

Synthesis of Methano-bridged Tetradehydro[36]annulene

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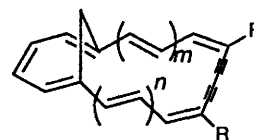
The title compound, 20,25-di-*tert*-butyl-21,22,23,24-tetradehydro-1,6-methano[36]annulene, was synthesized by the Wittig reaction of 1-(8-formylocta-1,3,5,7-tetraenyl)-6-(10-formyldeca-1,3,5,7,9-pentaenyl)cyclohepta-1,3,5-triene with triphenyl(3-*tert*-butylpent-2-en-4-ynyl)phosphonium bromide, followed by intramolecular oxidative coupling of the resulting acyclic diacetylenic compound. ¹H NMR and electronic spectral data suggest that the [36]annulene is atropic.

In our previous papers,^{1,2} we reported syntheses of a series of tetradehydromethanoannulenes 1–10 in which the ring size was increased systematically up to 38, in order to elucidate the upper limit of the ring size showing the ring current effect. We found that these methano-bridged tetradehydroannulenes show diatropism up to the 34-membered ring (compound 9) in the $[4n + 2]\pi$ -electron series and paratropism up to the 28-membered ring (compound 6) in $[4n]\pi$ -electron series, respectively, and that these compounds have high thermal and conformational stability, which is reasonably ascribed to considerable rigidity of the molecular skeleton imposed by the presence of the bridging methylene group and 1,3-diacetylenic linkage. The thermal stability enabled us to study the non-linear optical properties of these annulenes.³ However, in these studies the 36-membered ring has been missing.² Judging from the facts that both dia- and para-tropicity of the tetradehydromethanoannulenes 1–10 decreased with the increasing ring size, and that the [32]annulene 8 showed no ring current effect but was atropic,² it was predicted that the higher analogue of 8, the title [36]annulene 14 would also be atropic. To test this prediction and in connection with the study on non-linear optical properties of the two-dimensional conjugated system,⁴ the preparation of the tetradehydromethano[36]annulene 14 was required.

Results and Discussion

Synthesis.—The title [36]annulene 14 was synthesized according to the procedure reported for the lower homologues,² as illustrated in Scheme 1.

The Wittig reaction between 1-(8-formylocta-1,3,5,7-tetraenyl)-6-(10-formyldeca-1,3,5,7,9-pentaenyl)cyclohepta-1,3,5-triene 11⁵ and triphenyl(3-*tert*-butylpent-2-en-4-ynyl)phosphonium bromide 12² with butyllithium in tetrahydrofuran afforded the acyclic diacetylene 13 in 44% yield. The *E*-configurations for the newly formed double bonds of the isolated diacetylene 13 were confirmed by its IR spectrum and the ¹H chemical shifts of the acetylenic protons. Since compound 13 was unstable on exposure to diffused light and air, satisfactory elemental analysis was not obtained but its mass spectrum using the field-desorption method clearly showed the molecular ion peak. Intramolecular oxidative coupling of compound 13, carried out with copper(II) acetate monohydrate in pyridine-methanol under high dilution conditions with diethyl ether as an entraining solvent, gave rise to the monomeric cyclic product 14 in 36% yield. The formation of the monomeric product from compound 13 was confirmed by the

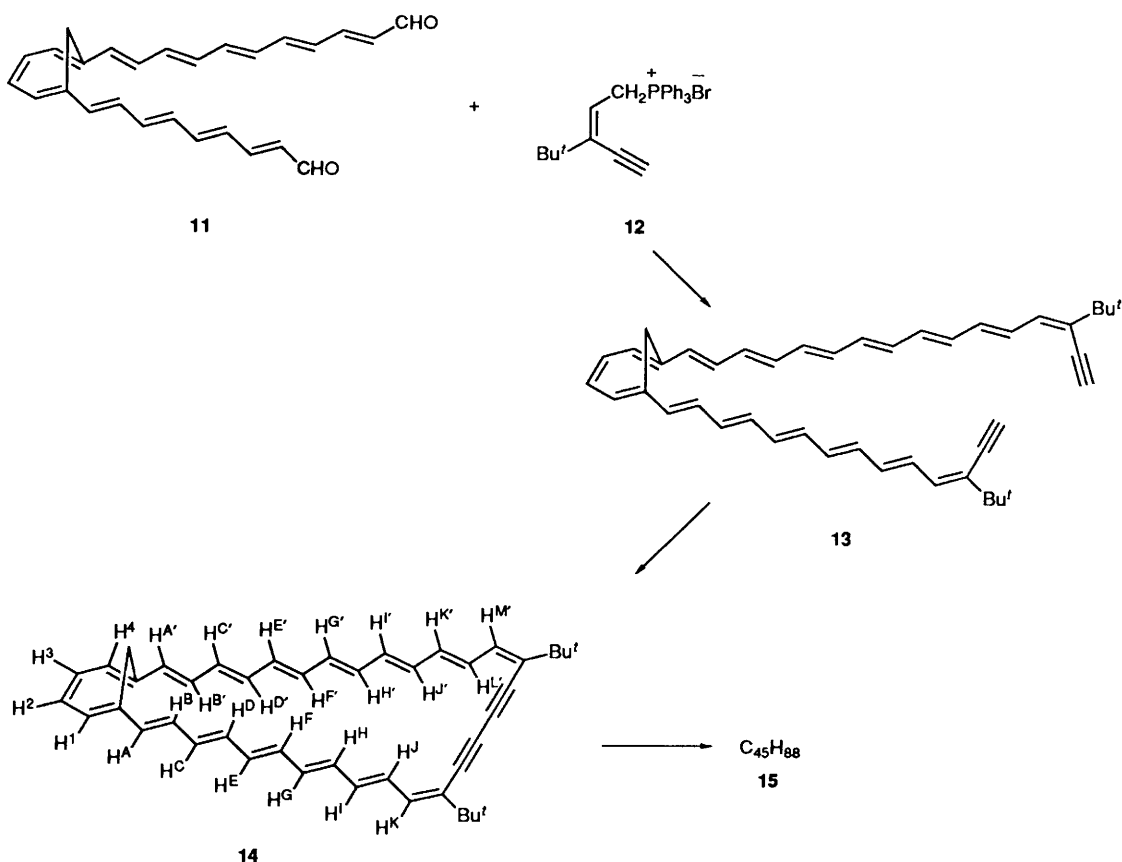


[18]-	1	R = Me, m = n = 1
[20]-	2	R = Me, m = 2, n = 1
[22]-	3	R = Me, m = n = 2
[24]-	4	R = Me, m = 3, n = 2
[26]-	5	R = Me, m = n = 3
[28]-	6	R = Me, m = 4, n = 3
[30]-	7	R = Me, m = n = 4
[32]-	8	R = Bu ^t , m = 5, n = 4
[34]-	9	R = Bu ^t , m = n = 5
[38]-	10	R = Bu ^t , m = n = 6

appearance of the molecular ion peak, m/z 589 ($M^+ + 1$), in the mass spectrum using the FAB method. The structural confirmation was further obtained by exhaustive hydrogenation of compound 14 to the corresponding saturated hydrocarbon, di-*tert*-butylmethanocyclohexatriacontane 15, which was obtained as colourless crystals with a low melting point and showed the molecular ion peak, m/z 629 (M^+), in the mass spectrum by the direct-inlet method. The tetradehydromethano[36]annulene 14 thus obtained was a black crystalline solid with a metallic lustre which was thermally more stable than monocyclic annulenes, dehydroannulenes⁶ and the corresponding methanoannulenes,⁷ as expected from the previous studies.^{1,2}

¹H NMR Spectral Study of Compound 14.—The ¹H NMR spectrum of the [36]annulene 14 is presented in Fig. 1 and the COSY spectrum of the olefinic protons is illustrated in Fig. 2.

Compound 14 has 28 olefinic protons and the structure shown by the formula predicts that 17 of these protons are located outside the macrocycle and 11 protons are inside. Integration of the olefinic proton signals indicated that the higher-field signals at δ 6.5–6.1 corresponded to 17 protons and the remaining lower-field signals at δ 7.6–6.8 amounted to 11 protons. This fact made us assume that the lower-field 11-proton signals were ascribed to the inner olefinic protons and the higher-field 17-proton signals to the outer protons. This hypothesis was supported by the COSY spectrum (Fig. 2),



Scheme 1

which clearly indicated that all the coupling partners of the lower-field signals at δ 7.6–6.8 were in the higher-field region of δ 6.5–6.1, although the individual assignments of the signals could not be made. In the previous studies,^{1,2} it was found that in the tetradehydromethanoannulenes 1–10 the inner olefinic protons near the cycloheptatriene ring and the 1,3-diacetylenic moiety always give their signals at a lower field than the other olefinic inner protons, owing to the local anisotropic effect of these moieties. Therefore, we can assign the lowest field doublet signal to the inner H^L proton. Next, we can assign the 3-proton signals at δ 7.4–7.2 to the H^B, H^J and H^B protons. Therefore, the remaining 7 proton signals at δ 7.1–6.8 are assigned to the other inner protons (H^D, H^D, H^F, H^F, H^H, H^H and H^J). The higher-field olefinic signals are assigned to the 17 outer olefinic protons. Of these, the multiplet centred at δ 6.45 will be assigned to the H² and H³ protons from the band shape, and the doublet at δ 6.40 is definitely assigned to H^M proton from the COSY data. Thus, it is apparent that the inner olefinic protons resonate to low field while the outer protons are to

high field. These results seem to suggest that the [36]annulene 14 is paratropic, as might be expected for a 36 π -electron system.

Our criterion on tropicity has been the difference in the proton chemical shifts between an annulene and the corresponding acyclic model compound. The [28]annulene 6 was concluded to be paratropic, as might be expected for a 28 π -electron system.² This followed from the fact that the outer protons (including methyl protons) in 6 resonated at a higher field than those of the corresponding protons in its precursor with two terminal acetylene groups, whereas the inner protons (including methylene protons) appeared at a lower field. By contrast, comparison of the chemical shifts of the protons of the [32]annulene 8 with those of the corresponding acyclic compound suggested that the [32]annulene 8 was atropic, since the resonances of compound 8 were at almost the same positions as those of the acyclic model.

The protons of the acyclic model compound 13 of the present [36]annulene 14 resonate at δ (CDCl₃) 6.84–6.17 (olefinic and 7-membered-ring H), 3.41 (C≡H), 2.71 (CH₂), 1.20 and 1.19 (Bu^t).

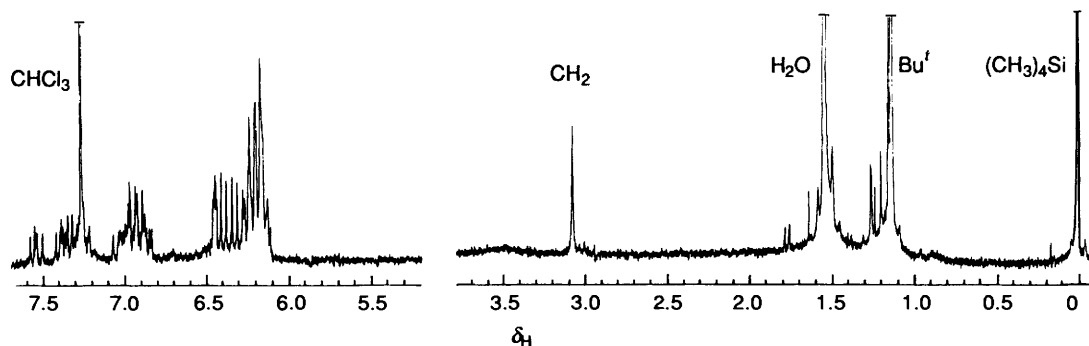


Fig. 1 ¹H NMR spectrum of the [36]annulene 14 in CDCl₃ at 22°C [360 MHz, δ values, internal standard, (CH₃)₄Si]

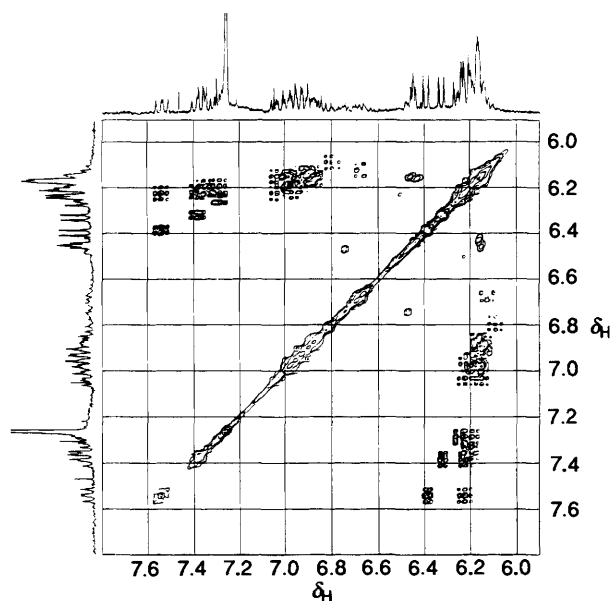


Fig. 2 The COSY spectrum of the olefinic protons of the [36]annulene 14 in CDCl_3 (500 MHz)

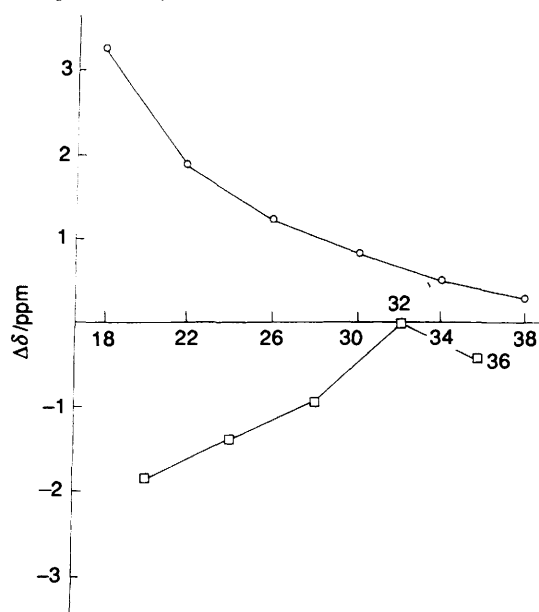


Fig. 3 A plot of chemical shift difference ($\Delta\delta$) of the methylene protons between the annulenes 1–10, 14 and the corresponding acyclic models vs. the ring size of the annulenes 1–10, 14

The inner protons in compound 14 resonate at a lower field than the corresponding protons in compound 13. Also, the inner methylene bridge proton signal appears at δ 3.10 and is at a lower field than those of the acyclic model compound 13 (δ 2.71) and the atropic [32]annulene 8 (δ 2.72).² However, the outer protons in compound 14 resonate at δ 6.5–6.1, almost the same position as the corresponding protons in compound 13. Various factors other than tropicity would contribute to the proton chemical shifts. Among them are the local anisotropy effects mentioned above, which mainly affect the chemical shifts of the inner protons. Thus, the chemical shifts of the outer protons seem to be more reliable as the criterion of tropicity. Therefore, it is most reasonable to conclude that compound 14 is atropic.

The signals of the bridged methylene protons always appear as a singlet in the tetrahydromethanoannulenes 1–10,^{1,2} indicating that flipping of the methano bridge through the average plane of the macrocycle takes place rapidly on the

NMR time scale. This feature is in contrast to the one in multi-bridged annulenes⁸ and methanoannulenes,⁷ in whose spectra the methylene protons usually appear as two doublets even at room temperature.

Fig. 3 shows a plot of the chemical shift differences ($\Delta\delta$) of the bridged methylene protons between 1–10, 14 and their corresponding acyclic models versus the ring size of the annulenes 1–10, 14.⁹ We can see from Fig. 3 that the chemical shift differences ($\Delta\delta$) in the $[4n + 2]\pi$ - and $[4n]\pi$ -systems tends downward and upward, respectively, with the increasing ring size, and in the latter case reaches zero at the 32-membered ring, and again tends to downward at the 36-membered ring. Thus, in these annulene series 1–10 and 14, the $[4n + 2]\pi$ -electron system gives a smooth correlation between the degree of tropicity and the chemical shift difference ($\Delta\delta$) of the methylene protons, while such a smooth correlation is not obtained in the $[4n]\pi$ -electron system. This may not be surprising if we admit that tropicity is not the only factor affecting the chemical shifts.

Electronic Spectrum of Compound 14.—The main absorption maxima (the strongest absorption maxima) of the annulenes 1–10 and 14 are listed in Table 1,^{1,2} from which it can be seen that the main maxima of $[4n + 2]\pi$ -annulenes, [18]-1, [22]-3, and [26]annulene 5, are at rather longer wavelengths than those of $[4n]\pi$ -annulenes, [20]-2, [24]-4 and [28]annulene 6, which is the same trend as has been demonstrated for monocyclic annulenes and dehydroannulenes.¹⁰ However, the maxima of [30]-7 and [34]annulene 9 are not at longer wavelengths than those of the [32]-8 and [36]annulene 14, respectively, which suggests that both of the [32]-8 and [36]annulene 14 are atropic, as is inferred by their ^1H NMR spectra.²

Thus, as we have concluded in the previous papers^{1,2} that the largest ring size annulene showing the ring current effect is the [34]annulene 9 in $[4n + 2]\pi$ -system and the [28]annulene 6 in $[4n]\pi$ -system, the result obtained from this study verifies the conclusion.

Experimental

M.p.s were determined on a hot-stage apparatus and are uncorrected. IR spectra were taken on a Hitachi 260–50 spectrophotometer and were calibrated against polystyrene; only significant maxima are reported. Electronic spectra were measured in tetrahydrofuran (THF) solution and run with a Hitachi 220A spectrophotometer. ^1H NMR spectra were measured on a JEOL FX-90Q (90 MHz), a JEOL GX-270 (270 MHz), a Bruker WM-360 (360 MHz) or a Bruker AM-500 spectrometer (500 MHz) and refer to solutions in CDCl_3 , SiMe_4 being used as an internal standard. Mass spectra were recorded with a JMS D-300 spectrometer operating at 75 eV using a direct inlet system or a JMS-D spectrometer equipped with field-desorption system. Fast atom bombardment mass spectrum (FAB MS) was obtained on a JEOL JMS-AX 505W high-resolution double-focusing mass spectrometer equipped with a D 5000 data system. Ions were generated by bombardment of the target *m*-nitrobenzyl alcohol matrix with a neutral xenon atom beam (derived from a Xe^+ ion beam accelerated at 2 kV). Merck alumina (activity II–III) was used for column chromatography. Progress of reactions was followed by TLC on Merck precoated silica gel F_{254} .

1-(12-*tert*-Butyltetradeca-1,3,5,7,9,11-hexaen-13-ynyl)-6-(14-*tert*-butylhexadeca-1,3,5,7,9,11,13-heptaen-15-ynyl)cyclohepta-1,-3,5-triene 13.—To a stirred suspension of the salt 12² (2.00 g, 4.30 mmol) in dry THF (61 cm^3) at -70°C was added dropwise a solution of butyllithium in hexane (1.6 mol dm^{-3} ; 2.70 cm^3 , 4.32 mmol) by a syringe during 5 min under argon. Then the mixture was stirred at -60°C for a further 1 h, after which a

Table 1 Electronic main absorption maxima (λ/nm) of annulenes 1–10 and 14 in THF ^a

[18]-1	[20]-2	[22]-3	[24]-4	[26]-5	[28]-6	[30]-7	[32]-8	[34]-9	[36]-14	[38]-10
343	324	367	355	388	383	406	406	425	429	440

^a See ref. 1 and 2.

solution of the dialdehyde **11**⁵ (240 mg, 0.63 mmol) in dry THF (60 cm³) was added dropwise at -60°C during 1 h. Then the temperature was allowed to rise to -4°C , and the solution was stirred for 3 h. After addition of ethyl acetate (10 cm³), the mixture was poured into brine and extracted with benzene. The combined organic layers were washed with brine and dried over sodium sulfate. The residue obtained after removal of the solvent was chromatographed on alumina (3.2 \times 8.0 cm). The fractions eluted with 10–20% ether in hexane afforded compound **13** (162 mg, 44%) as black needles, m.p. 102–105 $^\circ\text{C}$ (decomp.) (from hexane–benzene); m/z 590 (M^+) (field-desorption method) (Found: M^+ , 590.8); $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3280 ($\text{C}\equiv\text{CH}$), 2100 ($\text{C}=\text{C}$), 1000 and 990 [(*E*)-HC=CH]; $\lambda_{\text{max}}/\text{nm}$ 251 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 19 500), 309 (19 400), 401 (11 3000), 419 (121 000) and 448sh (22 000); δ_{H} (270 MHz) 6.84–6.17 (28 H, m, olefinic and 7-membered-ring H), 3.41 (2 H, s, $\text{C}\equiv\text{CH}$), 2.71 (2 H, s, CH_2), 1.20 (9 H, s, Bu^t) and 1.17 (9 H, s, Bu^t) (Found: C, 90.5; H, 8.6. $\text{C}_{45}\text{H}_{50}$ requires C, 91.5; H, 8.5%). Attempts to improve the elemental analysis failed.

21,22,23,24-Tetrahydro-20,25-di-tert-butyl-1,6-methano[36]-annulene **14**.—A solution of compound **13** (162 mg, 0.27 mmol) in a mixture of pyridine (63 cm³), diethyl ether (21 cm³) and methanol (20 cm³) was added dropwise during 4 h to a stirred and refluxing solution of copper(II) acetate monohydrate (2.23 g) in a mixture of pyridine (95 cm³), diethyl ether (150 cm³) and methanol (10 cm³) at 52 $^\circ\text{C}$. After being refluxed and stirred for a further 2 h, the mixture was poured into water and extracted with benzene. The combined extracts were washed successively with 5% HCl until they turned acidic to litmus, and then with aq. sodium hydrogen carbonate, and were then dried over sodium sulfate. The residue after removal of the solvent was chromatographed on alumina (3.2 \times 8.0 cm). The fractions eluted with hexane–ether (1 : 1) afforded the [36]annulene **14** (58 mg, 36%) as black needles, m.p. 234–235 $^\circ\text{C}$ (decomp.) (from toluene); m/z 589 ($\text{M}^+ + 1$) (FAB method) (Found: M^+ , 588.8); $\nu_{\text{max}}/\text{cm}^{-1}$ 2250 ($\text{C}\equiv\text{C}$) and 995 [(*E*)-HC=CH]; $\lambda_{\text{max}}/\text{nm}$ 261 (ϵ 35 300), 309sh (38 200), 322sh (44 900), 409 (12 2000), 429 (14 000) and 524sh (33 800); δ_{H} (500 MHz) 7.53 (1 H, dd, *J* 11.8 and 14.7, H^L), 7.39 (1 H, dd, *J* 11.2 and 14.3, H^J), 7.35 (1 H, dd, *J* 11.2 and 15.0, H^B or H^B), 7.29 (1 H, dd, *J* 11.1 and 14.7, H^B or H^B), 7.04 (1 H, dd, *J* 11.1 and 14.7, H^J), 6.98–6.85 (6 H, m, H^H, H^H, H^F, H^F, H^D and H^D), 6.46–6.44 (2 H, m, H² and H³), 6.39 (1 H, d, *J* 11.4, H^M), 6.33 (1 H, d, *J* 11.3, H^K), 6.27–6.10 (12 H, m, H^A, H^A, H^C, H^C, H^E, H^E, H^G, H^G, H^I, H^I, H^I and H⁴), 3.07 (2 H, s, CH_2), 1.14 (9 H, s, Bu^t) and 1.13 (9 H, s, Bu^t); and see also Figs. 1 and 2; (Found: C, 91.8; H, 8.2. $\text{C}_{45}\text{H}_{48}$ requires C, 91.8; H, 8.2%).

14,19-Di-tert-butyl-1-cycloheptyltriacontane **15**.—Compound **14** (12.3 mg, 0.021 mmol) in ethyl acetate (8.0 cm³) was hydrogenated over pre-reduced platinum oxide dihydrate (35 mg) with stirring for 2 h at room temperature under atmospheric pressure. Then the precipitates were filtered, and

benzene and water were added to the filtrate. The organic layer was washed successively with aq. sodium hydrogen carbonate and water, and were then dried over sodium sulfate. The residue after removal of the solvent was chromatographed on alumina (2.2 \times 7.5 cm). The fractions eluted with hexane afforded a colourless liquid (12 mg, 92%), which was dissolved in ethyl acetate–methanol. Crystals deposited on cooling of the solution in a refrigerator were collected and recrystallized from the same solvents to afford compound **15** as colourless low-melting crystals; m/z 629 (M^+ , 3%) and 565 (100) (Found: M^+ , 629.1); $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 2910, 2900, 1465, 1365, 980 and 725 (C–H); δ_{H} (90 MHz) 2.01 (4 H, br s, CH), 1.26 (66 H, s, CH_2) and 0.84 (18 H, s, Bu^t) (Found: C, 85.8; H, 13.7. $\text{C}_{45}\text{H}_{88}$ requires C, 85.9; H, 14.1%).

Acknowledgements

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