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Zipping up 'the crushed fullerene' $C_{60}H_{30}$: C_{60} by fifteen-fold, consecutive intramolecular H_2 losses†

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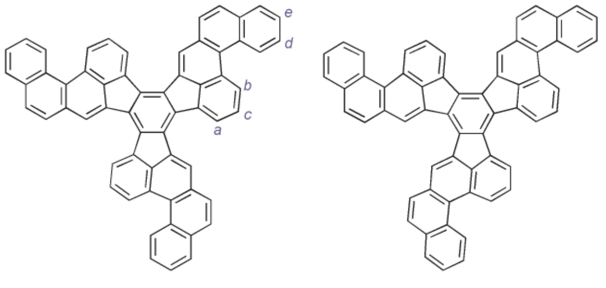
MALDI TOF-MS of tribenzo[*l*:l′:l″]benzo[1,2-*e*:3,4-*e′*:5,6-*e″*]triacephenanthrylene (1a, $C_{60}H_{30}$) gives $C_{60}^{\cdot+}$ by multiple intramolecular cyclodehydrogenation reactions.

The proposal that laser evaporation of graphite gives the fullerene C_{60},[1] followed by its isolation from arc-evaporated graphite soot[2] in sufficient quantities has had considerable impact. For example, the chemical modification of C_{60} has become a subject of intense research.[3] However, despite many efforts,[4] rational syntheses of any of the hitherto isolated fullerenes from unimolecular precursors still remain elusive. Only recently mass spectral (FT-ICR LD[5] and LD-TOF MS[6]) evidence has been reported showing that $C_{60}^{\cdot+}/C_{60}^{\cdot-}$ are accessible from the transient $C_{60}H_6$ cyclophane-like polyyne generated *in situ* in the mass spectrometer.

In a different approach inspired by the observation that in suitable flames C_{60} and C_{70} are formed besides the common (non)-alternant polycyclic aromatic hydrocarbon (PAH) effluents,[7] tribenzo[*l*:*l′*:*l″*]benzo[1,2-*e*:3,4-*e′*:5,6-*e″*]triacephenanthrylene [**1a**, $C_{60}H_{30}$, C_3; ΔH_f^0(AM1) 344.6 kcal mol^{-1}, Chart 1], was put forward as an unimolecular C_{60} precursor.[8–10]



1a, C_3 **1b**, C_1

Chart 1

Notice that **1a** has the exact carbon atom topology of the C_{60} Schlegel diagram (Fig. 1). Unfortunately, the initial synthesis of **1a** by S_8-mediated cyclotrimerization of 4,5-dihydro[*l*]benzacephenanthrylene [**2**, C_1, Chart 1][10,11]† lacked proper *regio*-chemical control.[8,12] Scrutiny of the cyclotrimerization mechanism using AM1[13] results strongly indicated that instead of **1a**, its unsymmetrical isomer tribenzo[*l*:*l′*:*l″*]benzo[1,2-*e*:3,4-*e′*:6,5-*e″*]triacephenanthrylene [**1b**, C_1; ΔH_f^0(AM1) 345.3 kcal mol^{-1}] will be the major $C_{60}H_{30}$ product (statistical *ratio* **1a**:**1b** 1:3).[8] Whilst **1a** can be converted into C_{60} *via* fifteen-fold, consecutive intramolecular H_2 losses accompanied by ring closures, **1b** will yield either a curved $C_{60}H_{12}$ or $C_{60}H_{10}$ PAH under identical conditions, *viz.* in the absence of rearrangements of its carbon skeleton. MALDI TOF-MS (positive-ion mode)‡ of the S_8-cyclotrimerization reaction mixture containing **1a**/**1b** corroborated these contentions. At a high laser fluence of *ca.* 440 μJ pulse^{-1} consecutive intramolecular H_2 losses from *m*/*z* 750 ($C_{60}H_{30}^{\cdot+}$) down to *m*/*z* 732/730 ($C_{60}H_{12}^{\cdot+}/C_{60}H_{10}^{\cdot+}$) were clearly discernible. However, no evidence for $C_{60}^{\cdot+}$ (*m*/*z* 720) formation was found.[8]†

Here we report that fifteen-fold, consecutive intramolecular cyclodehydrogenations occur if pure **1a**, prepared *via* triple Pd-catalysed arylation of *syn*-5,10,15-tris[2-(1-bromo)naphthylmethyl]truxene,[9,16] is subjected to similar MALDI TOF-MS conditions.

At a laser fluence of *ca.* 12 μJ pulse^{-1} the precursor ion **1a**$^{\cdot+}$ ($C_{60}H_{30}^{\cdot+}$, *m*/*z* 750) undergoes three-fold H_2 losses giving $C_{60}H_{28}^{\cdot+}$, $C_{60}H_{26}^{\cdot+}$ and $C_{60}H_{24}^{\cdot+}$ [*m*/*z* 748 (11%), 746 (3%) and 744 (2%)].‡§ No skeletal fragmentation of **1a** occurs. At a laser fluence of *ca.* 440 μJ per pulse, however, cyclodehydrogenation products spanning the mass range *m*/*z* 750 ($C_{60}H_{30}^{\cdot+}$) down to *m*/*z* 720 ($C_{60}^{\cdot+}$) are unequivocally identified [Fig. 2; *m*/*z* 748 (85%), 746 (72%), 744 (43%), 742 (23%), 740 (10%), 738 (6%), 736 (5%), 734 (4%), 732 (3%), 730 (2%), 728 (1%), 726 (2%), 724 (2%), 722 (6%) and 720 (5%)].‡§The stepwise character of the multiple cyclodehydrogenations is substantiated by the following additional observations:

i) At low laser fluences (*ca.* 12 μJ pulse^{-1}) decacyclene [**3**, $C_{36}H_{18}$ (D_3)[8,14,15,]†] and benzo[1,2-*e*:3,4-*e′*:6,5-*e″*]triacephenanthrylene [**4**, $C_{48}H_{24}$ (C_3)[16]†] like **1a** undergo stepwise three-fold intramolecular overall H_2 losses from $C_{36}H_{18}^{\cdot+}$ and $C_{48}H_{24}^{\cdot+}$ down to $C_{36}H_{12}^{\cdot+}$ [*m*/*z* 448 (10%), 446 (4%) and 444 (1%)][14,15] and $C_{48}H_{18}^{\cdot+}$ [*m*/*z* 598 (7%), 596 (3%) and 594

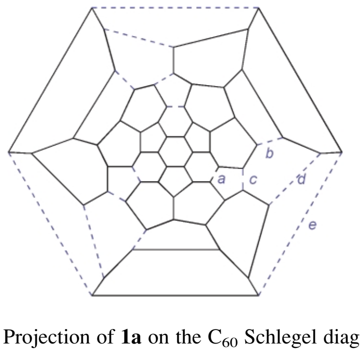


Fig. 1 Projection of **1a** on the C_{60} Schlegel diagram.†

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† Electronic supplementary information (ESI) available: AM1 optimised geometries, heats of formation, first ionisation potentials, Schlegel diagrams and MALDI TOF-MS spectrum of **1a**$^{\cdot+}$. See http://www.rsc.org/suppdata/cc/b1/b110587f/

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(1%)], respectively.§ In contrast at a laser fluence of 440 μJ per pulse $3^{\cdot+}$ in line with previous observations[15] fragments extensively, while $4^{\cdot+}$ still gives $C_{48}H_{22}^{\cdot+}$, $C_{48}H_{20}^{\cdot+}$ and $C_{48}H_{18}^{\cdot+}$.

Only in the case of $\mathbf{1a}^{\cdot+}$ are consecutive cyclodehydrogenations spanning the mass range *m*/*z* 750 down to *m*/*z* 720 ($C_{60}^{\cdot+}$) observed.§

ii) The *post-source-decay* (PSD)[17] spectra, in which $\mathbf{1a}^{\cdot+}$ is isolated prior to TOF-MS analysis, measured at different laser fluences, are nearly identical to the corresponding *in-source* spectra.† Similar observations were made for $3^{\cdot+}$ and $4^{\cdot+}$. Hence, intramolecular H_2 losses accompanied by ring closures originate from the precursor ions of **1a**, **3** and **4**, respectively.

Insight into the conversion of **1a** into C_{60} was obtained using AM1[13] calculations.†¶ Interestingly, the results indicate that cyclodehydrogenations occur with *regio*-chemical control. In propeller-like **1a** (C_3, ΔH_f^0 344.6 kcal mol^{-1} [8]) the three innermost, symmetry related C–*H(a)* pairs are congested due to interaction with a C–*H* moiety of a neighbouring unit [$H(a)\cdots H$ 1.89 Å]. Thus, they are susceptible to undergo ring-closure giving bowl-shaped $C_{60}H_{24}$ (C_3, ΔH_f^0 481.0 kcal mol^{-1}) in which three other C–*H(b)* pairs [$H(b)\cdots H$ 2.01 Å] become congested (Chart 1 and Fig. 1); this will facilitate $C_{60}H_{18}$ (C_3, ΔH_f^0 625.7 kcal mol^{-1}) formation. In $C_{60}H_{18}$ the C–*H(c)* pairs [$H(c)\cdots H$ 2.14 Å] are prone to undergo cyclodehydrogenation towards $C_{60}H_{12}$ (C_3, ΔH_f^0 777.2 kcal mol^{-1}). After closure of the next set of over-crowded C–*H(d)* bonds the ring-opened fullerene $C_{60}H_6$ (C_{3v}, ΔH_f^0 874.3 kcal mol^{-1}) is obtained. Closure of the latter into C_{60} (I_h, ΔH_f^0 973.4 kcal mol^{-1}) may involve three extra overall H_2 losses and ring closures, *i.e.* occur *via* ring-opened fullerenes $C_{60}H_4$ (C_s, ΔH_f^0 930.5 kcal mol^{-1}) and $C_{60}H_2$ (C_s, ΔH_f^0 977.5 kcal mol^{-1}),†¶ However, AM1 calculations also showed that the ring-closed isomer of $C_{60}H_6$ (C_{3v}, ΔH_f^0 865.3 kcal mol^{-1}†), accessible *via* a 2 + 2 + 2 cycloaddition, is 9 kcal mol^{-1} more stable.[18] Similarly, ring-closed analogues of ring-opened $C_{60}H_4$ (C_s, ΔH_f^0 901.1 and C_s, ΔH_f^0 892.2 kcal mol^{-1}†) and ring-opened $C_{60}H_2$ (C_s, ΔH_f^0 950.0 and C_{2v}, ΔH_f^0 931.2 kcal mol^{-1}†) were found to be 29.4/38.3 and 27.5/46.3 kcal mol^{-1}, respectively, more stable. Thus from **1a**, curling up and closure of the surface presumably involves three-fold 6-, 5-, 5-, and 6-membered ring closures, a 2 + 2 + 2 cycloaddition followed by three-fold overall H_2 losses. In line with the endothermic homolytic C–H bond scission energy (*ca.* 100 kcal mol^{-1} for PAH[19]) excess energy (high laser fluences), is required to accomplish all ring-closures and overall H_2 losses. Whereas for the consecutive conversion of $C_{60}H_{30}$ into $C_{60}H_{24}$, $C_{60}H_{18}$ and $C_{60}H_{12}$, respectively, similar ΔH_r [$= \Delta H_f^0(C_{60}H_x) - \Delta H_f^0(C_{60}H_{x-6})$] values (136.4, 144.7 and 151.5 kcal mol^{-1}) are found, $\Delta H_r(C_{60}H_{12} \rightarrow C_{60}H_6)$ (97.1 kcal mol^{-1}) is decisively smaller.†These results rationalise: i) cyclodehydrogenations of **1a** will be only discernible in the positive-ion mode TOF-MS spectra.[8]‡ ii) The similarity of the *in-source* and PSD[17] TOF-MS spectra of **1a**. iii) The gradual decrease in intensity of the mass peaks concomitant with an increasing number of overall H_2 losses. iv) The occurrence of near zero peak intensities in the mass range *m*/*z* 730–726.

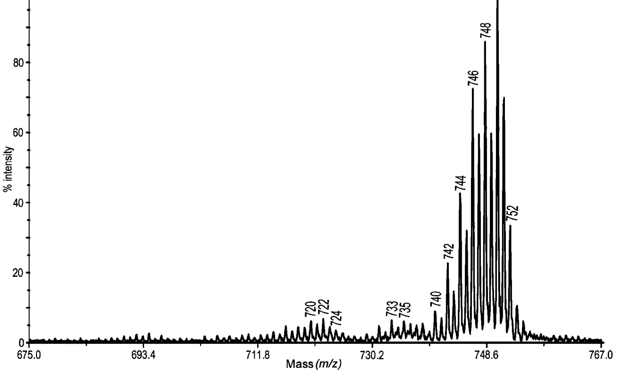

Fig. 2 MALDI TOF-MS spectrum of **1a** (laser fluence *ca.* 440 μJ pulse^{-1}). See ESI for the nearly identical *post-source-decay* (PSD)[17]†‡ MALDI TOF-MS spectrum of $\mathbf{1a}^{\cdot+}$ (*m*/*z* 750).

Isotope pattern analysis in the mass range *m*/*z* 720 to *m*/*z* 725 shows that at the high laser fluence (*ca.* 440 μJ pulse^{-1}) both $C_{60}^{\cdot+}$ and $C_{60}H_2^{\cdot+}$ are formed [*ratio* 1 : 1, natural isotope pattern: *calc.* 720 (4.9%), 721 (3.3%), 722 (6.0%), 723 (3.5%), 724 (1.1%) and 725 (0.3%); *found* 720 (5.0%), 721 (3.5%), 722 (6.0%), 723 (3.6%), 724 (2.0%) and 725 (0.9%), Fig. 2]. Just after we finished this work an independent report of the conversion of **1a** into $C_{60}^{\cdot+}$ using LDI MS appeared.[20]

In summary, at high laser fluences **1a** is converted stepwise into $C_{60}^{\cdot+}$. This renders **1a** a synthon for the formation of endohedral derivatives of C_{60};[21] experiments are in progress.

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Notes and references

‡ MALDI TOF-MS (positive-ion mode): Applied Biosystems/PerSeptive Biosystems Voyager-DE-RP MALDI TOF-MS [N_2 laser; λ_{exc} 337 nm (3 ns pulses)]. TOF-MS spectra were recorded in the reflection mode.[8]

Samples: **1a**[9], **3**[14,15] and **4**[16] were mixed with a dihydroxybenzoic acid solution (3 mg L^{-1}); 1 μL of the suspension was loaded on the Au-sample plate. At a laser fluence of *ca.* 8 μJ pulse^{-1} **1a** only gives a peak at *m*/*z* 750 [$C_{60}H_{30}^{+}$ natural isotope pattern: calc. 750 (100%), 751 (67%), 752 (22%) and 723 (6%); found 750 (100%), 751 (70%), 752 (33%) and 723 (10%)]. Cyclodehydrogenation reactions are not discernible in the negative-ion mode TOF-MS spectra (see text and ref. 8).

§ Besides pure ^{12}C peaks, natural isotope peaks corresponding to the presence of single and double ^{13}C isotopes are discernible.

¶ With the exception of the AM1[13] geometry of ring-opened (*5,6*) $C_{60}H_2$, all structures were identified as minima by harmonic analysis.†

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