Stability, thermal homolysis and intermediate phases of solid hydroazafullerene $C_{59}HN$†

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Density functional (DFT) calculations, high-temperature electron paramagnetic resonance (EPR) and transmission electron microscopy (TEM) results suggest that thermal homolysis of $C_{59}HN$ involves a remarkably stable intermediate $C_{59}N$–$C_{59}HN^{\bullet}$ structure characterised by charge redistribution from a $C_{59}N^{\bullet}$ radical to a bonded $C_{59}HN$.

One of the most striking achievements of fullerene chemistry is the possibility of substituting one or more cage carbon atoms with heteroatoms. A particularly prominent example is the azafullerenyl radical $C_{59}N^{\bullet}$.[1] However, $C_{59}N^{\bullet}$ is highly reactive and in crystals it dimerises, forming bis(azafullerene) $(C_{59}N)_2$.[2,3] The two $C_{59}N$ units in the dimer are only bound by ~18 kcal mol^{-1}.[4] UV or visible light illumination[5,6] as well as high-temperature treatment[7] can separate the dimer and form $C_{59}N^{\bullet}$ radicals, which are seen in EPR spectra as three equidistant sharp lines indicative of ^{14}N hyperfine interaction (a = 3.6 G) with the unpaired electron.[5,6,7] In order to stabilise the monomeric $C_{59}N^{\bullet}$ radicals, samples with diluted $C_{59}N^{\bullet}$ in a C_{60} matrix or even $C_{59}N^{\bullet}$ encapsulated within carbon nanotubes have been prepared[8,9,10] with the hope of developing novel spintronic devices.[11]

An alternative way to produce azafullerenyl radicals, to the best of our knowledge rarely explored to date, starts instead *via* the parent hydroazafullerene $C_{59}HN$.[12] Thermolysis and/or photolysis of $C_{59}HN$ and the detection of the radical formation has not been attempted yet, even though the hydrogen is expected to be only weakly bound to the azafullerene.[5] Recent vibrational infrared and Raman spectroscopy studies of $C_{59}HN$ powder showed full transformation from $C_{59}HN$ to $(C_{59}N)_2$ at 700 K, while an unknown intermediate metastable phase was identified above 540 K.[13] The transformation pathway from $C_{59}HN$ to bis(azafullerene) at high temperatures is thus not yet clear and calls for further investigation. The present study provides strong evidence for a unique rather stable intermediate phase grown by the bonding of a $C_{59}N^{\bullet}$ radical to a $C_{59}HN$ neighbour. The stability and possibility of controlled structural and electronic manipulation using the various high-temperature phases of $C_{59}HN$ qualify this material as another candidate for future spintronic devices.

The question is thus: what happens to $C_{59}HN$ when it is heated to high temperatures? It seems reasonable that on heating, a $C_{59}HN$ fullerene will eventually lose its hydrogen atom, which will diffuse away, forming H_2 and leaving the system. This results in a $C_{59}N^{\bullet}$ radical next to $C_{59}HN$, or at very high temperatures and after prolonged thermal treatment, next to another $C_{59}N^{\bullet}$ radical. Therefore, we performed DFT calculations under the local density approximation using the AIMPRO code[14] of isolated $C_{59}N^{\bullet}$, $C_{59}HN$, and combinations of the two (method given in the ESI†). This has previously been used to study azofullerenes such as $C_{58}N_2$.[15] Our calculated energy to form isolated $C_{59}N^{\bullet}$ and $H^{\bullet}$ radicals from $C_{59}HN$ is 68 kcal mol^{-1}, although it is more likely that hydrogen will diffuse over azafullerene surfaces and thus this is an upper limit only on the hydrogen binding energy.

Mulliken population analysis of the unpaired electron of isolated $C_{59}N^{\bullet}$ gives, as expected, the highest concentration (10.9%) on the α-carbon next to nitrogen (the atom sharing a hexagon–hexagon bond with nitrogen), 5.4% on the nitrogen itself, and the rest distributed at very low concentrations over the azafullerene. This agrees with other calculations[8,9] and explains the magnitude of the hyperfine coupling constant a measured by EPR.

$C_{59}N^{\bullet}$ is a chemically active radical and may thus bond to neighbouring neutral $C_{59}HN$. Our calculations found many thermodynamically stable structures in which the α-carbon in $C_{59}N^{\bullet}$ forms a weak covalent bond (1.66 Å) to a carbon atom in the neighbouring $C_{59}HN$ cage, with the binding energy dependent on which carbon atom of the $C_{59}HN$ cage forms the cross-link. In the range of representative carbon bonding sites at different distances from the substitutional nitrogen that were tested, the highest binding we found is 4.20 kcal mol^{-1}, for a structure shown in Fig. 1. We also note at this point that bonding *via* non-α carbons on the $C_{59}N^{\bullet}$ led to less stable structures and so are not considered further here.

For these structures, Mulliken population analysis shows the unpaired electron resides primarily on the $C_{59}HN$ rather than the $C_{59}N$ cage. For example in Fig. 1, by far the highest concentration (15.4%) of the electron resides on the carbon atom of $C_{59}HN$ marked with a red arrow, neighbouring the atom forming a covalent link with $C_{59}N$. Notably, only 1.3% (0.1%) of the electron resides on the nitrogen atom of the $C_{59}N$ ($C_{59}HN$) cage. Thus, the unpaired electron is transferred from the $C_{59}N$ onto the $C_{59}HN$ cage, far from both nitrogen atoms. This structure is electronically similar to $C_{59}N^{\bullet}$ bonded to C_{60}, proposed recently for $C_{59}N$ doped

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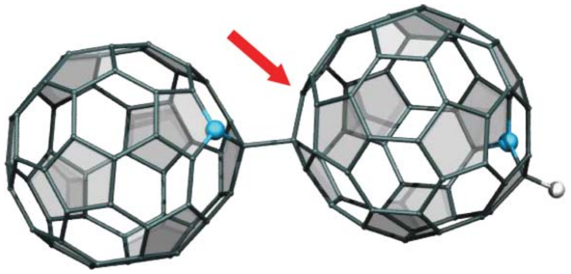

Fig. 1 $C_{59}N–C_{59}HN^{\bullet}$ (nitrogen: blue, hydrogen: white, pentagons: shaded). The unpaired spin is primarily localised on the carbon atom indicated by a red arrow.

C_{60}.[9] As a test, we also examined $C_{59}N^{\bullet}–C_{60}$, and our calculations reproduced the results of ref. 9: we find a weak 1.69 kcal mol^{-1} binding energy compared to the isolated fullerenes, a C–C bond length between C_{60} and $C_{59}N$ of 1.65 Å and a structure similar to our $C_{59}HN–C_{59}N$. Once again the unpaired electron was largely transferred from the $C_{59}N$ cage onto the C_{60}, 16.4% residing on the C_{60} carbon atom neighbouring the cross-linking carbon, only 1% on the nitrogen atom of $C_{59}N$, 2.9% on the C_{60} atom forming the cross-link and the rest distributed over the two cages.

To continue the investigation of possible high-temperature structures, we next consider what happens when $C_{59}N–C_{59}HN^{\bullet}$ loses its second hydrogen atom upon further heating. The lowest energy structure for bis(azafullerene) $(C_{59}N)_2$ is well-known, with cross bonding between the two α-carbon atoms sharing hexagon–hexagon bonds with a nitrogen atom. We obtain a binding energy of 17.0 kcal mol^{-1}, in good agreement with a previous calculated value of ~18 kcal mol^{-1},[4] however higher than experimental binding energies in the range 7–12 kcal mol^{-1} found in this and previous[7] studies. We therefore suggest that, instead of immediately forming this $(C_{59}N)_2$ isomer, there is an intermediate step in which the $C_{59}N–C_{59}HN^{\bullet}$ structure discussed above loses its hydrogen atom, without any reorganisation of the inter-fullerene bonding. In this case, we have an isomer with one $C_{59}N$ cage (referred to hereafter as the 'bonding fullerene') bonded into the rear of the second (the 'leading fullerene'). In other words, after releasing the second H, the resultant structure (referred to hereafter as $(C_{59}N)_2$*) needs extra energy to rearrange into a standard dimeric bis(azafullerene) $(C_{59}N)_2$ structure.

The binding energies for such intermediate structures fall in the range 5.4–10.3 kcal mol^{-1}, with the majority between 7–10 kcal mol^{-1}, depending on which carbon of the leading fullerene forms the cross-linking bond (compared to two isolated $C_{59}N$ cages). The most stable binding site (besides the standard dimeric bis(azafullerene)) is the non-hydrogenated form of Fig. 1. The barrier for this $(C_{59}N)_2$* to reconfigure to the standard $(C_{59}N)_2$ will also be around 10.3 kcal mol^{-1}, since rearrangement will require breaking and reforming the cross-linking bond.

We now summarise the proposed transformation sequence of $C_{59}HN$ (meta)stable structures that emerges from the calculations (Fig. S3†):

$$C_{59}HN \rightarrow C_{59}N–C_{59}HN^{\bullet} \text{ (Fig. 1)} \rightarrow (C_{59}N)_2^* \rightarrow (C_{59}N)_2$$

$C_{59}N–C_{59}HN^{\bullet}$ (Fig. 1) is a radical and should be observable in EPR. Additionally, the last standard bis(azafullerene) structure $(C_{59}N)_2$ is known to dissociate at high temperatures into monomeric $C_{59}N^{\bullet}$ radicals characterised by a typical N hyperfine splitting EPR signal.[7] $(C_{59}N)_2$* should behave similarly, also generating $C_{59}N^{\bullet}$ radicals with the same EPR signal.

Radical formation in $C_{59}HN$ powder was followed with a high-temperature EPR study. As-prepared $C_{59}HN$ powder already shows a structureless EPR signal at room temperature (referred to hereafter as **signal-1**, inset to Fig. 2). This signal has, at room temperature, a *g*-factor 2.0022(3), a linewidth 3.2(1) and its intensity corresponds to a concentration of about 800 ppm. We note that the *g*-factor is unusually high for a standard fullerene centre, for instance C_{60}^{-} has a *g*-factor of less than 2.[16] The high purity of starting material and the fact that it has been exposed to air for a prolonged time before being sealed in a quartz tube rules out the possibility that this is an impurity signal. On the other hand, a very similar signal with nearly identical *g*-factor was found in $C_{59}N$ doped C_{60}.[9] There, it was attributed to delocalised electrons, first over a cluster of $C_{59}N$ and its first C_{60} neighbours and at higher temperatures over larger distances. We remind the reader of the close resemblance between the calculated electronic structure of $C_{59}N–C_{59}HN^{\bullet}$ (Fig. 1) and $C_{59}N–C_{60}$. We therefore attribute **signal-1** to $C_{59}N–C_{59}HN^{\bullet}$ units. Our calculations show that the unpaired electron has transferred from the $C_{59}N$ onto the $C_{59}HN$, far from both nitrogen atoms, explaining the absence of a nitrogen hyperfine coupling in the EPR spectrum.

On heating, **signal-1** remains almost unchanged up to ~500 K, apart from a small decrease in its intensity due to increased temperature. This suggests that $C_{59}N–C_{59}HN^{\bullet}$ centres are largely thermodynamically stable from 300–500 K. Above 500–530 K, the intensity of **signal-1** starts to decrease rapidly and the original intensity is never restored again. Interestingly, after a first thermal cycle, the room temperature intensity of **signal-1** does not change so dramatically thereafter with further thermal cycling. Also, at 530 K, a very weak set of three equidistant lines appears on top of **signal-1**. Fitting of the high-temperature EPR spectra (inset to Fig. 2 and Fig. S4†) thus involves two main components, a line corresponding to **signal-1**, and a set of three equidistant lines. These three lines are typical of $C_{59}N^{\bullet}$, with the fitted *g*-factor and hyperfine coupling constant being 2.0013(4) and 3.56(2) G. Finally,

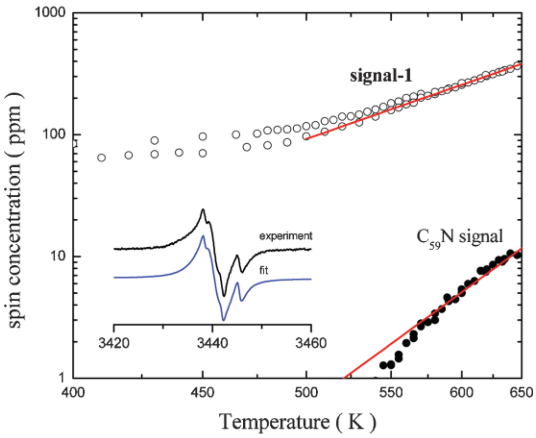

Fig. 2 The temperature dependence of the concentration of paramagnetic centres responsible for **signal-1** (○) and $C_{59}N^{\bullet}$ radical EPR signal (●) at high temperatures. Inset: experimental EPR spectrum taken at $T = 580$ K and corresponding fit with the **signal-1** and $C_{59}N$ components.

careful examination of the high-temperature spectra also shows a weak signal at g = 1.9985(7), attributed to a very small concentration of C_{60}^- centres.

These temperatures correlate well with both the DFT results presented here and the previous high-temperature IR studies.[13] We suggest that at around T = 540 K the $C_{59}N$–$C_{59}HN^{\bullet}$ radical loses its second hydrogen, forming diamagnetic $(C_{59}N)_2$*. On cooling, this structure cannot regain hydrogen, and the $C_{59}N$–$C_{59}HN^{\bullet}$ EPR signal is irrevocably lost, explaining the observed cycling behaviour. Since the stable $(C_{59}N)_2$ dimer separates into $C_{59}N^{\bullet}$ radicals upon heating,[7] it seems reasonable that $(C_{59}N)_2$* will behave similarly, explaining the observed $C_{59}N^{\bullet}$ radical signal above 540 K.

As mentioned above, the room temperature intensity of **signal-1** does not change much after the first high-temperature treatment. In Fig. 2 we show the variation of spin concentration responsible for **signal-1** and $C_{59}N^{\bullet}$ during the second thermal cycle (in all subsequent cycles we found analogous behaviour). The intensity of both signals increases with temperature, suggesting the creation of novel centres with increasing temperature. Interestingly, both centres appear at around 500–540 K with activated high-temperature behaviour. For the creation of $C_{59}N^{\bullet}$ centres we estimate the binding energy to be E_{bind} = 12(2) kcal mol^{-1}, comparable to (but larger than) the binding energy found in the previous bis(azafullerene) study.[7] This might suggest that the $C_{59}N^{\bullet}$ centres found in this study formed from $(C_{59}N)_2$ thermolysis. However, this binding energy does not match our calculated DFT value and is instead closer to that calculated for $(C_{59}N)_2$*. We thus propose that the binding energy E_{bind} = 12(2) kcal mol^{-1} in fact represents an average binding energy for $(C_{59}N)_2$*.

The binding energy for the creation of **signal-1** centres is much smaller, *i.e.* 5.3(6) kcal mol^{-1}. This matches extremely well the calculated binding energy for $C_{59}N$–$C_{59}HN^{\bullet}$, giving us extra confidence in the assignment of **signal-1**. The EPR results thus provide strong evidence for the first direct observation of hydrogen removal from $C_{59}HN$, creating intermediate $C_{59}N$–$C_{59}HN^{\bullet}$ units and high-temperature $C_{59}N^{\bullet}$ radicals simply by its thermal homolysis. In addition, the fact that both signals first appear at approximately the same temperature suggests that the thermal activation for hydrogen removal from $C_{59}HN$ and $C_{59}N$–$C_{59}HN^{\bullet}$ should be very close.

The exposed nitrogen of $(C_{59}N)_2$* will likely enhance van der Waals interaction with neighbouring species and probably even promote their self-organisation. The resultant aggregates will thus potentially contain many fullerenes. Such systems are beyond the scope of our DFT calculations, so we turn instead to TEM imaging. When a drop of $C_{59}HN$ in toluene was placed onto the TEM grid, almost perfectly spherical superstructures with average diameter of order 5–10 nm were observed (Fig. S5†). Their size corresponds to an assembly of approximately 50–500 $C_{59}HN$ fullerenes, almost three orders of magnitude smaller than the aggregate size of bis(azafullerene) $(C_{59}N)_2$ under the same preparation conditions.[17] These aggregates were stable under the strong focused electron beam during TEM observation. Although the details of the $C_{59}HN$ agglomeration are still under investigation, we stress that the present data suggest a tendency of the $C_{59}HN$ to self-assemble. Amongst other factors, such a tendency could be promoted by the presence of $C_{59}N$–$C_{59}HN^{\bullet}$ *via* enhanced interaction with hydroazafullerene molecules.

To conclude, we have investigated the high-temperature transformations of hydroazafullerene $C_{59}HN$ by DFT calculations, EPR spectroscopy and TEM microscopy. Evidence for a unique intermediate phase characterised by $C_{59}N$–$C_{59}HN^{\bullet}$ bonding was found. In these structures the unpaired spin density is shifted away from the $C_{59}N^{\bullet}$ radical to a bonded $C_{59}HN$ fullerene cage, as seen from both Mulliken population analysis and EPR spectra. This structure appears to be remarkably stable even at temperatures as high as 500 K and even after losing its second hydrogen atom. Further high-temperature treatment is needed to gradually transform to a known bis(azafullerene) $(C_{59}N)_2$ dimer. We speculate that the present results could be relevant for the preparation of $C_{59}N^{\bullet}$@CNT (CNT = carbon nanotube) peapod structures, recently proposed to be important building units in future spintronic devices.[10,11]

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