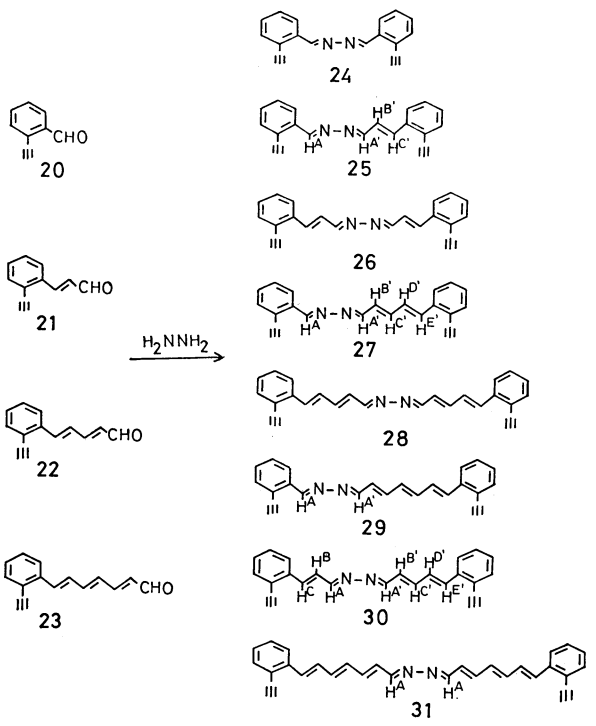
The conjugated mono-, di-, tri-, and tetraene, containing a terminal acetylene group were converted into a variety of symmetrical and unsymmetrical conjugated azines on treatment with aqueous hydrazine in ethanol. Oxidative couplings of these azines were attempted using anhydrous copper(II) acetate in pyridine and ether. Each of unsymmetrical azines, 3,16-dimethyl-8,9-diaza-3,5,7,9,11,13,15-octadecaheptaene-1,17-diyne and 1,10-bis(*o*-ethynylphenyl)-4,5-diaza-1,3,5,7,9-decapentaene, gave the corresponding two isomeric cyclic dimers: The former gave 7,12,25,30-tetramethyl-8,10,26,28-tetrakisdehydro-1,2,17,18-tetraaza[36]annulene and 7,12,25,30-tetramethyl-8,10,26,28-tetrakisdehydro-1,2,19,20-tetraaza[36]annulene, and the latter gave 6,7:12,13:24,25:30,31-tetrabenzo-8,10,26,28-tetrakisdehydro-1,2,17,18-tetraaza[36]annulene and 6,7:12,13:24,25:30,31-tetrabenzo-8,10,26,28-tetrakisdehydro-1,2,19,20-tetraaza[36]annulene, although only in poor yields. Coupling of symmetrical azines, 3,22-dimethyl-12,13-diaza-3,5,7,9,11,13,15,17,19,21-tetraeicosadecaene-1,23-diyne and 1,16-bis(*o*-ethynylphenyl)-8,9-diaza-1,3,5,7,9,11,13,15-hexadecaoctaene, furnished cyclic dimers, 11,16,35,40-tetramethyl-12,14,36,38-tetrakisdehydro-1,2,25,26-tetraaza[48]annulene and 10,11:16,17:34,35:40,41-tetrabenzo-12,14,36,38-tetrakisdehydro-1,2,25,26-tetraaza[48]annulene, respectively, in moderate yields. Examination of ^{1}H NMR spectra indicates that these tetraazaannulenes are atropic.

In 1974, Yamamoto and Sondheimer attempted oxidative couplings of conjugated azines **1a—c** using copper(II) acetate monohydrate in pyridine and ether under relatively dilute conditions in order to obtain the corresponding monomeric and/or dimeric cyclic compounds, which are macrocyclic analogs of pyridazine (**2**) and 1,2,4,5-tetrazine (**3**), respectively.[1] They obtained cyclic dimer **4**, a higher analog of **3**, only from azine **1b**. Subsequently, Darby *et al.* found that oxidative coupling of terminal diacetylenes to macrocyclic 1,3-diacetylenes usually proceeds in good yield when anhydrous copper(II) acetate instead of the monohydrate is employed.[2] We used advantageously the conditions for oxidative couplings of symmetrical conjugated, methylated azines **12**, **14**, **16** and their benzoannelated azines **24**, **26**, **28**. In practice, cyclic dimers **5** and **6** were obtained from azines **14** and **26**, respectively, as similarly as **4** formed from azine **1b**, and further we could also obtain cyclic dimer **7** from azine **16**.[3] However, we could not obtain monomeric cyclic compounds corresponding to higher analogs of pyridazine (**2**) from these azines even under the conditions reported by Darby *et al.*,[2] as well as under several different conditions. Thus, the failure of attempts to obtain monomeric compounds from these azines led us to consider the following.



Firstly, oxidative couplings should be attempted under high dilution conditions in order to obtain monomers from azines. Secondly, if symmetrical azines would be converted into the corresponding monomers, preparation of unsymmetrical azines available from aldehydes **8—11** and **20—23** is worthwhile, since we had it in mind that the unsymmetrical azines (**13**, **17**, **18**, **25**, **29**, **30**) make formally a potentially aromatic $(4n+2)\pi$-electron system on their intramolecular cyclization, in contrast that the symmetrical azines (**12**, **14**, **16**, **19**, **24**, **26**, **28**, **31**) do a nonaromatic $4n\pi$-system. This paper is concerned with synthesis and properties of title compounds together with attempts of oxidative couplings of symmetrical and unsymmetrical azines **12—19** and **24—31**, prepared from aldehydes **8—11** and **20—23**.





Results and Discussion

For preparation of azines **12**—**19**, a large amount of aldehydes **8**—**11** were required. Therefore, reported procedures[3,4] of preparation of aldehydes **9** and **10** were reexamined, since yields were variable (20—80% in different experiments on **8** and 15—55% in those on **9**). The starting material was (*Z*)-3-methyl-2-penten-4-ynal (**8**), which was prepared by acid treatment of 1-chloro-3-methyl-1-penten-4-yn-3-ol.[5] A homologation of **8** to (2*E*,4*Z*)-5-methyl-2,4-heptadien-6-ynal (**9**)[4] as well as a further homologation of **9** to (2*E*,4*E*,6*Z*)-7-methyl-2,4,6-nonatrien-8-ynal (**10**)[3] was modified, according to the procedure of that of (*Z*)-3-*t*-butyl-2-penten-4-ynal reported by Iyoda *et al.*[6] Isolation of diethyl acetal of **8**, condensation of the acetal with ethyl vinyl ether in the presence of boron trifluoride etherate, and then hydrolysis of the condensate with aqueous acetic acid containing sodium acetate gave the dienyne aldehyde **9** in 64% yield. The aldehyde **9** was then homologated to the trienyne aldehyde **10** in 70% yield in a similar manner to that of **8** to **9**, except without isolation of diethyl acetal of **9** (Experimental). Thus, modification of a reported procedure could be adapted to preparation of a large amount of aldehydes **9** and **10**.

For preparation of benzoannelated azines **24**—**31**, the starting material was *o*-ethynylbenzaldehyde (**20**), which was prepared as reported.[8] A homologation of **20** to **21**,[9] and subsequent homologations of **21**[10] to **22**[11] were carried out by Wittig condensation with [(1,3-dioxolan-2-yl)methyl]triphenylphosphonium bromide and lithium ethoxide, followed by hydrolysis, as reported previously.

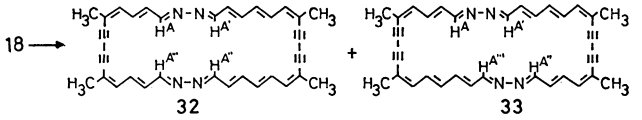
Treatment of aldehydes **8**—**11** and **20**—**23** in ethanol with aqueous hydrazine yielded the corresponding symmetrical azines **12**, **14**, **16**, **19**, **24**, **26**, **28**, **31**, respectively, as described previously.[3] Similarly, combination of two different aldehydes in each group of **8**—**11** and **20**—**23** in place of only one yielded a variety of unsymmetrical azines **13**, **15**, **17**, **18**, **25**, **27**, **29**, **30**. As expected in formation of unsymmetrical azines, the product was admixed with two different symmetrical azines: For formation of **13**, **12**, and **14** were also formed. Careful chromatography on alumina resulted in an almost complete separation of three azines. The yields and melting points of these unsymmetrical azines are summarized in Table 1, altogether with those of symmetrical azines **19** and **31**.

Table 1. Yields and melting points of azines

Compd	Yield %	Mp θ_m/°C
13	23	137—138 (decomp)
15	19	132—133 (decomp)
17	22	100—101 (decomp)
18	46	172—173 (decomp)
19	39	238—240 (decomp)
25	41	136—137
27	30	141—142
29	43	143—144
30	23	136—137
31	54	278—279 (decomp)

Oxidative couplings of these azines were attempted. At first, in order to obtain monomeric cyclic compounds from symmetrical azines **12**, **14**, **16**, an attempt was made under high dilution conditions. Thus, very slow addition of **12** was done to a stirred solution of anhydrous copper(II) acetate in a large volume of pyridine, ether, and methanol (*ca.* 2000 ml, 500 ml, 500 ml). After careful work up of the reaction mixture, the product was chromatographed on alumina. However, no monomeric and dimeric compounds were obtained. Oxidative couplings of azines **14** and **16** under high dilution conditions were carried out similarly to that of azine **12**. Neither azines **14** nor **16** gave monomers, but the respective dimers **5** and **7** in lower yields than in those under the conditions reported previously.[3]

These results led us to consider it impossible to obtain monomeric cyclic compounds from the other azines even if high dilution conditions would be used. Therefore, we turned out to investigate thereafter oxidation of azines, summarized in Table 1, using anhydrous copper(II) acetate in pyridine and ether at 50 °C under relatively dilute conditions as reported by Darby *et al.*[2]



Among the unsymmetrical methylated azines, none of **13**, **15**, and **17** gave monomeric and dimeric cyclic compounds in attempted oxidative couplings. On the other hand, an oxidative coupling of azine **18** resulted in a mixture of cyclic dimers in a yield of 3.5%, which,

upon chromatography on alumina, yielded a high melting isomer and a low melting isomer in a ratio of *ca.* 3:1. As the isomerism can reasonably be attributed to positional isomers due to two azine groups in tetrakisdehydro[36]annulene system, we tentatively assigned a high melting isomer to 7,12,25,30-tetramethyl-8,10,26,28-tetrakisdehydro-1,2,17,18-tetraaza-[36]annulene (**32**) and a low melting isomer to 7,12,25,30-tetramethyl-8,10,26,28-tetrakisdehydro-1,2,19,20-tetraaza[36]annulene (**33**). Both **32** and **33** were obtained as microcrystalline purple powders, and decomposed on exposure to diffused light and air within 1—2 d, and did at 144 °C and 112 °C, respectively, on attempted melting point determination. The gross structure of **32** and **33** was supported by mass spectra, which showed molecular ion peaks at *m/e* 520. The infrared spectra of **32** and **33** exhibited maxima at 2180 and 2190 (–C≡C–), 1615 and 1620 (C=N), respectively, and 995 cm^{-1} (*trans* C=C), but no maxima at −3300 cm^{-1} due to a terminal acetylene. The electronic spectra of both **32** and **33** in tetrahydrofuran, illustrated in Fig. 1, altogether with those of tetramethyl[32]- **5** and -[40]annulene **7**, showed main maxima at the same wavelength, 367 nm, which is middle

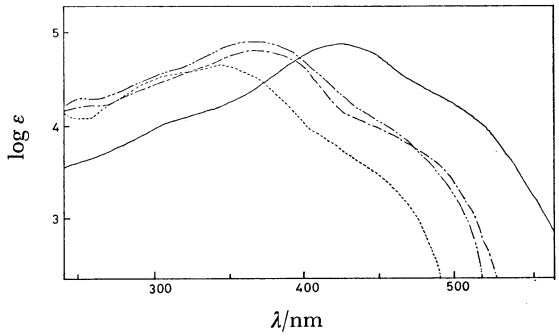


Fig. 1. Electronic spectra of tetraazatetrakisdehydroannulenes **5** (----), **32** (————), **33** (—————), and **7** (——) in THF.

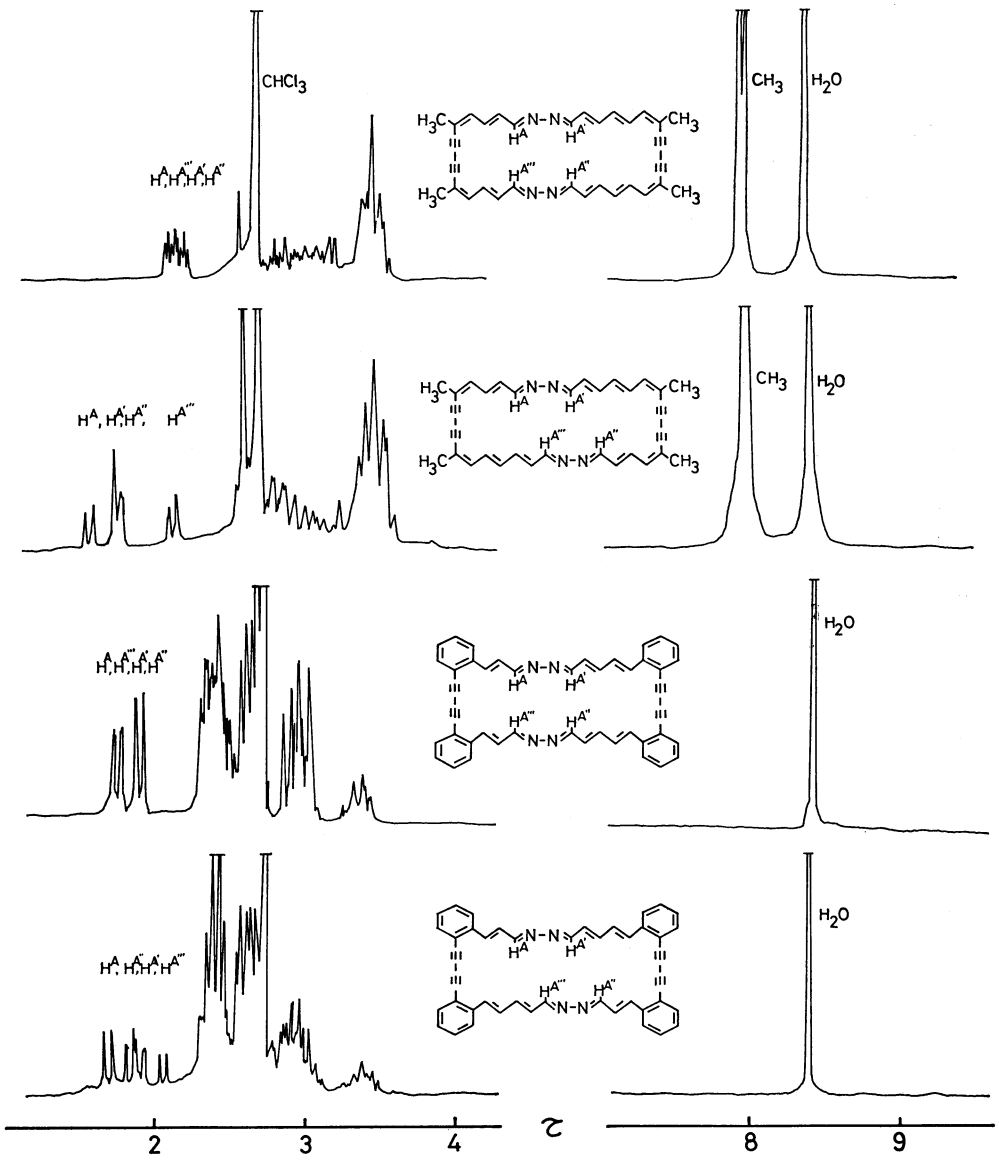
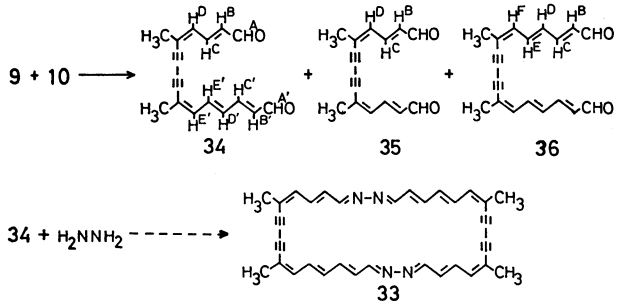


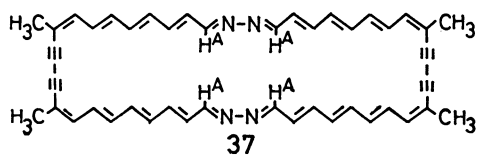
Fig. 2. The ^1H NMR FT spectra of **32**, **33**, **38**, and **39** in $CDCl_3$ at 200 MHz (internal standard, TMS).

one of the main maxima observed in **5** (339 nm) and **7** (381 nm), reflecting the number of double bonds in the cyclic conjugated system.

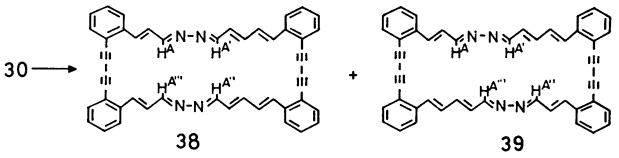
The ^{1}H NMR spectra were taken in $CDCl_3$ at 200 MHz, and are reproduced in Fig. 2. In these ^{1}H NMR spectra of cyclic tetraazaannulene system, it has been found that only protons adjacent to nitrogen atom resonate at relatively low field among olefinic protons. In annulenes **5** and **7** the protons (H^A) resonate at τ 2.30 and 2.03, respectively.[3] The spectrum of **32** consists of signals of τ 2.14 (1H, d, J=9 Hz, H^A), 2.16 (1H, d, J=9.5 Hz, $H^{A'''}$), 2.23 (1H, d, J=9.5 Hz, $H^{A'}$), 2.26 (1H, d, J=9 Hz, $H^{A''}$), *ca.* 2.6—3.6 (m, olefinic H), 7.98 (6H, s, Me), and 8.01 (6H, s, Me). On the other hand, the spectrum of **33** showed signals at τ 1.59 (1H, d, J=9.5 Hz, H^A), 1.77 (1H, d, J=9.5 Hz, $H^{A''}$), 1.78 (1H, d, J=10 Hz, $H^{A'}$), 2.14 (1H, d, J=10 Hz, $H^{A'''}$), *ca.* 2.6—3.6 (m, olefinic H), 8.00 (3H, s, Me), and 8.03 (3H, s, Me). Thus, the spectrum of **32** exhibits four doublets due to olefinic protons adjacent to nitrogen in narrow region and in high field as compared with those of the corresponding protons of **33**, although we have no explanation for these observations.



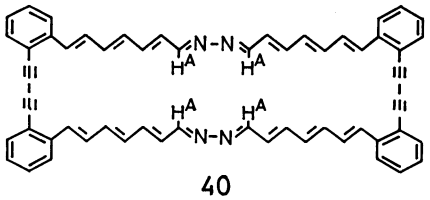
We attempted the following chemical means to determine which isomer should be assigned to the structure **33**. If the reaction similar to that of preparation of azines, between hydrazine and dialdehyde **34** would occur, an expected cyclic product have the structure **33** which is identical to that of one of the two isomers from azine **18**, eliminating the structure **32**. For this aim we prepared the pentaenediynedial **34**. The dialdehyde **34** was obtained in 25% yield from **9** and **10** by oxidative coupling, admixed with tetraenediynedial **35** and hexaenediynedial **36**. The dialdehyde **34** thus obtained was subjected to a reaction with aqueous hydrazine in ethanol. However, no evidence for the presence of the same product as that obtained from azine **18** was detected. Thus, although we could not elucidate the exact structual assignment between **32** and **33**, we believe that the isomer which shows four doublets at very narrow region (τ 2.14—2.26) in its ^{1}H NMR spectrum, has the structure of **32** as described above, from comparison with ^{1}H NMR spectra of annulenes **5** and **7**.



The azine **19** gave cyclic dimer, 11,16,35,40-tetramethyl-12,14,36,38-tetrakisdehydro-1,2,25,26-tetraaza-[40]annulene (**37**), on oxidation in 20% yield. The dimeric structure **37** was established by mass spectrum. The mass spectral measurement of **37** using direct inlet system was not satisfactory owing to decomposition during measurement. However, the spectrum by a field desorption technique was satisfactory one, revealing a molecular ion peak at *m/e* 676 (mol wt, 676). The electronic spectrum of **37** showed main maximum at 420 nm, exhibiting a bathochromic shift by 39 nm as compared with that of [40]annulene **7**. The ^{1}H NMR spectrum of **37** showed only one doublet at τ 1.98 due to olefinic protons (H^A) adjacent to nitrogen, revealing a symmetrical structure of **37**, a multiplet at τ 2.2—3.5 due to other olefinic protons, and a singlet at τ 8.04 due to methyl protons.



We carried out oxidative couplings of benzoannelated unsymmetrical azines **25**, **27**, **29**, **30** and symmetrical azine **31** under the same conditions as those for methylated azines. When these were done, we expected a stabilizing effect due to fused benzene rings on products of these reactions. However, we could not also obtain cyclic dimers from azines **25**, **27**, **29**, similarly to the cases of the corresponding methylated azines **13**, **15**, **17**. On the other hand, as in the case of the corresponding methylated azine **18**, azine **30** gave two cyclic dimers **38** and **39** in better yield (17%) than in that of **32** and **33** from azine **18**. The molecular weight of both **38** and **39** could not be determined by mass spectra owing to their low volatility. The structual assignment of **38** and **39** follows from examination of their IR, ^{1}H NMR, and electronic spectra, given in Experimental section. Both **38** and **39** showed main maxima at the same wavelength (355 nm) in tetrahydrofuran, as similarly to those observed in both **32** and **33**. The ^{1}H NMR spectra of **38** and **39**, illustrated in Fig. 2, resembled those of **32** and **33**, and the chemical shifts of H^A, $H^{A'}$, $H^{A''}$, $H^{A'''}$ protons are closer between **38** and **39** than between **32** and **33**.



Azine **31** afforded cyclic dimer **40**. The very low solubility and involatility of compound **40** prevented a complete characterization, but UV and ^{1}H NMR spectral data supported the structure **40**.

The chemical shifts of olefinic and methyl protons of the annulenes **32**, **33**, **37**, **38**, **39**, **40** indicates that these annulenes are atropic molecules.

In conclusion, oxidative couplings of conjugated azines **12**—**19** and **24**—**31** did not furnish cyclic monomers, but cyclic dimers in some cases. It was found that a possibility to obtain cyclic dimers is high from symmetrical azines than from unsymmetrical ones.

Experimental

All boiling and melting points are uncorrected. IR spectra were measured on Hitachi 260-50 spectrophotometer as KBr disk unless otherwise stated; only significant maxima are reported. Electronic spectra on Hitachi 124 or Hitachi 220 A spectrophotometer were recorded in nm, in tetrahydrofuran solution. The ε-values are given in parentheses, the shoulder being denoted by sh. Mass spectra were measured with JEOL JMS-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 EM-390 (90 MHz) or Varian XL-200 (200 MHz) spectrometer, and refer to solution in $CDCl_3$, in τ-values with TMS as an internal standard. The coupling constants (J) are given in Hz. The individual assignments are made on the basis of multiplicities and coupling constants. Alumina (II—III) was used for column chromatography. Progress of most reactions was followed by TLC using Merck precoated alumina. Preparative TLC was carried out on 20×20 cm alumina plates (Merck, 0.5 or 2 mm thick). Evaporation of solvents was performed at water aspirator pressure, and sodium sulfate was used as drying agent unless otherwise specified.

*Diethyl Acetal of (2Z)-3-Methyl-2-penten-4-ynal (**8**).* This compound was prepared by a slight modification of the reported procedure.[5b] A mixture of 3-methyl-2-penten-4-ynal (**8**)[5] (37.8 g, 0.40 mol), ammonium nitrate (3.0 g), and triethyl orthoformate (50.0 g, 0.38 mol) in abs ethanol (105 ml) was heated under reflux for 2 min. Then the mixture was poured onto dilute aq ammonia and extracted with benzene. The extracts were washed with dilute aq ammonia, and passed through Hyflo Super-Cel. The filtrate was concentrated to one-fourth its original volume and the concentrate was mixed with saturated aq sodium hydrogensulfite soln (440 ml). The mixture was stirred for 30 min at room temp. Then the mixture was passed through Hyflo Super-Cel and the precipitates formed were washed with benzene. The filtrate was washed with aq sodium chloride soln and dried over potassium carbonate. After removal of solvent, the residual dark red liquid was distilled, giving diethyl acetal of **8** (42.9 g, 69%) as a colorless liquid; bp 81 °C/19 mmHg** (lit,[5b] 59%, 77 °C/12 mmHg), MS *m/e* 168 (M^+, 37%) and 123 (100); mol wt 168.2; IR (neat) 3300 (-C≡CH), 2100 (-C≡C-), 1135, and 1060 cm^{-1} (C-O-C); ^{1}H NMR (90 MHz) τ=4.18 (d, 8, 1H, olefinic H), 4.70 (d, 8, 1H, $-C\underline{H}(OCH_2CH_3)_2$), *ca.* 6.2—6.5 (m, 4H, $-C\underline{H}_2CH_3$), 6.80 (-C≡CH), 8.07 (s, 3H, CH_3), and 8.78 (t, 7, 6H, $-CH_2C\underline{H}_3$).

*(2E,4Z)-5-Methyl-2,4-heptadien-6-ynal (**9**).* This compound was prepared with a modification of the previously described method.[4] To a soln of diethyl acetal of **8** (33.1 g, 0.20 mol) in dry benzene (244 ml) was added a soln of boron trifluoride etherate (243 mg) in dry benzene (12 ml) at 37 °C with stirring, and then a soln of ethyl vinyl ether (17.2 g, 0.24 mol) in dry benzene (63 ml) was added slowly dropwise during 1.5 h at 38—40 °C with stirring. After the mixture had been stirred at the same temp for 2 h, finely powdered potassium carbonate (22.5 g) was added. The inorganic material was removed by filtration and washed with ether. Then the filtrate was added to a mixture of sodium acetate trihydrate (104 g), water (66 ml), and acetic acid (1420 ml), and the soln was stirred under reflux for 3 h. After cooling, the reaction mixture was poured onto water and extracted with benzene. The combined extracts were washed with water, aq sodium hydrogencarbonate, and aq sodium chloride soln successively, and dried. After removal of solvent, the residual red liquid was chromatographed on alumina (200 g). The fractions eluted with hexane gave the aldehyde **9** (21.7 g, 92%, 64% based on **8**) as a red liquid. For spectral properties of **9**, see Ref. 4.

*(2E,4E,6Z)-7-Methyl-2,4,6-nonatrien-8-ynal (**10**).* This compound was prepared with a modification of the previously described method.[3] To a mixture of the dienyne aldehyde **9** (10.0 g, 83.2 mmol) and triethyl orthoformate (150 g, 0.91 mol) was added a soln of *p*-toluenesulfonic acid monohydrate (2.0 g) in abs ethanol (20 ml). After being stirred at room temp overnight, the reaction mixture was poured onto aq sodium hydrogencarbonate soln, and extracted with benzene. The extracts were washed with aq sodium hydrogencarbonate and sodium chloride soln, and dried over potassium carbonate. Evaporation of solvent yielded a crude diethyl acetal of **9** as a red liquid. The liquid was dissolved in dry benzene (100 ml) and warmed to 35 °C in a flask equipped with a dropping funnel, a condenser, and a magnetic stirrer. A soln of boron trifluoride etherate (238 mg) in dry benzene (7.5 ml) was added, and then a soln of ethyl vinyl ether (7.0 g, 97 mmol) in dry benzene (25 ml) was added during 3 h with stirring at 35—37 °C. After the mixture had been stirred for a further 1.5 h at the same temp, finely powdered potassium carbonate (22.0 g) was added. The inorganic material was removed by filtration and washed with ether. Then a mixture of the filtrate, sodium acetate trihydrate (33.0 g), acetic acid (493 ml), and water (23 ml) was heated under reflux with stirring at 79—80 °C for 3 h, and then allowed to cool to room temp. The mixture was poured onto aq sodium chloride soln and extracted with benzene. The extracts were washed successively with aq sodium hydrogencarbonate and aq sodium chloride soln, and dried. The residue obtained on evaporation of solvent was chromatographed on alumina (120 g). The fractions eluted with 10% ether in hexane yielded the trienyne aldehyde **10** (8.50 g, 70%, lit,[3] 50%) as an unstable red solid. For spectral and physical properties, see Ref. 3.

*(2E,4E,6E,8Z)-9-Methyl-2,4,6,8-undecatetraen-10-ynal (**11**).* This compound was prepared from **10** by Wittig condensation with [(1,3-dioxolan-2-yl)methyl]triphenylphosphonium bromide and lithium ethoxide, followed by hydrolysis with dilute hydrochloric acid, as reported previously.[7]

*3,12-Dimethyl-6,7-diaza-3,5,7,9,11-tetradecapentaene-1,13-diyne (**13**).* A soln of **8** (3.1 g, 33 mmol) and **9** (4.0 g, 33 mmol) in ethanol (98 ml) was added dropwise during 1.5 h to a stirred soln of hydrazine sulfate (5.0 g), sodium carbonate (6.1 g), and water (105 ml) at 12—19 °C. The mixture was stirred for a further 40 min at 17—18 °C. Then the mixture was poured onto aq sodium hydrogencarbonate soln and extracted with benzene. The extracts were washed with aq sodium hydrogencarbonate soln and dried over potassium carbonate. The residual dark red liquid, after solvent removal, was chromatographed on alumina (150 g). The early fractions eluted with hexane–ether (4:1—3:2) gave azine **12**[3] (1.58 g, 26%). The following fractions eluted with hexane–ether (2:3) gave azine **13** (1.59 g, 23%) as a solid. Recrystallization from hexane–benzene afforded yellow leaflets: mp 137—138 °C (decomp); MS *m/e* 210 (M^+, 80%) and 195 (100); mol wt 210.3; IR 3200 (-C≡CH),

**1 mm Hg≈133.322 Pa.

2150 (–C≡C–), 1615 (C=N), 1585 (C=C), 980, and 960 cm^{-1} (*trans* C=C); UV_{max} 273 (2860), 308 sh (9880), 326 sh (20000), 338 (23800), 353 (24800), and 370 nm (16200); ^1H NMR (90 MHz) τ=1.37 (d, 10, 1H, H^A), 1.73 (d, 10, 1H, $H^{A'}$), 2.78 (dd, 15, 11, 1H, $H^{C'}$), 3.37 (d, 11, 1H, H^B), 3.47 (d, 11, 1H, $H^{D'}$), 3.48 (dd, 15, 11, 1H, $H^{B'}$), 6.53 (s, 2H, –C≡CH), 7.88 (s, 3H, CH_3), and 7.95 (s, 3H, CH_3).

Found: C, 79.94; H, 6.70; N, 13.27%. Calcd for $C_{14}H_{14}N_2$: C, 79.96; H, 6.71; N, 13.32%.

The later fractions eluted with hexane–ether (1:1) gave azine **14**[3] (937 mg, 12%).

*3,14-Dimethyl-6,7-diaza-3,5,7,9,11,13-hexadecahexaene-1,15-diyne (**15**).* A soln of **8** (1.60 g, 17 mmol) and **10** (2.50 g, 17 mmol) in ethanol (50 ml) was added dropwise during 1.5 h to a stirred soln of hydrazine sulfate (2.6 g), sodium carbonate (3.1 g), and water (54 ml) at 17—21 °C. The mixture was stirred for a further 30 min at 20—21 °C. Then the mixture was worked up as in the preparation of **13**. The residual red liquid, after solvent removal, was chromatographed on alumina (200 g). The early fractions eluted with hexane–ether (2:3) gave azine **14** (887 mg, 29%). The following fractions eluted with hexane–ether (2:3—1:4) gave azine **15** (748 mg, 19%) as a solid. Recrystallization from chloroform–ethanol afforded orange needles: mp 132—133 °C (decomp); MS *m/e* 236 (M^+, 40%) and 39 (100); mol wt 236.3; IR 3200 (–C≡CH), 2100 (–C≡C–), 1620 (C=N), 1595 (C=C), and 990 cm^{-1} (*trans* C=C); UV_{max} 233 (13500), 277 (8410), 289 (8870), 342 sh (46100), 359 (64400), 377 (69400), and 395 nm (50300); ^1H NMR (90 MHz) τ=1.33 (d, 10, 1H, H^A), 1.75 (d, 10, 1H, $H^{A'}$), 2.88—3.70 (m, 6H, olefinic H), 6.52 (s, 1H, –C≡CH), 6.57 (s, 1H, –C≡CH), 7.87 (s, 3H, CH_3), and 7.97 (s, 3H, CH_3).

Found: C, 81.21; H, 6.87; N, 11.74%. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.83; N, 11.86%.

The later fractions eluted with ether gave azine **16**[3] (440 mg, 8.9%).

*3,16-Dimethyl-6,7-diaza-3,5,7,9,11,13,15-octadecaheptaene-1,17-diyne (**17**).* A soln of **8** (1.70 g, 18 mmol) and **11** (3.10 g, 18 mmol) in ethanol (53 ml) was added dropwise during 1 h to a stirred soln of hydrazine sulfate (2.70 g), sodium carbonate (3.30 g), and water (57 ml) at 23 °C. The mixture was stirred for a further 2 h at the same temp. After the mixture was worked up as in the preparation of **13**, the residual brown liquid was chromatographed on alumina (17×4 cm). The early fractions eluted with hexane–ether (3:7) gave azine **12**[3] (1.71 g, 52%). The following fractions eluted with hexane–ether (2:3) gave azine **17** (1.04 g, 22%) as a solid. Recrystallization from hexane–benzene afforded brown needles: mp 100—101 °C (decomp); MS *m/e* 262 (M^+, 35%) and 78 (100); mol wt 262.3; IR 3200 (–C≡CH), 2100 (–C≡C–), 1620 (C=N), 1570 (C=C), and 1000 cm^{-1} (*trans* C=C); UV_{max} 248 (11000), 293 (6940), 305 (7770), 359 sh (38300), 381 sh (58300), 397 (66400), and 417 nm sh (51500); ^1H NMR (90 MHz) τ=1.33 (d, 10, 1H, H^A), 1.75 (d, 10, 1H, $H^{A'}$), *ca.* 2.9—3.8 (m, 8H, olefinic H), 6.52 (s, 1H, –C≡CH), 6.58 (s, 1H, –C≡CH), 7.88 (s, 3H, CH_3), and 7.98 (s, 3H, CH_3).

Found: C, 82.04; H, 7.13; N, 10.98%. Calcd for $C_{18}H_{18}N_2$: C, 82.40; H, 6.92; N, 10.68%.

The later fractions eluted with benzene–chloroform gave azine **19** (405 mg, 6.6%). Azine **19** was also prepared from aldehyde **11** (*vide infra*).

*3,16-Dimethyl-8,9-diaza-3,5,7,9,11,13,15-octadecaheptaene-1,17-diyne (**18**).* A soln of **9** (2.00 g, 17 mmol) and **10** (2.40 g, 17 mmol) in ethanol (49 ml) was added dropwise during 1.5 h to a stirred soln of hydrazine sulfate (2.50 g), sodium carbonate (3.00 g), and water (32 ml) at 14—21 °C. The mixture was stirred for a further 30 min at 20 °C. After the mixture was worked up as in the preparation of **13**, the residual dark brown liquid was chromatographed on alumina (180 g). The early fractions eluted with hexane–ether (1:1) gave azine **14** (501 mg, 13%). The following fractions eluted with hexane–ether (3:7) gave azine **18** (1.99 g, 46%) as a solid. Recrystallization from chloroform–ethanol afforded yellow needles: mp 172—173 °C (decomp); MS *m/e* 262 (M^+, 33%) and 115 (100); mol wt 262.3; IR 3280 (–C≡CH), 2100 (–C≡C–), 1620 (C=N), 1575 (C=C), and 980 cm^{-1} (*trans* C=C); UV_{max} 246 (15000), 253 sh (14300), 262 sh (11900), 298 sh (13700), 310 sh (16000), 362 sh (62600), 377 (80500), 394 (85000), and 414 nm (59000); ^1H NMR (90 MHz) τ=1.72 (d, 10, 1H, H^A), 1.75 (d, 10, 1H, $H^{A'}$), *ca.* 2.6—3.7 (m, 8H, olefinic H), 6.54 (s, 1H, –C≡CH), 6.58 (s, 1H, –C≡CH), 7.95 (s, 3H, CH_3), and 7.97 (s, 3H, CH_3).

Found: C, 82.09; H, 7.01; N, 10.63%. Calcd for $C_{18}H_{18}N_2$: C, 82.40; H, 6.92; N, 10.68%.

The later fractions eluted with ether gave azine **16** (465 mg, 9.7%).

*3,22-Dimethyl-12,13-diaza-3,5,7,9,11,13,15,17,19,21-tetraeicosadecaene-1,23-diyne (**19**).* A soln of **11** (0.70 g, 4.1 mmol) in ethanol (39 ml) was added dropwise during 1.5 h to a stirred soln of hydrazine sulfate (2.8 g), sodium carbonate (3.8 g), and water (30 ml) at 27 °C. The mixture was stirred for a further 1 h at the same temp and worked up as in the preparation of **13**. The residual dark red liquid was chromatographed on alumina (4×12 cm). The fractions eluted with chloroform gave azine **19** (698 mg, 39%) as a partly crystallized liquid. Crystallization from a variety of solvents were unsuccessful in our hands owing to low solubility and instability of **19**. Repeated layer chromatography (0.5 mm thick) gave brown microcrystals: mp 238—240 °C (decomp); MS (field desorption method) *m/e* 340 (M^+); mol wt 340.4; IR 3300 (–C≡CH), 2090 (–C≡C–), 1620 (C=N), 1570 (C=C), and 1010 cm^{-1} (*trans* C=C); UV_{max} 293 (32200), 303 (31800), 402 sh (59900), 418 (73600), 437 (72500), and 468 nm sh (43500); ^1H NMR (200 MHz) τ=1.75 (d, 10, 2H, H^A), *ca.* 2.6—3.6 (m, 14H, olefinic H), 6.58 (s, 2H, –C≡CH), and 8.01 (s, 6H, CH_3).

*1,6-Bis(o-ethynylphenyl)-2,3-diaza-1,3,5-hexatriene (**25**).* A soln of **20** (3.0 g, 23 mmol) and **21** (3.6 g, 23 mmol) in ethanol (70 ml) was added dropwise during 1.5 h to a stirred soln of hydrazine sulfate (3.2 g), sodium carbonate (3.8 g), and water (32 ml) at 18 °C. The mixture was stirred for a further 2 h at the same temp. Then the mixture was worked up as in the preparation of **13**. The residual light yellow solid was chromatographed on alumina (250 g). The early fractions eluted with hexane–ether (17:3) gave azine **24**[3] (0.67 g, 10%). The following fractions eluted with hexane–ether (7:3) gave azine **25** (2.67 g, 41%) as a solid. Recrystallization from hexane–benzene afforded yellow needles: mp 136—137 °C; MS *m/e* 282 (M^+, 16%) and 139 (100); mol wt 282.3; IR 3280 (–C≡CH), 2105 (–C≡C–), 1630 (C=N), 1610 (C=C), 990, and 970 cm^{-1} (*trans* C=C); UV_{max} 236 (18700), 246 (16300), 253 sh (15700), 265 sh (10500), 322 sh (26700), 336 (30000), 348 sh (28400), and 360 nm sh (19000); ^1H NMR (90 MHz) τ=0.83 (s, 1H, H^A), 1.42 (d, 10, 1H, $H^{A'}$), 1.70—1.80 (m, 1H, benzenoid H), 2.19—2.93 (m, 9H, $H^{B'}$, $H^{C'}$, and benzenoid H), and 6.46 (s, 2H, –C≡CH).

Found: C, 85.25; H, 4.96; N, 9.94%. Calcd for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92%.

The later fractions eluted with hexane–ether (2:3) gave azine **26**[3] (1.68 g, 27%).

*1,8-Bis(o-ethynylphenyl)-2,3-diaza-1,3,5,7-octatetraene (**27**),*

A soln of **20** (4.3 g, 33 mmol) and **22** (6.0 g, 33 mmol) in ethanol (86 ml) was added dropwise during 2 h to a stirred soln of hydrazine sulfate (4.6 g), sodium carbonate (5.5 g), and water (46 ml) at 18 °C. The mixture was stirred for a further 2 h at the same temp, and worked up as in the preparation of **13**. The residual dark red solid was chromatographed on alumina (4×13 cm). The early fractions eluted with hexane–ether (9:1) gave azine **24** (3.0 g, 35%). The following fractions eluted with hexane–ether (4:1–3:2) gave azine **27** (3.0 g, 30%) as a solid. Recrystallization from hexane–benzene afforded yellow needles: mp 141—142 °C; MS *m/e* 308 (M^+, 100%); mol wt 308.3; IR 3325, 3290 (–C≡CH), 2110 (–C≡C–), 1610 (C=N), 1005, and 975 cm^{-1} (*trans* C=C); UV_{max} 235 (17200), 254 sh (14200), 288 (6340), 341 sh (33900), 357 (44200), 370 (44500), and 390 nm sh (28900); ^1H NMR (200 MHz) τ=0.88 (s, 1H, H^A), 1.59 (d, 10, 1H, $H^{A'}$), 1.76—1.83 (m, 1H, benzenoid H), 2.30—2.78 (m, 7H, benzenoid H), 2.94 (dd, 14, 11, 1H, $H^{C'}$), 2.96 (d, 16, 1H, $H^{E'}$), 2.97 (dd, 16, 11, 1H, $H^{D'}$), 3.30 (dd, 14, 11, 1H, $H^{B'}$), and 6.61 (s, 2H, –C≡CH).

Found: C, 85.90; H, 5.34; N, 9.02%. Calcd for $C_{22}H_{16}N_2$: C, 85.69; H, 5.23; N, 9.09%.

The later fractions eluted with ether gave azine **28**[3] (3.8 g, 32%).

*1,10-Bis(o-ethynylphenyl)-2,3-diaza-1,3,5,7,9-decapentaene (**29**).* A soln of **20** (3.4 g, 26 mmol) and **23** (5.4 g, 26 mmol) in ethanol (68 ml) was added dropwise during 1.5 h to a stirred soln of hydrazine sulfate (3.6 g), sodium carbonate (4.3 g), and water (36 ml) at 19 °C. The mixture was stirred for a further 3 h at the same temp. Then the mixture was poured onto aq sodium hydrogencarbonate soln and extracted with chloroform. The extracts were washed with aq sodium hydrogencarbonate soln and dried. The residual dark red liquid obtained after solvent removal was chromatographed on alumina (4×15 cm). The early fractions eluted with hexane–ether (9:1) gave azine **24**[3] (2.2 g, 32%). The following fractions eluted with hexane–ether (4:1–1:1) gave azine **29** (3.7 g, 43%) as a solid. Recrystallization from hexane–benzene afforded yellow needles: mp 143—144 °C; MS *m/e* 334 (M^+, 25%) and 129 (100); mol wt 334.4; IR 3280 (–C≡CH), 2100 (–C≡C–), 1620 (C=N), 1600, 1590 (C=C), and 1005 cm^{-1} (*trans* C=C); UV_{max} 227 (27900), 260 sh (14800), 267 sh (13400), 277 sh (10400), 292 (8130), 307 sh (9180), 380 sh (56300), 392 (59100), and 410 nm sh (46000); ^1H NMR (200 MHz) τ=0.89 (s, 1H, H^A), 1.60 (d, 10, 1H, $H^{A'}$), 1.78—1.84 (m, 1H, benzenoid H), 2.33—2.80 (m, 7H, benzenoid H), 2.94—3.46 (m, 6H, olefinic H), and 6.61 (s, 2H, –C≡CH).

Found: C, 86.32; H, 5.33; N, 8.35%. Calcd for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; N, 8.38%.

The later fractions eluted with chloroform gave azine **31** (2.8 g, 26%). Azine **31** was also prepared from aldehyde **23** (*vide infra*).

*1,10-Bis(o-ethynylphenyl)-4,5-diaza-1,3,5,7,9-decapentaene (**30**).* A soln of **21** (5.2 g, 33 mmol) and **22** (6.0 g, 33 mmol) in ethanol (86 ml) was added dropwise during 2.5 h to a stirred soln of hydrazine sulfate (4.6 g), sodium carbonate (5.5 g), and water (46 ml) at 15 °C. The mixture was stirred for a further 3 h at the same temp. Then the mixture was worked up as in the preparation of **13**, the residual brown liquid was chromatographed on alumina (4×13 cm). The early fractions eluted with hexane–ether (4:1) gave azine **26**[3] (2.9 g, 29%). The following fractions eluted with hexane–ether (3:2) gave azine **30** (2.6 g, 23%) as a solid. Recrystallization from hexane–benzene afforded yellow needles: mp 136—137 °C; MS *m/e* 334 (M^+, 30%) and 180 (100); mol wt 334.4; IR 3310, 3280 (–C≡CH), 2110 (–C≡C–), 1630 (C=N), 1610, 1600 (C=C), 1010, and 990 cm^{-1} (*trans* C=C); UV_{max} 227 (27900), 257 (17500), 296 sh (8100), 360 sh (51400), 372 (57100), 387 (54500), and 410 nm sh (52000); ^1H NMR (200 MHz) τ=1.57 (d, 10, 1H, H^A), 1.67 (d, 10, 1H, $H^{A'}$), 2.26—3.06 (m, 13H, H^B, H^C, $H^{C'}$, $H^{D'}$, $H^{E'}$, and benzenoid H), 3.52 (dd, 14, 11, 1H, $H^{B'}$), 6.58 (s, 1H, –C≡CH), and 6.60 (s, 1H, –C≡CH).

Found: C, 86.10; H, 5.15; N, 8.60%. Calcd for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; N, 8.38%.

The later fractions eluted with ether gave azine **28** (4.2 g, 35%).

*1,16-Bis(o-ethynylphenyl)-8,9-diaza-1,3,5,7,9,11,13,15-hexadecaoctaene (**31**).* A soln of **23** (0.50 g, 2.4 mmol) in ethanol (5.7 ml) was added dropwise during 30 min to a stirred soln of hydrazine sulfate (0.31 g), sodium carbonate (0.37 g), and water (3.1 ml) at 15 °C. The mixture was stirred for a further 2 h at the same temp. Then the mixture was worked up as in the preparation of **29**, the residual red solid was chromatographed on alumina (3×10 cm). The fractions eluted with chloroform gave azine **31** (268 mg, 54%) as a solid. Recrystallization from chloroform–ethanol afforded red needles: mp 278—279 °C (decomp); MS *m/e* 412 (M^+, 25%) and 178 (100); mol wt 412.5; IR 3280 (–C≡CH), 2100 (–C≡C–), 1620 (C=N), 1600, 1580 (C=C), and 1005 cm^{-1} (*trans* C=C); UV_{max} 230 (16700), 268 (11700), 295 sh (9110), 357 sh (17700), 418 (62600), 437 (62300), and 459 nm sh (41700); ^1H NMR (200 MHz) τ=1.73 (d, 10, 2H, H^A), 2.34—2.80 (m, 8H, benzenoid H), 2.95—3.49 (m, 12H, olefinic H), and 6.62 (s, 2H, –C≡CH).

Found: C, 87.34; H, 5.79; N, 6.85%. Calcd for $C_{30}H_{24}N_2$: C, 87.34; H, 5.87; N, 6.79%.

*Oxidative Coupling of **18** to Two Isomeric Tetramethyl[36]annulenes **32** and **33**.* A soln of azine **18** (2.68 g, 10.2 mmol) in pyridine (160 ml) and dry ether (53 ml) was added dropwise during 4 h to a stirred soln of anhyd copper(II) acetate (13.0 g) in pyridine (355 ml) and dry ether (120 ml) kept at 50 °C; the mixture was stirred for a further 1 h at the same temp. Then the mixture was chilled and filtered through Hyflo Super-Cel. After the precipitates formed were washed with benzene, the filtrate was poured onto water. The organic layer combined with the benzene extracts from aq layer was washed with water fifteen times to remove pyridine, and dried over potassium carbonate. The residual dark red liquid, after solvent removal, was passed through a short column of alumina. The red liquid thus obtained was chromatographed on alumina (4×10 cm). The fractions eluted with hexane–ether (3:7–2:3) gave a slightly crude **32** (132 mg, 2.5%) as a crystalline liquid. Repeated thin layer chromatography gave a solid. Recrystallization from chloroform–ethanol afforded purple microcrystals: mp 144 °C (decomp); MS *m/e* 520 (M^+, 25%) and 115 (100); mol wt 520.6; IR 2190 (–C≡C–), 1620 (C=N), and 1000 cm^{-1} (*trans* C=C); UV_{max} 252 (17200) and 367 nm (62800), and see Fig. 1; ^1H NMR (200 MHz) τ=2.14 (d, 9, 1H, H^A), 2.16 (d, 9.5, 1H, $H^{A'''}$), 2.23 (d, 9.5, 1H, $H^{A'}$), 2.26 (d, 9, 1H, $H^{A''}$), *ca.* 2.6—3.6 (m, 16H, olefinic H), 7.98 (s, 6H, CH_3), and 8.01 (s, 6H, CH_3), and see Fig. 2. Compound **32** formed crystals containing 1 mol of chloroform.

Found: C, 69.59; H, 5.39; N, 8.89%. Calcd for $C_{36}H_{32}N_2 \cdot CHCl_3$: C, 69.43; H, 5.21; N, 8.76%.

The following fractions eluted with hexane–ether (2:3) gave a slightly crude **33** (50 mg, 0.90%) as a partly crystallized liquid. Thin layer chromatography gave a solid. Recrystallization from chloroform–ethanol afforded purple microcrystals: mp 112 °C (decomp); MS *m/e* 520 (M^+, 7%) and 18 (100); mol wt 520.6; IR 2180 (–C≡C–), 1615 (C=N),

and 1000 cm^{-1} (*trans* C=C); UV_{max} 251 (16000) and 367 nm (58400), and see Fig. 1; ^1H NMR (200 MHz) τ=1.59 (d, 9.5 1H, H^A), 1.77 (d, 9, 1H, $H^{A''}$), 1.78 (d, 10, 1H, $H^{A'}$), 2.14 (d, 10, 1H, $H^{A''}$), *ca.* 2.6—3.6 (m, 16H, olefinic H), 8.00 (s, 6H, CH_3), and 8.03 (s, 6H, CH_3), and see Fig. 2.

*5,10-Dimethyl-2,4,10,12,14-hexadecapentaene-6,8-diynedial (**34**).* A soln of **9** (3.30 g, 27.5 mmol) and **10** (4.00 g, 27.4 mmol) in pyridine (74 ml) and methanol (74 ml) was added dropwise during 1 h to a stirred soln of copper(II) acetate monohydrate (37.0 g) in pyridine (298 ml) and methanol (298 ml) at 20 °C. After being stirred at room temp overnight, the reaction mixture was poured onto aq sodium chloride soln and extracted with benzene. The extracts were washed with 3 M† hydrochloric acid until it turned acidic, and then with aq sodium hydrogencarbonate soln, and dried. The residual red liquid, after solvent removal, was chromatographed on alumina (4×10 cm). The early fractions eluted with hexane–ether (3:2) gave the tetraenediynedial **35** (840 mg, 13%) (*vide infra*). The following fractions eluted with hexane–ether (1:1) gave the desired pentaenediynedial **34** (1.79 g, 25%) as a solid. Recrystallization from benzene afforded orange needles: mp 48—49 °C; MS *m/e* 264 (M^+, 10%) and 78 (100); mol wt 264.3; IR 2190 (–C≡C–), 1670 (CHO), 1610 (C=C), 1010, 990, and 980 cm^{-1} (*trans* C=C); UV_{max} 257 sh (10100), 268 (10800), 318 (23800), 340 sh (23800), 375 (27400), and 405 nm sh (19800); ^1H NMR (90 MHz) τ=0.27 (d, 8, 1H, CH^AO), 0.33 (d, 8, 1H, $CH^{A'}O$), 2.42 (dd, 16, 11, 1H, H^C), 2.60 (s, 6H, benzene), 2.74 (dd, 16, 12, 1H, $H^{E'}$), 2.83 (dd, 16, 11, 1H, $H^{C'}$), 3.33 (d, 12, 1H, H^D), 3.43 (d, 12, 1H, $H^{F'}$), 3.45 (dd, 16, 12, $H^{D'}$), 3.78 (dd, 16, 8, 2H, H^B and $H^{B'}$), 7.90 (s, 3H, CH_3), and 7.95 (s, 3H, CH_3).

Found: C, 83.92; H, 6.39%. Calcd for $C_{18}H_{16}O_2 \cdot C_6H_6$: C, 84.17; H, 6.47%.

Compound **34** formed crystals containing 1 mol of benzene.

The later fractions eluted with hexane–ether (3:2) gave the hexaenediynedial **36** (607 mg, 7.6%) (*vide infra*).

The teraenediynedial **35** and the hexaenediynedial **36** were also prepared from **9** and **10**, respectively, in higher yields than in those described above.

*5,10-Dimethyl-2,4,10,12-tetradecatetraene-6,8-diynedial (**35**).* A soln of **9** (3.00 g, 25 mmol) in pyridine (35 ml) and methanol (35 ml) was added dropwise during 30 min to a stirred soln of copper(II) acetate monohydrate (18.0 g) in pyridine (138 ml) and methanol (138 ml) at 20 °C. After being stirred at room temp overnight, the reaction mixture was worked up as in the preparation of **34**. The residual red liquid obtained after solvent removal was chromatographed on alumina (4×10 cm). The fraction eluted with hexane–ether (3:2) gave the teraenediynedial **35** (1.65 g, 54%) as a crystalline liquid. Crystallization from hexane–benzene afforded yellow needles: mp 160—161 °C; MS *m/e* 238 (M^+, 4%) and 165 (100); mol wt 238.2; IR 2200 (–C≡C–), 1675 (CHO), 1610 (C=C), 1000, and 980 cm^{-1} (*trans* C=C); UV_{max} 245 sh (13200), 254 (17200), 293 (23900), 339 (25700), 62 (25200), and 387 nm (20600); ^1H NMR (90 MHz) τ=0.25 (d, 8, 2H, CHO), 2.43 (dd, 15, 12, 2H, H^C), 3.31 d, 12, 2H, H^D), 3.78 (dd, 15, 11, 2H, H^B), and 7.87 (s, H, CH_3).

Found: C, 80.94; H, 5.99%. Calcd for $C_{16}H_{14}O_2$: C, 0.64; H, 5.92%.

*7,12-Dimethyl-2,4,6,12,14,16-octadecahexaene-8,10-diynedial (**36**).* A soln of the aldehyde **10** (6.00 g, 43 mmol) in pyridine (59 ml) and methanol (59 ml) was added dropwise during 1 h to a stirred soln of copper(II) acetate monohydrate (30.0 g) in pyridine (235 ml) and methanol (235 ml) at 19 °C. After being stirred at room temp overnight, the reaction mixture was worked up as in the preparation of **34**. The residual red liquid obtained after solvent removal was chromatographed on alumina (4×15 cm). The hexaenediynedial **36** (2.50 g, 40%) was obtained from the fractions eluted with hexane–ether (2:3). Recrystallization from hexane–benzene afforded orange needles: mp 130—131 °C; MS *m/e* 290 (M^+, 18%) and 203 (100); mol wt 290.3; IR 2200 (–C≡C–), 1680 (CHO), 1610, 1590 (C=C), 1010, and 985 cm^{-1} (*trans* C=C); UV_{max} 239 (18300), 283 (17600), 321 sh (31600), 334 (35400), 377 (32500), 391 sh (31300), and 423 nm (21900); ^1H NMR (90 MHz) τ=0.32 (d, 8, 2H, CHO), 2.72 (dd, 15, 12, 2H, H^E), 2.85 (dd, 15, 12, 2H, H^C), 3.43 (dd, 16, 12, 2H, H^D), 3.45 (d, 12, 2H, H^F), 3.76 (dd, 15, 8, 2H, H^B), and 7.93 (s, 6H, CH_3).

Found: C, 82.70; H, 6.32%. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25%.

*The Reaction of **34** with Hydrazine Sulfate.* A soln of pentaenediynedial **34** (1.15 g, 4.36 mmol) in ethanol (26 ml) was added dropwise during 1.5 h to a stirred soln of hydrazine sulfate (0.66 g) and sodium carbonate (0.80 g) in water (19 ml) at room temp. The mixture was stirred for a further 1 h at the same temp. Then the mixture was worked up as in the preparation of **13**. The residual red liquid obtained after solvent removal was chromatographed on alumina. However, we could not detect the fractions containing cyclic products corresponding to **33**.

*Oxidative Coupling of **19** to Tetramethyl[48]annulene **37**.* A soln of **19** (3.30 g, 9.69 mmol) in pyridine (152 ml) and dry ether (51 ml) was added dropwise during 1 h to a stirred soln of anhyd copper(II) acetate (12.0 g) in pyridine (337 ml) and dry ether (113 ml) kept at 45 °C; the mixture was stirred for a further 30 min at the same temp. Then the mixture was chilled and filtered through Hyflo Super-Cel. The precipitates formed were washed with chloroform, and the filtrate was poured onto water. The organic layer combined with the chloroform extracts from aq layer was washed with water ten times to remove pyridine and dried. The residual brown liquid obtained after solvent removal was chromatographed on alumina (4×12 cm). The early fractions contained pyridine. The following fractions eluted with chloroform contained the desired **37**. The dark red liquid obtained was again chromatographed on alumina (4×9 cm). The fractions eluted with benzene–chloroform (1:1) gave **37** (618 mg, 19%) as a crystalline liquid. Although crystallization was unsuccessful in our hands due to low solubility of **37**, thin layer chromatography (0.5 mm thick) afforded purple microcrystals: mp 175—176 °C (decomp); MS (field desorption method) *m/e* 676 (M^+); mol wt 676.8; IR 2180 (–C≡C–), 1620 (C=N), 1595 (C=C), and 1000 cm^{-1} (*trans* C=C); UV_{max} 300 sh (10300) and 420 nm (73200); ^1H NMR (200 MHz) τ=1.98 (d, 10, 1H, H^A), *ca.* 2.4—3.5 (m, 20H, olefinic H), and 8.04 (s, 12H, CH_3).

*Oxidative Coupling of **30** to Two Isomeric Tetrabenzo[36]annulenes **38** and **39**.* A soln of azine **30** (1.2 g, 36 mmol) in pyridine (66 ml) and dry ether (22 ml) was added dropwise during 2.5 h to a stirred soln of anhyd copper(II) acetate (4.5 g) in pyridine (125 ml) and dry ether (42 ml) kept at 50 °C; the mixture was stirred for a further 2 h at the same temp and chilled. After work up as in the preparation of **37**, the residual red liquid obtained by solvent removal was chromatographed on alumina (3×8 cm). The fractions eluted with ether–benzene (1:4) gave a mixture of **38** and **39** as a brown liquid. The liquid was again chromatographed on alumina (4×15 cm). The early fractions eluted

† 1 M = 1 mol dm^{-3}.

with benzene–chloroform gave **38** (118 mg, 9.8%) as a solid. Recrystallization from chloroform–ethanol afforded yellow microcrystals: mp 182 °C (decomp); IR 2200, 2150 (–C≡C–), 1620 (C=N), 1605, 1600 (C=C), 1000, and 980 cm^{-1} (*trans* C=C); UV_{max} 238 (68100), 263 (52200), 307 sh (59000), and 355 nm (95100); ^1H NMR (200 MHz) τ= 1.76 (d, 9.5, 1H, H^A), 1.77 (d, 9.5, 1H, $H^{A'''}$), 1.90 (d, 10, 1H, $H^{A'}$), 1.91 (d, 10, 1H, $H^{A''}$), and *ca.* 2.3—3.8 (m, 28H, olefinic and benzenoid H), and see Fig. 2. The following fractions eluted with benzene–chloroform gave **39** (86 mg, 7.0%) as a solid. Recrystallization from chloroform–ethanol afforded yellow microcrystals: mp 234 °C (decomp); IR 2220, 2150 (–C≡C–), 1630 (C=N), 1610, 1600 (C=C), 1000, and 980 cm^{-1} (*trans* C=C); UV_{max} 267 sh (39200), 282 (50400), 355 (90700), 410 sh (31100), and 435 nm sh (17100); ^1H NMR (200 MHz) τ=1.70 (d, 9.5, 1H, H^A), 1.85 (d, 9.5, 1H, $H^{A''}$), 1.89 (d, 9.5, 1H, $H^{A'}$), 2.06 (d, 9.5, 1H, $H^{A'''}$), and *ca.* 2.3—3.7 (m, 37H, olefinic and benzenoid H), and see Fig. 2.

*Oxidative Coupling of **31** to Tetrabenzo*[48]*annulene **40**.* A soln of azine **31** (2.80 g, 6.79 mmol) in pyridine (124 ml) and dry ether (41 ml) was added dropwise during 1 h to a stirred soln of anhyd copper(II) acetate (8.50 g) in pyridine (236 ml) and dry ether (79 ml) kept at 50 °C; the mixture was stirred for a further 30 min at the same temp. After work up as in the preparation of **37**, the residual dark red liquid obtained by solvent removal was chromatographed on alumina (4×10 cm). The early fractions contained pyridine. The later fractions eluted with chloroform gave **40** (414 mg, 15%) as a dark red gum, which resisted attempted crystallization and did not run from the base line on preparative layer chromatography. Precipitates formed from chloroform solution afforded purple powders: mp 235—240 °C (decomp); IR 2200, 2140 (–C≡C–), 1620 (C=N), 1590, 1580 (C=C), and 1000 cm^{-1} (*trans* C=C); UV_{max} 290 (27300), 416 (92200), and 470 nm sh (44700); ^1H NMR τ=1.99 (d, 9, 4H, H^A), and *ca.* 2.3—3.6 (m, 40H, olefinic and benzenoid H).

*Oxidative Couplings of Azines **13**, **15**, **17**, **25**, **27**, **29**.* These oxidative couplings were carried out under almost the same conditions as those described for azines **18** and **30**. However, in attempted runs, no monomeric and dimeric cyclic compounds were obtained.

*Oxidative Coupling of **14** to Tetramethyl*[32]*annulene **5**[3] under High Dilution Conditions.* A soln of azine **14** (2.1 g, 8.9 mmol) in ether (77 ml), methanol (77 ml), and pyridine (309 ml) was added dropwise during 8 h to a stirred soln of anhyd copper(II) acetate (16.2 g) in pyridine (2100 ml), ether (525 ml), and methanol (525 ml) kept at 68—70 °C. After being refluxed for a further 2 h at the same temp, the mixture was allowed to stand overnight at room temp. Then the mixture was concentrated to 150 ml *in vacuo* on a water bath kept below 45 °C. The concentrate was chilled, diluted with benzene (200 ml), and filtered through Hyflo Super-Cel. The precipitates formed were washed with benzene, and the filtrate was poured onto water. The organic layer combined with benzene extracts from aq layer was washed with water ten times to remove pyridine and dried over potassium carbonate. After removal of solvent, the residual red liquid was chromatographed on alumina (150 g). The fractions eluted with ether–benzene (7:3) gave the corresponding cyclic dimer **5** (116 mg, 2.8%). No monomeric product could be obtained.

*Oxidative Coupling of **16** to Tetramethyl*[40]*annulene **7**[3] under High Dilution Conditions.* A soln of azine **16** (3.40 g, 11.8 mmol) in ether (102 ml), methanol (102 ml), and pyridine (410 ml) was added dropwise during 7 h to a stirred and refluxing soln of anhyd copper(II) acetate (18.0 g) in pyridine (2141 ml), ether (410 ml), and methanol (410 ml) kept at 72—74 °C. After being stirred for a further 1.5 h, the mixture was worked up as in the isolation of **5**, as described above. The residual red liquid obtained after solvent removal was chromatographed on alumina (180 g). The fractions eluted with benzene–chloroform gave the corresponding cyclic dimer **7** (330 mg, 9.8%).

*Oxidative Coupling of Azine **12**.* This was carried out in almost the same scale as that for azine **14** described above. However, no desired cyclic products could be obtained.

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