Synthesis of 1,6-diethynylcyclohepta-1,3,5-triene and its oxidative coupling to dimethano-bridged octadehydro[20]annulene and trimethano-bridged dodecadehydro[30]annulene

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1,6-Diethynylcyclohepta-1,3,5-triene 27 was synthesized from 1,6-diacetylcyclohepta-1,3,5-triene 24. Oxidative coupling of the diacetylene 27 with copper(ii) acetate in pyridine (Eglinton conditions) led to the cyclic 'dimer', a dimethano-bridged octadehydro[20]annulene 28, in 18% yield and the cyclic 'trimer', a trimethano-bridged dodecadehydro[30]annulene 29, in 19% yield. Both compounds 28 and 29 consisted of an equilibrating mixture of two conformers which differed in the relative disposition of the methano bridges. Oxidative coupling of compound 27 with oxygen, copper(i) chloride and ammonium chloride (Glaser conditions) afforded 2,3,4,5-tetrachloro-1,6-methano[10]annulene 32 in 3.5% yield together with compounds 28 and 29.

Introduction

Recently, acyclic and cyclic polyalkynes carrying a conjugated carbon backbone have become the subject of increasing studies because of their potentially useful optical and electronic properties.[1] Among them, cyclic compounds incorporating 1,3-diyne groupings, which normally form a straight rod consisting of six carbon atoms but are sometimes bent because of ring formation, have been synthesized by the oxidative coupling of terminal diacetylenes under either Eglinton conditions[2] or Glaser conditions.[3] However, the mechanisms of these two coupling reactions were not studied in detail.[3]

A variety of nonfused and fused 1,5-diynes have been subjected to the oxidative coupling under either Eglinton or Glaser conditions. Hexa-1,5-diyne 1 and (Z)-hex-3-ene-1,5-diyne 4 gave the corresponding cyclic trimers 2[4] and 5[5] but no cyclic dimers under Eglinton conditions, while hexa-1,5-diyne 1 afforded the cyclic dimer 3 under Glaser conditions.[6] On the other hand, o-diethynylbenzene 6, 1,2-diethynylcyclohexene 8 and 9,10-diethynylphenanthrene 10 gave the corresponding cyclic dimers 7,[7,8] 9[9] and 11[10] respectively in high yields, but no cyclic trimers under Eglinton conditions. Among other fused diynes, 1,8-diethynylanthracene 12 afforded the cyclic dimer 13[11] under Eglinton conditions, while 1,8-diethynylnaphthalene 14 gave the cyclic dimer 15[12] under Glaser conditions.

Preferential formation of the cyclic trimers 2 and 5 from the nonfused 1,5-diynes 1 and 4, and of the cyclic dimers 13 and 15 from the 1,8- 12 and 1,6-diynes 14 may be reasonable because the two ethynyl groups in the starting diynes have the relative orientation suitable for cyclization and thus the formed cyclic compounds are almost strain free. However, the exclusive formation of the highly strained cyclic dimers 7, 9 and 11 from the fused 1,5-diynes 6, 8 and 10, respectively, is surprising. The presence of six-membered rings such as benzene and cyclohexene in fused diynes may presumably be responsible for the differential results, although the exact reason for this difference is unknown.

It is therefore quite interesting to study the product(s) in the oxidative coupling reaction of 1,6-diethynylcyclohepta-1,3,5-

triene 27. On the basis of the most stable boat conformation of the parent cyclohepta-1,3,5-triene, the two ethynyl groups of substrate 27 form an angle of ~80°, which is even greater than the corresponding angles of ~60° in hexa-1,5-diyne 1 and (Z)-hex-3-ene-1,5-diyne 4. However, compound 27 is conformationally flexible so that the angle may easily decrease to allow formation of the cyclic dimer.

Another feature of interest is that the Glaser couplings often afford chlorine-containing compounds as well as the normal coupling products.[9,13]

In a previous paper, we have reported unexpected formation of annulenediones 20–22 containing a 1,4-dichlorobutatriene moiety from a series of the symmetrical diketones 17–19 carrying terminal acetylene groups under Glaser conditions.[14] We have also found the formation of the tricyclic annulenediones 23 containing two and three chlorine atoms from the unsymmetrical diketone 16.[15] These were the first reports in which oxidation products containing chlorine atoms were characterized in the Glaser coupling. It is of interest to study whether chlorine-containing product(s) is/are obtained in the Glaser coupling of compound 27.

Bearing these in mind we studied the synthesis of 1,6-diethynylcyclohepta-1,3,5-triene 27 and its oxidative coupling under both Eglinton and Glaser conditions.

Results and discussion

Synthesis

The starting material for the synthesis of compound 27 was 1,6-diacetylcyclohepta-1,3,5-triene 24, which was prepared by the method of Vogel et al.[16] Treatment of the diacetyl derivative 24 under Vilsmeier conditions[17] gave the dialdehyde 25 in 12% yield. The (Z)-configuration of the two newly formed double bonds was confirmed by NOE (nuclear Overhauser enhancement) between the methylene protons and H[A].[18] Treatment of compound 25 with aq. potassium hydroxide in N,N-dimethylformamide (DMF)[17b] caused dehydrochlorination to afford the monoaldehyde 26 in 46% yield with concomitant release
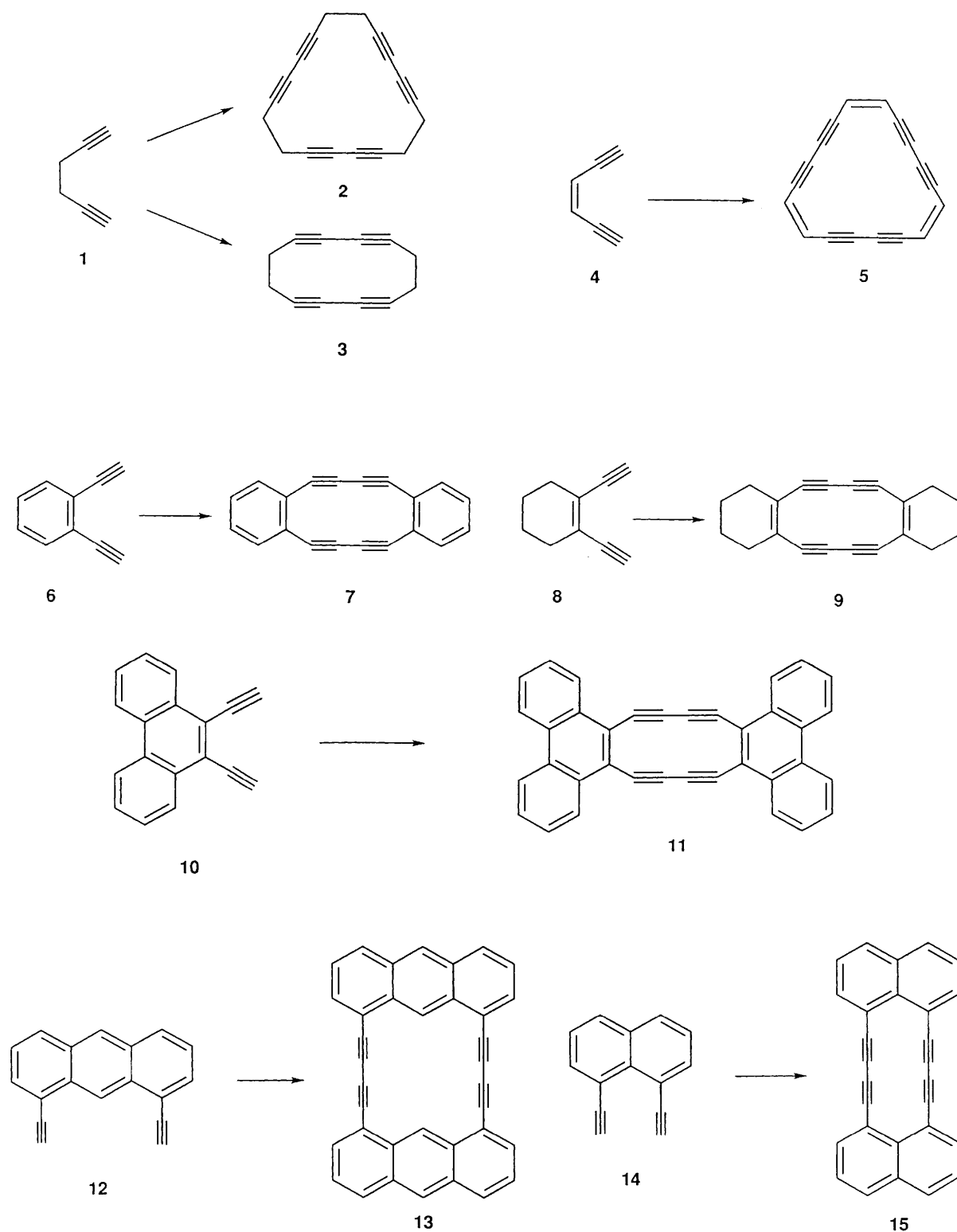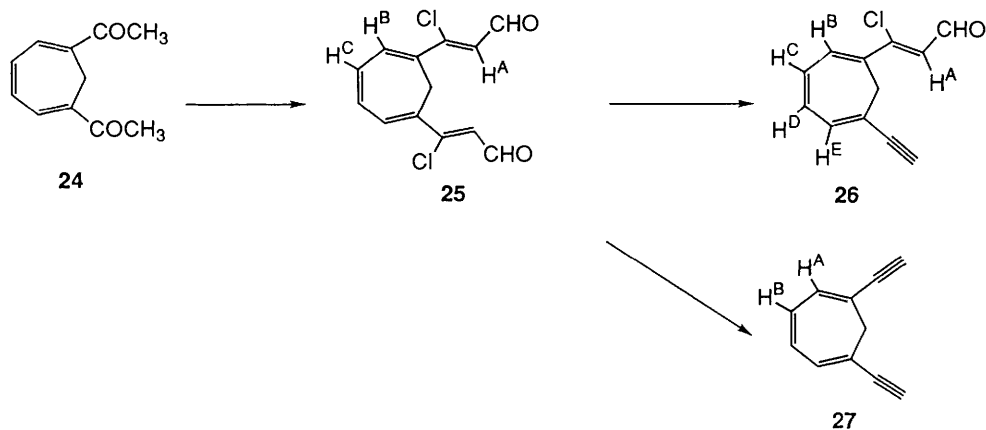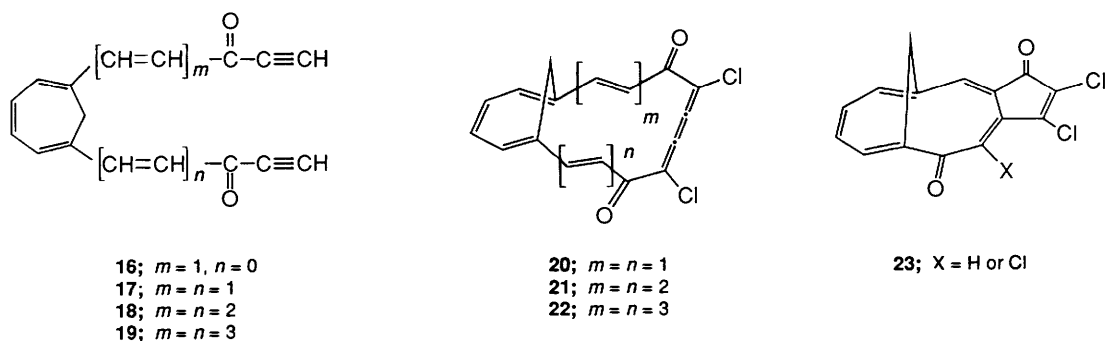
of carbon monoxide, but treatment of **25** with aq. sodium hydroxide in 1,4-dioxane–water[17c] afforded the diacetylene **27** in 75% yield as a somewhat unstable red liquid (Scheme 1).
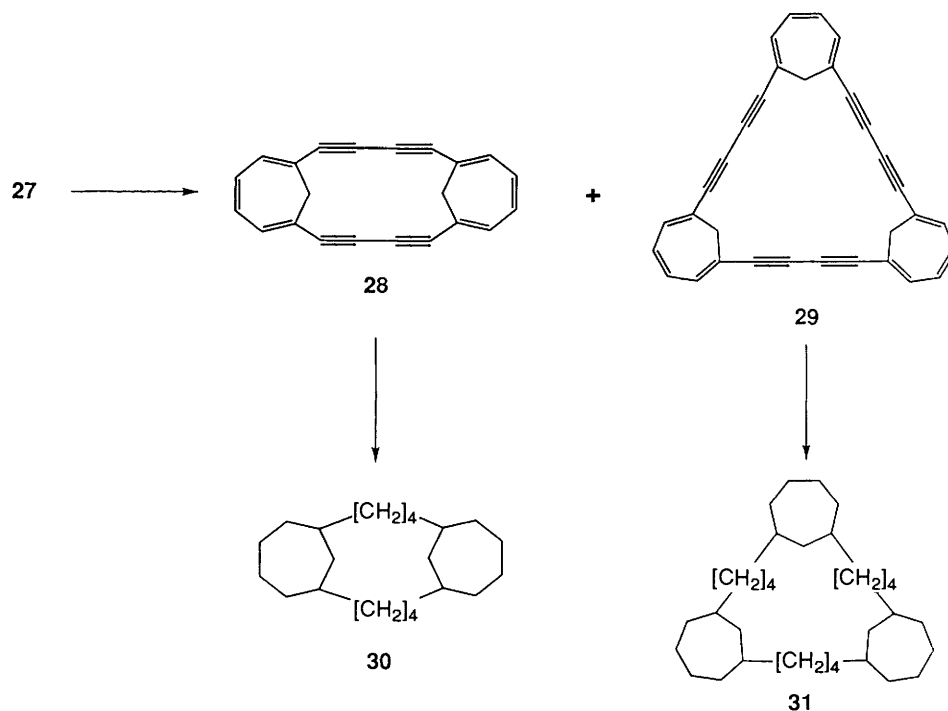
Oxidative coupling of the diacetylene **27** with copper(II) acetate monohydrate in pyridine (Eglinton conditions)[2] at 48 °C for 0.5 h led to the cyclic dimer, 7,8,9,10,17,18,19,20-octadehydro-1,6:11,16-dimethano[20]annulene **28** in 18% yield and the cyclic trimer, 7,8,9,10,17,18,19,20,27,28,29,30-dodecadehydro-1,6:11,16:21,26-trismethano[30]annulene **29** in 19% yield (Scheme 2). Both compounds **28** and **29** proved

to be relatively stable on exposure to air and light at room temperature.

Oxidative coupling of compound **27** was also attempted using anhydrous copper(II) acetate in pyridine–diethyl ether since it was found that oxidative coupling of a compound carrying two terminal acetylenes to give the corresponding monomeric product proceeds in higher yield when anhydrous copper(II) acetate is employed instead of its monohydrate.[19] Upon use of this procedure compound **27** afforded the cyclic dimer **28** in 30% yield and the cyclic trimer **29** in 5% yield. Thus, the yield of

16; $m = 1, n = 0$
17; $m = n = 1$
18; $m = n = 2$
19; $m = n = 3$

20; $m = n = 1$
21; $m = n = 2$
22; $m = n = 3$

23; X = H or Cl

Scheme 1

Scheme 2

the dimer **28** was improved using anhydrous copper(II) acetate, whilst the yield of the trimer **29** decreased.

Exhaustive hydrogenation of hexaenetetrayne **28** in ethyl acetate over a platinum catalyst yielded the saturated tricyclic compound **30** in 87% yield as a liquid. Mass spectrum of **30** showed the expected relative molecular mass (304) while ^{1}H and

^{13}C NMR spectra were complex, indicating the presence of various stereoisomers. Hydrogenation of compound **29** yielded the saturated tetracyclic compound **31** in 74% yield as a mixture of stereoisomers.

Attempts to prepare charge-transfer (CT) complexes of compounds **28** and **29** with 7,7,8,8-tetracyanoquinodimethane
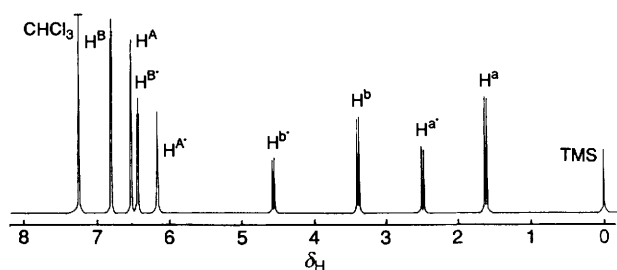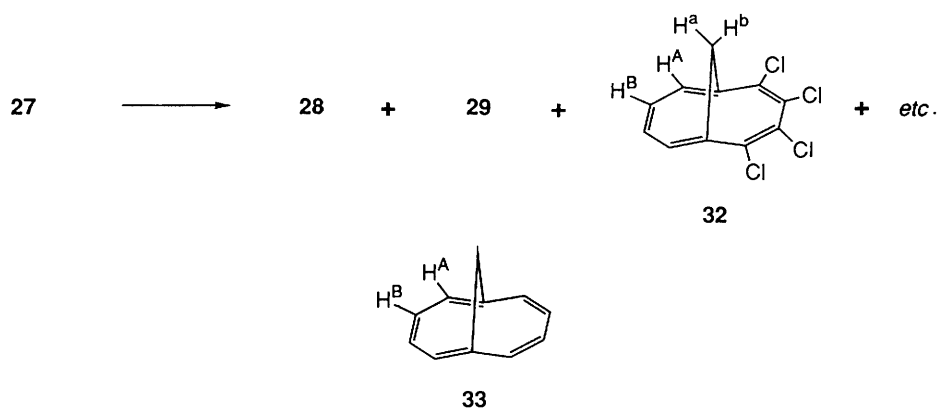
27 ⟶ 28 + 29 + [structure] + etc.

32

33

Fig. 1 400 MHz ^{1}H NMR spectra of compound **28** at 26 °C in $CDCl_3$

Fig. 2 Time dependence at -4 °C of the olefinic proton region of the sample prepared by dissolving crystalline **28** in $CDCl_3$ at ~ -20 °C. Only the signals due to isomer **28a** are observed at $t = 0$. Peaks marked $\times$ are due to impurities.

or 2,4,7-trinitro-9-fluorenone were unsuccessful presumably owing to the presence of the methano-bridges or the weak π-donor property of compounds **28** and **29**.

Glaser coupling[3] was carried out by bubbling oxygen through a mixture of the diacetylene **27**, copper(I) chloride and ammonium chloride in aq. ethanol–benzene with conc. hydrochloric acid at 60 °C. Column chromatography of the reaction mixture on alumina afforded yellow needles in 3.5% yield from the initial fractions eluted with hexane. The product was identified as 2,3,4,5-tetrachloro-1,6-methano[10]annulene **32** from its spectral data and elemental analysis. In particular, the ^{1}H NMR spectrum of compound **32** showed a similar pattern to that for 1,6-methano[10]annulene **33** prepared by Vogel et al.[20] The later fractions from the chromatography afforded the cyclic dimer **28** and the cyclic trimer **29**.

^{1}H NMR spectra of compounds 27–29 and 32
The ^{1}H NMR parameters for compounds **27–29** and **32** are listed in Table 1 together with those of the closely related compound **33**;[20] the spectra of compounds **28** and **29** are illustrated in Figs. 1 and 3 respectively, together with the signal assignments. Fig. 1 shows that compound **28** exists in $CDCl_3$ at 26 °C as a mixture of two isomers in the ratio ~ 5:3. Structures **28a** and **28b**, which differ in the relative disposition of the two methano bridges, are tentatively assigned to these isomers. The methylene protons are diastereotopic in either isomer. The higher-field doublet is assigned to H^a located above the seven-membered ring while the lower-field doublet assigned to H^b shows further splitting due to W-letter coupling with H^A.

We can estimate the extent of paratropicity of the two isomers expected of a 20π-electron system. The olefinic protons $H^{A'}$ and $H^{B'}$ of the minor isomer **28b** resonate at higher field than those of the reference compound **27**, while the methylene protons resonate at lower field (by 0.86 ppm on average). On the other hand, in the major isomer **28a** neither the upfield shift of the olefinic protons nor the downfield shift of the methylene protons is observed. Therefore we conclude that the minor
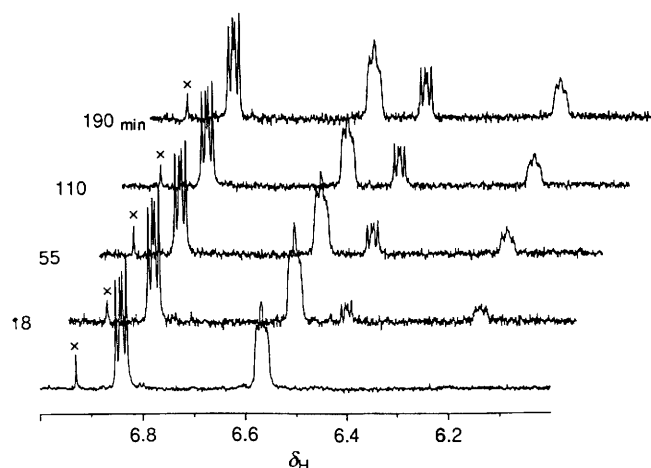
isomer **28b** shows paratropicity, while the major isomer **28a** is atropic.

We have recently reported that the syn-isomer **34a** of the tetradehydrodimethano[21]annulenone showed paratropicity, while the anti-isomer **34b** did not.[21] Thus, the molecular skeleton of the syn-isomer **34a** was inferred to be more planar than that of the anti-isomer **34b**. By analogy with this finding we suppose that the minor isomer **28b** showing paratropicity must be the syn-isomer, while the major isomer **28a** without tropicity would be the anti-isomer.

When a crystalline sample of compound **28** was dissolved in $CDCl_3$ below -20 °C and the solution was immediately subjected to NMR measurement at -20 °C, only the signals due to the major isomer **28a** were observed. This clearly indicates that compound **28** exists as a single conformer in the crystalline state. In solution at higher temperatures compound **28** gradually isomerized, finally to afford an equilibrium mixture of two isomers **28a** and **28b** (Fig. 2). Kinetic analysis of the isomerization as a first-order reversible reaction gave the rate constant for the conversion from isomer **28a** into isomer **28b** as 9.1×10^{-5} s^{-1} at -4 °C with an equilibrium constant **[28b]/[28a]** of 0.51. The rate constant corresponds to a free energy of activation of 20.7 kcal mol^{-1}.†

These findings suggested that X-ray crystallographic analysis of compound **28** would afford a final conclusion as to the

† 1 cal = 4.184 J.

28a   28b

34a   34b
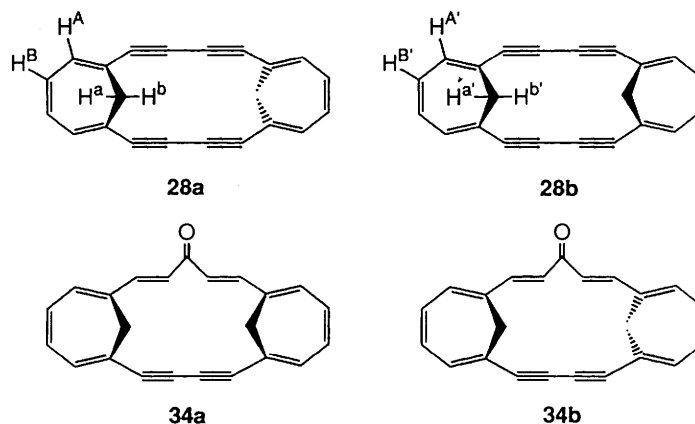
Table 1 ¹H NMR chemical shifts (δ) of compounds 27–29, 32 and 33[a,b]

Compd.	H^A (H^A')	H^B (H^B')	H^a (H^a', H^a'')	H^b (H^b', H^b'')	C≡CH
27		6.579s		2.664s	2.879s
28a	6.534m	6.813m	1.620d (11.6)	3.384dt (11.6, 1.2)	
28b	6.174m	6.439m	2.488d (11.6)	4.561dt (11.6, 1.2)	
29		6.668s		2.629s	
29a[c]		6.75s	1.85d (12.8)	2.93d (12.8)	
29b[c]		6.65s	2.01 1 H br / 2.06 2 H br	3.21 1 H br / 3.23 2 H br	
32	7.22–7.15m	7.79–7.71m	−0.011d (10.7)	0.183d (10.7)	
33[d]		7.5–6.8m	−0.5s		

[a] Obtained at 400 MHz in CDCl₃ at ambient temperature unless otherwise stated. [b] J Values (Hz) are given in parentheses. [c] At 600 MHz in CD₂Cl₂ at −85 °C. [d] See ref. 20.

syn/anti disposition of the compound and thus the relation between tropicity and conformation. However, our extensive efforts to grow crystals suitable for X-ray crystallography have so far been unsuccessful.

In order to obtain further information on the interconversion between the isomers of compound **28**, ¹H NMR spectra were measured at high temperatures. At 85 °C the methylene signals showed slight broadening, but at higher temperatures extensive decomposition of the sample took place and no information on the exchange rates was obtained. Thus we relied on saturation-transfer experiments.[22] At 62 °C, irradiation of the H^A' signal of the minor isomer **28b** at δ 6.17 caused a decrease in the intensity of the signal at δ 6.53 due to H^A of the major isomer **28a**. Quantitative analysis of the dependence of the signal intensity upon the duration of the irradiation afforded a rate constant of 0.33 s⁻¹ for the conversion of **28a** into **28b** at this temperature, which correspond to a $\Delta G^{\ddagger}$-value of 20.4 kcal mol⁻¹. The equilibrium constant was 0.57 at 62 °C. The similar values of the free energy of activation obtained at −4 and 62 °C may be reasonable because the entropy of activation is usually very small for conformational interconversion.

The spectra of compound **29** at 26 °C and at −85 °C are shown in Figs. 3(a) and 3(b) respectively. The methylene protons appeared as a sharp singlet at 26 °C, indicating that the flipping of the methylene bridge is rapid on the NMR time-scale. At −85 °C, the flipping is significantly frozen on the NMR time-scale. The spectrum shows that the compound exists as a mixture of two isomers in the ratio ~ 3:1. In the major isomer the methylene protons afford one pair of sharp doublets, indicating that all three methano bridges are on the same side of the average plane of the macrocyclic ring and thus this is the

29a

29b
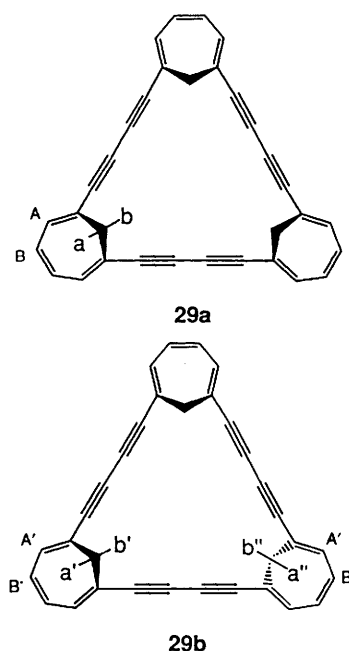
syn-isomer **29a**. In the minor isomer the flipping is not yet completely frozen at −85 °C and the methylene protons appear as two pairs of broad peaks in an intensity ratio of 2:1, which indicates that one of the methano bridges is on the other side of
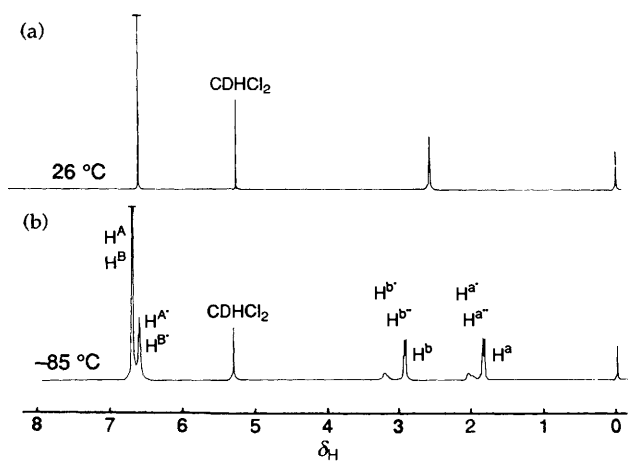
(a)

CDHCl₂

26 °C

(b)

Hᴬ
Hᴮ

Hᴬ'
Hᴮ'   CDHCl₂

Hᵇ'   Hᵃ'
Hᵇ''   Hᵃ''

−85 °C   Hᵇ   Hᵃ

8 7 6 5 4 3 2 1 0
δ_H

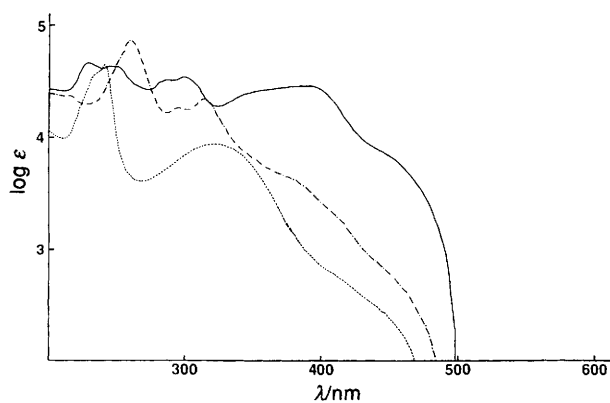Fig. 3   600 MHz ¹H NMR spectra of compound 29 (a) at 26 °C and (b) at −85 °C in CD₂Cl₂

Fig. 4 Electronic absorption spectra of compound 27 (-- -- --), compound 28 (— · — · —) and compound 29 (———) in THF

the plane of the macrocyclic ring from the remaining two, i.e. the anti-isomer 29b.

The olefinic protons of compound 29 accidentally afforded a singlet at ambient temperature and two singlets with a 3:1 intensity ratio at −85 °C, each peak corresponding to one isomer. Lineshape analysis of the signal at −66 °C gave a rough estimate of the rate constant as ~50 s⁻¹ for the conversion from the major isomer 29a to the minor isomer 29b, which corresponds to a free energy of activation of 10.4 kcal mol⁻¹.

Either isomer of compound 29 is concluded to be atropic since both the olefinic protons and the methylene protons of compound 29a or compound 29b show no appreciable shifts from those of the model compound 27.

The diatropicity of compound 32 expected for a 10π-electron system is smaller than that of the parent compound 33 since the methylene protons in compound 32 resonate at a lower field (~ 0.3 ppm on the average) than those of compound 33, as shown in Table 1. This is ascribed to two reasons; (i) the four adjacent chlorine atoms in compound 32 might distort the molecular planarity of compound 32, and (ii) the electron-withdrawing property of chlorine atoms might decrease the π-electron overlapping for conjugation.

Electronic spectra of compounds 27–29
The electronic absorption spectra of compounds 27–29 in tetrahydrofuran (THF) are shown in Fig. 4. As is seen from Fig. 4, the spectrum of compound 29 is similar in shape to that of compound 27 but differs in the wavelength and intensity of each

band, while the spectrum of compound 28 is different in shape from that of compound 27. This suggests that the conjugated π-electron systems of compounds 27 and 29 are almost identical and that of compound 29 is the extended one of compound 27 without perturbation, but the system of compound 28 is different from those of compounds 27 and 29.

Mechanism for the formation of compound 32
Our reports on the syntheses of compounds 20–23[14,15] were the first examples of formation of chlorine-containing annulene derivatives. A tentative mechanism for the formation of compound 23 was presented.[15] A similar mechanism would operate in the formation of compound 32 as given in Scheme 3.

Copper(I) chloride used in the Glaser coupling often contains copper(II) chloride as an impurity which may chlorinate the initially formed bis[copper(I) acetylide] 35 to give the bis(vinyl copper) 36. The tetrachloro derivative 36 may then cyclize to form bicycle 32 by radical coupling.

In summary, it was found from this study that the diethynyl compound 27 gives rise to the cyclic dimer and the cyclic trimer under both Eglinton and Glaser coupling conditions. If we consider that the diacetylene 27 is a nonfused compound and the cyclic dimer 28 is a less strained system than that (7) from o-diethynylbenzene, the finding may not be surprising.

Experimental
Mps were determined on a hot-stage apparatus and are uncorrected. IR spectra were taken with a JASCO-7300 spectrophotometer as KBr discs, unless otherwise specified; only significant maxima are described for compounds 25–29 and 32, but all the absorptions are shown for compounds 30 and 31. Electronic (UV-visible) spectra were measured in THF solution and run with a Shimadzu 2200A spectrophotometer. Mass spectra were recorded with a JEOL JMS-D 300 spectrometer operating at 75 eV using a direct-inlet system. ¹H NMR spectra at ambient temperature were recorded in CDCl₃ solutions with a JEOL FX-90Q (90 MHz), a JEOL GX-400 (400 MHz), a Bruker AM-500 (500 MHz) or a Bruker AM-600 (600 MHz) spectrometer, SiMe₄ (TMS) being used as internal standard. J Values are given in Hz. ¹³C NMR spectra were recorded as CDCl₃ solution on a GX-400, a AM-500 or a AM-600 at 100.40, 125.76 or 150.90 MHz with internal SiMe₄ as a reference.

Progress of all reactions was followed by TLC on Merck precoated silica gel. Alumina (Merck, activity II–III) and silica gel (Daiso gel 1001 W) were used for column chromatography. Compounds were preadsorbed from diethyl ether or benzene solution onto the adsorbent before column chromatography. Dry DMF was prepared by being stirred with calcium hydride overnight and then by distillation before use. Organic extracts were washed with saturated aq. sodium chloride and dried over anhydrous sodium sulfate prior to removal of solvent. Solvents were evaporated off under water-pump pressure. Ether refers to diethyl ether.

1,6-Bis[(Z)-1-chloro-2-formylethenyl]cyclohepta-1,3,5-triene 25
Phosphoryl trichloride (102 g, 0.67 mol) was added dropwise to dry, stirred DMF (280 cm³) during 30 min at room temperature and the solution was stirred for further 30 min at room temperature. To the resultant red solution was added dropwise during 10 min a solution of 1,6-diacetylcyclohepta-1,3,5-triene 24[16] (23.0 g, 0.14 mol) in dry benzene (30 cm³) and then the stirred mixture was kept at 40 °C for 2 days. The mixture was poured onto water (1000 cm³) and the resultant solution was neutralized (pH 7.0) by addition of solid NaHCO₃ in small
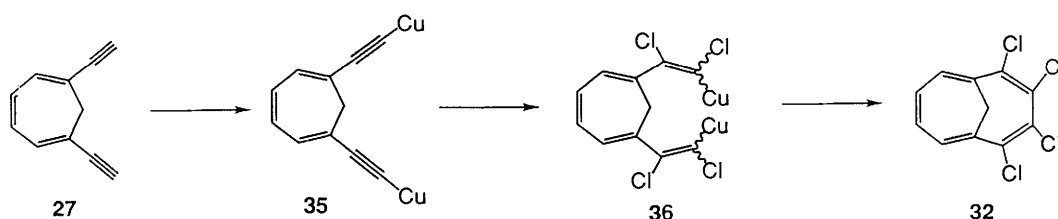
Scheme 3

portions. Then the mixture was filtered and the inorganic material residue was washed with water. The combined filtrate and washings were extracted with dichloromethane. The extracts were washed with saturated aq. $NaHCO_3$ and dried. The residual yellow solid obtained after removal of the solvent was chromatographed on silica gel (4.7 × 10.0 cm). The fractions eluted with hexane–benzene (1:4) afforded the *dialdehyde* **25** (4.1 g, 12%) as yellow needles, mp 149–150 °C (from hexane–benzene); m/z 268 (M^+, 5%) and 139 (100) ($C_{13}H_{10}Cl_2O_2$ requires M, 268.1); λ_{max}/nm 289 ($\varepsilon/dm^3\ mol^{-1}$ cm^{-1} 49 300) and 370 (7890); ν_{max}/cm^{-1} 2872, 2856, 2747 (CHO), 1671 (C=O) and 1596 and 1564 (C=C); δ_H(500 MHz) 10.176 (2 H, d, J 6.8, CHO), 7.16–7.10 (2 H, m, H^B), 6.97–6.91 (2 H, m, H^C), 6.491 (2 H, d, J 6.7, H^A) and 2.963 (2 H, s, CH_2); δ_C(125.67 MHz) 191.43 (t, CHO), 149.09 (q, ClC), 133.44 (t, CH^C), 130.74 (t, CH^B), 128.94 (q), 124.81 (t, CH^A) and 29.44 (s, CH_2) (Found: C, 58.35; H, 3.8. $C_{13}H_{10}Cl_2O_2$ requires C, 58.2; H, 3.8%).

(Z)-3-Chloro-3-(6-ethynylcyclohepta-1,3,5-trienyl)propenal 26
To a stirred solution of the dialdehyde **25** (708 mg, 2.6 mmol) in dry DMF (17 cm^3) was added dropwise aq. KOH (15 mol dm^{-3}; 0.2 cm^3) during 1 h at room temperature. After addition of benzene (100 cm^3), the mixture was poured onto water and extracted with benzene. The combined extracts were washed with brine and dried. The residue after removal of the solvent was chromatographed on silica gel (4.2 × 6.0 cm). The fractions eluted with hexane–benzene (1:1) afforded the *aldehyde* **26** (0.25 g, 46%) as red brown plates, mp 63–64 °C (from hexane–benzene); m/z 204 (M^+, 14%) and 139 (100) ($C_{12}H_9ClO$ requires M, 204.6); λ_{max}/nm 260sh (ε 19 000), 268 (20 200) and 341.5 (6310); ν_{max}/cm^{-1} 3262 (C≡CH), 2867, 2760 (CHO), 2088 (C≡C), 1656 (C=O), 1582 and 1562 (C=C); δ_H(90 MHz) 10.22 (1 H, d, J 6.8, CHO), 7.28–7.16 (1 H, m, H^E), 6.84–6.60 (4 H, m, H^A, H^B, H^C and H^D), 3.00 (1 H, s, C≡CH) and 2.75 (2 H, s, CH_2) (Found: C, 70.6; H, 4.6. $C_{12}H_9ClO$ requires C, 70.4; H, 4.4%).

1,6-Diethynylcyclohepta-1,3,5-triene 27
A solution of NaOH (3.0 g, 75 mmol) in a mixture of 1,4-dioxane–water (1:1; 45 cm^3) was heated to 60 °C and the dialdehyde **25** (1.90 g, 7.1 mmol) was added in one portion. The reaction mixture immediately turned dark. The mixture was stirred for 1.5 h at 60 °C, poured onto brine and extracted with dichloromethane. The extracts were washed with water and dried. The residue left after removal of the solvent was chromatographed on silica gel (3.1 × 3.5 cm). The fractions eluted with hexane afforded the *diacetylene* **27** (742 mg, 75%) as a red liquid; m/z 140 (M^+, 43%) and 139 (100) ($C_{11}H_8$ requires M, 140.1); λ_{max}/nm 234sh (ε 37 200), 240 (44 800) and 318 (8740) and see Fig. 4; ν_{max}(neat)/cm^{-1} 3310 (C≡CH), 2092 (C≡C) and 1597 (C=C); for ^1H NMR data see Table 1; δ_C(100.40 MHz) 132.40 (t, CH^A or CH^B), 131.02 (t, CH^B or CH^A), 113.36 (q), 85.48 (q, –C≡), 74.85 (t, ≡CH) and 37.53 (s,

CH_2) (Found: C, 94.1; H, 6.05. $C_{11}H_8$ requires C, 94.25; H, 5.75%).

Oxidative coupling of the diacetylene 27 with copper(II) acetate monohydrate in pyridine. 7,8,9,10,17,18,19,20-octadehydro-1,6:11,16-dimethano[20]annulene 28 and 7,8,9,10,17,18,19,-20,27,28,29,30-dodecadehydro-1,6:11,16:21,26-trimethano-[30]annulene 29
A solution of the diacetylene **27** (602 mg, 4.28 mmol) in pyridine (6.5 cm^3) was added during 30 min to a solution of copper(II) acetate monohydrate (9.00 g, 74.4 mmol) in pyridine (56 cm^3) preheated at 48 °C, and the solution was stirred for 0.5 h at 48 °C. Then the mixture was poured onto water and extracted with benzene. The combined extracts were washed successively with dil. HCl until they turned acidic to litmus, and then with aq. $NaHCO_3$ and brine, and were dried. The residue obtained after removal of the solvent was chromatographed on alumina (5.0 × 7.0 cm). The initial fractions eluted with hexane–benzene (98:2) afforded the cyclic dimer, *compound* **28** (106 mg, 18%), as yellow needles, mp 177–178 °C (decomp.) (from hexane–benzene); m/z 276 (M^+, 100%) ($C_{22}H_{12}$ requires M, 276.2); λ_{max}/nm 260 (ε 74 000), 294.5 (18 300) and 313 (22 400) and see Fig. 4; ν_{max}/cm^{-1} 2165 (C≡C) (Found: C, 95.6; H, 4.6. $C_{22}H_{12}$ requires C, 95.6; H, 4.4%); The ^1H NMR spectrum of compound **28** showed it to be a 5:3 mixture of two stereoisomers. For ^1H NMR data see Table 1, Figs. 1 and 2. The major isomer **28a**: δ_C(100.40 MHz) 131.20 (t), 127.56 (t), 110.09 (q), 89.44 (q, –C≡), 75.91 (q, –C≡) and 43.25 (s, CH_2); the minor isomer **28b**: δ_C 131.07 (t), 125.92 (t), 112.45 (q), 87.74 (q, –C≡), 75.47 (q, –C≡) and 47.05 (s, CH_2).

The later fractions eluted with 10% ether in hexane afforded the cyclic trimer, *compound* **29** (114 mg, 19%), as red needles, mp 198–202 °C (decomp.) (from hexane–benzene); m/z 414 (M^+, 9%) and 119 (100) ($C_{44}H_{18}$ requires M, 414.4); λ_{max}/nm 226 (ε 45 200), 228 (47 200), 234 (43 000), 245 (43 600), 249.5 (42 800), 287 (31 700), 299 (33 700), 342 (24 200) and 389 (28 500) and see Fig. 3; ν_{max}/cm^{-1} 2179 (C≡C) and 1586 (C=C) (Found: C, 95.8; H, 4.6. $C_{33}H_{18}$ requires C, 95.6; H, 4.4%). The ^1H NMR spectrum of compound **29** at − 85 °C showed it to be a 3:1 mixture of two stereoisomers. For ^1H NMR data see Table 1 and Fig. 3; δ_C(150.90 MHz) 134.14 (t, CH^A), 132.41 (t, CH^B), 112.88 (q), 84.65 (q, –C≡), 72.95 (q, –C≡) and 38.18 (s, CH_2).

Oxidative coupling of the diacetylene 27 with anhydrous copper(II) acetate in pyridine–ether [19]
A solution of the diacetylene **27** (660 mg, 4.71 mmol) in pyridine–ether (3:1; 210 cm^3) was added to a solution of anhydrous copper(II) acetate (11.0 g, 61 mmol) in pyridine–ether (3:1; 140 cm^3) preheated at 55 °C. The mixture was worked up as for the isolation of compounds **28** and **29**. The product was chromatographed on alumina (5.2 × 4.0 cm). The initial fractions eluted with hexane afforded the cyclic dimer **28**

(198 mg, 30%). The later fractions eluted with hexane–ether (98:2) afforded the cyclic trimer **29** (33 mg, 5.1%).

Catalytic hydrogenation of compound 28 to give tricyclo-[14.4.1.1^{6,11}]docosane 30

Compound **28** (40 mg, 0.145 mmol) in stirred ethyl acetate (52 cm^3) was hydrogenated over pre-reduced platinum(IV) oxide (226 mg) for 2 h at room temperature under atmospheric pressure. Then the precipitates were filtered off and washed with ethyl acetate. The combined filtrate and washings were evaporated and the residue was chromatographed on alumina (2.0 × 9.0 cm). The fractions eluted with hexane afforded the *compound* **30** (38 mg, 87%) as a liquid; ν_{max}(neat)/cm^{-1} 2922, 2854, 2695, 1460, 1377, 1296 and 722; δ_H(90 MHz) 1.73–0.75 (m) (Found: M$^+$, 304.3127; C, 86.5; H, 13.4. C$_{22}$H$_{40}$ requires M, 304.3127; C, 86.8; H, 13.2%).

Catalytic hydrogenation of compound 29 to give tetracyclo-[24.4.1.1^{6,11}.1^{16,21}]tritriacontane 31

Compound **29** (67.7 mg, 0.163 mmol) in stirred ethyl acetate (80 cm^3) was hydrogenated over pre-reduced platinum(IV) oxide (62 mg, 0.273 mmol) for 2 h at room temperature and the mixture was worked up as for the isolation of compound **30**. The product was chromatographed on alumina (2.3 × 9.0 cm). The fractions eluted with hexane afforded *compound* **31** (55.1 mg, 74%) as a liquid; ν_{max}(neat)/cm^{-1} 2921, 2853, 2692, 1460, 1364, 1284, 1091 and 724; δ_H(400 MHz) 1.70–0.80 (m) (Found: M$^+$, 456.4688; C, 86.9; H, 12.8. C$_{33}$H$_{60}$ requires M, 456.4693; C, 86.8; H, 13.2%).

2,3,4,5-Tetrachloro-1,6-methano[10]annulene 32

A solution of the diacetylene **27** (540 mg, 3.85 mmol) in benzene (10 cm^3)–ethanol (13 cm^3) was added dropwise during 30 min to a stirred solution of copper(I) chloride (14.0 g, 0.141 mol), ammonium chloride (20 g), water (53 cm^3) and conc. HCl (0.2 cm^3) at 60 °C. After stirring of the mixture for 5 min, further quantities of benzene (31 cm^3) and ethanol (9 cm^3) were added to the mixture. Then the mixture was stirred for 1 h at 60 °C whilst gaseous oxygen was bubbled through it. The mixture was then cooled, poured onto water and extracted with benzene. The combined extracts were washed successively with 2 mol dm^{-3} HCl and aq. NaHCO$_3$ and dried. The residue obtained after removal of the solvent was chromatographed on alumina (5.2 × 4.0 cm). The initial fractions eluted with hexane afforded the *tetrachloromethano*[10]*annulene* **32** (38 mg, 3.5%) as yellow needles, mp 97–98 °C (from hexane); *m/z* 282 [(M + 2)$^+$, 15%], 280 (M$^+$, 31), 279 [(M − 1)$^+$, 16], 278 [(M − 2)$^+$, 24] and 243 (100) (C$_{11}$H$_6$Cl$_4$ requires M, 280.0); λ_{max}/nm 249 (ε 12 500), 288.5 (44 000) and 343.5 (5100); ν_{max}/cm^{-1} 697 and 670 [(Z)-HC=CH]; for ^{1}H NMR data see Table 1; δ_C(100.40 MHz) 132.48 (q), 131.12 (t), 130.19 (t), 125.28 (q), 114.48 (q) and 33.29 (s, CH$_2$) (Found: C, 47.3; H, 2.3. C$_{11}$H$_6$Cl$_4$ requires C, 47.2; H, 2.2%).

The following fractions eluted with 1% ether in hexane afforded the cyclic dimer **28** (8.5 mg, 1.6%).

The later fractions eluted with 5% ether in hexane afforded a liquid (8.3 mg) which could not be identified owing to its instability for air and diffused light.

The final fractions eluted with 10% ether in hexane afforded the cyclic trimer **29** (23 mg, 4.3%).

Acknowledgements

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