PERKIN 2
COMMUNICATION

Electronic absorption and vibrational spectroscopy of azafullerene $C_{59}HN$ and its oxide $C_{59}HNO$

Nikos Tagmatarchis,[a] **Hisanori Shinohara,***[a] **Thomas Pichler,**[bc] **Matthias Krause**[b] **and Hans Kuzmany**[b]

[a] *Department of Chemistry, Nagoya University, Nagoya 464-8602, Japan*
[b] *Universität Wien, Institut für Materialphysik, Strudlhofgasse 4, A-1090 Wien, Austria*
[c] *Institut für Festkoerper und Werkstofforschung e.V., PO Box 270016, 01171 Dresden, Germany*

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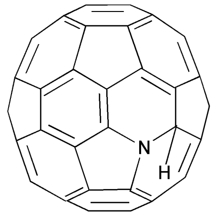
Monomeric hydroazafullerene $C_{59}HN$ has been synthesized and isolated by HPLC in its pure form, which has been efficiently oxidized to give $C_{59}HNO$ in the presence of oxygen under irradiation with a UV lamp; mid-IR, UV–Vis–NIR and FT-Raman spectra have been measured. Analyses of the electronic absorption and vibrational spectra of $C_{59}HN$ and $C_{59}HNO$ are also reported.

The introduction of heteroatoms into fullerene networks fundamentally affects their structural and electronic properties.[1–4] Exchange of one carbon atom in the C_{60} molecule with nitrogen, a trivalent element with a lone pair of electrons, produces the azafullerene radical $C_{59}N^{\bullet}$ which is found either to rapidly dimerise yielding bisazafullerene $(C_{59}N)_2$[5] or to abstract a hydrogen atom to form the parent hydroazafullerene $C_{59}HN$.[6] Due to the lowering of the symmetry, the t_{1u} triplet LUMO of the $C_{59}N^{\bullet}$ radical is no longer triply degenerate. Moreover, it is an open shell with a partially occupied t_{1u} orbital with reduced energy.[7] Although the bulk synthesis of the monomeric form of azafullerene $C_{59}HN$ was described four years ago, no further studies of its structural, electronic and solid state properties or its chemical reactivity and potential applications have been performed.



$C_{59}HN$ Hydroazafullerene

In this communication we report the reaction conditions we have applied for the synthesis of $C_{59}HN$ that guarantee more than 99.9% pure isolated material after HPLC treatment. The species are characterized *via* FT-IR, FT-Raman and UV–Vis–NIR absorption spectroscopy. Also, an oxide derivative $C_{59}HNO$ is synthesized and a direct comparison with its precursor is made.

Starting from C_{60} and following a two-step literature procedure a [60]-N-MEM ketolactam was isolated.[5] Then, a large excess of 100 equivalents of *p*-TsOH was added to an *o*-dichlorobenzene solution of the ketolactam and after degassing with Ar the system was refluxed for 7 minutes.[8] A rapid reaction occurred and after quickly cooling down the system to room temperature by immersing the reaction flask in an ice bath to prevent further dimerisation, hydroazafullerene $C_{59}HN$ was isolated by flash column chromatography with toluene as eluent. The product was purified further by high performance liquid chromatography on a 5PYE column.[9]

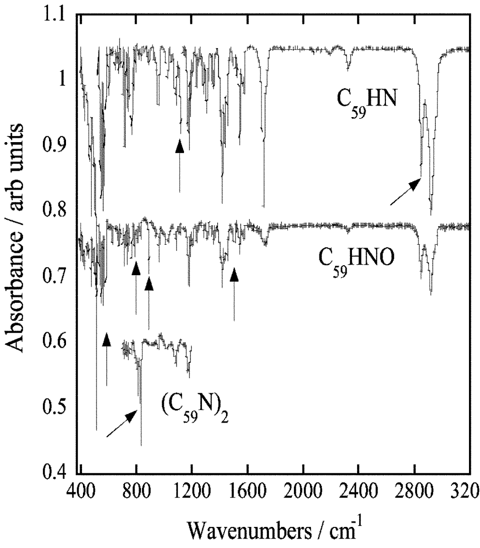


Fig. 1 Mid-IR spectra of $C_{59}HN$ (top) and $C_{59}HNO$ (middle) and a partial spectrum of $(C_{59}N)_2$ (bottom). The arrows on each spectrum identify characteristic lines for each compound.

In order to obtain the oxide derivative a slow stream of molecular oxygen was bubbled into a toluene solution of $C_{59}HN$ and the solution was irradiated with a UV lamp for a period of 40 minutes.[10] In addition, we have recently found that both $C_{59}HN$ and $(C_{59}N)_2$ can produce sufficient amounts of singlet oxygen and therefore sensitize the photooxygenation of olefins.[11]

For the FT-IR and Raman measurements thin films of the isolated compounds were prepared by the drop-coating technique on gold-coated silicon substrates with condensed toluene samples. Fig. 1 shows the mid-IR spectra of $C_{59}HN$, $C_{59}HNO$ and a partial region of the dimer $(C_{59}N)_2$[12] for comparison. Interestingly, in the spectrum of $C_{59}HNO$ the appearance of at least four new absorbance peaks with respect to the $C_{59}HN$ was observed. The new lines appear at 587, 792, 895 and 1506 cm^{-1} and should most probably be attributed to the N–O bending and the stretching modes rather than to any C–O[13] vibrational mode. The disappearance of the absorption modes at 820–840 cm^{-1} from the bisazafullerene and the simultaneous growth of new ones at 1170 cm^{-1} clearly show that the two materials possess different absorption spectra and therefore can be easily distinguished from each other.[14] Thus, for the first time we are able to unambiguously provide fingerprint regions for all of this novel class of materials.

Fig. 2 shows the UV–Vis–NIR electronic absorption spectra of $C_{59}HN$ and $C_{59}HNO$ in carbon disulfide solution. The onset of $C_{59}HN$ lies at a high energy around 900 nm. Basically, the onset of a UV–Vis–NIR spectrum corresponds to the lowest

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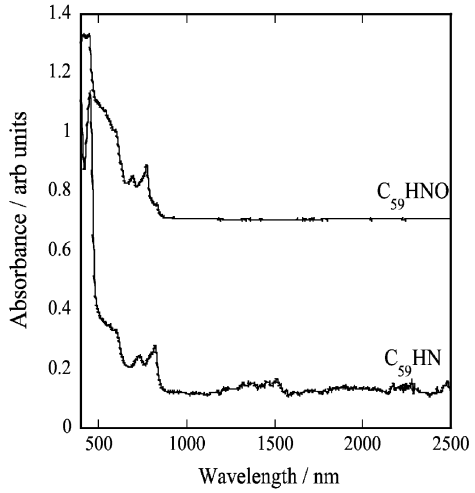

Fig. 2 UV–Vis–NIR absorption spectra of $C_{59}HN$ (bottom) and $C_{59}HNO$ (top).

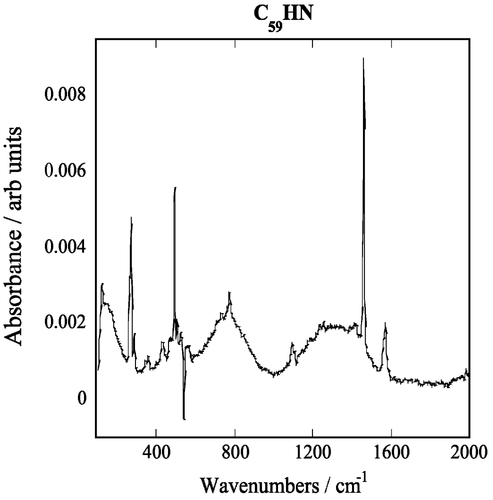

Fig. 3 FT-Raman vibrational spectrum of the hydroazafullerene $C_{59}HN$.

electronic transitions and thus is a good measure of the HOMO–LUMO energy gap. This means that hydroazafullerene $C_{59}HN$ should possess a large HOMO–LUMO band-gap which is also consistent with its remarkable stability both in solution and in the solid state. There are also other characteristic features observed for the monomer $C_{59}HN$ at 450, 600, 740, 816 nm and also a couple of broad peaks at around 1300 and 1950 nm. A separate measurement of its electronic absorption spectrum was performed in the solid state in order to verify that the broad peaks that appeared after the onset do not come from the background. We found that the onset of the hydroazafullerene in the solid state is continuous down to 2400 nm; this would most probably be attributable to a higher excited state of the material. An overall comparison with the electronic absorption spectrum of its oxide derivative $C_{59}HNO$ reveals close similarities between the two materials.

We have also measured the FT-Raman spectrum of $C_{59}HN$ which is presented in Fig. 3.[15] As expected, the transformation from C_{60} to $C_{59}HN$ results in an increase of the Raman active modes as a consequence of lowering the overall molecular symmetry from I_h to C_s. The strongest lines appear at 270, 492, 1460 and 1570 cm^{-1}. Overall the modes are slightly shifted towards lower energies with respect to those of C_{60} as a result of the symmetry reduction and the higher molecular mass of the material. Excitation with lasers having different wavelengths and temperature dependent studies of this unique material would allow a direct comparison with previous results based on the dimer derivative[16] and provide information on its stability and detailed electronic properties, a study which is currently underway.

It is worth mentioning that the material was found to be remarkably stable during all these studies. Time dependent infrared studies showed that neither dimerisation nor derivatisation to any oxidation adducts occurred in the solid state. Also the material remains unchanged in toluene solution in the dark for at least several weeks.

In summary, for the first time, we have prepared, in a very pure form, the parent hydroazafullerene from a [60]-N-MEM ketolactam under reaction conditions different from those of the literature method. Also, its *N*-oxide derivative was synthesized and UV–Vis–NIR absorption electronic spectra as well as FT-Raman and mid-IR vibrational spectra were recorded, analysed and compared.

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8 Further refluxing of the system (*ca.* 15 minutes) produces bisazafullerene as the major product and only minor amounts of the monomeric material.

9 The material shows low affinity for both 5PYE and buckyprep columns. The retention time on a 5PYE column was 7.9 minutes, with toluene as eluent at a 10 ml min^{-1} flow rate.

10 LD-TOF mass spectrometry of the *N*-oxide derivative either with or without dithranol as matrix shows a base peak at a mass-to-charge ratio $m/z = 739$. Under similar conditions the mass-to-charge ratio for the parent hydroazafullerene is at $m/z = 723$.

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13 Previous measurements did not reveal any infrared fingerprint mode of the epoxy group in $C_{60}O$. This is further evidence that the oxidation has happened on the nitrogen rather than on the carbon of the fullerene skeleton to form an epoxide. See also: M. Krause, L. Dunsch, G. Seifert, P. W. Fowler, A. Gromov, W. Kraetschmer, R. Gutierez, D. Porezag and T. Frauenheim, *J. Chem. Soc.*, *Faraday Trans.*, 1998, **94**, 2287.

14 Surprisingly, in the first report of the synthesis of $C_{59}HN$ (ref. 6) both its infrared and UV–VIS spectra are quite similar to the ones of the dimer $(C_{59}N)_2$.

15 FT-Raman scattering of the *N*-oxide derivative was also measured (not shown) though the background of the spectrum was very high due to luminescence.

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