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Heterofullerenes

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The state of the art in heterofullerene chemistry and physics is reviewed with emphasis on azafullerenes. The macroscopic synthetic methods that have been developed for aza[60]fullerene compounds since 1995 have led to a whole new and rich area in the science of fullerenes: cage modification chemistry. The synthetic routes towards aza[60]fullerene and its derivatives are reviewed in Sect. 2. The synthetic routes for aza[70]fullerene and its derivatives are summarized in Sect. 3. Section 4 comprises the theoretical and experimental work on the physicochemical properties of azafullerene compounds. Finally, in Sect. 5, the literature regarding heterofullerenes other than monoazafullerenes is reviewed.

Abbreviations

MEM   2-methoxyethoxymethyl
SEM   2-(trimethylsilyl)ethoxymethyl
ODCB   1,2-dichlorobenzene
pTsOH   *para*-toluenesulfonic acid

1
Introduction

Heterofullerenes ("dopeyballs", "heterohedral" fullerenes) are fullerenes in which one or more carbon atoms that form the cage structure is replaced by a non-carbon atom, i.e. a heteroatom. Fullerenes are defined by IUPAC as poly-hedral closed cages made up entirely of *n* three-coordinate carbon atoms and having 12 pentagonal and (*n*/2–10) hexagonal faces, where *n* is equal to or grea-ter than 20. Carbon cages that do not fulfill the requirement are referred to as *quasi*-fullerenes; the hetero-analogues of such structures being hetero-*quasi*-fullerenes and they will not be reviewed in this chapter. Since most inorganic (non-carbon) cage and cluster structures do not fulfill the requirement, these compounds are also not considered here. Thus, this review concerns mainly hetero-analogues of [60]fullerene (Buckminsterfullerene C_{60}) and [70]fullerene.

In 1991, 6 years after the experimental discovery of the fullerenes [1] and one year after the discovery of a method for bulk preparation of fullerenes [2], the first spectroscopic observation of gas-phase formation of heterofullerene ions was reported by the Smalley group [3]. Very soon thereafter, other groups found spectroscopic evidence for gas-phase heterofullerene ion formation and some theoretical studies concerning the electronic structure and thermodynamic stability of heterofullerenes emerged (see Sect. 5). From the beginning, hetero-fullerenes have been considered as interesting molecules and materials, mainly because it was envisioned that through modification of the cage structure, sig-nificant modification of geometry, chemical functionality and electronic char-acter of the fullerenes would occur. Consequently, it was anticipated that these heterofullerenes should exhibit a variety of properties, e.g. superconductivity (leading to superconducting materials with improved thermodynamic stability) or altered electronegativity (making them interesting candidates for photo-diode-based devices).

In 1995, three chemistry research groups found independently that, during mass spectroscopic analysis, certain exohedrally nitrogen-containing [60]fuller-ene *derivatives* showed efficient gas-phase rearrangements to aza[60]fullerene ions [4–6]. Based on the gas-phase observation and after rationalization of the events that take place during the rearrangement process, the first and highly

efficient synthetic method for the bulk preparation of aza[60]fullerene was developed in Santa Barbara (USA) in 1995 [7]. Soon thereafter, the Hirsch group succeeded in converting their gas-phase process into a preparative method [8]. These developments have enabled scientists to synthesize and study a variety of aza[60]- and aza[70]fullerene compounds. Since there are no such synthetic methods for other fullerenes to date, azafullerenes are by far the most studied heterofullerenes until now. Hence, this review concerns mainly the preparation of aza[60]fullerene and its derivatives (Sect. 2), aza[70]fullerene and derivatives (Sect. 3), and the properties of aza[60]- and aza[70]fullerene compounds (Sect. 4). In Sect. 5, we will summarize the work concerning presently observed or considered (mainly [60]-) heterofullerenes other than aza[60]- and aza[70]fullerene.

Although the field is very young, a number of reviews concerning heterofullerenes and heteroatom-containing versions of carbon nanotubes have appeared recently. In some of these, with varying success, efforts have been made to cover the whole area [9–12], in others only part of the field is concerned [13–15], while in some articles the authors summarize their own work on heterofullerenes almost exclusively [16–21].

The nomenclature that has been used for fullerenes, fullerene derivatives, and heterofullerenes, has been until now rather haphazard. In this review, we will generally try to comply with the latest IUPAC nomenclature, as described in the article by Godly and Taylor [22].

2
Synthesis of Aza[60]fullerene

2.1
Introduction

The potential influence of substitution of a carbon atom by a nitrogen atom in the C_{60} cage structure on its electronic and optical properties has attracted the theoretical interest of a considerable number of scientific groups since 1992. Neutral aza[60]fullerene (CAS: 2H-1-aza[5,6]fulleren-C_{60}-I_h-yl) is an open shell molecule due to the trivalency of nitrogen leaving a "dangling bond" on an adjacent carbon atom in the cage (structure **1** in Fig. 1). Aza[60]fullerene in the first oxidized state is sometimes called aza[60]fulleronium (CAS: azonia[5,6]fulleren-C$_{60}$-I_h), for which one resonance structure is shown (**2**, see Fig. 1).
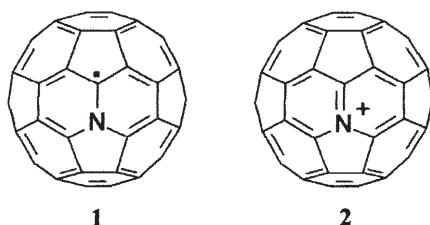

Fig. 1. Important resonance structures of aza[60]fullerene radical (**1**) and aza[60]fulleronium (**2**)

The first preparative efforts, using the arc-discharge method in an atmosphere of helium and nitrogen, ammonia, or methylamine, followed by MS analysis of the toluene extraction of the resultant soot, pointed towards the formation of several nitrogen-containing heterofullerenes, but not $C_{59}N$ [23,24]. Gas-phase formation of $C_{59}N$ (as $C_{59}N^+$) was first reported by Christian et al. in 1992 [25]. An experiment in which a N^+ ion beam was collided with an evaporated mixture of C_{60} and C_{70} (~ 85 : 15) and the collision products were collected by the ion guide and mass analyzed by a double-focusing mass spectrometer and counted by an on-axis Daly detector, yielded evidence for the formation of $C_{59}N^+$. It was reported that the $C_{59}N^+$ thus formed decayed primarily by CN elimination (analogous to the "shrink-wrap" mechanism found for fullerenes) to C_{58}^+. In hindsight, this proves that their $C_{59}N^+$ was almost certainly aza[60]fulleronium, since this shrink-wrap pattern was also observed later in mass spectra of pure samples of $(C_{59}N)_2$ [7]. Arc vaporization of graphite in the presence of pyrrole vapor was reported to yield "N-doped" fullerenes. The products were analyzed by a series of spectroscopic methods, yielding little structural evidence for $C_{59}N$ [26, 27]. Negative mode mass spectroscopic analysis of products from arc vaporization of graphite in an atmosphere of pure nitrogen showed a relatively increased intensity of the peak at m/e 722, which was interpreted as proof for the presence of $C_{59}N^-$ [28]. Products from a similar experiment were also characterized by XPS [29]. Other investigators analyzed similarly obtained products by MS, UV-Vis and IR spectroscopy [30]. Mass spectroscopy, ESR, Raman scattering, and IR analysis of Soxhlet extracts of soot from arc vaporization of graphite rods of which one was filled with boron nitrite, were interpreted as if $C_{59}N$ would exist as an open shell monomer at ambient conditions [31], which is not the case. Laser ablation of graphite in a heated nitrogen gas atmosphere revealed ions with masses in accordance with $C_{59}N^+$ and $C_{69}N^+$ in FT mass spectroscopy. The presence of nitrogen in the product was confirmed by isotope labeling experiments with $^{15}N_2$. The nitrogen 1s level was found to be at 400.7 eV using XPS [32,33]. A hot plasma method for the preparation of all kinds of heterofullerenes including azafullerenes has been patented [34].

This summarizes all the theoretical and gas-phase preparation work that has been done up to now with respect to aza[60]fullerene, except for the developments that led to the realization of actual bulk preparation of [60]- and aza[70]fullerene dimers and derivatives and the investigations of these products. This work will be described in detail in the remainder of this section.

2.2
Synthesis of Aza[60]fullerene Dimer $(C_{59}N)_2$

In 1995, three different but related ways were found that first led to *efficient* gas-phase preparation of aza[60]fulleronium **2**. These findings subsequently gave way to two closely related synthetic methods for bulk preparation of $C_{59}N$ in its dimeric form [4–8]. Since all of these methods start with the chemical modification of C_{60} or C_{70} using the addition of azides, we will review the work related to this reaction first in Sect. 2.2.1. A second step in the synthesis is de-

scribed in Sect. 2.2.2 and the two approaches for the final synthetic step are described in Sects. 2.2.3 and 2.2.4.

2.2.1
The Addition of Azides and Nitrenes to C60

In 1993, it was found that alkyl azides react with C_{60} in a 1,3-dipolar cycloaddition manner [35]. The course of the reaction is closely analogous to the 1,3-dipolar addition of alkyl diazo compounds. Preliminary results on the reaction of C_{60} with organic azides were complicated. Treatment of C_{60} with SEM azide in refluxing chlorobenzene afforded two major products **3** and **4** (Fig. 2). While ^{15}N-^{13}C spin-spin coupling experiments supported the structure for **4**, the ^{13}C NMR spectrum of **3** contained a resonance at 160 ppm coupled to ^{15}N, which was not compatible with the expected triazoline.
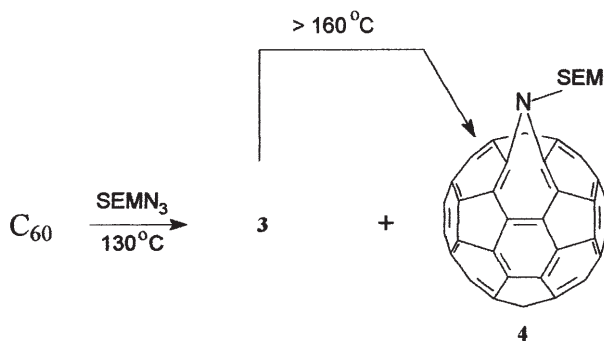
Fig. 2. The addition of $SEMN_3$ to C_{60}

The initial monoaddition product from the reaction with MEM azide across a [6,6] bond of C_{60}, the triazoline **5**, is stable enough to allow isolation at room temperature and confirmation of the structure through X-ray analysis of single crystals [36]. Thermolysis of the monoadduct, triazoline **5**, followed by concomitant loss of nitrogen, gives rise to azafulleroid (azahomofullerene; IUPAC: 1a-aza-1(6)a-homo[60]fullerene; CAS: 2a-aza-1,2(2a)-homo[5,6]fullerene-C_{60}-I_h) **6** and azirenofullerene ("fulleroaziridine", 1,2-(dihydro-1H-aziridino)-[60]fullerene; aziridinofullerene; IUPAC: 1,2-epimino[60]fullerene or 1′H-azireno[2′,3′:1,2][60]fullerene; CAS: 1′H-[5,6]fullereno-C_{60}-I_h-[1,9-b]azirene) **7** in 15 and 5% yield, respectively (Fig. 3) [35]. Azirenofullerenes and azafulleroids can also be obtained directly from C_{60} at higher reaction temperatures (160–180 °C).

Interestingly, when MEM azide addition reactions are carried out at temperatures ranging from 60–140 °C, in addition to the formation of the azafulleroid and azirenofullerene, a bisazafulleroid (diazabishomofullerene) **8** is formed and is the major product [37]. For reasons which are not well understood, the double bonds adjacent to the nitrogen bridge are more reactive towards further cyclo-
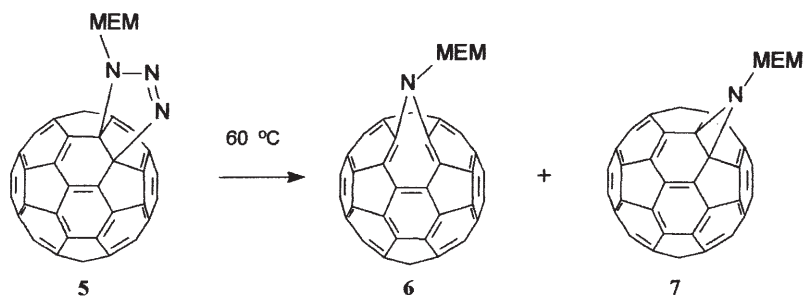
Fig. 3. Thermolysis products from MEM-substituted triazoline **5**
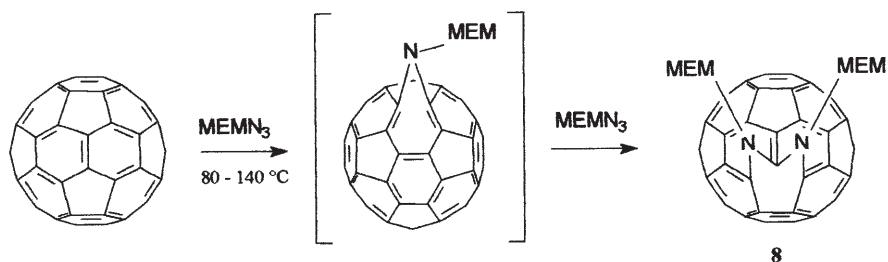
Fig. 4. Chemo- and regioselective formation of bisazafulleroid **8** from C_{60}

addition of alkyl azides than the other double bonds in the fullerene framework. Upon heating above 140 °C, **8** (or a MEM analogue of **3**) reverts back to the mono adduct **6**. The appearance of a carbon resonance at 160 ppm for **8** (**3**) is consistent with a carbon atom adjoined to two nitrogen atoms. (Fig. 4)

Investigation of this phenomenon led to the finding that not only is the azide addition chemoselective, it is also regioselective, as indicated by the isolation of the bisadduct **8**, and not **9** or **10** (Fig. 5). The preparation of bisazafulleroid compounds has been patented [38].

Several groups have noted similar findings for azide addition, in which the structure of the bisadduct depends on the nature of the starting alkyl azide or bisazide [39–41]. Even chiral bisazafulleroids have been prepared [42, 43]. As an interesting example, it was found that subsequent addition of azido ester to N-ethoxycarbonyl-azirenofullerene resulted in the formation of bisadduct **12** and not **11** [40]. Structure **12** constitutes the first fullerene derivative having [6, 6] open bridges (Fig. 6). Before that, all [5,6] adducts were found to adopt an open bridged structure and all [6, 6] adducts to adopt closed bridged structures.

In the case of **12**, electronic factors exceed the normal characteristic of fullerene derivatization; that is the tendency to avoid endocyclic double bonds in five-membered rings. Prior to this work, Banks claimed the existence of a [5, 6]
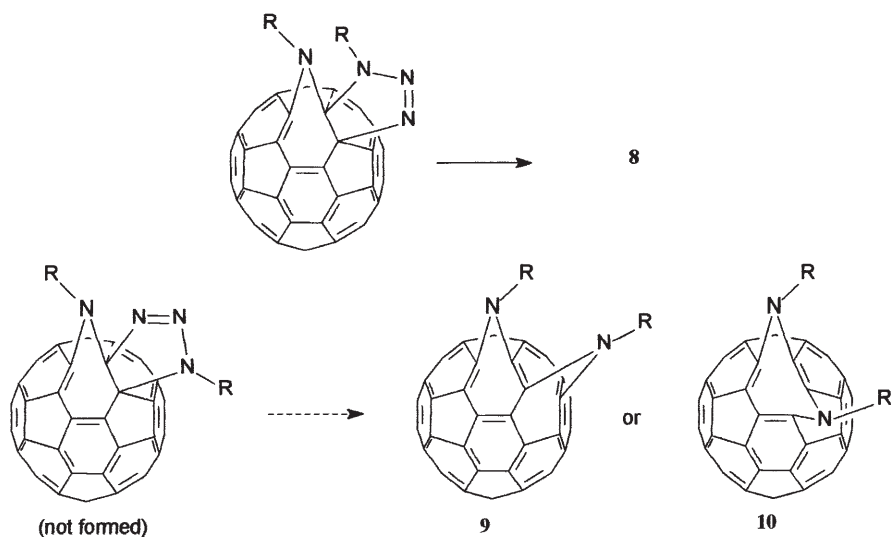
Fig. 5. Expected additional bisazafulleroid isomers **9** and/or **10** in the case of non-regioselective addition of $MEMN_3$ to MEM-azafulleroid **6**
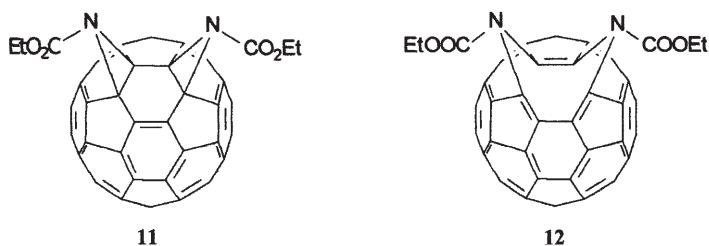
Fig. 6. Addition of azidoester to N-ethoxycarbonyl-azireno[60]fullerene results in formation of bisadduct **12** and not **11**

closed structure, but this was corrected by the Hirsch group [44, 45]. The existence of the [6,6] open structure **12** is well established; ^{15}N labeling experiments were used to determine the bonding of these unique bisadducts [40]. Azirenofullerenes are formed in good yield by the reaction of in situ formed nitrenes (either photochemically or thermally from azides) with C_{60}. Averdung and Mattay and co-workers investigated the addition to C_{60} of nitrenes derived from aroylazides and tert-butylazidoformate and found that the parent azirenofullerene **14** can be obtained upon chromatography of the N-t-butoxycarbonyl compound **13** over a column of neutral alumina (Fig. 7) [46–48]. Banks et al. found a similar route to **14** independently [49]. The parent azirenofullerene **14** can be derivatized on the nitrogen atom by addition of electrophiles to yield a urethane, an amide, or a sulfonamide [50].
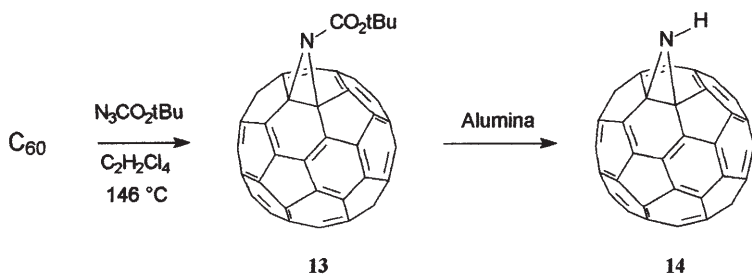
Fig. 7. Two-step synthesis of azireno[60]fullerene **14** from C_{60}

In contrast to the N-MEM (N-alkyl) analogue (see Sect. 2.2.2), N-aryl-aza-fulleroids, obtained from the thermal reaction of aryl azides with C_{60}, can be photochemically isomerized to azirenofullerenes [51]. This closely resembles the difference in the photochemical behavior of C-aryl- and C-alkyl fulleroids obtained from the reaction of diazo compounds with C_{60} (e.g. [5,6] $C_{61}H_2$ is photochemically stable). After some initial studies (see for example [52–55]), the addition of azides and nitrenes to C_{60} has been investigated and used for the preparation of a series of functional fullerene derivatives by a number of other investigators, but their work is not relevant in relation to the preparation of aza[60]fullerene. The addition of azides to fullerenes has been briefly reviewed previously [56–58].

2.2.2
Gas-Phase Observation of Aza-dihydro[60]fullerene and Azafulleronium Ions from Aazirenofullerenes and Bisazafulleroids

Averdung et al. found in 1995 that when azirenofullerene **14** was subjected to desorptive chemical ionization (DCI) mass spectroscopy, using ammonia as reagent gas and a rhenium wire as heater, peaks at m/z 723 and 724 were found, next to $[M+H]^+$, C_{60}^+, and $C_{60}H^+$ [6]. These peaks were rationalized as dihydro-aza[60]fullerene ions $C_{59}NH^{+\cdot}$ and $C_{59}NH_2^+$. A normal exact mass determination was not possible, but the calculated centroid masses of the peaks for $C_{59}NH^+$ and $C_{59}NH_2^+$ were reported to fit the experimentally found values. Based on quantum-chemical calculations, the authors proposed a 1,2-closed structure as the most stable for both the neutral $C_{59}NH$ and the charged species $C_{59}NH_2^+$ (structures **15** and **16** in Fig. 8).

The exact mechanism of this formation of heterofullerene ions remains unclear, although a possible mechanism involving NH_3 addition to azafulleroid (presumably formed by isomerization of the azirenofullerene) was later proposed [18]. The authors reported on several occasions on this gas-phase transformation [17, 59–61]. The proposed structure for $C_{59}NH$ was later confirmed by the Wudl group upon the bulk synthesis of this compound (see Sect. 2.3).

Also in 1995, Lamparth et al. found that when bisadducts **12** and **17** (Fig. 9) were submitted to FAB-MS, aza[60]fulleronium $C_{59}N^+$ was formed in high yield,
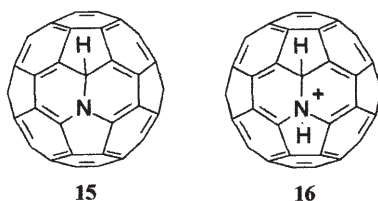
Fig. 8. Structures for neutral $C_{59}NH$ (**15**) and $C_{59}NH_2^+$ (**16**), proposed by Averdung et al.

R = CH$_2$COOMe
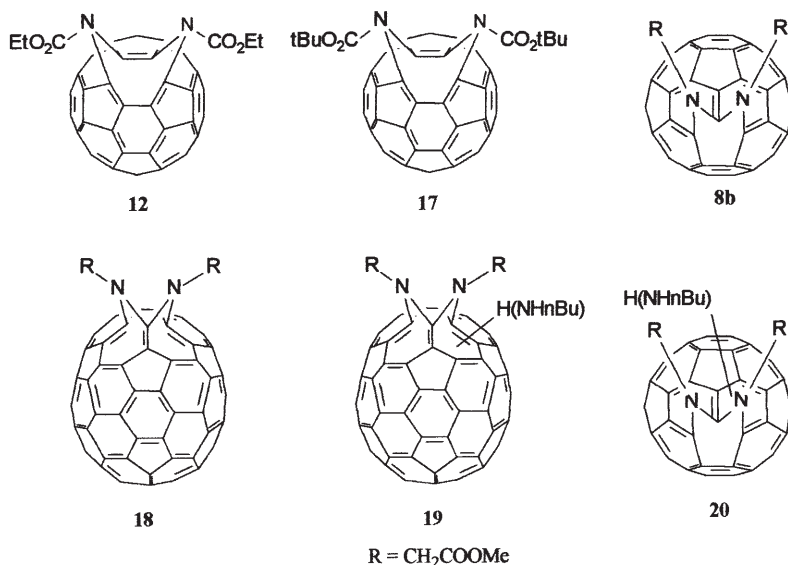
Fig. 9. Precursors for the gas phase formation of $C_{59}N^+$ (**8b, 12, 17, 20**) and $C_{69}N^+$ (**18, 19**) in FAB-MS. Compounds **19** and **20** are the products of the reaction of butylamine/DBU with bisazafulleroids **18** and **8b**, respectively

whereas the mass spectra of the bisazafulleroids show only the typical characteristics of fullerene adducts (a relatively small M^+ peak and, at 720, C_{60}^+, the base peak) [5].

In the case of **12** and **17** the peak at m/z 722 ($C_{59}N^+$) was the base peak, and the 720 peak showed a relative intensity of 80%. The well-known shrink-wrap degradation was observed, supporting the fullerene structure of this material. Furthermore, it was found that treatment of bisazafulleroids **8b** and **18** with one equivalent of butylamine in the presence of DBU yielded (presumably regioselective monoaddition) products that fragmented in FAB-MS with efficient formation of aza[60]fulleronium and aza[70]fulleronium ions, respectively ($C_{60}^+/C_{59}N^+ \sim 1:1$ and $C_{70}^+/C_{69}N^+ \sim 1:2$). Exact mass determination confirmed the proposed formulae. The synthetic method for the preparation of azafullerenes, based on these findings, is described in Sect. 2.2.5.

2.2.3
Controlled Chemical Opening of the Fullerene Cage

From the fact that azide addition to fullerenes yields specific bisadducts with high selectivity, it is clear that the two identical "enamine" C=C bonds in aza-fulleroids are relatively activated in certain reactions. In an attempt to expand the scope of the chemoselectivity of the azafulleroids, other cycloadditions were performed. Taking advantage of the fullerenes as effective triplet sensitizers, Hummelen et al. showed that self-sensitized photo-oxygenation of N-MEM aza[60]fulleroid **6** afforded the cage-opened [60]N-MEM ketolactam **22** in 65% yield [62]. This was the first step towards the controlled opening of the fullerene cage. By causing oxidative rupture of a double bond adjacent to the 5,6 bridged nitrogen atom, an 11-membered ring was created. It is assumed that the reaction proceeds through a 1,2-dioxetane intermediate **21** (Fig. 10).
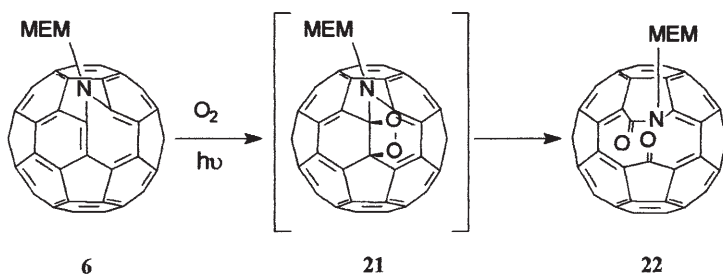
Fig. 10. Controlled opening of the fullerene cage by self-sensitized photo-oxygenation of **6**

Product **22** was fully characterized by ^{13}C and ^{1}H NMR, FTIR, UV-Vis and FAB-MS spectroscopy and elemental analysis. In the course of the characterization, FAB-MS revealed a base peak at m/z=722 (and no peak at all at 720!) and smaller peaks at m/z=780 (95%) and 856 (M+H$^+$). The exact mass of the m/z 722 ion, 721.9991, was consistent with the molecular formula $C_{59}N^+$. Further confirmation was found in the shrink-wrap fragmentation pattern [63]: loss of CN, m/z = 696, followed by the successive loss of C_2, m/z 672 and 648. Examination of the FAB mass fragmentation pattern of N-MEM ketolactam 22 to azaful-leronium $C_{59}N^+$ led to the proposed mechanism of formation as depicted in Fig. 11.

The relatively intense peak at m/z=780 is due to loss of 2-methoxyethanol from the protonated M to yield the N-methyl carbonium ion **23** which is, in turn, transformed to the four-membered 1,3-oxazetidinium ring in **24**. The latter eliminates formaldehyde to yield intermediate **25**, followed by the loss of carbon monoxide to yield the azafulleronium ion.

When bisazafulleroid **8** was submitted to self-sensitized photooxygenation, the expected symmetrical oxidation product was not observed, but instead the asymmetric mono-oxidized product **26** was isolated in low yield (Fig. 12). The
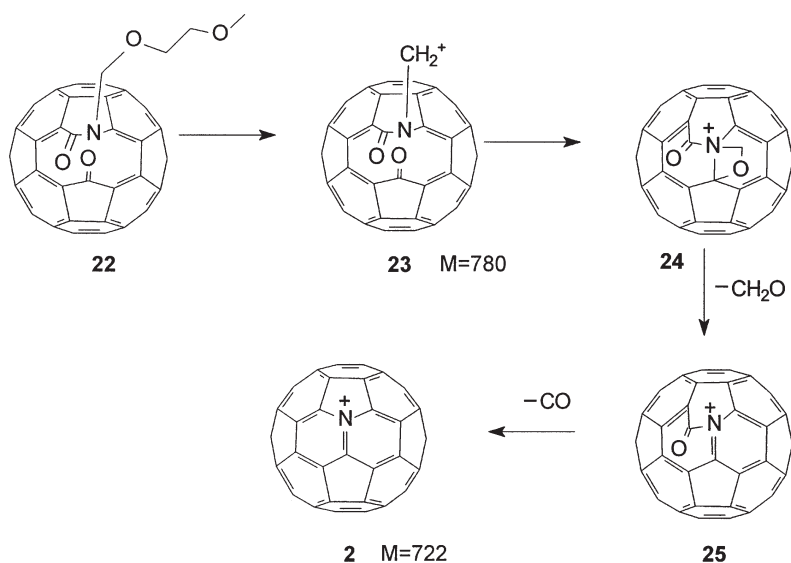
Fig. 11. Possible mechanism of gas-phase formation of $C_{59}N^+$ from ketolactam **22** in FAB-MS
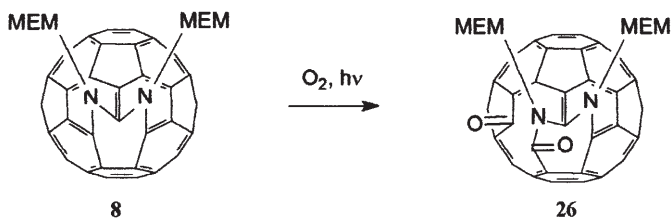
Fig. 12. Regioselective self-sensitized photo-oxygenation of bisazafulleroid **8**

FAB-MS degradation pattern of **26** gave further support for the proposed mechanism of azafulleronium formation, because, next to the M^+ peak at m/z = 958, and the base peak at 722, peaks at m/z = 883 (17 %) and 853 (35 %) were observed, corresponding to subsequent loss of 2-methoxyethanol and formaldehyde from **26** [7].

These gas-phase observations paved the way for the first synthetic route towards azafullerenes, as described in the next section. The cage-opened structures **22** and **26** are asymmetric. Ketolactam **22** was later resolved on a chiral HPLC column, and the circular dichroism of the enantiomers was determined [64].

2.2.4
(C₅₉N)₂ from a Cage-Opened Fullerene

Soon thereafter, during the search for a synthetic method that would mimic the events depicted above to obtain macroscopic quantities of "$C_{59}N$", a fast and remarkable reaction was observed when N-MEM ketolactam was treated with a large excess (15–20 equiv.) of pTsOH-H_2O in ODCB at reflux temperature under an atmosphere of nitrogen [7]. The color of the reaction mixture changed from red-brown to green-brown upon the formation of a non-polar major product in high yield. After purification by HPLC, the latter (green in solution) was shown by cyclic voltammetry, ^{13}C NMR, FTIR, UV-Vis, elemental analysis and mass spectrometry (electrospray) to be the azafullerene dimer $(C_{59}N)_2$. A strong argument for the dimer was obtained from the cyclic voltammogram (CV), which showed three pairs of reversible one-electron reductions. The appearance of closely spaced pairs of waves in the CV suggested that this system consisted of two (identical) weakly interacting electrophores. The ^{13}C NMR spectrum of $(C_{59}N)_2$ showed 29 lines in the region between 156 and 124 ppm, which is consistent with a highly symmetrical dimer structure. Other resonances (i.e. sp³-hybridized carbon atoms) were not observed. The absence of a resonance in the 70–110 ppm region in the ^{13}C NMR spectrum forced the investigators to consider the [6,6]-open structure **27** as a possible structure for the azafullerene, as the only alternative to the [6,6]-closed structure **28** (symmetry arguments ruled out all other structures; Fig. 13). Electrospray mass spectroscopy was the only MS technique that allowed the detection of the dimer M⁺ peak (at m/z = 1445). In FAB-MS, MALDI, EI and CI MS, only the monomer $C_{59}N^+$ or $C_{59}N^-$ (depending on the detection mode) ions were observed, with shrink-wrap peaks in FAB-MS.

After establishing the dimeric structure, the following rationale for the molecule's formation process was proposed (Fig. 14): the azafulleronium ion is
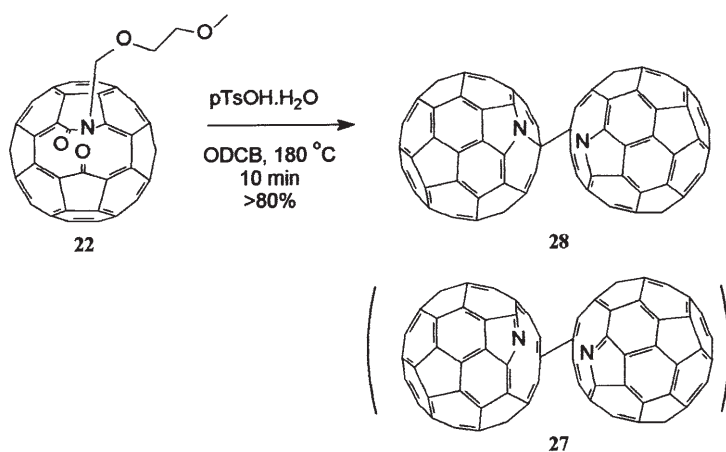
Fig. 13. Synthesis of $(C_{59}N)_2$ from MEM-ketolactam **22**

formed first in a manner that mimics the gas-phase formation of azafulleronium, i.e. the acid protonates the MEM moiety, inducing the loss of 2-methoxyethanol, followed by rearrangement and loss of formaldehyde and carbon monoxide to yield the azafulleronium ion. In the presence of the 2-methoxyethanol (or water) the azafulleronium ion can be reduced to the azafullerenyl radical. Finally, this radical dimerizes to yield $(C_{59}N)_2$.

Repeating the synthetic sequence $C_{60} \rightarrow$ **28** starting with ^{15}N-labeled MEM azide afforded ^{15}N-labeled **28**. Using various NMR techniques, the [6,6]-closed structure of $(C_{59}N)_2$ (i.e. structure **28**) was be proven unambiguously [65].

The Wudl group later optimized the three-step synthetic route from C_{60} to $(C_{59}N)_2$ to a reproducible overall yield of 15 % on larger scale to yield gram quantities of the dimer. The synthetic method is potentially applicable to all fullerenes (see Sect. 3). When oxygen was not rigorously excluded during the reaction **22 → 28**, some oxidized dimeric material was formed. The structure of this material was proposed to be the N-oxide **29** (Fig. 15) [66]. Further support for
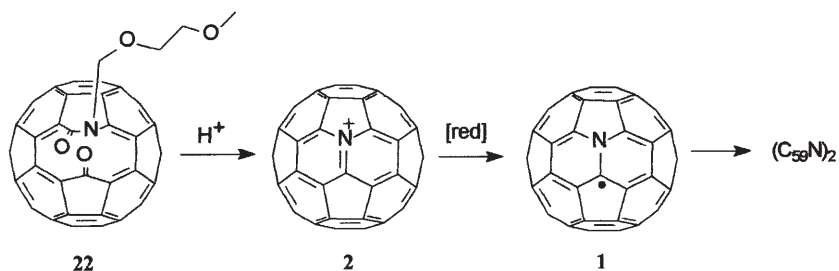
Fig. 14. Mechanism of formation of $(C_{59}N)_2$ from MEM-ketolactam **22**
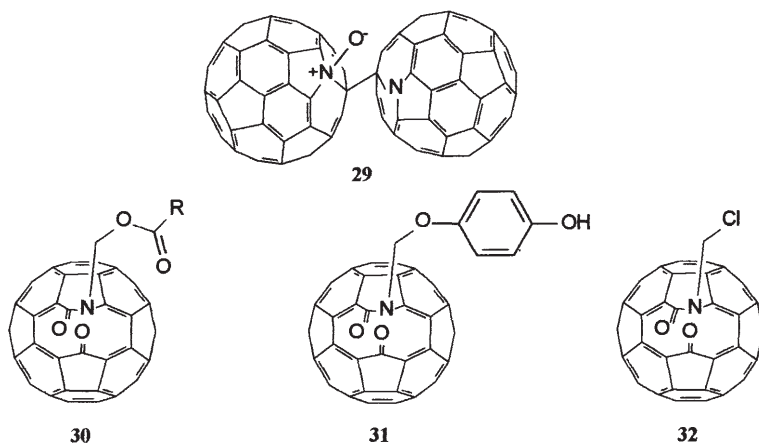
Fig. 15. N-oxide **29** is formed during the reaction **22 → 28** in the presence of traces of oxygen. Holeyballs **30, 31**, and **32** are carbonium ion intermediate **23** trapping products from the reaction **22 → 28** in the presence of nucleophiles

the proposed mechanism for the formation of $(C_{59}N)_2$ was obtained when the reaction was carried out in the presence of nucleophiles to trap the proposed carbonium ion intermediate **23** [67]. This led to the isolation of new holeyballs **30, 31**, and **32**, fullerenes with a ring larger than a hexagon (Fig. 15).

2.2.5
(C₅₉N)₂ from a Bisazafulleroid

Based on their gas-phase observation of $C_{59}N^+$, a second route to $(C_{59}N)_2$ was developed by Hirsch and co-workers [7, 8]. When bisazafulleroid **8** was treated with butylamine and DBU in toluene at room temperature, "aminofullerides" were formed, which yielded a mixture of dimer **28** and aza[60]fullerene deriva- tive **33** in 12–15% yield after heating with 20 equivalents of pTsOH in ODCB at reflux temperature over 8 min (Fig. 16). The reaction did not occur when **8b**, the bis-NCH₂CO₂Me analogue of 8, was used as starting material. The dimer **28** obtained by this method was identical to the material obtained earlier by the Wudl group.
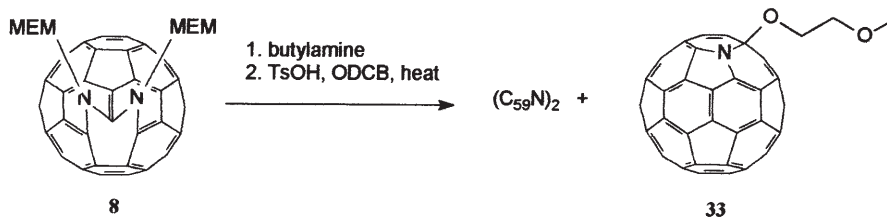
Fig. 16. Synthetic route towards azafullerene compounds, reported by Hirsch et al.

The reaction was also applied to the C_{70} analogue (see Sect. 3), which implies that this three-step route from C_{60} to $(C_{59}N)_2$ can also be applied to all fullerenes. The exact mechanism of the reaction is, however, not known.

2.3
Synthesis of Aza[60]fullerene Derivatives

Up to now, two types of synthetic methods towards monomeric aza[60]fullerene derivatives have been developed: Method (a) starting from non-azafullerene precursors and Method (b) starting from the dimer $(C_{59}N)_2$.

Method (a). The first example of a reaction according to this method has alrea- dy been mentioned in the preceding section. Another example is the reaction depicted in Fig. 17. Hence, when a 15-fold excess (relative to **8**) of hydroquinone was added to the reaction mixture that otherwise yielded the azafullerene dimer, the intermediate azafulleronium ion **2** was reduced to azafullerenyl radical **1**, which was subsequently trapped by the hydroquinone to give the parent mono-
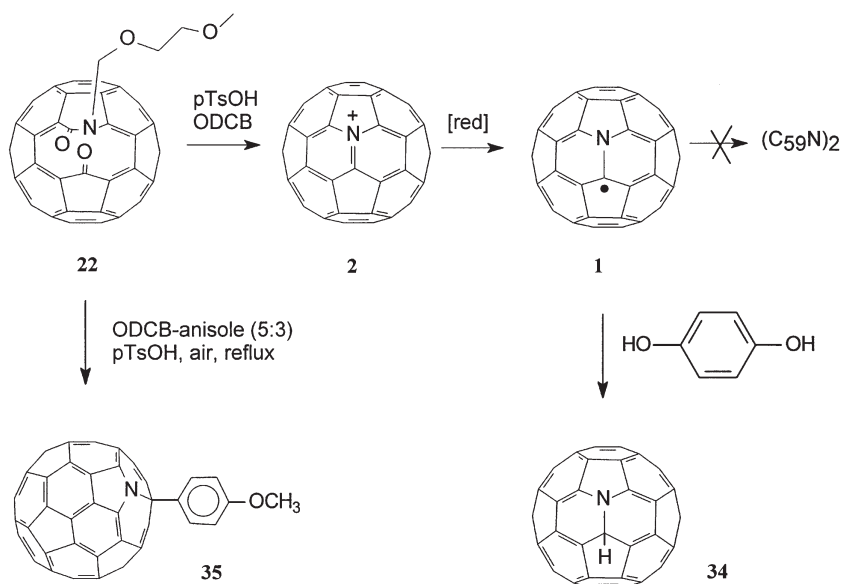
Fig. 17. More trapping products of the reaction **22→28**. Trapping of azafullerenyl radical intermediate **1** by hydroquinone leads to the formation of hydroaza[60]fullerene **34**. Trapping of intermediate azafulleronium **2** by anisole yields arylated azafullerene **35**

meric azafullerene, hydroazafullerene **34**, in a high yield [67]. As was mentioned in Sect. 2.2.4, a larger (75-fold) excess of hydroquinone resulted in the trapping of an earlier intermediate in this reaction, i.e. carbonium ion **23**.

Negative ion ES-MS of **34** showed a base peak at m/z = 723. DCI mass spectroscopy shows shrink-wrap peaks at m/z = 696, 672, 648, and 624. Compound **34**, like dimer **28** and derivative **33**, is green in common organic solvents. A clear resonance signal at 72.1 ppm in the ^{13}C NMR allowed for unambiguous assignment of the [6,6]-closed structure to hydroazafullerene **34**.

Recently, it was found that when the reaction is carried out in the presence of a large excess of anisole and air, arylated azafullerene **35** can be obtained in 38 % yield [68] (Fig. 18). Compound **35** was also obtained, but in a much lower yield, directly from bisazafulleroid **8**, when the reaction shown in Fig. 16 was carried out in the presence of anisole and air. When the same reaction was carried out in pure 1-chloronaphthalene at 220 °C, a mixture of arylated products **36** was obtained in 46 % isolated yield [68].

Method (b). Several examples of the preparation of monomeric aza[60]fullerene derivatives from the dimer **28** have been reported. First, it was found that treatment of the dimer with excess diphenylmethane in refluxing ODCB for 48 h afforded, after chromatographic purification, 2-diphenylmethyl-azafullerene **37** in 42 % yield, as depicted in Fig. 19 [69].

A short free-radical chain mechanism has been proposed to explain the result. Hence, thermal homolysis of the dimer generates $C_{59}N^{\cdot}$, which either
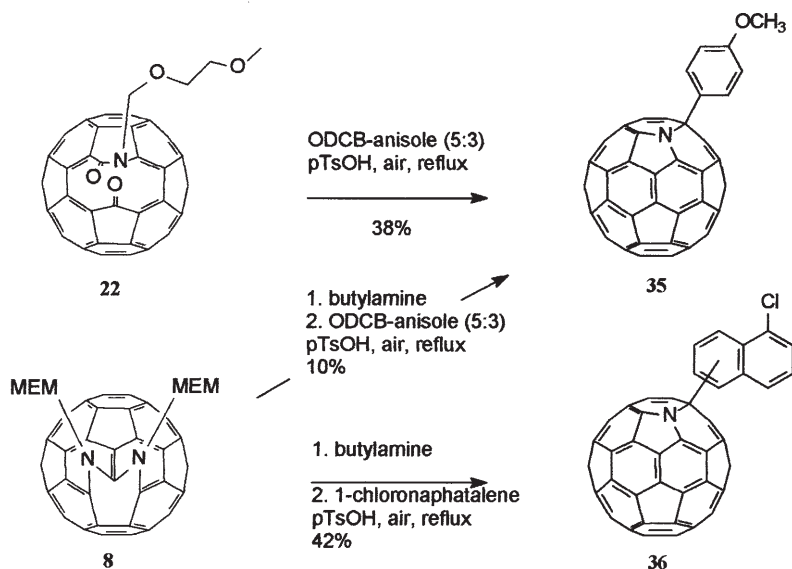
Fig. 18. Arylation products from the common azafulleronium intermediate **1**, formed in some reactions of **22** and **8**
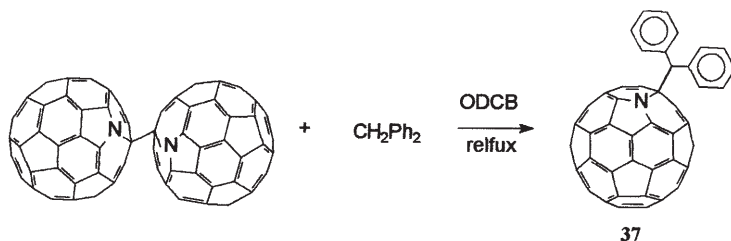
Fig. 19. Thermal homolysis of $(C_{59}N)_2$ in the presence of diphenylmethane yields azafullerenyl radical trapping product **37**

abstracts a hydrogen atom from the hydrogen donor diphenylmethane or re-combines with the thus formed diphenylmethyl radical. The hydroazafullerene is not stable under these reaction conditions and generates more dimer:

$$(C_{59}N)_2 \rightarrow 2\,C_{59}N^{\cdot}$$

$$C_{59}N^{\cdot} + Ph_2CH_2 \rightarrow C_{59}NH + Ph_2CH^{\cdot}$$

$$Ph_2CH^{\cdot} + C_{59}N^{\cdot} \rightarrow C_{59}(CHPh_2)N$$

$$2\,C_{59}NH \text{ (with trace of } O_2) \rightarrow (C_{59}N)_2 + H_2O_2$$
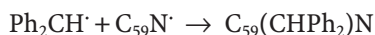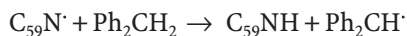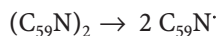
This mechanism is supported by two control experiments: (a) a fresh sample of hydroazafullerene **34** was found to dimerize on standing at room temperature,

even in the solid state; (b) treatment of **34** with diphenylmethane in refluxing ODCB for 24 h afforded 73% of **37**, 7% of dimer **28**, and 5% of recovered starting material.

Treatment of $(C_{59}N)_2$ with diphenylmethane under photolytic conditions at room temperature was expected to produce **37**. However, after five hours of irradiation, HPLC analysis of an aliquot of the reaction mixture showed no formation of **37**, but instead revealed the formation of material with proposed *N*-oxide structure **38** (25%), next to recovered $(C_{59}N)_2$ (75%). It was assumed that trace amounts of $^1O_2$ initiate this conversion (Fig. 20). Because fullerenes are excellent sensitizers for the conversion of triplet to singlet oxygen, any oxygen in the reaction flask is converted to $^1O_2$ under these reaction circumstances [66].

Thermal treatment of the dimer with anisole, toluene, and 1-chloronaphthalene in the presence of a large excess of pTsOH and air leads to the formation of mono-arylated azafullerenes in 78–90% isolated yields [68]. The reaction with anisole and toluene yield *para*-substitution products **35** and **39**, while 1-chloronaphthalene is substituted at various positions (Fig. 21). The reaction does not take place in the absence of air or pTsOH. The reaction is presumed to proceed through electrophilic aromatic substitution by $C_{59}N^+$, which was proposed as being formed via thermal homolysis of the dimer, followed by oxidation with O_2.

Very recently, Reuther and Hirsch have found that **35**, **39**, and yet another arylated azafullerene **40**, react with iodine monochloride in a reaction closely analogous to the one found by Taylor and co-workers, yielding tetra-chlorinated compounds **41**, **42**, and **43**, respectively, in 50–60% yields [70,71]. An interesting point is that the five-membered ring containing the nitrogen atom adopts the
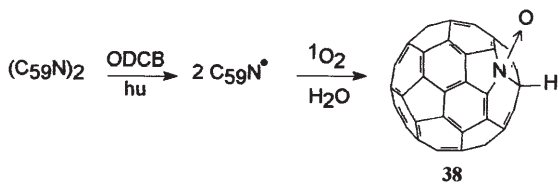
Fig. 20. Formation of N-oxide **38** by photolysis of $(C_{59}N)_2$ in the presence of traces of oxygen
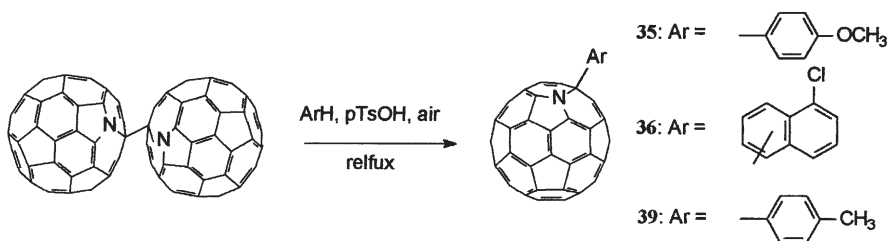
Fig. 21. Azafulleronium arylation products from oxidative thermolysis of $(C_{59}N)_2$
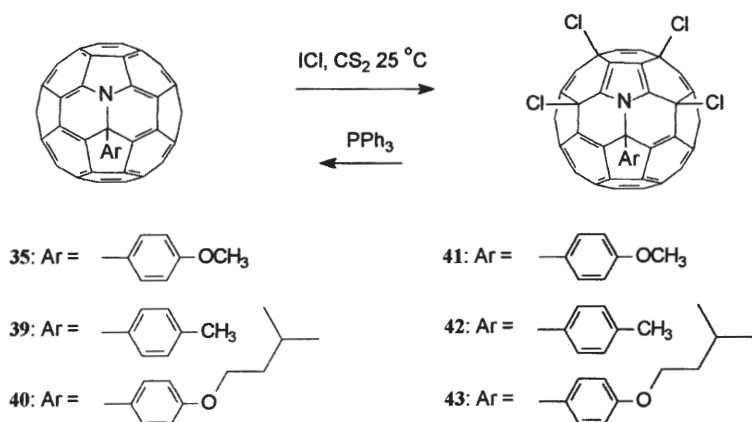
Fig. 22. Formation of tetra-chlorinated compounds **41 – 43** upon the regioselective reaction of 2-Aryl-azafullerenes with ICl. The reverse reaction takes place with excess PPh_3 in ODCB at 25°C

pyrrole configuration (Fig. 22). As a result, the UV-Vis spectrum of these compounds is very similar to that of $C_{60}Cl_6$. AM1 calculations support the pyrrole configuration. The reaction can be reversed upon treatment of the tetrachloro adducts with excess triphenylphosphine in ODCB at room temperature.

The authors envision that compounds like **41**, **42**, and **43** could have potential as precursors for diaza[60]fullerene $C_{58}N_2$ derivatives by way of an azide addition/dechlorination sequence.

This summarizes all presently known chemistry towards aza[60]fullerene compounds, and with that all preparative chemistry related to hetero[60]fullerenes in general.

3
Synthesis of Aza[70]fullerene

The preparation of pure aza[70]fullerene dimers and derivatives is an even more challenging endeavor than the aza[60]fullerene case, because, in principle, there is more than one possible isomer of $C_{69}N$. This complication was recognized from the beginning [8] and has been worked out in detail by Bellavia-Lund and Wudl [20, 72]. C_{70} (D_{5h}) has five different types of carbon atoms (a – e in Fig. 23), therefore there are five isomers of $C_{69}N$, of which the oxidized forms **44 – 48** are shown in Fig. 23. Simultaneous formation of all five corresponding radicals could lead to 15 distinct $C_{69}N$ dimers (if bound by specific[6,6]-α-carbon atoms!).

The IUPAC names for these fulleronium compounds are 2-azonia[70]fullerene (**44**), 1-azonia[70]fullerene (**45**), 5-azonia[70]fullerene (**46**), 7-azonia[70]fullerene (**47**), and 20-azonia[70]fullerene (**48**), respectively (The CAS names and numbering are different again!). The corresponding most stable radicals are expected to be 2-aza[70]fulleren-1-yl (from **44**), 1-aza[70]fulleren-2-yl (from **45**), 5-aza[70]fulleren-6-yl (from **46**), 7-aza[70]fulleren-21-yl (from **47**), and 20-aza[70]fulleren-19(or 21)-yl (from **48**).
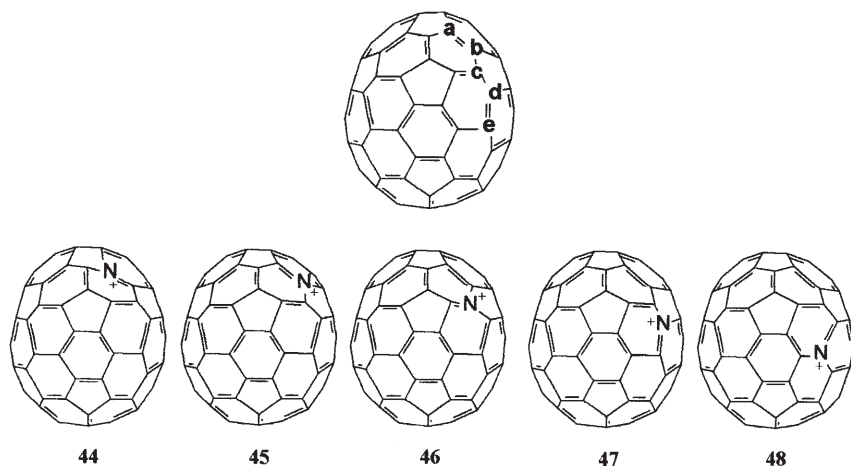
Fig. 23. C$_{70}$ has five different types of carbon atoms **a**-**e** (*above*). Hence, there are five possible isomers of aza[70]fulleronium C$_{69}$N$^+$: **44–48**

Experiments leading to gas-phase observations of C$_{69}$N$^+$ have already been mentioned in Sects. 2.1 and 2.2.2, and will not be reviewed again here [5, 25, 32, 33].

3.1
Synthesis of Aza[70]fullerene Dimers (C$_{69}$N)$_2$ and Aza[70]fullerene Derivatives

The groups of Hirsch and Wudl both applied their own synthetic methods for the preparation of aza[60]fullerene dimer to C$_{70}$. Since both methods start with the preparation of aza[70]fulleroids and bisaza[70]fulleroids as precursors, we will summarize these results first.

The 1,3-dipolar addition of azide could, in theory, give rise to a maximum of six triazoline isomers (Fig. 24), where addition across a [6,6] bond between two different types of carbon atoms in general gives rise to a pair of regio-isomers [73, 74]. C$_{60}$ gains its reactivity as a result of inherent strain in the molecule. In the case of C$_{70}$, having lower symmetry, the strain is not uniform over the entire molecule. Hawkin's studies on the osmylation of C$_{70}$ revealed that most of the strain is localized at the poles rendering the [a–b] bond most reactive [75].

Treatment of C$_{70}$ with an excess of MEMN$_3$ in ODCB at room temperature for 48 h afforded, upon chromatography, one band which contained a mixture of triazoline isomers **49, 50,** and **51** (32% yield, 60% based on consumed C$_{70}$) [72]. When the mixture of the three isomers was heated to 55 °C overnight, only one azirenofullerene (**55**) and one azafulleroid (**56**) were found, next to **49, 50,** and a little C$_{70}$ (Fig. 25). Hence, **51** was converted selectively, which allowed the separation and complete characterization of both **49** and **50** as well as for separately heating of these isomers to yield the *same* azirenofullerene **57** and azafulleroids **58** and **56**, respectively.
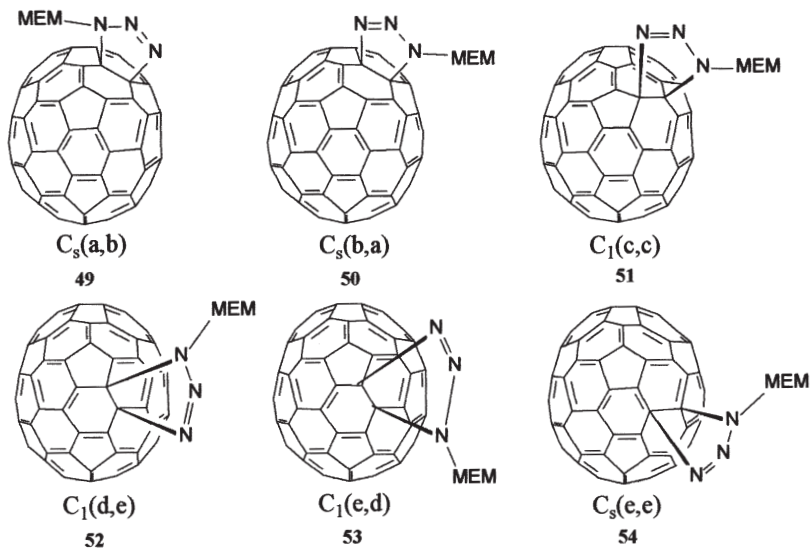
Fig. 24. The six possible triazoline isomers from the reaction of MEM-azide with C_{70}
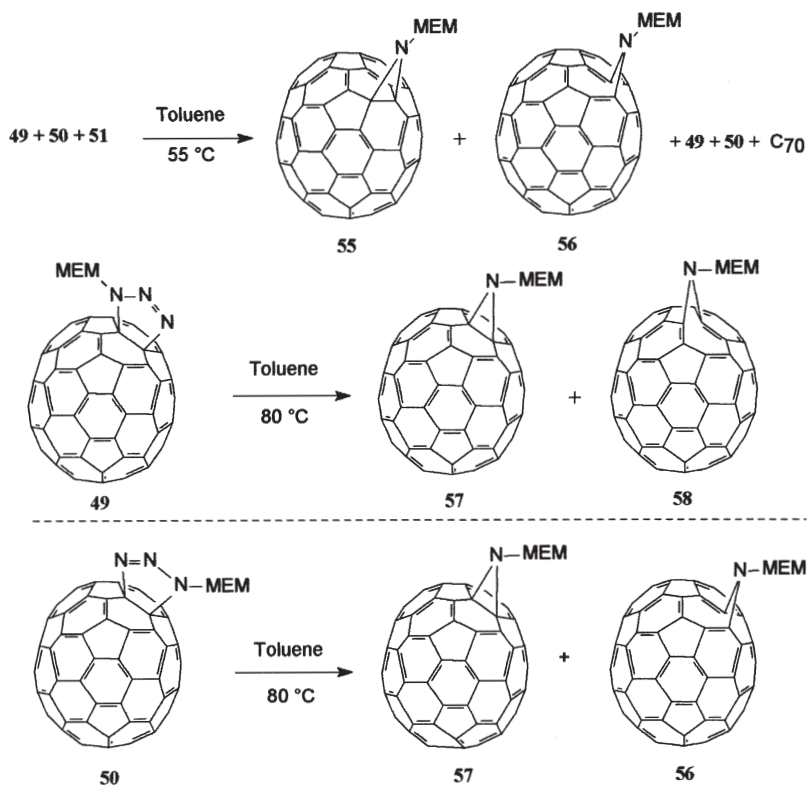
Fig. 25. Selective thermal decomposition of triazolino[70]fullerene **51**, present in a mixture of three isomers **49–51** (*above*). Separate thermal decomposition of triazolino[70]fullerene isomers **49** and **50**, leading to a common product, azireno[70]fullerene **57**, and isomeric aza[70]fulleroids **58** and **56**, respectively (*below*)

Differentiation between **49** and **50** was accomplished by thermolysis of a solution of **50** and **51**, affording the azirenofullerenes **57** and **59** [supposedly the (c,c)-isomer] as well as a common azafulleroid **56** [76]. In conclusion, perseverance afforded two well-characterized aza[70]fulleroids **56** and **58**, that were used for further transformation to aza[70]fullerenes (see below).

Nuber and Hirsch, in the meantime, prepared bisaza[70]fulleroid **60** in a one-step synthesis from C_{70} with MEM azide in ODCB at 120 °C. They observed that while **60** was formed preferentially, another bisadduct isomer [presumably the (1,6);(1,9)-isomer, according to *modern* IUPAC numbering] was formed as a byproduct. When this material was subjected to the reaction conditions that afforded aza[60]fullerenes from **8** (see Sect. 2.2.5), an analogous aza[70]fullerene dimer, most likely with the structure **61**, and the methoxyethoxy derivative **62** could be isolated from the mixture in 10 and 15 % yield, respectively (Fig. 26) [8]. The detection of a resonance at 96.4 ppm in the ^{13}C NMR spectrum of **62** is indicative for the presence of an sp^3-hybridized carbon atom next to nitrogen. Hence, the aza[70]fullerene has a [6,6]-closed structure as shown in Fig. 26.
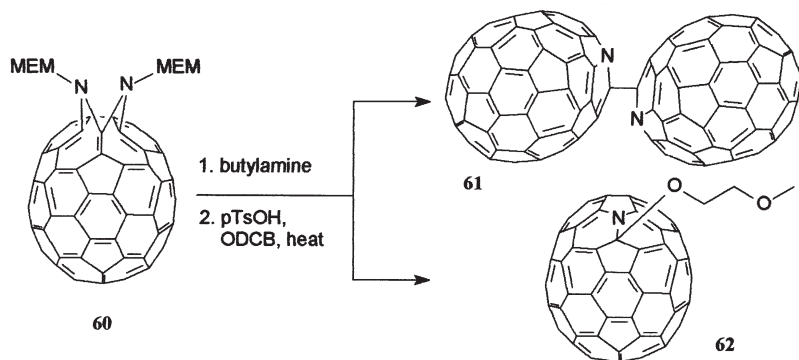
Fig. 26. Aza[70]fullerene compounds obtained from bisazafulleroid **60** by the method of Hirsch et al.

Compound **62** (as its aza[60]fullerene analogue **33**) is unstable and decomposes slowly into insoluble products, which show carbonyl vibrations in IR. A rigorous proof of the structure of **61**, using ^{13}C NMR, was impossible due to the low solubility of the material.

Photooxygenation of C_s symmetric aza[70]fulleroid **56** yielded a single (chiral) oxidized product, ketolactam **63**, in good yield [20]. The structure of **63** was fully characterized by spectroscopic methods (Fig. 27).

The analogous photooxygenation of C_1 symmetric **58** yielded two ketolactam products **64** and **65** (4 : 1). Interestingly, and unlike the UV-Vis spectra of the isomeric aza[70]fulleroids, the UV-Vis spectra of the ketolactam isomers are not superimposible. Isomer **63** is brick red, **64** is orange red, and **65** is brownish green in solution. Similar to the [60] analog, the FAB-MS of all three ketolactams revealed a base peak at m/z = 842, consistent with $C_{69}N^+$.
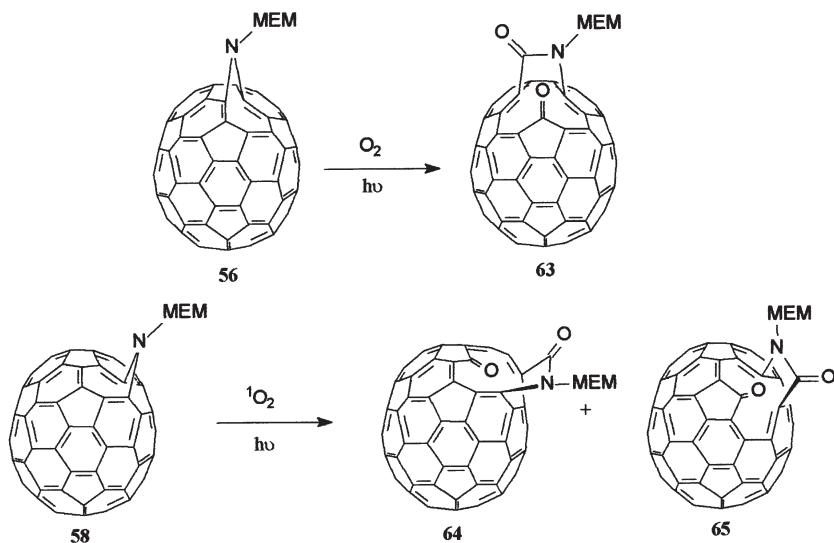
Fig. 27. Self-sensitized photo-oxygenation products from aza[70]fulleroids: symmetric fulleroid **56** yields one ketolactam **63**, while asymmetric azafulleroid **58** yields the two possible ketolactam isomers **64** and **65** (4:1)
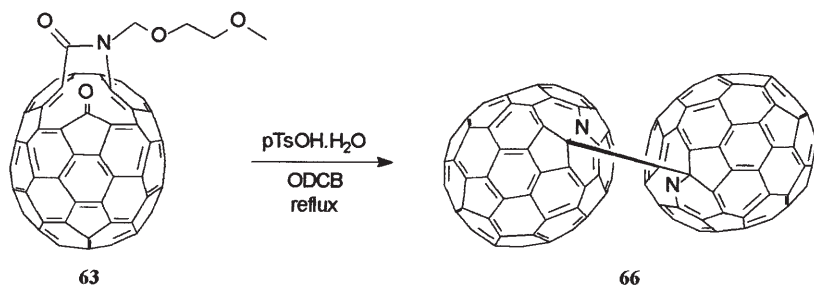
Fig. 28. Formation of the "**a-a**" $(C_{69}N)_2$ isomer **66** from ketolactam **63**

Treatment of ketolactam **63** with an excess of pTsOH in refluxing ODCB produced a single non-polar product, aza[70]fullerene dimer **66** (Fig. 28). Electrospray mass analysis confirmed the elemental composition of **66**, showing a molecular ion at m/z = 1685 and a strong base peak at m/z = 842. The ^{13}C NMR spectrum revealed 29 peaks in the sp^2 region, illustrating the high symmetry of the isomer. Because of the low solubility of the dimer and the tendency for sp^3 carbons adjacent to nitrogen to have long T_1 times, no resonances in the sp^3 region were detected. Dimer **66** is most likely the same dimer as **61**, described by Nuber and Hirsch, but this cannot be fully confirmed by comparison of the data presently reported for the latter [8, 76, 77].

Analysis of the decomposition of the ketolactam isomers **64** and **65** according to the proposed mechanism suggests that each ketolactam isomer should give a different single $(C_{69}N)_2$ isomer. Decomposition of **64** leads to the exchange of carbon "b" for nitrogen (Fig. 23) and decomposition of **65** leads to exchange of carbon "c". Hence, 64 should initially yield azafulleronium **45**, while **65** is expected to give azafulleronium **46** before reduction to its corresponding radical. Interestingly, the symmetries of **45** and **46** are different, allowing for the distinction between the two dimers, **67** and **68**. Ketolactams **64** and **65** were indeed reported to yield the expected aza[70]fullerene dimers, as shown in Fig. 29, but rigorous proof of the structure of 68 is still awaited from ^{13}C NMR analysis [76].

The three isomeric dimers show different retention times on a Cosmosil Buckyprep HPLC column. In the reaction **65** → **68**, a byproduct was formed, which was assigned to hydroaza[70]fullerene **69**.
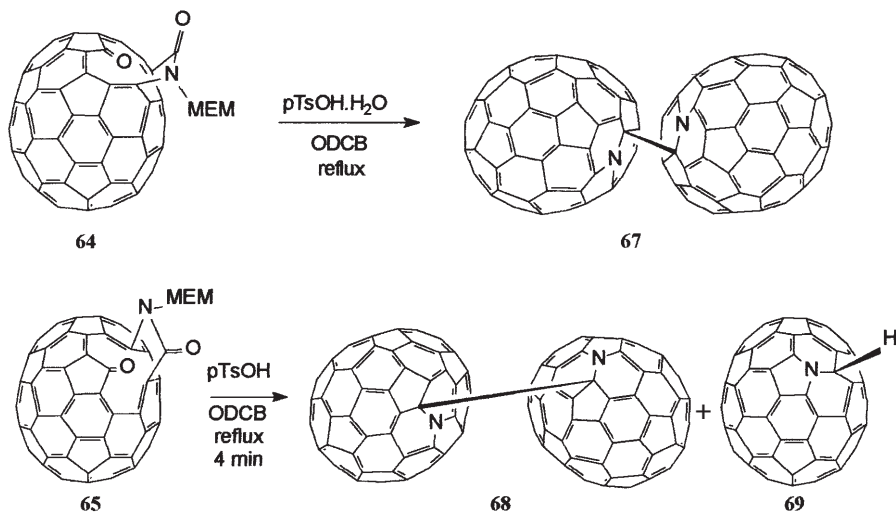
Fig. 29. Formation of the "**b-b**" $(C_{69}N)_2$ isomer **67** from ketolactam **64** (*above*). Formation of the "**c-c**" $(C_{69}N)_2$ isomer **68** and hydroaza[70]fullerene **69** from ketolactam **65** (*below*)

The $C_{69}N$ dimer, in which carbon atom "e" is exchanged with a nitrogen atom, cannot be made following the above procedure, since the nitrogen atom in position "e" is not part of a five-membered ring. As a consequence, the corresponding azafulleroid cannot exist. Formation of an isomer in which carbon "d" is replaced by nitrogen is theoretically possible, using the above mentioned sequence of steps, but not probable. Its formation would require several extra steps, i.e. blocking the more reactive sites, prior to the addition of azide.

In conclusion, three of the five possible homodimers of aza[70]fullerene and two monomeric aza[70]fullerene derivatives have been synthesized up to now.

3.2
The Mixed Dimer $C_{59}N-C_{69}N$

The inter-dimer bond in aza[60]fullerene and aza[70]fullerene dimers is by far the weakest bond in these structures, with an estimated bond energy of ~ 18 kcal mol^{-1}. This has been used in the syntheses of monomeric azafullerene derivatives as described in Sect. 2.3: heating the dimer to 180°C in ODCB in the presence of a radical scavenger yields monomeric products after thermal rupture of the dimer bond. It was found that at 80 °C no net reaction had occurred. In order to gain a better perspective on the nature of the $C_{59}N^{\cdot}$ radical, the equilibrium with a radical source which has a similar binding energy, i.e. $C_{69}N-C_{69}N$ was studied. The investigation of the formation of the heterodimer, $C_{59}N-C_{69}N$, was not only to provide information about the binding energy of the $C_{59}N$ dimer, but also to shed some light on the reactivity of the aza[60]fullerene radical towards its higher analog aza[70]fullerene radical. In addition, this study furnished the first fullerene with commingled properties from both heterofullerenes [78]. Bellavia-Lund and Wudl took two approaches to this study [76].

First, the formation of the dimers from their corresponding ketolactams was investigated. Treatment of a 1:1 molar solution of [60]ketolactam **8** and [70]ketolactam **64** with pTsOH in refluxing ODCB for 5 min resulted in the formation of $(C_{59}N)_2$, $C_{69}HN$, $(C_{69}N)_2$, and the heterodimer $C_{59}N-C_{69}N$ **70**, as determined by HPLC and UV-Vis analysis (Fig. 30). (The aza[70]fullerene moiety is of the type present in dimer **67**).
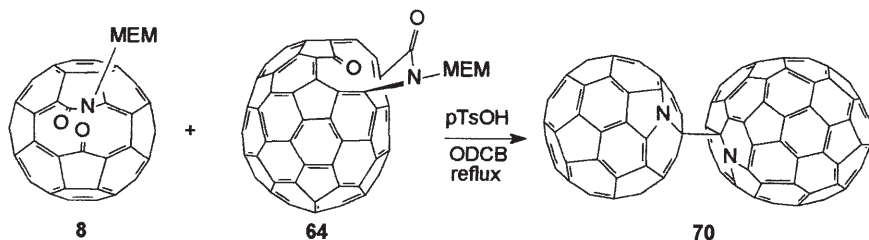
Fig. 30. Method 1 for the preparation of mixed azafullerene dimers: through generation of a mixture of azafullerene radicals from the corresponding ketolactams. The mixed dimer obtained from a mixture of **8** and **64** is proposed to have the structure **70**, the $C_{59}N$-"**b**"-$C_{69}N$ isomer with the dimer bond position on the a-"**a**" carbon atom of the $C_{69}N$ moiety

Second, an equimolar solution of $(C_{59}N)_2$ (**28**) and aza[70]fullerene dimer **66** in ODCB was degassed and refluxed overnight. HPLC analysis of the resulting mixture revealed the presence of $(C_{59}N)_2$, $(C_{69}N)_2$, and the heterodimer $C_{59}N-C_{69}N$ **71** (Fig. 31).

Interestingly, the three dimers were formed in essentially a 1:1:2 ratio of **28**, **66**, and **71**, respectively, suggesting that at the elevated temperature they are in equilibrium with each other, as determined by statistical mixing. The overlapping UV-Vis spectra of $(C_{59}N)_2$, $C_{59}N-C_{69}N$, and $(C_{69}N)_2$, in which the heterodimer spectrum contains equal features of both homo-dimers, are shown in Fig. 32a.
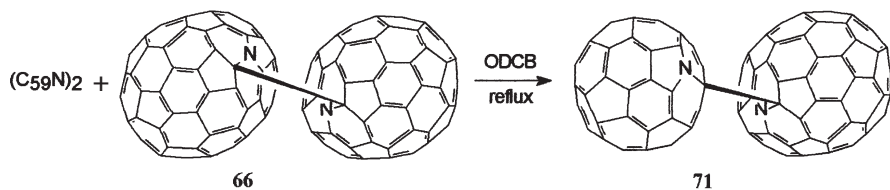
Fig. 31. Method 2 for the preparation of mixed azafullerene dimers: through generation of a mixture of azafullerene radicals from the two corresponding homodimers. The mixed dimer obtained from a mixture of $(C_{59}N)_2$ **28** and "**a-a**" $(C_{69}N)_2$ dimer **66** is proposed to have the structure **71**, the $C_{59}N$-"**a**"-$C_{69}N$ isomer with the dimer bond position on the **a**-"**b**" carbon atom of the $C_{69}N$ moiety

The fact that heterodimer **71** contains a different $C_{69}N$ moiety than **70** was clear from the difference in the HPLC retention times and the the UV-Vis spectra of these compounds. The UV-Vis spectra of **70** and **71** are shown in Fig. 32b.

Heterodimers **70** and **71** are the first examples of what is theoretically an enormous family of possible (hetero)fullerene heterodimers. It is expected that fullerene heterodimers will exhibit interesting electronic (optical, electron accepting) properties. Nuber and Hirsch recognized the fact that they had obtained a mixture of three aza[70]fullerene dimers upon treatment of a mixture of two isomeric bisaza[70]fulleroids. One of their products is most likely a mixed dimer [8]. This is a "hetero"-dimer in a sense that differs from **70** and **71**;
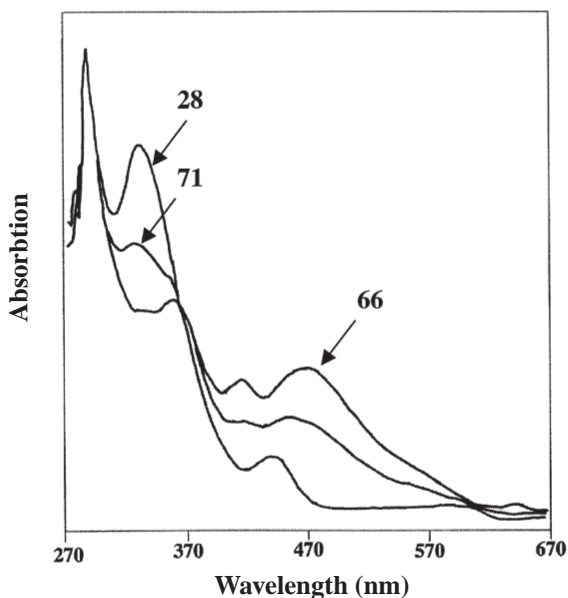
Fig. 32 a. UV-Vis spectrum of mixed $C_{59}N$-$C_{69}N$ azafullerene dimer **71** and of both corresponding homodimers $(C_{59}N)_2$ (**28**) and $(C_{69}N)_2$ isomer **66**
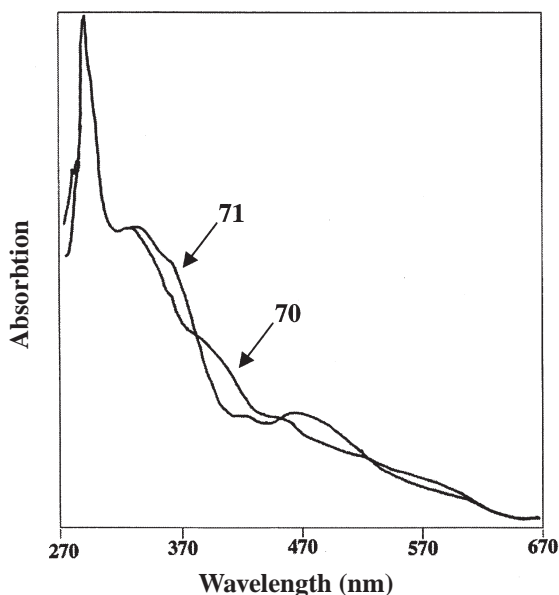
Fig. 32 b. UV-Vis spectra of $C_{59}N$-$C_{69}N$ azafullerene dimers **70** and **71**

however, it could be called a "heteroisomeric" dimer, since the two parts are isomers of each other.

The theoretical possibility of a "donor-acceptor" dimer, i.e. a Lewis acid/base complex $C_{59}N - C_{59}B$, has been mentioned by Wang et al., who calculated on their hypothetical heterodimeric structures $C_{60} - C_{59}N$, $C_{60} - C_{59}B$, and $C_{59}B - C_{59}N$ [79]. These workers, however, only considered structures in which dimer bonds are formed by the heteroatoms, a highly unlikely situation in our opinion. Andreoni et al. also envisaged the possibility of a $C_{59}B - C_{59}N$ dimer, bound in part by charge exchange between donor and acceptor states [80]. We regard a C–C'-bonded heterodimer $C_{59}B - C_{59}N$, with marginal "donor-acceptor" properties, perhaps more feasible.

4
Physicochemical Properties of Azafullerenes

4.1
Theory

Andreoni et al. calculated the impurity states in $C_{59}N$ (and $C_{59}B$) using the Car–Parrinello method and found that the deformation of the fullerene cage is limited to the environment of the "impurity" [80,81]. From the calculated cohesive energy, it was concluded that $C_{59}N$ could exist. Kurita et al. calculated the

molecular structure, binding energies and electronic properties of $C_{59}N$ (also of $C_{59}B$ and $C_{59}S$) using the Harris approximation [82]. Liu et al. used a tight-binding approximation method for calculating the electronic structure [83]. Rosen and Oestling did molecular cluster calculations on $C_{59}N$ within the local density approximation [84]. Chen et al. considered the possible electronic effects of metal complexation of $C_{59}N$ (and $C_{59}B$) [85]. In 1994, the geometrical structure and relative stability of $C_{59}N$ were also calculated using LCAO MO and molecular mechanics methods [86]. Jiang and Xing and co-workers calculated the structural and electronic properties [87], the third-order nonlinear polarizability [88, 89], the linear optical absorption [90], and the second-order nonlinear susceptibility [91] of $C_{59}N$, all using the Su–Schrieffer–Heeger model and the sum-over-states method. Some nonlinear optical properties had been calculated previously by Rustagi et al. using a tight-binding method [92]. It has even been speculated that $C_{59}N$ (and C_{60}) could be formed via a modified isoprene mechanism as an abiotic terpenoid [93]. Piechota and Byszewski reported on the calculation of the electronic structure of $C_{59}N^+$ [94]. These authors also claimed to have prepared samples containing $C_{59}N$, $C_{59}B$, and $C_{58}BN$, which would be at least quite remarkable, if not just plain unlikely (see Sect. 5). The reported ESR spectrum of their material does not fit the data obtained from pure azafullerene (see next section). Andreoni is unique among the theoreticians by anticipating the synthetic preparation of the *real* heterofullerenes $(C_{59}N)_2$ and $C_{59}NH$. While most of the work of her group has been published together with that of the experimentalists (see below), part of it has appeared independently in the literature [95–97].

4.2
The Dimer Bond in Azafullerene Dimers; Generation and Study of Aza[60]fulleren-2-yl and Aza[70]fullerenyl Radicals

Soon after the first preparation of $(C_{59}N)_2$, when the "6,6-closed" structure of the azafullerene moieties was not yet fully established, Andreoni et al. calculated the optimized structure and the energetically favored conformation of the dimer using Car-Parrinello molecular dynamics [98]. It was found that the two balls are linked in a *trans*-configuration by one bond and that the molecule has C_{2h} symmetry. The link is made by the carbon atoms 2 and 2′ (making the hexagon-hexagon fusions together with the nitrogen atoms), with the C^2–N bond length being 1.520 Å (i.e. the "6,6-closed" configuration). The *trans*-conformation minimizes the repulsion of the nitrogen electron clouds. The C–C′ dimer bond was further calculated to be 1.609 Å, i.e. 0.05 Å longer than that between two average sp^3 carbons. The binding energy was calculated to be ~ 18 kcal mol^{-1}, a value in the range of the formation enthalpies of dimers of C_{60} with monoalkyl radical adducts.

Synthetically, the weakness of the dimer bond was used to prepare azafullerene monomer derivatives from the dimer and mixed dimers from two different dimers, as was discussed in Sects. 2.3 and 3.2, respectively. The dimer can be cleaved both thermally and photochemically, yielding two $C_{59}N^{\cdot}$ radicals **1** [69]. $C_{59}N^{\cdot}$ and $C_{69}N^{\cdot}$ radicals are isoelectronic with $C_{60}^{\cdot-}$ and $C_{70}^{\cdot-}$, respectively. Initial

attempts to observe aza[60]fullerenyl radicals by thermal generation yielded erroneous results [4]. Photochemical generation of the radicals appears to be the method of choice. Gruss et al. found that light-induced ESR measurement (LESR) of a solution of $(C_{59}N)_2$ in 1-chloronaphthalene, using 532 nm laser pulses, yielded a spectrum with three equidistant lines of equal intensity, indicative of ^{14}N hyperfine interaction [99]. The hyperfine coupling constant is 3.73 G [100]. The isotropic coupling constant of 10.4 MHz is similar to that of $C_{69}N^{\cdot}$ radical 72 (Fig. 33). The reported values for the g factor of $C_{59}N^{\cdot}$ are 2.0011(1) and 2.0013(2). This value is higher than that of $C_{60}^{\cdot-}$, 1.9991 [101]. The unusually low g value of the C_{60} radical anion was explained in terms of Jahn-Teller distortion that splits the triply degenerate t_{1u} states, thus leading to quenching of angular momentum. Hasharoni et al. give two possible explanations for the positive g shift in the heterofullerene radical: (a) the lower symmetry of $C_{59}N^{\cdot}$ relative to that of $C_{60}^{\cdot-}$ removes the distortion; and (b) the nitrogen heavy atom effect increases spin-orbit coupling in $C_{59}N^{\cdot}$. The symmetry argument is somewhat weakened by the fact that "dissymmetrized" radical anions of C_{60} derivatives (methanofullerenes and fulleroids) show g-values closer to that of C_{60} [102]. Most likely, the major decay channel of the $C_{59}N^{\cdot}$ radicals is redimerization, since a train of more than 10^5 light pulses did not decrease the signal intensity.

LESR measurements on two isomers of $(C_{69}N)_2$, structures 66 and 67, were performed to study the two isomeric $C_{69}N^{\cdot}$ radicals 2-aza[70]fulleren-1-yl 72 and 1-aza[70]fulleren-2-yl 73, respectively [100] (Fig. 33).

The LESR spectrum of dimer 66 also features a reasonably clean three-line spectrum due to ^{14}N hyperfine splitting that has a more positive g-factor, 2.0024(2), and a larger hyperfine coupling, 4.74 G, than those of $C_{59}N^{\cdot}$. This indicates that the unpaired electron and nitrogen wave functions overlap to a greater extent in azafullerenyl 72 and, thus, the electron is more localized in the vicinity of the nitrogen atom.

The LESR spectrum obtained from dimer 67 is more complicated: it shows two ^{14}N hyperfine splittings. The first is identical to that of 72 [g-value 2.0025(2), hfc 4.78 G] and the second stems from a different radical with a g-value of 1.9973(2) and hfc of 0.49 G. This was explained by assuming that the radical 73 actually has two different electron localization sites, where in one of them the unpaired electron is at the pole position as shown for 73 and in the other it is forced to be on the equatorial site because of strain in the molecule [100]. More
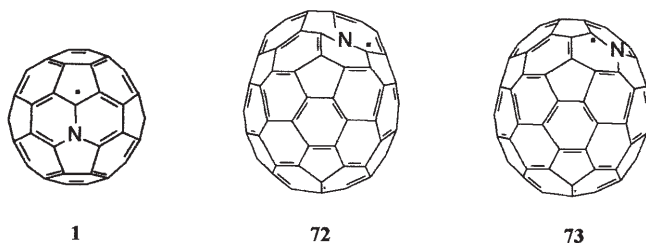
Fig. 33. Azafullerene radical $C_{59}N^{\cdot}$ (1) and $C_{69}N^{\cdot}$ radicals 2-aza[70]fulleren-1-yl (72) and 1-aza[70]fulleren-2-yl (73)

proof of this phenomenon awaits the detection of LESR signals from preferably all five different aza[70]fullerene homodimers!

4.3
Solid-Phase Properties of Azafullerenes

Solid-Phase Structure of $(C_{59}N)_2$. As was the case for the theoretical calculations mentioned above, the driving force for solving the crystal structure of the dimer was the lack of a ^{13}C NMR signal in the expected region of the spectrum. After several attempts to obtain crystals by sublimation, Prassides' group was able to get a crystalline powder whose XRD spectrum could not easily be interpreted, even after use of a high-resolution synchrotron X-ray diffraction source [103]. The problem was that the dominant peaks were those of a pseudo-cubic solid with lattice dimensions in the same order as those of C_{60}! However, the authors noted the importance of a weak, broad peak at ca 3° that was due to a superlattice which indexed as $(1/2,1/2,1/2)_{cubic}$ within the fundamental cubic cell. This demanded an enlargement of the unit cell to orthorhombic. From the dimensions of this unit cell one could now accommodate the dumbbell-shaped $(C_{59}N)_2$. Further examination revealed that the dumbbells were rotated along their long axis relative to the axis of the lattice, forcing further revision of the structure to monoclinic. With additional help from the theoretical calculations by Andreoni mentioned above, the structure was solved.

In attempts to solve the structure via electron diffraction by TEM, it was discovered during preliminary SEM examination, that the morphology of the heterofullerene dimer was that of spheres of spheres. Giant hollow spheres of ca. 2–8 µm in diameter had formed from smaller (50–100 nm) ones in the process of "crystallization" [104, 105]. Later, Bellavia-Lund discovered the same behavior for $(C_{69}N)_2$ [76]. The $(C_{59}N)_2$ spheres were only poorly crystalline, giving only five lines superimposed on a broad amorphous background. The lines could be indexed to a hexagonal unit cell with a = 9.97 Å and c = 16.18 Å.

The Effect of Pressure on Solid $(C_{59}N)_2$. Synchrotron X-ray powder diffraction experiments on crystalline $(C_{59}N)_2$ up to 22.5 GPa were determined [106]. Upon deriving the pressure-volume equation of state, it was discovered that the material observed at atmospheric pressure remained stable up to the highest hydrostatic compression studied. The bulk modulus (E_o) of 21.5 GPa and its pressure derivative, $dE_o/dP = 4.2$, were only slightly lower than the values observed for C_{60} ($E_o = 18.1$ GPa, $dE_o/dP = 5.7$). By analyzing the pressure dependence of the three lattice constants it was possible to determine various bonding interactions in the solid. For example, the absence of strong anisotropy in compressibility was rationalized as resulting from the nonalignment of the dumbbell's long axis with that of the unit cell axis, mentioned above (Sect. 4.3). However, as the pressure increased, the interdimer distances decreased more than the intradimer ones. By the time a pressure of ca. 6.5 GP had been applied, both distances were observed to become of comparable magnitude, forcing the authors to conclude that a novel solid state structure with almost isotropic bonding between spheres had been produced.

Potassium Doping of $(C_{59}N)_2$. As stated before, the electronic structure of aza[60]fullerene is dramatically different from that of C_{60}, such that the equivalent of K_3C_{60} would be $K_2C_{59}N$. Since the intercluster bond of the dimer was calculated to be very weak, and since addition of a number of electrons to the dimer forces breakage of the intercluster bond (see Sect. 4.4), it was not surprising that treatment of the dimer with excess potassium metal at elevated temperature led to the formation of $K_6C_{59}N$ [107]. Interestingly, the bcc symmetry crystal structure of this salt was found to be identical to that of its C_{60} congener [108,109]. There were subtle differences, however; for example, the unit cell parameter was slightly smaller, giving an intercluster distance of 9.80 Å, compared to 9.86 Å for K_6C_{60}. Because the crystal structures of both potassium salts were so similar and because $C_{59}N$, under stringent conditions (heating in a tungsten crucible to more than 500 °C [110] or electron impact with greater than 70 keV [111]), was known to produce C_{60}, the synchrotron X-ray sample was reported to have been re-oxidized in the presence of pTsOH, to produce a mixture of $C_{59}HN$ and $(C_{59}N)_2$. The modified electronic structure of the azafullerene relative to the all-carbon cage required that in $K_6C_{59}N$ there should be an unfilled band resulting from interaction with the open shell $C_{59}N^{-6(\cdot)}$ in the solid state; in contrast to K_6C_{60}, where the hexa-anion is closed shell due to complete filling of the triply degenerate t_{1u} level, leading to a filled band and the expected insulating state. Hence, in contrast to the all-carbon case, the azafullerene salt was found to be a conductor at room temperature. The partial filling of the band was also reflected in the magnetic susceptibility, which indicated Curie–Weiss behavior [112]. In principle, the most interesting salts would be $K_2C_{59}N$ and $K_1C_{59}N$, where the former is isoelectronic with the superconducting phase of C_{60}. Many attempts by the Sussex group have so far failed to produce a stable phase of either stoichiometry of the K and Rb salts [113]. Some evidence for the formation of "$Rb_{0.7}(C_{59}N)_2$" and "$Rb_{1.8}(C_{59}N)_2$" compositions, with the intercalated Rb residing in the octahedral interstices, has been reported more recently [114]. Preliminary DC magnetization measurements showed a Curie-like paramagnetic component, superimposed on a temperature-independent background.

The Electronic Structure of $(C_{59}N)_2$ and Its Alkali-Metal Salts. The electronic properties of $(C_{59}N)_2$ in thin films were studied using photoemission spectroscopy (PES) and electron energy-loss spectroscopy (EELS). The HOMO of $(C_{59}N)_2$ is clearly different from that of C_{60}, with the electron density strongly concentrated on the N atoms and along the axis of the dimer bond [115,116]. In contrast, the LUMO has mainly C-character. When $(C_{59}N)_2$ was compared to the C_{60}^--dimer in dimerized Rb_1C_{60}, a lowering of the HOMO and HOMO-1 states of the heterofullerene dimer was observed. This reduces the splitting of the occupied electronic levels in $(C_{59}N)_2$. The N 1s excitation edge of $(C_{59}N)_2$ resembles that of polypyrrole much more than that of polymethineimine. This is in agreement with a [6,6]-closed structure for the [60]azafullerene moieties. The optical gap of the dimer is ~1.4 eV, slightly smaller than that of C_{60} (1.8 eV) [117,118]. For $(C_{59}N)_2$, a static dielectric constant $\varepsilon_1(0) \sim 5.6$ was obtained from the energy-loss functions. This value is larger than that of C_{60} [$\varepsilon_1(0) \sim 4$], reflecting the smaller energy gap of the heterofullerene dimer.

The electronic structure of $A_xC_{59}N$ salts (A = K, Rb, Cs) was determined analogously using PES and EELS [119]. Intercalation of the three different metals in $(C_{59}N)_2$ results in very similar PES spectra. The spectrum for very low K content resembles that of the solid solution "α phase" in the KC_{60} system. Upon increasing intercalation, an additional feature at ~1.2 eV binding energy appears; further increase in K content results in the appearance of a broad structure at ~0.5 eV. Upon K saturation, this last feature grows in weight and shifts to 0.7 eV, a situation similar to that observed for K_6C_{60}. No density of states at the Fermi level was observed at any time during the intercalation experiment (analogous to the situation observed for Rb_xC_{70} and K_xC_{70}). All of the PES and EELS spectra are very similar to that of K_6C_{60}. This is still somewhat of a puzzle, if one assumes that the saturated heterofullerene salts have the $A_6C_{59}N$ stoichiometry, since one would expect to find some sign of a singly occupied MO, that is to be present in $C_{59}N^{6-}$.

4.4
Electrochemistry of Azafullerenes

The cyclic voltammogram (CV) of $(C_{59}N)_2$ showed three overlapping pairs of reversible one-electron reductions within the solvent window (E_1 = –997 mV, E_2 = –1071 mV, E_3 = –1424 mV, E_4 = –1485 mV, E_5 = –1979 mV, E_6 = –2089 mV; ferrocene/ferrocenium couple, internal standard) [7]. A combination of linear sweep voltammetry and chronoamperometry established that all overlapping waves were two-electron reductions [120]. There was also an irreversible two-electron oxidation with a peak potential at +886 mV, that is 0.2 V more negative (easier to oxidize) than C_{60} [121]. The appearance of closely spaced pairs of waves in the CV was interpreted in terms of two (identical) weakly interacting electrophores, similar to the dianthrylalkanes [122]. After the third double wave, the process is irreversible, this was interpreted as irreversible cleavage of the dimer bond.

The situation with the electrochemistry of $C_{59}HN$ is somewhat more complicated because the redox waves correspond to electrochemically irreversible steps, a result which was interpreted as arising from the weak C–H bond [66]. The first and second reduction waves occur at more negative potentials (E_1 = –1106 mV, E_2 = –1500 mV; ferrocene/ferrocenium couple, internal standard) than the dimer but very slightly more positive potentials than C_{60} and significantly more positive potentials than any dihydro C_{60} derivative, a reflection of the higher electronegativity of nitrogen vs. carbon. The observed irreversible oxidation wave at +823 mV (vs. ferrocene/ferrocenium couple, internal standard; 570 mV easier to oxidize than C_{60}!) may also be a reflection of the weak C–H bond, or may stem from the ionization of one of the lone pair electrons on the nitrogen atom.

5
Miscellaneous Reports on Other Heterofullerenes

In this section we will briefly summarize the literature with respect to reports on heterofullerenes other than aza[60]fullerene and aza[70]fullerenes. Since we

limit ourselves to heterofullerenes in the narrow sense of the definition, non-carbon clusters and most C_mX_n and $C_mX_nY_p$ clusters are neglected here to leave reports on $C_{59}X$, $C_{58}X_2$, $C_{57}X_3$, $C_{58}XY$, and the corresponding heterofullerenes derived from C_{70} to be reviewed.

Theoretically, even this limitation still leaves us with an enormous number of structures: while for every X there is only one $C_{59}X$ isomer, for hetero[60]fullerenes $C_{58}X_2$ there are already 23 possible isomers (of which some are chiral), not to mention the number of isomers of the hetero[60]fullerenes $C_{57}X_3$! In Fig. 34, the 23 isomers of $C_{58}X_2$ are shown, together with the IUPAC numbering [22].

Borafullerenes. Borafullerenes were the first heterofullerenes to be reported by the Smalley group in 1991 and thereafter [123–126]. Laser vaporization of a graphite/boron nitride composite disk and analysis of the formed clusters by the Fourier transform ion cyclotron resonance (FT-ICR) device yielded mass spectra with "clusters" of peaks corresponding to C_n and $C_{n-x}B_x$ (with n even and > 44). From the deconvoluted mass spectra, the approximate amounts of the bora[60]fullerene ions, relative to C_{60}^+ (= 100 %), were calculated to be 95 % $C_{59}B^+$, 109 % $C_{58}B_2^+$, 82 % $C_{57}B_3^+$, 42 % $C_{56}B_4^+$, 18 % $C_{55}B_5^+$, and 9 % $C_{54}B_6^+$. Upon exposure of this set of ions to NH_3 at low pressure, a new series of peaks was observed, corresponding to adducts with formulas $C_{59}B(NH_3)$, $C_{58}B_2(NH_3)_2$, etc, with the same relative abundance. A similar series of bora[70]fullerene ions was observed around the m/z = 840 cluster. The authors speculate that since every boron atom appears to be able to bind an ammonia molecule, the boron atoms are likely to be well separated on the surface of the cage. Further support for the heterofullerene structure of these gas-phase ions was found in the photophysical behavior: exposure to laser pulses yielded spectra showing the typical fullerene "shrink-wrap" peaks from successive loss of C_2 fragments. Later, when a KCl/boron/graphite composite target was laser vaporized in a 1200 °C tube furnace, material was collected that showed peaks in FT-ICR mass spectra that were ascribed to $C_{59}B$, $K@C_{59}B$, and $K@C_{58}B_2$ ions. Laser photolysis of these ions again led to the appearance of shrink-wrap peaks [124].

In 1996, Muhr et al. reported on the macroscopic preparation of borafullerenes using the arc-evaporation method on graphite rods doped with either boron nitride, boron carbide, or boron [127]. An extraction and enrichment scheme was used for the heterofullerene content of the soot, involving pyridine extraction and subsequent treatments of the extract with CS_2 (yielding extract 1) and pyridine (extract 2). Negative mode TOF mass spectroscopy of extract 2 showed clear contributions of $C_{59}B^-$ and $C_{69}B^-$ ions to the m/z = 720 and 840 peak clusters. The use of ^{10}B-enriched material confirmed the MS interpretation. Only monoborafullerene ions were observed. XPS spectra of the extract showed a peak at 188.8 eV that was assigned to boron (1s core level) in borafullerene ($C_{59}B$ mainly). Treatment of the soot with THF supposedly led to extraction of the "borafullerenes", and also to their decomposition. These workers further report that the extracted materials appear to be moisture sensitive, leading to the formation of boron oxide or boric acid. Piechota et al. performed a similar production experiment and extracted the soot in the standard manner with toluene
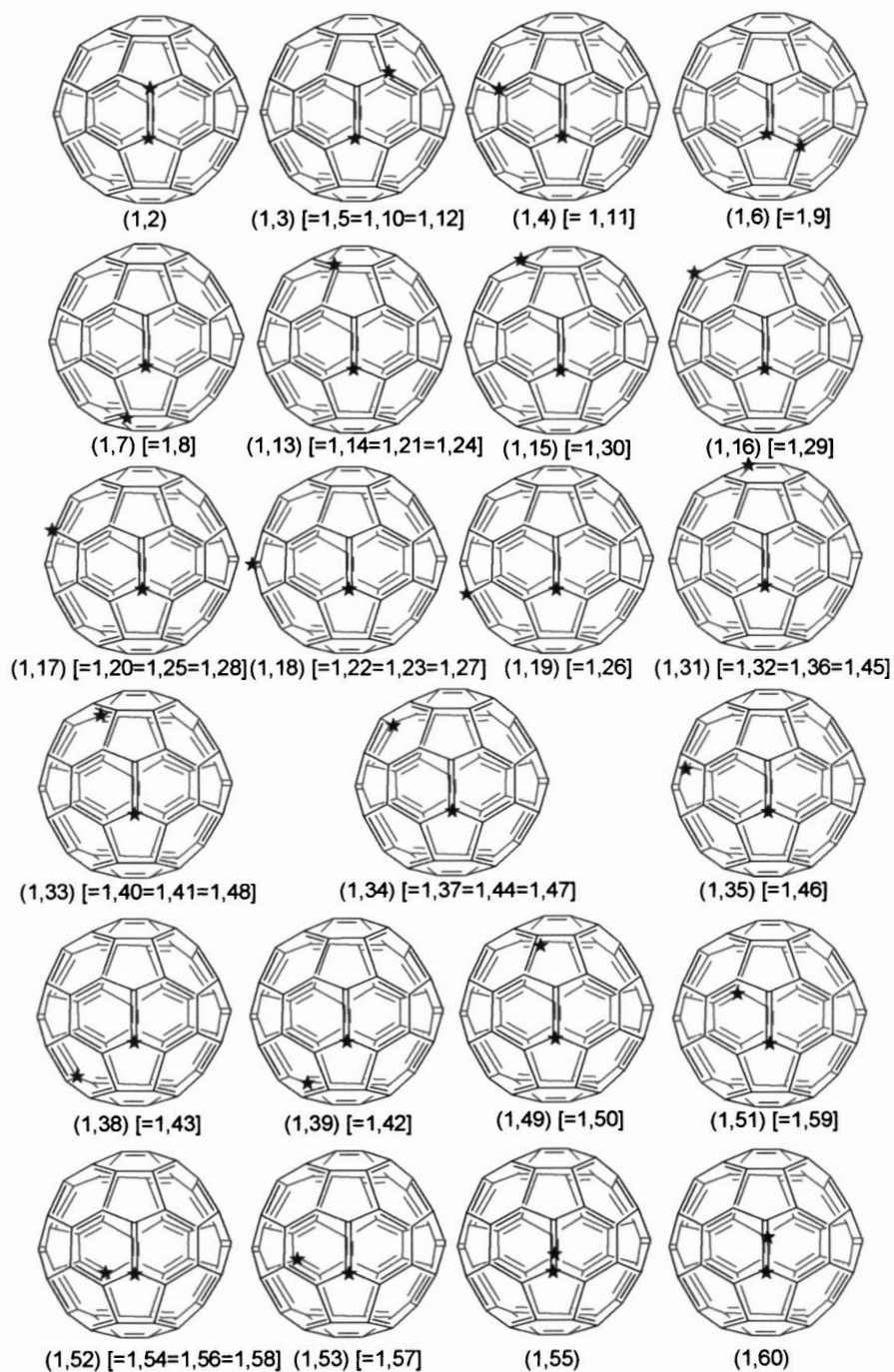
Fig. 34. The 23 possible positions of two heteroatoms in heterofullerenes with formula $C_{58}X_2$ (the positions of the heteroatoms are indicated by *; atom numbering according to IUPAC rules)

and analyzed the extract without any further purification, since too much material seemed to be bound irreversibly to alumina when the latter was used as solid phase for column chromatography. MS analysis of the crude extract did not indicate the presence of "borafullerenes", however [31]. Surprisingly, in none of the two reports was it mentioned that, based on the previously published properties of $C_{59}N$, isolating neutral and unsubstituted monomeric $C_{59}B$ would be very unlikely since it is an open shell molecule. In Chemical Abstracts we found a Chinese report on a gas-phase preparation method that yielded materials showing mass spectra with peaks interpreted as $C_{59}B$, $C_{58}B_2$, and $C_{57}B_3$ ions [128].

Bora[60]fullerene (CAS name for the radical: $2H$-1-bora[5,6]fulleren-C_{60}-I_h-2-yl) has been the subject of various types of calculations. Andreoni et al. used the Car–Parrinello method that proved quite accurate in calculating a number of properties of C_{60}. It was found that the B atom remains threefold coordinated and most of the distortion is localized on the B–C bonds. The length of the "6,6" B–C bond increases by 10 %, while that of the "5,6" B–C bonds increases by 7.5 % relative to C_{60}, according to these calculations. Hence, the bora[60]fullerene cage is expected to be closed. The "impurity state" is strongly localized, as in $C_{59}N$. A radial, inward directed, dipole moment of ~1.4 D was calculated [80]. Kurita et al., in a series of papers, reported calculated molecular structures, binding energies, and electronic properties of $C_{59}B$, $C_{58}B_2$, and several other heterofullerenes using a MO method with Harris approximation [129–131]. They envisioned only a 4.2 and 4.7 % increase, respectively, in the "6,6" C–B and "5,6" C–B bond lengths in $C_{59}B$. The binding energies for C_{60}, $C_{59}B$, and $C_{59}N$ were found to be almost identical. For $C_{58}B_2$, only two isomers were considered, namely one with the two boron atoms as "nearest-neighbor sites in a pentagon" (i.e. 1,6-bibora[60]fullerene) and one with the boron atoms on opposite sites (i.e. 1,60-dibora[60]fullerene), the latter appearing to have very much the same properties as $C_{59}B$. In the 1,6 isomer, a heavy distortion was found, already evident from the B–B bond length, calculated to be 1.65 Å. However, according to the calculation, this did not significantly affect the binding energy. $C_{59}B$ (and sometimes $C_{58}B_2$) was also considered and compared to $C_{59}N$ with respect to electronic structure, (nonlinear) optical properties, and in metal complexes in several other theoretical studies, already mentioned in Sect. 4.1 [31, 79, 83, 85, 87–89, 92]. 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 using the Su–Schrieffer–Heeger (SSH) model and found that the results were not always consistent with those obtained by the SCF-MO method [132]. Xu et al. used the SSH model to compute the third-order polarizability of 1,6- and 1,60-$C_{58}B_2$ and compared the calculated γ-values with those of the N-analogs and $C_{59}X$. 1,60-$C_{58}B_2$ has the largest γ-values [133,134]. Chen and Lin considered all 23 isomers of $C_{58}B_2$ in their calculations on a PC [135].

Xia et al. found in their calculations that in $C_{58}B_2$ isomers in which the two boron atoms were further apart on the surface of the ball, the open shell diradical form becomes more favorable than the closed shell structure [136].

Miyamoto et al. calculated the electronic structure of solid $C_{59}B$ as a metallic fullerene material consisting of single molecules [137]. Taking the experimen-

tally observed consistent dimerizing tendency of the known fullerene mono-radicals and monoradical ions into account, this seems to be a highly hypothe-tical situation!

Zou et al. calculated the electronic states of C_nB, with n = 59, 179, 239, 419, 539, 719, 779, finding a localized distortion and a "mid-gap state", appearing in the original gap of the pristine fullerenes [138].

In our opinion, by far 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 the dimer, a salt or a derivative), most likely starting from C_{60}, as was done for aza[60]fullerene.

Azafullerenes with More Than One Nitrogen Atom. Up to now, no diaza[60]ful-lerene has been prepared, most likely not even in the gas phase. Since all $C_{58}N_2$ isomers, especially the ones with two adjacent nitrogen atoms, should, in princi-ple, be able to relax to closed shell structures, monomeric pristine $C_{58}N_2$ seems a feasible target. In 1991, it was reported that mass spectroscopy of the toluene extract of soot, obtained by contact-arc vaporization of graphite in the presence of N_2, showed peaks that were tentatively attributed to formulas such as $C_{70}N_2$, $C_{59}N_6$, $C_{59}N_4$, and $C_{59}N_2$. Since no further experimental evidence was given for such structures, this interpretation is pure speculation [23,24]. Glenis et al. reported on a similar experiment, but using pyrrole gas as the source of nitro-gen atoms. Elemental analysis of the soot showed almost 1% N-content. The toluene extract was chromatographed on alumina, resulting in a "yellow-oran-ge", a "yellow-green", and a "dark orange" band, subsequently. The material from the second band was analyzed by mass spectroscopy, UV-Vis and fluorescence spectroscopy [26]. Mass spectroscopy revealed peaks at almost every even m/z value between 640 and 790. Especially between 720 and 790 amu, only even mas-ses were observed. The authors conclude from this spectrum that, next to $C_{59}N$, only molecules with even-numbered ratios of C to N atoms are formed (like $C_{58}N_2$, $C_{56}N_4$, etc., etc.). We, however, consider it impossible that *any* heteroful-lerene would show even mass peaks *only*, unless pure ^{12}C-graphite was used in the experiment! Later, the extract was submitted to HPLC, using a GPC column, to yield ten separated fractions, that were regrettably not submitted to mass spectroscopy but analyzed by absorption and fluorescence spectroscopy only [27].

Diaza[60]fullerenes have been the subject of several theoretical considera-tions and calculations, however – Karfunkel et al. considered the ten possible isomers of $C_{58}N_2$, with the nitrogen atoms separated by maximally three carbon atoms [139]. Some thermochemical and electronic properties of the closed shell structures were calculated using various methods. It was found that 1,7-dia-za[60]fullerene, with the two nitrogen atoms in a 1,3-fashion in the same penta-gon, appears to be of remarkable stability (15 kcal mol^{-1} more stable than the next most stable isomer, according to an AM1 calculation). The geometry of all isomers appears to be very much like that of C_{60}, but the predicted vibrational spectra and the HOMO and LUMO values differ significantly. These workers also considered some "truncated" heterofullerenes, based on the C_{60} skeleton. Some of the structures, with formula $C_{54}N_4$, show some resemblance to porphyrins. In

several computational studies, efforts were made to compare various properties of $C_{58}N_2$ with those of $C_{58}B_2$ (see above) [79, 83, 92] (23 isomers), [130–134, 136]. The Hirsch group has mentioned an idea for a synthetic route towards $C_{58}N_2$, starting from C_{60} [70]. The remarkable regioselectivity in the bisaddition of azides to C_{60} has prevented a simple "bis-version" of the synthetic routes, described for $C_{59}N$ and $C_{69}N$ compounds. Addition of bisazides in which the two azide moieties are tethered by a (removable) spacer might also be considered as a first step in a route towards certain isomers of $C_{58}N_2$. The synthesis of $C_{58}N_2$ is possibly complicated if the formation of the two N-sites is not simultaneous: in that case, an open shell intermediate, as found in the synthesis of $(C_{59}N)_2$, might give rise to an undesired reaction path.

Bühl has proposed that hexaaza[60]fullerene, $C_{54}N_6$, could be an aromatic molecule, being isoelectronic with C_{60}^{6-} [140]. An ab initio study of six highly symmetrical $C_{54}N_6$ isomers indicated that two isomers with D_{3d} symmetry may have large endohedral chemical shieldings, much more than the other isomers with D_3 symmetry.

Azabora[60]fullerene. Of the many possible isomers of $C_{58}BN$, most (computational) attention has been given to the 1,2-, 1,6- and the 1,60-isomer. There are no reports of formation of $C_{58}BN$ in gas-phase heterofullerene preparation experiments. This may be due to the fact that $C_{58}BN$ has a mass of 720/721 amu ($\sim 1:4$), apart from ^{13}C contributions, which makes it very hard to be detected unambiguously in the MS of mixtures that also contain C_{60}. Piechota et al. do indeed mention a higher 721/720 ratio in their possibly heterofullerene-containing product than in the product from a carbon-only experiment, but found no other proof for $C_{58}BN$ [31]. These workers calculate a HOMO-LUMO gap of 2.2 and 1.8 eV for the 1,2- and 1,6 isomer, respectively, using the so-called Dgauss program, while Liu et al. found similar gaps of ~ 2 eV for a non-specified "nearest neighbor" BN structure and the 1,60-isomer, using a tight-binding approximation quantum mechanical method [83]. Rustagi et al., without much scientific ado, envision interesting nonlinear optical effects in 1,60-azabora[60]fullerene [92]. Xia et al. found in their calculations that all isomers of $C_{58}BN$ are preferably in the closed shell configuration (in contrast to $C_{58}B_2$). In the 1,2-isomer, B and N have estimated charge densities of $+0.0523$ and -0.1450, respectively, while in the (presumably) 1,3-isomer and the 1,60-isomer both heteroatoms have negative charge density [136]. Others calculated bond lengths and HOMO-LUMO gaps of the 1,6- and the 1,60-isomer and found a B–N bond of 1.61 Å in the 1,6-isomer and a factor 8.6 difference in the energy gap between the two isomers [131]! Esfarjani et al. performed computations on the 1,2- and 1,60-isomers of $C_{58}BN$ in the solid state [141–143]. These workers discuss the various possibilities for the nature of the B–N bond in the 1,2-isomer, the limits being "covalent" (ylide $> B^- = N^+ <$), "ionic" ("open" structure with $> B^+$ and $N^- <$), and "no charge transfer" (with a single $> B–N < \sigma$-bond). Calculations on the fcc solid-state electronic structure indicated the presence of a single B–N bond with slight charge transfer from N to B. However, since the B–N bond length was fixed *a priori* at 1.40 Å, this computational result, reasonable as it may seem, may still be of limited value, as was recognized by the authors [142].

[60]Heterofullerenes with Heteroatoms Other Than N, B. After unsuccessful attempts by the Smalley group, Clemmer et al. reported the formation of C_nNb^+ (n = 28–50) clusters upon pulsed laser vaporization of a mixed NbC/graphite composite rod [144]. From the difference between even and odd n C_nNb^+ ions in their chemical reactivity towards O_2 and N_2, evidence was found for the odd-C numbered cages to be (quasi)heterofullerenes instead of endohedral complexes. No clusters with a C/Nb ratio of ~ 60 : 1 were detected, however.

In our opinion, heterofullerenes with divalent heteroatoms, like O and S, are potentially interesting compounds because they could possibly exist as neutral ylide structures with $>{}^-C{-}O^+<$ and $>{}^-C{-}S^+<$ bonds, respectively. Alternative structures for $C_{59}O$ and $C_{59}S$ are less ionic truncated quasi-fullerene structures bearing a carbonyl or thiocarbonyl moiety, as shown in Fig. 35.

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, a HOMO-LUMO gap of 0.63 eV, and an atomic charge of + 0.5 on the S atom [129]. Later, Glenis et al. tried to prepare thiafullerenes analogously to their previously reported method of contact-arc vaporization of graphite, but in the presence of thiophene or 3-methylthiophene instead of pyrrole [145]. We find it striking that column chromatography of the soot extract (containing 2% S by elemental analysis) yielded three bands with the same colors as in the case of their attempted azafullerene preparation (see above). Many peaks with tempting amu numbers were observed in mass spectroscopy, but there was no proof for any heterofullerene structure.

Of the oxygen-containing heterofullerene family, oxa[60]fullerene, $C_{59}O$, has only been mentioned as possibly present in the form of $C_{59}O^+$ ions in gas-phase experiments by Christian et al. [25,146]. At collision energies between 15 and 75 eV, O^+ ions and gas-phase C_{60} yielded peaks in MS that were interpreted as odd-sized "fullerene oxide" ions of the form $C_{59-2n}O^+$ (n = 0–4), decomposing primarily by C_2 loss, retaining the O atom. The possibility of the structures being $CO@C_{58-2n}$ was slightly favored by the authors, however. Karfunkel et al. reported on a philosophy about truncated heterofullerenes containing O atoms or N and O atoms in such a way that crown-ether-like structures would be present as part of the cage [139].

Purely hypothetical are the mono- and the 23 diphospha[60]fullerene isomers, $C_{59}P$ and $C_{58}P_2$, considered using a PC-based calculation by Chen and Lin [135].
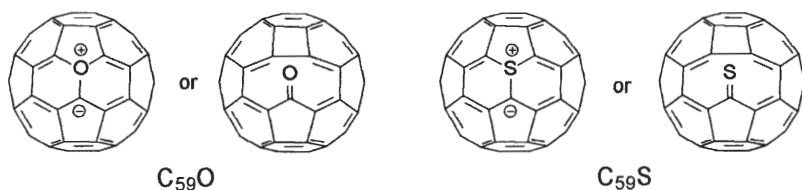

$C_{59}O$ or $C_{59}S$

Fig. 35. Possible structures for $C_{59}O$ and $C_{59}S$: ylide heterofullerenes or open-cage (thio)carbonyl quasi-fullerenes

Lastly, we found two reports on silafullerenes [147,148]. In 1993, Jelski et al. computed the structures and relative stability of $C_{59}Si$, 1,2-, 1,6,- and 1,60-$C_{58}Si_2$, and a $C_{48}Si_{12}$ isomer by a AM1 method. These structures were predicted to be stable and to show a steady decrease of the band gaps with the increasing number of Si atoms. These workers did not hesitate to mention the possibility of a polysiloxane type 1,60-disila[60]fullerene polymer. Kimura et al. analyzed the products from pulsed-laser vaporization of silicon-carbon composite ("bulk siliconized carbon") rods by time-of-flight MS. Only small peaks were observed that would match the masses of "SiC_n^+-clusters" ($61 \geq n \geq 56$). Since no further evidence was given, silafullerenes are still best considered as hypothetical structures.

Considering the fact that, at best, scarce proof was given for the existence of only some of the heterofullerenes mentioned in Sect. 5, there are already a surprising number of patents covering, among other things, the preparation and/or uses of such materials [34,149–153]!

6
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