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Heterofullerenes

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1. Heterofullerenes: An Introduction

In heterofullerenes,[1−3] one or more carbon atoms that form the fullerene carbon cage are replaced by a non-carbon atom, i.e., a heteroatom. Consequently, substitution of an odd number of C atoms by trivalent atoms such as nitrogen or boron leads to radicals which can be stabilized by dimerization, whereas the replacement of an even number of C atoms would directly result in closed-shell systems. However, also heteroatoms with other valencies are plausible. Conceptually, the systematic substitution of cage C atoms by heteroatoms, i.e., the transition from fullerenes to heterofullerenes, represents the three-dimensional counterpart of the transition from planar aromatics to heteroaromatics. A number of reviews concerning heterofullerenes appeared between 1995 and 2000,[1,3−16] spanning the period only of heterofullerenes' discovery and seminal syntheses. Some of them cover the whole area of heterofullerenes;[1−8] in others only a part of the field (e.g., azafullerenes) is reviewed.[9−16] During the first years of the new century, derivatization and exohedral chemistry became the main focus of heterofullerene chemistry. The aim of the present review is to provide a complete and up-to-date evaluation of the chemistry and physics of heterofullerenes. Special emphasis is given to functional derivatives of azafullerenes.

Six years after the experimental discovery of the fullerenes[17] and shortly after the elaboration of bulk syntheses of fullerenes,[18] Smalley and co-workers reported on the gas-phase formation and mass spectrometric detection of borafullerenes $C_{60-n}B_n$ ($n = 1-6$), generated by laser vaporization of graphite/boron nitride composites.[19] In the following year, the preparation of a number of C_nN_m clusters formed by contact-arc vaporization in a partial N_2 or NH_3 atmosphere and by reactive collision scattering of N^+ with C_{60}, respectively, was reported.[20,21] However, none of these species have been isolated or structurally characterized. In 1994, Clemmer et al. presented evidence for the formation of metal heterofullerenes C_nNb^+ ($n = 28-50$) upon pulsed laser vaporization of a mixed NbC/graphite rod.[22] No clusters with a C:Nb ratio of ~60:1 were detected, however. Muhr et al. reported on the preparation of monoborafullerenes $C_{59}B$, $C_{69}B$, and higher homologues by arc evaporation of doped graphite rods in a modified fullerene reactor.[23] However, presumably due to the instability of these systems no material could be isolated and completely characterized.

The real preparative heterofullerene chemistry began in 1995, when Mattay[24] and Hirsch,[25] respectively, discovered that certain exohedrally *N*-substituted epiminofullerenes and azahomofullerenes (azafulleroids) represent suitable precursors for a gas-phase rearrangement forming positively charged heterofullerenium ions such as $C_{59}N^+$ and $C_{69}N^+$. In the same year, the group of Wudl[26] accomplished the first synthesis of heterofullerenes in bulk quantities with the preparation of aza[60]fullerene ($C_{59}N$, **1**) and its dimer [$(C_{59}N)_2$, **2**]. Shortly afterward, the group of Hirsch also succeeded in the bulk preparation of **1** and **2**.[27] Subsequently, azafullerenes became by far the most studied heterofullerenes till now. As a consequence, the major part of this review covers nitrogen heteroanalogues of [60]fullerene (C_{60}) and [70]fullerene (C_{70}) and their derivatives.

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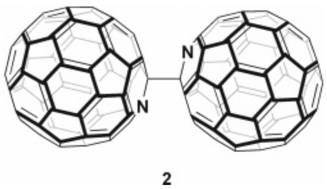

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2. Azafullerenes

2.1. Azafullerenes from Exohedral Imino Derivatives of C_{60}

A convenient route for the direct formation of nitrogen heterofullerenes is the cluster rearrangement within exohedral fullerene derivatives such as iminofullerenes and azafulleroids. The first hints for this approach were obtained from mass spectrometry investigations of the *cis*-1-diazabishomo-

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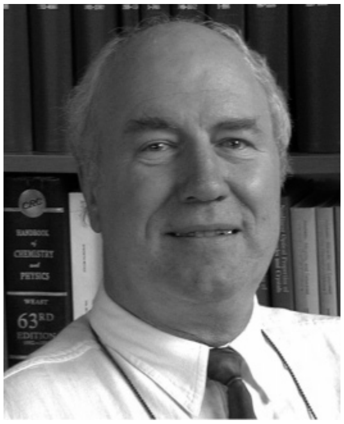
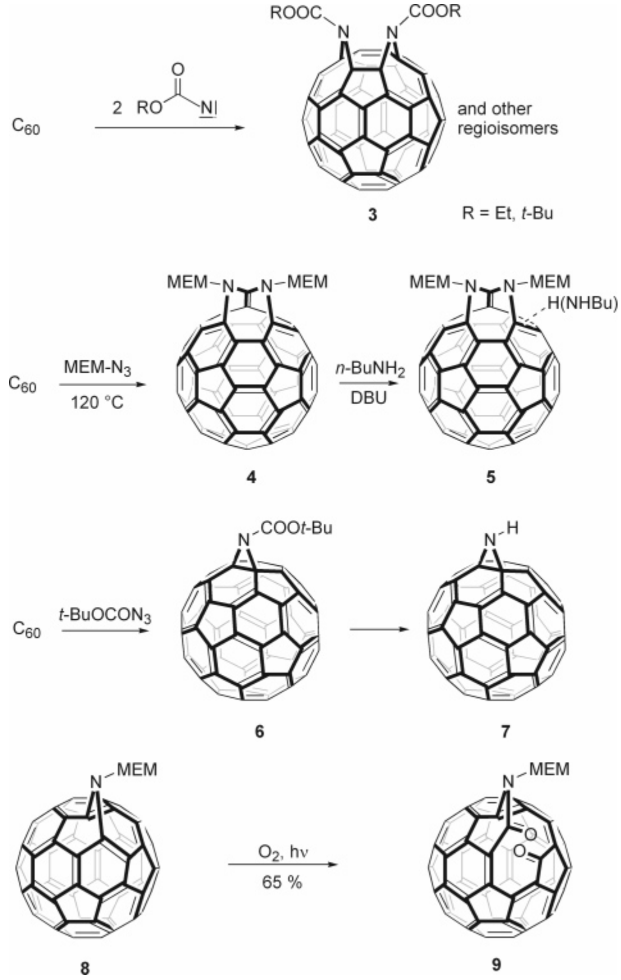
Andreas Hirsch was born in Esslingen, Germany, in 1960. He studied chemistry at the University of Tübingen, Germany, and obtained his Ph.D. in 1990 under Michael Hanack. After a postdoctoral stay at the Institute for Polymers and Organic Solids in Santa Barbara, CA, with Fred Wudl, he returned in 1991 to Tübingen as a research associate at the Institute for Organic Chemistry. After his Habilitation in 1994 he joined the faculty of the Department of Chemistry at the University of Karlsruhe as a professor. Since October 1995, he has been Full Professor of Organic Chemistry at Friedrich-Alexander-Universität, Erlangen-Nürnberg. His main research activities have been focused on the development of methodologies for efficient syntheses of exohedral derivatives of fullerenes and their use as structural templates and building blocks for supramolecular architectures and nanomaterials. Other research interests are in the area of dendrimers, calixarene conjugates, oligoynes and polyynes, synthetic lipids and amphiphiles, model compounds for photoinduced charge separation, and chemical derivatization and solubilization of carbon nanotubes and the investigation of their synthetic potential and properties as new materials.



Otto Vostrowsky was born in 1944 in Vienna, Austria. He received his chemical education at the University of Vienna, Austria, where he obtained his Ph.D. in 1971 at the Institute for Organic Chemistry with M. Pailer. In 1972 he took a postdoctoral position at the Department of Organic Chemistry at Friedrich-Alexander-Universität, Erlangen-Nürnberg. with H. J. Bestmann, where he is currently working as Akademischer Direktor with Andreas Hirsch. His main research interests have included synthetic phosphorus chemistry, the structure elucidation and synthesis of insect semiochemicals, the analysis of essential oils, the use of plant constituents as an integrated tool in pest management, and general natural product chemistry and mass spectrometry. For more than 10 years, his research goals have shifted to the chemistry of fullerenes and nanomaterials.

Scheme 1. Syntheses of *cis*-1-Diazabishomo[60]fullerene 3, the *n*-Butylamine Adduct 5, the 1,2-Epiminofullerene 7, and the Cluster-Opened Ketolactam 9



[60]fullerene **3**,[25] the *n*-butylamine adduct **5**,[25] the 1,2-epiminofullerene **7**,[24] and the cluster-opened ketolactam **9** (Scheme 1).[26] *cis*-1-Diazabishomo[60]fullerene **3** was obtained from the 2-fold addition of the corresponding nitrenes to C_{60}.[28] The addition of MEM azide to C_{60} afforded the bisazafulleroid **4**, which upon treatment with *n*-BuNH$_2$/DBU reacted to give butylamine adduct **5** (Scheme 1).[27] The parent 1,2-epimino[60]fullerene (**7**) was generated via deprotection from the carbamate **6** (Scheme 1).[24] *N*-MEM ketolactam **9** was obtained from self-sensitized photooxygenation of *N*-MEM-aza[60]fulleroid **8** (Scheme 1).[29]

The mass spectra of the exohedral imino derivatives **3**, **5**, **7**, and **9** revealed an unprecedented fragmentation behavior. Whereas the usual exohedral adducts of C_{60} show the typical characteristics, namely, relatively small M^+ peaks and the peaks of the fullerene fragment ions C_{60}^+ at $m/z = 720$ as the most intense signals, the fragmentation (FAB mass spectrometry) of cluster-opened **3** and the isomeric mixture of *n*-butylamine adducts **5** led most efficiently to ions with masses of 722. This must be assigned to the heterofullerenium ion $C_{59}N^+$,[25] which is isoelectronic with C_{60}. After the first "shrink wrapping",[19,25] the signals of the fragment ions $C_{57}N^+$ were also of pronounced intensity, the ^{15}N-labeled analogues of **5** gave rise to the most intensive fragmentation signals at $m/z = 723$, and the high-resolution MS signal with $m/z = 722$ was consistent with the formula $C_{59}N^+$. The parent **7** under the conditions of DCI (desorptive chemical ionization) mass spectrometry (reagent gas NH_3) afforded fragmentation signals at $m/z = 723$ and 724, due to $C_{59}NH^+$ and $C_{59}NH_2^+$.[24] Under FAB mass spectrometric conditions, ketolactam **5** efficiently fragmented to $C_{59}N^+$[26] and no fragmentation to C_{60} was observed at all.

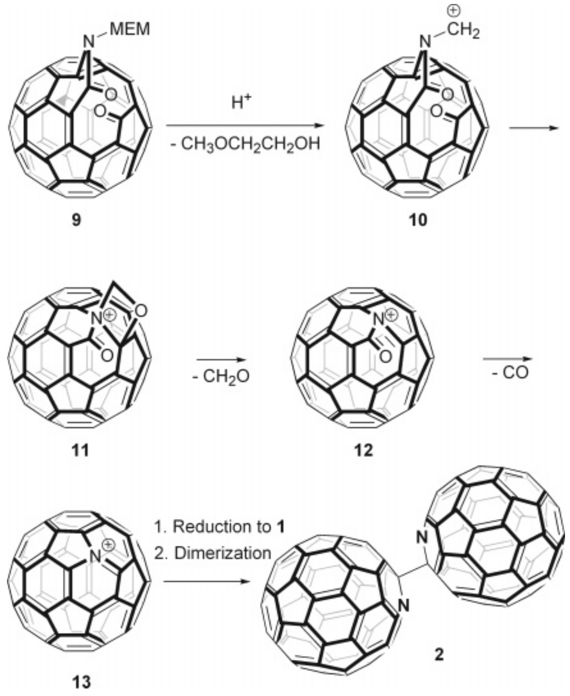
The formation of nitrogen heterofullerene $C_{59}N$ following laser ablation of a series of fullerene derivates, all of which were substituted with organic ligands bound to the carbon cage through a nitrogen atom, has been investigated by Hirsch and Drewello et al. utilizing laser desorption/ionization mass spectrometry.[30] This approach was found to be a new and efficient way to implement the initially exohedral nitrogen atom into the carbon network and to produce azafullerenes in the gas phase.

The synthesis of highly ^{13}C isotope enriched azafullerene $C_{59}N$, embedded in C_{60} and to be used for nuclear spin labeling, was reported by Kuzmany and co-workers.[31] ^{13}C-enriched fullerenes, produced by the Krätschmer−Huffman process, were subjected to a N_2 discharge that produced ^{13}C-enriched $C_{59}N$ in low yield. Raman spectroscopy of the products indicated a homogeneous ^{13}C distribution.

2.2. Synthesis of Bis(aza[60]fullerenyl) [$(C_{59}N)_2$, 2]

On the basis of the mass spectrometric results, synthetic routes were designed to mimic these fragmentation processes in the gas phase. Refluxing **9** in *o*-dichlorobenzene (ODCB) in the presence of a 12−20-fold excess of *p*-TsOH led to the formation of heterofullerene "$C_{59}N$", which exhibits a green color in solution. However, instead of **1**, which is an open-shell system, as demonstrated by cyclovoltammetry, ESR, and ^{13}C NMR spectroscopy, the diamagnetic dimer **2** was isolated (Scheme 2).[26] The suggested mechanism for the formation of **2** involves the acid-catalyzed cleavage of the MEM group of **9** as the first step, followed by an intramolecular ring formation to the 1,3-oxazetidinium system **11**. This intermediate then loses first formaldehyde to form **12** and second CO to form the aza[60]fullerenium ion ($C_{59}N^+$, **13**). The latter is subsequently reduced to the $C_{59}N$ monomer (**1**), which undergoes dimerization to the bisazafullerenyl **2**. This mechanism was supported by trapping experiments with nucleophiles,[32] and the reducing agent was proposed to be 2-methoxyethanol from the MEM group or water. Neutral aza[60]fullerene [CAS name for the radical: 2*H*-1-aza[5,6]fulleren-C_{60}-I_h-yl] (**1**) is an open-shell molecule, due to the trivalency of nitrogen leaving a "dangling bond" on an adjacent carbon atom in the cage. Thus, the final step results in the dimerization of **1** to give **2**.[26]

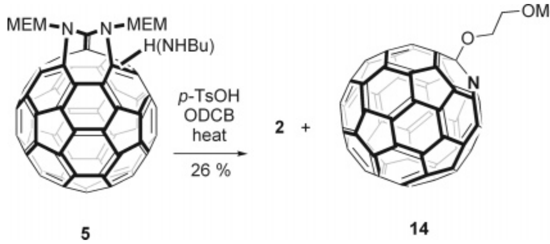
Scheme 2. Formation of Bisaza[60]fullerene [$(C_{59}N)_2$, 2], Starting from the Ketolactam 9 via *N*-Methylcarbenium Ion 10, 1,3-Oxazetidinium Intermediate 11, and the Azafullerenium Ion 13[a]



[a] Reduction stands for a general reducing agent in the reaction mixture, e.g., methoxyethanol.

The second synthetic approach to heterofullerenes in bulk quantities is based on the gas-phase fragmentation of **5** (Scheme 3).[25,26] The reaction of **5** with 20 equiv of *p*-TsOH in refluxing ODCB in an argon atmosphere gave rise to the formation of **2** in an optimized yield of 26%. It is of interest that together with the dimer **2** the alkoxy-substituted monomeric compound **14** was formed. This exohedral heterofullerene adduct, however, decomposes to form a cluster-opened system exhibiting carbonyl vibrations in the IR spectra.[27] Nevertheless, ^{13}C NMR investigations on **14** showed for the first time the resonance of the sp^3 fullerene C atom carrying the addend at $\delta = 90.03$[27] similar to that of the inter-fullerene bond within **2**.[33]

Scheme 3. Formation of Bisaza[60]fullerene [$(C_{59}N)_2$, 2], Starting from Activated Bisazafulleroid 5, and the Structure of the Trapping Product 14



Although the mechanism of the fragmentation reaction is not fully understood at present, mass spectrometric investigations of **5** with ^{15}N-labeled imino bridges revealed the formation of the fragment ion $C_{59}{}^{15}N^+$ (FAB-MS), demonstrating that the nitrogen atom within the azafullerene framework must originate from one of the imino bridges of the diazabishomo[60]fullerene precursor **5**.[25]

2.3. Synthesis of Bis(aza[70]fullerenyl) [$(C_{69}N)_2$]

The concept of fragmentation of activated diazabishomofullerenes was also applied by Hirsch et al. for the first synthesis of aza[70]fullerenes.[27] Since the parent fullerene C_{70} (D_{5h}) possesses five inequivalent types of carbon atoms (A, B, C, D, and E in Figure 1), five different isomeric $C_{69}N\bullet$ radicals can in principle be considered. The simultanous formation and dimerization of all five different radicals (by specific [6,6]-α-carbon atom bonds) could lead to 15 distinct $(C_{69}N)_2$ dimers.[1] The C_s-symmetric diazabis[70]homofullerene **15** with a 1,6:1,9-addition pattern is the precursor of aza-[70]heterofullerenes, where a C atom of set A (Figure 1) is replaced by a N atom, whereas C_s-symmetric **16** with a 2,3:2,12-addition pattern serves as the starting material for

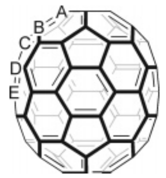
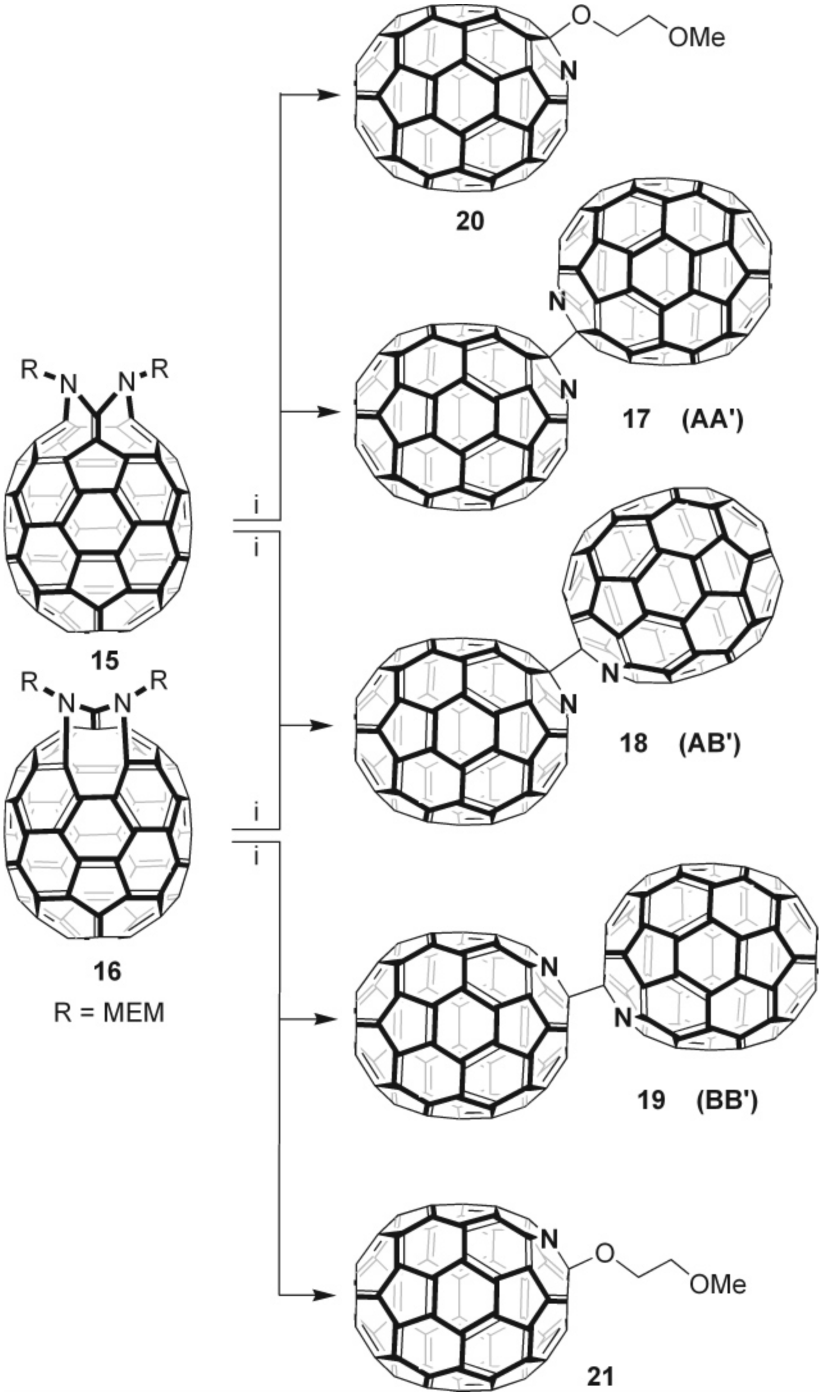


Figure 1. Five sets (A, B, C, D, E) of different C atoms in C_{70}.

Scheme 4. Synthesis of Aza[70]fullerenes $(C_{69}N)_2$ 17, 18, and 19, Starting from Bisazafulleroids 15 and 16[a]



[a] Reagents and conditions: (i) *n*-butylamine, *p*-TsOH, ODCB, heat.

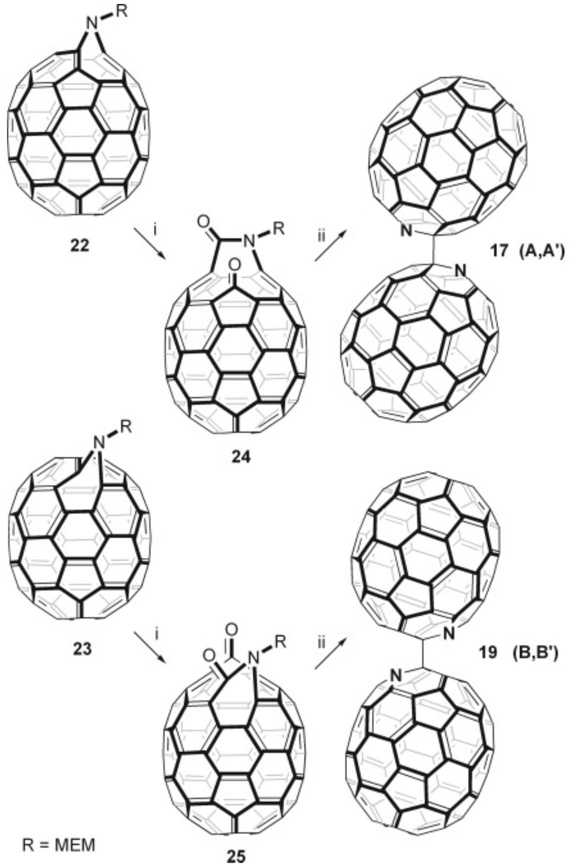
heterofullerene isomers containing the N atom in the B position (Figure 1). When a 4:1 mixture of **15** and **16** was allowed to form heterofullerenes under the same conditions used for the synthesis of **2**,[27] a mixture of all three possible dimers **17**−**19** with AA′, AB′, and BB′ substitution patterns was formed (Scheme 4).[27]

The ratio of the constitutional AA′, AB′, and BB′ isomers **17**−**19** as determined by HPLC was 16:3:1. Similarly to the synthesis of the aza[60]fullerenes, alkoxy-substituted aza[70]fullerene monomers **20** and **21** were formed together with the dimers **17**−**19** (Scheme 4).[27] The two monomers **20** and **21** appeared in a ratio of 7:1. ^{13}C NMR spectroscopy revealed a closed structure; e.g., the signal of the sp^3 C atom of **20** appeared at $\delta = 96.42$. In conclusion, three of the five possible homodimers of aza[70]fullerene and two monomeric aza[70]fullerene derivatives had been synthesized up to that time.

The Wudl group also applied their method of heterofullerene formation to synthesize aza[70]fullerenes. Starting from the [5,6]-bridged azahomo[70]fullerenes **22** (C_s symmetry) and **23** (C_1 symmetry), they selectively synthesized the AA′ aza[70]fullerene isomer **17** and the BB′ isomer **19** by photooxygenation and specific decomposition of the ketolactams **24** and **25**, respectively (Scheme 5).[34] A third minor $(C_{69}N)_2$ isomer, derived from **23**, could not be characterized because of the minute yield of formation.[1]

Upon a modified procedure the isolation of the C_1-symmetrical *N*-MEM-azahomo[70]fullerene isomer **23** was

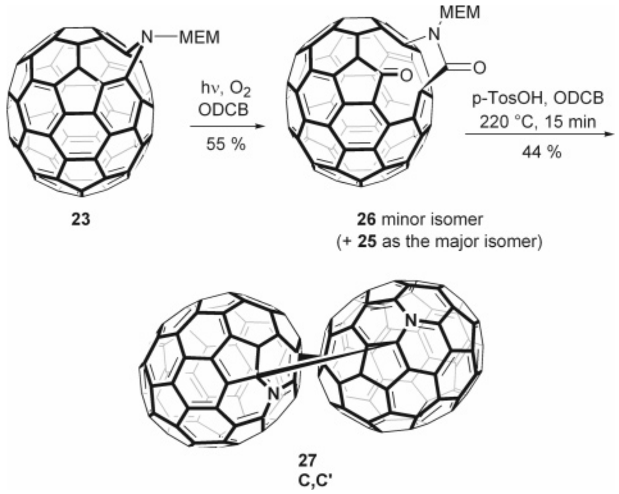
Scheme 5. Synthesis of Aza[70]fullerenes 17 and 19 Starting from Aza[70]fulleroids 22 and 23[a]



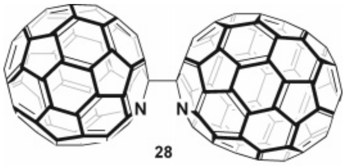
[a] Reagents and conditions: (i) $^1O_2$; (ii) *p*-TsOH, ODCB, heat.

achieved in excellent yields by Shinohara's group in 2000.[35] The photooxygenation of **23** enabled the isolation and characterization of two ketolactams, the major ketolactam **25** and the minor constituent ketolactam **26** (Scheme 6). The latter served as the precursor compound for the synthesis of the third less abundant isomer $(C_{69}N)_2$ **27**. The synthesis yield of **27** was sufficient for a complete spectroscopical characterization. The HPLC retention time of **27** on a 5PYE column is between those of the two other more abundant species **17** and **19**.[35]

Scheme 6. Synthesis of the Less Abundant $(C_{69}N)_2$ Isomer 27 Starting from the Minor Ketolactam Isomer 26



The first mixed $C_{59}N-C_{69}N$ heterodimers **28** and **29** were synthesized in a similar way.[1] Treatment of a 1:1 molar solution of [60]ketolactam **9** and [70]ketolactam **25** with *p*-TsOH in refluxing ODBC and subsequent HPLC analysis revealed the presence of $(C_{59}N)_2$, $(C_{69}N)_2$, and the heterodimer $C_{59}N-C_{69}N$ **28**.[1] In another aproach, an equimolar solution of aza[60]fullerene $(C_{59}N)_2$ (**2**) and aza[70]fullerene $(C_{69}N)_2$ **17** was heated in refluxing ODBC, and the homodimers **2** and **17** and the heterodimer $C_{59}N-N_{69}N$ **29** were found in the product mixture.[1] The three dimers were formed in a 1:1:2 ratio (**2**:**17**:**29**), suggesting an equilibrium with statistical mixing with each other.[1]



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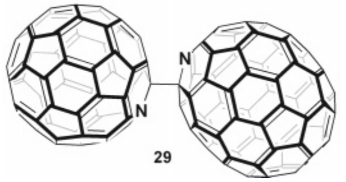

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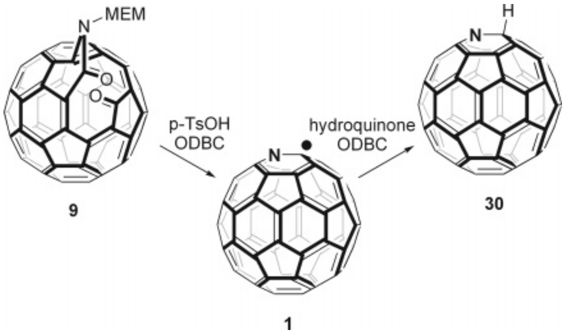
2.4. Chemistry of the Azafullerenes

The first heterofullerene derivatives, namely, the monomeric alkoxy-sustituted derivatives **14**, **20**, and **21**, were formed during the formation of azafullerenes and dimers (Schemes 3 and 4). Similar to these ether derivatives, a number of monosubstituted heterofullerene adducts are plausible by trapping the intermediate azafullerenyl radical with radicals, by reduction of the azafullerenyl with hydrogen donors, or by reaction of the corresponding azafullerenium ion $C_{59}N^+$ with nucleophiles. In all cases, the substituents are positioned at the 2-position next to the nitrogen atom, which is the carbon atom constituting the N−C [6,6]-bond. In addition, since all aza[60]fullerene monoderivatives have 16 different carbon [6,6]-double bonds, access to a broad variety of bisadducts and polyadducts is in principle possible by subsequent additions to the azafullerene core. Two types of synthetic methods toward monomeric aza[60]fullerene derivatives have to be considered, i.e., route A, starting from a nonaza[60]fullerene precursor, and route B, starting from the dimer **2**. The first example of a heterofullerene derivative synthesized according to route A was the parent hydroaza[60]fullerene ($C_{59}NH$, **30**). It was obtained by the treatment of precursor ketolactam **9** with *p*-TsOH and a 15-fold excess of hydroquinone.[32] The hydroquinone is assumed to reduce the $C_{59}N$ radical intermediate **1** (Scheme 7). ^{13}C NMR spectroscopy allowed for unambiguous assignment of the [6,6]-closed structure to **30**. The symmetry of the parent **30** as well as that of all monomeric hetero[60]fullerene derivatives, derived from reaction of the azafullerenyl radical or the corresponding azafullerenium ion $C_{59}N^+$, with the addend attached to the 2-position is C_s. Sixteen regioisomeric bisadducts are possible upon a subsequent cycloaddition to the [6,6]-bond of the heterofullerene core, three of them with C_s symmetry (two different *e* positions and *trans*-1) and thirteen with C_1 symmetry (for the regiochemistry of multiple addition to C_{60} and symmetry considerations of fullerene C_{60} adducts, see ref 36). This lowering of symmetry, compared to that of C_{60} adducts, makes the assignment of carbon atoms

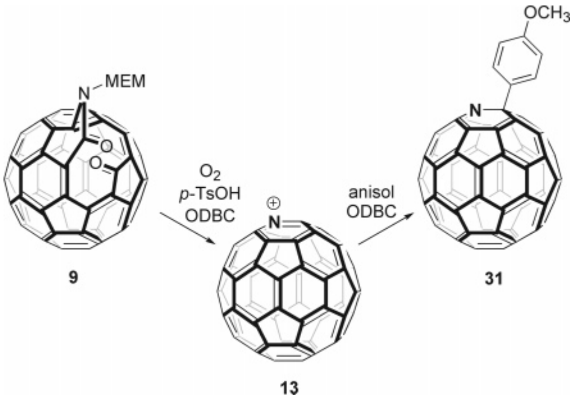
Scheme 7. Synthesis According to Route A and Proposed Reaction Mechanism of the Parent Hydroaza[60]fullerene ($C_{59}NH$, 30) from Treatment of Precursor Ketolactam 9 with *p*-TsOH and Hydroquinone in ODBC



of heterofullerenes by ^{13}C NMR spectroscopy almost impossible.

When the azafullerene synthesis was carried out with the precursor ketolactam **9** or with bisazafulleroid **5** in the presence of a large excess of anisole and air, arylated azafullerene **31** was obtained in 38% yield.[34] The yield is lower compared to that of the synthesis starting from dimer **2** (see below); however, one reaction step is saved with this method (Scheme 8).

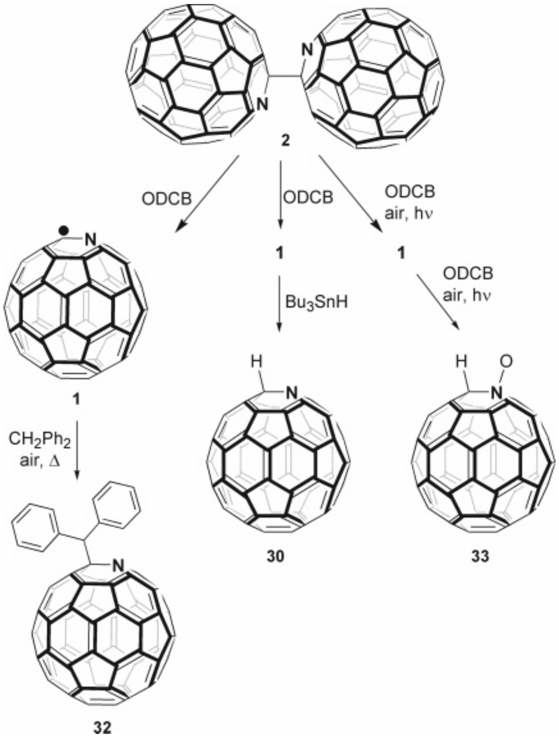
Scheme 8. Formation of Arylated Azafullerene 31 from Ketolactam 9 in the Presence of an Excess of Anisole and Air



Route B using dimer **2** as the precursor allows for access to a broad variety of azafullerene monoadducts. This route requires the homolytical cleavage of the central dimer bond of **2**. This bond appeared to be very long and to have a very low bond energy, as calculated by Car−Parinello molecular dynamics.[38] Consequently, an easy homolytical cleavage can be achieved thermally or photochemically. The monomeric radical **1** bears a valuable synthetic potential, as was demonstrated with the thermal treatment of **2** in ODCB in the presence of excess diphenylmethane (Scheme 9).[39] The resulting formation of C_s-symmetrical **32** is consistent with a free radical chain mechanism. Similarly, the parent system **30** was obtained by the thermal treatment of **1** in ODCB in the presence of Bu$_3$SnH as the hydrogen donor. Interestingly, treatment of **2** with diphenylmethane under photolytic conditions in the presence of air does not produce **32**, but the C_s-symmetrical *N*-oxide **33** (Scheme 9).[39]

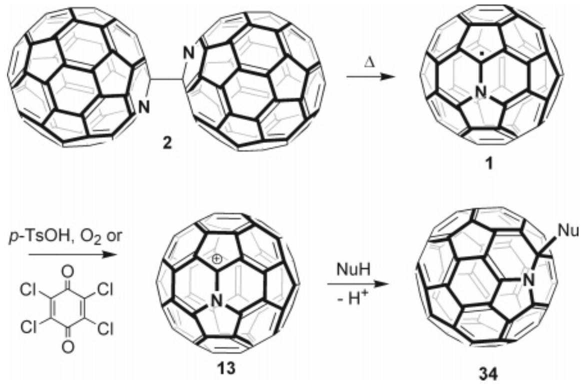
The synthetically most valuable intermediate in heterofullerene chemistry so far is **13**. It can be generated in situ by the thermally induced homolytical cleavage of **2** and subsequent oxidation, for example, with O$_2$ or chloranil.[37,40−43]

Scheme 9. Route B, Using the Dimer ($(C_{59}N)_2$) (2) as the Precursor for the Preparation of the Parent Hydroazafullerene 30, Diphenylmethyl Derivative 32, and *N*-Oxide 33



The reaction intermediate **13** can subsequently be trapped with a variety of nucleophiles such as electron-rich aromatics, enolizable carbonyl compounds, alkenes, and alcohols to form functionalized heterofullerenes **34** (Scheme 10).

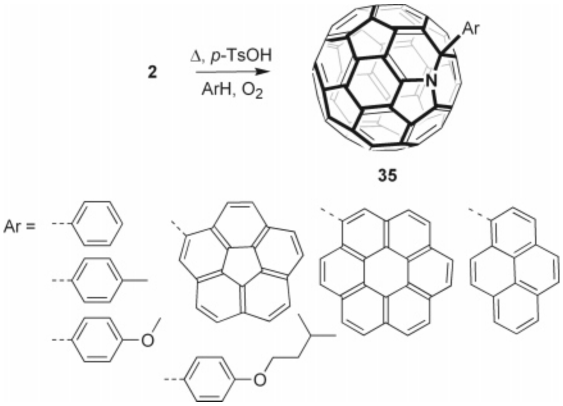
Scheme 10. Formation of Functionalized Heterofullerenes 34 via the Azafullerenium Intermediate 13



The treatment of **2** with electron-rich aromatics such as nucleophilic reagent NuH in the presence of air and an excess of *p*-TsOH leads to C_s-symmetrical arylated aza[60]fullerene derivatives such as **35** in yields up to 90% (Scheme 11). A great variety of arylated derivatives **35** including those containing planar and parabolic polycyclic aromatics such as corannulene, coronene, and pyrene addends have been synthesized, in which the aromatic moieties are connected to the spherical heterofullerene by a single σ-bond.[37,41−44]

The polycyclic aromatics directly connected to heterofullerenes resemble molecular satellite dishes. Together with the fact that heterofullerenes are good acceptors within photoinduced electron- or energy-transfer events implied that

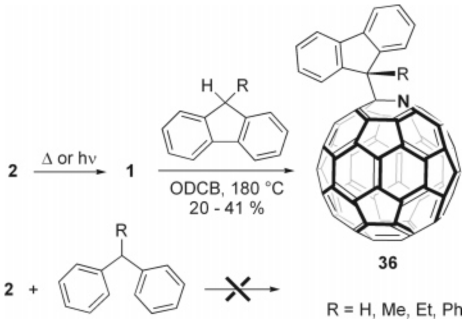
Scheme 11. Formation of Arylated Heterofullerenes $C_{59}NAr$ 35 According to Route B



this geometrical analogy is accompanied by a functional analogy. Insight into the electronic interaction between the $C_{59}N$ core and the respective arene moieties came from steady-state fluorescence spectroscopy.[44] In particular, the arene emission is nearly quantitatively quenched. Parallel with the fluorescence quenching, we noted the appearance of the $C_{59}N$ emission in the near-infrared region. Additional excitation spectra of the $C_{59}N$ fluorescence, which reveal the ground-state transitions of the arenes, led to postulation of an efficient and quantitative transfer of singlet excited-state energy from the highly energetic arene singlet excited state (~3.0 eV) to the low-lying singlet excited state of $C_{59}N$ (1.5 eV). The results suggested that the strong $C_{59}N$−arene coupling features extremely fast intramolecular transfer dynamics.[44]

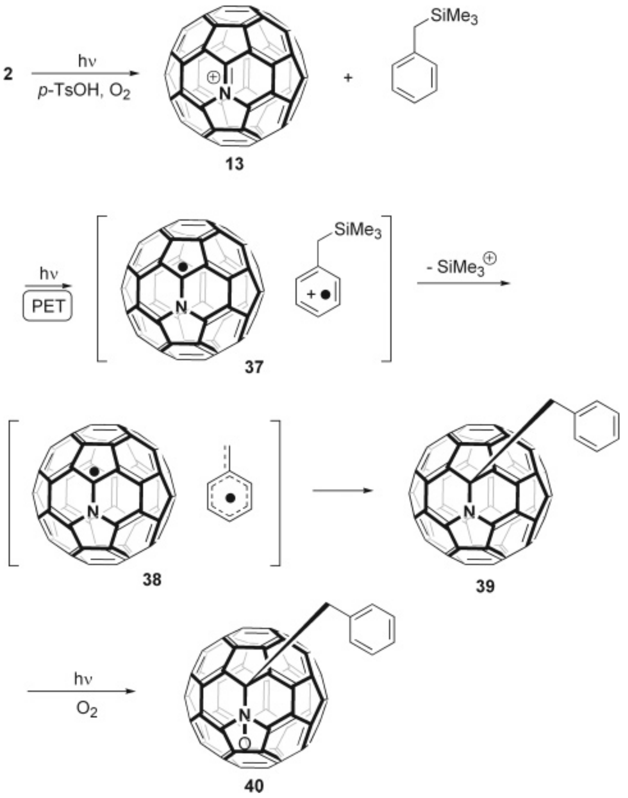
The reaction of **13** with toluene and anisole has been mechanistically studied by Orfanopoulos et al.[45] The measured intermolecular kinetic isotope effects were consistent with an electrophilic aromatic substitution mechanism, the electrophilic attack of **13** on the electron-rich aromatics representing the first reaction step. An efficient reaction between the azafullerene dimer **2** and 9-substituted fluorenes led to the formation of new azafullerene monoadducts **36** (Scheme 12).[46] However, diphenylmethanes, structurally related to the corresponding fluorenes, gave no adducts with dimer **2** under the same experimental conditions.

Scheme 12. Reactions of the Azafullerene Radical 1, Generated from Dimer 2, with Substituted Fluorenes To Yield Fluorenyl Derivatives 36



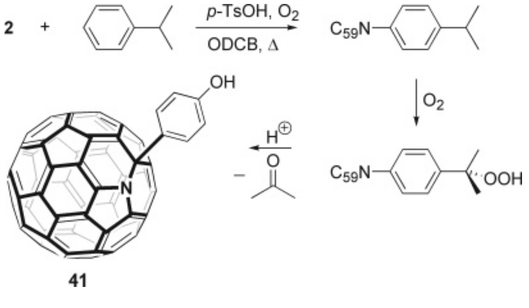
In two consecutive papers, Orfanopoulos et al. observed a photoinduced electron transfer (PET) between **13**, generated from **2**, and benzyltrimethylsilane and the formation of benzyl-substituted aza[60]fullerene *N*-oxide **40** via **39**. According to the proposed mechanism, PET from the silane to **13** gives the radical cation pair **37** (stabilized α-amino radical and benzylsilyl radical cation), while concomitant loss of the $SiMe_3^+$ group from the benzylic position leads to the neutral radical pair **38** (Scheme 13).[47]

Scheme 13. Photoinduced Electron Transfer (PET) between Aza[60]fullerenium Cation (13) and Benzyltrimethylsilane and Proposed Mechanism for the Formation of Benzyl-Substituted Aza[60]fullerene *N*-Oxide 40



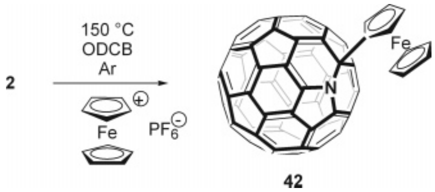
By an adaption of the cumol synthesis from phenol and acetone, Hirsch et al. succeeded in the synthesis of an aza[60]fullerene adduct with phenol.[48] When cumol is subjected to the conditions mentioned above, the arylation is followed immediately by oxygenation, rearrangement, and cleavage to **41** (Scheme 14).

Scheme 14. Formation of the Phenol Adduct 41 via Reaction with Cumol and Subsequent Oxidative Degradation



A special case for the aza[60]fullerene arylation is the reaction of **2** with a 25-fold excess of ferrocenium hexafluorophosphate at 150 °C in an argon atmosphere, which afforded the ferrocenylhydroaza[60]fullerene dyad **42** (Scheme 15).[42] In this case, ferrocenium hexafluorophosphate serves as the oxidizing reagent for the generation of **13** and the simultaneously generated ferrocene as its trapping reagent. Compound **42** represents the first example of a fullerene-based dyad where two electroactive groups are connected

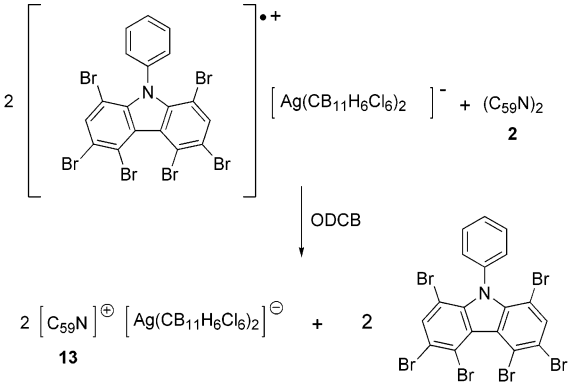
Scheme 15. Synthesis of the Ferrocenyl Hydroazafullerene 42



by only one single σ-bond. The cyclic voltammetry of **42** shows strong electronic coupling between the two chromophores in the ground state. Photophysical studies revealed an intramolecular photoinduced electron transfer with the formation of the charge-separated $C_{59}N^{\bullet-}-Fc^{\bullet+}$ radical pair.[42]

Isolation and subsequent characterization of **13** by X-ray crystallography was achieved via oxidation of **2** with the radical cation hexabromo(phenyl)carbazole ($HPPC^{\bullet+}$) in dry ODCB (Scheme 16).[49] The counterion is the silver(I) complex carborane ion $[Ag(CB_{11}H_6Cl_6)_2]^-$. The solid salt $[C_{59}N][Ag(CB_{11}H_6Cl_6)_2]$ was crystallized as dark green crystals by diffusion of hexane vapor and was reasonably air stable. The X-ray crystal structure of the $13^+[Ag(CB_{11}H_6Cl_6)_2]^-$ salt with three ODBC solvate molecules provided final proof of the structure of the azafullerenium ion (Figure 2).

Scheme 16. Preparation and Isolation of the Aza[60]fullerenium Ion (13) by Oxidation of 2 with the Hexabromo(phenyl)carbazole ($HPPC\bullet^+$) Radical Cation



13 has almost the same structure as C_{60} including the bond length alternation between the shorter [6,6]-bonds and the longer [5,6]-bonds. Semiempirical calculations showed that the positive charge density is predominantly located in the neighborhood of the nitrogen substituent (Figure 3).[25] Therefore, the resonance structures depicted in Figure 3 are the most important.

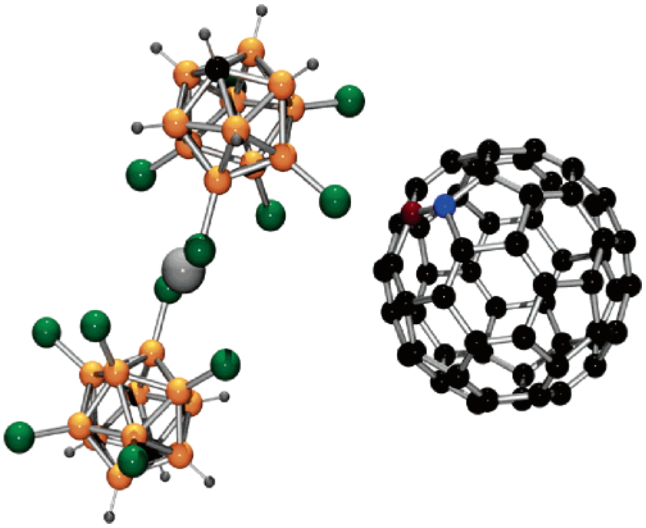


Figure 2. X-ray single-crystal structure of $[C_{59}N^+][Ag(CB_{11}H_6Cl_6)_2^-]$.

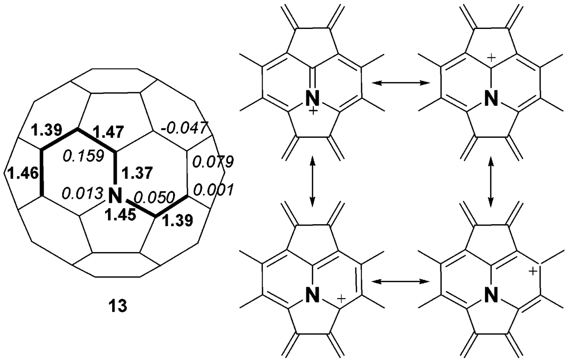
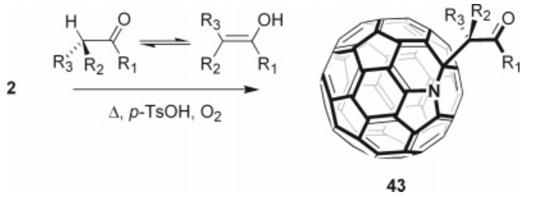


Figure 3. Characteristic bond lengths (Å) (bold), Mulliken charges, and the most important resonance structures of $C_{59}N^+$ (**13**), showing both carbenium and iminium ion character.

A very versatile tool for the synthesis of monomeric aza[60]fullerene derivatives **43** is the Mannich functionalization (Scheme 17), where **2** is typically treated in ODCB with an excess of the enolizable carbonyl compound and 40 equiv of p-TsOH at 150 °C in a constant stream of O_2.[40,41,50] After 15 min, the conversion is usually completed and the Mannich bases are formed in good yield and complete regioselectivity.

Scheme 17. Reaction of $(C_{59}N)_2$ (2) with Enolizable Carbonyl Compounds To Obtain Ketoazafullerene Derivatives 43

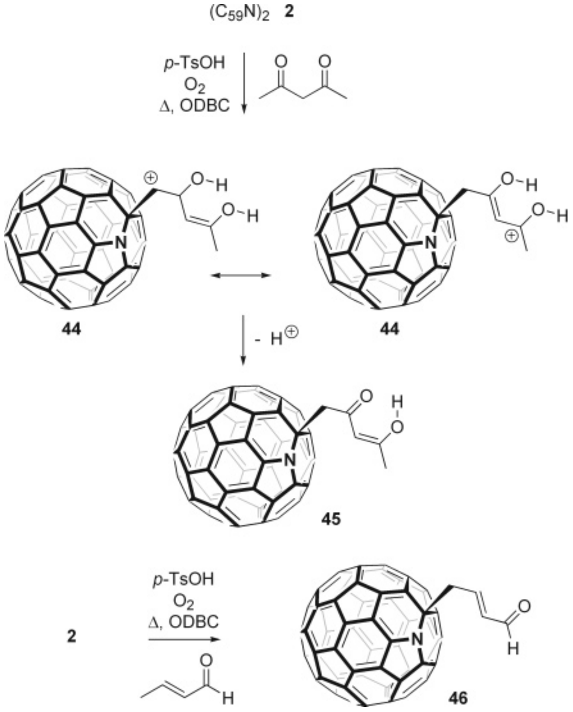


Allowing acetylacetone as a 1,3-dicarbonyl compound to react with dimer **2**, the diacetyl derivative **45** is obtained, bearing the $C_{59}N$ moiety at a terminal carbon atom of the acetylacetone (Scheme 18).[41] The preferred terminal attack is due to the thermodynamical stability of the corresponding cationic intermediate **44**. Treatment of **2** with 20 equiv of the α,β-unsaturated carbonyl compound crotonaldehyde under the same reaction conditions leads to an exclusive γ-attack accompanied by the formation of product **46**.[41]

Upon treating the azafullerene dimer **2** with a series of enolizable acetyl fluorophores and p-TsOH at 150 °C in ODBC under a constant stream of air, a novel series of fluorophore−heterofullerene conjugates, **47**−**51**, were obtained.[51] The fluorophores range from benzene to naphthalene, phenanthrene, fluorene, and pyrene. NMR spectroscopy and quantum mechanical calculations demonstrated that, contrary to the direct-arylation conjugates **35**, the flexible acetyl linker allows for the possibility of efficient $\pi-\pi$ stacking interactions between the fullerene and the aromatics.[51]

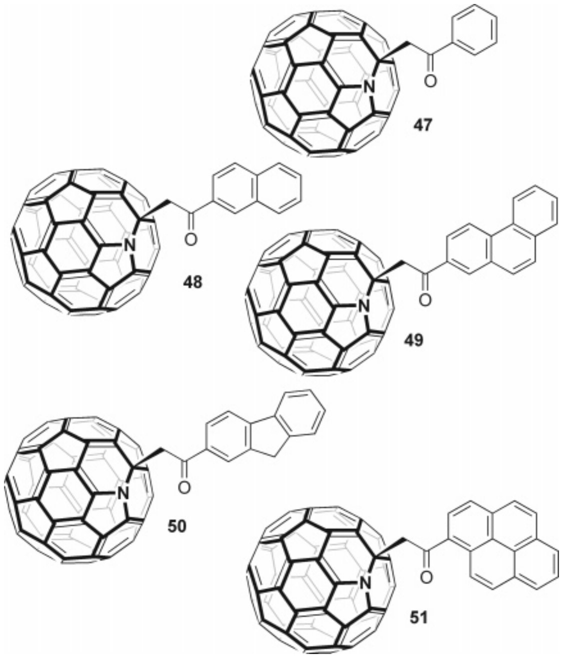
Photophysical steady-state and time-resolved measurements clearly showed the photosensitization effect of the fluorophores that act as an antenna system and transmit their excited-state energy to the covalently attached $C_{59}N$ moiety.

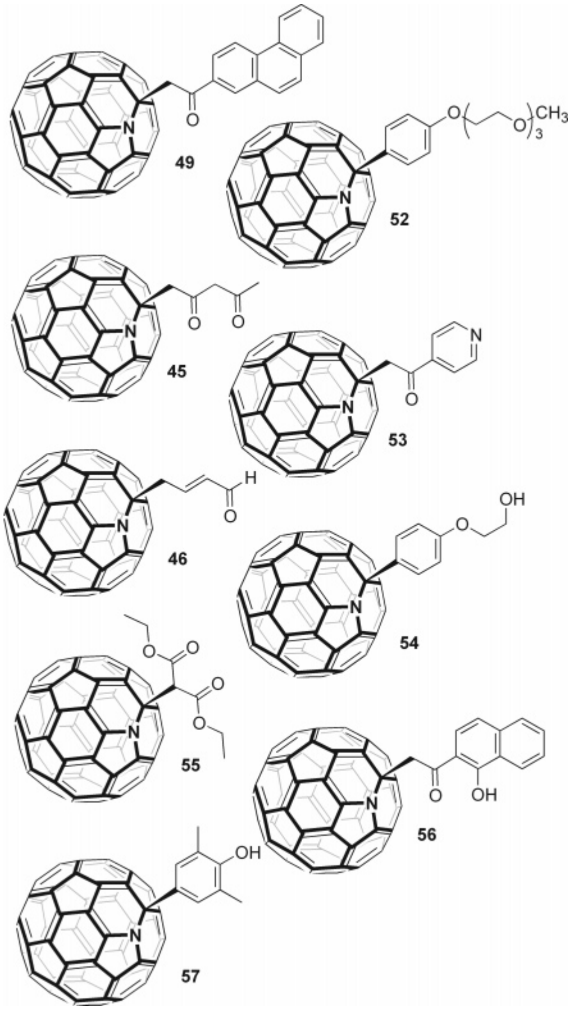
Scheme 18. Reaction of $(C_{59}N)_2$ (2) with Acetylacetone as a 1,3-Dicarbonyl Compound, Formation of Diacetyl Derivative 45, and Reaction of 2 with Crotonaldehyde as an α,β-Unsaturated Aldehyde To Yield 4-Azafullerenyl-but-2-enal (46)



This enables the efficient $C_{59}N$ triplet generation, even in a wavelength region where the fullerene absorption is comparatively weak. The electronic interactions between the two subsystems are reflected in a series of ground-state and excited-state assays ranging from fluorescence studies to fast transient absorption measurements. The results confirmed an efficient singlet−singlet energy-transfer mechanism controlling the deactivation of the photoexcited fluorophore in fluorophore−heterofullerene conjugates **47**−**51**.[51]

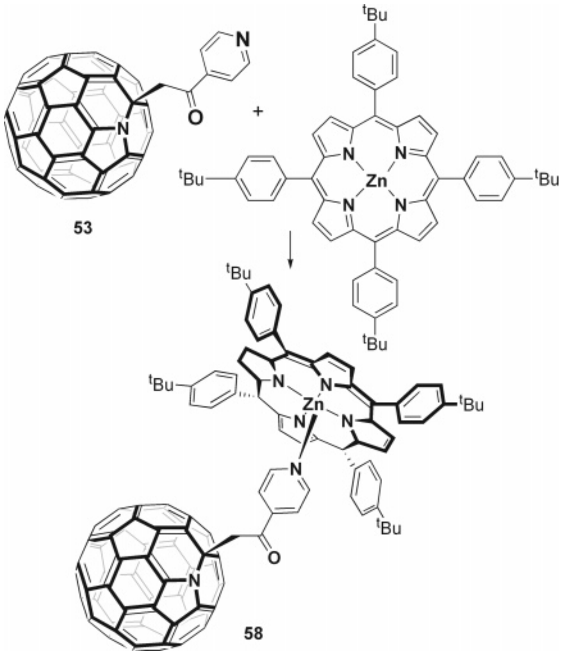
A series of hydroazaheterofullerene derivatives $RC_{59}N$, **45**, **46**, **49**, and **52**−**57**, with a wide variety of different side chains R have recently been synthesized accordingly, and their spectroscopic and photophysical properties have been investigated and compared with those of C_{60}.[52] The ground-state absorption spectra, fluorescence spectra, fluorescence quantum yields Φ_F, singlet-state lifetimes τ_F, triplet-state absorption spectra, triplet molar absorption coefficients ϵ_T, singlet oxygen (Φ_Δ) and triplet-state (Φ_T) quantum yields were determined; the replacement of a carbon of the C_{60} fullerene sphere by a nitrogen strongly affected most of the spectroscopic and photophysical properties.[52]





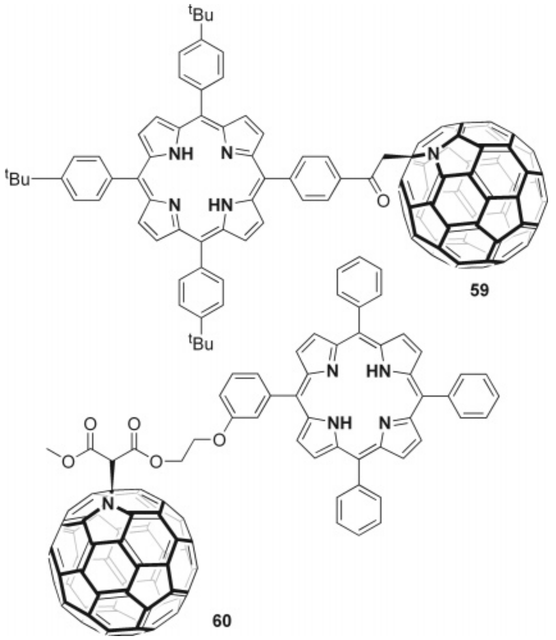
A novel supramolecular dyad, zinc [tetrakis(*p*-*tert*-butylphenyl)porphyrinyl]pyridine−$C_{59}N$ [Zn-(ttbpp)pyridine−$C_{59}N$, **58**]−with a quasi-linear geometry−involving a heterofullerene acceptor and a zinc tetrakis(*p*-*tert*-butylphenyl)-porphyrin (Zn-ttbpp) donor was assembled via axial coordination.[43] 1-(4-Pyridyl)ethanone was attached to dimer **2**, leading to an anchor system, **53**. Upon dissolving an equimolar amount of the heterofullerene anchor **53** and Zn-ttbpp in ODCB, the heterofullerene−tetraphenylporphyrin **58** was obtained (Scheme 19). Depending on the solvent, either photoinduced singlet−singlet energy transfer or electron transfer was observed for the molecular assembly of the two redox-active components. The latter process takes place in *o*-dichlorobenzene as the solvent and leads to the corresponding charge-separated state, that is, the π-radical anion of $C_{59}N$ and the π-radical cation of Zn-ttbpp. The substantial increase of the solvent polarity of ODCB (ϵ = 9.98) brings about the large exothermic driving force for this charge-separation pathway. In line with this energetic

Scheme 19. Synthesis of the Supramolecular Dyad Zn-(ttbpp)pyridine−$C_{59}N$ (58) with a Heterofullerene Acceptor and a Zinc Tetrakis(*p-tert*-butylphenyl)porphyrin (Zn-ttbpp) Donor



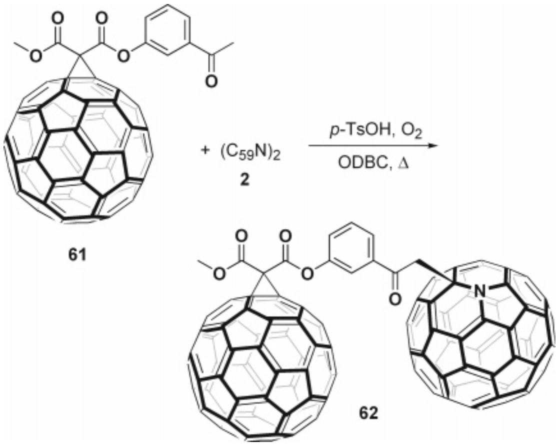
presumption, no appreciable heterofullerene emission could be detected in the steady-state or time-resolved measurements in ODCB, prompting an intramolecular electron transfer.[43]

Recently, covalently linked heterofullerene−porphyrin conjugates **59** and **60** have been synthesized as novel artificial light-harvesting antennae and as new model systems for long-lived intramolecular charge separation.[53] The reaction of two suitable porphyrin derivatives with an equimolar amount of heterofullerene dimer **2** and 30 equiv of *p*-TsOH at 150 °C in ODBC afforded dyad conjugates **59** and **60** in moderate yields. The two conjugates were purified by flash chromatography and isolated in high purity.[53]



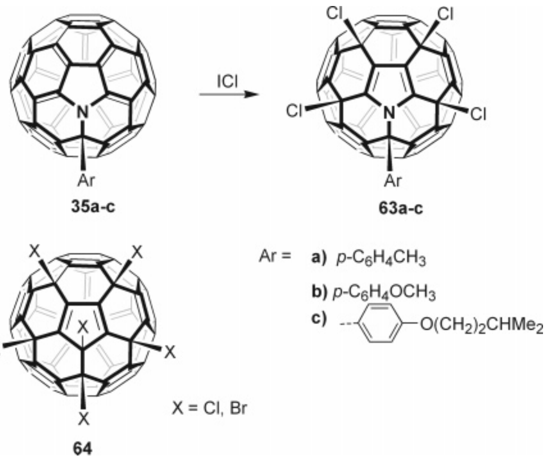
The synthesis of the first fullerene−heterofullerene dyad was achieved by selectively attaching the bifunctional acetylphenyl methyl malonate to C_{60} to afford Bingel monoadduct **61**. The latter underwent a regioselective reaction with azafullerene dimer **2** to yield the unsymmetrical fullerene−heterofullerene dyad **62** (Scheme 20).[50] This type of fullerene−heterofullerene conjugate represents a new scaffold for directional energy transduction.

Scheme 20. Synthesis of the Fullerene−Heterofullerene Dyad 62



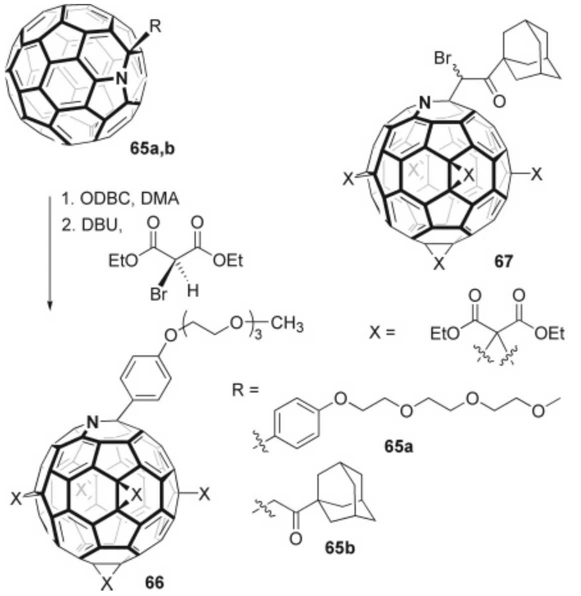
Since monomeric aza[60]fullerene derivatives carrying an organic addend adjacent to the *N*-substituent are stable, exhibit favorable solubility properties, and are obtainable in high yields, they represent ideal starting materials for the investigation of the behavior of the $C_{59}N$ core toward addition reactions. As an example, the chlorination of monoarylated **35a−c** with ICl in CS_2 at room temperature leads to the exclusive formation of the tetrachlorinated heterospheres Cl_4-$ArC_{59}N$ **63a−c**, which were isolated as orange microcrystals in 50−60% yield (Scheme 21).[54] The structures of **63a−c** were determined by ^{13}C NMR spectroscopy, and they appeared as closely related to the hexachlorides and hexabromides $C_{60}X_6$ (X = Cl, Br) **64**, described by Birkett et al.[55] In analogy to the cyclopentadiene subunit in **64**, compounds **63** contain an integral pyrrole moiety decoupled from the conjugated π-system of the fullerene cage. The chlorine addends can be easily removed from the cage by treating **63** with an excess of PPh_3 at room temperature.[54] The reversible binding could provide a useful strategy for protection of several double bonds of the fullerene core.

Scheme 21. Chlorination of the Aryl Adducts 35a−c, Yielding the Tetrachlorinated Compounds 63a−c Containing an Integral Pyrrole Moiety within the Fullerene Framework



Multiple functionalization of an aza[60]fullerene was also achieved via template-mediated addition of malonates into the octahedral [6,6]-bonds of the heterofullerene framework.[56] This method was originally developed for the highly regioselective hexaaddition of C_{60}[57] and allows for the synthesis of pentakisadducts derived from $RC_{59}N$ containing a C_s-symmetrical addition pattern. For example, the monoaryl adduct **65a** was stirred with a 5-fold excess of dimethylanthracene (DMA) in ODCB for 3 h and subsequently reacted with a 10-fold excess of DBU and diethyl bromomalonate. After chromatography the pentamalonate **66** was isolated in 20% yield (Scheme 22). The reaction of the adamantyl derivative **65b** applying the same reaction conditions afforded compound **67**. Obviously, the 5-fold cyclopropanation of **65b** at octahedral positions was accompanied by bromination of the methylene group of the ketone addend. The facile formation of **67** clearly demonstrates that the deprotonation with the base DBU generated an intermediate enolate which was able to attack diethyl bromomalonate to efficiently form a brominated ketone.[56]

Scheme 22. Highly Regioselective Formation of the Pentamalonates 66 and 67



30 and **2** sensitize the reaction of olefins with molecular oxygen under photolytic conditions. 2-Methyl-2-butene and α-terpinene undergo ene and Diels−Alder photooxygenation reactions, respectively, in the presence of minute amounts of azafullerenes to produce the corresponding hydroperoxides and peroxides.[58]

2.5. Electronic Structure and Physical and Physicochemical Properties of Azafullerenes and Azafullerene Derivatives

A number of computational calculations on the possible existence, relative stability, molecular and electronic structure, binding energies, and physical properties of heterofullerenes, mainly aza[60]fullerene, appeared in the "presynthetic" heterofullerene era from 1992 to 1995.[59,60] Karfunkel et al. computed the enormous structural diversity of heterofullerenes and predicted their structural, electronic, and thermochemical properties using semiempirical methods.[59] Jiang, Xing, and co-workers calculated the structural and electronic properties, the nonlinear polarizability, the optical absorption, and the nonlinear susceptibility of $C_{59}N$.[61] The same nonlinear optical properties had been calculated previously by Rustagi et al.[62] Piechota and Byszewski reported on the calculation of the electronic structure of $C_{59}N^+$.[63] Jiao et al. studied the monodoped heterofullerenes $C_{59}X$ and $C_{59}X^{6-}$ ($X = N^+, B^-, P^+, As^+$, Si), isoelectronic to C_{60} and $C_{60}{}^{6-}$, at the B3LYP/6-31G* level of density functional theory.[64] On the basis of the computed NICS values at the cage center and at the center of individual rings as magnetic criteria, heterofullerenes with 60 π-electrons are as aromatic as the parent C_{60}, while those with 66 π-electrons are much less aromatic than $C_{60}{}^{6-}$. The very distinct endohedral chemical shifts of the 66-π-electron systems may be useful to identify the heterofullerenes through their endohedral ^{3}He NMR chemical shifts.[64]

When heterofullerenes became reality, the first experimental investigations on the electronic structure of **2** were carried out by Haffner et al.[65,66] using photoemission spectroscopy (PES) and electron energy loss spectroscopy (EELS). The researchers compared the results with those of C_{60} and its dimer $[(C_{60}{}^-)_2]$, isostructural and isoelectronic to **2**, respectively. The EELS spectra of the carbon 1s level show no great difference apart from a line broadening attributed to the dimerization and substitution of one carbon atom by nitrogen. This demonstrates that the introduction of N (and thus one additional electron) into the cage does not lead to a significant population of the unoccupied frontier orbitals in C_{60} and points to a localization of the additional electron at the N atom. In combination with theoretical results it can be concluded that the HOMO of $(C_{59}N)_2$ is located mainly on the N atoms and the sp^3 carbons of the intermolecular bond. The main difference between the $(C_{60}{}^-)_2$ dimer and **2** consists of the higher charge of the nitrogen core in **2**. This leads to a lower energy of the occupied frontier orbitals in **2** and to a lower distance between the occupied electronic levels. Andreoni et al. calculated the formation of the heterofullerenes **2** and **30**.[67]

The correct [6,6],[6,6]-closed structure, the energetically favored transoid conformation of the linking bond, and the C_{2h} symmetry of **2** have been predicted by Andreoni et al. on the basis of DFT calculations.[38] However, the final experimental proof of this structure had been missing for quite a long time, since it had not been possible to detect the signal for the sp^3 carbon atom with ^{13}C NMR spectroscopy. However, Wudl et al. found that the relaxation time of the two sp^3 carbon atoms in question is very much longer than usual, and they detected the missing sp^3 signal at 90.4 ppm with a pulse delay time of 16 s.[33] The use of $Cr(acac)_3$ as a paramagnetic relaxation reagent[68] and pulse delay times of about 1 s have the same effect.[69] In the meantime, the signal for the sp^3 carbon could also be found in the ^{13}C CP-MAS spectrum of solid aza[60]fullerene.[70] By the synthesis of the ^{15}N-labeled dimer **2**, hydroazafullerene **30**, and diphenylmethyl adduct **32**, Wudl's group was also able to assign the resonances of the cage carbons in the near neighborhood of the N atom (Figure 4) by analysis of the ^{15}N-coupled ^{13}C NMR spectra.[33]

Also the cyclic voltammogram of **2** provided strong evidence for its dimeric structure.[26] It consists of three overlapping pairs of reversible one-electron reduction waves. The appearance of closely spaced pairs of waves in the cyclic voltammogram was interpreted in terms of two (identical) weakly interacting electrophores, similar to dianthrylalkanes.[71] After the third double wave, the process is irreversible, interpreted as an irreversible cleavage of the dimer bond.

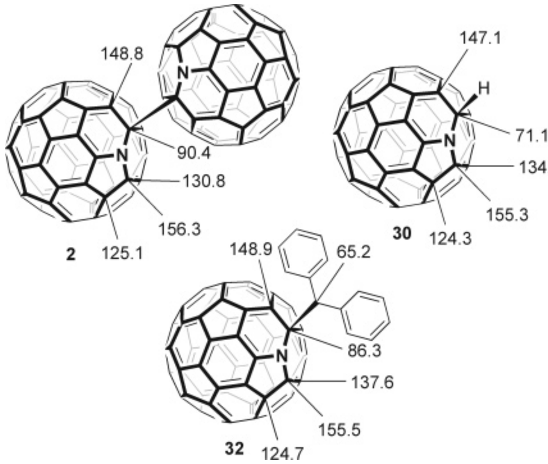


Figure 4. ^{13}C chemical shifts of azafullerene dimer **2**, hydroazafullerene **30**, and diphenylmethyl adduct **32** assigned by analysis of $^{15}N-^{13}C$ coupling in the ^{15}N-labeled compounds **2**, **30**, and **32**.

The interlink between the two balls of dimer **2** is made by carbon atoms 2 and 2′ (making hexagon−hexagon fusions together with the nitrogen atom), with the C-2−N bond length being 1.520 Å (“[6,6]-closed”). The *trans* conformation minimizes the repulsion of the nitrogen electron clouds. Theoretical calculations predicted a relatively low binding energy of about 18 kcal/mol for the intermolecular bond in bisazafullerenyl **2**.[38] Bellavia-Lund et al. found evidence for a thermally induced cleavage of the dimer by heating a solution of **2** in ODCB together with an excess of the hydrogen donor diphenylmethane.[39] They were able to quench $(CHPh_2)C_{59}N$ (**32)** from the reaction mixture and ensured a free radical mechanism initiated by the thermal homolysis of the dimer **2**.

Conventional experiments for the detection of the aza[60]fullerenyl radical **1** by EPR under thermolytic conditions proved unsuccessful. However, **1** could be detected by means of light-induced continuous-wave EPR (LESR), repeatedly irradiating a solution of dimer **2** with 532 nm laser pulses.[72] A spectrum with three equidistant lines with equal intensity was obtained, indicating ^{14}N hyperfine interaction. The use of a Xe lamp is also possible, as similar results of the Wudl group have shown.[34] When FT-EPR is used, it is possible to obtain time-resolved spectra, which show that the breakage of the intermolecular bond is preceded by intersystem crossing into a metastable triplet state.[72]

Studies on the electronic structure of **2**, using EELS, were presented by Pichler et al.[73] The dielectric function of **2** was calculated in the low-energy region, and a static dielectric function at zero energy of approximately 5.6 was found. In continuation of this work, Golden et al. examined the electronic structure of $C_{59}N$ and its salts $A_xC_{59}N$ (A = K, Rb, Cs) using a combination of results from photoemission, electron energy loss spectroscopy, and gradient-corrected density functional calculations.[74] Optical spectra and Raman spectra of dimer **2** were presented by Plank et al.[75] and compared to Raman spectra of the isostructural singly bonded dimeric fullerene $(C_{60}^-)_2$. The spectra of both materials exhibit strong correlations with respect to splitting, line position, and line intensity.

Extensive investigations of dimer **2** and the heterofullerene salt $K_6C_{59}N$ [76] using X-ray powder diffraction techniques, together with electron diffraction by TEM and additional theoretical calculations, have been undertaken to solve the structure.[77] Samples of **2** obtained by recrystallization from CS_2 exhibit a hexagonal structure (space group $P6_3/mmc$ or a subgroup), which remains intact at pressures of up to 22 GPa.[78] The diffraction patterns point to a CS_2 content of about 1/2 molecule per formula unit. Removing CS_2 by sublimation leads to a monoclinic structure; the space group is most probably $C2/m$. $K_6C_{59}N$ crystallizes in the body-centered cubic space group $Im3$ and shows, in contrast to the corresponding C_{60} salts, a pronounced electrical conductivity.[76]

The gas-phase formation of endohedrally metal-doped azafullerene ions $La_2@C_{79}N^+$ and $La@C_{81}N^+$ succeeded by FAB-MS fragmentation of the adducts of the reactions of benzyl azide with $La_2@C_{80}$ and $La@C_{82}$.[79]

2.6. Azafullerenes with More Than One Nitrogen Atom

No diaza[60]fullerene has been prepared till now, not even in the gas phase. However, monomeric $C_{58}N_2$ seems to be a feasible synthesis target and future preparative challenge, especially isomeric diazafullerenes such as **68**−**70** (Figure 5) as stable diamagnetic monomers.[80] All $C_{58}N_2$ isomers, especially the ones with two adjacent nitrogen atoms, should be able to relax to closed-shell structures. In 1991, it was speculated that mass spectroscopy of the toluene extract of soot, obtained by contact-arc vaporization of graphite in the presence of N_2, showed peaks tentatively attributed to formulas such as $C_{70}N_2$, $C_{59}N_6$, $C_{59}N_4$, and $C_{59}N_2$.[20] Glenis et al., using pyrrole gas as the source of nitrogen on a similar experiment, reported the analysis of N-containing chromatographic fractions by mass spectroscopy and UV−vis and fluorescence spectroscopy.[81] The authors conclude from mass spectral data that, next to $C_{59}N$, only molecules with even-numbered ratios of C to N atoms were formed (e.g., $C_{58}N_2$, $C_{56}N_4$, etc.). Later, the extract was submitted to GPC−HPLC to yield separated fractions, which were regrettably not submitted to mass spectroscopy but analyzed by absorption and fluorescence spectroscopy only.[82]

Figure 5. Possible constitutional isomers **68**, **69**, and **70** of diaza[60]fullerene ($C_{58}N_2$).

Hirsch et al. proposed an idea for a synthetic route toward $C_{58}N_2$, starting from C_{60}.[15,54] Functionalizing C_{60} with a suitable malonate Bingel reagent which carries two free azide groups with a tailored spacer may lead to a “prefunctionalized” C_{60} monoadduct. Subsequently, the azide groups can be fixed to the C_{60} cage, and final photooxygenation/acid treatment should open a synthetic route toward certain isomers of $C_{58}N_2$ derivatives.

Diaza[60]fullerenes have been the subject of several theoretical calculations. Xu et al. calculated in a systematic investigation all possible isomers of $C_{48}N_2$ (and $C_{48}B_2$) using AM1 and MNDO level semiempirical methods.[83] The results indicated that the most stable isomer corresponds to 1,4-substitution in the six-membered ring located at the equator for both $C_{48}N_2$ and $C_{48}B_2$.[83] Possible structures of heterofullerenes $C_{60-n}N_n$ and $C_{60-n}B_n$ ($n = 2-8$) and $C_{70-n}N_n$ and

$C_{70-n}B_n$ ($n = 2-10$) and their substitution patterns, thermodynamic data, and electronic properties have been calculated by Karfunkel et al.[59] and Chen et al.[84] using semiempirical MNDO, AM1, PM3, and ab initio methods. Karfunkel et al. compared the computational data of all $C_{58}N_2$ topological isomers, where the shortest path between the two nitrogens consists of at most three carbons, with those of C_{60} (Figure 6). Out of the 10 $C_{58}N_2$ isomers, it was found that 1,7-diaza[60]fullerene structure $C_{58}N_2$ (**d**), with the nitrogen atoms in a 1,3-fashion in the same pentagon, exhibited remarkable stability with a heat of formation difference of about 15 kcal/mol from the next most stable isomer.[59] The heterofullerenes $C_{70-n}X_n$ are less stable than their all-carbon analogues, and the N-doped fullerenes are thermodynamically more stable than their B-doped analogues.[84] Bühl calculated relative energies for the D_{3d}- and D_3-symmetrical isomers of hexaaza[60]fullerene ($C_{54}N_6$) and proposed that some isomers of $C_{54}N_6$ could be potentially aromatic molecules, being isoelectronic with $C_{60}{}^{6-}$.[85] The global and local aromaticity of two S_6-symmetrical isomers of $C_{48}X_{12}$ (X = N, P, B, Si) were evaluated by their NICS values.[86] Triphenylene units, appearing in one of the isomers, attribute to the greater stability compared to that of the other isomers, due to the local aromaticity.

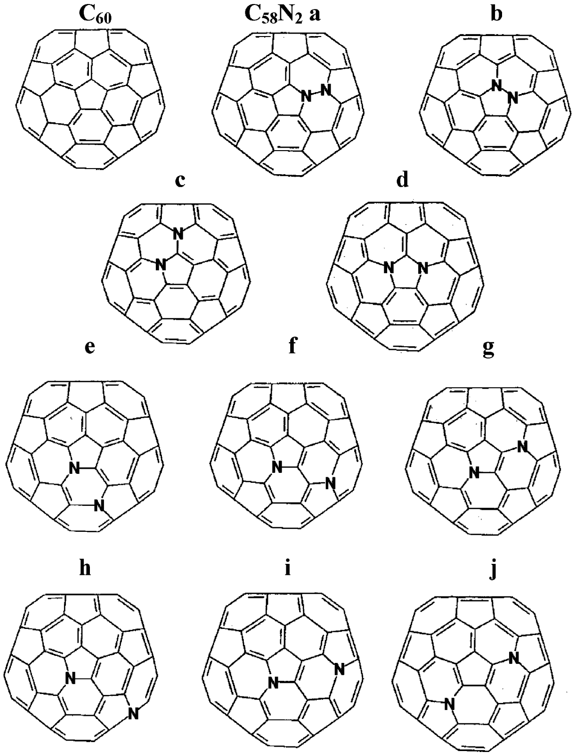


Figure 6. Structures of C_{60} and 10 $C_{58}N_2$ isomers, **a**−**j**, where the shortest path between two nitrogens consists of at most three carbons.

3. Heterofullerenes Other Than Azafullerenes

Only a small number of reports on heterofullerenes other than aza[60]fullerenes and aza[70]fullerenes are found in the literature. Furthermore, most of the reported investigations comprise "virtual chemistry" only.

3.1. Borafullerenes

Bora[60]fullerenes were the first heterofullerenes (see section 1) found as positive ion clusters $C_{n-x}B_x{}^+$ by FT-ICR mass spectrometry of the products formed by laser vaporization of a graphite/boron composite as reported by Smalley's group in 1991.[19] In 1996 Muhr et al.[23] reported the macroscopic preparation of borafullerenes via arc evaporation of graphite doped with boron nitride, boron carbide, or boron. According to mass spectrometric analysis only monosubstituted fullerenes such as $C_{59}B$, $C_{69}B$, and higher homologues could be extracted and enriched using pyridine as the solvent. In the following year, Cao et al. claimed the synthesis of macroscopic amounts of boron-doped fullerenes such as $C_{60-n}B_n$ and $C_{70-n}B_n$ for $n = 1$, 2, and 3 by dc arc burning of graphite and B_4C/graphite rod electrodes[87] and their characterization by FD mass spectroscopy only. Similarly, heterofullerenes $C_{59}B$ and $C_{58}BN$ were prepared by laser ablation of B_4C/graphite and BC_2N/graphite.[88] However, isolating macroscopic amounts of neutral and unsubstituted monomeric $C_{59}B$ or $C_{69}B$, representing an open-shell molecule, is very unlikely because of kinetic instability, as was assumed by Aihara.[89]

Bora[60]fullerene [CAS name for the radical: 2*H*-1-bora-[5,6]fulleren-C60-I_h-2-yl] has been the subject of various types of calculations. Andreoni et al. found that the B atom remains 3-fold coordinated and the bora[60]fullerene cage is closed.[60a] In a series of papers, Kurita et al. reported on the calculated molecular structures, binding energies, and electronic properties of $C_{59}B$, two isomers of $C_{58}B_2$, and several other heterofullerenes.[60c,90] Furthermore, Liu et al. calculated the electronic properties of 1,2-, 1,3-, 1,58-, 1,59-, and 1,60-dibora[60]fullerene and the corresponding diaza[60]fullerene isomers.[91] Chen and Lin considered all 23 possible isomers of $C_{58}B_2$ in theoretical calculations.[92] The bonding, electronic polarizability, and vibrational and magnetic properties of heterofullerene $C_{48}B_{12}$ were studied by Xie et al.[93] and IR and Raman-active vibrational frequencies assigned. Eight ^{13}C and two ^{11}B NMR spectral signals were predicted. The average second hyperpolarizability is about 180% larger than that of C_{60}.[93] However, still the most important and challenging future work to be done on borafullerenes is to design and perform a rational synthesis for $C_{59}B$ as was done for azafullerenes.

In the class of mixed azaborafullerenes such as $C_{58}BN$, most computational attention has been given to the 1,2-, 1,6-, and 1,60-isomers. Piechota et al.[94] calculated a HOMO−LUMO gap of 2.2 and 1.8 eV for the 1,2- and 1,6-isomers, respectively, while Liu et al.[60d] found similar gaps of ~2 eV for a nonspecified "nearest-neighbor" BN structure and the 1,60-isomer. Xia et al. found in their calculations that in contrast to $C_{58}B_2$ all isomers of $C_{58}BN$ are preferred in the closed-shell configuration.[95] Esfarjani et al. performed computations on the electronic properties and chemical bonding of the 1,2- and 1,60-isomers of $C_{58}BN$ in the solid state[96] and discussed the various possibilities for the nature of the B−N bond in the 1,2-isomer. From the computed NICS values at the cage center and at the center of individual rings of the heterofullerenes, Chen et al. found that $C_{58}BN$, $C_{54}(BN)_3$, $C_{48}(BN)_6$, and $C_{12}(BN)_{24}$ are slightly more aromatic than C_{60}, whereas the corresponding hexaanions are significantly less aromatic than C_{60}.[6−97] The geometrical structure and the vibrational and excitation spectra of mixed heterofullerene $C_{48}(BN)_6$ were reported using density functional calculations.[98] The structure and electronic properties of mixed azaboraheterofullerene $C_{30}B_{15}N_{15}$ has been investigated by semiempirical MO calculations at the PM3 level and density functional theory at the B3LYP level including MP2 correlation correction.[99]

Reports on the gas-phase formation of $C_{58}BN$ appeared in 2001 and 2003, when Nakamura et al. proved the generation of the azabora[60]fullerene upon a BN substitution reaction of fullerene C_{60} upon irridiation with a KrF excimer laser at room temperature.[100]

3.2. [60]Heterofullerenes with Heteroatoms Other Than N and B

In 1994, Clemmer et al. reported the formation of C_nNb^+ ($n = 28-50$) clusters upon pulsed laser vaporization of a mixed NbC/graphite composite rod and found evidence for the odd-C-numbered cages to be (quasi)heterofullerenes.[22]

Heterofullerenes containing sulfur or oxygen as divalent heteroatoms such as thiafullerenes **71** and **72** and oxafullerenes **73** and **74**, respectively, could be either neutral open-cage quasi-fullerene structures bearing a thiocarbonyl or carbonyl moiety or represent closed molecules, even formulated as ylide heterofullerenes **74** (Figure 7).

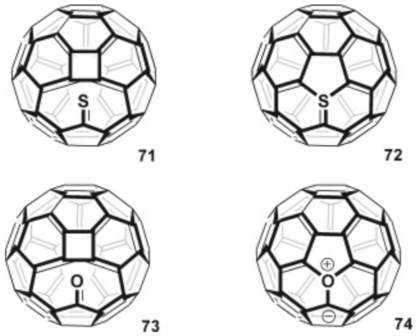


Figure 7. Open-cage and closed forms of heterofullerenes containing sulfur (**71** and **72**) or oxygen (**73** and **74**).

Kurita et al. calculated a $C_{59}S$ cluster and found a heavily distorted structure with C−S "bond lengths" of 2.01 and 2.16 Å, a rather low binding energy of 5.1 eV/atom, and an atomic charge of +0.5 on the S atom.[60c] In 1996, Glenis et al. claimed evidence for the replacement of fullerene cage carbon atoms by sulfur atoms during arc vaporization of graphite in the presence of thiophene from elucidation of the photophysical properties of the products.[101]

Oxa[60]fullerene ($C_{59}O$) was mentioned as possibly present in the form of $C_{59}O^+$ ions in gas-phase MS collision experiments with O^+ ions and C_{60} by Christian et al.[21,102] in 1992. Oxafullerene $C_{59}O$ was computationally reinvestigated by semiempirical PM3 calculations in 2001 by a Chinese group.[103] The investigators found that in contrast to former less accurate INDO/2 calculations the O−C single bond was slightly longer than the C−C single bond of the fullerene C_{60} cage.

Purely hypothetical only were the monophospha[60]fullerene and the 23 diphospha[60]fullerene isomers ($C_{59}P$ and $C_{58}P_2$, respectively) considered using a PC-based calculation by Chen and Lin in 1997.[92] However, in 1999 the gas-phase formation of stable phosphorus heterofullerenes $C_{59}P$ and $C_{69}P$ was reported by Moeschel and Jansen, achieved by simultaneous evaporation of P and C in a radio frequency furnace.[104] P-doped phosphafullerene $C_{59}P$ was studied via semiempirical and density functional theory calculations by Lu et al.[105] Geometry optimization showed that structural deformation occurs in the vicinity of the dopant atom, resulting in a P−C bond significantly longer than the C−C bond of the all-carbon fullerene cage.

In 1993, Jelski et al. computed the structures and stability of sila[60]fullerenes ($C_{59}Si$), 1,2-, 1,6-, and 1,60-$C_{58}Si_2$, and one $C_{48}Si_{12}$ isomer.[106] The structures were predicted to be stable; however, the authors did not hesitate to mention the possibility of a polysiloxane-type 1,60-disila[60]fullerene polymer. Kimura et al.[107] analyzed the products from pulsed-laser vaporization of silicon−carbon composite rods by TOF-MS. Only small peaks were observed to match the masses of SiC_n^+ clusters ($56 < n < 61$), resulting in silafullerenes to be best considered as hypothetical structures. Clusters $C_{2n-q}Si_q$ with $2n = 32-100$ and $q < 4$ were generated by laser vaporization from defined Si:C targets.[108] The abundance distribution analysis and photofragmentation TOF spectra revealed the appearance of fullerene geometry, the Si atoms located close to each other in the fullerene network, corroborated by ab initio calculations.

First-principles calculations of Si-doped fullerenes $C_{59}Si$ and $C_{58}Si_2$ revealed charge transfer from the dopant atoms to the nearest-neighbor C atoms and that the bonding of Si in the fullerene cage consists of two single bonds and one weak double bond.[109] A systematic investigation on the molecular structures of silicon-substituted fullerenes $C_{59}Si$ and $C_{69}Si$ has been performed by using semiempirical MNDO, AM1, and PM3 methods.[110] PM3 semiempirical calculations on heterofullerenes $C_{59}Si$, $C_{58}Si_2$, and $C_{57}Si_3$ have been used to evaluate their stability and reactivity.[111] Optimization of geometrical structures using ab initio methods and simulation of the spectra of third-order nonlinear optical polarizabilities in $C_{59}Si$ and $C_{58}Si_2$ was reported by Cheng et al.[112]

Density functional calculations and structural geometry minimization techniques gave clear evidence of stable fullerene-like cage structures for multi-silicon-doped silafullerenes $C_{54}Si_6$, $C_{48}Si_{12}$, $C_{40}Si_{20}$, $C_{36}Si_{24}$, and $C_{30}Si_{30}$.[113−115] In the case of $C_{54}Si_6$, the thermally most stable arrangements were those when all Si atoms were found on a hexagon. The analysis of the charge topology revealed that the amount of charge on each atom depends on the number of heterogeneous bonds, due to significant charge transfer from the Si atoms to the neighboring C atoms.[113] The most stable isomer of $C_{48}Si_{12}$ featured a compact Si pattern consisting of three adjacent subunits, two hexagons and one pentagon.[114] An extensive isomer search showed that in the case of $C_{40}Si_{20}$ the most stable arrangements were those in which the Si atoms and the C atoms form two distinct homogeneous subnetworks. Due to charge transfer from Si to C, opposite charges are found in neighboring Si and C sites.[115] A threshold instability in highly Si-doped heterofullerenes was proven by transition from thermally stable to unstable $C_{60-m}Si_m$ systems at $m = 20$.[116] The structural and thermal properties and fragmentation behavior of exohedrally and substitutionally silicon-doped C_{60} containing 1−12 Si atoms were investigated by extensive molecular-dynamics simulations, performed by López et al.[117] The substitutional $C_{60-m}Si_m$ heterofullerenes undergo different structural transformations above the bond-breaking temperature T_b, prior to fragmentation and ejection of atoms and small molecules. This was demonstrated by snapshots, extracted along the simulation trajectories.[117b]

Germanium-containing heterofullerenes were produced by the arc-discharge technique under a 100 Torr He atmosphere and extracted from soot using CS_2. The mass distribution of the extract was analyzed by FAB mass spectrometry and showed the stability of heterofullerene structures.[118]

The networked iron fullerene $C_{59}Fe$, obtained by replacing a C atom of C_{60} by an Fe atom and subsequent self-consistently relaxing, has a closed-cage structure, but locally deformed in the vicinity of the Fe dopant atom. This was the result of first-principles calculations of its geometric and electronic structure.[119]

Fullerenes with metal atoms substituted into the C framework were observed in laser ablation studies of electrochemically deposited C_{60}/Pt polymeric films.[120] $[C_{58}Pt]^-$ and $[C_{56}Pt]^-$ were produced, resulting from the substitution of a Pt atom for two C atoms, and $[C_{57}Pt_2]^-$ was produced with two Pt atoms incorporated into the cage.[120] A systematic search of the regioisomers of the platinum heterofullerenes $C_{57}Pt_2$ and $C_{56}Pt_2$ to find the most stable structures has been carried out by Campanera et al. utilizing density functional calculations.[121] Both heterofullerenes incorporate two metal atoms into the fullerene core; in $C_{57}Pt_2$ one Pt atom substitutes one C atom of C_{60} and the other Pt replaces a C−C bond, whereas in $C_{56}Pt_2$ each Pt atom replaces one C−C bond of C_{60}.

A general formation of microscopic amounts of heteroatom-doped fullerenes from homofullerenes was achieved by a recoil process following nuclear processes.[122] From the traces of radioactivity detected after HPLC separation, the formation of heterofullerenes was proven. However, under the conditions of high kinetic energy insertion of atoms into homofullerenes, the formation of endohedrally doped fullerenes also has to be considered.[122] Radioactive heterofullerenes As^*C_{59} and As^*C_{69} ($As^* = {}^{71}As$, ${}^{72}As$, ${}^{74}As$) and ${}^{69}GeC_{59}$ and their polymers were detected by radiochemical and radiochromatographic techniques already in 1999.[123] The formation of Se atom-incorporated fullerenes has been investigated using radionuclides produced by nuclear reactions, and the presence of ${}^{75}Se$ as part of the fullerene framework was suggested. Ab initio molecular dynamics simulations were performed to support these findings.[124] Sb-incorporated fullerenes were synthesized by mixing C_{60} fullerene powder with Sb_2O_3 followed by irradiation with bremsstrahlung of 50 MeV. The formation of Sb derivatives was corroborated by tracing the radioactivity of ${}^{120}Sb$ and ${}^{122}Sb$.[125]

4. Conclusion and Outlook

Heterofullerene chemistry is still a very young discipline within synthetic organic chemistry. So far, it is still restricted to azafullerenes. However, since its possible structural diversity is enormous, heterofullerene chemistry still offers preparative challenges for the future. Access to new and unknown diazafullerenes $C_{58}N_2$, higher substituted azafullerenes $C_{60-n}N_n$, heterofullerenes containing other elements such as thiafullerenes, oxafullerenes, borafullerenes, and other elementafullerenes, as either closed- or open-shell molecules,[80] new heterofullerene dimers such as bisborafullerenyl, and finally truncated heterofullerenes remains to be discovered. Making these structures available will lead to the development of new synthetic approaches in synthetic fullerene chemistry. Exciting and unprecedented physical and chemical properties of these fascinating cage molecules and their derivatives can be expected.

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