Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2015, **25**, 273–274

Mendeleev Communications

Circular dichroism spectra of new optically active terpenoid spiro homofullerenes

Airat R. Tuktarov,*[a] Leonard M. Khalilov,[a] Kirill K. Babievskii,[b] Arslan R. Akhmetov,[a] Viacheslav I. Sokolov[b] and Usein M. Dzhemilev[a]

[a] *Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, 450075 Ufa, Russian Federation. Fax: +7 347 284 2750; e-mail: tuktarovar@gmail.com*

[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2015.07.014

New optically active spiro homofullerenes were prepared by Pd-catalyzed cycloaddition of diazo derivatives of both enantiomers of menthone and camphor to C_{60} and were examined by circular dichroism spectroscopy.

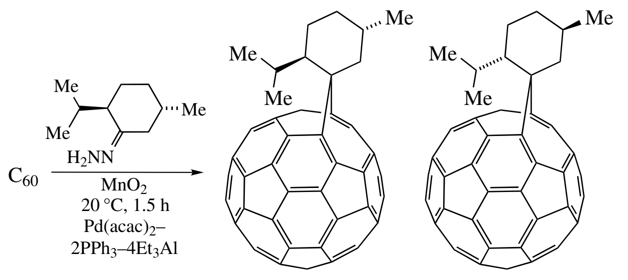
The chemistry of fullerenes is one of the most rapidly developing areas of modern synthetic chemistry,[1–5] although information about chiral carbon clusters is limited. Currently, there are available C_{76} enantiomers with chiral skeleton[6] and several derivatives with a chiral arrangement of two achiral ligands on the C_{60} spheroid.[7] The general access to optically active fullerenes (mainly C_{60}) is their derivatization with chiral addends.[8,9]

In literature including the extensive review[10] the details of preparation of optically active spiro homofullerenes were not documented because of their difficult selective synthesis.

Earlier,[11–16] we reported the selective cycloaddition of achiral cyclic and acyclic diazoalkanes, generated *in situ* by oxidation of hydrazones, to C_{60} in the presence of the three-component catalyst $Pd(acac)_2$–$2PPh_3$–$4Et_3Al$ to afford individual homofullerenes.

In a recent publication, we described[17] the Pd-catalyzed synthesis of optically active spiro homofullerenes *via* the interaction between C_{60} and chiral cyclic diazo compounds generated *in situ* from hydrazones of (–)-menthone and *d*-(+)-camphor, and optical rotation of the synthesized spiro C_{60} derivatives was also determined. For a more detailed study of the stereochemistry of chiral 5,6-open cycloadducts of C_{60}, as well as for better understanding the CD spectra of fullerene derivatives,[9(f)] we examined the complete set of enantiomeric spiro homofullerenes resulting from cycloaddition between C_{60} and diazo derivatives of (+)- and (–)-menthone as well as (+)- and (–)-camphor.

Following the developed procedure[17] (20 °C, 1 h, *o*-dichlorobenzene), fullerene C_{60} was reacted with (2*R*,5*S*)-1-diazo-2-isopropyl-5-methylcyclohexane (generated *in situ* by oxidation of (+)-menthone hydrazone with MnO_2) in the presence of 20 mol% $Pd(acac)_2$–$2PPh_3$–$4Et_3Al$ as a catalyst. An individual spiro homofullerene **1** was thus obtained in 40% yield (Scheme 1).†



1 **1′**

Scheme 1

The structure of **1** was proved by means of one- (^{1}H, ^{13}C) and two-dimensional homo- (COSY, NOESY) and heteronuclear (HSQC, HMBC) NMR experiments and fully consistent with published data[17] for its enantiomer **1′**.

The wavelengths of induced Cotton effects (CE) in the CD spectra‡ of **1** and its antipode **1′** (Figure 1) were identical and close to 'mirror images' of one another for all observed extrema in the wavelength range of 300–800 nm. Both of these compounds exhibited extrema at 589 and 650 nm, characteristic of the electronic π–π transitions of the fullerene derivatives. CEs were positive for **1** and negative for its antipode **1′**. The short wavelength parts of the spectra of compounds **1** and **1′** also contain other extrema (432 and 550 nm), which have opposite signs.

Similarly, we have synthesized spiro homofullerene **2**. Its antipode **2′** was obtained by us previously.[17]

In the case of compounds **2** and **2′**, prepared on the basis of (1*R*)- and (1*S*)-camphor, mirror images of CE extrema are also observed in the CD spectra (Figure 2).

Addends in all investigated homofullerenes are saturated alkanes without any chromophore groups. Hence, Cotton effects observed in the 300–750 nm region in the CD spectra should

† *General procedure*. Solutions of $Pd(acac)_2$ (2.78 μmol) in *o*-dichlorobenzene (0.4 ml) and PPh_3 (5.56 μmol) in *o*-dichlorobenzene (0.4 ml) were mixed in a glass flask, and a solution of Et_3Al (11.12 μmol) in toluene (0.1 ml) was added dropwise with stirring under nitrogen flow at –5 °C. The colour of the solution changed from pale yellow to light brown. A solution of fullerene C_{60} (13.9 μmol) in *o*-dichlorobenzene (0.1 ml) was added to the resultant catalyst at room temperature, and the colour of the solution turned dark green. A solution of the corresponding optically active hydrazone (69.5 μmol) in toluene (0.5 ml) and MnO_2 were added. The reaction mixture was stirred for 1–1.5 h at ambient temperature, then treated with aqueous HCl and extracted with toluene (7 ml). The organic layer was passed through a short column of silica gel. The products **1**, **2** and fullerene C_{60} were separated by preparative HPLC using toluene as eluent. Spectral characteristics of compounds **1** and **2** are identical with those previously described.[17]

‡ The CD spectra of solutions of **1**, **1′** and **2**, **2′** in chloroform were recorded in a wavelength range of 200–800 nm on an SKD-2 dichrograph (designed and produced at the Institute of Molecular Biology and the Institute of Spectroscopy, Russian Academy of Sciences) at 23 °C, in a 1-cm quartz cell. All measurements were carried out with a spectral resolution of 3 nm, an accumulation of 2.4 s, and a scan rate of 35 nm min^{-1}. In all figures the dichroism values are given in Δ*A*.

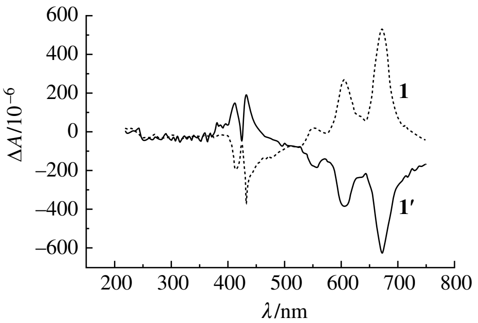
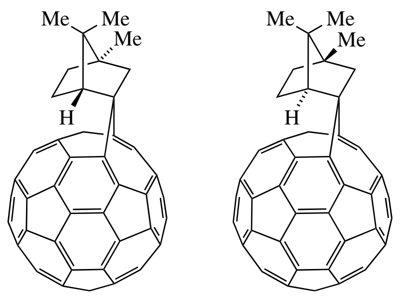


Figure 1 The CD spectra of spiro homofullerenes **1** and **1′** in chloroform (c = 2.0 g dm^{-3}).



2 **2′**

occur due to asymmetrically perturbed electronic transitions in the fullerene core itself, or, less possible, due to electron transfer from addends to the fullerene core. In isotropic UV-visible spectra of C_{60} and other fullerenes weak electronic transitions do not occur, but the corresponding Cotton effects can be observed in the CD spectra due to chiral environment. It is known that UV-VIS spectra of methanofullerenes show the characteristic weak band at 430 nm, which is not displayed in the spectra of homofullerenes. However, the Cotton effects corresponding to this wavelength are present in the CD spectra of all 5,6-opened compounds studied. This means that electronic transitions occur in spiro homofullerenes as well, however, in the isotropic spectrum they are of low intensity or symmetry-forbidden.

Taking into account that optically pure (–)-, (+)-menthone and *d*-, *l*-camphor were used as substrates, we attempted to measure the optical rotations of the synthesized homofullerenes **1** and **2**. Experiments were performed on a Perkin Elmer model 341 polarimeter with a sodium lamp (λ = 589 nm). The rotations of the optically active cycloadducts **1′** and **2′** were recorded previously.[17]

The average $[\alpha]_D^{20}$ values of compounds **1** and **2** are about –173±4 (c 0.028, $CHCl_3$) and –114±2 (c 0.028, $CHCl_3$), while those for are **1′** and **2′** are +176±5[17] and +120±2,[17] respectively. The solutions of higher concentrations of **1** and **2** are dark-coloured and significantly absorb at the measured wavelength. Hence, we were unable to measure the rotation angle of more concentrated solutions.

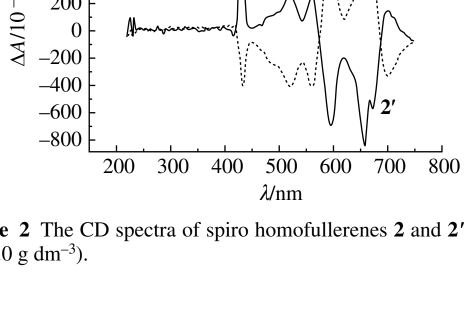


Figure 2 The CD spectra of spiro homofullerenes **2** and **2′** in chloroform (c = 2.0 g dm^{-3}).

The comparison of the enantiomeric homofullerenes with the addend possessing the same absolute configuration can be challenging for future discussions.

This work was supported by Presidium of the Russian Academy of Sciences (programme 'Fundamental Sciences for Medicine'), FTP 'Scientific and Pedagogical Staff of Innovative Russia' (grant no. 14.740.11.0014), Russian Foundation Basic Research (project no. 11-03-00252) and Division of Chemistry and Materials Science of the Russian Academy of Sciences (programme 01).

References

1 A. B. Kornev, A. S. Peregudov, V. M. Martynenko, G. V. Guseva, T. E. Sashenkova, A. Yu. Rybkin, I. I. Faingold, D. V. Mishchenko, R. A. Kotelnikova, N. P. Konovalova, J. Balzarin and P. A. Troshin, *Mendeleev Commun*., 2013, **23**, 323.
2 U. M. Dzhemilev, A. R. Tuktarov, I. R. Yarullin and A. R. Akhmetov, *Mendeleev Commun*., 2013, **23**, 326.
3 V. S. Lebedeva, F. M. Karmova, F. V. Toukach and A. F. Mironov, *Mendeleev Commun*., 2015, **25**, 32.
4 O. L. Kobzar, V. V. Trush, V. Yu. Tanchuk, I. I. Voronov, A. S. Peregudov, P. A. Troshin and A. I. Vovk, *Mendeleev Commun.*, 2015, **25**, 199.
5 Q. Zhang, B. Jin, R. Peng, S. Lei and S. Chu, *Mendeleev Commun*., 2015, **25**, 204.
6 J. M. Hawkins and A. Meyer, *Science*, 1993, **260**, 1918.
7 J. M. Hawkins, A. Meyer and M. Nambu, *J. Am. Chem. Soc*., 1993, **115**, 9844.
8 (*a*) A. Vasella, P. Uhlmann, C. A. Waldraff, F. Diederich and C. Thilgen, *Angew. Chem., Int. Ed. Engl*., 1992, **31**, 1388; (*b*) M. Prato, A. Bianco, M. Maggini, G. Scorrano, C. Toniolo and F. Wudl, *J. Org. Chem.*, 1993, **58**, 5578; (*c*) Y. Wang, D. I. Schuster, S. R. Wilson and C. J. Welch, *J. Org. Chem.*, 1996, **61**, 5198; (*d*) J. C. Hummelen, M. Keshavarz-K, J. L. J. van Dongen, R. A. J. Janssen, E. W. Meijer and F. Wudl, *Chem. Commun*., 1998, 281; (*e*) S. R. Wilson, Q. Lu, J. Cao, Y. Wu, C. J. Welch and D. I. Schuster, *Tetrahedron*, 1996, **52**, 5131; (*f*) V. I. Sokolov, *Russ. J. Org. Chem.*, 1999, **35**, 1257 (*Zh. Org. Khim*., 1999, **35**, 1289); (*g*) N. V. Abramova, K. K. Babievskii, S. M. Peregudova, A. S. Peregudov and V. I. Sokolov, *Russ. Chem. Bull., Int. Ed.*, 2011, **60**, 2010 (*Izv. Akad. Nauk, Ser. Khim*., 2011, 1974); (*h*) V. S. Romanova, K. K. Babievsky and I. A. Yamskov, *Russ. Chem. Bull., Int. Ed.*, 2010, **59**, 665 (*Izv. Akad. Nauk, Ser. Khim*., 2010, 650); (*i*) F. Giacalone, J. L. Segura and N. Martin, *J. Org. Chem.*, 2002, **67**, 3529.
9 (*a*) V. V. Bashilov, P. V. Petrovskii and V. I. Sokolov, *Russ. Chem. Bull.*, 1993, **42**, 392 (*Izv. Akad. Nauk, Ser. Khim*., 1993, 428); (*b*) V. V. Bashilov, P. V. Petrovskii, V. I. Sokolov, F. M. Dolgushin, A. I. Yanovsky and Yu. T. Struchkov, *Russ. Chem. Bull.*, 1996, **45**, 1207 (*Izv. Akad. Nauk, Ser. Khim*., 1996, 1268); (*c*) H. Zhang, C. F. Zhu, L. Li, W. Zou, Y. Q. Huang and J. X. Gao, *Chin. Chem. Lett*., 2004, **15**, 1411; (*d*) V. V. Bashilov, F. M. Dolgushin, P. V. Petrovski, V. I. Sokolov, M. Sada, T. Benincori and G. Zotti, *J. Organomet. Chem*., 2005, **690**, 4330; (*e*) V. I. Sokolov, *Russ. J. Coord. Chem*., 2009, **35**, 553 (*Zh. Koord. Khim*., 2009, **35**, 563); (*f*) V. I. Sokolov, V. V. Bashilov, F. M. Dolgushin, N. V. Abramova, K. K. Babievskii, A. G. Ginzburg and P. V. Petrovskii, *Tetrahedron Lett*., 2009, **50**, 5347; (*g*) M. V. Tsikalova, S. I. Zheludkov, E. I. Vorontsov, V. V. Bashilov, K. K. Babievskii, V. I. Sokolov and Yu. N. Novikov, *Mendeleev Commun.*, 2011, **21**, 256.
10 C. Thielgen and F. Diederich, *Chem. Rev.*, 2006, **106**, 5049.
11 A. R. Tuktarov, V. V. Korolev, L. M. Khalilov, A. G. Ibragimov and U. M. Dzhemilev, *Russ. J. Org. Chem.*, 2009, **45**, 1594 (*Zh. Org. Khim*., 2009, **45**, 1608).
12 A. R. Tuktarov, V. V. Korolev and U. M. Dzhemilev, *Russ. J. Org. Chem*., 2010, **46**, 588 (*Zh. Org. Khim*., 2010, **46**, 595).
13 A. R. Tuktarov, V. V. Korolev, D. Sh. Sabirov and U. M. Dzhemilev, *Russ. J. Org. Chem*., 2011, **47**, 41 (*Zh. Org. Khim*., 2011, **47**, 45).
14 A. R. Tuktarov, V. V. Korolev, A. R. Tulyabaev, V. M. Yanjbin, L. M. Khalilov and U. M. Dzhemilev, *Russ. Chem. Bull., Int. Ed*., 2010, **59**, 977 (*Izv. Akad. Nauk, Ser. Khim.*, 2010, 956).
15 U. M. Dzhemilev, A. R. Tuktarov, V. V. Korolev and L. M. Khalilov, *Petroleum Chem.*, 2011, **51**, 123 (*Neftekhimiya*, 2011, **51**, 134).
16 A. R. Tuktarov, A. R. Akhmetov, V. V. Korolev, A. A. Khuzin, L. L. Khasanova, N. R. Popod'ko and L. M. Khalilov, *Arkivoc*, 2011, **(viii)**, 54.
17 A. R. Tuktarov, V. V. Korolev, A. R. Tulyabaev, N. R. Popod'ko, L. M. Khalilov and U. M. Dzhemilev, *Tetrahedron Lett*., 2011, **52**, 834.

Received: 12th January 2015; Com. 15/4541