Crystal Structure of 1,2 : 5,6 : 9,10 : 13,14 : 17,18 : 21,22 : 25,26 : 29,30 : 33,34 : 37,38 Decabenzo-3,7,11,15,19,23,27,31,35,39-decadehydro[40]annulene ($C_{80}H_{40}$), a 40-membered Macrocyclic Ring and the Synthesis and Characterization of its 80- ($C_{160}H_{80}$), 120- ($C_{240}H_{120}$), 160- ($C_{320}H_{160}$) and 200- ($C_{400}H_{200}$) membered Ring Homologues

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The crystal structure of 1,2 : 5,6 : 9,10 : 13,14 : 17,18 : 21,22 : 25,26 : 29,30 : 33,34 : 37,38-Decabenzo-3,7,11,15,19,23,27,31,35,39-decadehydro[40]annulene $C_{80}H_{40}$ (DBC), and the isolation and characterization of its higher homologues $C_{160}H_{80}$, $C_{240}H_{120}$, $C_{320}H_{160}$ and $C_{400}H_{200}$ by time of flight secondary ion mass spectrometry (TOFSIMS) are reported.

Cyclic phenyl alkynes are currently being synthesized by us in order to explore their transformation into tubules and conjugated helical π-systems. Theoretical calculations predict that small diameter tubules may have significant metallic character.[1] Cyclynes such as DBC may undergo a cyclic self capping Bergman reaction[2] which would result in a molecular belt. We also intend to examine the lithium induced cyclization on cyclynes such as DBC, a reaction which has been shown to form conjugated π-systems of a helical nature.[3] Conjugated π-systems lying in a helical conformation may lead to increased solubility as compared to planar systems of comparable molecular weight.

DBC, (Fig. 1, $n = 7$), has been synthesized by combining the two compounds in Fig. 2 with a palladium–copper catalyst[4] and characterized by ^1H NMR, ^{13}C NMR, UV–VIS, MS and elemental analysis. Here, we report the X-ray structure of DBC,† and the isolation and characterization of its higher homologues $C_{160}H_{80}$ (Fig. 1, $n = 17$), $C_{240}H_{120}$ (Fig. 1, $n = 27$), $C_{320}H_{160}$ (Fig. 1, $n = 37$) and $C_{400}H_{200}$ (Fig. 1, $n = 47$) by TOFSIMS.

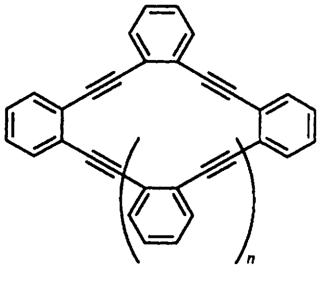

Fig. 1

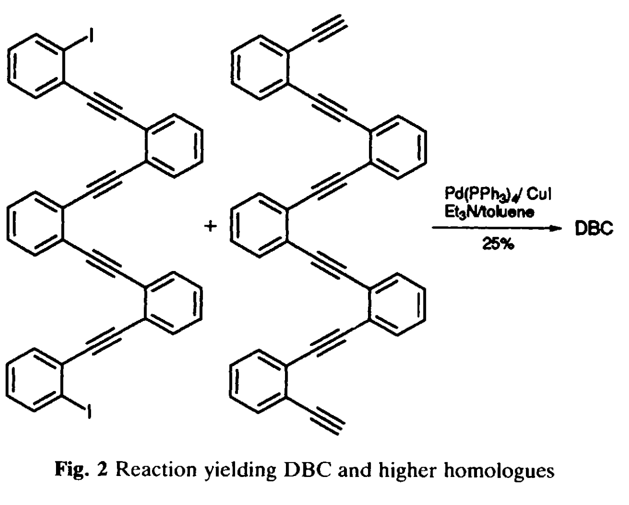

Fig. 2 Reaction yielding DBC and higher homologues

Low-temperature X-ray data were collected on a $P2_1$ diffractometer using molybdenum radiation. Room temperature X-ray data were collected on a Rigaku AFC5R diffractometer with graphite monochromated Cu-Kα radiation and a 12 kW rotating anode generator. The structure was successfully solved using the SAP191 direct methods[5] portion of the TEXSAN package of crystallography programs and expanded using Fourier techniques.[6] The thermal ellipsoid plot of the low temperature study is shown in Fig. 3. Two interacting phenyl rings [one phenyl ring containing C(20) and the other phenyl ring containing C(44)], prohibit DBC from lying in a crown conformation (Fig. 3). The perpendicular distance between the least squares phases of these two phenyl rings is 3.600 Å.‡ No symmetry other than C_1 is observed in its molecular structure. The closest analogue to DBC is HBC (Fig. 1, $n = 3$).[7] HBC is also prohibited from lying in a crown conformation due to two interacting phenyl rings. In the room temperature structure the phenyl ring containing C(78) is disordered, but in the low temperature structure it is ordered.

From the reaction outlined in Fig. 2, the higher homologues $C_{160}H_{80}$, $C_{240}H_{120}$, $C_{320}H_{160}$ and $C_{400}H_{200}$ were isolated and characterized by TOFSIMS. Molecular ion peaks were found at 2107–2109, 3108, 4108 and 5108 representing Ag+$C_{160}H_{80}$, Ag+$C_{240}H_{120}$, Ag+$C_{320}H_{160}$ and Ag+$C_{400}H_{200}$.§

After DBC was collected on a silica column with 15% ethyl acetate in hexanes, a gradient was applied by slowly increasing the ethyl acetate concentration to 40%. $C_{160}H_{80}$ was isolated and characterized by ^1H NMR and ^{13}C NMR.¶ The yield of $C_{160}H_{80}$ was less than 5%. The higher homologues were

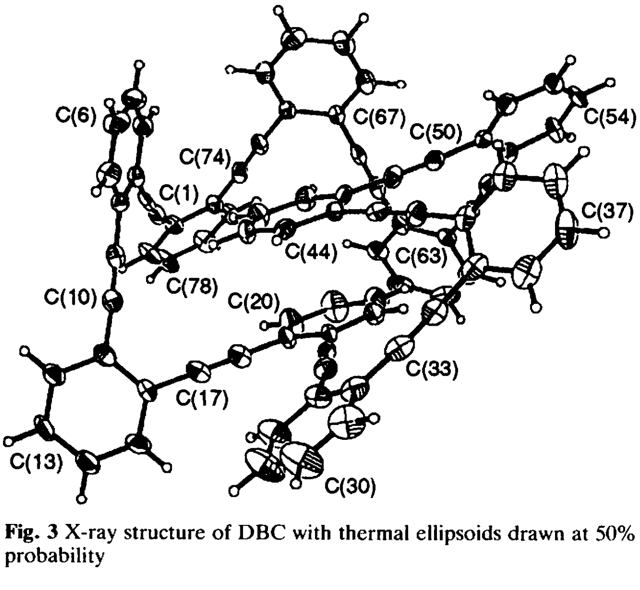

Fig. 3 X-ray structure of DBC with thermal ellipsoids drawn at 50% probability

obtained by increasing the concentration of ethyl acetate slowly to 50%. They came off the column together and were only characterized by TOFSIMS. Their total combined weight indicated that each of their yields were also under 5%. We are currently synthesizing these compounds by a more direct route and plan to examine the formation of tubules and the effect of lithium on these systems.

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Footnotes

† *Crystal data* for $C_{80}H_{40}$, monoclinic, space group $P2_1/c$, a = 11.196(3), b = 10.956(3), c = 47.429(2) Å, β = 91.406(9), Z = 4, V = 5815(1) Å^3, D = 1.143 g cm^{-3}, Cu–Kα radiation, λ = 1.54178 Å. $6.0 \leqslant 2\theta \leqslant 100.1°$. Rigaku AFC5R diffractometer. 6822 reflections were collected of which 2656 unique reflections, $[I > 2.00\sigma(I)]$ were used for refinement (691 parameters), converging to R = 0.062 and R_w = 0.050.

Low temperature crystal data for $C_{80}H_{40}$, monoclinic, space group $P2_1/c$, a = 11.134 (2), b = 10.831(2), c = 46.955(9) Å. β = 91.55(3)°, Z = 4, V = 5660(2) Å^3, D_c = 1.175 g cm^{-3}, Mo–Kα radiation, λ = 0.71073 Å, $3.5 \leqslant 2\theta \leqslant 45.0°$. Syntex $P2_1$ diffractometer. 8822 Reflections were collected of which 4164 unique reflections $[F > 4.0\sigma(F)]$ were used for refinement (722 parameters), converging to R = 0.076 and R_w = 0.0617. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ The distance between the two phenyl rings was determined by calculating the centroid of each phenyl ring and then joining the centroids.

§ The 3108 peak is reported because the resolution of the 3107 and 3109 peaks could not be resolved individually. For the same reason 4108 and 5108 are reported.

¶ $C_{160}H_{80}$: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.4431 (20 H, m), 7.0885 (20 H, m); ^{13}C NMR (600 MHz, $CDCl_3$) δ 132.10, 127.93, 125.61, 92.45.

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