Towards the total synthesis of cyclo[*n*]carbons and the generation of cyclo[6]carbon

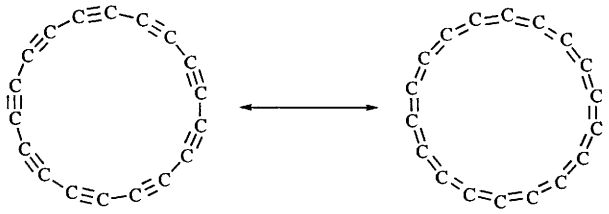
George A. Adamson and Charles W. Rees

Department of Chemistry, Imperial College of Science, Technology & Medicine, London SW7 2AY, UK

We describe efforts towards the synthesis of some allotropes of carbon, the cyclo[*n*]carbons where *n* = 18, 24 and 30. The key intermediate 11 is hexa-1,3,5-triyne with the central triple bond masked as a 1-amino-1,2,3-triazole derivative. Cyclo-oligomerisation of this by oxidative coupling gives macrocyclic precursors of C_{18}, C_{24} and C_{30}. C_{30} is a proposed intermediate in the formation of C_{60} and we also describe some attempts at the synthesis of C_{60} *via* the chemical generation of benzotriyne, cyclo[6]carbon.

Cyclo[*n*]carbons

Cyclo[*n*]carbons have generated much interest in recent years as a new allotropes of carbon. Each carbon atom is sp hybridised, achieved by having a polyalkyne species curved into a large ring to satisfy the terminal valencies. This causes curvature in the polyalkyne, but this is possible for large enough rings since each alkyne is only slightly distorted from linearity, which introduces relatively little strain (for distortions less than 20°). The smallest cyclo[*n*]carbon predicted to be thermodynamically stable is C_{18} **1a** which would have a strain energy of 72 kcal mol^{-1}.[1] Calculations using a different set of parameters suggest that this structure is more stable as the polycumulene **1b**.[2] Polymeric all-carbon networks based on alkynic



1a **1b**

structures[3] have been predicted to display useful semiconductor and non-linear optical properties.[4] Also of great interest is the role of such species as intermediates in the formation of fullerenes[5] as indicated by ion chromatography.[6]

We wished to devise a flexible synthesis of such species which would allow the preparation of substantial quantities of these new carbon allotropes, thus facilitating an investigation of their properties and chemistry. Diederich has already reported impressive work aimed at the synthesis of these compounds, employing the strategy of masking certain alkyne units for stability, for more favourable bond angles for macrocyclic ring construction, and for easier preparation of the building blocks. A hexatriyne unit with the central alkyne masked was used as the 'monomer' which was cyclo-oligomerised using the techniques pioneered by Sondheimer in his work on dehydroannulenes.[7] This allowed for rapid construction of the macrocyclic rings in one step (trimer, tetramer and pentamer were produced in varying ratios depending upon the precursor) by the use of terminal alkyne oxidative coupling under high dilution. Although the yields were not high, the cyclisation process represented a large increase in molecular complexity in the products. This approach was made possible by the symmetry of the target molecules, which was disrupted minimally by the introduction of the alkyne masking groups. The masking groups employed by Diederich were cyclopropenone,[8] cyclobutenedione,[8,9] an anthracene derivative[1,10] (for a retro-Diels–Alder reaction), and a dicobalt carbonyl residue.[10,11] Although none of these have yet resulted in the isolation of the desired all-carbon species because of the vigorous reaction conditions required for the removal of the masking groups, the cyclobutenedione precursor did result in cyclo[18]carbon generation under mass spectral conditions.[12] Evidence for the production of cyclo[18]carbon was also obtained upon irradiation of the cyclobutenedione precursor at a suitable wavelength to induce the removal of the alkyne masking groups in a low temperature glass.[10] As irradiation continued, IR detection showed the disappearence of a carbonyl band in the starting material and the appearence of a ketene band. Irradiation at a different wavelength showed the disappearence of the ketene band and appearence of the band for carbon monoxide (the all-carbon molecule should only show weak IR activity). This suggests a fragmentation pathway which was considered to be an equilibrium since the carbon monoxide could not diffuse away from the product as it was trapped in the glass.

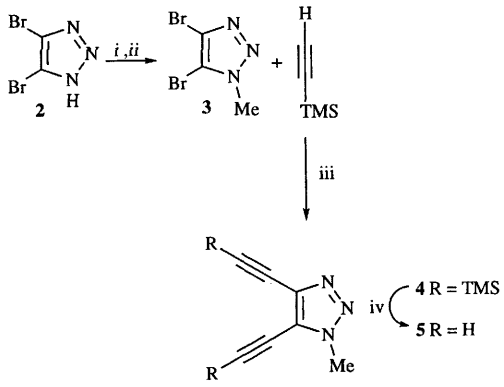
We planned to follow the same general synthetic scheme, which is efficient, uses the symmetry of the target molecules as much as possible, and could provide C_{18} (formally aromatic), C_{24} (less strained but formally antiaromatic) and C_{30} (a precursor for C_{60}).[12] However, we chose the 1-amino-1,2,3-triazolo unit as the alkyne precursor since the 'deprotection' is very rapid and virtually quantitative under very mild conditions [$Pb(OAc)_4$, CH_2Cl_2, −78 °C], providing little chance of interference from intermediates.[13] The successful removal of two 1-aminotriazole units simultaneously has been demonstrated in the formation of a benzodiyne.[14]

Our monomeric unit would thus be a suitably protected 1-amino-4,5-bis(ethynyl)-1,2,3-triazole, with the alkyne groups most readily introduced by Pd^0 cross-coupling with the 4,5-dibromotriazole **7**.

Results and discussion

1,2,3-Triazole was prepared by cycloaddition of benzyl azide to acetylenedicarboxylic acid followed by double decarboxylation and debenzylation[15] on a 400 g scale. As 1,2,3-triazole cannot easily be isolated from the reaction mixture, it was used crude in the bromination step by dissolving in the minimum volume of water and adding bromine over 48 h *until* a brown colour persisted. Recrystallisation from methanol gave 4,5-dibromo-1,2,3-triazole **2** (178 g, 29% overall).

To investigate the Pd^0 cross-coupling in a model reaction, the dibromotriazole **2** was methylated with iodomethane and sodium hydride in THF (Scheme 1). The mixture of 1- and 2-



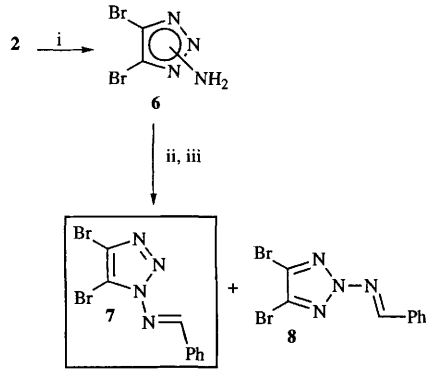
Scheme 1 *Reagents and conditions:* i, NaH (1 equiv.), THF, room temp., 10 min, then MeI (1 equiv.), reflux, 16 h; ii, fractional crystallisation; iii, CuI (10.4 mol%), $Pd(PPh_3)_2Cl_2$ (5.7 mol%), Et_3N, toluene (6:1), 80 °C, 12 h; iv, KOH (aq), MeOH, room temp., 10 min

isomers could be separated readily by chromatography or by fractional crystallisation from ether. Treatment of the 1-isomer **3** with trimethylsilylethyne (2.4 equiv.), copper(I) iodide (10.4 mol%), palladium bis(triphenylphosphine) dichloride (5.7 mol%) in a mixture of triethylamine–toluene (6:1) at 80 °C for 12 h in a sealed tube provided the desired diyne **4** in 81% yield after chromatography (Scheme 1). The terminal alkynes were quantitatively deprotected with potassium hydroxide in methanol to give the free diyne **5**; the use of tetrabutylammonium fluoride (TBAF) resulted in instantaneous destruction of the starting material.

Attempts to couple **3** with dimethylhexylsilylbutadiyne[16] under similar conditions met with low yield owing to the thermal instability of the starting butadiyne.

Attempts to cyclo-oligomerise the deprotected model compound **5** using several oxidative coupling techniques [Hay catalyst in acetone at several dilutions or copper(II) acetate in pyridine–methanol] were unsuccessful.

We then turned to the N-amination of 4,5-dibromo-1,2,3-triazole **2** *via* electrophilic amination of its sodium salt. As this is not very nucleophilic, a highly active electrophilic aminating agent, mesitylenesulfonyl-*O*-hydroxylamine (MSH) was chosen. This was prepared using the only literature method which worked well;[17] attempts to dry the reagent and isolate it as a pure solid always met with rapid decomposition so it was used as an undried ether solution. The amination was complete in 30 min; extending this time caused a reduction in yield. This reaction could be carried out on a 60 g scale successfully. ^1H NMR showed the product to be an equimolar mixture of the 1- and 2-isomers **6** (60–70%) (Scheme 2). The use of different

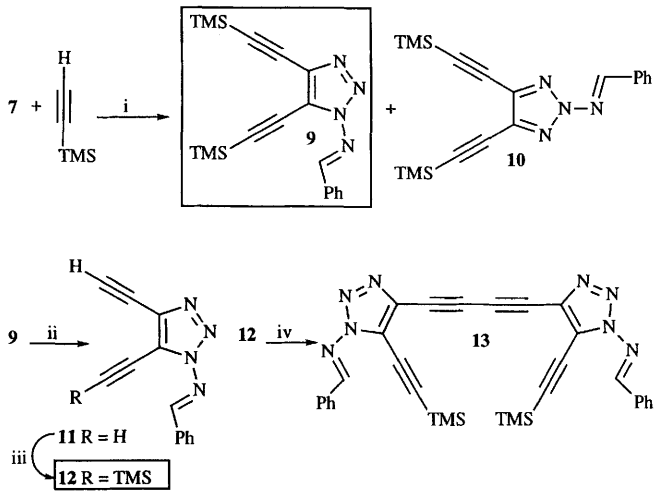


Scheme 2 *Reagents and conditions:* i, NaH (1 equiv.), MSH (1.25 equiv.), THF, 0 °C, 30 min; ii, $PhCH(OMe)_2$, MeOH, H_2SO_4 (cat.), room temp., 16 h; iii, fractional crystallisation

counterions to alter this ratio was not successful. It should be noted that the undesired 2-isomer could always be reconverted into the triazole by treatment with nitrous acid.[13]

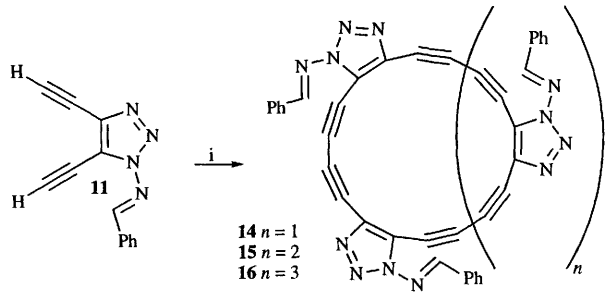
Since two of the subsequent steps of the synthesis were likely to involve copper salts, it was considered necessary to mask the amino residue fully. The crude mixture of amines **6** were protected as their benzylidene derivatives by treatment with benzaldehyde dimethyl acetal in methanol with sulfuric acid as catalyst. The two isomers were separated by fractional crystallisation with alternation between methanol and light petroleum (bp 60–80 °C) as the solvents. This fractional crystallisation allowed the reaction to be carried out on a large scale without purification problems, and gave the desired 4,5-dibromo-1-(phenylmethylideneamino)-1,2,3-triazole **7** (33 g, 41%) along with a similar quantity of the undesired 2-isomer **8** (Scheme 2).

Attempts to effect the Pd^0 cross coupling of **7** with trimethylsilylethyne using the conditions described in Scheme 1 were unsuccessful, the starting material being partially destroyed in the reaction conditions. Whilst adjusting the conditions, it became apparent that triethylamine was the cause of the degradation; its use as a solvent was to solubilise the copper species, as well as to neutralise the acid generated. By using the more soluble copper(I) bromide dimethyl sulfide complex in place of copper(I) iodide, the amount of triethylamine could be reduced from that of solvent to just a few equivalents. Once this change was made, the desired bis-coupled product **9** was isolated in 79% yield (Scheme 3). This



Scheme 3 *Reagents and conditions:* i, $CuBr{\cdot}SMe_2$ (10.4 mol%), $Pd(PPh_3)_2Cl_2$ (3 mol%), Et_3N (4 equiv.), toluene, 80 °C, 12 h; ii, K_2CO_3 (1 equiv.), MeOH, room temp.; 25 min; iii, LDA (1 equiv.), THF, −78 °C, 25 min, TMSCl (1.1 equiv.), to room temp.; iv, CuCl·TMEDA (0.6 equiv.), O_2, acetone, room temp., 4 h

reaction was then scaled up by using a pressure bottle in place of a sealed tube (because of the volatility of the trimethylsilylethyne) to 2 g. On this scale, another side reaction was observed in which the *N*-substituent migrated from the 1- to the 2-position after the cross coupling had occurred to give **10** as up to 15% of the product. By adjusting the amount of the catalysts, a probable cause of this rearrangement was found to be the relatively high palladium catalyst concentration, and reducing this quantity from 5.7 to 3 mol% suppressed the rearrangement. The reason for this rearrangement is unclear although the palladium may coordinate with the nitrogens of the triazole ring enhancing its leaving group ability and so allowing rearrangement to the presumably more stable 2-isomer. On a 2 g scale, using 2.4 equiv. of trimethylsilylethyne, 4 equiv. triethylamine, 10.4 mol% of copper(I) bromide dimethyl sulfide complex and palladium bis(triphenylphosphine) dichloride



Scheme 4 *Reagents and conditions:* i, CuCl·TMEDA (1 equiv.), O_2, acetone, room temp., 50 min

(3 mol%) in toluene, the desired bis-coupled product **9** could be isolated in 75–85% yield.

To allow for the possibility of stepwise construction of the macrocyclic rings, it seemed desirable to differentiate between the two alkynes present on the triazole ring. Experiments with the methylated compounds had failed to yield a set of conditions mild enough to allow mono-alkyne coupling of **3**, and attempts to mono-desilylate the bis-coupled product **4** using the procedure described by Holmes[18] also failed. Attempts to mono-desilylate the adduct **9** were similarly unsuccessful, and so full deprotection was accomplished by treatment with potassium carbonate in methanol. This gave the free diyne **11** almost quantitatively as an unstable solid which could not be stored for any length of time under any conditions (Scheme 3).

Treatment of **11** in THF with one equivalent of lithium diisopropylamide (LDA) at −78 °C followed by a slight excess of trimethylsilyl chloride gave the mono-silylated diyne **12** usually as an oil, contaminated with a little **9**. Owing to the lack of hydrogens in close proximity, NOE spectroscopy was not able to show which ethyne the silyl group resided on. A later derivative of this compound for which an X-ray structure determination was made confirmed that it was the 5-ethynyl group which was protected. This may result from the polarisation of the triazole ring which would stabilise negative charge on the 5- more than on the 4-ethynyl group.

Cyclo-oligomerisation of the monomer **11** would now give, if successful, a large increase in molecular complexity by providing the macrocyclic ring precursors of C_{18}, C_{24} and C_{30}. Some of the experimental techniques subsequently published by Diederich[4] appeared to be a better starting point than those previously attempted for the model compound **5**. However, this large change in molecular complexity made prediction of stability, solubility and TLC mobility difficult. In addition to this, the benzylidene protecting group is unstable towards copper(II)–pyridine due to weak Lewis acidity;[19] its stability towards copper(II)–TMEDA was unknown.

The mono-protected precursor **12** was dissolved in acetone, a solution of Hay catalyst (CuCl·TMEDA) added, and the mixture saturated with oxygen for 4 h. This allowed the isolation of the dimer **13** (45%) in a moderate yield; extended reaction times caused a reduction in yield (Scheme 3). Complete desilylation and subsequent mono-silylation of the dimer gave a mixture of compounds containing the mono-protected derivative which was subjected to the oxidative coupling conditions. The mixture formed by this was complex but probably contained some of the tetrameric species, and was used to gain some indication of the stability, solubility and TLC mobility of the macrocyclic rings which survived the reaction conditions reasonably well. An X-ray structure determination[20] of the dimer **13** established the regiochemistry of the earlier mono-silylation.

The bis-ethynyl monomer **11** was dissolved in acetone (0.002 mol l^{-1}) and saturated with oxygen; a solution of Hay catalyst (1 equiv.) was added and the mixture stirred for 50 min. This reaction was carried out on up to a 1 g scale. Since aqueous workup was found to be laborious owing to the formation of emulsions, the reaction mixture was degassed, evaporated and then filtered through a pad of silica with chloroform as the eluent. After evaporation, the acetone oligomers present were removed by high vacuum evaporation since they presented a polar medium which complicated subsequent chromatographic separation of the mixture. The dark mixture was then decolourised with activated charcoal in chloroform before filtration and evaporation to give a residue (*ca.* 30% yield). TLC showed three fluorescent bands of compounds which were assumed to be the trimer **14**, tetramer **15** and pentamer **16** (Scheme 4). Mass spectral analysis (FAB^+) showed a weak signal at 1092 for the pentamer (MH^+), a weaker signal for the tetramer at 872 (MH^+), but the trimer was not observed. This may be due to the increasing strain of the macrocylic rings as the oligomer size decreases. Attempts to separate the mixture were complicated by the fact that each sized ring existed as a mixture of regioisomers: two for the trimer, and four each for the tetramer and pentamer.

Several chromatographic separations were necessary to obtain the three cyclo-oligomers in reasonable purity, and there was no sign of separation of the regioisomers. The compounds were isolated in a ratio of about 2:2:1 for the trimer, tetramer and pentamer, respectively. As expected, ^1H NMR only showed resonances for the benzylidene protecting group and none for the terminal alkynes. A ^{13}C NMR of the trimer could be tentatively assigned (with help from that of the dimer **13** prepared previously) as being the desired structure with the more symmetrical isomer predominating, possibly because of reduced steric interaction between the phenylmethylideneamino groups.

Acid hydrolysis of the benzylidene protecting groups of trimer **14** proved to be unsuccessful under a range of conditions such as aqueous hydrochloric acid at room temperature or under reflux, aqueous trifluoroacetic acid or concentrated sulfuric acid. No reaction occurred either with the macrocyclic ring derivative or with 4,5-dibromo-2-(phenylmethylideneamino)-1,2,3-triazole **8** which was used as a model compound for the deprotection. Diederich had shown that his macrocyclic carbon frameworks were stable to acidic conditions, and our chosen protecting group was supposedly acid labile, so the failure of this step was unexpected.

By warming the model compound **8** in methanol with potassium hydroxide (5 equiv.), some deprotection was observed by TLC and so the same reaction was carried out on the cyclic trimer **14**. Although signs of deprotection were again observed (TLC), the reaction was complex and no appropriate peak was observed in the FAB^+ mass spectrum of the products; since **14** itself did not show a peak in its FAB^+ spectrum, this may not mean that the desired product is not present in the mixture.

The use of the more acid-labile 4-methoxybenzylidene group will be tested to see whether it will survive the other conditions necessary for the synthesis. It is felt that this strategy is worth pursuing since every step up to and including the cyclo-oligomerisation was carried out on at least a 1 g scale and, with the exception of the cyclo-oligomerisation, all steps could be carried out without the need for column chromatography. The formation of C–C bonds in this synthesis is efficiently achieved in just two C–C forming operations, owing to the symmetry of the target molecules.

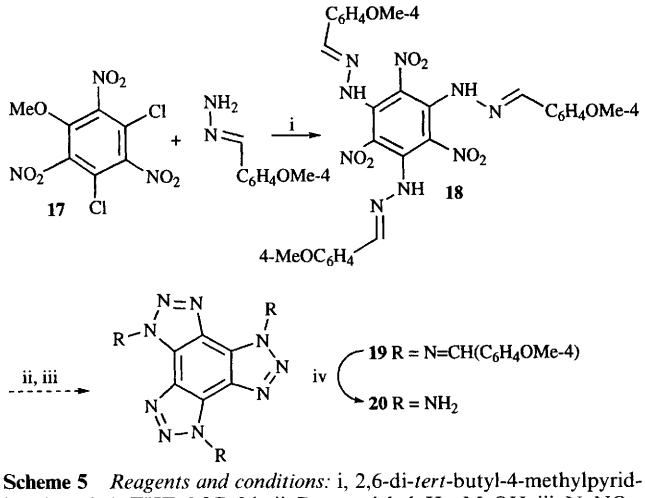
Fullerene 60

Diederich has reported evidence for the conversion of two units of cyclo[30]carbon in the gas phase to C_{60} by dimerisation and rearrangement into the thermodynamically more stable fullerene species.[12] During the course of our work, we explored a few other, potentially more direct, routes to C_{60} as alternatives to the methods currently available. We hoped to

avoid the need for resistive heating or plasma discharge techniques, and the formation of C_{70} which is hard to separate from C_{60}. We envisaged the chemical generation of a C_6 unit which, under the appropriate conditions, would coagulate into a fullerene species; if the C_6 units do not fragment during the cluster growth period, C_{60} could be formed but not C_{70}. The chemical generation of such a species was based on benzene with three further units of unsaturation introduced *via* chemical reactions analogous to those used to generate benzyne.

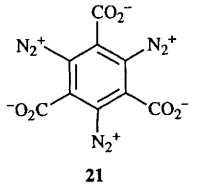
Results and discussion

By analogy with the work described above, the preparation of the tris(1-aminotriazolo)benzene **20** was initially considered, by a route similar to that for 1-aminobenzotriazole which commences with diazotisation of 2-nitroaniline and subsequent condensation with an active methylene compound to give a hydrazone.[13] However, diazotisation of 1,3,5-triamino-2,4,6-trinitrobenzene was unsuccessful despite the use of diazotisation conditions which work for 2,4,6-trinitroaniline.[21] This may be attributed to the reduction of amine nucleophilicity due to the strong hydrogen bonding that this compound is known to exhibit.[22] Attempts to introduce three hydrazone units simultaneously onto 3,5-dichloro-2,4,6-trinitroanisole **17** (treatment with ammonia gave the required 1,3,5-triamino-2,4,6-trinitrobenzene)[22] met with limited success (Scheme 5). It was



Scheme 5 *Reagents and conditions:* i, 2,6-di-*tert*-butyl-4-methylpyridine (3 equiv.), THF, 0 °C, 2 h; ii, Raney nickel, H_2, MeOH; iii, $NaNO_2$, HCl, H_2O; iv, H_3O^+, base

found that only hydrazones with no α-methylene groups would work adequately, possibly due to undesirable reactions with an enamine mode of nucleophilicity; the use of a weakly nucleophilic base (2,6-di-*tert*-butyl-4-methylpyridine) was also found to suppress some side reactions. The hydrazone **18** was prepared from 3,5-dichloro-2,4,6-trinitroanisole **17** and 4-methoxyphenylhydrazone, but was heavily contaminated with the azine derived from hydrazone disproportionation upon its preparation and so this route was unsuccessful. Improvement of this procedure should allow the subsequent nitro group reduction (which has been demonstrated in the presence of an aromatic imino moiety[23]), diazotisation and ring closure to give the C_6 precursor **19** with protected amino groups. The preparation of another C_6 precursor, benzene-1,3,5-tris(diazonium)-2,4,6-tris(carboxylate) **21** was attempted. Trinitration of mesitylene with a fuming nitric–conc. sulfuric acid mixture gave 2,4,6-trinitromesitylene in good yield but all attempts to oxidise the methyl groups to carboxylic acids failed. Even use of harsh oxidants such as sodium dichromate, potassium permanganate, with and without phase transfer catalysis, and tetrabutylammonium permanganate in pyridine all failed. Free radical chain bromination of the benzylic positions followed by hydrolysis and oxidation was equally unsuccessful. Although literature precedents exist for all of these processes, our substrate was resistant, possibly because it is hexasubstituted and very sterically hindered.



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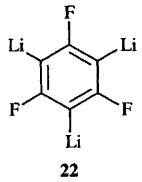

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Another C_6 precursor, 1,3,5-trifluoro-2,4,6-trilithiobenzene **22** was formed by the action of Bu^{t}Li on 1,3,5-trifluorobenzene in THF at −100 °C (internal temperature). All three hydrogens could be substituted with trimethylsilyl groups when quenched with trimethylsilyl chloride. To show that this was not a stepwise lithiation and quench sequence of one position at a time (trimethylsilyl chloride and Bu^{t}Li are compatible at the temperature used), the reaction solution was allowed to warm up to room temperature slowly. Any excess of Bu^{t}Li would be expected to attack any didehydroaromatic species present to give products incorporating *tert*-butyl groups. ^{1}H NMR showed no such species (these were observed in reactions run at −78 °C) and indicated that all of the Bu^{t}Li had been consumed before elimination of lithium fluoride. Rapid heating (refluxing THF) of the trilithio species **22** in an attempt to promote lithium fluoride elimination and subsequent oligomerisation was unsuccessful. Although high mass oligomers were formed, none corresponded to fullerenes, and were likely to be polyaryl derivatives formed by aryl lithium attack on dehydro species. The formation of dehydro species was probably not fast enough to give an adequate concentration of C_6. The use of the mixed base system sodium *tert*-butoxide and BuLi, which has been reported to alter the reactivity of benzyne,[24] was also unsuccessful.

More encouraging results were obtained in the use of mellitic trianhydride **24** as a C_6 precursor. This was easily prepared from commercially available mellitic acid **23** by heating in an excess of acetic anhydride.[25] Various pyrolytic techniques were attempted with this precursor; flash vacuum pyrolysis was unsuccessful because the trianhydride is not sufficiently volatile, and solution spray pyrolysis was also unsuccessful as no suitable solvent could be found which was inert at the high furnace temperatures (1100 °C) required for the anhydride decomposition. However, pyrolysis of the solid trianhydride under vacuum with a microburner gave loss of gas, blackening of the remaining solid and, after extended intermittent heating, mass spectral evidence showed the presence of trace quantities of a species with the same M^+ as C_{60}. On one occasion, a peak for $C_{55}O$ was observed; this corresponds to nine C_6 units and one C=O. However, these species were barely detectable even by mass spectral analysis and so, in an attempt to improve the yield, the reactions were carried out under more dilute conditions.

In the high concentration of the solid state, reactive intermediates would probably combine immediately to form extended carbon networks. Under more dilute conditions, some intramolecular rearrangements might occur at rates competitive with intermolecular additions to allow formation of the five membered rings required to induce the curvature and eventual sphere formation necessary for fullerene production. This could be considered analogous to the annealing process required for the formation of fullerenes under resistive carbon arc production;[26] such rearrangements are known for benzyne generated by pyrolysis of phthalic anhydride.[27]

When a 0.1 mol l^{-1} solution of mellitic trianhydride **24** in degassed diphenyl ether was heated at reflux (*ca.* 250 °C) under an atmosphere of argon, the formation of C_{60} was increased as indicated by mass spectral data; however, this process was not

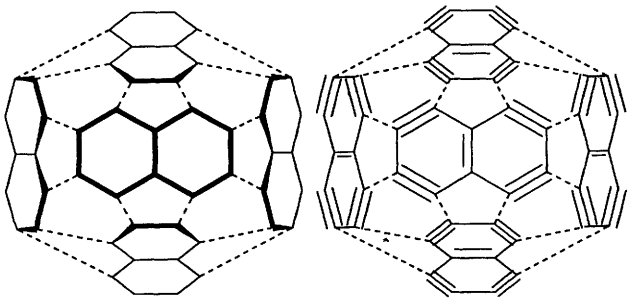
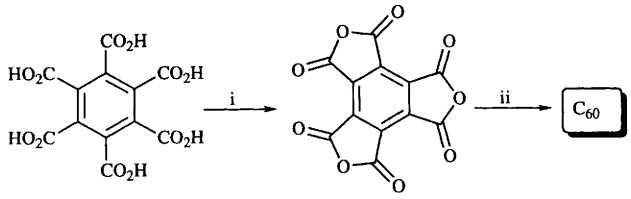


Fig. 1 Formation of fullerene 60 from C_{10} (naphthotetrayne) units (rear unit omitted for clarity)



23 **24**

Scheme 6 *Reagents and conditions:* i, Ac_2O, reflux, 16 h; ii, Ph_2O, reflux, 24 h

always reproducible (Scheme 6). No C_{70} was observed mass spectrometrically from any of these pyrolyses. Just as for the resistive arc methods of C_{60} production, our thermolysis conditions are likely to be critical to ensure the correct balance between oligomer growth and rearrangement to introduce curvature in the growing carbon structure.

Extension of the generation of C_6 (benzotriyne) to the generation of C_{10} (naphthotetrayne) could be of great interest since C_{60} can be formed from six C_{10} units without the necessity for any rearrangement of the naphthalene structure by a thermally allowed, concerted sequence of cycloaddition reactions (Fig. 1).

Experimental

Nitrogen and argon were dried by passage through solid calcium chloride and potassium hydroxide. All Carius tube reactions were performed under dry nitrogen rather than argon to avoid its liquefaction. Aromatic hydrocarbon solvents and diethyl ether ('ether') were dried over sodium wire. Where stated, chlorinated solvents were distilled from phosphorus pentoxide, otherwise they were used untreated. Acetone was dried over potassium carbonate; methanol was dried by distillation from magnesium methoxide. THF was distilled from sodium benzophenone ketyl and trimethylsilyl chloride was used immediately after distillation from sodium wire. Amines were distilled from calcium hydride and stored over potassium hydroxide under nitrogen. Chromatography was carried out on Rhône Poulenc Sorbsil C60 40–60 H silica or, if stated, BDH active neutral alumina Grade 1; TLC was run on Merck Kieselgel 60 F_{254} plates. For column chromatography, the crude compound was preadsorbed onto dry magnesium sulfate unless otherwise stated.

Melting points were measured on a Reichert hotstage apparatus and are uncorrected. Microanalyses were carried out at Medac Ltd, and on a Perkin-Elmer Elemental Analyser 2400 CHN, at Imperial College. UV spectra were taken on a Philips PU 9740 UV–VIS scanning spectrophotometer or a Perkin-Elmer Lambda 2 UV–VIS spectrometer. Infra-red spectra were taken on Perkin-Elmer PP1 FTIR and Perkin-Elmer 1600 series FTIR spectrometers. ^1H NMR spectroscopy was carried out on the following instruments: 250 MHz spectra on a Bruker WM 250, and 270 MHz spectra on a JEOL GSX 270. ^{13}C NMR spectra were run on a Bruker AM 500 machine and ^{19}F NMR spectra on a JEOL FX90 Q. Mass spectra were obtained on VG Micromass 70/70B and VG Autospec instruments or obtained from the SERC mass spectroscopy service, Swansea.

Reactions were usually carried out under an inert atmosphere using dry solvents, with the required apparatus being assembled and flushed well with dry nitrogen or argon. The apparatus was then flame dried with a Bunsen burner under a stream of dry inert gas. Preweighed starting materials were placed quickly into similarly prepared flasks and these vessels once again flushed. The reagents were then added in the desired order at the required temperature as solutions prepared in the appropriate solvent, either by syringe, cannular or dropping funnel. If the reagent was insoluble, it was quickly placed in the reaction vessel which was then flushed with an inert gas. For reactions carried out under Schlenk conditions, a similar procedure was followed with the exception that the vessels concerned were flame dried under vacuum and flushing was replaced with flask evacuation and vacuum quench with a dried inert gas. Standard workup procedures were employed unless otherwise stated; the reaction mixture was poured into an aqueous–solvent bilayer, separated, the aqueous layer extracted further and the combined organic solvents were washed and dried; the solvent was evaporated on a rotary evaporator with a water aspirator.

4,5-Dibromo-1,2,3-triazole 2

1-Benzyl-1,2,3-triazole (104 g, 0.63 mol) was dissolved in THF (300 ml) and to this was added liquid ammonia (1000 ml). Under a Cardice condenser and calcium chloride guard tube protection, sodium metal was added with stirring until a persistent blue colour was observed. Solid ammonium chloride was added until an almost colourless suspension was seen. The ammonia was then allowed to evaporate and the THF was evaporated to give crude 1,2,3-triazole.[28]

This process was repeated twice more on the same scale. The residues from each reaction were combined and suspended in water (400 ml). With ice cooling and stirring, bromine (201 g, 2 equiv.) was added in portions (15 to 20 ml). Stirring was continued for 72 h and further portions of bromine were added as necessary until a persistent bromine colour was seen. The suspension was filtered off and recrystallised from methanol to give 4,5-dibromo-1,2,3-triazole **2** (178 g, 40%) identical with an authentic sample.[29]

4,5-Dibromo-2-methyl-1,2,3-triazole and 4,5-dibromo-1-methyl-1,2,3-triazole 3

To a suspension of washed sodium hydride (60% in mineral oil; 1.16 g, 29 mmol) in dry THF (20 ml) was added a solution of 4,5-dibromo-1,2,3-triazole **2** (6.54 g, 1 equiv.) in dry THF (40 ml). After gas evolution ceased, iodomethane (1.8 ml, 1 equiv.) was added and the mixture heated at reflux for 16 h. On cooling, the reaction mixture was poured into a water–ether bilayer, separated, and the aqueous layer was extracted with two further portions of ether. The combined organic layers were dried ($MgSO_4$) and evaporated to give a mixture of the two products. These were purified by chromatography with 20% ether in light petroleum (bp 40–60 °C) to elute 4,5-dibromo-2-methyl-1,2,3-triazole (1.95 g, 28%); recrystallised from light petroleum (bp 40–60 °C), mp 53–54.5 °C (lit.,[29] 53 °C). The eluent polarity was then increased to 50% ether to give 4,5-dibromo-1-methyl-1,2,3-triazole **3** (3.72 g, 54%); recrystallised from ether, mp 124 °C (lit.,[29] 123 °C).

1-Methyl-4,5-bis(trimethylsilylethynyl)-1,2,3-triazole 4

4,5-Dibromo-1-methyl-1,2,3-triazole **3** (300 mg, 1.25 mmol), palladium(II) bis(triphenylphosphine) dichloride (50 mg, 5.7 mol%) and copper(I) iodide (25 mg, 10.4 mol%) were placed in a dry Carius tube and the system was flushed with nitrogen. Dry triethylamine (3 ml), toluene (0.5 ml) and trimethylsilylacetylene (0.42 ml, 2.4 equiv.) were added. The tube was sealed under nitrogen whilst immersed in liquid nitrogen and well mixed

before heating at 80 °C for 12 h. On cooling the tube was opened and the contents poured into a water–ether bilayer. The layers were separated and the aqueous layer was extracted with two further portions of ether. The combined organic layers were washed with brine, dried ($MgSO_4$) and evaporated. The residue was purified by chromatography, eluting with 25% ether in light petroleum (bp 40–60 °C) to give a slowly crystallising oil further purified by vacuum sublimation to give 1-*methyl*-4,5-*bis*-(*trimethylsilylethynyl*)-1,2,3-*triazole* **4** as a crystalline product (280 mg, 81%), mp 48–49 °C (vacuum sublimation) (Found: C, 56.7; H, 7.7; N, 15.6. $C_{13}H_{21}N_3Si_2$ requires C, 56.7; H, 7.7; N, 15.25%); λ_{max}EtOH/nm 225 ($\log_{10}$ ε/dm^3 mol^{-1} cm^{-1} 6.34), 275 (5.54) and 283sh (5.54); ν_{max}/cm^{-1} 2920br (C–H), 2174 (C≡C), 1462s (triazole), 1250s (C–Si), 760s (C–Si); δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.26 (9 H, s, TMS), 0.29 (9 H, s, TMS), 4.03 (3 H, s, NMe); δ_C(125.7 MHz; $CDCl_3$; Me_4Si) −0.56 (TMS), −0.41 (TMS), 35.60 (NMe), 87.61 and 92.71 (C≡*C*Si), 101.57 and 110.73 (*C*≡CSi), 124.68 and 133.99 (triazole C); *m*/*z* (100 °C) 275 (M^+, 5.9%), 260 (5.1), 247 (100), 232 (66.3), 202 (14.8), 191 (41.1), 160 (19.5), 97 (39.7), 73 (50.6).

4,5-Bis(ethynyl)-1-methyl-1,2,3-triazole 5

1-Methyl-4,5-bis(trimethylsilylethynyl)-1,2,3-triazole **4** (100 mg, 0.36 mmol) was dissolved in methanol (5 ml) and this was added to aqueous potassium hydroxide (1 mol l^{-1}; 10 ml). The reaction was stirred for 10 min and aqueous hydrochloric acid (3 mol l^{-1}; 5 ml) added. Water (20 ml) was added and the solution neutralised with solid sodium hydrogen carbonate. The aqueous layer was extracted with three portions of ether, dried ($MgSO_4$) and the combined organic layers were evaporated. The crude mixture was purified by filtration through active, neutral alumina with ether as the eluent. This gave 4,5-*bis*(*ethynyl*)-1-*methyl*-1,2,3-*triazole* **5** as a slightly unstable crystalline solid (34.4 mg, 72%), mp 154–155.5 °C (with decolourisation from 133 °C) (vacuum sublimation) (Found: C, 63.7; H, 3.8; N, 31.8. $C_7H_5N_3$ requires C, 64.1; H, 3.8; N, 32.0%); λ_{max}EtOH/nm 238sh ($\log_{10}$ ε/dm^3 mol^{-1} cm^{-1} 6.12), 246 (6.14); ν_{max}/cm^{-1} 3244 (C≡C–H), 2925br (C–H), 2102 (C≡C), 1462 (triazole); δ_H(270 MHz; $CDCl_3$; Me_4Si) 3.41 (1 H, s, C≡CH), 3.89 (1 H, s, C≡CH), 4.08 (3 H, s, NMe); δ_C(125.7 MHz; [$^2H_6$]DMSO; Me_4Si) 35.83 (NMe), 67.45 and 72.34 (C≡*C*H), 86.68 and 95.22 (*C*≡CH), 123.84 and 132.02 (triazole C); *m*/*z* (160 °C) 131 (M^+, 53.1%), 103 (47.5), 88 (45.2), 62 (100).

1-Amino-4,5-dibromo-1,2,3-triazole and 2-amino-4,5-dibromo-1,2,3-triazole 6

N-*tert*-Butoxycarbonyl-*O*-mesitylenesulfonylhydroxylamine (100 g, 317 mmol), prepared according to the literature,[17] was dissolved in trifluoroacetic acid (265 ml) and stirred at 0 °C until gas evolution ceased. The solution was then poured into water (600 ml) and the solution neutralised (solid sodium hydrogen carbonate). The resulting solid mesitylenesulfonyl-*O*-hydroxylamine (MSH) was filtered off and dissolved in ether (90 ml). Water was separated and the ether layer used immediately without further drying.

To a suspension of washed sodium hydride (60%; 10 g, 0.79 equiv.) in ether (1000 ml) was added a solution of 4,5-dibromo-1,2,3-triazole **2** (57.5 g, 0.80 equiv.) in ether (270 ml) and the mixture stirred at 0 °C until gas evolution ceased. The ether solution of mesitylenesulfonyl-*O*-hydroxylamine was added and the mixture stirred at 0 °C for 30 min. The resulting suspension was filtered off, and the cake washed with ether. The ether layer was washed with water, 20% aqueous potassium hydrogen carbonate, 25% aqueous sodium bisulfite, brine, dried ($MgSO_4$) and evaporated to give a crude mixture of the aminated triazoles **6** (46–52 g, 75–85%), *m*/*z* (CI$^+$) 243 (M^+, 100%).

4,5-Dibromo-2-(phenylmethylideneamino)-1,2,3-triazole 8 and 4,5-dibromo-1-(phenylmethylideneamino)-1,2,3-triazole 7

To a stirred solution of the crude 1- and 2-amino-4,5-dibromo-1,2,3-triazoles **6** (75% pure by NMR; 78.97 g, 245 mmol) in dry methanol (160 ml) was added benzaldehyde dimethyl acetal (36.3 ml, 1 equiv.). Concentrated sulfuric acid (4 drops) was added and the mixture stirred for 16 h. The resultant reaction mixture was evaporated, preadsorbed onto silica and the products filtered through a pad of silica with ether as the eluent. The ether layer was evaporated and the residue recrystallised from ether. The recrystallised product mixture was fractionally crystallised alternately from methanol and light petroleum (bp 60–80 °C) with seeding of the solutions. This allowed full separation of the two isomers until the final 2 g of mixture remained. This mixture was then chromatographed with 5% ether in light petroleum (bp 40–60 °C) to give 4,5-*dibromo*-2-(*phenylmethylideneamino*)-1,2,3-*triazole* **8** as a crystalline solid. This was combined with the material separated by fractional crystallisation (33.9 g, 42%), mp 116.5–118 °C [from light petroleum (bp 60–80 °C)] (Found: C, 32.8; H, 1.8; N, 17.0. $C_9H_6Br_2N_4$ requires C, 32.8; H, 1.8; N, 17.0%); λ_{max}EtOH/nm 245 ($\log_{10}$ ε/dm^3 mol^{-1} cm^{-1} 3.68), 313 (4.43), 323 (4.43); ν_{max}/cm^{-1} 3000 (C–H), 1600 (N=C), 1451 (triazole); δ_H(270 MHz; $CDCl_3$; Me_4Si) 7.52 and 7.92 (5 H, m, N=CH*Ph*), 9.14 (1 H, s, N=C*H*Ph); δ_C(125.7 MHz; $CDCl_3$; Me_4Si) 124.92 (Ph quaternary C), 129.04 (Ph *m*-C), 129.24 (Ph *o*-C), 131.16 (triazole C), 132.70 (Ph *p*-C), 154.17 (N=C); *m*/*z* (160 °C) 330 (M^+, 65.2%), 286 (1.7), 221 (2.5), 199 (4), 172 (1.3), 118 (65.9), 90 (100), 77 (16.9). The eluent polarity was then increased to 25% ether to give 4,5-*dibromo*-1-(*phenylmethylideneamino*)-1,2,3-*triazole* **7** which was combined with the material isolated by fractional crystallisation (33.1 g, 41%), mp 133.5–135 °C [light petroleum (bp 60–80 °C)] (Found: C, 33.0; H, 1.8; N, 17.2. $C_9H_6Br_2N_4$ requires C, 32.8; H, 1.8; N, 17.0%); λ_{max}EtOH/nm 275infl ($\log_{10}$ ε/dm^3 mol^{-1} cm^{-1} 4.21), 296 (4.29); ν_{max}/cm^{-1} 2950 (C–H), 1596s (N=C), 1485 (triazole); δ_H(270 MHz; $CDCl_3$; Me_4Si) 7.54 and 7.94 (5 H, m, N=CH*Ph*), 9.34 (1 H, s, N=C*H*Ph); δ_C(125.7 MHz; $CDCl_3$; Me_4Si) 112.41 and 123.33 (triazole C), 129.1 (Ph *m*-C), 129.46 (Ph *o*-C), 131.28 (Ph quaternary C), 133.18 (Ph *p*-C), 157.43 (N=C); *m*/*z* (100 °C) 330 (M^+, 0.4%), 302 (0.1), 223 (0.2), 199 (2.1), 142 (5.6), 118 (8.9), 103 (100), 77 (62.3).

4,5-Bis(trimethylsilylethynyl)-1-(phenylmethylideneamino)-1,2,3-triazole 9

(i) 4,5-Dibromo-1-(phenylmethylideneamino)-1,2,3-triazole **7** (100 mg, 0.3 mmol), palladium(II) bis(triphenylphosphine) dichloride (11 mg, 5.2 mol%) and copper(I) bromide dimethyl sulfide complex (6.48 mg, 10.4 mol%) were placed in a dry Carius tube under an atmosphere of nitrogen. Dry toluene (1.2 ml), dry triethylamine (0.17 ml, 4 equiv.) and trimethylsilylethyne (0.1 ml, 2.4 equiv.) were added and the vessel sealed under nitrogen whilst immersed in liquid nitrogen. The tube was heated at 100 °C for 12 h in an oven. On cooling, the tube was opened and the reaction mixture was poured into a water–ether bilayer and the layers separated. The aqueous layer was extracted with two further portions of ether, the combined organic layers were washed with brine, dried ($MgSO_4$) and evaporated. The residue was chromatographed using 7.5% ether in light petroleum (bp 60–80 °C) to give 4,5-*bis*(*trimethylsilylethynyl*)-1-(*phenylmethylideneamino*)-1,2,3-*triazole* **9** (87.6 mg, 79%), mp 79–81 °C (from ether) (Found: C, 62.5; H, 6.6; N, 15.4. $C_{19}H_{24}N_4Si_2$ requires C, 62.6; H, 6.6; N, 15.4%); λ_{max}EtOH/nm 227 ($\log_{10}$ ε/dm^3 mol^{-1} cm^{-1} 4.33), 255sh (4.29), 268 (4.31), 297 (4.21); ν_{max}/cm^{-1} 2960 (C–H), 2176 (C≡C), 1602 (N=C), 1450 (triazole), 1252s (C–Si), 845 (C–Si); δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.29 (9 H, s, TMS), 0.33 (9 H, s, TMS), 7.53 and 7.92 (5 H, m, N=CH*Ph*), 9.33 (1 H, s, N=C*H*Ph); δ_C(125.7 MHz; $CDCl_3$; Me_4Si) −0.47 (TMS), −0.36 (TMS), 87.36 and 92.52 (C≡*C*Si), 102.45 and 111.57 (*C*≡CSi), 122.71 (triazole C), 129.04 (Ph *m*-C), 129.35 (Ph *o*-C), 131.74 (Ph quaternary C), 132.88 (Ph *p*-C), 134.22 (triazole C), 156.89 (N=C); *m*/*z* (200 °C) 336 ([M^+ − N_2],

7.5%), 246 (2.1), 203 (18.9), 118 (84.3), 103 (8.8), 90 (100), 77 (12).

(ii) On a larger scale, the reaction was carried out in a pressure bottle using the following modified conditions. 4,5-Dibromo-1-(phenylmethylideneamino)-1,2,3-triazole **7** (2 g, 6.06 mmol), palladium bis(triphenylphosphine) dichloride (128 mg, 3 mol%) and copper(I) bromide dimethyl sulfide complex (150 mg, 12 mol%) were placed in a dry pressure bottle. To this was added dry toluene (10 ml), dry triethylamine (3.38 ml, 4 equiv.) and trimethylsilylethyne (3 ml, 3.5 equiv.) The mixture was sealed under nitrogen and then heated, with efficient stirring, at 80 °C *for 12 h*. The reaction mixture was poured into a water–ether bilayer and the layers separated. The aqueous layer was extracted with two further portions of ether and the combined organic layers were washed with brine, dried ($MgSO_4$) and evaporated to give a tarry residue. The residue was preadsorbed onto silica and filtered through a pad of silica with light petroleum (bp 40–60 °C) as the eluent; non-polar residues were removed by this and the eluent gradient was increased to 25% ether in light petroleum (bp 40–60 °C) to obtain a residue which was then crystallised from ether to give 4,5-bis(trimethylsilylethynyl)-1-(phenylmethylideneamino)-1,2,3-triazole **9** identical with that described above, in yields ranging between 75 and 85%.

4,5-*Bis*(*trimethylsilylethynyl*)-2-(*phenylmethylideneamino*)-1,2,3-*triazole* **10** was also produced by rearrangement in this reaction; mp 98–100 °C [from light petroleum (bp 40–60 °C)] (Found: C, 62.4; H, 6.4; N, 15.4. $C_{19}H_{24}N_4Si_2$ requires C, 62.6; H, 6.6; N, 15.4%); λ_{max}EtOH/nm 260 ($\log_{10}$ ε/dm^3 mol^{-1} cm^{-1} 4.08), 270infl (3.96), 330sh (4.33), 340 (4.39), 356infl (4.11); ν_{max}/cm^{-1} 2961 (C–H), 2169 (C≡C), 1471 (N=C), 1251s (C–Si), 994 (triazole), 843vs (C–Si); δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.29 (18 H, s, TMS), 7.43–7.58 and 7.88–7.98 (5 H, m, N=CH*Ph*), 9.21 (1 H, s, N=C*H*Ph); δ_C(125.7 MHz; $CDCl_3$; Me_4Si) −0.42 (TMS), 91.65 (C≡*C*Si), 103.65 (*C*≡CSi), 129.07 (Ph *m*-C), 129.32 (Ph *o*-C), 131.63 (Ph quaternary or triazole C), 132.67 (Ph *p*-C), 133.79 (Ph quaternary or triazole C), 155.65 (N=C); *m*/*z* (230 °C) 364 (M^+, 10.6%), 349 (5.7), 246 (1.4), 231 (2.3), 217 (2.7), 103 (100), 93 (38.7), 77 (20.9), 73 (56.6).

4,5-Bis(ethynyl)-1-(phenylmethylideneamino)-1,2,3-triazole 11

4,5-Bis(trimethylsilylethynyl)-1-(phenylmethylideneamino)-1,2,3-triazole **10** (2 g, 5.49 mmol) was dissolved in methanol (18 ml) and the solution added to solid potassium carbonate (379 mg, 1 equiv.). The mixture was stirred for 25 min and poured into a water–CH_2Cl_2 bilayer. The layers were separated and the aqueous layer was extracted with two further portions of CH_2Cl_2. The combined organic layers were washed with brine, dried ($MgSO_4$) and evaporated to give a residue which was filtered through a pad of active, neutral alumina with CH_2Cl_2 as the eluent. The solution was evaporated to give 4,5-*bis*(*ethynyl*)-1-(*phenylmethylideneamino*)-1,2,3-*triazole* **11** as an unstable solid (1.19 g, 99%), ν_{max}/cm^{-1} 3289vs (C–H), 2930 (C–H), 2122 (C≡C), 3132 (C≡C), 1598 (N=C), 1537 (triazole), 1450 (triazole); δ_H(270 MHz; $CDCl_3$; Me_4Si) 3.49 and 3.91 (1 H, s, C≡CH), 7.44–7.63 and 7.91–8.01 (5 H, m, N=CH*Ph*), 9.36 (1 H, s, N=C*H*Ph).

4-Ethynyl-5-trimethylsilylethynyl-1-(phenylmethylideneamino)-1,2,3-triazole 12

4,5-Bis(ethynyl)-1-(phenylmethylideneamino)-1,2,3-triazole **11** (600 mg, 2.7 mmol) was dissolved in dry THF (14 ml) and the solution cooled to −78 °C. A solution of lithium diisopropylamide (LDA) (0.5 mol l^{-1} in THF–pentanes; 5.45 ml, 1 equiv.) was added dropwise and the mixture stirred for 25 min. Trimethylsilylchloride (0.35 ml, 1.05 equiv.) was added and the mixture allowed to warm to room temperature. The mixture was poured into a water–ether bilayer and the layers separated. The aqueous layer was extracted with two further portions of ether and the combined organic layers were washed with brine, dried ($MgSO_4$) and evaporated to give an oil. Chromatography with 5% ether in light petroleum (bp 40–60 °C) gave 4-*ethynyl*-5-*trimethylsilylethynyl*-1-(*phenylmethylideneamino*)-1,2,3-*triazole* **12** (574 mg, 73%), mp 97.5–100 °C (from ether) (Found: C, 65.6; H, 5.5; N, 19.0. $C_{16}H_{16}N_4Si$ requires C, 65.7; H, 5.5; N, 19.2%); λ_{max}EtOH/nm 253infl ($\log_{10}$ ε/dm^3 mol^{-1} cm^{-1} 4.05) 258 (4.10), 300 (4.30); ν_{max}/cm^{-1} 3290 (C–H), 2960 (C–H), 2174 (C≡C), 1601s (N=C), 1508 (triazole), 1450 (triazole), 1253vs (C–Si); δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.33 (9 H, s, TMS), 3.48 (1 H, s, C≡CH), 7.45–7.60 and 7.91–7.99 (5 H, m, N=CH*Ph*), 9.33 (1 H, s, N=C*H*Ph); δ_C(125.7 MHz; $CDCl_3$; Me_4Si) −0.49 (TMS), 72.30 (*C*≡CH), 84.04 (C≡*C*H), 87.05 (C≡*C*Si), 111.78 (*C*≡CSi), 122.96 (triazole C), 129.07 (Ph *m*-C), 129.35 (Ph *o*-C), 131.75 (Ph quaternary C), 132.93 (triazole C), 132.93 (Ph *p*-C), 157.07 (N=C); *m*/*z* (160 °C) 264 ([$M^+ - N_2$], 0.8%), 249 (1.5), 199 (1.5), 146 (4.2), 118 (23.5), 104 (24), 90 (100), 77 (29.7).

1,4-Bis[1-(phenylmethylideneamino)-5-trimethylsilylethynyl-1,2,3-triazol-4-yl]butadiyne 13

4-Ethynyl-5-trimethylsilylethynyl-1-(phenylmethylideneamino)-1,2,3-triazole **12** (1 g, 3.4 mmol) was placed in a Schlenk tube in dry acetone (34 ml) and degassed.

Hay catalyst was prepared by placing purified copper(I) chloride in a Schlenk tube and adding dry, degassed acetone (39 ml). To the degassed solution was added *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (0.62 ml, 1.2 equiv.) and the mixture stirred for 30 min before being allowed to settle. Half of the solution containing the Hay catalyst was then syringed into the prepared substrate solution and the mixture stirred for 20 min. A balloon of oxygen was then used to flush the vessel out and the atmosphere of oxygen was maintained for 4 h. The mixture was then poured into a water–ether bilayer and the layers separated. The aqueous layer was extracted with two further portions of ether, the organic layers were combined, washed with brine, dried ($MgSO_4$) and evaporated. Chromatography with 7.5% ether in light petroleum (bp 40–60 °C) gave a residue which was further purified by recrystallisation from ethyl acetate to give 1,4-*bis*[1-(*phenylmethylideneamino*)-5-*trimethylsilylethynyl*-1,2,3-*triazol*-4-*yl*]*butadiyne* **13** as a crystalline solid (448 mg, 45%), mp >290 °C (with discolouration from 200 °C) (from ethyl acetate) (Found: C, 65.9; H, 5.4; N, 19.1. $C_{32}H_{30}N_8Si_2$ requires C, 65.95; H, 5.2; N, 19.2%); λ_{max}EtOH/nm 227 ($\log_{10}$ ε/dm^3 mol^{-1} cm^{-1} 4.74), 262 (4.58), 284 (4.58), 304 (4.51), 314 (4.51), 324 (4.49), 333sh (4.43); ν_{max}/cm^{-1} 2960 (C–H), 2252 (C≡C), 2179 (C≡C), 1602 (N=C), 1451s (triazole), 1253 (C–Si); δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.37 (18 H, s, TMS), 7.44–7.62 and 7.91–7.99 (10 H, m, N=CH*Ph*), 9.34 (2 H, s, N=C*H*Ph); δ_C(125.7 MHz; $CDCl_3$; Me_4Si) −0.50 (TMS), 71.90 (*C*≡C–C≡*C*), 79.69 (C≡*C*–*C*≡C), 86.87 (C≡*C*Si), 113.04 (*C*≡CSi), 123.89 (triazole C), 129.11 (Ph *o*-C), 129.41 (Ph *m*-C), 131.69 (Ph quaternary or triazole C), 132.30 (Ph quaternary or triazole C), 133.05 (Ph *p*-C), 157.31 (N=C); *m*/*z* (FAB$^+$, NOBA matrix) 583 (M^+, 10%), 527 (2), 437 (6.4), 334 (2.5), 1167 (5.2).

Cyclic trimer 14, tetramer 15 and pentamer 16

Freshly prepared 4,5-bis(ethynyl)-1-(phenylmethylideneamino)-1,2,3-triazole **11** (1148 mg, 1.3 mmol) was dissolved in dry acetone (650 ml) and the solution was degassed and then saturated with oxygen using Schlenk techniques as described above.

A solution of Hay catalyst was prepared by placing copper(I) chloride (2.91 g, 5.65 equiv.) in a Schlenk tube and adding dry, degassed acetone (29 ml). To this was added TMEDA (1.57 ml, 2 equiv.) and the mixture stirred for 30 min before being allowed to settle. Half of the solution containing the Hay catalyst (14.5 ml, 1 equiv.) was added to the oxygen saturated solution prepared above by syringe, and the mixture stirred vigorously for 50 min with periodic saturation with oxygen. The solution was evaporated and the residue filtered through a pad

of silica with chloroform as the eluent. The solution was concentrated and evaporation was completed using a Cardice rotary evaporator, the residue then being dried under vacuum. The residue was taken up in chloroform and decolourised thoroughly with activated charcoal, filtered and evaporated to give a residue (240 mg). Chromatography using 40% chloroform in light petroleum (bp 40–60 °C) provided three dispersed bands that streaked on TLC. These needed 3 or 4 chromatographic separations to give reasonable separation of the three products in a ratio of about 2:2:1. The crude mixture (after the decolourisation process) showed; ν_{max}/cm^{-1} 2962vs (C–H), 2248 (C≡C), 1723 (N=C), 1450 (triazole); δ_H(270 MHz; $CDCl_3$; Me_4Si) 7.40–7.62 and 7.81–8.07 (N=C*H*Ph), about 9.37 (N=C*H*Ph); *m/z* (FAB$^+$, NOBA matrix) 872 (tetramer **15**, $C_{52}H_{24}N_{16}$ requires 872.8) and 1092 (pentamer **16**, $C_{65}H_{30}N_{20}$ requires 1091.1). After separation by column chromatography, trimer **14** was submitted for ^{13}C and the major regioisomer (the most symmetrical one as shown in **14**) showed the following characteristics; δ_C(125.7 MHz; $CDCl_3$; Me_4Si) 68.89, 83.82, 118.92, 126.46, 126.84 (C≡C and a triazole C), 129.14 (Ph *m*-C), 129.54 (Ph *o*-C), 131.60 (triazole), 131.64 (Ph quaternary C), 133.10 (Ph *p*-C), 157.28 (N=C).

1,3,5-Tris(4-methoxyphenylmethylidenehydrazino)-2,4,6-trinitrobenzene 18

4-Methoxybenzaldehyde hydrazone was prepared according to a literature method;[30] this gave a mixture of only 17% purity, the main impurity being the azine.

Methoxybenzaldehyde hydrazone (17% purity; 1.70 g, 3 equiv.) was suspended in dry THF (5 ml) and a solution of 2,6-di-*tert*-butyl-4-methylpyridine (395 mg, 3 equiv.) in dry THF (4 ml) added. To this mixture, at 0 °C with stirring, was added a solution of 3,5-dichloro-2,4,6-trinitroanisole **17** (200 mg, 0.64 mmol) in dry THF (4 ml). The mixture was stirred at 0 °C for 2 h and allowed to warm to room temperature. The mixture was then allowed to stir for 48 h and poured into a water–chloroform bilayer. The layers were separated and the aqueous layer was extracted with three further portions of chloroform, the organic layers were combined, washed with brine, dried ($MgSO_4$) and evaporated to give a solid. This was found to contain some of the desired compound 1,3,5-trinitro-2,4,6-tris(4-methoxyphenylmethylidenehydrazino)benzene **18**; *m/z* (FAB$^+$, NOBA matrix) (MH$^+$ 659, 1.2%) ([$C_{30}H_{28}N_9O_9$]$^+$ requires 658.6).

1,3,5-Trimethyl-2,4,6-trinitrobenzene

A mixture of nitric acid (90%, 25 ml, 6 equiv.) and sulfuric acid (94%; 56.7 ml, 12 equiv.) was cooled to −10 °C and mesitylene (11.5 ml, 83 mmol) was added dropwise slowly, not allowing the temperature to rise above 10 °C. The mixture was then heated to 75 °C for 1 h, allowed to cool and poured onto ice. The solid was filtered off, washed with water and dried *in vacuo*. This gave 1,3,5-trimethyl-2,4,6-trinitrobenzene as a crystalline compound (19.49 g, 92%), mp 220–235 °C (from chloroform) (lit.,[31] 236–238 °C); ν_{max}/cm^{-1} 1532, 1355 (N=O), 872 (C–NO_2); δ_H(270 MHz; $CDCl_3$; Me_4Si), 2.43 (s, Me).

1,3,5-Trifluoro-2,4,6-trilithiobenzene 22

1,3,5-Trifluorobenzene (200 mg, 1.5 mmol) was dissolved in dry THF (2 ml) and this was added dropwise to a solution of Bu^{t}Li (1.18 mol l^{-1} in pentanes; 3.8 ml, 3 equiv.) in dry THF (24 ml) at −100 °C (pentane–liquid nitrogen, internal temperature). The mixture was stirred at −100 °C for 2 h.

(*a*) To this solution was added trimethylsilyl chloride (0.6 ml, 3 equiv.). The mixture was allowed to warm to room temperature and stirred for 16 h. The mixture was poured into a water–ether bilayer and the layers separated. The aqueous layer was extracted with two further portions of ether. The organic layers were combined, washed with brine, dried ($MgSO_4$) and evaporated to give a yellow oil. The residue was chromatographed with light petroleum (bp 40–60 °C) as the eluent. This gave 1,3,5-*trifluoro*-2,4,6-*tris*(*trimethylsilyl*)*benzene* as an oil (308 mg, 59%) (accurate mass 348.1373. $C_{15}H_{27}F_3Si_3$ requires 348.13725); λ_{max}EtOH/nm 262 ($\log_{10}$ ε/dm^3 mol^{-1} cm^{-1} 2.62); ν_{max}/cm^{-1} 2959 (C–H), 1364 (C–F), 1253 (C–Si), 846s (C–Si), 725 (C–F); δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.32 (s, TMS); δ_C(125.7 MHz; $CDCl_3$; Me_4Si) complex due to long range C–F couplings; δ_F(84.3 MHz; $CDCl_3$; $CFCl_3$) −94.76 (ArF); *m/z* (200 °C) 348 (M$^+$, 7.5%), 276 (19.1), 241 (10.8), 189 (17.1), 165 (55.5), 77 (100), 73 (52.7).

(*b*) The solution of the anion was warmed rapidly in a water bath and then a preheated graphite bath to reflux in 2 min and then heated at reflux for 16 h. The mixture was cooled, evaporated and the residue submitted for mass spectral analysis.

Mellitic trianhydride (benzenehexacarboxylic trianhydride) 24[25]

Mellitic acid (benzenehexacarboxylic acid) **23** (1.05 g, 3 mmol) was added to acetic anhydride (4.9 ml, 17 equiv.) and the mixture heated at reflux for 16 h. The mixture was evaporated to dryness to give mellitic trianhydride **24** as a green solid (crude, 100%) which was stored away from moisture; mp > 300 °C; ν_{max}/cm^{-1} 1798 (C=O, anhydride); *m/z* (320 °C) (M$^+$ 288, 0.2%), 244 (43), 216 (0.5), 200 (4.6), 172 (27), 128 (5.3), 100 (23.7), 72 (35.8), 44 (100).

Solid pyrolysis of mellitic trianhydride. Mellitic trianhydride **24** (0.85 mg, 0.003 mmol) was placed in a small quartz tube which was evacuated. This was heated intermittently with a microburner which resulted in the evolution of gas from the solid and blackening of the substrate; some starting material sublimed. A sample of the black residue was submitted for mass spectroscopy; *m/z* (FAB$^+$, NOBA matrix) (M$^+$ 721) ([C_{60}]$^+$ requires 720.7).

Solution pyrolysis of mellitic anhydride. Mellitic trianhydride **24** (30 mg, 0.1 mmol) was suspended in diphenyl ether (1 ml) and the mixture thoroughly degassed with argon. The mixture was then heated at reflux for 24 h under argon; the mixture darkened with time. After cooling, a sample of the pyrolysate solution was submitted for mass spectral analysis; *m/z* (FAB$^+$, NOBA matrix) (M$^+$ 721) ([C_{60}]$^+$ requires 720.7).

The solution was subjected to high vacuum distillation to remove the diphenyl ether and the residue subjected to soxhlet extraction with benzene in an unsuccessful attempt to isolate any soluble fullerenes present.

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