Tetrahedron Letters 54 (2013) 2146–2148

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Catalytic cycloaddition of diazo amides to fullerene C_{60}

Airat R. Tuktarov *, Liliya L. Khuzina, Natal'ya R. Popod'ko, Usein M. Dzhemilev

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, 141 Prospekt Oktyabrya, Ufa 450075, Russia

ARTICLE INFO

Article history:
Received 8 December 2012
Revised 24 January 2013
Accepted 13 February 2013
Available online 20 February 2013

Keywords:
[60]Fullerene
Diazo compounds
Diazo amides
Cycloaddition
Metal complex catalyst
Pyrazolinofullerene
Methanofullerene

ABSTRACT

A general catalytic procedure for the cycloaddition of diazo amides to fullerene C_{60} in the presence of the three-component catalyst, $Pd(acac)_2$–PPh_3–Et_3Al, has been developed. Depending on the reaction conditions, pyrazolinofullerenes or methanofullerenes are formed.

1,3-Dipolar cycloaddition between diazo compounds and fullerene C_{60} is the most effective and convenient route to homo- and methanofullerenes, which are of special interest as new materials for science and technology, as evidenced by numerous reviews[1–6] covering methods for synthesizing fullerenes[1–4] and aspects of their use.[5,6]

Analysis of the literature, however, has shown that thermal cycloadditions of diazo compounds to fullerene C_{60} proceed non-selectively and produce a mixture of methano- and stereoisomeric homofullerenes.[7–11]

Metal complex catalysts (based upon palladium and rhodium) can direct the cycloaddition reaction towards the predominant formation of individual homo-, methano- or pyrazolinofullerenes.[4,12–18]

At the onset of our research, only a thermal reaction of diazo amides with C_{60} to afford a mixture of 6,6-close and stereoisomeric 5,6-open cycloadducts had been described in the literature.[19] Information concerning catalytic cycloadditions between diazo amides and fullerenes was absent from the literature.

In continuation of our work[13–18] on both the cycloaddition reactions of diazo compounds to fullerenes under the action of metal complex catalysts, and to develop effective methods for the synthesis of synthetically important functionalized fullerenes, we have studied the catalytic 1,3-dipolar cycloadditions of various diazo amides to fullerene C_{60}.

Diazo amides derived from glycine and cyclohexylamine were selected as model compounds.

Previously, we showed that the three-component catalytic system, $Pd(acac)_2$–PPh_3–Et_3Al, favoured cycloadditions of diazo alkanes,[13–16] diazo acetates,[17,20–23] diazo ketones[24] and diazo thioates[18,25] to fullerene C_{60} with high yields and selectivity. These studies also revealed that the ratios of the starting reagents defined the direction of the reaction leading to the formation of homofullerenes or methanofullerenes. Taking into account these findings we performed further research in this arena.

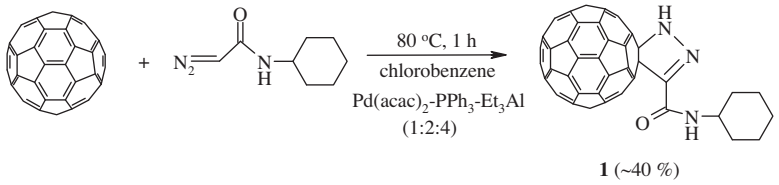
Our experiments revealed that the reaction between fullerene C_{60} and a fivefold molar excess of *N*-cyclohexyl-2-diazoacetamide (80 °C, 1 h, chlorobenzene),[26] in the presence of 20 mol % of the three-component catalytic system, $Pd(acac)_2$–PPh_3–Et_3Al (1:2:4), gave a single pyrazolinofullerene **1**[27] in 40% yield relative to the starting fullerene C_{60} (Scheme 1). An elevated temperature (100 °C) and increased reaction time (3 h) did not significantly increase the yield of the target [2+3] cycloadduct **1**. This reaction, without a catalyst, leads to a formation of a mixture of methano- and stereoisomeric homofullerenes, as reported previously[19] for the thermal cycloaddition of diazo amides to fullerene C_{60}.

The MALDI–TOF mass spectrum of pyrazolinofullerene **1**, which was isolated by preparative HPLC, contained an intense molecular ion peak $[M+H]^+$ at *m*/*z* 888.112 (ca. 888.114) along with a fragment ion peak $[C_{60}N_2H]^+$ at *m*/*z* 749.033, which provided strong evidence for the proposed structure.

The one-dimensional (^1H, ^{13}C) and two-dimensional (COSY, HSQC, HMBC) NMR experiments on compound **1** also gave evidence for the presence of the pyrazoline ring linked to the amide group. The ^{13}C NMR spectrum of the pyrazoline moiety exhibited three signals. Two of them (δ_C 80.09 and 87.30) were due to

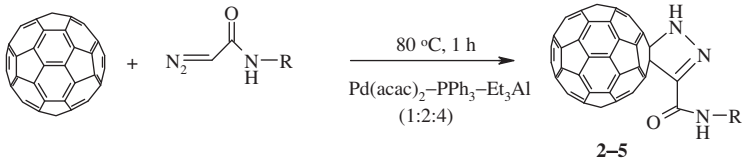
* Corresponding author. Tel./fax: +7 347 2842750.
E-mail address: tuktarovar@gmail.com (A.R. Tuktarov).

0040-4039/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetlet.2013.02.037

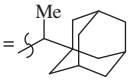
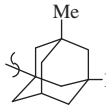


1 (~40 %)

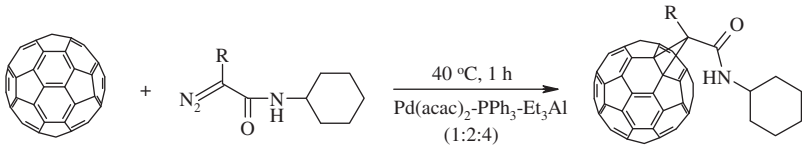
Scheme 1. Catalytic cycloaddition of *N*-cyclohexyl-2-diazoacetamide to [60]fullerene.



2–5

2: R = Ph (~33%); **3:** R =  (~39%); **4:** R =  (~30%); **5:** R=  (~36%)

Scheme 2. Catalytic synthesis of pyrazolinofullerenes **2**–**5**.



6–8

6: R= Me (50%); **7:** R= *i*-Bu (47%); **8:** R= -$(CH_2)_2$SMe (40%)

Scheme 3. Reactions of [60]fullerene with diazo amides bearing a substituent alpha to the diazo group.

annelated sp^3 hybridized C-atoms of the fullerene skeleton, while the third signal (δ_C 136.23) was assigned to the carbon atom attached to the nitrogen of the five-membered heterocycle by a double bond.

Additionally, between δ_C 25 and δ_C 50 in the ^{13}C NMR spectrum of pyrazolinofullerene **1**, we observed low frequency signals attributable to the cyclohexyl moiety [δ_C 25.38 (2C), 26.05 (1C), 33.31 (2C), 49.08 (1C)]. Also seen were high frequency signals characteristic of the fullerene skeleton (25 signals in the region between δ_C 137 and δ_C 149), and the carbonyl carbon atom (δ_C 157.61).

In order to extend the application of this fullerene cycloaddition and to investigate patterns in the yield and selectivity on the size and structure of the substituent on the amide group of the diazo compound, we studied the reactions between fullerene C_{60} and sterically hindered diazo amides, based on glycine or aniline, and also derived from adamantane-containing amines (Scheme 2).

Thus, under the optimized conditions [80 °C, 1 h, $Pd(acac)_2$–$2PPh_3$–$4Et_3Al$] the corresponding monoadducts **2**–**5**[28–31] were obtained in moderate yields (up to 40%). The experiments also showed that bulky substituents on the amide group did not influence the reaction pathway.

It is known that pyrazolinofullerenes derived from fullerene C_{60} and diazo acetates[17,32] or diazothioates[18] can undergo thermal transformations to afford the corresponding methanofullerenes. Refluxing [2+3] cycloadducts **1**–**5** for 100 h in 1,2-dichlorobenzene did not result in the formation of methanofullerenes, and in all the experiments the starting pyrazolinofullerenes remained unchanged.

Earlier,[18] we showed that the substituent alpha to the diazo group of the diazo compound was able to destabilize the pyrazolinofullerene formed giving rise to a [2+1] cycloadduct. In the hope of developing a selective method for the synthesis of methanofullerenes, we studied the reactions between C_{60} and α-substituted diazo amides derived from alanine, leucine, methionine and cyclohexylamine.

The reactions between the above diazo amides and fullerene C_{60} under the optimized conditions (40 °C, 1 h) in the presence of 20 mol% of $Pd(acac)_2$–PPh_3–Et_3Al (1:2:4), led exclusively, to methanofullerenes **6–8**[33–35] in 40–50% yields (Scheme 3).

The structures of methanofullerenes **6**–**8** were reliably established by means of standard analytical (1D and 2D NMR, IR, UV, MALDI–TOF) methods.

The intense molecular ion peak at *m*/*z* 873.120 (ca. 873.115) in the MALDI–TOF spectrum of compound **6** provided strong evidence for the formation of the [2+1]-cycloadduct.

The ^{13}C NMR spectrum of compound **6** contained 27 resonances in the fullerene region between δ_C 138 and δ_C 149, and three with twice the intensity. The cyclopropane fragment has a plane of symmetry and in the spectrum exhibited two signals resonating at δ_C 78.30. The signals of the bridge carbon atom (δ_C 62.00) bound to the amide group (δ_C 165.95) and the methyl group (δ_C 17.32), which in the ^1H NMR spectrum manifested itself as a singlet at δ_H 2.54, also provided evidence for the formation of the cyclopropane–annelated 6,6-substituted fullerene.

In conclusion, for the first time, we have reported catalytic cycloadditions between diazo amides and fullerene C_{60} under the influence of the three-component catalytic system, $Pd(acac)_2$–PPh_3–Et_3Al, to produce pyrazolinofullerenes or methanofullerenes depending on the reaction conditions.

References and notes

1. Diederich, F.; Thilge, C. *Science* **1996**, *271*, 317.
2. Yurovskaya, M. A.; Trushkov, I. V. *Russ. Chem. Bull.* **2002**, *51*, 367.
3. Thilgen, C.; Diederich, F. *Chem. Rev.* **2006**, *106*, 5049.
4. Tuktarov, A. R.; Dzhemilev, U. M. *Russ. Chem. Rev.* **2010**, *79*, 585.
5. Troshin, P. A.; Lyubovskaya, R. N.; Razumov, V. F. *Nanotechnol. Russ.* **2008**, *3*, 242.
6. Da Ros, T.; Prato, M. *Chem. Commun.* **1999**, 663.
7. Prato, M.; Lucchini, V.; Maggini, M.; Stimpfl, E.; Scorrano, G.; Eiermann, M.; Suzuki, T.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 8479.
8. Li, Z.; Bouhadir, K. H.; Shevlin, P. *Tetrahedron Lett.* **1996**, *37*, 4652.
9. Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 1231.
10. Zhu, C. C.; Xu, Y.; Liu, Y. Q.; Zhu, D. B. *J. Org. Chem.* **1997**, *62*, 1996.
11. Nakamura, Y.; Inamura, K.; Oomuro, R.; Laurenco, R.; Tidwell, T. T.; Nishimura, J. *Org. Biomol. Chem.* **2005**, *3*, 3032.
12. Roberti, M.; Natalini, B.; Andrisano, V.; Seraglia, R.; Gioiello, A.; Pellicciari, R. *Tetrahedron* **2010**, *66*, 7329.
13. Tuktarov, A. R.; Korolev, V. V.; Sabirov, D. Sh.; Dzhemilev, U. M. *Russ. J. Org. Chem.* **2011**, *47*, 41.
14. Dzhemilev, U. M.; Tuktarov, A. R.; Korolev, V. V.; Khalilov, L. M. *Petroleum Chem.* **2011**, *51*, 123.
15. Tuktarov, A. R.; Korolev, V. V.; Tulyabaev, A. R.; Popod'ko, N. R.; Khalilov, L. M.; Dzhemilev, U. M. *Tetrahedron Lett.* **2011**, *52*, 834.
16. Tuktarov, A. R.; Khuzin, A. A.; Korolev, V. V.; Dzhemilev, U. M. *Russ. J. Org. Chem.* **2012**, *48*, 99.
17. Tuktarov, A. R.; Khuzina, L. L.; Dzhemilev, U. M. *Russ. Chem. Bull.* **2011**, *60*, 662.
18. Tuktarov, A. R.; Khuzin, A. A.; Popod'ko, N. R.; Dzhemilev, U. M. *Tetrahedron Lett.* **2012**, *53*, 3123.
19. Skiebe, A.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1994**, 335.
20. Tuktarov, A. R.; Akhmetov, A. R.; Kamalov, R. F.; Khalilov, L. M.; Pudas, M.; Ibragimov, A. G.; Dzhemilev, U. M. *Russ. J. Org. Chem.* **2009**, *45*, 1168.
21. Tuktarov, A. R.; Akhmetov, A. R.; Sabirov, D. Sh.; Khalilov, L. M.; Ibragimov, A. G.; Dzhemilev, U. M. *Russ. Chem. Bull.* **2009**, *58*, 1724.
22. Tuktarov, A. R.; Akhmetov, A. R.; Kirichenko, G. N.; Glazunova, V. I.; Khalilov, L. M.; Dzhemilev, U. M. *Russ. J. Appl. Chem.* **2010**, *83*, 1238.
23. Tuktarov, A. R.; Akhmetov, A. R.; Khasanova, L. L.; Khalilov, L. M.; Dzhemilev, U. M. *Russ. Chem. Bull.* **2010**, *59*, 1959.
24. Tuktarov, A. R.; Akhmetov, A. R.; Khalilov, L. M.; Dzhemilev, U. M. *Russ. Chem. Bull.* **2010**, *59*, 611.
25. Tuktarov, A. R.; Khuzin, A. A.; Popod'ko, N. R.; Dzhemilev, U. M. *Fullerenes Nanotubes Carbon Nanostruct.* **2013**. http://dx.doi.org/10.1080/1536383X.2012.690463.
26. *Catalytic cycloaddition of diazo amides to [60]fullerene (general procedure).* $Pd(acac)_2$ (0.00278 mmol) in chlorobenzene (0.2 mL) and PPh_3 (0.00556 mmol) in chlorobenzene (0.21 mL) were loaded into a glass reactor. The mixture was cooled to −5 to 0 °C. Et_3Al (0.01112 mmol) in toluene (0.1 mL) was added under a dry argon current, and on stirring the mixture, the color changed from light-yellow to light-brown. To the obtained catalyst, fullerene C_{60} (0.0139 mmol) in chlorobenzene (1.5 mL) was added at ~20 °C and the solution became deep-green in color. The mixture was heated to 80 °C, the diazo compound (0.0695 mmol) in chlorobenzene (0.2 mL) was added dropwise over 2–3 min, and the mixture was stirred for 1 h. The mixture was cooled to ~20 °C and treated with aqueous HCl. Toluene (7 mL) was added, and the organic layer passed through a column containing a small amount of silica gel. The reaction products and the starting fullerene C_{60} were separated by preparative HPLC, with toluene as the eluent.
27. *N*-Cyclohexylcarboamidyl-1′*H*-[1,2]pyrazolino[4′,5′:1,9](C_{60}–I_h)-[5,6]fullerene (**1**) (isolated yield 40%). IR: 527, 750, 1179, 1457, 1523, 1633 cm^{-1}. UV ($CHCl_3$), λ_{max}, nm: 260, 316, 427. ^1H NMR (400 MHz, $CDCl_3$): δ 1.37 and 1.78 (both m, 2H, CH_2), 1.46 and 2.16 (both m, 4H, $2CH_2$), 1.88 (m, 4H, $2CH_2$), 4.01 (m, 1H, CH), 6.78 (s, 1H, NH), 8.08 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.38, 26.05, 33.31, 49.08, 80.09, 136.23, 137.11, 140.28, 141.87, 141.94, 142.29, 142.41, 142.52, 142.67, 142.87, 142.93, 143.17, 144.18, 144.38, 144.67, 145.23, 145.41, 145.76, 146.02, 146.06, 146.36, 146.45, 147.17, 147.53, 147.86, 148.39, 157.61. MALDI–TOF, *m*/*z* 888.027 $[M+H]^+$ ($C_{68}H_{13}N_3O$).
28. *N*-Phenylcarboamidyl-1′*H*-[1,2]pyrazolino[4′,5′:1,9](C_{60}–I_h)-[5,6]fullerene (**2**) (isolated yield 33%). IR: 526, 756, 1180, 1364, 1480, 1635 cm^{-1}. UV ($CHCl_3$), λ_{max}, nm: 260, 330, 430. ^1H NMR (400 MHz, $CDCl_3$): δ 7.23 (m, 1H, CH), 7.43 (m, 2H, 2CH), 7.73 (m, 2H, 2CH), 8.81 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 62.90, 88.18, 119.92, 125.28, 127.67, 136.36, 137.06, 137.17, 140.33, 140.35, 141.93, 141.94, 142.27, 142.44, 142.56, 142.65, 142.69, 142.91, 142.96, 142.98, 143.19, 144.08, 144.20, 144.40, 144.64, 145.26, 145.29, 145.40, 145.85, 146.06, 146.61, 146.43, 146.49, 147.21, 147.57, 147.89, 148.69, 156.09. MALDI–TOF, *m*/*z* 881.065 $[M]^+$ ($C_{68}H_7N_3O$).
29. *N*-[1-(1-Adamantyl)ethyl]carboamidyl-1′*H*-[1,2]pyrazolino[4′,5′:1,9](C_{60}–I_h)-[5,6]fullerene (**3**) (isolated yield 39%). IR: 526, 752, 1180, 1448, 1520, 1671 cm^{-1}. UV ($CHCl_3$), λ_{max}, nm: 257, 316, 427. ^1H NMR (400 MHz, $CDCl_3$): δ 1.29 (d, 3H, CH_3, J = 5.6 Hz), 1.55 (m, 6H, $3CH_2$), 1.79 (m, 6H, $3CH_2$), 2.13 (m, 3H, 3CH), 3.96 (m, 1H, CH), 6.94 (d, 1H, NH, J = 9.6 Hz), 8.01 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.76, 29.01, 36.40, 37.46, 38.79, 53.81, 76.14, 136.24, 136.31, 137.08, 137.19, 140.28, 140.30, 141.86, 141.89, 141.95, 141.97, 142.23, 142.26, 142.41, 142.53, 142.68, 142.87, 142.88, 142.90, 142.93, 142.94, 143.18, 144.18, 144.37, 144.41, 144.43, 145.67, 144.69, 145.23, 145.25, 145.41, 145.43, 145.77, 146.02, 146.05, 146.06, 146.37, 146.38, 146.45, 147.17, 147.54, 147.62, 147.86, 148.47, 158.20. MALDI–TOF, *m*/*z* 968.221 $[M+H]^+$ ($C_{74}H_{21}N_3O$).
30. *N*-(1-Adamantyl)carboamidyl-1′*H*-[1,2]pyrazolino[4′,5′:1,9](C_{60}–I_h)-[5,6]fullerene (**4**) (isolated yield 30%). IR: 523, 750, 1181, 1455, 1519, 1672 cm^{-1}. UV ($CHCl_3$), λ_{max}, nm: 257, 327, 424. ^1H NMR (400 MHz, $CDCl_3$): δ 1.76 (m, 6H, $3CH_2$), 2.05 (m, 6H, $3CH_2$), 2.21 (m, 3H, 3CH), 6.84 (s, 1H, NH), 8.08 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.10, 36.66, 41.86, 53.16, 66.09, 80.03, 136.22, 140.27, 140.32, 141.89, 141.94, 142.25, 142.41, 142.52, 142.67, 142.86, 142.93, 142.99, 144.19, 144.39, 144.48, 144.68, 145.22, 145.24, 145.42, 145.75, 146.01, 146.05, 146.36, 146.45, 147.16, 147.57, 147.84, 148.71, 157.25. MALDI–TOF, *m*/*z* 940.147 $[M+H]^+$ ($C_{72}H_{17}N_3O$).
31. *N*-(3,5-Dimethyl-1-adamantyl)carboamidyl-1′*H*-[1,2]pyrazolino[4′,5′:1,9](C_{60}–I_h)-[5,6]fullerene (**5**) (isolated yield 36%). IR: 526, 754, 1180, 1454, 1518, 1674 cm^{-1}. UV ($CHCl_3$), λ_{max}, nm: 260, 326, 427. ^1H NMR (400 MHz, $CDCl_3$): δ 1.13 (s, 6H, 2 CH_3), 1.3–1.5 (m, 10H, $5CH_2$), 2.06 (m, 1H, CH), 2.21 (m, 2H, CH_2), 6.86 (s, 1H, NH), 8.08 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.46, 31.38, 32.36, 38.35, 40.49, 42.83, 47.52, 48.59, 50.71, 66.21, 79.98, 136.30, 140.29, 140.31, 141.73, 141.93, 142.16, 142.40, 142.48, 142.59, 142.86, 142.94, 143.18, 144.11, 144.34, 144.49, 144.72, 145.15, 145.31, 145.74, 146.15, 146.21, 147.16, 147.31, 147.69, 148.13, 148.95, 149.40, 158.70. MALDI–TOF, *m*/*z* 967.208 $[M]^+$ ($C_{74}H_{21}N_3O$).
32. Wang, G.-W.; Li, Y.-J.; Peng, R.-F.; Liang, Z.-H.; Liu, Y.-C. *Tetrahedron* **2004**, *60*, 3921.
33. 1′-Methyl-1′-[*N*-cyclohexylamidyl](C_{60}–I_h)[5,6]fullero[2′,3′:1,9]cyclopropane (**6**) (isolated yield 50%). IR: 527, 577, 722, 748, 1021, 1182, 1431, 1456, 1685 cm^{-1}. UV ($CHCl_3$), λ_{max}, nm: 259, 328, 426. ^1H NMR (400 MHz, $CDCl_3$): δ 1.39 and 2.18 (both m, 4H, $2CH_2$), 1.52 and 1.93 (both m, 4H, $2CH_2$), 1.77 (m, 2H, CH_2), 2.54 (s, 3H, CH_3), 4.29 (m, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.32, 25.46, 26.05, 33.53, 49.69, 62.00, 78.30, 138.07, 138.82, 139.33, 141.19, 141.54, 141.69, 142.04, 142.24, 142.31, 142.48, 142.83, 143.04, 143.18, 143.56, 143.71, 143.84, 143.90, 144.01, 144.13, 144.33, 144.54, 144.87, 145.23, 145.55, 146.39, 147.65, 148.32, 165.95. MALDI–TOF, *m*/*z* 873.120 $[M]^+$ ($C_{69}H_{15}NO$).
34. 1′-*iso*-Butyl-1′-[*N*-cyclohexylamidyl](C_{60}–I_h)[5,6]fullero[2′,3′:1,9]cyclopropane (**7**) (isolated yield 47%). IR: 527, 573, 1093, 1176, 1448, 1508, 1636 cm^{-1}. UV ($CHCl_3$), λ_{max}, nm: 261, 329, 427. ^1H NMR (400 MHz, $CDCl_3$): δ 0.99 (d, 6H, $2CH_3$, J = 6.0 Hz), 1.30 (m, 1H, CH), 1.38 and 2.15 (both m, 4H, $2CH_2$), 1.51 and 1.83 (both m, 4H, $2CH_2$), 1.60 (m, 2H, CH_2), 1.72 (m, 2H, CH_2), 4.23 (m, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.12, 25.30, 25.97, 26.20, 33.47, 40.34, 49.23, 63.98, 79.32, 137.95, 138.14, 138.71, 138.41, 140.51, 141.42, 141.56, 142.11, 142.19, 142.27, 142.29, 142.52, 142.90, 143.13, 143.18, 143.24, 143.51, 143.63, 143.87, 144.22, 144.78, 144.87, 145.17, 145.28, 147.32, 147.61, 148.87, 165.88. MALDI–TOF, *m*/*z* 915.169 $[M]^+$ ($C_{72}H_{21}NO$).
35. 1′-[2″-(Methylthio)ethyl]-1′-[*N*-cyclohexylamidyl](C_{60}–I_h)[5,6]fullero[2′,3′:1,9]cyclopropane (**8**) (isolated yield 40%). IR: 525, 578, 735, 1028, 1182, 1428, 1675 cm^{-1}. UV ($CHCl_3$), λ_{max}, nm: 260, 328, 426. ^1H NMR (400 MHz, $CDCl_3$): δ 1.39 and 2.74 (both m, 4H, $2CH_2$), 1.54 and 1.88 (both m, 4H, $2CH_2$), 1.78 (m, 2H, CH_2), 2.14 (s, 3H, CH_3), 3.12 (t, 2H, CH_2, J = 7.2 Hz), 3.25 (t, 2H, CH_2, J = 7.2 Hz), 4.27 (m, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.20, 25.64, 25.73, 30.17, 31.33, 33.31, 49.35, 63.82, 79.07, 137.09, 137.87, 138.10, 138.16, 139.19, 140.53, 141.44, 141.79, 142.15, 142.20, 142.26, 142.37, 142.44, 142.99, 143.16, 143.26, 143.48, 143.74, 143.90, 144.23, 144.35, 144.53, 144.80, 144.88, 145.13, 145.25, 145.39, 145.53, 146.57, 147.30, 147.53, 147.85, 165.93. MALDI–TOF, *m*/*z* 933.193 $[M]^+$ ($C_{71}H_{19}NOS$).