ChemComm

COMMUNICATION



View Article Online View Journal | View Issue

Cite this: Chem. Commun., 2014, 50, 2021

Received 5th November 2013, Accepted 19th December 2013

DOI: 10.1039/c3cc48461k

www.rsc.org/chemcomm

Selective oxidative conversion of triaryldihydro[C₅₉N]fullerenes: a model case for oxygenation of carbon allotropes[†]

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The photooxidation of triaryldihydro[C_{59} N]fullerenes was achieved by treatment with air and light leading to a new selective core functionalization of azafullerenes, which serves as a model case for oxygenation of carbon allotropes.

To date, azafullerenes, in which one carbon atom of the C₆₀ skeleton is substituted by nitrogen, are the only class of heterofullerenes that are accessible in macroscopic quantities.^{1,2} In general, carbon allotropes like fullerenes, carbon nanotubes and graphene represent an emerging research field.³⁻⁵ Particularly, graphene based materials have gained enormous attention due to their fascinating electronic properties.⁶ In this regard, graphene oxide⁷ plays an important role as a promising precursor for wet chemical synthesis of graphene with minimal defects.8 Its structure contains epoxy and hydroxyl groups in addition to carboxylic acids at the edges of the graphene oxide layers according to the Lerf-Klinowski model.9,10 However, the oxygenation mechanism behind structures like graphene oxide is still not understood. Even the structure elucidation is still in progress.¹¹ In addition, the chemical doping of graphene with nitrogen leads to promising materials that have already shown superior preferences towards various applications.¹² However, chemical reactions on N-doped graphenes are an unaddressed issue. In this context, fullerenes, in general, provide a very suitable model system to study oxygenation reactions and the stability of products due to their monodispersity and the possibility of using unambiguous characterization methods such as mass spectrometry, NMR spectroscopy and X-ray single crystal analysis. Here, we report on selective oxygenation reactions of azafullerene derivatives providing valuable insights into carbon allotrope oxides and their formation mechanism.

The azafullerene dimer can be obtained by a three-step reaction starting from C60.1,2 Covalent functionalization of C₅₉N monoadducts such as C₅₉NAr has been investigated quite extensively;13,14 however, heterofullerene derivatives with a higher degree of addition have only been generated in a few cases,¹⁵⁻²¹ in contrast to the corresponding rich chemistry of the isocyclic fullerene C_{60} . However, the establishment of a C_s -symmetrical 6,8,12,15,18addition motif, also known for C60 fullerene derivatives, 22,23 was first demonstrated by our group with the successful synthesis of tetrachlorinated aryladduct C₅₀NArCl₄ bearing an integral pyrrole moiety within the π -system of the fullerene surface.¹⁶ Recently, we explored the formation of pentaarylazafullerene C50NAr5 by an acid catalyzed reaction of a C59N precursor with electron-rich aromatic compounds. During the course of these reactions, triaryldihydroazafullerenes $C_{59}NAr_3H_2$ **1–4** were formed as stable intermediates.^{20,21} Furthermore, they exhibit the same pentakisaddition pattern, but contain an unusual pyrrole substructure with allylic hydrogen atoms. The reactivity of these triaryldihydroazafullerenes is still unexplored, despite the possibility of substituting the H-atoms by aryl moieties as we have recently demonstrated.^{20,21} We have now discovered that these triaryldihydro derivatives 1-4 exhibit a pronounced reactivity towards air and light induced oxygenation. As a consequence, for the first time a new class of compounds, namely oxofunctionalized azafullerenes were formed, isolated and characterized. In an initial photooxidation experiment of a mixture of the isomers 1-4 (Scheme 1), we recognized that isomer 2 was converted much faster than 1, 3 and 4 (Fig. S1, ESI[†]). After a short exposure (15 min) of the reaction mixture to light and air, isomer 2 was oxidized to its green oxygenated product 5. As a consequence, we conclude that this isomer 2 with both hydrogen atoms in the α' position (Scheme 1) is the most reactive of all four isomers.

Earlier studies have already shown that the tetraarylmonohydro-[C_{59} N]fullerene C_{59} NAr₄H with only one hydrogen atom in the α' position is more reactive towards further arylation than its isomer bearing the hydrogen in the β' position.^{20,21} The reaction product 5 exhibits a MALDI-MS peak consistent with one additional oxygen atom and one hydroxyl group. Advantageously, the isolation of the main product 5 was achieved by column chromatography using

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[†] Electronic supplementary information (ESI) available. CCDC 967868. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c3cc48461k



Scheme 1 (a) Reaction scheme of the photooxidation of the mixture of triaryldihydroazafullerene isomers **1–4** leading to main product **5** and (b) the depicted ¹H NMR spectrum of **5** shows a ⁴J coupling constant of **1**.3 Hz between the hydrogen addend and the hydroxyl group.

silica gel, and no HPLC separation was necessary as it is required for the separation of the pure isomers **1–4**. Oxidation side-products from the other isomers **1**, **3** and **4** were obtained in minor amounts, too.

To gain more insight into this reaction we took a closer look at isomer 2. Single crystals of compound 2 were obtained from a mixture of isomers 2 and 3 in CDCl₃. The X-ray structure of 2 is shown in Fig. 1a with the pyrrole unit in the middle, highlighted in green, and the two hydrogen addends in the α' position. Interestingly, isomer 2 crystallizes in a straight-stacking motif with the stacking axis in direction *b* of the unit cell (Fig. 1c). The closest intermolecular C···C distance is between two azafullerene cores of adjacent stacks and measures 3.19 Å (Fig. 1d). The co-crystallized solvent molecules (CDCl₃, omitted for clarity in Fig. 1) are disordered and confined to channels along the stacking axis.

The pure isomer 2 can be converted to 5 like the mixture of 1-4 described above. The transformation of isomer 2 to the oxidation product 5 was monitored by ¹H NMR experiments (Fig. S2, ESI[†]).

Full characterization of the isolated oxygenated product 5 was provided by ¹H, ¹³C, COSY, HSQC, HMBC and ROESY NMR analyses, as well as by MS, HRMS, UV/Vis and IR spectroscopy. The experimental data are consistent with the structure displayed in Scheme 1 involving a newly formed double bond and one additional epoxy and hydroxyl group on the azafullerene core. The hydroxyl group is adjacent to the hydrogen on the fullerene. Coupling between the two protons H_a and H_b with 4J = 1.3 Hz is shown in the ¹H NMR spectrum (Scheme 1). We assume that the proton of the hydroxyl group is involved in a hydrogen bond presumably oriented towards the epoxy group because it gives rise to a very sharp doublet. The ¹³C NMR spectrum clearly reveals C_1 symmetry and the resonance signals of the epoxy structure and the hemi-aminal structure appear at δ = 75.22, 77.51 and 91.95 ppm. The signals of the pyrrole-like C-atoms of the starting material disappeared and the signals of the newly formed enamine double bond could be clearly observed at δ = 109.34 ppm and 160.19 ppm. No indication of carbonyl groups was found by IR and ¹³C NMR spectroscopy.



Fig. 1 (a) Single crystal structure of isomer **2** with two H- atoms in the α' position, stick representation (C yellow/green, N blue, O red, H white); (b) DFT calculated HOMO (B3LYP/6-31-G(d)) of **2**; (c) space-filling representation of the packing motif (C yellow/purple, N light blue, O red, H white) and (d) part of the crystal structure showing the closest intermolecular C···C distances. Solvent molecules (CDCl₃) are omitted for clarity.

In preliminary experiments the oxygenated product 5 was further irradiated in order to test its stability under ambient and inert (argon) conditions. The experiment shows that 5 completely decomposes within 1.5 h. In a control experiment a degassed sample of the mixture of 1-4 showed no reaction at all upon irradiation for over 30 min. Therefore, we conclude that oxygen is crucial for this initial reaction.

The first step of the observed oxygenation of 2 can be explained by a Schenck ene type reaction.²⁴ It is well known that azafullerenes as well as fullerenes can sensitize very efficiently the formation of singlet oxygen upon illumination.25,26 Moreover, the highest occupied molecular orbital (HOMO) of 2 is located at the pyrrolic double bonds according to theoretical DFT calculations at the B3LYP/6-31G(d) level (Fig. 1b). The generated singlet oxygen can attack the allylic and the rather electron poor double bond of 2 to give a hydroperoxide intermediate 6 (Scheme 2). In contrast, electron-rich olefins under these conditions form 1,2-dioxetanes.27-29 The latter mechanism is also observed for the formation of C60-N-MEM-oxo-lactam, the precursor of the C₅₉N dimer.³⁰ Furthermore, we suggest that the lone pair of the nitrogen atom plays an activating role to give the iminium ion intermediate 7 after hydroxide elimination. Subsequently, the nucleophilic hydroxide can attack the imminium intermediate 7 to form the oxygenated product 5. Scheme 2 shows a plausible ionic mechanism, however, a radical mechanism cannot be excluded. The oxidation of pyrrole derivatives is well studied and various oxidation products depending on the substitution pattern of pyrroles have been described.^{28,31} However, an oxidation product such as 5 bearing



Scheme 2 Proposed reaction mechanism for the formation of oxygenated product 5.



Fig. 2 The oxygenation products 8 and 9 obtained by photooxidation of pure isomers 1 and 4, respectively.

an enamine moiety next to aryl, epoxy and hydroxyl substituents has not been reported so far.

We also analysed the oxygenation of isomers 1, 3 and 4. Photooxidation of pure isomers 1 and 4 also led to the formation of green oxidation products. We suggest the structures 8 and 9, respectively, according to the proposed Schenck ene type mechanism. This assumption is further corroborated by NMR investigations as well as MS, IR and UV/Vis spectroscopy. The ¹³C NMR data for the oxygenated products of 1 and 4 show a similar structure like that of the oxygenated product 5. Moreover, in the ¹H NMR spectra of compounds 8 and 9 no coupling of the sp³-CH- and the OH-signals is observed. Consequently, these two functional groups must be located at remote positions. These results are consistent with the structures depicted in Fig. 2. However, upon photooxidation of isomer 3 the formation of a green reaction product was not observed. Instead, isomer 3 (Scheme 1) reacts to give orange products whose structures have not been revealed.

Interestingly, we also observed an orange intermediate during the photooxidation of either pure isomer 1 or 4. However, these intermediates are unstable and react *in situ* even in the dark to the oxyfunctionalized products 8 and 9, respectively. This observation supports the view that intermediates are present during the oxygenation as proposed for the mechanism (Fig. 2). In the case of the oxygenation of isomer 2, however, we assume that the reaction proceeded very fast since such an intermediate was not observed. Hence, this explains that the oxygenated azafullerene 5 could be isolated as the main product after a short time treatment with air and light followed by a subsequent work-up.

In conclusion, we have discovered that triaryldihydroazafullerenes with their characteristic pyrrole addition pattern involving allylic hydrogen atoms are very sensitive towards light induced oxygenation reactions. The hydrogen addends of the triaryldihydro adduct 2 in the α' position are highly reactive towards photooxidation leading to a new functionalization pattern on the heterofullerene core. We propose an oxygenation mechanism that follows a Schenk ene type reaction leading, for the first time, to new oxygenated azafullerenes. Due to the preactivated structure of the pyrrole subunit, triaryldihydroazafullerenes are ideal model compounds to analyze defined oxygenated products and the mechanism behind this photooxidation process. Investigations on oxygenation reactions and their products are of great interest especially for carbon allotropes regarding the use of graphene oxide.

The authors thank the Deutsche Forschungsgemeinschaft (DFG – SFB 953, Project A1, "Synthetic Carbon Allotropes") and the project "Solar Technologies Go Hybrid" (State of Bavaria) for financial support.

Notes and references

- 1 J. C. Hummelen, B. Knight, J. Pavlovich, R. González and F. Wudl, Science, 1995, 269, 1554–1556.
- 2 B. Nuber and A. Hirsch, Chem. Commun., 1996, 1421-1422.
- 3 A. Hirsch and M. Brettreich, *Fullerenes, Chemistry and Reactions*, Wiley-VCH, Weinheim, Germany, 2005.
- 4 D. Tasis, N. Tagmatarchis, A. Bianco and M. Prato, *Chem. Rev.*, 2006, **106**, 1105–1136.
- 5 N. O. Weiss, H. Zhou, L. Liao, Y. Liu, S. Jiang, Y. Huang and X. Duan, *Adv. Mater.*, 2012, 24, 5782–5825.
- 6 A. K. Geim, Science, 2009, 324, 1530-1534.
- 7 D. R. Dreyer, S. Park, C. W. Bielawski and R. S. Ruoff, *Chem. Soc. Rev.*, 2010, **39**, 228–240.
- 8 S. Eigler, M. Enzelberger-Heim, S. Grimm, P. Hofmann, W. Kroener, A. Geworski, C. Dotzer, M. Röckert, J. Xiao, C. Papp, O. Lytken, H.-P. Steinrück, P. Müller and A. Hirsch, *Adv. Mater.*, 2013, 25, 3583–3587.
- 9 A. Lerf, H. He, M. Forster and J. Klinowski, J. Phys. Chem. B, 1998, 102, 4477-4482.
- 10 L. B. Casabianca, M. A. Shaibat, W. W. Cai, S. Park, R. Piner, R. S. Ruoff and Y. Ishii, *J. Am. Chem. Soc.*, 2010, **132**, 5672–5676.
- 11 S. Eigler, C. Dotzer, F. Hof, W. Bauer and A. Hirsch, *Chem.-Eur. J.*, 2013, **19**, 9490–9496.
- 12 H. Wang, T. Maiyalagan and X. Wang, ACS Catal., 2012, 2, 781-794.
- 13 F. Hauke and A. Hirsch, Tetrahedron, 2001, 57, 3697-3708.
- 14 G. C. Vougioukalakis, M. M. Roubelakis and M. Orfanopoulos, J. Org. Chem., 2010, 75, 4124–4130.
- 15 F. Hauke and A. Hirsch, Chem. Commun., 2001, 1316-1317.
- 16 U. Reuther and A. Hirsch, Chem. Commun., 1998, 1401-1402.
- 17 G. Zhang, S. Huang, Z. Xiao, Q. Chen, L. Gan and Z. Wang, J. Am. Chem. Soc., 2008, 130, 12614–12615.
- 18 N. B. Shustova, I. V. Kuvychko, A. A. Popov, M. von Delius, L. Dunsch, O. P. Anderson, A. Hirsch, S. H. Strauss and O. V. Boltalina, *Angew. Chem.*, 2011, **123**, 5651–5654.
- 19 N. B. Shustova, I. V. Kuvychko, A. A. Popov, M. von Delius, L. Dunsch, O. P. Anderson, A. Hirsch, S. H. Strauss and O. V. Boltalina, *Angew. Chem., Int. Ed.*, 2011, **50**, 5537–5540.
- 20 R. Neubauer, F. W. Heinemann, F. Hampel, Y. Rubin and A. Hirsch, Angew. Chem., 2012, 124, 11892–11896.
- 21 R. Neubauer, F. W. Heinemann, F. Hampel, Y. Rubin and A. Hirsch, Angew. Chem., Int. Ed., 2012, 51, 11722–11726.
- 22 A. G. Avent, P. R. Birkett, J. D. Crane, A. D. Darwish, G. J. Langley, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1994, 1463–1464.
- 23 Y. Matsuo and E. Nakamura, Chem. Rev., 2008, 108, 3016-3028.
- 24 G. Schenck, Naturwissenschaften, 1948, 35, 28-29.
- 25 N. Tagmatarchis, H. Shinohara, M. Fujitsuka and O. Ito, J. Org. Chem., 2001, 66, 8026–8029.
- 26 J. W. Arbogast, A. P. Darmanyan, C. S. Foote, F. N. Diederich, R. L. Whetten, Y. Rubin, M. M. Alvarez and S. J. Anz, J. Phys. Chem., 1991, 95, 11–12.
- 27 M. Prein and W. Adam, Angew. Chem., Int. Ed., 1996, 35, 477-494.
- 28 Singlet Oxygen, ed. H. H. Wasserman and R. W. Murray, Academic Press, Inc., New York, London, 1979.
- 29 M. N. Alberti and M. Orfanopoulos, in *CRC Handbook of Organic Photochemistry and Photobiology*, ed. M. O. Axel Griesbeck and F. Ghetti, CRC Press, Third edn, 2012, vol. 1, pp. 765–787.
- 30 J. C. Hummelen, M. Prato and F. Wudl, J. Am. Chem. Soc., 1995, 117, 7003–7004.
- 31 M. N. Alberti, G. C. Vougioukalakis and M. Orfanopoulos, J. Org. Chem., 2009, 74, 7274–7282.