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Amination of [60]Fullerene by Ammonia and by Primary and Secondary Aliphatic Amines—Preparation of Amino[60]fullerene Peroxides

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In memory of Roger Taylor

Abstract: Ammonia and aliphatic amines react readily in the oxygen-rich regions of the C_s symmetric fullerene peroxides $C_{60}(O)(OOtBu)_4$ (**1**) and $C_{60}(OH)(Br)(OOtBu)_4$ (**2c**). Michael addition-type hydroamination of the 1,4-diene moiety on the central skew-pentagon was observed when **1** was treated with ammonia or with nonbulky primary amines, while sterically demanding primary amines opened the epoxy moiety to form vicinal aminohydroxy fullerene compounds with the amino group on the central pentagon. In **2c** the bromo group was replaced under similar conditions by ammonia and primary amines. Cyclic secondary amines showed different reaction patterns, forming hydrogenation products or aminoketal-fullerenes when treated with **1** and **2c**, respectively. Single-electron transfer (SET) is the key step in all the proposed mechanisms. The compounds were characterized by their spectroscopic data, and in addition, three single-crystal X-ray structures were obtained.

Keywords: amines · fullerenes · peroxides · radicals · single-electron transfer

Introduction

Amination of fullerene, one of the first reactions in fullerene chemistry to be investigated, has been studied intensively.[1] Back in 1992, Wudl and co-workers reported that primary and secondary aliphatic amines react readily with C_{60} to give multiple adducts,[2] which usually contain some oxygen if molecular oxygen is present in the reaction medium. Oxygen incorporated in these multiple adducts could be in the form of epoxy, hydroxy, or other groups, but it was not possible to determine the exact structures of such complex mixtures. Later, several groups reported isomerically pure adducts of secondary amines: piperidine adds to C_{60} to form well characterized mono- and bisadducts,[3] Hirsch et al. found that secondary amines present in excess react with C_{60} to form 1,4-addition adducts such as tetrakismorpholino[60]fullerene epoxide,[4a] and good yields of similar compounds were reported by Nakamura et al.[4b,c] Troshin et al. prepared highly water-soluble fullerene derivatives by treating the tetraaminofullerene derivative C_{60}(*N*-(2-pyridyl)piperazine)$_4$O with acids.[4d] There are no fullerenic C–H bonds in these fullerene amino-adducts, although hydroaminofullerene adducts have been observed in reactions between C_{60} and azacrown ethers.[5] Tertiary amines can also react with fullerenes to form pyrrolidinofullerenes.[6] So far there is still no well characterized fullerene adduct containing a primary amine moiety, even though primary amines react readily with C_{60}. Remarkably, though, boiling of a polyamine solution of C_{60} affords the C_{3v} symmetric $C_{60}H_{18}$ in high yield.[7]

We have previously reported the fullerene mixed peroxide **1** (Scheme 1), which exhibits versatile reactivity toward various Lewis acids to form compounds such as **2**.[8] In an effort to prepare fullerene derivatives containing both oxygen and nitrogen addends, we investigated the reactions between

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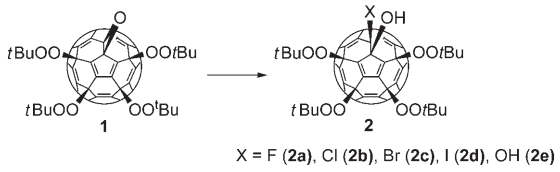
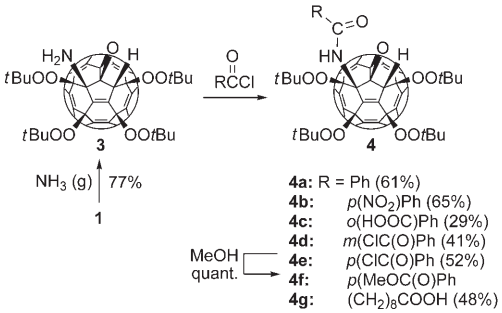
amines and fullerene mixed peroxides and here we report the preparation of fullerene adducts with ammonia and with primary and secondary amines.



Scheme 1. Epoxide opening in **1** by a Lewis acid.

Results and Discussion

Reactions between 1 and amines: The interaction between ammonia and C_{60} is very weak: liquid ammonia has been used to prepare alkali metal fullerides without addition of ammonia to C_{60}.[9] In contrast with its weak interaction with pristine C_{60}, however, ammonia gas reacted readily with the fullerene mixed peroxide **1** under atmosphere pressure (Scheme 2) in a reaction performed in darkness to avoid light-induced fragmentation of the peroxy moieties. Even though an excess of NH_3 was present, only the monoaminated product **3** was obtained as a major product. Heating of the solution slows down the reaction as a result of lower concentrations of NH_3 at higher temperatures.

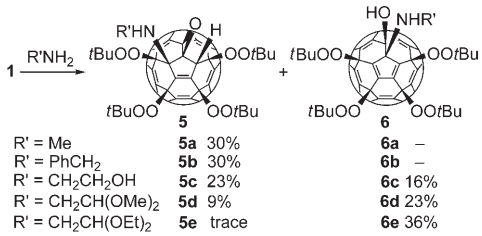


Scheme 2. Reaction between **1** and ammonia.

The more readily available aqueous ammonia would also react with **1**, but the reaction was much slower. Various solvents such as CCl_4 and CH_2Cl_2 may be used as the reaction medium; the nonpolar solvent CCl_4 was chosen because the reaction solution could be directly purified by chromatography without concentration on a rotary evaporator, thus avoiding a lower yield caused by the formation of uncharacterizable products.

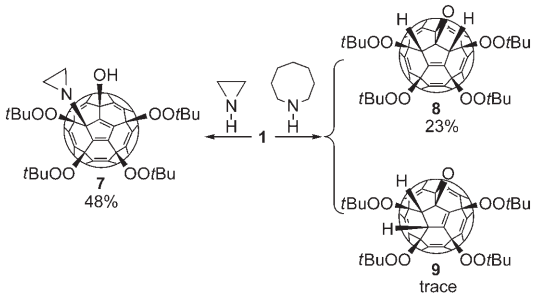
The amino group in **3** appears to be the most reactive site toward electrophiles, despite its unfavorable steric hindrance. Amide derivatives **4a–g** were obtained in moderate yields when **3** was treated with acyl chlorides such as benzoyl chloride and sebacoyl chloride. Compound **4g** has a carboxylic group relatively far away from the C_{60} cage and may be useful for further functionalization as we have done for the sebacoyl pyrrolidinofullerene derivative.[10]

Primary amines reacted with **1** slightly differently: while methylamine and benzylamine gave the analogous **5a** and **5b**, respectively, as the only isolable monoaddition products, 2,2-diethoxyethylamine gave mainly the C_s symmetric **6e**, while the other two medium-sized amines gave a mixture of isomers **5c**,**d** and **6c**,**d** (Scheme 3). *n*-Butylamine also yielded two isomeric products, but these were quite difficult to separate. The yields of compounds **5** were much lower than those obtained in the ammonia reaction as a result of poor selectivity. Benzylamine is more reactive than NH_3 and readily affords multiple addition products containing two or three benzylamino groups.[11]



Scheme 3. Reactions between **1** and aliphatic primary amines.

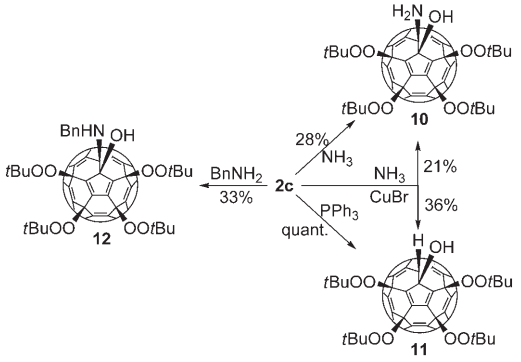
Secondary amines showed different reactivity toward **1**. Aziridine opens the epoxy moiety in **1** to give compound **7**, containing a hydroxy group (Scheme 4), while with bulkier cyclic amines the reaction could not be stopped at the single addition step, adducts containing two amino addends instead being obtained in the cases of pyrrolidine and piperidine, with the conversion of one *t*BuOO group into a hydroxy group in the process.[11] The even bulkier cycloheptylamine did not attach onto the fullerene cage, but acted as a hydrogenation agent to give two isomeric hydrogenated derivatives **8** and **9**.



Scheme 4. Reactions between **1** and cyclic secondary amines (the structure of **7** is tentative; see spectroscopic data and structure assignments section for discussion).

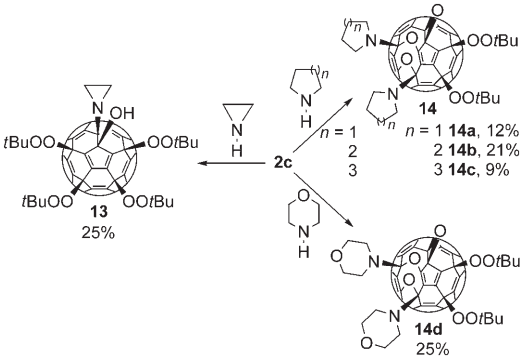
Reactions between 2c and amines: Compound **2c** contains a vicinal bromohydroxy moiety corresponding to the epoxy location of **1**, and the presence of the hydroxy group on the central pentagon completely blocks amino addition at the cyclopentadiene unit as observed for **1**. The bromo group in **2c** was eliminated in all the reactions with amines, with am-

monia and benzylamine replacing the bromine to give the C_s symmetric compounds **10** and **12**, respectively (Scheme 5). In an effort to increase the efficiency of the ammonia reaction, some CuBr was added. This reaction then afforded the hydrohydroxy derivative **11** together with **10**. Quantitative formation of **11** was observed when **2c** was treated with an excess of triphenylphosphine.



Scheme 5. Reactions between **2c** and ammonia and aliphatic primary amines.

Compound **2c** also reacted readily with secondary amines to give compounds **13** and **14** (Scheme 6). In this case aziridine showed the same reaction pattern as ammonia and benzylamine, the bromine being replaced to form the C_s symmetric product **13**, while the use of bulkier cyclic amines resulted in the conversion of two *tert*-butylperoxy groups into two aminoketal moieties to form compounds **14**. In addition, the net mass change indicated that one HBr molecule was lost from the vicinal bromohydroxy moiety to form the epoxy moiety.



Scheme 6. Reactions between **2c** and cyclic secondary amines.

X-ray structures of compounds 4a, 6d, and 14a: To establish the exact locations of the addends in the above compounds, various methods to grow suitable single crystals were tested. Slow evaporation of mixtures of solvents appeared to be efficient, with single crystals of compounds **4a** and **6d** being obtained by evaporation from $CHCl_3/CS_2/CH_3CN$ and CS_2/EtOH at 5 °C, respectively, while storage of an NMR sample of **14a** in $CDCl_3$ in the refrigerator at 0 °C resulted in rectangular crystals. Compounds **4a**[12] and **6d**[13] (Figure 1) showed some disorder for the solvent molecules and *t*BuOO groups (one for **6d** and two for **4a**). One of the two pyrrolidine rings in **14a**[14] is also slightly disordered, but these disorder problems do not affect the regiochemistry assignment on the fullerene cage.

The bonding features shown by the X-ray analyses are consistent with the structures depicted in the reaction schemes. The unique double bond in the central pentagon of **4a** is the shortest double bond in all the three crystal structures (C54–C55 1.325 Å), while the two double bonds in the central pentagon of **6d** are slightly longer (C56–C60 1.335 Å and C58–C59 1.348 Å), due to the cyclopentadienyl-type conjugation, but still shorter than the other fullerene double bonds in the cage. Except for the one in the epoxide moiety, single bonds between two sp^3 fullerene carbons are longer than a normal fullerene single bond, the longest single bond being the one in **4a** (C59–C60 1.601 Å) with adjacent amino and *t*BuOO groups. The hydroxy group in **6d** forms a hydrogen bond with the adjacent nitrogen, while the hydrogen atoms in the amino groups of both **4a** and **6d** each form a hydrogen bond with the neighboring *t*BuOO group. In all the structures we have so far obtained, the oxygen atom forming the hydrogen bond is the one bonding the *tert*-butyl group rather than the fullerene cage.[8]

The unsaturated carbons in the central pentagon show less deviation from planar sp^2 hybridization than the pyramidalized sp^2 fullerene carbons (Figure 2): the torsion angles of the sp^2 orbitals in **4a** are around 175° for the two carbons forming the double bond on the central pentagon, while in the aminoketal derivative **14a** the sp^2 orbitals of the central pentagon carbon connecting to the aminoketal moiety at the 6,6-junction are essentially planar, with torsion angles around 179°. The torsion angles of the sp^2 orbitals in **6d** range from 157 to 162° for the four carbons on the central pentagon, which is still much larger than those of the other sp^2 fullerene carbons (around 140°). These structural characteristics can partially explain the unique ^{13}C NMR chemical shifts observed for the carbons on the central pentagon as discussed below.

Spectroscopic data and structure assignments: In the light of the above X-ray crystal analysis results, the structures of other compounds were deduced from their spectroscopic data. The presence of amino groups provides ideal protonation sites for positive ESI-MS, so molecular ion signals can be easily detected and usually appear as the most intensive signal in aminated fullerene peroxides. For those fullerene peroxides not containing an amino group, molecular ion signals are detected as $[M+NH_4]^+$, which is common in ESI-MS spectra. Thanks to the presence of multiple *tert*-butyl groups these fullerene derivatives are very soluble in common organic solvents—usually more than 30 mg mL^{-1} in $CHCl_3$—which greatly facilitates NMR measurements, especially the ^{13}C NMR spectra. From their MS and NMR spec-

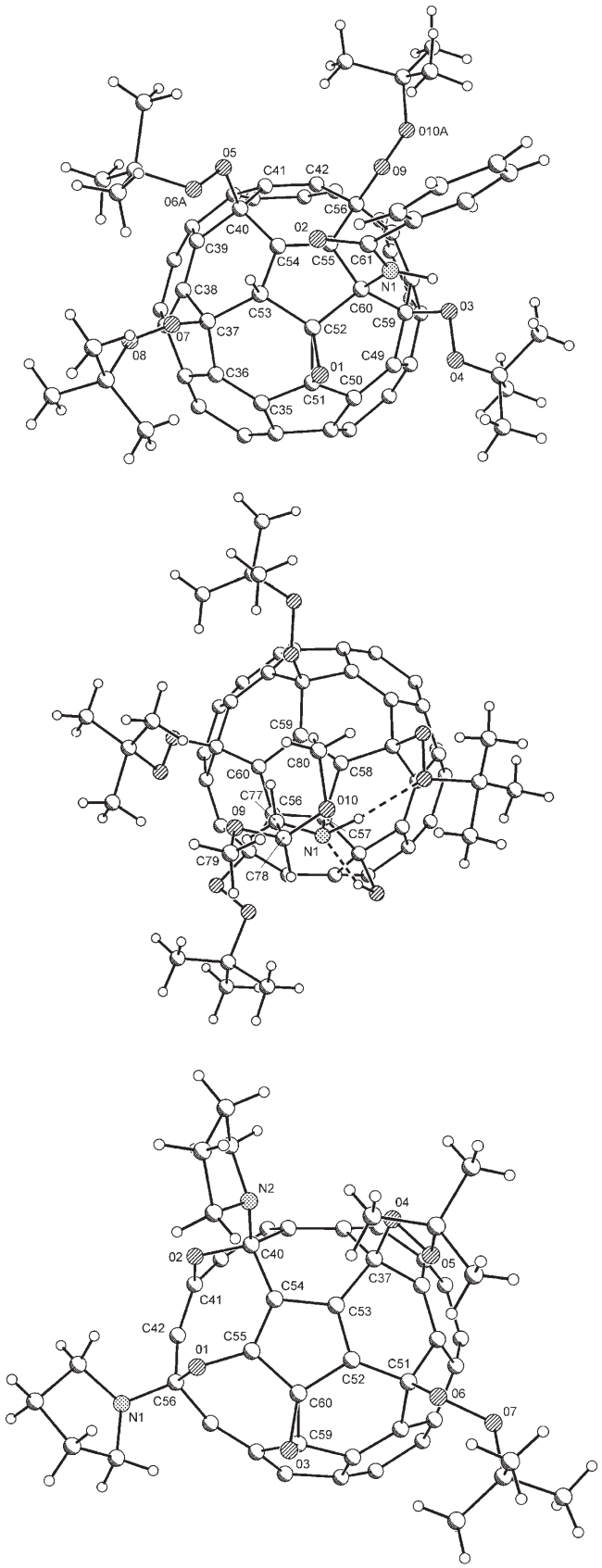


Figure 1. Single-crystal molecular structures of **4a** (top), **6d** (middle), and **14a** (bottom); some atoms of the C_{60} cage have been omitted for clarity.

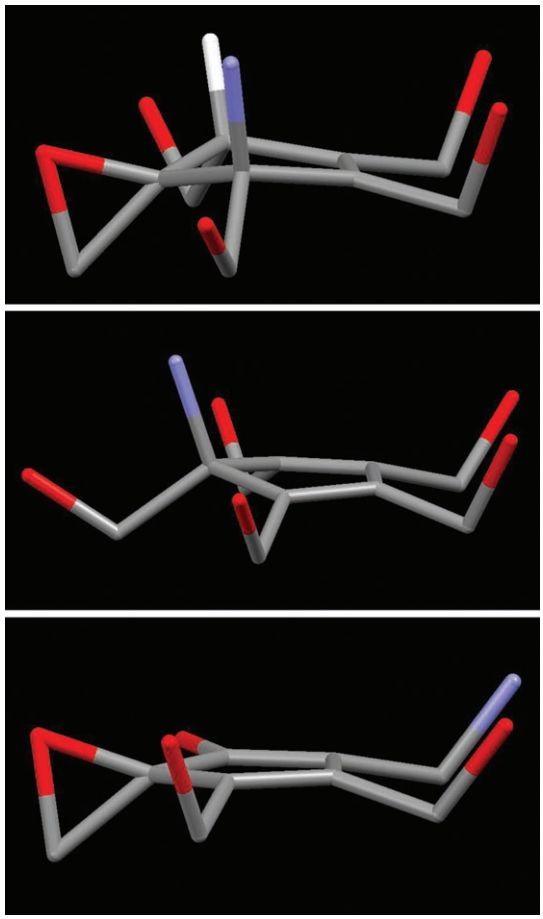


Figure 2. X-ray structures showing the central skew-pentagon regions in compounds **4a** (top), **6d** (middle), and **14a** (bottom), red O, blue N, gray C, white H.

tra it is possible to obtain unambiguous formulas, but assignment of the relative locations of addends is problematic.

Compounds 3, 4a–g, and 5a–d: Comparison of NMR data with those obtained for X-ray-established structures played a crucial role for the structure assignment. Compounds **3**, **4**, and **5** are quite similar, differing only in the groups attached to the nitrogen and each possessing a characteristic fullerene proton, as is evident in their NMR spectra. Their ^{13}C NMR patterns are similar, especially in the case of the eight sp^3 fullerene carbons, three of which appear below the solvent ($CDCl_3$) signal (including the one connecting to the hydrogen: around 48 ppm, confirmed by DEPT spectra), two at relatively low field (around δ 88 and 89 ppm), and the other three between δ 80 to 85 ppm. It is thus reasonable to conclude that they all have the same basic structure as compound **4a**, which was established by X-ray analysis.

Steric hindrance is a key factor affecting the properties of compounds **5a** to **5d**: as the steric hindrance increases from **5a** to **5d**, the rotation of the amino group becomes more hindered and the ^1H NMR signals of the amino group become broader. Geminal coupling in the benzyl group of

5b is clear, but the methylene signals of **5c** and **5d** appear as broad multiplets and as a flat hump, respectively. This steric phenomenon correlates with the decreasing yields from **5a** to **5e**.

Compounds 6c–e, 10, 12, and 13: The presence of the mirror planes in compounds **6**, **10**, **12**, and **13** makes the structural assignment much easier. These compounds show the expected ^{1}H coupling patterns: the $CHCH_2$ protons on the amino groups of compounds **6d** and **6e**, for example, appear as a triplet at around 4.8 ppm and a doublet at 3.4 ppm, while the methylene protons in the OCH_2CH_3 moiety in **6e** appear as a doublet of quartets due to germinal coupling. The number of fullerene skeleton signals in the ^{13}C NMR spectra is consistent with the C_s symmetry. The steric hindrance here is smaller than that in compounds **5**, as can be seen from the relatively sharp ^{1}H NMR signals of compounds **6d** and **6e**.

Two regioisomers are possible for these C_s symmetric compounds with the two groups on the mirror plane being switched, one on the central pentagon and the other on the neighboring pentagon. The three compounds **6** (**c**, **d**, **e**) are all obtained under similar conditions from starting compound **1** and their ^{13}C NMR spectra each show two characteristic signals at around 72 and 75 ppm, attributable to the sp^3 fullerene carbons connected to the amino and the hydroxy groups, while the other fullerene carbons exhibit the same NMR pattern. Compounds **6c** and **6e** should thus have the same structure as compound **6d**, which was established by X-ray analysis: that is, with the amino group on the central pentagon.

In contrast with compounds **6c–e**, compounds **10**, **12**, and **13** have the hydroxy group on the central pentagon and the amino group on the neighboring pentagon. These three compounds are all obtained from the starting vicinal bromohydroxy derivative **2c**, and their ^{13}C NMR spectra each show two unique signals at δ 62–71 and 81–84 ppm, attributable to the two sp^3 fullerene carbons connected to the amino and hydroxy groups, respectively. Chemical shifts of hydroxy groups on the central pentagon appear in the δ 80–84 ppm range for a series of related compounds.[8]

HMBC spectra further confirmed the chemical shift assignment for hydroxy groups on the central pentagon. We have recently reported the single-crystal structure of the chlorohydroxy derivative **2b**.[8d] The HMBC spectrum of **2b** showed a correlation between the OH proton and the sp^2 fullerene carbons on the central pentagon at 157.3 ppm, a unique signal at the lowest field, considerably separated from other sp^2 fullerene carbon signals. The ^{1}H NMR spectrum of the hydrohydroxy derivative **11** showed two singlets at δ 4.6 and 5.2 ppm, and a D_2O exchange experiment indicated that the 4.6 ppm signal was due to the OH group. In the case of **11**, the HMBC spectrum showed correlation of the OH signal with the sp^2 fullerene carbons on the central pentagon at 155.0 ppm.

The HMBC spectrum of the aziridine adduct **13** (Figure 3) showed correlation between the OH proton and

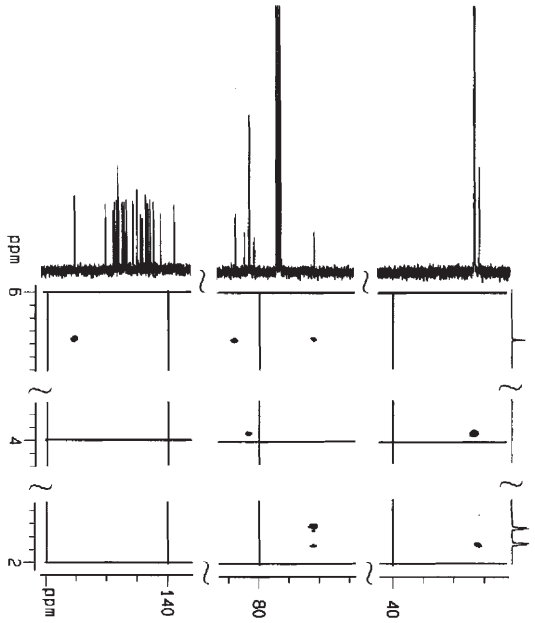


Figure 3. HMBC spectrum of compound **13**.

the carbons at δ 71.0, 84.1, and 155.5 ppm, which can be assigned to the sp^3 fullerene carbons connected to the aziridine, the OH, and the two equivalent sp^2 carbons on the central pentagon, respectively. There are two signals correlating to the *t*BuOO group for the broad hump at 4.2 ppm in Figure 3, which may be due to a H-bonded water molecule HOH···O*t*Bu.

Compounds 14a–d: These compounds are all C_1 symmetric, while only compound **14a** was characterized by X-ray analysis. As above, comparison of the NMR data for **14b–d** with those for **14a** indicates that they have analogous structures as depicted in Scheme 6. Compounds **14a–d** each show four fullerene sp^3 signals at δ 70.0, 71.3, 83.1, and 83.4–83.7 ppm (Figure 4), attributable to those connected to the epoxy and the two *t*BuOO groups. The two aminoketal fullerene carbons appear at δ 100–104 and 110–115 ppm. The signal at 125.0 ppm for all four compounds is at a rather high field for a normal sp^2 fullerene skeleton carbon and is probably due to the carbon on the central pentagon connected to the aminoketal moiety at the 5,6-junction. As discussed in the case of the spectra of compounds **5**, steric hindrance is also clearly observable in the NMR spectra of compounds **14**. One of the NCH_2 groups in the cyclic amine is broad at RT, but became a sharp signal at elevated temperature (cf., for example, the two spectra for **14b** at the bottom of Figure 4).

Compounds 8 and 9: Compounds **8** and **9** are regioisomers, differing only in their hydrogen locations. Extensive NMR spectra were obtained in order to derive their structures: the ^{1}H NMR spectrum of **9** showed the expected coupling between the two fullerene protons with a coupling constant of 10.1 Hz. The DEPT spectra of **8** and **9** confirmed fullerene sp^3 signals connected to the hydrogens at δ 49.0 ppm for

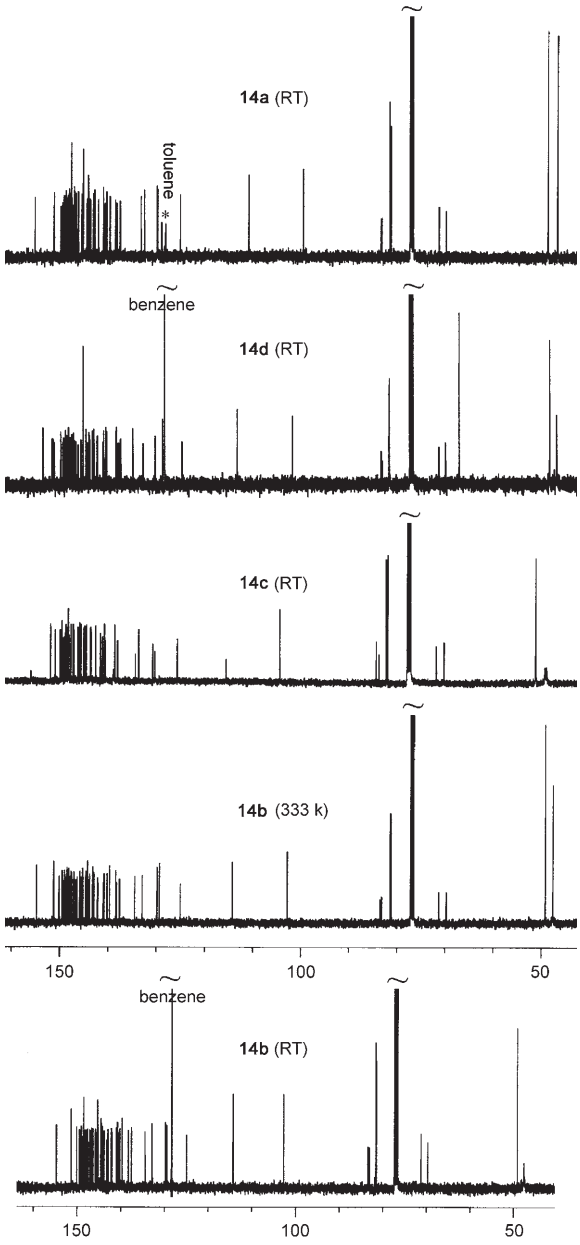


Figure 4. ^{13}C NMR spectra of compounds **14**.

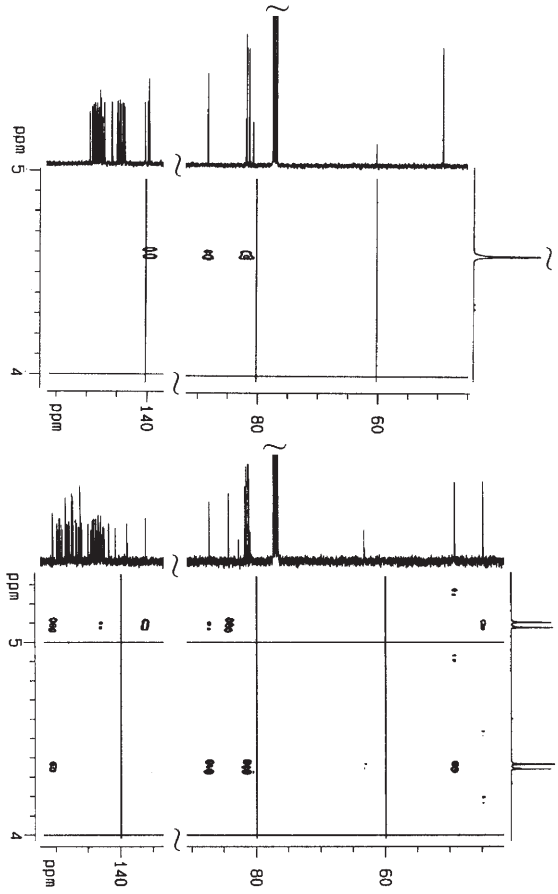


Figure 5. HMBC spectra of compounds **8** (above) and **9** (below).

8 and at 49.3 and 44.9 ppm for **9**. The signal near 49 ppm is essentially the same as those observed in compounds **3**, **4**, and **5**.

The HMBC spectrum of the C_s symmetric **8** showed correlation of hydrogens with sp^3 carbons connected to the *t*BuOO groups and sp^2 carbons on the central pentagon, at the highest field (139.4 ppm) for sp^2 skeleton carbons in **8** (Figure 5). The HMBC spectrum of **9** is more informative. The H at δ 5.1 ppm exhibits correlation to both the two sp^2 carbons on the central pentagon at the lowest (150.6 ppm) and the highest (136.2 ppm) fields in the sp^2 region and it is reasonable to assign this proton as the one closer to the epoxy unit. The other proton on the central pentagon is relatively more shielded by the surrounding *tert*-butylperoxy groups and appears at higher field (4.4 ppm). Correlations of these two protons with sp^3 carbons connected to the *t*BuOO groups indicate that the higher-field signal (at 84.3 ppm) and the lower-field signal (at 87.3 ppm) are due to the carbons further away from and closer to the epoxy moiety, respectively. From these data and from earlier results, a tentative partial assignment of the NMR data as shown in Figure 6 is suggested.

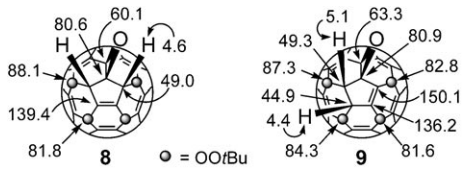
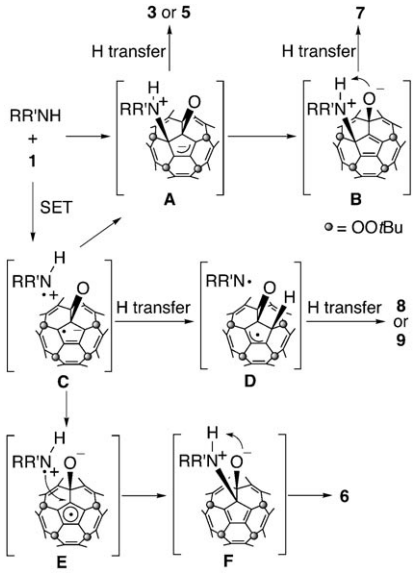


Figure 6. Partial assignment of chemical shifts for compounds **8** and **9**.

Compound 7: The structure assignment for compound **7** is less conclusive, crystallization efforts having failed to produce suitable single crystals. The structure for **7** depicted in Scheme 4 is consistent with its spectroscopic data, with the two methylene groups on the aziridine ring differing because of restricted rotation. Four proton and two carbon signals were observed in the ^1H and ^{13}C NMR spectra, respectively.

Mechanism consideration: The mechanisms of reactions between amines and fullerenes are not well understood. It has been confirmed, though, that radical species are involved through single-electron transfer (SET) processes,[2] and singlet oxygen has been shown to be essential in a few cases.[6d] Informative pathways based on the characterization of isomerically pure aminofullerene adducts have been suggested for the addition of secondary[1c,4] and tertiary amines,[6] while a zwitterionic allyl-type intermediate was suggested to explain the substitution of 1,4-diaminofullerene by another cyclic secondary amine.[15] In the case of primary amines, however, little progress has been made since the first report by Wudl et al. The lack of any isomerically pure primary amine adduct makes it difficult to propose a conclusive mechanism.

Scheme 7 shows a possible pathway for the reactions between **1** and amines. The cyclopentadienyl moiety in the skew-pentagon of **1** should be more reactive than the other

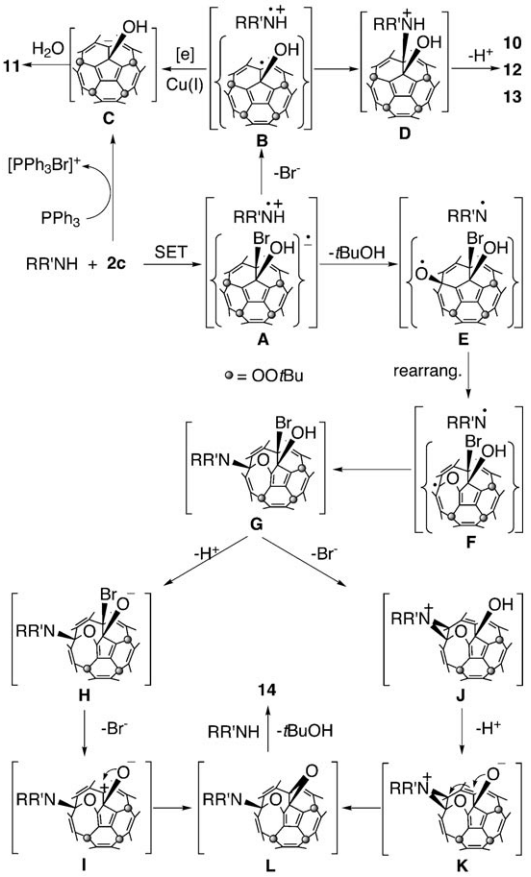


Scheme 7. Possible pathways for reactions of **1**.

double bonds on the surface, but it is sterically hindered by the four *tert*-butylperoxy groups, so the steric size of the amine is thus the key factor determining the addition mechanism. For less bulky amines the formal 1,4-addition products **3** and **5** are formed through intermediate **A**, which may be the results either of Michael-type addition or of radical coupling within the cage complex intermediate **C**. The decreasing yields of **5a**–**e** are consistent with the increasing sizes of the amines. The negative charge of the allyl anion in intermediate **A** can also be transferred onto the epoxy oxygen to give the epoxy-opened intermediate **B**, which can then yield **7** after a proton transfer step. In the case of bulky nucleophiles such as dimethoxyethylamine the radical coupling is relatively slow, and intermediate **C** can rearrange to the more stable cyclopentadienyl radical **E** before the coupling. The epoxy moiety is opened in this rearrangement process and addition of the amino group can then take place next to the oxygen anion to form **F** preferentially, both for steric reasons and because of electrostatic charge attraction. Finally, a proton transfer step affords **6** from **F**. The proton transfer step could also occur before the amino addition, or the two processes may be concerted.

For even bulkier amines such as cycloheptylamine, addition at the nitrogen is severely hindered, so another hydrogen atom, instead of the amino group, adds to the pentagon to form the isomeric dihydrogenfullerene derivatives **8** or **9**. This second hydrogen atom could be one of the methylene protons α to the nitrogen-centered radical RR′N$^{\bullet}$ nearby or hydrogen on the nitrogen from another amine molecule. This bishydrogenation reaction is probably analogous to the formation of $C_{60}H_{18}$ when C_{60} was heated with polyamines.[7]

As in the reaction mechanisms of **1**, SET is also the key step in the reactions of **2c** (Scheme 8). Steric hindrance also plays an important role in the different reaction patterns. In the case of sterically undemanding amines the bromo group is simply replaced through intermediates **A**, **B**, and **D**, and when reducing agent Cu^{I} is present, intermediate **B** can be further reduced to the anion intermediate **C**, protonation of which yields **11**. Because of its relatively strong reducing ability the bulky triphenylphosphine reacts efficiently with **2c** to form **C**. In the case of bulky amines, simple replacement of the bromo group is unfavorable, so there is less



Scheme 8. Possible pathways for reactions of **2c**.

driving force for the detachment of the bromo group from **A**. Cleavage of the peroxy bond thus takes place instead, to form intermediate **E**, which rearranges to **F** before coupling with the amino radical. We have reported analogous hemiketalfullerenes with hydroxy groups at the same position as the amino group in **G**. The formation of the epoxy moiety in compound **14** could follow either the S_N1-type mechanism, as shown from **G**→**H**→**I**→**L**, or the amino group-assisted double intramolecular S_N2' mechanism as shown from **G**→**J**→**K**→**L**. Repetition of the aminoketal formation steps with **L** results in the stable product **14**. The epoxy moiety must be formed after the aminoketal, since compound **1** did not give **14** under similar conditions. It is possible that the epoxy moiety is formed after the second aminoketal moiety rather than the first one, as shown in Scheme 8.

The replacement reaction mechanism for **10**, **12**, and **13** is reminiscent of the well known $S_{RN}1$ chain mechanism,[16] in which the nucleophile does not react directly with the substrate RX but with the radical R$^{\bullet}$ resulting from reductive cleavage of the R−X bond. Kitagawa and Komatsu reported the electron-induced substitution of alkylated C_{60} chloride by 1,8-bis(dimethylamino)naphthalene, in which a $S_{RN}1$ chain mechanism was observed.[17] In the present case, it is less likely that the formation of compounds **10**, **12**, and **13** would follow the same chain mechanism, since the aliphatic amines used here cannot form the relatively stable delocalized radical as with aminonaphthalene.

Conclusion

Fullerene peroxides react readily with primary and secondary aliphatic amines around their peroxy addends to form various aminofullerene peroxides, including simple hydroamination products and aminoketo derivatives. Cleavage of peroxy O−O and fullerene C−C and C−O bonds is involved in these reactions. The observed chemo- and regioselectivities can be explained in terms of SET process and steric hindrance. The *tert*-butylperoxy groups in these compounds form an effective wall isolating the central skew-pentagon, and stabilize otherwise unstable products.

The oxygen-rich region on the fullerene surface has been shown here to exhibit enhanced reactivity. This observation provides valuable insight into the chemistry of nanotubes, such as the controversial mechanism of the ammonia gas sensor property reported for oxidized SWNTs.[18] Characterization of the covalently bonded ammonia derivative **3** supports chemisorption—rather than physisorption—of ammonia onto oxidized nanotubes.

Chirality is an important aspect in fullerene chemistry.[19] All the C_1 symmetric fullerene derivatives reported here are isolated as racemic mixtures, and pairs of enantiomers are observed in the unit cells of **4a** and **14a**. Aromatic amines did not give characterizable products under these conditions. Preliminary results indicate that some of the above compounds can react further with aliphatic amines and Lewis acids to form interesting structures. Further work to characterize these products and to explore their potential as precursors for heterofullerenes is in progress.[20]

Experimental Section

General: NMR spectra were recorded on a Bruker ARX 400 (^{1}H, 400 MHz, ^{13}C, 100 MHz) spectrometer at RT (298 K) except when noted. Chemical shifts are given in ppm relative to TMS or $CDCl_3$ (for ^{13}C NMR). ESI-MS spectra were recorded on a LCQ Decaxp Plus Spectrometer with $CHCl_3/CH_3OH$ or $CDCl_3/CH_3OH$ as the solvent, and positive mode spectra were reported except when noted. FTIR spectra were recorded on a Nicolet Magna-IR 750 instrument in microscope mode. All reagents were used as received. Reactions were performed under air at RT except where noted. Thin layer chromatography (TLC) Macherey–Nagel GmbH & Co. silica gel 60 UV254. Chromatographic purifications were carried out with 200–300 mesh silica gel.

CAUTION: *Large amounts of peroxide are involved in some reactions, so care must be taken to avoid possible explosions.*

2-Amino-6,12,15,18-tetrakis(*tert*-butylperoxy)-2,5,6,12,15,18-hexahydrooxireno[2′,3′:1,9](C$_{60}$-I_h)[5,6]fullerene (3):[21] Compound **1** (150 mg, 0.14 mmol) was dissolved in CCl_4 (50 mL), and ammonia gas was bubbled through the solution, which was stirred at RT in darkness. The progress of the reaction was monitored by TLC. After about 5 h, the solution was transferred directly onto a silica gel column and purified by chromatography, with elution with benzene. A small amount of unreacted **1** was eluted as the first band, followed by compound **3** (117 mg, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.65 (s, 1H), 3.08 (s, 2H), 1.532 (s, 9H), 1.405 (s, 9H), 1.327 (s, 9H), 1.323 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 149.5, 149.3, 149.2, 148.9, 148.8, 148.6, 148.5, 148.38, 148.35, 148.32, 148.29, 148.26, 148.24, 148.14, 148.10, 148.05, 147.96, 147.88, 147.85, 147.77, 147.6, 147.5, 147.4, 147.3, 147.22, 147.18, 146.4, 145.72, 145.66, 145.0, 144.79, 144.75, 144.63, 144.60, 144.5, 144.40, 144.38 (2C), 144.3, 144.0, 143.9, 143.7, 143.6, 143.5 (2C), 143.1, 142.4, 142.0, 140.5, 139.2, 139.1, 138.6, 88.7, 88.1, 84.0, 81.90, 81.85, 81.7, 81.2, 80.9, 80.4, 65.6, 61.5, 47.5 (C−H, confirmed by DEPT), 26.8 (3×CH_3), 26.7 (3×CH_3), 26.7 ppm (6×CH_3); FT-IR (microscope): $\tilde{\nu}$ = 3391, 3322, 2979, 2931, 1466, 1455, 1387, 1364, 1260, 1243, 1192, 1120, 1110, 1081, 1055, 1008, 907, 873, 733 cm^{-1}; ESI-MS: *m*/*z* (%): 1110 (100) $[M+H]^+$.

2-(Benzoylamino)-6,12,15,18-tetrakis(*tert*-butylperoxy)-2,5,6,12,15,18-hexahydrooxireno[2′,3′:1,9](C$_{60}$-I_h)[5,6]fullerene (4a): Compound **3** (70 mg, 0.06 mmol) was dissolved in $CHCl_3$ (35 mL). Excess benzoyl chloride (3 drops) and K_2CO_3 (10 mg, 0.07 mmol) were added, and the solution was stirred at RT in darkness. Progress of the reaction was monitored by TLC. After 36 h, the solution was transferred onto a silica gel column and purified by chromatography, with elution with benzene. Product **4a** was eluted as the first band (47 mg, 61%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.48 (s, 1H), 8.14 (m, 2H), 7.57–7.53 (m, 3H), 5.81 (s, 1H), 1.48 (s, 9H), 1.37 (s, 9H), 1.35 (s, 9H), 1.20 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 165.5, 149.22, 149.19, 149.0, 148.78, 148.75, 148.71, 148.6, 148.41 (2C), 148.36 (2C), 148.30, 148.24, 148.20, 148.1, 148.0, 147.9 (2C), 147.7 (2C), 147.58, 147.56, 147.4, 147.3, 147.1, 147.0, 146.1, 145.70, 145.65, 145.1, 144.9, 144.80, 144.78 (2C), 144.68 (2C), 144.5, 144.3, 144.27, 144.25, 144.0, 143.9, 143.9, 143.5, 143.4, 143.3, 143.0, 140.5, 139.5, 139.3, 138.5, 136.8, 136.0, 131.1, 128.3 (2C), 127.4 (2C), 90.5, 87.9, 83.2, 81.6, 81.31, 81.28, 81.0, 80.9, 80.5, 65.2, 61.1, 49.8 (C−H, confirmed by DEPT), 26.8 (3×CH_3), 26.8 (3×CH_3), 26.7 (3×CH_3), 26.5 ppm (3×CH_3); FT-IR (microscope): $\tilde{\nu}$ = 3428, 2978, 2931, 2872, 1691, 1518, 1487, 1475, 1456, 1387, 1364, 1307, 1291, 1260, 1244, 1192, 1122, 1095, 1082, 1049, 1013, 1001, 869, 708 cm^{-1}; ESI-MS: *m*/*z* (%): 1214 (100) $[M+H]^+$.

Single crystals were obtained by slow evaporation of a solution of **4a** in CS_2/EtOH 1:1.[12]

6,12,15,18-Tetrakis(*tert*-butylperoxy)-2-(4-nitrobenzoylamino)-2,5,6,12,15,18-hexahydrooxireno[2′,3′:1,9](C$_{60}$-I_h)[5,6]fullerene (4b): Compound **3** (100 mg, 0.09 mmol) was dissolved in $CHCl_3$ (40 mL). *p*-Nitrobenzoyl chloride (40 mg, 0.22 mmol) and K_2CO_3 (30 mg, 0.21 mmol)

were added, the solution was stirred at RT in darkness, and progress was monitored by TLC. After 20 h, the solution was purified by chromatography on a silica gel column, with elution with benzene. The product was eluted as the first band. The eluted solution of **4b** was evaporated and washed with acetonitrile three times (75 mg, 65%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.56 (s, 1H), 8.41 (d, 2H), 8.31 (d, 2H), 5.75 (s, 1H), 1.46 (s, 9H), 1.37 (s, 9H), 1.35 (s, 9H), 1.20 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 400 MHz): δ = 163.3, 149.5, 149.2 (2C), 149.0, 148.7 (2C), 148.6, 148.5, 148.41, 148.39, 148.36, 148.29, 148.22, 148.16 (2C), 148.11, 148.0, 147.9 (2C), 147.6 (2C), 147.5, 147.4, 147.3, 147.2, 147.1, 146.5, 146.0, 145.7, 145.5, 145.3, 144.8, 144.78 (2C), 144.76, 144.6 (2C), 144.42, 144.34, 144.29, 144.3, 144.0, 143.9, 143.8, 143.6, 143.4, 143.3, 142.8, 142.4, 140.3, 139.4, 139.2, 138.2, 135.4, 128.5 (2C), 123.7 (2C), 90.5, 87.8, 83.6 (2C), 81.5 (*C*-$(CH_3)_3$), 81.3 (2×*C*-$(CH_3)_3$), 80.8 (*C*-$(CH_3)_3$), 80.4, 65.3, 61.2, 49.7 (C−H), 26.9 (3×CH_3), 26.7 (3×CH_3), 26.7 (3×CH_3), 26.5 ppm (3×CH_3); FT-IR (microscope): $\tilde{\nu}$ = 3420, 2978, 2931, 2868, 1698, 1604, 1529, 1485, 1364, 1345, 1295, 1193, 1095, 1012, 867, 851, 756, 716 cm^{-1}; ESI-MS: *m*/*z* (%): 1259 (75) $[M+H]^+$, 1281(100) $[M+Na]^+$.

6,12,15,18-Tetrakis(*tert*-butylperoxy)-2-(*o*-chlorocarbonyl-benzoylamino)-2,5,6,12,15,18-hexahydrooxireno[2′,3′:1,9](C$_{60}$-*I*$_h$)[5,6]fullerene (4c): *o*-Phthaloyl dichloride (32 μL, 0.22 mmol) was added to a solution of **3** (60 mg, 0.054 mmol) in CCl_4 (20 mL). The solution was stirred at RT in darkness and progress was monitored by TLC. After stirring for 9 h at RT, the solution was purified by chromatography on a silica gel column, with elution with toluene/ethyl acetate 5:1. Compound **4c** was eluted as the first band (20 mg; 29%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.76 (s, 1H), 8.43–8.46 (m, 1H), 8.17–8.20 (m, 1H), 7.68–7.75 (m, 2H), 5.06 (s, 1H), 1.45 (s, 9H), 1.39 (s, 9H), 1.30 (s, 9H), 1.23 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, all signals represent 1C except as noted): δ = 170.4, 167.3, 149.2 (2C), 149.0, 148.8, 148.7, 148.6, 148.41, 148.39 (2C), 148.3 (2C), 148.24, 148.15 (2C), 148.0, 147.84, 147.82, 147.61, 147.58, 147.5, 147.31, 147.27, 147.18, 147.08, 146.6, 146.5, 146.0, 145.3, 145.0, 144.82 (2C), 144.79, 144.7, 144.52, 144.50, 144.45, 144.37, 144.28, 144.25, 144.01, 143.95, 143.7, 143.6, 143.5, 143.2, 142.7, 140.4, 139.6, 139.0, 138.1, 137.8, 135.4, 134.5, 134.3, 131.84, 131.78, 131.6, 129.0, 90.1, 87.6, 83.6, 81.9, 81.8, 81.4, 80.9, 80.7, 80.5, 65.9, 61.1, 49.5, 26.7 (3×CH_3), 26.7 (3×CH_3), 26.6 (3×CH_3), 26.5 ppm (3×CH_3); FT-IR (microscope): $\tilde{\nu}$ = 3407, 2978, 2925, 2851, 1731, 1699, 1525, 1455, 1388, 1364, 1291, 1261, 1244, 1192, 1084, 1012, 870, 756 cm^{-1}; ESI-MS: *m*/*z* (%): 1216 (100) $[M-CO_2+H]^+$, 1258 (80) $[M-2H+H]^+$.

6,12,15,18-Tetrakis(*tert*-butylperoxy)-2-(*m*-carboxybenzoyl-amino)-2,5,6,12,15,18-hexahydrooxireno[2′,3′:1,9](C$_{60}$-*I*$_h$)[5,6]fullerene (4d): Isophthaloyl dichloride (29 mg, 0.14 mmol) was added to a solution of **3** (38 mg, 0.034 mmol) in CCl_4 (12 mL). The solution was stirred at RT in darkness and progress was monitored by TLC. After stirring for 9.5 h at RT, the solution was purified by chromatography on a silica gel column, with elution with toluene/ethyl acetate 5:1. Compound **4d** was eluted as the first band (18 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (t, *J* = 3.2 Hz, 1H), 8.52 (s, 1H), 8.47–8.50 (m, 1H), 8.36–8.38 (m, 1H), 7.73 (t, *J* = 15.6 Hz, 1H), 5.77 (s, 1H), 1.47 (s, 9H), 1.37 (s, 9H), 1.35 (s, 9H), 1.19 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, all signals represent 1C except as noted): δ = 168.0, 163.7, 149.3, 149.2, 149.0, 148.81, 148.76, 148.60, 148.57, 148.43 (2C), 148.40, 148.30, 148.25, 148.24, 148.21, 148.1, 148.0, 147.9 (2C), 147.7 (2C), 147.6, 147.5, 147.34, 147.25, 147.1, 146.9, 146.1, 145.7, 145.6, 145.3, 144.82 (3C), 144.77, 144.71, 144.66, 144.5, 144.4, 144.32, 144.29, 144.0, 143.9, 143.8, 143.6, 143.37, 143.34, 142.9, 140.5, 139.5, 139.1, 138.3, 137.9, 135.4, 134.4, 134.0, 133.7, 129.4, 129.3, 90.4, 87.8, 83.6, 81.6, 81.4, 81.3, 80.88, 80.86, 80.5, 65.3, 61.2, 49.8, 26.9 (3×CH_3), 26.8 (3×CH_3), 26.7 (3×CH_3), 26.50 ppm (3×CH_3); FT-IR (microscope): $\tilde{\nu}$ = 3419, 2979, 2930, 1729, 1697, 1518, 1388, 1364, 1301, 1262, 1244, 1192, 1014, 871, 733 cm^{-1}; ESI-MS: *m*/*z* (%): 1272 (100) $[M+H+OMe-Cl]^+$.

6,12,15,18-Tetrakis(*tert*-butylperoxy)-2-(*p*-chlorocarbonyl-benzoylamino)-2,5,6,12,15,18-hexahydrooxireno[2′,3′:1,9](C$_{60}$-*I*$_h$)[5,6]fullerene (4e): Terephthaloyl dichloride (66 mg, 0.33 mmol) was added to a solution of **3** (90 mg, 0.081 mmol) in CCl_4 (30 mL). The solution was stirred at RT in darkness and progress was monitored by TLC. After stirring for 3 h at RT, the solution was purified by chromatography on a silica gel column, with elution with toluene. Compound **4e** was eluted as the first band (54 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (s, 1H), 8.26–8.30 (m, 4H), 5.75 (s, 1H) 1.47 (s, 9H), 1.37 (s, 9H), 1.36 (s, 9H), 1.20 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, all signals represent 1C except as noted): δ = 168.0, 163.7, 149.20, 149.18, 148.9, 148.7 (2C), 148.6, 148.5, 148.39, 148.37, 148.33, 148.26, 148.20, 148.16, 148.14, 148.09, 148.0, 147.8 (2C), 147.6 (2C), 147.5, 147.4, 147.3, 147.2, 147.1, 146.6, 146.0, 145.6, 145.5, 145.3, 144.78, 144.76 (2C), 144.7, 144.58, 144.57, 144.4, 144.31, 144.26, 144.23, 144.0, 143.9, 143.8, 143.5, 143.32, 143.28, 142.81, 142.80, 140.3, 139.4, 139.2, 138.2, 135.5, 135.2, 131.5, 131.4, 130.9, 128.0, 90.4, 87.8, 83.5, 81.5, 81.3 (2C), 80.81, 80.79, 80.4, 65.3, 61.1, 49.7, 26.9 (3×CH_3), 26.7 (3×CH_3), 26.6 (3×CH_3), 26.5 (3×CH_3) cm^{-1}; ESI-MS: *m*/*z* (%): 1272 (100) $[M+H+OMe-Cl]^+$.

6,12,15,18-Tetrakis(*tert*-butylperoxy)-2-(*p*-methoxycarbonyl-benzoylamino)-2,5,6,12,15,18-hexahydrooxireno[2′,3′:1,9](C$_{60}$-*I*$_h$)[5,6]fullerene (4f): MeOH (1 mL) was added to a solution of **4e** (54 mg, 0.042 mmol) in $CHCl_3$ (5 mL). After stirring for 8 min at RT, the solution was purified by chromatography on a silica gel column, with elution with toluene/petroleum ether/ethyl acetate 10:10:1. Compound **4f** was eluted as the first product band (54 mg, quantitative). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (s, 1H), 8.21 (s, 4H), 5.78 (s, 1H), 4.00 (s, 3H), 1.47 (s, 9H), 1.37 (s, 9H), 1.35 (s, 9H), 1.19 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, all signals represent 1C except as noted): δ = 166.5, 164.5, 149.21, 149.19, 149.0, 148.8, 148.7, 148.6 (2C), 148.39, 148.35, 148.28, 148.26, 148.22, 148.17, 148.09, 147.98, 147.85 (2C), 147.6 (2C), 147.54, 147.49, 147.3, 147.2, 147.1, 146.8, 146.1, 145.6, 145.5, 145.3 (2C), 144.80 (2C), 144.76, 144.70, 144.66, 144.63, 144.5, 144.33, 144.25 (2C), 144.00, 143.9, 143.8, 143.5, 143.33, 143.31, 142.9, 140.8, 140.4, 139.4, 139.2, 138.3, 135.8, 132.4, 129.7 (2C), 127.5 (2C), 90.5, 87.8, 83.4, 81.6, 81.3 (2C), 80.9, 80.8, 80.5, 65.3, 61.1, 52.4, 49.7, 26.9 (3×CH_3), 26.7 (3×CH_3), 26.7 (3×CH_3), 26.5 ppm (3×CH_3); FT-IR (microscope): $\tilde{\nu}$ = 3424, 2979, 2932, 1728, 1693, 1522, 1364, 1278, 1245, 1192, 1106, 1013, 868, 755, 728 cm^{-1}; ESI-MS: *m*/*z* (%): 1272 (100) $[M+H]^+$.

6,12,15,18-Tetrakis(*tert*-butylperoxy)-2-(9-carboxynonanoyl-amino)-2,5,6,12,15,18-hexahydrooxireno[2′,3′:1,9](C$_{60}$-*I*$_h$)[5,6]fullerene (4g): Sebacoyl chloride (92%, 4 drops) was added to a solution of **3** (60 mg, 0.054 mmol) in CCl_4 (20 mL) and the flask was wrapped with aluminum foil. After stirring for 20 min at RT, the solution was purified by chromatography on a silica gel column, with elution with toluene/ethyl acetate 5:1. Compound **4g** was collected as the second band (35 mg, 47.8%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (s, 1H), 5.65 (s, 1H), 2.47–2.57 (m, 2H), 2.40 (t, *J* = 14.9 Hz, 2H), 1.90–1.95 (m, 2H), 1.68–1.71 (m, 2H), 1.50–1.54 (m, 2H), 1.46 (s, 9H), 1.42 (s, 6H), 1.39 (s, 2H), 1.36 (s, 18H), 1.35 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, all signals represent 1C except as noted): δ = 178.6, 170.7, 149.2, 149.2, 149.0, 148.7 (2C), 148.62, 148.57, 148.4 (2C), 148.34, 148.26 (2C), 148.21, 148.18, 148.1, 148.0, 147.9 (2C), 147.7, 147.60, 147.57, 147.5, 147.31, 147.25, 147.12, 147.08, 146.1, 145.6, 145.4, 144.81 (3C), 144.77, 144.75, 144.7, 144.6, 144.5, 144.30, 144.25, 144.23, 144.9, 143.9, 143.8, 143.5, 143.4, 143.3, 143.0, 140.5, 139.5, 139.1, 138.5, 136.0, 90.1, 87.8, 82.9, 81.6, 81.3 (2C), 81.0, 80.8, 80.5, 64.7, 61.1, 49.7, 38.6, 33.9, 29.5, 29.3, 29.1, 29.1, 26.8 (3×CH_3), 26.7 (3×CH_3), 26.7 (6×CH_3), 26.2, 24.7 ppm; FT-IR (microscope): $\tilde{\nu}$ = 3425, 2978, 2930, 2856, 1729, 1706, 1665, 1514, 1387, 1364, 1192, 1014, 1004, 871, 756, 735 cm^{-1}; ESI-MS: *m*/*z* (%): 1294 (100) $[M+H]^+$.

6,12,15,18-Tetrakis(*tert*-butylperoxy)-2-(methylamino)-2,5,6,12,15,18-hexahydrooxireno[2′,3′:1,9](C$_{60}$-*I*$_h$)[5,6]fullerene (5a): NH_2CH_3 (aq., 64 μL, 4.03 mmol) was added to a solution of **1** (90 mg, 0.082 mmol) in CH_2Cl_2 (18 mL). The solution was stirred at RT in darkness and progress was monitored by TLC. After stirring for 30 min at RT, the solution was purified by chromatography on a silica gel column, with elution with toluene/ethyl acetate 10:1. Unreacted **1** was collected as the first band (30 mg), **5a** as the second, red band (28 mg, 30.3%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.54 (s, 1H), 3.11 (s, 3H), 1.49 (s, 9H), 1.37 (s, 9H), 1.32 ppm (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, all signals represent 1C except as noted): δ = 149.8, 149.6, 149.2, 149.1, 148.9, 148.7, 148.5, 148.4, 148.3, 148.2 (2C), 148.2, 148.11, 148.06, 147.9, 147.80, 147.77, 147.72, 147.70, 147.6, 147.34, 147.32, 147.2, 147.14 (2C), 147.12, 146.8, 145.7, 145.6, 145.2, 144.81, 144.76, 144.40, 144.38 (2C), 144.3 (2C), 144.23,

144.18, 144.1, 143.9, 143.8, 143.6, 143.5, 143.5 (2C), 143.2, 139.72, 139.68, 139.5, 138.6, 138.5, 89.9, 87.9, 83.1, 81.7, 81.6, 81.4, 81.1, 80.6, 80.3, 70.0, 61.5, 48.6, 31.9, 26.8 ($3\times CH_3$), 26.7 ($3\times CH_3$), 26.70 ($3\times CH_3$), 26.65 ppm ($3\times CH_3$); FT-IR (microscope): $\tilde{\nu}$ = 3373, 2957, 2926, 2855, 1730, 1463, 1387, 1364, 1286, 1272, 1193, 1122, 1073, 1041, 1018, 873, 743 cm^{-1}; ESI-MS: *m*/*z* (%): 1124 (100) $[M+H]^+$.

2-(Benzylamino)-6,12,15,18-tetrakis(*tert*-butylperoxy)-2,5,6,12,15,18-hexahydrooxireno[2′,3′:1,9](C$_{60}$-*I*$_h$)[5,6]fullerene (5b): Compound **1** (67 mg, 0.06 mmol) was dissolved in CCl_4 (20 mL), and excess benzylamine (4 drops) was added. The solution was stirred at RT in darkness and progress of the reaction was monitored by TLC. After 3 h, the solution was purified by chromatography on a silica gel column, with elution with benzene and petroleum ether 2:1, to give **5b** as the first product band (22 mg, 30%). Other bands were collected as multiple adducts, structures of which remained to be assigned. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.73 (d, 2H), 7.45 (t, 2H), 7.34 (t, 1H), 4.71 (d, *J* = 12.2 Hz, 1H), 4.62 (d, *J* = 12.2 Hz, 1H), 4.60 (s, 1H), 3.49 (s, 1H), 1.477 (s, 9H), 1.337 (s, 9H), 1.327 (s, 9H), 1.252 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 149.99, 149.74, 149.26, 149.14, 148.93, 148.73, 148.59, 148.41, 148.38, 148.30, 148.27 (2C), 148.16, 148.13, 147.95, 147.84, 147.82, 147.79, 147.77, 147.75, 147.37, 147.29, 147.26, 147.21, 147.16 (2C), 146.62, 145.68, 145.63, 145.17, 144.87, 144.78, 144.44 (4C), 144.41, 144.39, 144.30, 144.26, 144.02, 143.81, 143.68, 143.57, 143.51, 143.50, 143.33, 141.69, 139.80 (2C), 139.37, 138.62, 138.44, 128.23 (2C), 128.22 (2C), 126.73, 90.09, 88.06, 83.10, 81.81, 81.61, 81.58, 81.27, 80.84, 80.25, 69.72, 61.56, 48.83 (CH_2, confirmed by DEPT), 48.71 (C–H, confirmed by DEPT), 26.78 ($3\times CH_3$), 26.75 ppm ($9\times CH_3$); FT-IR (microscope): $\tilde{\nu}$ = 3353, 3033, 2978, 2928, 2868, 1466, 1455,1387, 1363, 1260, 1243, 1192, 1121, 1095, 1078, 1009, 874, 677 cm^{-1}; ESI-MS: *m*/*z* (%): 1200 (100) $[M+H]^+$.

6,12,15,18-Tetrakis(*tert*-butylperoxy)-2-(2-hydroxyethylamino)-2,5,6,12,15,18-hexahydrooxireno[2′,3′:1,9](C$_{60}$-*I*$_h$)[5,6]fullerene (5c) and 6,12,15,18-tetrakis(*tert*-butylperoxy)-9-hydroxy-1-(2-hydroxyethylamino)-1,6,9,12,15,18-hexahydro(C$_{60}$-*I*$_h$)[5,6]fullerene (6c): Ethanolamine (80 μL, 1.36 mmol) was added to a solution of **1** (150 mg, 0.136 mmol) in CH_2Cl_2 (15 mL) and the flask was wrapped with aluminum foil. After stirring for 25 min at RT, the solution was purified by chromatography on a silica gel column, with elution with toluene/ethyl acetate 10:1. Unreacted **1** was collected as the first band (18 mg), **5c** was collected as the second band (36 mg, 22.7%), and the third band was **6c** (25 mg, 15.8%).

Compound 5c: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.45 (s, 1H), 3.95–3.97 (m, 2H), 3.57–3.58 (m, 2H), 3.3–3.5 (br s, 1H), 3.11 (s, 1H), 1.48 (s, 9H), 1.37 (s, 9H), 1.33 ppm (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, all signals represent 1C except as noted): δ = 149.8, 149.6, 149.2, 149.1, 148.9, 148.7, 148.6, 148.4, 148.33, 148.30, 148.25, 148.20, 148.1 (2C), 147.9, 147.8 (2C), 147.70 (2C), 147.66, 147.4, 147.3, 147.2, 147.13, 147.11, 147.09, 146.3, 145.6, 145.6, 145.2, 144.8, 144.7, 144.6, 144.5, 144.43, 144.39, 144.37, 144.2 (2C), 144.0, 143.9, 143.8, 143.6, 143.44, 143.39, 143.35, 143.29, 140.0, 139.3, 139.1, 138.4, 138.3, 89.8, 88.0, 82.2, 82.0, 82.7, 81.6, 81.3, 80.9, 80.2, 69.1, 62.6, 61.3, 48.5, 45.4, 26.7 ppm ($12\times CH_3$); FT-IR (microscope): $\tilde{\nu}$ = 3350, 2978, 2930, 2870, 1466, 1387, 1364, 1192, 1010, 873, 756, 733 cm^{-1}; ESI-MS: *m*/*z* (%): 1154 (100) $[M+H]^+$.

Compound 6c: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.09 (s, 2H), 3.44 (t, *J* = 10.3 Hz, 2H), 2.17 (s, 1H), 1.45 (s, 18H), 1.38 ppm (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, all signals represent 2C except as noted): δ = 156.3, 151.7, 150.4, 149.1, 148.9, 148.6, 148.4 (1C), 148.3, 148.13, 148.10, 147.39, 147.35, 147.31 (1C), 147.27, 147.1, 145.8, 145.64, 145.62, 145.0, 144.6, 144.5, 144.4, 143.9, 143.4, 142.7, 142.5, 141.5, 136.7, 82.4, 82.1, 81.5, 80.7, 75.1, 72.4, 61.5, 48.6, 26.8 ($6\times CH_3$), 26.7 ppm ($6\times CH_3$); FT-IR (microscope): $\tilde{\nu}$ = 3288, 2979, 2929, 2870, 1457, 1387, 1364, 1193, 1138, 1118, 1103, 1090, 1049, 1019, 872, 757, 734 cm^{-1}; ESI-MS: *m*/*z* (%): 1154 (100) $[M+H]^+$.

6,12,15,18-Tetrakis(*tert*-butylperoxy)-2-(2,2-dimethoxyethylamino)-2,5,6,12,15,18-hexahydrooxireno[2′,3′:1,9](C$_{60}$-*I*$_h$)[5,6]fullerene (5d) and 6,12,15,18-tetrakis(*tert*-butylperoxy)-1-(2,2-dimethoxy-ethylamino)-9-hydroxy-1,6,9,12,15,18-hexahydro(C$_{60}$-*I*$_h$)[5,6]fullerene (6d): Aminoacetaldehyde dimethyl acetal (440 μL, 4.02 mmol) was added to a solution of **1** (110 mg, 0.10 mmol) in CH_2Cl_2 (20 mL) and the flask was wrapped with aluminum foil. After stirring for 25 min at RT, the solution was purified by chromatography on a silica gel column, with elution with toluene/ethyl acetate 10:1. Unreacted **1** was collected as the first band (24 mg), and the second, red band was collected as a mixture of **5d** and **6d**. The mixture of **5d** and **6d** was repurified by chromatography on a silica gel column, with elution with toluene/petroleum ether/ethyl acetate 10:10:1 to give pure **5d** (11 mg, 9.0%) and **6d** (29 mg, 23.8%) as the first and second bands, respectively.

Compound 5d (322 K): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.81 (s, 1H), 4.47 (s, 1H), 3.60 (s, 6H), 1.48 (s, 9H), 1.38 (s, 9H), 1.33 ppm (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, all signals represent 1C except as noted): δ = 150.0, 149.8, 149.2, 149.1, 148.9, 148.7, 148.6, 148.4, 148.3, 148.27, 148.25, 148.18, 148.09, 148.07, 148.03, 147.9, 147.8 (2C), 147.7 (2C), 147.5, 147.3, 147.2, 147.18, 147.16, 147.13, 147.09, 147.6, 145.7, 145.6, 145.3, 144.79, 144.76, 144.5, 144.4 (2C), 144.39, 144.34, 144.25, 144.23, 143.9, 143.7, 143.6, 143.47 (2C), 143.45, 143.2, 140.0, 139.0, 138.6, 138.3, 128.9, 105.2, 89.7, 88.1, 81.5, 81.2, 80.9, 80.3, 69.1, 61.2, 48.5, 26.7 ($3\times CH_3$), 26.7 ($6\times CH_3$), 26.6 ($3\times CH_3$), 26.5 ppm ($3\times CH_3$).

Compound 5d (298 K): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.75 (s, 1H), 4.43 (s, 1H), 3.59 (s, 6H), 1.49 (s, 9H), 1.39 (s, 9H), 1.33 ppm (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, all signals represent 1C except as noted): δ = 149.2, 149.1, 148.9, 148.7, 148.5, 148.33, 148.32, 148.27, 148.23, 148.17, 148.08, 148.06, 147.98, 147.9, 147.78, 147.76 (2C), 147.69, 147.66, 147.4, 147.3, 147.2, 147.14, 147.07, 147.0, 145.61, 145.56, 144.8, 144.7, 144.5, 144.43, 144.41 (2C), 144.33, 144.26, 144.23, 143.9, 143.7, 143.6, 143.47, 143.45, 143.41, 143.2, 139.9, 138.9, 138.3, 125.2, 105.0, 89.7, 88.0, 81.5, 81.3, 80.8, 80.2, 69.1, 61.3, 48.5, 26.7 ($3\times CH_3$), 26.69 ($3\times CH_3$), 26.66 ($3\times CH_3$), 26.60 ppm ($3\times CH_3$). Not all ^{13}C signals were detected because the signals are broad as a result of steric effects. FT-IR (microscope): $\tilde{\nu}$ = 3358, 2978, 2929, 2832, 1466, 1387, 1364, 1261, 1243, 1193, 1128, 1082, 1010, 874 cm^{-1}; ESI-MS: *m*/*z* (%): 1198 (100), $[M+H]^+$.

Compound 6d: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.78 (t, *J* = 11.1 Hz, 1H), 4.02 (s, 1H), 3.57 (s, 6H), 3.38 (d, *J* = 5.5 Hz, 2H), 1.45 (s, 18H), 1.39 ppm (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, all signals represent 2C except as noted): δ = 156.4, 151.8, 149.1, 148.9, 148.6, 148.4, 148.3 (2C), 148.1, 147.37, 147.35, 147.32, 147.27, 147.1, 145.8, 145.7, 145.6, 144.9, 144.7, 144.5, 144.4, 143.9, 143.3, 142.7, 142.5, 141.5, 136.8, 128.3, 103.0, 82.2, 82.0, 81.4, 80.7, 74.8, 72.0, 53.4, 47.7, 26.72 ($6\times CH_3$), 26.66 ppm ($6\times CH_3$); FT-IR (microscope): $\tilde{\nu}$ = 3285, 2978, 2929, 2871, 2857, 1463, 1388, 1364, 1287, 1263, 1245, 1193, 1120, 1103, 1075, 1020, 872, 849 cm^{-1}; ESI-MS: *m*/*z* (%): 1198 (100), $[M+H]^+$.

Single crystals were obtained by slow evaporation of a solution of **6d** in $CHCl_3/CS_2/CH_3CN$ 1:1:1.[13]

6,12,15,18-Tetrakis(*tert*-butylperoxy)-1-(2,2-diethoxyethylamino)-9-hydroxy-1,6,9,12,15,18-hexahydro(C$_{60}$-*I*$_h$)[5,6]fullerene (6e): Aminoacetaldehyde diethyl acetal (590 μL, 4.03 mmol) was added to a solution of **1** (110 mg, 0.10 mmol) in CH_2Cl_2 (22 mL) and the flask was wrapped with aluminum foil. After stirring for 35 min at RT, the solution was purified by chromatography on a silica gel column, with elution with toluene/ethyl acetate 10:1. Unreacted **1** was collected as the first band (8 mg), and the second, red band was collected as a mixture of **5e** and **6e**. The mixture of **5e** and **6e** was repurified by chromatography on a silica gel column, with elution with toluene/petroleum ether/ethyl acetate 10:10:1, to give pure **5e** (trace) and **6e** (44 mg, 35.7%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.88 (t, *J* = 10.8 Hz, 1H), 3.86–3.92 (m, 2H), 3.73–3.79 (m, 2H), 3.42 (d, *J* = 5.19 Hz, 2H, 1.46 (s, 18H), 1.39 (s, 18H). 1.36 ppm (t, *J* = 14.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, all signals represent 2C except as noted): δ = 156.6, 151.7, 150.3, 149.1, 148.9, 148.6, 148.33 (1C), 148.26, 148.14, 148.10, 147.38, 147.35, 147.34 (1C), 147.28, 147.1, 145.8, 145.7, 145.6, 144.9, 144.7, 144.44, 144.37, 143.8, 143.3, 142.8, 142.4, 141.5, 136.7, 128.3, 101.5, 82.3, 81.9, 81.4, 80.7, 74.8, 72.1, 61.7, 49.4, 26.8 ($6\times CH_3$), 26.7 ($6\times CH_3$), 15.5 ppm; FT-IR (microscope): $\tilde{\nu}$ = 3290, 2978, 2929, 1456, 1387, 1363, 1193, 1136, 1119, 1090, 1054, 1017, 873, 756 cm^{-1}; ESI-MS: *m*/*z* (%): 1226 (100) $[M+H]^+$.

2-(Aziridin-1-yl)-6,12,15,18-tetrakis(*tert*-butylperoxy)-9-hydroxy-2,6,9,12,15,18-hexahydro(C$_{60}$-*I*$_h$)[5,6]fullerene (7): Compound **1** (70 mg, 0.06 mmol) was dissolved in CH_2Cl_2 (15 mL) and a solution of $HCl{\cdot}NH_2CH_2CH_2Br$ (322 mg, 1.6 mmol) and NaOH (109 mg, 2.7 mmol)

in water (2 mL) was added.[22] The solution was stirred at RT in darkness and progress was monitored by TLC. After 24 h, the solution was washed three times with water and then purified by chromatography on a silica gel column, with elution with toluene and ethyl acetate 2:1, to give **7** as the first product band (35 mg, 48%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.17 (s, 1H), 2.63 (m, 1H), 2.41 (t, J = 9.9 Hz, 1H), 2.25 (m, 1H), 2.16 (t, J = 9.9 Hz, 1H), 1.48 (s, 9H), 1.46 (s, 9H), 1.36 ppm (s, 18H); ^{13}C NMR ($CDCl_3$, 400 MHz): δ = 159.6, 153.5, 152.3, 149.7, 149.14, 149.08, 148.98, 148.93, 148.61, 148.60, 148.5, 148.4, 148.3, 148.3, 148.2, 148.14, 148.11, 148.0, 147.9, 147.6, 147.54 (2C), 147.52, 147.4, 147.3, 147.2, 147.0, 146.9, 146.6 (2C), 146.0, 145.9, 145.7, 145.4, 144.9, 144.61, 144.57, 144.4, 144.3, 144.1, 143.7, 143.64, 143.62, 143.4, 143.3, 143.0, 142.90 (2C), 142.88, 142.84, 142.1, 140.6, 140.2, 140.0, 86.2, 82.3, 82.6 ($C(CH_3)_3$), 81.42 ($C(CH_3)_3$), 81.35 ($C(CH_3)_3$), 81.2 ($C(CH_3)_3$), 80.5, 80.1, 79.6, 73.5, 32.9 (CH_2), 26.9 ($3\times CH_3$), 26.9 ($3\times CH_3$), 26.8 ($3\times CH_3$), 26.7 ($3\times CH_3$), 22.6 ppm (CH_2); FT-IR (microscope): $\tilde{\nu}$ = 3284, 2978, 2930, 2870, 1473, 1455, 1387, 1363, 1193, 1101, 1090, 1044, 1022, 1008, 871 cm^{-1}; ESI-MS: m/z (%): 1136 (100) $[M+H]^+$.

6,12,15,18-Tetrakis(*tert*-butylperoxy)-2,5,6,12,15,18-hexahydrooxireno[2′,3′:1,9](C_{60}-I_h)[5,6]fullerene (8) and 6,12,15,18-tetrakis(*tert*-butylperoxy)-2,3,6,12,15,18-hexahydrooxireno[2′,3′:1,9](C_{60}-I_h)-[5,6]fullerene (9): Compound **1** (60 mg, 0.05 mmol) was dissolved in CCl_4 (20 mL), and an excess of heptamethyleneimine (four drops) was added. The solution was stirred at 55°C in darkness and progress was monitored by TLC. After 5.5 h, the solution was purified by chromatography on a silica gel column, with elution with toluene and petroleum ether 1:1. The first band was a mixture of **1** and **9**, and the second, red band was **8** (14 mg, 23%). It was difficult to separate the mixture of **1** and **9**, but pure **9** was obtained by extending the reaction time to consume all the starting material **1**.

Compound 8: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.60 (s, 2H), 1.46 (s, 18H), 1.33 ppm (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz, all signals represent 2C except when noted): δ = 149.2, 148.8, 148.6, 148.4, 148.4, 148.1, 147.98, 147.95 (1C), 147.7, 147.47, 147.45, 147.3, 147.1, 147.0 (1C), 146.8, 145.6, 144.7, 144.6, 144.3, 144.2, 144.1, 143.7, 143.6, 143.5, 140.1, 139.6, 139.4, 88.1, 81.8, 81.7 ($2\times C(CH_3)$), 81.2 ($2\times C(CH_3)$), 80.6, 60.1, 49.0 (C–H), 26.7 ($6\times CH_3$), 26.7 ppm ($6\times CH_3$); FT-IR (microscope): $\tilde{\nu}$ = 2979, 2931, 1467, 1387, 1363, 1193, 1094, 1013, 905, 875, 733 cm^{-1}; ESI-MS: m/z (%): 1095 (100) $[M+H]^+$.

Compound 9: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.09 (br s, J = 10.15 Hz, 1H), 4.35 (b, J = 10.14 Hz, 1H), 1.47 (s, 9H), 1.39 (s, 9H), 1.38 (s, 9H), 1.34 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, all signals represent 1C except as noted): δ = 150.6, 150.0, 149.7, 149.5, 149.2, 148.6 (2C), 148.5, 148.40, 148.37, 148.25, 148.18, 148.14, 148.07, 148.0, 147.7, 147.6 (2C), 147.52 (2C), 147.47, 147.06, 147.02, 146.9, 146.5, 146.3 (2C), 146.12, 146.09, 145.1, 144.6, 144.5, 144.39, 144.37, 144.28, 144.17, 143.94, 143.90, 143.89, 143.6, 143.5, 143.3, 143.21, 143.16, 143.12, 143.11, 142.8, 142.6, 141.9, 140.9, 139.1, 136.2, 87.3, 84.3, 82.8, 81.8, 81.61, 81.55, 81.3, 81.1, 80.9, 63.3, 49.3 (CH), 44.9 (CH), 26.8 ($3\times CH_3$), 26.8 ($3\times CH_3$), 26.8 ($3\times CH_3$), 26.7 ppm ($3\times CH_3$); FT-IR (microscope): $\tilde{\nu}$ = 2978, 2929, 1472, 1455, 1387, 1363, 1193, 1106, 1075, 1013, 873, 734 cm^{-1}; ESI-MS (neg. mode): m/z (%): 1094 (100) $[M]^-$.

9-Amino-6,12,15,18-tetrakis(*tert*-butylperoxy)-1-hydroxy-1,6,9,12,15,18-hexahydro(C_{60}-I_h)[5,6]fullerene (10): Compound **2c**[8d] (50 mg, 0.04 mmol) was dissolved in $CHCl_3$ (20 mL), and dry NH_3 was bubbled through. The solution was stirred at RT in darkness and progress was monitored by TLC. After 3.5 h, the solution was purified by chromatography on a silica gel column as the first product band, with elution with benzene and ethyl acetate 10:1 (13 mg, 28%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.5 (s, 1H), 2.8 (d, 2H), 1.47 (s, 18H), 1.46 ppm (s, 18H); ^{13}C NMR ($CDCl_3$, 400 MHz, all signals represent 2C except when noted): δ = 156.1, 152.6, 150.0, 149.1, 149.0, 148.7, 148.6, 148.5 (1C), 148.44, 148.36, 147.6, 147.39, 147.37, 147.25 (1C), 147.1, 145.9, 145.4, 145.3, 144.9, 144.5, 144.3, 143.87, 143.85, 143.4, 142.9, 142.5, 141.5, 137.0, 82.5, 82.2 ($C(CH_3)_3$), 81.9, 81.8 ($C(CH_3)_3$), 81.0, 62.7, 26.8 ($6\times CH_3$), 26.7 ppm ($6\times CH_3$); FT-IR (microscope): $\tilde{\nu}$ = 3510, 3389, 3317, 2978, 2929, 2868, 1474, 1463, 1387, 1363, 1193, 1093, 1048, 1019, 872, 733 cm^{-1}; ESI-MS: m/z (%): 1110 (100) $[M+H]^+$.

6,12,15,18-Tetrakis(*tert*-butylperoxy)-1-hydroxy-1,6,9,12,15,18-hexahydro-(C_{60}-I_h)[5,6]fullerene (11): *Method 1*: Compound **2c** (12 mg, 0.01 mmol) was dissolved in $CHCl_3$ (5 mL), an excess of PPh_3 (10 mg, 0.038 mmol) was added, the solution was stirred at RT in darkness, and progress was monitored by TLC. After 5 min the solution was purified by chromatography on a silica gel column, with elution with benzene, as the only visible band. Yield: quantitative. Yield was 81% when the scale was increased to 122 mg.

Method 2: Compound **2c** (50 mg, 0.04 mmol) was dissolved in CH_2Cl_2 (20 mL), and CuBr (25 mg, 0.17 mmol) was added. Ammonia gas (NH_3) was bubbled through the solution, which was stirred at RT in darkness, and progress was monitored by TLC. After 20 min the solution was purified by chromatography on a silica gel column, with elution with benzene and ethyl acetate 20:1. The first product band was **11** (17 mg, 36%). The second product band was **10** (10 mg, 21%). **11**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.20 (s, 1H), 4.56 (s, 1H), 1.48 (s, 18H), 1.45 ppm (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz, all signals represent 2C except when noted): δ = 155.0, 150.6, 149.9, 149.2, 148.9, 148.7, 148.4, 148.2 (1C), 148.2 (4C), 147.6, 147.4, 147.2 (4C), 146.4 (1C), 146.3, 145.79, 145.76, 145.66, 144.60, 144.55, 144.3, 143.9, 143.6, 142.7, 142.3, 141.2, 137.7, 83.6, 82.7, 82.3 ($2\times C(CH_3)_3$), 81.8 ($2\times C(CH_3)_3$), 81.2, 53.6, 26.8 ($6\times CH_3$), 26.8 ppm ($6\times CH_3$); FTIR (microscope): $\tilde{\nu}$ = 3521, 2978, 2928, 2851, 1473, 1461, 1363, 1243, 1193, 1100, 1022, 871, 754 cm^{-1}; ESI-MS: m/z (%): 1112 (100) $[M+NH_4]^+$.

9-Benzylamino-6,12,15,18-tetrakis(*tert*-butylperoxy)-1-hydroxy-1,6,9,12,15,18-hexahydro(C_{60}-I_h)[5,6]fullerene (12): Compound **2c** (60 mg, 0.05 mmol) was dissolved in CCl_4 (30 mL) and an excess of benzylamine (3 drops) was added. The solution was stirred at RT in darkness and progress was monitored by TLC. After 13 h the solution was purified by chromatography on a silica gel column, with elution with benzene, to give **12** as the first band (21 mg, 33%). Other bands were collected as uncharacterized products. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.42 (d, 2H), 7.36 (d, 2H), 7.17 (s, 1H), 6.08 (s, 1H), 4.34 (s, 2H), 1.47 (s, 18H), 1.41 ppm (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz, all signals represent 2C except when noted): δ = 155.4, 150.6, 150.5, 149.1, 149.0, 148.6, 148.5, 148.4, 148.4 (3C), 147.6, 147.4 (3C), 147.2 (1C), 147.0, 145.9, 145.3, 145.1, 145.0, 144.38, 144.36, 144.0, 143.8, 143.4, 143.0, 142.4, 141.5, 139.0, 137.9, 128.6, 128.3, 127.6 (1C), 82.7, 82.4, 81.9 ($C(CH_3)_3$), 81.8 ($C(CH_3)_3$), 81.0, 67.3, 52.3 (CH_2), 26.8 ($6\times CH_3$), 26.7 ppm ($6\times CH_3$); FT-IR (microscope): $\tilde{\nu}$ = 3507, 3327, 2979, 2931, 2869, 1473, 1455, 1387, 1364, 1193, 1141, 1100, 1069, 1047, 1020, 1008, 908, 872, 732 cm^{-1}; ESI-MS: m/z (%): 1200 (100) $[M+H]^+$.

9-(Aziridin-1-yl)-6,12,15,18-tetrakis(*tert*-butylperoxy)-1-hydroxy-1,6,9,12,15,18-hexahydro(C_{60}-I_h)[5,6]fullerene (13s): A solution of $HCl{\cdot}NH_2CH_2CH_2Br$ (400 mg, 2.0 mmol) and NaOH (156 mg, 3.9 mmol) in water (3 mL) was stirred at 50°C for 1 hour and the product was then extracted three times with CH_2Cl_2 (5 mL). The extracts were combined and concentrated[21] and the concentrated extract was added to compound **3** (150 mg, 0.13 mmol) dissolved in CH_2Cl_2 (20 mL). The solution was stirred at RT in darkness and progress was monitored by TLC. After 1.5 h, the solution was washed three times with water and then purified by chromatography on a silica gel column, with elution with toluene and ethyl acetate 10:1, to give **13** as the first band (36 mg, 25%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.6 (s, 1H), 2.49 (d, J = 3.74 Hz, 2H), 2.15 (d, J = 3.74 Hz, 2H), 1.48 (s, 18H), 1.44 ppm (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz, all signals represent 2C except when noted): δ = 155.5, 150.5, 149.1, 148.9, 148.5, 148.4 (5C), 148.3, 147.7, 147.6, 147.4, 147.3, 147.2 (1C), 146.92, 145.90, 145.2 (4C), 144.6, 144.4, 144.3, 143.77, 143.76, 143.4, 143.1, 142.5, 141.4, 139.1, 84.1, 82.7, 81.9 ($C(CH_3)_3$), 81.8 ($C(CH_3)_3$), 81.0, 71.1, 26.7 ($6\times CH_3$), 26.7 ($6\times CH_3$), 26.0 ppm ($2\times CH_2$); FT-IR (microscope): $\tilde{\nu}$ = 3512, 3063, 2978, 2930, 1474, 1464, 1387, 1363, 1193, 1100, 1047, 1021, 1004, 871, 732 cm^{-1}; ESI-MS: m/z (%): 1136 (100) $[M+H]^+$.

6,18-Bis(*tert*-butylperoxy)-12,15-bis(pyrrolidin-1-yl)-6,12,15,18-tetrahydrooxireno[2′,3′:1,9]-2a,14a-dioxa-2(12)a,14(15)a-dihomo(C_{60}-I_h)[5,6]-fullerene (14a): Compound **2c** (90 mg, 0.08 mmol) was dissolved in CCl_4 (120 mL), and an excess of pyrrolidine (25 μL) in CCl_4 (20 mL) was added. The solution was stirred at 0°C in darkness and progress of the reaction was monitored by TLC. After 15 min, the solution was purified

by chromatography on a silica gel column, with elution with toluene, to give **14a** as the first band. Yield: 10 mg (12%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.5–3.3 (m, 8H), 2.0 (m, 8H), 1.40 (s, 9H), 1.39 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 155.2, 151.3, 151.2, 149.9, 149.5, 149.3, 149.0, 148.9, 148.8, 148.7, 148.5, 148.4, 148.2, 148.13, 148.08, 147.8, 147.7 (2C), 147.6, 147.4, 147.09, 147.06, 146.7, 146.3, 145.5, 145.4 (2C), 145.3 (2C), 144.6, 144.4, 144.24, 144.23, 144.16, 143.9, 143.8, 143.2, 142.90, 142.85, 142.12, 142.08, 141.13, 141.12, 140.8, 140.4, 139.7, 138.6, 138.3, 137.6, 133.3, 132.6, 130.0, 129.8, 125.2, 110.9, 99.6, 83.4, 83.1, 81.6, 81.3, 71.3, 69.8, 48.6 (CH_2), 46.6 (CH_2), 26.7 ($3\times CH_3$), 26.6 ($3\times CH_3$), 25.5 (CH_2), 24.9 ppm (CH_2); FT-IR (microscope): $\tilde{\nu}$ = 2973, 2926, 2870, 2853, 1461, 1386, 1375, 1363, 1260, 1242, 1194, 1091, 1046, 993, 857, 756 cm^{-1}; ESI-MS: *m*/*z* (%): 1016 (100) $[M-C_4H_8N]^+$, 1087 (20) $[M+H]^+$; negative mode: *m*/*z*: 1117 (100) $[M+CH_3O]^-$.

Single crystals were obtained by slow evaporation of a solution of **14a** in $CDCl_3$.[14]

6,18-Bis(*tert*-butylperoxy)-12,15-bis(piperidin-1-yl)-6,12,15,18-tetrahydrooxireno[2′,3′:1,9]-2a,14a-dioxa-2(12)a,14(15)a-dihomo(C_{60}-I_h)[5,6]-fullerene (14b): Compound **2c** (50 mg, 0.04 mmol) was dissolved in $CHCl_3$ (20 mL), and an excess of piperidine (30 μL) in $CHCl_3$ (2 mL) was added. The solution was stirred at RT in darkness and progress of the reaction was monitored by TLC. After 3 min the solution was purified by chromatography on a silica gel column, with elution with toluene, to give **14b** as the first band (10 mg, 21%).

Compound 14b (298 K): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.6–3.0 (m, 8H), 1.5–1.8 (m, 8H), 1.46 (s, 9H), 1.38 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 154.8, 151.36, 151.35, 151.3, 150.1, 149.5, 149.4, 149.0, 148.9, 148.8, 148.5 (2C), 148.3, 148.2 (2C), 147.8, 147.7, 147.7, 147.6, 147.5, 147.13, 147.07, 146.7, 146.4, 145.8, 145.5, 145.33 (2C), 145.25, 144.53 (2C), 144.45, 144.32, 144.29, 144.0, 143.8, 143.3, 143.0, 142.9, 142.2, 142.1, 141.0, 140.8, 140.6, 140.2, 139.7, 138.33, 138.27, 137.6, 134.5, 132.9, 129.8, 129.5, 125.0, 114.3, 102.7, 83.4, 83.1, 81.6, 81.5, 71.3, 69.8, 49.2 (CH_2), 26.8 ($3\times CH_3$), 26.8 ($3\times CH_3$), 26.2 (CH_2), 26.1 (CH_2), 24.7, 24.2 ppm (CH_2); FT-IR (microscope): $\tilde{\nu}$ = 2977, 2934, 2852, 1463, 1452, 1442, 1385, 1363, 1197, 1090, 886, 855, 733 cm^{-1}; ESI-MS: *m*/*z* (%): 1030 (100) $[M-(CH_2)_5N]^+$, 1115 (25) $[M+H]^+$; negative mode: *m*/*z*: 1146 (100) $[M+MeOH]^-$.

Compound 14b (333 K): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.25–3.35 (m, 8H), 1.76 (m, 4H), 1.70(m, 4H), 1.60 (m, 4H), 1.41 (s, 9H), 1.38 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 154.3, 151.33, 151.32, 151.28, 150.2, 149.5, 149.4, 149.0, 148.9, 148.8, 148.51, 148.48, 148.3, 148.2, 148.1, 147.8, 147.72, 147.67, 147.6, 147.5, 147.13, 147.07, 146.7, 146.4, 145.9, 145.5, 145.3, 145.3, 145.2, 144.6, 144.5, 144.3, 144.2 (2C), 144.0, 143.8, 143.2, 142.9, 142.9, 142.13, 142.06, 141.0, 140.9, 140.8, 140.2, 139.7, 138.4, 138.2, 137.6, 134.5, 133.0, 130.0, 129.4, 125.0, 114.3, 102.8, 83.5, 83.2, 81.4, 81.2, 71.3, 69.8, 49.1 (CH_2), 47.6 (CH_2), 26.8 ($3\times CH_3$), 26.7 ($3\times CH_3$), 26.2 (CH_2), 26.0 (CH_2), 24.6 (CH_2), 24.2 (CH_2), assignment was confirmed by DEPT spectrum.

12,15-Bis(azepan-1-yl)-6,18-bis(*tert*-butylperoxy)-6,12,15,18-tetrahydrooxireno[2′,3′:1,9]-2a,14a-dioxa-2(12)a,14(15)a-dihomo(C_{60}-I_h)[5,6]fullerene (14c): Compound **2c** (90 mg, 0.08 mmol) was dissolved in CH_2Cl_2 (15 mL) and an excess of hexamethyleneimine[23] was added. The solution was stirred at RT in darkness and progress was monitored by TLC. After 5 min, the solution was washed three times with water and then purified by chromatography on a silica gel column, with elution with toluene and petroleum ether 1:1, to give **14c** as the first band. Yield: 8 mgn (9%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.7–3.2 (m, 8H), 1.9–1.5 (m, 16H), 1.42 (s, 9H), 1.36 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 155.4, 151.31, 151.27, 150.4, 150.3, 149.3, 149.2, 148.99, 148.98, 148.8, 148.5, 148.2, 148.1, 148.1, 148.96, 147.78, 147.7 (2C), 147.6, 147.5, 147.1, 147.0, 146.6, 146.4, 145.6, 145.3, 145.23, 145.16, 145.0, 144.5, 144.3, 144.22, 144.16, 144.01, 143.97, 143.8, 143.0, 143.0, 142.9, 142.0 (2C), 141.00, 140.98, 140.6, 140.2, 139.9, 138.3, 138.0, 137.4, 133.8, 133.1, 130.2, 129.8, 125.1, 115.0, 103.8, 83.7, 83.1, 81.7, 81.4, 71.3, 69.6, 50.6 ($2\times CH_2$), 48.7 ($2\times CH_2$), 48.3 ($2\times CH_2$), 29.5 ($2\times CH_2$), 27.3 ($4\times CH_2$), 27.7 ($3\times CH_3$), 26.7 ppm ($3\times CH_3$); FT-IR (microscope): $\tilde{\nu}$ = 2977, 2925, 2852, 1460, 1363, 1241, 1193, 1158, 872, 858, 756 cm^{-1}; ESI-MS: *m*/*z* (%): 1044 (100) $[M-C_6H_{12}N]^+$, 1143(50) $[M+H]^+$; negative mode: *m*/*z*: 1175 (100) $[M+NH_2OH]^-$.

6,18-Bis(*tert*-butylperoxy)-12,15-bis(morpholin-4-yl)-6,12,15,18-tetrahydrooxireno[2′,3′:1,9]-2a,14a-dioxa-2(12)a,14(15)a-dihomo(C_{60}-I_h)[5,6]-fullerene (14d): Compound **2c** (50 mg, 0.04 mmol) was dissolved in $CHCl_3$ (20 mL), and an excess of morpholine (40 μL) in $CHCl_3$ (1 mL) was added. The solution was stirred at RT in darkness and progress was monitored by TLC. After 50 min, the solution was purified by chromatography on a silica gel column, with elution with benzene and ethyl acetate 10:1, to give **14d** as the first band (11 mg, 25%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.89–3.82 (m, 8H), 3.4–3.3 (m, 8H), 1.43 (s, 9H), 1.39 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 153.5, 151.6, 151.4, 151.2, 149.8, 149.4, 149.3, 149.1, 148.9, 148.7, 148.6, 148.5, 148.3, 148.17, 148.15, 147.9, 147.8, 147.7, 147.6, 147.5, 147.2, 147.0, 146.7, 146.3, 145.6, 145.2 (3C), 145.1, 144.6, 144.5, 144.31, 144.28, 144.0, 143.9, 143.8, 143.2, 142.9, 142.9, 142.3, 142.2, 141.1, 140.9, 140.5, 140.3, 138.4, 138.2, 137.8, 137.4, 134.9, 132.8, 130.2, 128.7, 124.7, 113.2, 101.7, 83.3, 83.0, 81.7, 81.5, 71.3, 69.9, 67.0 (CH_2), 48.2 (CH_2), 46.7 (CH_2), 26.8 ($3\times CH_3$), 26.7 ppm ($3\times CH_3$); FT-IR (microscope): $\tilde{\nu}$ = 2977, 2915, 2893, 2853, 1584, 1453, 1387, 1364, 1298, 1269, 1197, 1173, 1117, 1092, 1042, 1018, 984, 893, 856, 756 cm^{-1}; ESI-MS: *m*/*z* (%): 1032 (100) $[M-C_4H_8NO]^+$, 1119 (50) $[M+H]^+$; negative mode 1150 (100) $[M+MeOH]^-$.

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[11] Isomerically pure products were isolated, but it is not possible to assign their structures at present.

[12] Crystal data for **4a**: $C_{87}H_{55}NO_{12}$, $M = 1306.32$, triclinic, $P\bar{1}$, $a = 9.961(2)$, $b = 13.569(3)$, $c = 24.135(5)$ Å, $\alpha = 91.30(3)$, $\beta = 91.51(3)$, $\gamma = 109.84(3)°$, $V = 3065.8(11)$ Å^3, $T = 143(2)$ K, $Z = 2$, $\rho_{calcd} = 1.415$ Mg m^{-3}, graphite monochromatized $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, crystal size $0.60 \times 0.40 \times 0.12$ mm^3. Data collected on a Rigaku RAXIS RAPID IP diffractometer, 10659 unique reflections ($R_{int} = 0.04579$). Refinement on F^2, final residuals $R1 = 0.0693$ for 4640 reflections with $I > 2\sigma I$), $wR2 = 0.1913$ for all data. CCDC-284233 (**4a**), -284234 (**6d**), and -290716 (**14a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] Crystal data for **6d**: $C_{81}H_{48}Cl_{13}NO_{11}$, $M = 1317.55$, monoclinic, $P2(1)/c$, $a = 23.629(5)$, $b = 13.811(3)$, $c = 19.000(4)$ Å, $\alpha = 90$, $\beta = 99.96(3)$, $\gamma = 90°$, $V = 6107(2)$ Å^3, $T = 143(2)$ K, $Z = 4$, $\rho_{calcd} = 1.433$ Mg m^{-3}, graphite monochromatized $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, crystal size $0.35 \times 0.20 \times 0.08$ mm^3. Data collected on a Rigaku RAXIS RAPID IP diffractometer, 10700 unique reflections ($R_{int} = 0.0538$). Refinement on F^2, final residuals $R1 = 0.0558$ for 3408 reflections with $I > 2\sigma I$), $wR2 = 0.1103$ for all data.

[14] Crystal data for **14a**: $C_{79}H_{37}Cl_{19}N_2O_7$, $M = 1445.16$, triclinic, $P\bar{1}$, $a = 9.7211(19)$, $b = 13.513(3)$, $c = 23.003(5)$ Å, $\alpha = 88.89(3)$, $\beta = 87.79(3)$, $\gamma = 76.64(3)°$, $V = 2969.9(10)$ Å^3, $T = 143(2)$ K, $Z = 2$, $\rho_{calcd} = 1.616$ Mg m^{-3}, graphite monochromatized $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, crystal size $0.40 \times 0.20 \times 0.12$ mm^3. Data collected on a Rigaku RAXIS RAPID IP diffractometer, 13297 unique reflections ($R_{int} = 0.0363$). Refinement on F^2, final residuals $R1 = 0.0553$ for 7966 reflections with $I > 2\sigma I$), $wR2 = 0.1620$ for all data.

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