Synthesis and Properties of Methano-bridged Tetradehydro-[26]-, -[28]-, -[30]-, -[32]-, -[34]-, and -[38]-annulene

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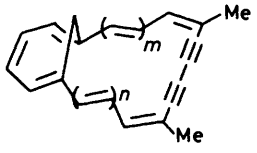
Title annulenes (**21**)—(**28**) have been synthesized by a Wittig reaction of 1,6-bis-(4-formylbuta-1,3-dienyl)cyclohepta-1,3,5-triene (**5**) and the vinylogous dicarbaldehydes (**6**)—(**10**) with 3-methylpent-2-en-4-ynyl(triphenyl)phosphonium bromide (**11**) or triphenyl-(3-t-butylpent-2-en-4-ynyl)phosphonium bromide (**12**), followed by intramolecular oxidative coupling of the resulting acyclic diacetylenes, and their properties are discussed on the basis of ^{1}H n.m.r. and electronic spectra.

In 1965, Dewar and Gleicher predicted from calculation that the limiting ring size of Hückel's prediction on aromaticity [1] should occur at a 22-membered ring.[2] However, a tetradehydro[30]-annulene [3] and didehydro[26]annulene [4] have been shown to be diatropic. Thus, although theory predicts that the ring size should be below a certain limit, the exact value of this limit is still uncertain.

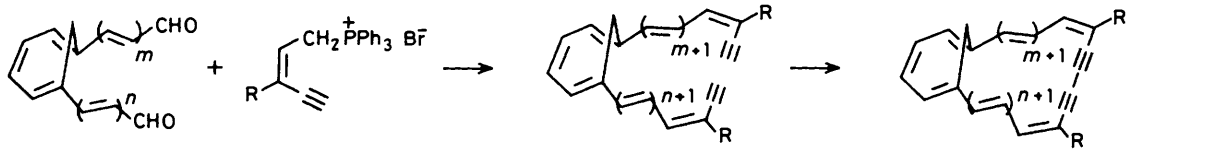
In our previous paper, we reported that the tetradehydromethano-[18]- (**1**), -[20]- (**2**), -[22]- (**3**), and -[24]-annulene (**4**) show diatropism and paratropism, and high thermal and conformational stability, which is reasonably ascribed to a fair amount of rigidity of the molecular skeleton imposed by the presence of the bridging methylene group and a 1,3-diacetylenic linkage.[5] It seemed to us that the tetradehydromethanoannulene system such as that in (**1**)—(**4**), which is expected to have a rather rigid perimeter and a slight perturbation with respect to π-electron conjugation, is a desirable model for a study to elucidate the upper limit of the ring size showing the ring-current effect. While keeping possible changes in stereochemistry to a minimum, we have now extended our work to the synthesis of the tetradehydromethano[38]annulene (**28**) as well as its lower homologues (**21**)—(**27**).[6] The alkylated compounds (**21**)—(**28**) are members of a series of tetradehydromethanoannulenes in which the number of double bonds is increased systematically, and hence a study of their spectral properties is particularly informative. It should be pointed out that the tetradehydro-1,6-methano-[28]-(**22**) and -[34]-annulene (**27**) are the first examples of paratropic 28π- and diatropic 34π-electron neutral annulenes, respectively.[7]

Results and Discussion

Synthesis.—The efficient synthesis of the annulenes (**21**)—(**28**) was the same as that for the preparation of fewer-membered annulenes (**1**)—(**4**),[5] as illustrated in Scheme 1. It begins with



[18]- (**1**) $m = n = 1$
[20]- (**2**) $m = 2, n = 1$
[22]- (**3**) $m = n = 2$
[24]- (**4**) $m = 3, n = 2$



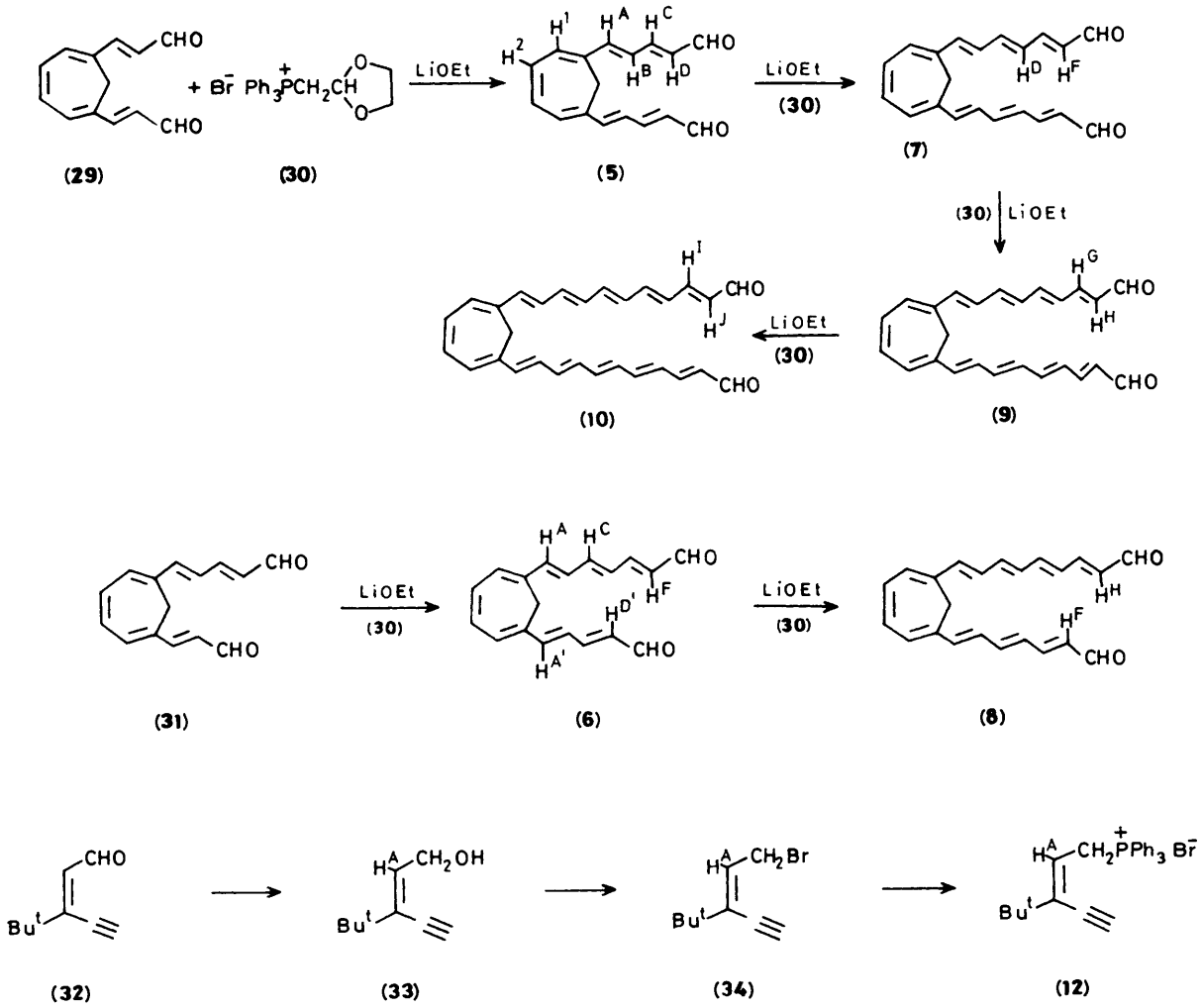
(**5**) $m = n = 2$
(**6**) $m = 3, n = 2$
(**7**) $m = n = 3$
(**8**) $m = 4, n = 3$
(**9**) $m = n = 4$
(**10**) $m = n = 5$

(**11**) R = Me
(**12**) R = Bu^t

(**13**) R = Me, $m = n = 2$
(**14**) R = Me, $m = 3, n = 2$
(**15**) R = Me, $m = n = 3$
(**16**) R = Me, $m = 4, n = 3$
(**17**) R = Me, $m = n = 4$
(**18**) R = Bu^t, $m = 4, n = 3$
(**19**) R = Bu^t, $m = n = 4$
(**20**) R = Bu^t, $m = n = 5$

[26]- (**21**) R = Me, $m = n = 2$
[28]- (**22**) R = Me, $m = 3, n = 2$
[30]- (**23**) R = Me, $m = n = 3$
[32]- (**24**) R = Me, $m = 4, n = 3$
[34]- (**25**) R = Me, $m = n = 4$
[32]- (**26**) R = Bu^t, $m = 4, n = 3$
[34]- (**27**) R = Bu^t, $m = n = 4$
[38]- (**28**) R = Bu^t, $m = n = 5$

Scheme 1.



Scheme 2.

the dicarbaldehydes (**5**)—(**10**), which were prepared from the lower vinylogues (**29**)[5] and (**31**),[5] as depicted in Scheme 2, by iterative sequences of Wittig condensation of [(1,3-dioxolan-2-yl)methyl]triphenylphosphonium bromide (**30**)[8] (8 mol equiv.) and lithium ethoxide in *N*,*N*-dimethylformamide (DMF) at 75 °C, followed by hydrolysis with dilute hydrochloric acid at room temperature, affording the bis-homologated dicarbaldehydes in each step. The Wittig reactions between the dicarbaldehydes (**5**)—(**10**) and the salt (**11**)[5] [or the salt (**12**), see below] were carried out with butyl-lithium in tetrahydrofuran (THF) from −70 °C to room temperature, successfully giving rise to the corresponding acyclic diacetylenes (**13**)—(**20**), respectively, in 25—50% yield. Although the stereoisomeric products from these reactions were not followed up, the *E*-configuration for the newly formed double bonds of the isolated compounds (**13**)—(**20**) was confirmed by both examination of their i.r. spectra and, occasionally, of ^{1}H n.m.r. signals for acetylenic protons. These acyclic compounds proved to be unstable. Accordingly, in some cases, satisfactory mass spectra and elemental analyses were not obtained (see Experimental section). Oxidative couplings of the acyclic compounds (**13**)—(**20**) were carried out with anhydrous copper(II) acetate in pyridine and ether at 50 °C under relatively dilute conditions, giving rise to the monomeric cyclic products (**21**)—(**28**) in 30—50% yield. Thus, the intramolecular oxidative couplings were achieved without employing a high-dilution technique, presumably because of the presence of the 1,6-methanol bridge in the acyclic polyenes (**13**)—(**20**) containing terminal acetylene groups. Among the annulenes prepared, the ^{1}H n.m.r. spectra of the methylated [32]-annulene (**24**) and [34]-annulene (**25**) could not be measured satisfactorily owing to poor solubility in various n.m.r. solvents. This prompted us to prepare t-butyl-substituted annulenes for the larger ring systems, since t-butylated derivatives of dehydroannulenes are known to be usually more soluble in common solvents and to have enhanced thermal stability compared with the methylated ones.[9,10] This route thus required preparation of the t-butylated salt, triphenyl-(3-t-butylpent-2-en-4-ynyl)phosphonium bromide (**12**), which was obtained from the bromide (**34**) and triphenylphosphine by the same manner as that for the preparation of the methylated salt (**11**).[5,11] The bromide (**34**) was obtained from 3-t-butylpent-2-en-4-ynal (**32**)[9] *via* the corresponding alcohol (**33**).[12] Thus, the t-butyl-substituted [32]- (**26**), [34]- (**27**), and [38]-annulene (**28**) were also prepared as illustrated in Scheme 1. All the tetradehydromethanoannulenes (**21**)—(**28**) thus obtained were deep coloured crystals with a metallic lustre. It is noteworthy that these annulenes are also thermally more stable than monocyclic annulenes and dehydroannulenes[7] and the corresponding methanoannulenes,[13] presumably due to rigidity of the

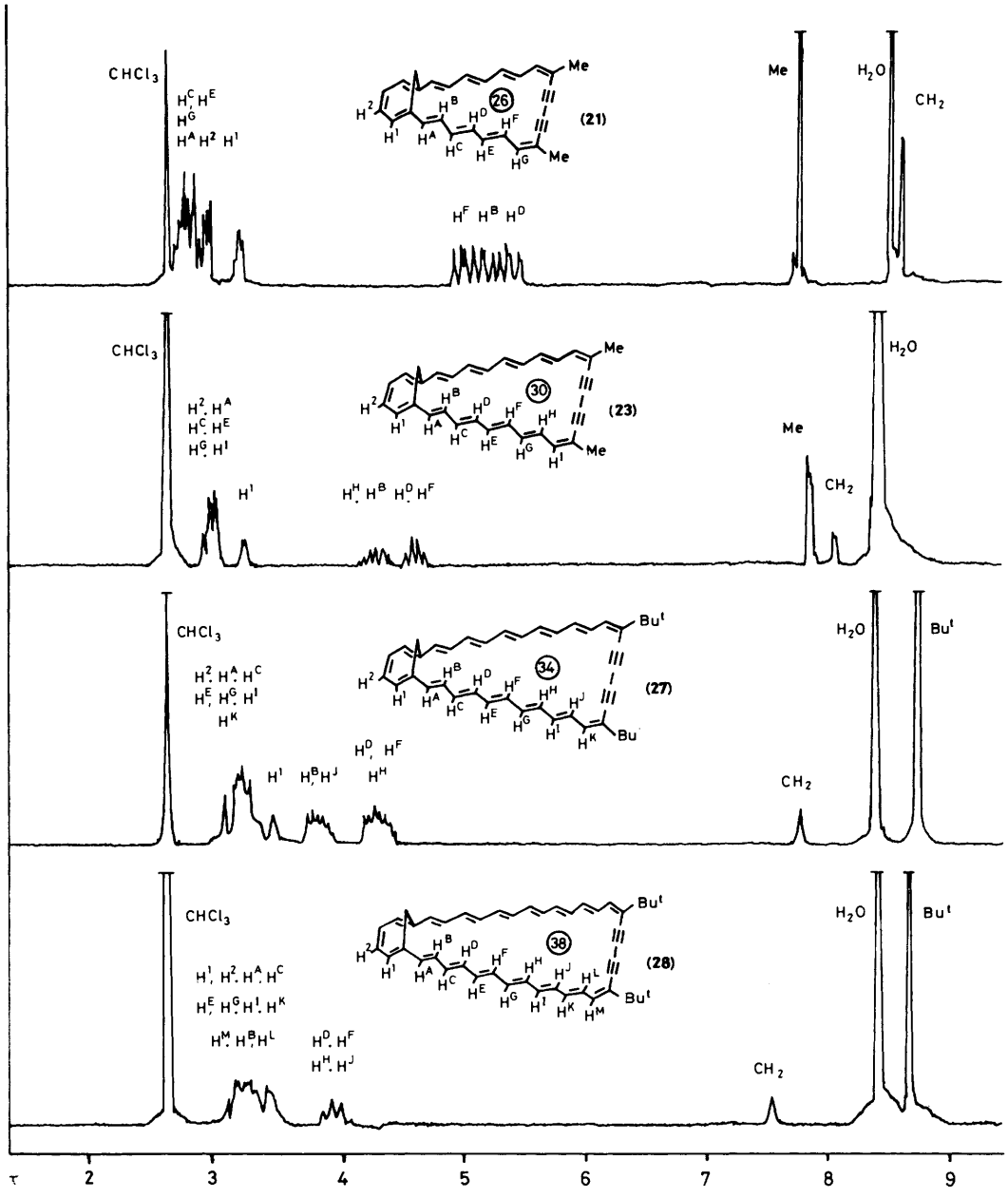


Figure 1. ^{1}H N.m.r. spectra of tetradehydro-[26]- (**21**), -[30]-(**23**), -[34]-(**27**), and -[38]-annulene (**28**) in $CDCl_3$ at 200 MHz, determined at 21 °C (τ-values)

molecular skeleton arising from both a methano bridge and a 1,3-diacetylenic linkage in the molecular perimeter.

^{1}H N.m.r. Spectra.—The ^{1}H n.m.r. spectra of the annulenes (**21**)—(**28**) [except (**24**) and (**25**); see above] and their corresponding acyclic compounds (**13**)—(**20**) were obtained using the Fourier transform technique. In the case of the methylated [32]-annulene (**24**), only the resonances of the methylene and the methyl protons could be detected.

The spectra of the tetradehydro[4*n* + 2]-membered series, [26]- (**21**), [30]- (**23**), [34]- (**27**), and [38]-annulene (**28**), are presented in Figure 1, and the spectra of the tetradehydro[4*n*]-membered series, [28]-(**22**) and [32]-annulene (**26**), are in Figure 2. Individual assignments were made on the basis of multiplicities and coupling constants given in the Experimental section and were further clarified by decoupling experiments or from examination of their two-dimensional spectra taken on a JEOL GX-270 or a Brucker WM-360 spectrometer.

The resonances of the olefinic, the methylene, and the methyl (or t-butyl) protons of the acyclic compounds (**13**)—(**20**) appear, respectively, at almost the same field position for each compound. The protons of the model acyclic compounds (**13**)—(**20**) resonate at τ($CDCl_3$) 3.09—3.91 (olefinic and 7-membered ring-H), 6.56—6.64 (C≡CH), 7.27—7.30 (CH_2), 8.00—8.04 (Me), and 8.80—8.84 (Bu^t). As can be seen from Figure 1 (see also Experimental section), comparison of the chemical shifts of the various protons of the tetradehydro-[26]-(**21**), -[30]- (**23**), and -[34]-annulene (**27**) with those of the respective corresponding acyclic compounds (**13**), (**15**), and (**19**) indicates that the annulenes (**21**), (**23**), and (**27**) are diatropic, as might be expected of 26π-, 30π- and 34π-electron systems, respectively. This follows from the fact that the outer protons

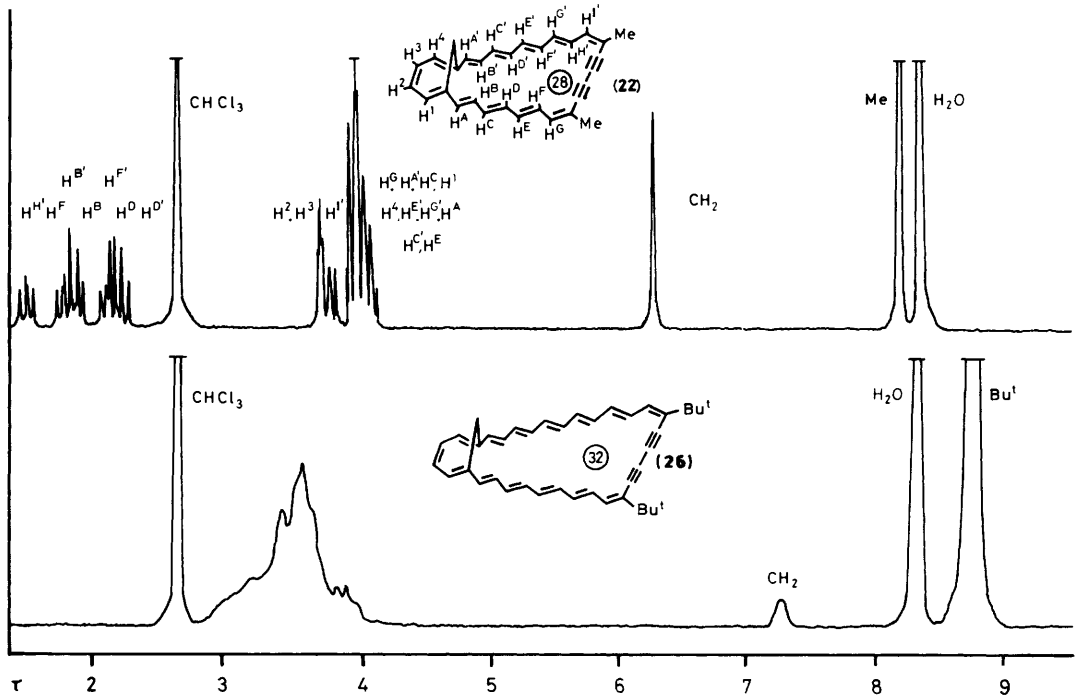


Figure 2. ^{1}H N.m.r. spectra of tetradehydro-[28]- (**22**) and -[32]-annulene (**26**) in $CDCl_3$ at 200 MHz, determined at 21 °C (τ-values)

Table 1. ^{1}H N.m.r. chemical shifts of methylene and methyl (t-butyl) protons of the annulenes (**1**)—(**4**), (**21**)—(**24**), and (**26**)—(**28**) in $CDCl_3$ at 200, 270, or 360 MHz (τ-values, $SiMe_4$ internal standard)[a]

	[18]-(**1**)	[20]-(**2**)	[22]-(**3**)	[24]-(**4**)	[26]-(**21**)	[28]-(**22**)	[30]-(**23**)	[32]-(**24**)	[32]-(**26**)	[34]-(**27**)	[38]-(**28**)
CH_2	10.45	5.36	9.19	5.88	8.50	6.35	8.07	7.28	7.28	7.78	7.60
Me	7.47	8.44	7.64	8.36, 8.39	7.76	8.27, 8.29	7.86	8.01, 8.02	8.80	8.74	8.76

[a] The methylene and the methyl (or t-butyl) protons of the acyclic precursors of these annulenes resonate at τ 7.15—7.29 and 8.00—8.05 (or 8.80—8.84), respectively (see text and ref. 5).

(including methyl protons) in compounds (**21**), (**23**), and (**27**) resonate at lower field than the corresponding protons in the acyclic compounds (**13**), (**15**), and (**19**), respectively, whereas the inner protons (including methylene protons) resonate at higher field. On the other hand, as is seen from Figure 2, the [28]-annulene (**22**) is paratropic, as might be expected of a 28π-electron system. This follows from the fact that the outer protons (including methyl protons) in (**22**) resonate at higher field than the corresponding protons in its precursor (**14**), whereas the inner protons (including methylene protons) resonate at lower field. By contrast, comparison of the chemical shifts of the protons of [32]- (**26**) and [38]-annulene (**28**) (Figures 1 and 2) with those of the corresponding acyclic compounds (**18**) and (**20**) indicates that the annulenes (**26**) and (**28**) are atropic, since the resonances of (**26**) and (**28**) are at almost the same position as those of the acyclic models (**18**) and (**20**).

It is evident from Figures 1 and 2 that in the spectra of [4*n* + 2]π-annulenes (**21**), (**23**), and (**27**) the olefinic inner protons resonate at higher field than the outer protons, while in the spectrum of [4*n*]π-annulene (**22**) the olefinic inner protons resonate at lower field than the outer protons. Also, in the spectra of [26]- (**21**), [28]- (**22**), [30]- (**23**), [34]- (**27**), and [38]-annulene (**28**) the olefinic inner protons near the cycloheptatriene and 1,3-diacetylenic moieties always resonate at lower field than the other olefinic inner protons, owing to the local anisotropic effect of these two moieties. In the spectra of the atropic [32]- (**26**) and [38]-annulene (**28**), both the olefinic inner and outer protons resonate at almost the same field position. Thus, Figures 1 and 2 show that the above described variation of tropicities in annulenes (**21**)—(**23**) and (**26**)—(**28**) can be deduced without having to make comparisons with the corresponding precursor models.

The chemical shifts of the methylene and the methyl protons of the tetradehydroannulenes (**21**)—(**24**) and (**26**)—(**28**) are listed in Table 1, together with those of the fewer-membered annulenes (**1**)—(**4**). The simplest test for the nature of the ring currents in these tetradehydromethanoannulenes (**1**)—(**4**), (**21**)—(**24**), and (**26**)—(**28**) is provided by the chemical shifts of the methylene and the methyl protons, since these must always be internal and external, respectively, and can readily be recognized. The alternation of the methylene and the methyl proton resonances between the [4*n* + 2]π-annulenes (**1**), (**3**), (**21**), (**23**), and (**27**) (relatively high- and low-field, respectively) and the [4*n*]π-annulenes (**2**), (**4**), and (**22**) (relatively low- and high-field, respectively) confirms the diatropicity of the former and the paratropicity of the latter. By contrast, the chemical shifts of the methylene and the methyl protons of the [32]-annulenes (**24**) and (**26**), and the [38]-annulene (**28**), are nearly the same as for the corresponding monocyclic models (**16**), (**18**),

Table 2. Variable-temperature ^{1}H n.m.r. parameters of the annulenes (**21**), (**26**), and (**27**) at 90 MHz (τ-values)

Compound	T (°C)				CH_2	Me
[26]- (**21**)	+60				8.50	7.78
	+23				8.51	7.77
	−30				8.77	7.75
	−60				8.81	7.74
		Olefinic and 7-membered-ring H			CH_2	Bu^t
[32]- (**26**)	+60	3.10—3.96			7.29	8.80
	+23	3.1—3.9			7.28	8.80
	−30	3.1—3.9			7.28	8.79
	−60	3.10—3.96			7.28	8.80
		Outer H	H^B, H^I	H^D, H^F, H^H	CH_2	Bu^t
[34]- (**27**)	+60	3.10—3.60	3.70—3.90	4.02—4.48	7.76	8.74
	+23	3.11—3.60	3.74—3.90	4.06—4.48	7.77	8.74
	−30	3.08—3.58	3.78—4.00	4.10—4.50	7.84	8.73
	−60	3.04—3.58	3.88—4.02	4.12—4.50	7.96	8.73

and (**20**) (see above), respectively, indicating that these annulenes are atropic.

In addition, comparison of the chemical shifts of both the methylene and the methyl protons indicates that the diatropicity in [4*n* + 2]π-annulenes falls off in the sequence [18]- (**1**) > [22]-(**3**) > [26]- (**21**) > [30]- (**23**) > [34]-annulene (**27**), while the paratropicity in [4*n*]π-annulenes falls in the order [20]- (**2**) > [24]- (**4**) > [28]-annulene (**22**). Thus, the observation that both the diamagnetic ring current effect in [4*n* + 2]π-electron systems and the paramagnetic ring current effect in [4*n*]π-electron systems become less as the ring size increases seems to reflect both a decrease of tropicity with an increase in ring size[2] and an increasing flexibility of the tetradehydroannulene perimeter, as has been observed in monocyclic annulenes and dehydroannulenes,[7] albeit that these annulenes have a methano-bridge and a 1,3-diacetylenic linkage in the rings. Thus, with increasing ring size, the chemical shifts of the methylene proton resonances tend towards and reach those of the acyclic model compounds at the 38-membered-ring system in [4*n* + 2]π-systems and at the 32-membered-ring system in [4*n*]π-systems, indicating that the [38]- (**28**) and the [32]-annulene (**26**) are atropic. However, the methylene proton resonance of the atropic [38]-annulene (**28**) does not fully correlate with that of the acyclic model, but is at higher field than that of the atropic [32]-annulene (**26**). This might be explained by a homoconjugative effect, due to the cycloheptatriene moiety, for the bridging methylene protons in the [4*n* + 2]π-, 38π-electron perimeter. To test the presence of a homoconjugative effect of the cycloheptatriene moiety, preparation of the next higher [4*n* + 2]π-membered compound, a [42]-annulene, was desirable. However, even in the t-butylated annulene series a dramatic decrease (see above) of solubility in deuteriochloroform with increasing ring size discouraged us from preparing the [42]-annulene.

Variable-temperature ^{1}H n.m.r. spectra of the [26]- (**21**), [28]- (**22**), [30]- (**23**), [32]- (**26**), and [34]-annulene (**27**) were run at 90 MHz over the range −60 to 60 °C. In the case of the [28]-(**22**), the [30]- (**23**), and the [38]-annulene (**28**), satisfactory spectra could not be obtained owing to poor solubility in deuteriochloroform, and in spectra of the [26]-annulene (**21**) only the resonances of the methyl and the methylene protons were detected. The results, summarized in Table 2, show all the spectra of compounds (**21**), (**26**), and (**27**) to be essentially temperature-independent, ruling out any conformational change of these annulenes between these temperatures, although, with decreasing temperature, the resonances of the inner (including methylene protons) and the outer (including methyl or t-butyl) protons of the diatropic [26]- (**21**) and [34]-annulene (**27**) move to slightly higher and lower field, respectively, reflecting the fact that these annulenes (**21**) and (**27**) have a higher planarity at low temperatures. Temperature-independency of the spectrum of the [32]-annulene (**26**) indicates that (**26**) is still atropic at low temperatures. Thus, it is rather surprising that the resonances of the bridged methylene protons in compounds (**21**), (**26**), and (**27**) always appear as a singlet between these temperatures, in contrast to the cases of multi-bridged annulenes[14] and methano-bridged annulenes,[13] in whose spectra the bridged methylene protons usually appear as two doublets even at room temperature. This also might be attributable to the rigidity of the molecular skeleton due to both a 1,6-methano bridge and a 1,3-diacetylenic linkage on these annulene perimeters.

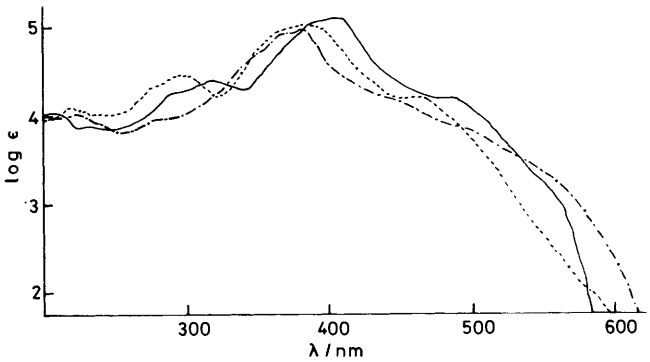


Figure 3. Electronic absorption spectra of tetradehydro-[26]- (**21**) (· · · ·), -[28]-annulene (**22**) (– • – • –), and -[30]-annulene (**23**) (——) in THF

Electronic Spectra.—The electronic absorption spectra of tetradehydro-[26]-(**21**), -[28]- (**22**), and -[30]-annulene (**23**) are illustrated in Figure 3. When compared with the spectra of the [26]- (**21**) and the [30]-annulene (**23**), the spectrum of the [28]-annulene (**22**) shows a rather broad absorption curve, as recognized in the spectra of monocyclic [4*n*]π-annulenes and dehydroannulenes.[7] However, the difference in the shape of the absorption curves between the [4*n* + 2]π- (**21**) and (**23**) and [4*n*]π-annulene (**22**) is smaller than that between the fewer-membered [4*n* + 2]π-, [18]- (**1**), [22]- (**3**) and the [4*n*]π-, [20]- (**2**), [24]-annulene (**4**),[5] suggesting that the annulene character decreases with increasing ring size.

The absorption maxima of all tetradehydromethanoannulenes (**21**)—(**28**), together with the wavelengths of the main absorption maxima of (**1**)—(**4**), are listed in Table 3, from which it can be seen that the main maxima of [4*n* + 2]π-annulenes [18]- (**1**), [22]- (**3**), and [26]-annulene (**21**) are at rather longer wavelengths than those of [4*n*]π-annulenes [20]- (**2**), [24]- (**4**), and [28]-annulene (**22**). However, the maximum of [30]-annulene (**23**) is not at longer wavelength than that of the [32]-annulene (**24**), suggesting that the [32]-annulene (**24**) is not paratropic, but is atropic, as is revealed by its ^{1}H n.m.r. spectrum (see above). Thus, it is evident that in these tetradehydromethanoannulenes having tropicity the same alternation in the wavelengths of the main absorption maxima between (4*n* + 2) and (4*n*) systems occurs, as has been demonstrated for monocyclic annulenes and dehydroannulenes.[15]

Experimental

M.p.s were determined with a hot-stage apparatus and are uncorrected. I.r. spectra were taken with a Hitachi 260-50

Table 3. Electronic absorption maxima of annulenes (**1**)—(**4**) and (**21**)—(**28**) in THF [$\lambda_{max.}$(nm) ($\varepsilon_{max.}$)]. The strongest absorption is indicated in bold type

[18]-(**1**) **343** nm[a]	[20]-(**2**) **324** nm[a]	[22]-(**3**) **367** nm[a]	[24]-(**4**) **355** nm[a]

[26]-(**21**) 273sh (18 800), 294 (27 800), 305sh (26 200), 369sh (93 300), **388 (104 000)**, 426sh (27 200), 469sh (14 000)
[28]-(**22**) 276 (8 620), 289sh (9 140), 350sh (50 200), 367 (81 500), **383 (96 900)**, 445sh (15 600)
[30]-(**23**) 290sh (17 800), 316 (25 200), 395sh (121 000), **406 (131 000)**, 488sh (14 900)
[32]-(**24**) 240 (14 000), 254sh (12 800), 294 (12 400), 308sh (19 300), 368sh (68 100), 390 (114 000), **409 (127 000)**, 519sh (12 900)
[34]-(**25**) 245sh (17 200), 307sh (21 300), 348sh (33 500), 410sh (115 000), **425 (122 000)**, 508sh (23 600)
[32]-(**26**) 221 (20 100), 291sh (13 500), 309 (16 800), 365sh (52 600), 388 (94 800), **406 (108 000)**
[34]-(**27**) 247 (13 900), 307sh (24 100), 330sh (31 800), 410sh (148 000), **425 (163 000)**, 503sh (26 300)
[38]-(**28**) 262 (24 000), 325sh (31 300), 425sh (178 000), **440 (199 000)**, 520sh (29 300)

[a] See also ref. 5.

spectrophotometer as KBr discs and were calibrated against polystyrene; only significant maxima are described. U.v. spectra were measured in THF solution and run with a Hitachi 220A spectrophotometer. Mass spectra were recorded with a JEOL JMS-300 spectrometer operating at 75 eV using a direct-inlet system or JMS-D spectrometer equipped with field-desorption system. ^{1}H N.m.r. spectra were recorded as $CDCl_3$ solutions (unless otherwise stated) with a FX-90Q (90 MHz), a Varian XL-200 (200 MHz), a JEOL GX(270 (270 MHz), or a Brucker WM-360 (360 MHz) spectrometer, tetramethylsilane being used as an internal standard. Assignments were clarified by the use of decoupling experiments where necessary. Merck alumina (activity II—III) and silica gel were used for column chromatography. Progress of most reactions was followed by t.l.c. using Merck precoated silica gel. Organic extracts with benzene or dichloromethane were washed with saturated aqueous sodium chloride and dried over anhydrous sodium sulphate prior to removal of solvent. Solvents were evaporated under water-pump pressure.

1,6-*Bis*-(4-*formylbuta*-1,3-*dienyl*)*cyclohepta*-1,3,5-*triene* (**5**).—Lithium ethoxide solution prepared from lithium (319 mg, 46 mmol) in dry ethanol (78 ml) was added dropwise during 4 h under nitrogen to a stirred solution of 1,6-bis-(2-formylvinyl)-cyclohepta-1,3,5-triene (**29**)[5] (1.51 g, 7.55 mmol) and the salt (**30**)[8] (19.5 g, 45.3 mmol) in DMF (179 ml) at 70 °C. After being stirred for a further 1.5 h at 70 °C, the solution was cooled to room temperature, poured onto water, and then extracted with benzene. The extracts were washed with brine, and dried. After removal of solvent, the residue was dissolved in THF (78 ml) and mixed with 15% hydrochloric acid (52 ml), and the mixture was stirred for 1.5 h at room temperature. Then the mixture was separated and the aqueous layer was extracted with dichloromethane. The combined organic layer was washed with aqueous sodium hydrogen carbonate, and dried. The residue after removal of solvent was chromatographed on silica gel (4.2 × 13 cm). The fractions eluted with 50—60% ether in hexane afforded the *dialdehyde* (**5**) (1.06 g, 56%). It formed red needles, m.p. 155—156 °C (from hexane–benzene); *m/z* 252 (M^+, 100%); *M*, 252.3; $\lambda_{max.}$ 318 (ε 72 600) and 418 nm (14 200); $\nu_{max.}$ 1 680 (CHO), 1 610 (C=C), 1 010, and 980 cm^{-1} (*E* C=C); τ (270 MHz) 0.40 (2 H, d, *J* 8 Hz, CHO), 2.80 (2 H, dd, *J* 15 and 10 Hz, H^C), 3.21—3.27 (6 H, m, H^1, H^A, and H^B), 3.46—3.49 (2 H, m, H^2), 3.73 (2 H, dd, *J* 15 and 8 Hz, H^D), and 7.22 (2 H, s, CH_2) (Found: C, 81.2; H, 6.5. $C_{17}H_{16}O_2$ requires C, 80.9; H, 6.4%).

1-(4-*Formylbuta*-1,3-*dienyl*)-6-(6-*formylhexa*-1,3,5-*trienyl*)-*cyclohepta*-1,3,5-*triene* (**6**).—Lithium ethoxide solution prepared from lithium (527 mg, 75 mmol) in dry ethanol (130 ml) was added dropwise during 4 h to a stirred solution of 1-(2-formylvinyl)-6-(4-formylbuta-1,3-dienyl)cyclohepta-1,3,5-triene (**31**)[5] (2.13 g, 9.40 mmol) and the salt (**30**) (32.3 g, 75.2 mmol) in DMF (400 ml) at 65 °C. After being stirred for a further 1.5 h at 65 °C, the mixture was worked up as described above. The residue after removal of solvent was dissolved in THF (260 ml) and mixed with 15% HCl (170 ml). After being stirred for 1 h at room temperature, the mixture was worked up as for the isolation of (**5**). The product was chromatographed on silica gel (4.5 × 18 cm). The fractions eluted with 80% ether in hexane afforded the *dialdehyde* (**6**) (1.42 g, 54%). It formed red needles, m.p. 136—137 °C (from hexane–benzene); *m/z* 278 (M^+, 100%); *M*, 278.3; $\lambda_{max.}$ 280sh (ε 12 600), 328sh (73 900), 338 (77 800), and 433 nm (14 300); $\nu_{max.}$ 1 670 (CHO), 1 605, 1 595 (C=C), 995, and 985 cm^{-1} (*E* C=C); τ (90 MHz) 0.41 (1 H, d, *J* 8 Hz, CHO), 0.42 (1 H, d, *J* 8 Hz, CHO), 2.65—3.04 (3 H, m, H^A, $H^{A'}$, and H^C), 3.22—3.64 (9 H, m, olefinic and 7-membered-ring H), 3.74 (1 H, dd, *J* 15 and 8 Hz, $H^{D'}$), 3.78 (1 H, dd, *J* 15 and 8 Hz, H^F), and 7.24 (2 H, s, CH_2) (Found: C, 82.15; H, 6.5. $C_{19}H_{18}O_2$ requires C, 82.0; H, 6.5%).

1,6-*Bis*-(6-*formylhexa*-1,3,5-*trienyl*)*cyclohepta*-1,3,5-*triene* (**7**).—Lithium ethoxide solution prepared from lithium (1.00 g, 142 mmol) in dry ethanol (206 ml) was added dropwise during 3 h under nitrogen to a stirred solution of the dialdehyde (**5**) (4.60 g, 17.8 mmol) and the salt (**30**) (61.0 g, 142 mmol) in DMF (800 ml) at 75 °C. After being stirred for a further 2.5 h, the mixture was worked up in the usual manner. The residue after removal of solvent was dissolved in THF (350 ml) and mixed with 7% HCl (307 ml). After being stirred overnight at room temperature, the mixture was worked up as before. The product was chromatographed on silica gel (5.0 × 18 cm). The fractions eluted with 70% ether in hexane afforded the *dialdehyde* (**7**) (2.70 g, 49.8%). It formed dark red needles, m.p. 194—195 °C (from hexane–benzene); *m/z* 304 (M^+, 100%); *M*, 304.3; $\lambda_{max.}$ 352 (ε 97 400) and 448 (15 100); $\nu_{max.}$ 1 670 (CHO), 1 610, 1 600, 1 590 (C=C), 1 010, and 990 cm^{-1} (*E* C=C); τ (90 MHz) 0.42 (2 H, d, *J* 8 Hz, CHO), 2.83 (2 H, dd, *J* 15 and 10 Hz, H^D), 3.26—3.62 (12 H, m, olefinic and 7-membered-ring H), 3.81 (2 H, dd, *J* 15 and 8 Hz, H^F), and 7.26 (2 H, s, CH_2) (Found: C, 83.1; H, 6.7. $C_{21}H_{20}O_2$ requires C, 82.9; H, 6.6%).

1-(6-*Formylhexa*-1,3,5-*trienyl*)-6-(8-*formylocta*-1,3,5,7-*tetraenyl*)*cyclohepta*-1,3,5-*triene* (**8**).—Lithium ethoxide solution prepared from lithium (765 mg, 110 mmol) in dry ethanol (177 ml) was added dropwise during 4 h under nitrogen to a stirred solution of the dialdehyde (**6**) (3.80 g, 13.7 mmol) and the salt (**30**) (47.0 g, 110 mmol) in DMF (554 ml) at 75 °C. After being stirred for a further 1 h, the mixture was worked up in the usual manner. The residue after removal of solvent was dissolved in THF (363 ml) and mixed with 7% HCl (238 ml). After being stirred overnight at room temperature, the mixture was worked up as for the isolation of (**5**). The product was chromatographed on silica gel (4.9 × 22 cm). The fractions eluted with 60—70% ether in hexane afforded the *dialdehyde* (**8**) (3.06 g, 67.6%). It formed black cubes, m.p. 184—185 °C (from hexane–THF); *m/z* 330 (M^+, 82%) and 162 (100); *M*, 330.4; $\lambda_{max.}$

298sh (ε 15 900), 350sh (85 600), 367 (114 000), and 457 nm (20 500); $\nu_{max.}$ 1 670 (CHO), 1 600, 1 570 (C=C), 1 015, and 995 cm^{-1} (*E* C=C); τ (90 MHz) 0.42 (1 H, d, *J* 8 Hz, CHO), 0.43 (1 H, d, *J* 8 Hz, CHO), 2.70—3.61 (16 H, m, olefinic and 7-membered-ring H), 3.81 (1 H, dd, *J* 15 and 8 Hz, H^F), 3.82 (1 H, dd, *J* 15 and 8 Hz, H^H), and 7.26 (2 H, s, CH_2) (Found: C, 83.3; H, 6.9. $C_{23}H_{22}O_2$ requires C, 83.6; H, 6.7%).

1,6-*Bis*-(8-*formylocta*-1,3,5,7-*tetraenyl*)*cyclohepta*-1,3,5-*triene* (**9**).—Lithium ethoxide solution prepared from lithium (112 mg, 16 mmol) in dry ethanol (35 ml) was added dropwise during 1.5 h under nitrogen to a stirred solution of the dialdehyde (**7**) (471 mg, 1.56 mmol) and the salt (**30**) (6.90 g, 16 mmol) in DMF (150 ml) at 75 °C. After being stirred for a further 1 h at 75 °C, the mixture was worked up in the usual manner. After removal of solvent, the residue was dissolved in THF (180 ml) and mixed with 10% HCl (90 ml). After being stirred overnight at room temperature, the mixture was worked up as for the isolation of (**5**). The product was chromatographed on silica gel (4.2 × 15 cm). The fractions eluted with 80% ether in hexane afforded the *dialdehyde* (**9**) (295 mg, 53%). It formed black needles, m.p. 199—200 °C (from benzene); *m/z* 356 (M^+, 100%); *M*, 356.4; $\lambda_{max.}$ 265 (ε 9 290), 368sh (87 500), 380 (98 200), and 459 nm (19 200); $\nu_{max.}$ 1 670 (CHO), 1 615 (C=C), 1 015, and 990 cm^{-1} (*E* C=C); τ (90 MHz) 0.43 (2 H, d, *J* 8 Hz, CHO), 2.85 (2 H, dd, *J* 15 and 10.5 Hz, H^G), 3.10—3.70 (16 H, m, olefinic and 7-membered-ring H), 3.84 (2 H, dd, *J* 15 and 8 Hz, H^H), and 7.27 (2 H, s, CH_2) (Found: C, 84.2; H, 6.7. $C_{25}H_{24}O_2$ requires C, 84.2; H, 6.8%).

1,6-*Bis*-(10-*formyldeca*-1,3,5,7,9-*pentaenyl*)*cyclohepta*-1,3,5-*triene* (**10**).—Lithium ethoxide prepared from lithium (128 mg, 18.4 mmol) in dry ethanol (55 ml) was added dropwise during 3 h under nitrogen to a stirred solution of the dialdehyde (**9**) (821 mg, 2.3 mmol) and the salt (**30**) (7.90 g, 18.4 mmol) in DMF (230 ml) at 65 °C. After being stirred for a further 1 h at 65 °C, the mixture was worked up in the usual manner. After removal of solvent, the residue was dissolved in THF (105 ml) and mixed with 7% HCl (65 ml). After being stirred overnight at room temperature, the mixture was worked up as for the isolation of (**5**). The product was chromatographed on silica gel (4.7 × 20 cm). The fractions eluted with ethyl acetate–chloroform (1:1) afforded the *dialdehyde* (**10**) (447 mg, 47.6%). It formed dark brown needles, m.p. 208—209 °C (decomp.) (from benzene); *m/z* 408 (M^+, 50%) and 78 (100); *M*, 408.5; $\lambda_{max.}$ 292 (ε 15 300), 395sh (11 500), 411 (138 000), and 490sh nm (28 700); $\nu_{max.}$ 1 660 (CHO), 1 605 (C=C), 1 020, and 1 000 cm^{-1} (*E* C=C); τ (90 MHz) 0.44 (2 H, d, *J* 8 Hz, CHO), 2.84 (2 H, dd, *J* 15 and 10 Hz, H^I), 3.20—3.70 (20 H, m, olefinic and 7-membered-ring H), 3.84 (2 H, dd, *J* 16 and 8 Hz, H^J), and 7.27 (2 H, s, CH_2) (Found: C, 85.1; H, 6.8. $C_{29}H_{28}O_2$ requires C, 85.3; H, 6.7%).

1,6-*Bis*-(8-*methyldeca*-1,3,5,7-*tetraen*-9-*ynyl*)*cyclohepta*-1,3,5-*triene* (**13**).—To a stirred suspension of the salt (**11**)[5] (1.70 g, 4.13 mmol) in dry THF (60 ml) at −70 °C was added dropwise a solution of butyl-lithium (1.67M; 2.5 ml) in hexane by a syringe during 15 min under argon. After being stirred for 2 h at −70 °C, the mixture was treated dropwise with a solution of the dialdehyde (**5**) (298 mg, 1.18 mmol) in dry THF (40 ml) during 2.5 h at −70 °C. Then the solution temperature was allowed to rise to −10 °C, and the solution was stirred for 2 h. After addition of ethyl acetate (15 ml), the mixture was poured onto brine, and the aqueous layer was extracted with benzene. The combined organic layer was washed with brine and dried. The product was passed through a short column of alumina (3.7 × 7.0 cm). The fractions eluted with ether (400 ml) were collected and the residual dark red semi-solid obtained after removal of solvent was chromatographed on silica gel (4.2 × 12 cm). The fractions eluted with 15% ether in benzene afforded *compound* (**13**) (101 mg, 22.5%). It formed dark red needles, m.p. 114—115 °C (decomp.) (from hexane–chloroform); *m/z* 376 (M^+, 68%) and 374 (100); *M*, 376.5; $\lambda_{max.}$ 265 (ε 4 840), 335sh (34 400), 351 (66 700), 367 (90 300), and 453 nm (9 100); $\nu_{max.}$ 3 300 (C≡CH), 2 100 (C≡C), 1 000, and 970 cm^{-1} (*E* C=C); τ (270 MHz) 3.12—3.70 (18 H, m, olefinic and 7-membered-ring H), 6.61 (2 H, s, C≡CH), 7.29 (2 H, s, CH_2), and 8.04 (6 H, s, Me) (Found: C, 92.7; H, 7.5. $C_{29}H_{28}$ requires C, 92.5; H, 7.5%).

15,16,17,18-*Tetrahydro*-14,19-*dimethyl*-1,6-*methano*[26]-*annulene* (**21**).—A solution of compound (**13**) (43.5 mg, 0.144 mmol) in pyridine and dry ether (3:1; 40 ml) was added dropwise during 3 h to a stirred solution of anhydrous copper(II) acetate (4.0 g) in pyridine and dry ether (3:1; 204 ml) at 51 °C, and the mixture was stirred for a further 20 min at the same temperature. Then the mixture was poured onto water and extracted with benzene. The extracts were washed successively with 5% HCl until acid, and then with aqueous sodium hydrogen carbonate, and were dried and concentrated. The residue was chromatographed on alumina (4.0 × 14 cm). The fractions eluted with 30—40% ether in hexane afforded the [26]-*annulene* (**21**) (14.7 mg, 34%). It formed red needles, m.p. 295—296 °C (decomp.) (from benzene); *m/z* 374 (M^+, 100%); *M*, 374.5; for u.v. data see Table 3 and Figure 3; $\nu_{max.}$ 2 160 (C≡C) and 995 cm^{-1} (*E* C=C); τ (200 mHz) 2.83—2.94 (8 H, m, H^A, H^C, H^E, and H^G), 3.00—3.03 (2 H, m, H^2), 3.23—3.26 (2 H, m, H^1), 5.03 (2 H, dd, *J* 15 and 11 Hz, H^F), 5.17 (2 H, dd, *J* 15 and 11 Hz, H^B), 5.36 (2 H, dd, *J* 15 and 11 Hz, H^D), 7.76 (6 H, s, Me), and 8.50 (2 H, s. CH_2) (see Figure 1) (Found: C, 92.8; H, 6.9. $C_{29}H_{26}$ requires C, 93.0; H, 7.0%).

1-(8-*Methyldeca*-1,3,5,7-*tetraen*-9-*ynyl*)-6-(10-*methyldodeca*-1,3,5,7,9-*pentaen*-11-*ynyl*)*cyclohepta*-1,3,5-*triene* (**14**).—To a stirred suspension of the salt (**11**)[5] (3.0 g, 7.05 mmol) in dry THF (50 ml) at −75 °C was added dropwise a solution of BuLi (1.69M; 6.0 ml) in hexane by a syringe during 10 min under argon. After the mixture had been stirred for 1 h at −75 °C, a solution of the dialdehyde (**6**) (393 mg, 1.41 mmol) in dry THF (21 ml) was added dropwise during 2 h, and the mixture was stirred for 1 h at −72 °C and for a further 30 min at room temperature. Then the mixture was worked up as for the isolation of (**13**). The product was passed through a short column of alumina (4.0 × 5.0 cm). The fractions eluted with benzene (400 ml) were collected and evaporated. The residue was chromatographed on alumina (4.3 × 17 cm). The fractions eluted with hexane–ether (1:1) afforded *compound* (**14**) (211 mg, 37%). It formed brown needles, m.p. 118—119 °C (decomp.) (from hexane–benzene); *m/z* 402.2474 ($C_{31}H_{30}$ requires *M*, 402.2348); $\lambda_{max.}$ 224 (ε 15 900), 277sh (17 100), 366 (80 800), 382 (89 500), and 462sh nm (16 200); $\nu_{max.}$ 3 280 (C≡CH), 2 080 (C≡C), and 995 cm^{-1} (*E* C=C); τ (270 MHz) 3.16—3.70 (20 H, m, olefinic and 7-membered-ring H), 6.64 (2 H, s, C≡CH), 7.30 (2 H, s, CH_2), and 8.04 (6 H, s, Me) (Found: C, 91.6; H, 7.5. $C_{31}H_{30}$ requires C, 92.5; H, 7.5%). Attempts to improve the elemental analysis failed.

15,16,17,18-*Tetrahydro*-14,19-*dimethyl*-1,6-*methano*[28]-*annulene* (**22**).—A solution of compound (**14**) (126 mg, 0.312 mmol) in pyridine and dry ether (3:1, 48 ml) was added dropwise during 3 h to a stirred solution of anhydrous copper(II) acetate (1.90 g) in pyridine and dry ether (3:1; 87 ml) at 52 °C, and the mixture was stirred for a further 30 min at the same temperature. Then the mixture was worked up as for the isolation of (**21**). The product was chromatographed on alumina (4.2 × 8.5 cm). The fractions eluted with 10—20% ether in hexane afforded the [28]-*annulene* (**22**) (61.1 mg, 48.9%). It formed brown needles, m.p. 198—199 °C (decomp.)

(from benzene); *m/z* 400 (M^+, 100%); *M*, 400.5; for u.v. data see Table 3 and Figure 3; $\nu_{max.}$ 2 150 (C≡C) and 985 cm^{-1} (*E* C=C); τ (360 MHz) 1.54 (1 H, dd, *J* 15 and 11 Hz, $H^{H'}$), 1.85 (1 H, dd, *J* 15 and 11 Hz, F^F), 1.91 (1 H, dd, *J* 15 and 11 Hz, $H^{B'}$), 1.95 (1 H, dd, *J* 15 and 11 Hz, H^B), 2.18 (1 H, dd, *J* 15 and 12 Hz, $H^{F'}$), 2.24 (2 H, dd, *J* 15 and 11 Hz, H^D and $H^{D'}$), 3.72—3.75 (2 H, m, H^2 and H^3), 3.83 (1 H, d, *J* 12 Hz, H'), 3.98—4.16 (10 H, m, H^G, $H^{A'}$, H^C, H^1, H^4, $H^{E'}$, $H^{G'}$, H^A, $H^{C'}$, and H^E), 6.35 (2 H, s, CH_2), 8.27 (3 H, s, Me), and 8.29 (3 H, s, Me) (see Figure 2) (Found: C, 92.7; H, 7.0. $C_{31}H_{28}$ requires C, 92.95; H, 7.05%).

1,6-*Bis*-(10-*methyldodeca*-1,3,5,7,9-*pentaen*-11-*ynyl*)*cyclohepta*-1,3,5-*triene* (**15**).—To a stirred ylide solution, prepared from the salt (**11**)[5] (3.92 g, 9.30 mmol) in dry THF (150 ml) by using BuLi (1.69M; 5.5 ml) in hexane as described above, at −70 °C was added dropwise a solution of the dialdehyde (**7**) (471 mg, 1.55 mmol) in dry THF (100 ml) during 1.5 h and the mixture was stirred for a further 2 h at room temperature. Then the mixture was worked up as for the isolation of (**13**). The product was chromatographed on alumina (4.2 × 8.0 cm). The fractions eluted with ether–chloroform (1:1) afforded *compound* (**15**) (265 mg, 40%). It formed dark purple needles, m.p. 110—111 °C (decomp.) (from hexane–benzene); *m/z* (field-desorption) 428 (M^+); *m*, 428.5; $\lambda_{max.}$ 232 (ε 13 900), 284 (9 600), 357sh (60 900), 374 (99 300), 391 (116 000), and 464sh nm (17 000); $\nu_{max.}$ 3 290 (C≡CH), 2 090 (C≡C), and 990 cm^{-1} (*E* C=C); τ (270 MHz) 3.15—3.90 (22 H, m, olefinic and 7-membered-ring H), 6.64 (2 H, s, C≡CH), 7.28 (2 H, s, CH_2), and 8.04 (6 H, s, Me) (Found: C, 91.5; H, 7.6. $C_{33}H_{32}$ requires C, 92.5; H, 7.5%). Attempts to improve the elemental analysis failed.

17,18,19,20-*Tetrahydro*-16,21-*dimethyl*-1,6-*methano*[30]-*annulene* (**23**).—A solution of compound (**15**) (61.0 mg, 0.14 mmol) in pyridine and dry ether (3:1; 24 ml) was added dropwise during 4 h to a stirred solution of anhydrous copper(II) acetate (1.0 g) in pyridine and dry ether (3:1; 48 ml) at 52 °C, and the mixture was stirred for a further 1 h at the same temperature. Then the mixture was worked up as for the isolation of (**21**). The product was chromatographed on alumina (4.2 × 10.0 cm). The fractions eluted with ether–dichloromethane (1:1) afforded the [30]-*annulene* (**23**) (19.0 mg, 31.3%). It formed black needles, m.p. 241—242 °C (decomp.) (from toluene); *m/z* 426 (M^+, 27%) and 44 (100); *M*, 426.5; for u.v. data see Table 3 and Figure 3; $\nu_{max.}$ 2 150 (C≡C) and 990 cm^{-1} (*E* C=C); τ (270 MHz) 3.06—3.18 (12 H, m, H^2, H^A, H^C, H^E, H^G, and H^1), 3.41—3.43 (2 H, m, H^1), 4.36—4.47 (4 H, m, H^H and H^B), 4.71—4.77 (4 H, m, H^D and H^F), 7.86 (6 H, s, Me), and 8.07 (2 H, s, CH_2) (see Figure 1) (Found: C, 92.7; H, 7.0. $C_{33}H_{30}$ requires C, 92.9; H, 7.1%).

1-(10-*Methyldodeca*-1,3,5,7,9-*pentaen*-11-*ynyl*)-6-(12-*methyltetradeca*-1,3,5,7,9,11-*hexaen*-13-*ynyl*)*cyclohepta*-1,3,5-*triene* (**16**).—To a stirred ylide solution, prepared from the salt (**11**) (3.20 g, 7.80 mmol) in dry THF (200 ml) and BuLi (1.69M; 4.6 ml) in hexane at −72 °C, was added dropwise a solution of the dialdehyde (**8**) (516 mg, 1.56 mmol) in dry THF (94 ml) during 3 h and the mixture was stirred for a further 30 min at room temperature. After addition of ethyl acetate (25 ml), the mixture was poured onto brine and extracted with dichloromethane. The extracts were washed with brine, and dried. The dark red liquid, after removal of solvent, was chromatographed on alumina (5.2 × 13 cm). The fractions eluted with 10—15% ether in hexane afforded *compound* (**16**) (266 mg, 37.5%). It formed black needles, m.p. 124—125 °C (decomp.) (from hexane–benzene); *m/z* (field desorption) 454 (M^+); *M*, 454.6; $\lambda_{max.}$ 242 (ε 15 900), 295 (13 200), 348sh (37 200), 385 (110 000), 402 (12 900), and 462sh (21 300); $\nu_{max.}$ 3 280 (C≡CH), 2 080 (C≡C), and 995 cm^{-1} (*E* C=C); τ (270 MHz) 3.13—3.91 (24 H, m, olefinic and 7-membered-ring H), 6.64 (2 H, s, C≡CH), 7.29 (2 H, s, CH_2), and 8.04 (6 H, s, Me) (Found: C, 90.7; H, 7.7. $C_{35}H_{34}$ requires C, 92.5; H, 7.5%). Attempts to improve the elemental analysis failed.

17,18,19,20-*Tetrahydro*-16,21-*dimethyl*-1,6-*methano*[32]-*annulene* (**24**).—A solution of compound (**16**) (95.3 mg, 0.210 mmol) in pyridine and dry ether (3:1; 32 ml) was added dropwise during 2 h to a stirred solution of anhydrous copper(II) acetate (1.29 g) in pyridine and dry ether (3:1; 64 ml) at 52 °C. After being stirred for a further 30 min at 52 °C, the mixture was worked up as for the isolation of (**21**). The product was chromatographed on alumina (4.2 × 90 cm). The fractions eluted with ether–dichloromethane (1:1) afforded the [32]-*annulene* (**24**) (38.6 mg, 40.6%). It formed black needles, m.p. 191—192 °C (decomp.) (from toluene); *m/z* 452 (M^+, 100%); *M*, 452.6; for u.v. data see Table 3; $\nu_{max.}$ 2 190 (C≡C) and 995 cm^{-1} (*E* C=C); for ^1H n.m.r. data see text and Table 1 (Found: C, 92.7; H, 7.0. $C_{35}H_{32}$ requires C, 92.9; H, 7.1%).

1,6-*Bis*-(12-*methyltetradeca*-1,3,5,7,9,11-*hexaen*-13-*ynyl*)*cyclohepta*-1,3,5-*triene* (**17**).—To a stirred ylide solution, prepared from the salt (**11**)[5] (1.50 g, 3.54 mmol) in dry THF (100 ml) and BuLi (1.69M; 2.1 ml) in hexane, at −63 °C was added dropwise a solution of the dialdehyde (**9**) (210 mg, 0.59 mmol) in dry THF (100 ml) during 2 h and the mixture was stirred for a further 2 h at 0 °C. Then the mixture was worked up as for the isolation of (**13**). The product was chromatographed on alumina (4.2 × 15 cm). The fractions eluted with dichloromethane afforded *compound* (**17**) (135 mg, 48%). It formed black needles, m.p. 123—125 °C (decomp.) (from hexane–benzene); $\lambda_{max.}$ 245 (ε 25 600), 301 (24 000), 375sh (105 000), 392 (145 000), 409 (162 000), and 500sh nm (25 600); $\nu_{max.}$ 3 250 (C≡CH), 2 060 (C≡C), and 990 cm^{-1} (*E* C=C); τ (270 MHz) 3.10—3.91 (26 H, m, olefinic and 7-membered-ring H), 6.64 (2 H, s, C≡CH), 7.29 (2 H, s, CH_2), and 8.00 (6 H, s, Me) (Found: C, 90.8; H, 7.5. $C_{37}H_{36}$ requires C, 92.45; H, 7.55%). Attempts to improve the elemental analysis failed.

19,20,21,22-*Tetrahydro*-18,23-*dimethyl*-1,6-*methano*[34]-*annulene* (**25**).—A solution of compound (**17**) (56.0 mg, 0.117 mmol) in pyridine and dry ether (3:1; 96 ml) was added dropwise during 4 h to a stirred solution of anhydrous copper(II) acetate (1.0 g) in pyridine and dry ether (3:1; 64 ml) at 52 °C. After being stirred for a further 1 h at 52 °C, the mixture was worked up as for the isolation of (**21**). The product was chromatographed on alumina (4.2 × 15 cm). The fractions eluted with ether–dichloromethane (1:1) afforded the [34]-*annulene* (**25**) (19 mg, 34.1%). It formed black needles, m.p. 223 °C (decomp.) (from toluene); *m/z* 478 (M^+, 8%) and 57 (100); *M*, 478.6; for u.v. data see Table 3; $\nu_{max.}$ 2 180 (C≡C) and 1 000 cm^{-1} (*E* C=C) (Found: C, 93.0; H, 7.0. $C_{37}H_{34}$ requires C, 92.8; H, 7.2%).

3-*t*-*Butylpent*-2-*en*-4-*yn*-1-*ol* (**33**).—This compound was prepared as reported.[12] A mixture of the aldehyde (**32**)[9] (5.65 g, 41.5 mmol) and sodium borohydride (1.57 g, 41.5 mmol) in dry ethanol (208 ml) was stirred for 1.5 h at room temperature. Then 2M-hydrochloric acid (125 ml) and water (20 ml) were added to the ice-cooled mixture, which was then poured onto water and extracted with benzene. The extracts were washed with brine, and dried. The residue, after removal of solvent, was distilled to give the alcohol (**33**) (4.0 g, 70%) as a pale yellow liquid; b.p. 72—73 °C at 2 mmHg; $\nu_{max.}$ 3 300 (OH), 3 280 (C≡CH), 2 090 (C≡C), and 1 620 cm^{-1} (C=C); τ (90 MHz) 4.04 (1 H, t, *J* 7 Hz, H^A), 5.62 (2 H, d, *J* 7 Hz, CH_2), 6.76 (1 H, s, C≡CH), 7.59 (1 H, br s, OH), and 8.84 (9 H, s, Bu^t).

5-*Bromo*-3-*t*-*butylpent*-3-*en*-1-*yne* (**34**).—To a stirred, ice-cooled solution of the alcohol (**33**) (6.80 g, 49.3 mmol) in dry dichloromethane (16 ml) was added dropwise during 2 h a solution of phosphorus tribromide (9.10 g, 33.2 mmol) in dry dichloromethane (7 ml). After being stirred for 1 h at room temperature, the mixture was poured onto water and extracted with dichloromethane. The extract was washed successively with water, aqueous sodium hydrogen carbonate, and brine, and dried. The residue obtained on removal of the solvent was distilled to give the bromide (**34**) (7.50 g, 76%) as a pale yellow liquid; b.p. 56—57 °C at 1 mmHg; $\nu_{max.}$ 3 280 (C≡CH), 2 090 (C≡C), and 1 600 cm^{-1} (C=C); τ (90 MHz) 3.96 (1 H, t, *J* 8 Hz, H^A), 5.77 (2 H, d, *J* 8 Hz, CH_2), 6.63 (1 H, s, C≡CH), and 8.86 (9 H, s, Bu^t).

Triphenyl-3-*t*-*butylpent*-2-*en*-4-*ynyl*)*phosphonium Bromide* (**12**).—To a stirred solution of triphenylphosphine (12.1 g, 46.1 mmol) in ethyl acetate (54 ml) at 5 °C was added dropwise a solution of the bromide (**34**) (7.50 g, 37.3 mmol) in ethyl acetate (5 ml) during 30 min under argon, and the mixture kept overnight at room temperature. The precipitate formed was collected by filtration, and washed with ethyl acetate, then with ether, to give the *salt* (**12**) (12.0 g, 69.4%). It formed white plates, m.p. 222—224 °C (from dry ethanol); τ (90 MHz; CF_3CO_2D) 2.0—2.5 (15 H, m, ArH), 4.07—4.30 (1 H, m, H^A), 5.68 (2 H, dd, *J* 15.5 and 7.5 Hz, CH_2), 6.67 (1 H, s, C≡CH), and 8.89 (9 H, s, Bu^t) (Found: C, 69.8; H, 6.1. $C_{27}H_{28}BrP$ requires C, 70.0; H, 6.1%).

1-(10-t-*Butyldodeca*-1,3,5,7,9-*pentaen*-11-*ynyl*)-6-(12-*t*-*butyltetradeca*-1,3,5,7,9,11-*hexaen*-13-*ynyl*)*cyclohepta*-1,3,5-*triene* (**18**).—To a stirred ylide solution, prepared from the salt (**12**) (3.89 g, 8.40 mmol) in dry THF (150 ml) and BuLi (1.69M; 10.0 ml) in hexane, at −72 °C was added dropwise a solution of the dialdehyde (**8**) (398 mg, 1.20 mmol) in dry THF (100 ml) during 3 h and the mixture was stirred for a further 30 min at room temperature before being worked up as for the isolation of (**13**). The product was chromatographed on alumina (4.2 × 12.5 cm). The fractions eluted with 30—40% ether in hexane afforded *compound* (**18**) (242 mg, 37.4%). It formed black needles, m.p. 115—116 °C (decomp.) (from hexane–benzene); $\lambda_{max.}$ 292 (ε 11 600), 359sh (53 900), 381 (96 300), 396 (107 000), and 458 nm (21 000); $\nu_{max.}$ 3 270 (C≡CH), 2 080 (C≡C), and 995 cm^{-1} (*E* C=C); τ (270 MHz) 3.07—3.88 (24 H, m, olefinic and 7-membered-ring H), 6.58 (2 H, s, C≡CH), 7.29 (2 H, s, CH_2), and 8.83 (18 H, s, Bu^t) (Found: C, 89.4; H, 8.5. $C_{41}H_{46}$ requires C, 91.4; H, 8.6%). Attempts to improve the elemental analysis failed.

17,18,19,20-*Tetradehydro*-16,21-*di*-*t*-*butyl*-1,6-*methano*[32]-*annulene* (**26**).—A solution of compound (**18**) (152 mg, 0.282 mmol) in pyridine and dry ether (3:1, 43 ml) was added dropwise during 2 h to a stirred solution of anhydrous copper(II) acetate (1.73 g) in pyridine and dry ether (3:1; 85 ml) at 52 °C. After being stirred for a further 1 h at 52 °C, the mixture was worked up as for the isolation of (**21**). The product was chromatographed on alumina (4.2 × 11 cm). The fractions eluted with 20% ether in hexane afforded the [32]-*annulene* (**26**) (57 mg, 38%). It formed brown needles, m.p. 165—166 °C (decomp.) (from hexane–benzene); *m*/*z* 536 (M^+, 5%) and 57 (100); *M*, 536.7; for u.v. data see Table 3; $\nu_{max.}$ 2 190 (C≡C) and 995 cm^{-1} (*E* C=C); τ (200 MHz) 2.98—3.93 (24 H, m, olefinic and 7-membered-ring H), 7.28 (2 H, s, CH_2), and 8.80 (18 H, s, Bu^t) (see Figure 2) (Found: C, 91.7; H, 8.1. $C_{41}H_{44}$ requires C, 91.7; H, 8.3%).

1,6-*Bis*-(12-*t*-*butyltetradeca*-1,3,5,7,9,11-*hexaen*-13-*ynyl*)-*cyclohepta*-1,3,5-*triene* (**19**).—To a stirred ylide solution, prepared from the salt (**12**) (2.70 g, 5.88 mmol) in dry THF (120 ml) and BuLi (1.69M; 4.6 ml) in hexane, at −63 °C was added dropwise a solution of the dialdehyde (**9**) (350 mg, 0.98 mmol) in dry THF (200 ml) during 1.5 h, and the mixture was stirred for 30 min at −63 °C, and for a further 2 h at room temperature, before being worked up as for the isolation of (**16**). The product was passed through a short column of alumina (4.2 × 4 cm). The fractions eluted with dichloromethane (200 ml) were collected and evaporated to give a dark red liquid, which was chromatographed on alumina (4.2 × 9 cm). The fractions eluted with 30—40% ether in hexane afforded *compound* (**19**) (319 mg, 57%). It formed black needles, m.p. 140—142 °C (decomp.) (from hexane–benzene); *m*/*z* (field desorption) 564 (M^+); *M*, 564.8; $\lambda_{max.}$ 248 (ε 12 100), 302 (10 500), 375sh (63 100), 393 (112 000), 412 (145 000), and 480sh nm (20 600); $\nu_{max.}$ 3 280 (C≡CH), 2 090 (C≡C), and 995 cm^{-1} (*E* C=C); τ (200 MHz) 3.10—3.89 (26 H, m, olefinic and 7-membered-ring H), 6.57 (2 H, s, C≡CH), 7.29 (2 H, s, CH_2), 8.80 (9 H, s, Bu^t), and 8.83 (9 H, s, Bu^t) (Found: C, 91.7; H, 8.4. $C_{43}H_{48}$ requires C, 91.4; H, 8.6%).

19,20,21,22-*Tetradehydro*-18,23-*di*-*t*-*butyl*-1,6-*methano*[34]-*annulene* (**27**).—A solution of compound (**19**) (147 mg, 0.26 mmol) in pyridine and dry ether (3:1; 80 ml) was added dropwise during 2.5 h to a stirred solution of anhydrous copper(II) acetate (2.0 g) in pyridine and dry ether (3:1; 120 ml) at 52 °C. After being stirred for a further 1.5 h at 52 °C, the mixture was worked up as for the isolation of (**21**). The product was chromatographed on alumina (4.2 × 11 cm). The fractions eluted with 30% dichloromethane in ether afforded the [34]-*annulene* (**27**) (65 mg, 44%). It formed dark brown needles, m.p. 235—237 °C (decomp.) (from benzene); *m*/*z* 563 (M^+, 13%) and 57 (100); *M*, 562.8; for u.v. data see Table 3; $\nu_{max.}$ 2 175 (C≡C) and 995 cm^{-1} (*E* C=C); τ (270 MHz) 3.17—3.39 (14 H, m, H^A, H^G, H^2, H^C, H^E, H^K, and H^I), 3.51—3.55 (2 H, m, H^1), 3.83—3.96 (4 H, m, H^J and H^B), 4.19—4.38 (6 H, m, H^H, H^F, and H^D), 7.78 (2 H, s, CH_2), and 8.74 (18 H, s, Bu^t) (see Figure 1) (Found: C, 91.7; H, 8.1. $C_{43}H_{46}$ requires C, 91.8; H, 8.2%).

1,6-*Bis*-(14-*t*-*butylhexadeca*-1,3,5,7,9,11,13-*heptaen*-15-*ynyl*)-*cyclohepta*-1,3,5-*triene* (**20**).—To a stirred ylide solution, prepared from the salt (**12**) (2.98 g, 6.44 mmol) in dry THF (230 ml) and BuLi (1.69M; 3.8 ml) in hexane, at −72 °C was added dropwise a solution of the dialdehyde (**10**) (375 mg, 0.92 mmol) in dry THF (150 ml) during 2.5 h, and the mixture was stirred for 30 min at −72 °C. After being stirred for a further 1.5 h at room temperature, the mixture was passed through a short column of alumina (4.4 × 50 cm). The fractions eluted with dichloromethane (500 ml) were collected and evaporated to give a dark red liquid, which was chromatographed on alumina (4.2 × 11 cm). The fractions eluted with 80—90% ether in hexane afforded *compound* (**20**) (283 mg, 50%). It formed black needles, m.p. 132—134 °C (decomp.) (from hexane–benzene); $\lambda_{max.}$ 316 (ε 9 430), 392sh (66 700), 411 (108 000), 430 (131 000), and 495sh nm (23 200); $\nu_{max.}$ 3 280 (C≡CH), 2 080 (C≡C), and 1 000 cm^{-1} (*E* C=C); τ (200 MHz) 3.09—3.88 (30 H, m, olefinic and 7-membered-ring H), 6.56 (2 H, br s, C≡CH), 7.27 (2 H, s, CH_2), 8.80 (9 H, s, Bu^t), and 8.84 (9 H, s, Bu^t) (Found: C, 91.0; H, 8.5. $C_{47}H_{52}$ requires C, 91.5; H, 8.5%). Attempts to improve the elemental analysis failed.

21,22,23,24-*Tetradehydro*-20,25-*di*-*t*-*butyl*-1,6-*methano*[38]-*annulene* (**28**).—A solution of compound (**20**) (166 mg, 0.27 mmol) in pyridine and dry ether (3:1; 80 ml) was added dropwise during 2.5 h to a stirred solution of anhydrous copper(II) acetate (3.0 g) in pyridine and dry ether (3:1; 128 ml) at 52 °C. After being stirred for a further 1.5 h at 52 °C, the mixture was worked up as for the isolation of (**21**). The product was chromatographed on alumina (4.2 × 12 cm). The fractions

eluted with ether–dichloromethane (1:1) afforded the [38]-*annulene* (**28**) (49 mg, 30%). It formed dark brown microcrystals, m.p. 205—207 °C (decomp) (from benzene); *m/z* 614 (M^+, 2%) and 78 (100); *M*, 614.8; for u.v. data see Table 3; $\nu_{max.}$ 2 180 (C≡C) and 1 000 cm^{-1} (*E* C=C); τ (270 MHz) 3.28—3.68 (22 H, m, H^1, H^2, H^A, H^C, H^E, H^G, H^I, H^K, H^M, H^B, and H^L), 3.93—4.10 (8 H, m, H^D, H^F, H^H, and H^J), 7.60 (2 H, s, CH_2), and 8.76 (18 H, s, Bu^t) (see Figure 1) (Found: C, 91.6; H, 8.2. $C_{47}H_{50}$ requires C, 91.8; H, 8.2%).

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References

1 E. Hückel, *Z. Physik*, 1931, **70**, 204; *Z. Elektrochem.*, 1937, **43**, 751; 'Grundzüge der Theorie ungesättigter und aromatischer Verbindungen,' Verlag Chemie, Berlin, 1938.
2 M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, 1965, **87**, 685.
3 M. Iyoda and M. Nakagawa, *Tetrahedron Lett.*, 1973, 4743.
4 B. W. Metcalf and F. Sondheimer, *J. Am. Chem. Soc.*, 1971, **93**, 5271.
5 J. Ojima, E. Ejiri, T. Kato, S. Kuroda, S. Hirooka, and M. Shibutani, *Tetrahedron Lett.*, 1986, **27**, 2467; J. Ojima, E. Ejiri, T. Kato, M. Nakamura, S. Kuroda, S. Hirooka, and M. Shibutani, *J. Chem. Soc., Perkin Trans. 1*, 1987, 831.
6 Part of this work has been reported in a preliminary form, J. Ojima, S. Fujita, M. Masumoto, E. Ejiri, T. Kato, S. Kuroda, Y. Nozawa, and H. Tatemitsu, *J. Chem. Soc., Chem. Commun.*, 1987, 534.
7 See, for example, F. Sondheimer, *Pure Appl. Chem.*, 1971, **28**, 331; *Acc. Chem. Res.*, 1972, **5**, 81; M. Nakagawa, *Pure Appl. Chem.*, 1975, **44**, 885.
8 T. M. Cresp, M. V. Sargent, and P. Vogel, *J. Chem. Soc., Perkin Trans. 1*, 1974, 37.
9 S. Tomita and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 302.
10 D. Lloyd, 'Non-benzenoid Conjugated Carbocyclic Compounds,' Elsevier, Amsterdam, 1984, pp. 295.
11 O. Isler, L. H. Chopard-did-Jean, M. Montavon, R. Rüegg, and P. Zeller, *Helv. Chim. Acta*, 1957, **40**, 1256.
12 M. Iyoda, S. Tanaka, Y. Aso, and M. Nakagawa, *Chem. Lett.*, 1984, 2001.
13 K. Yamamoto, S. Kuroda, Y. Nozawa, S. Fujita, and J. Ojima, *J. Chem. Soc., Chem. Commun.*, 1987, 199; K. Yamamoto, S. Kuroda, M. Shibutani, Y. Yoneyama, J. Ojima, S. Fujita, E. Ejiri, and K. Yanagihara, following paper.
14 For example, see E. Vogel, *Pure Appl. Chem.*, 1982, **54**, 1015.
15 P. J. Garratt and K. Grohmann in Houben-Weyl, 'Methoden der Organischen Chemie,' Georg Thieme Verlag, Stuttgart, 1972, vol. 4, Id, pp. 533—535.

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