Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2015, **25**, 470–472

Mendeleev Communications

Synthesis of [60]fulleropyrrolidine–dithienylethene conjugates and DFT calculations of their photochromic properties

Airat R. Tuktarov,* Artur A. Khuzin, Leonard M. Khalilov, Artur R. Tulyabaev, Arslan R. Akhmetov and Usein M. Dzhemilev

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

DOI: 10.1016/j.mencom.2015.11.025

Dithienylethene-containing fulleropyrrolidines were synthesized by 1,3-dipolar cycloaddition of *in situ* generated appropriately derivatized azomethine ylides to C_{60}. The photochromic properties of these cycloadducts were predicted resorting to DFT calculations.

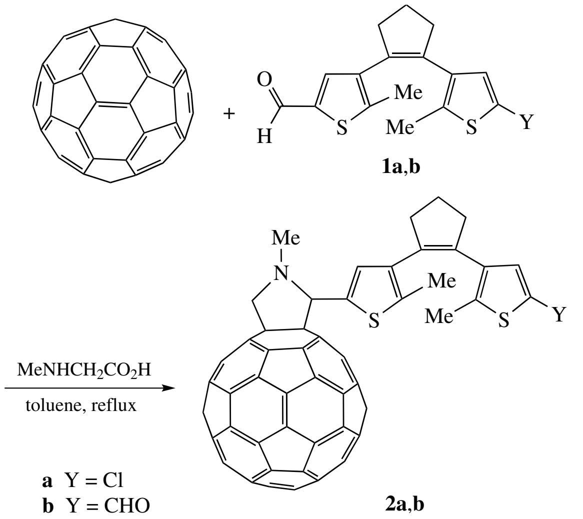
Organic molecules existing as two or more thermodynamically stable isomers find use not only as devices for molecular electronics and photonics but also for the control of dynamic properties of materials, targeted transport of biochemical information and signal transfer through biological membranes as well as for invention of photochemically and electrochemically switchable catalytic, enzymatic, bio- and chemosensor systems.[1] Nanoelectronics is one more perspective application of these photochromic compounds.

Several classes of organic compounds capable of *cis–trans*-isomerization or pericyclic transformations as well as topological isomers of supramolecules are considered as the most promising photochromic materials.[2–6] A special place is occupied by diarylethenes being thermally irreversible photochromes with high cycling rate. Currently, a broad range of various 1,2-diarylethene derivatives have been synthesized,[2] differing in the nature of the ethene or (het)aryl moieties or the nature of substituents in the latter. After the discovery of fullerenes in 1985,[7] the range of photochromic compounds was extended due to the use of derivatives of the carbon clusters.[8–10] The photochromic properties of fullerene adducts may be caused by electronic recombinations in both the fullerene cage[11] and the attached moiety, including the hetarylethene moiety.[12–14]

In order to extend the scope of application of photochromic derivatives of the carbon clusters and to study the effects of fullerene and diarylethene on the electronic properties and stability of a new photochromic molecule, we synthesized [60]fulleropyrrolidine–dithienylethene conjugates by the Prato reaction.[15]

In fact, 1,3-dipolar cycloaddition of dithienylethene **1a**,[16] containing a chlorine atom and an aldehyde group in the molecule, to fullerene C_{60} in the presence of sarcosine affords the corresponding fulleropyrrolidine **2a** in ~60% yield (Scheme 1).[†]

The structure of individual fulleropyrrolidine **2a** was reliably determined by one- (^1H and ^{13}C) and two-dimensional (COSY, HSQC, HMBC) NMR spectroscopy and MALDI TOF/TOF mass spectrometry (for details, see Online Supplementary Materials). The ^1H NMR spectrum of compound **2a** contains two singlets at δ_H 2.88 and 5.11 ppm corresponding to the methyl and methine protons, respectively, and two doublets for the geminal methylene protons (δ_H 4.22 and 4.96 ppm, ^2J 9.5 Hz) characteristic of pyrrolidinofullerenes.[17] In the HMBC experiment, the signal of the methine proton (δ_H 5.11 ppm) of the pyrrolidine ring in fulleropyrrolidine **2a** correlates with the carbon signals of the thiophene ring of the attached photochromic moiety (δ_C 129.39 and 153.28 ppm). The presence of a chiral centre in the pyrrolidine moiety of molecule **2a** in the direct vicinity of the fullerene core and of the unsymmetrical heteroaromatic substituent results in



Scheme 1

[†] *The Prato cycloaddition of dithienylethene aldehydes to [60]fullerene (general procedure).* A solution of C_{60} (0.14 mmol, 100 mg), sarcosine (0.28 mmol, 25 mg) and the corresponding photochromic aldehyde **1a**,**b** (0.67 mmol, 20 mg) in chlorobenzene (10 ml) was stirred at reflux temperature for 2 h, then the solvent was removed *in vacuo*. Chromatographic purification on SiO_2 (100% toluene as an eluent) afforded the target products **2a**,**b**.

2-{4-[2-(5-Chloro-2-methylthiophen-3-yl)cyclopenten-1-yl]-5-methylthiophen-2-yl}-1-methyl-3,4-fulleropyrrolidine **2a**: brown powder, yield 62% (92 mg). ^1H NMR (500 MHz, $CDCl_3$–CS_2, 1:5) δ: 1.74 (s, 3H, Me), 2.04 (s, 3H, Me), 2.07 (m, 2H, CH_2), 2.77 (t, 2H, CH_2, *J* 7.5 Hz), 2.84 (t, 2H, CH_2, *J* 7.5 Hz), 2.88 (s, 3H, Me), 4.22 (d, 1H, CH_2, *J* 9.5 Hz), 4.96 (d, 1H, CH_2, *J* 9.5 Hz), 5.11 (s, 1H, CH), 6.53 (s, 1H, CH), 7.07 (s, 1H, CH). ^{13}C NMR (125 MHz, $CDCl_3$–CS_2, 1:5) δ: 14.39, 14.86, 23.27, 38.64, 38.76, 40.31, 68.73, 69.93, 79.49, 126.75, 129.39, 133.18, 133.73, 134.81, 135.06, 135.08, 135.70, 135.88, 136.72, 139.70, 140.05, 140.25, 141.68, 141.75, 141.98, 142.06, 142.13, 142.22, 142.24, 142.30, 142.67, 142.70, 142.77, 143.06, 143.16, 143.22, 144.41, 144.44, 144.71, 144.78, 145.22, 145.33, 145.39, 145.42, 145.44, 145.55, 145.62, 145.67, 145.86, 146.01, 146.02, 146.15, 146.16, 146.18, 146.23, 146.26, 146.35, 146.39, 146.55, 146.81, 147.36, 153.19, 153.28, 153.92, 155.91. MS (MALDI-TOF), *m/z*: 1068.061 $[M-H]^+$ ($C_{78}H_{19}ClNS_2$).

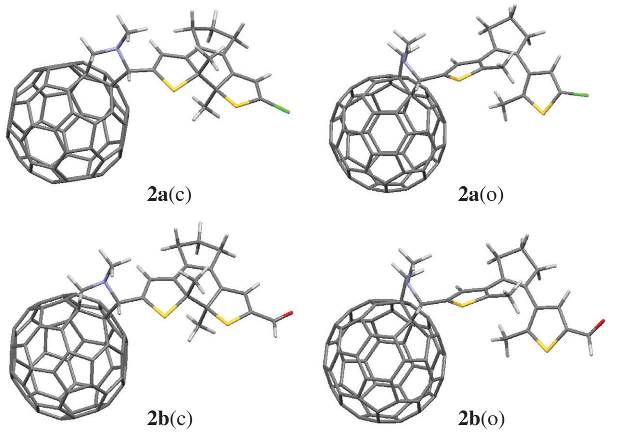

2a(c) **2a**(o)
2b(c) **2b**(o)

Figure 1 Open and closed antiparallel isomers of compounds **2a**,**b**.

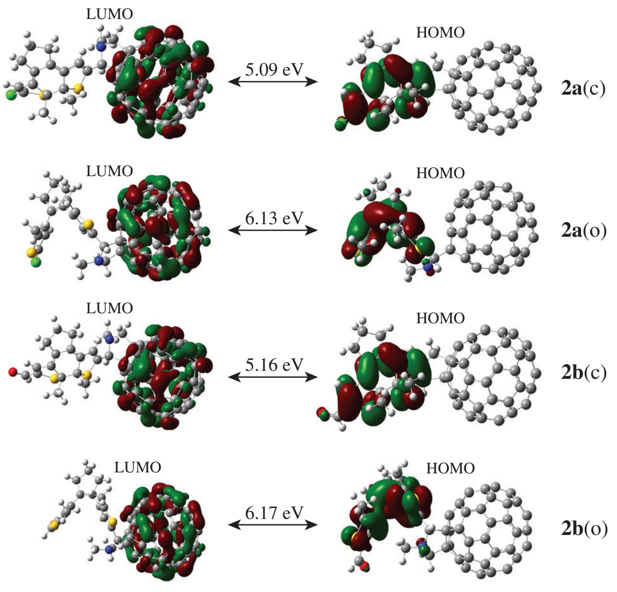


Figure 2 HOMO and LUMO of compounds **2a**,**b**.

the fullerene core of fulleropyrrolidine being responsible for 48 signals in the ^{13}C NMR spectrum. The structure of fulleropyrrolidine **2a** was also reliably established by means of MALDI TOF/TOF mass spectrometry; the spectrum of **2a** exhibited an intense fragment ion peak $[M-H]^+$ at *m/z* 1068.061.

We expected that the use of dithienylethene **1b** with two aldehyde groups could afford bis-adduct with two C_{60} fragments. However, the Prato reaction of fullerene C_{60} with dithienylethene **1b** involved only one aldehyde group giving the monoadduct **2b**.[‡] An increase in the reaction time and temperature and varying the reactant ratio did not cause the formation of bis-adduct.

In order to examine the photochromic properties of the resulting open and closed forms of compounds **2a**,**b**, we performed theoretical calculations of their 3D structure (Figure 1). The geometric parameters of the open and closed forms of fullerene adducts with dithienylethenes in the antiparallel and parallel conformation states were calculated by the PBE/3z method implemented in the PRIRODA program package.[18–21]

According to published data,[22–24] diarylethenes with the thiophene rings can exist in the parallel and antiparallel conformation states. In the former case, two heterocyclic rings are symmetrical with respect to the mirror plane, whereas the point group of symmetry of the latter state corresponds to the C_2 type.

The key factor responsible for the photochromic properties of hetarylethenes is the distance between the thiophene-ring α-carbon atoms involved in the ring closure, which should not exceed 4.2 Å.[25] In the antiparallel open type isomer **2a**(o), the theoretical distance between these carbon atoms is 3.642(3) Å, while the distance between these α-carbon atoms in **2b**(o) is 3.653(4) Å. In isomers **2a**(o) and **2b**(o), which occur in parallel conformations, these distances are longer being 4.359(6) and 4.346(5) Å, respectively. Therefore, the formation of the closed forms **2a**(c) and **2b**(c) is possible only owing to the antiparallel confiormational isomers. Moreover, the possibility of increasing the quantum yields of the closed isomers **2a**(c) and **2b**(c) can be achieved due to the large dihedral angle between the two thiophene rings, which are 67.12(7)° and 63.38(5)° for the antiparallel conformers **2a**(o) and **2b**(o), respectively. In the parallel conformers of open forms **2a**(o) and **2b**(o), these angles are 61.84(9)° and 71.77(6)°, respectively.

Simultaneously the molecular orbitals of the open and closed forms of **2a** and **2b** were analyzed by the B3LYP/6-31G(d) method using Gaussian software[26] (Figure 2). The highest occupied molecular orbital (HOMO) of the closed form **2a**(c) was shown to be located on the fullerene cage, whereas the lowest unoccupied molecular orbital (LUMO) is on the attached moiety. The energy difference between the two orbitals for compound **2a**(c) is about 5.09 eV, which is comparable with published data.[27] Similar results were obtained for other forms of compounds **2a** and **2b**.

Considering the above calculation data, one can conclude that in compounds **2a**,**b**, the fullerene cage is a potent acceptor of electron density, which readily migrates to the attached dithienylethene moiety upon ring closure or ring transformation. This is reflected in an increase in the quantum yield of the closed forms of the adducts on exposure to light and, hence, an increase in the performance of such compounds as molecular switches.

Thus, we synthesized fulleropyrrolidines containing dithienylethene moieties and theoretically predicted the photochromic properties of these compounds. The calculations of the geometric parameters of the open and closed forms of the fullerene adducts in the antiparallel and parallel conformation states demonstrated that introduction of a fullerene moiety as an electron acceptor into a dithienylethene molecule would maximize the quantum yield of the ring closure reaction of the open forms of the photochromes.

This work was supported by the Russian Science Foundation (grant no. 14-13-00296). The authors are grateful to Professor N. L. Asfandiarov (Institute of Molecule and Crystal Physics, Ufa Scientific Center of the RAS) for discussion of the results of theoretical calculations.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2015.11.025.

[‡] *2-{4-[2-(5-Formyl-2-methylthiopen-3-yl)cyclopent-1-yl]-5-methylthiophen-2-yl}-1-methyl-3,4-fulleropyrrolidine* **2b**: brown powder, yield 60% (89 mg). ^{1}H NMR (400 MHz, $CDCl_3$–CS_2, 1:5) δ: 1.92 (s, 3H, Me), 2.01 (s, 3H, Me), 2.10–2.20 (m, 2H, CH_2), 2.74–2.83 (m, 4H, 2CH_2), 2.87 (s, 3H, Me), 4.22 (d, 1H, CH_2, *J* 9.5 Hz), 4.95 (d, 1H, CH_2, *J* 9.5 Hz), 5.09 (s, 1H, CH), 7.05 (s, 1H, CH), 7.43 (s, 1H, CH), 9.69 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$–CS_2, 1:5) δ: 14.84, 15.53, 23.32, 38.84, 38.88, 40.28, 68.72, 69.94, 79.36, 129.13, 133.08, 134.53, 135.01, 136.64, 137.22, 137.61, 139.52, 140.04, 140.26, 140.28, 140.67, 141.72, 141.77, 141.87, 142.06, 142.09, 142.13, 142.20, 142.25, 142.29, 142.70, 142.73, 142.80, 143.09, 143.26, 144.43, 144.69, 144.81, 145.24, 145.35, 145.43, 145.53, 145.63, 145.66, 145.82, 146.04, 146.12, 146.17, 146.25, 146.27, 146.31, 146.39, 146.51, 146.70, 147.37, 152.94, 153.07, 153.74, 155.73, 181.30. MS (MALDI-TOF), *m/z*: 1062.159 $[M-H]^+$ ($C_{79}H_{20}NOS_2$).

References

1 V. I. Minkin, *Russ. Chem. Rev*., 2013, **82**, 1.

2 M. Irie, *Chem. Rev.*, 2000, **100**, 1685.

3 V. Z. Shirinian, D. V. Lonshakov, A. G. L'vov and M. M. Krayushkin, *Russ. Chem. Rev*., 2013, **82**, 511.

4 D. E. Korshin, N. V. Nastapova, S. V. Kharlamov, G. R. Nasybullina, T. Yu. Sergeeva, E. G. Krasnova, E. D. Sultanova, R. K. Mukhitova, S. K. Latypov, V. V. Yanilkin, A. Yu. Ziganshina and A. I. Konovalov, *Mendeleev Commun*., 2013, **23**, 71.

5 D. V. Lonshakov, V. Z. Shirinian, A. G. Lvov and M. M. Krayushkin, *Mendeleev Commun*., 2013, **23**, 268.

6 A. V. Mumyatov, L. I. Leshanskaya, D. V. Anokhin, N. N. Dremova and P. A. Troshin, *Mendeleev Commun*., 2014, **24**, 306.

7 H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 162.

8 P. A. Liddell, G. Kodis, J. Andreasson, L. de la Garza, S. Bandyopadhyay, R. H. Mitchell, T. A. Moore, A. L. Moore and D. Gust, *J. Am. Chem. Soc*., 2004, **126**, 4803.

9 S. D. Straight, J. Andreasson, G. Kodis, A. L. Moore, T. A. Moore and D. Gust, *J. Am. Chem. Soc.*, 2005, **127**, 2717.

10 M. E. El-Khouly, J. H. Kim, K.-Y. Kay, C. S. Choi, O. Ito and S. Fukuzumi, *Chem. Eur. J*., 2009, **15**, 5301.

11 A. R. Tuktarov, A. R. Akhmetov and U. M. Dzhemilev, in *Fullerene: Chemistry, Natural Sources and Technological Applications*, ed. S. B. Ellis, Nova Publishers, New York, 2014, pp. 123–166.

12 J. Jeong, E. Yun, Y. Choi, H.-Y. Jung, S. J. Chung, N. W. Song and B. H. Chung, *Chem. Commun*., 2011, **47**, 10668.

13 J. Frey, G. Kodis, S. D. Straight, T. A. Moore, A. L. Moore and D. Gust, *J. Phys. Chem. A*, 2013, **117**, 607.

14 S. Castellanos, A. A. Vieira, B. M. Illescas, V. Sacchetti, C. Shubert, J. Moreno, D. M. Guldi, S. Hecht and N. Martin, *Angew. Chem. Int. Ed.*, 2013, **52**, 13985.

15 M. Prato, M. Maggini, C. Giacometti, G. Scorrano, G. Sandona and G. Farnia, *Tetrahedron Lett*., 1996, **52**, 5221.

16 L. N. Lucas, J. J. D. de Jong, J. H. van Esch, R. M. Kellogg and B. L. Feringa, *Eur. J. Org. Chem*., 2003, 155.

17 T. Da Ros, M. Prato, F. Novello, M. Maggini and E. Banfi, *J. Org. Chem*., 1996, **61**, 9070.

18 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett*., 1996, **77**, 3865.

19 D. N. Laikov, *Chem. Phys. Lett*., 1997, **281**, 151.

20 D. N. Laikov and Yu. A. Ustynyuk, *Russ. Chem. Bull., Int. Ed*., 2005, **54**, 820 (*Izv. Akad. Nauk, Ser. Khim*., 2005, 804).

21 D. N. Laikov, *PhD Thesis*, Moscow State University, 2000.

22 R. M. Kellogg, M. B. Groen and H. J. Wynberg, *Org. Chem*., 1967, **32**, 3093.

23 M. Irie, K. Sakemura, M. Okinaka and K. J. Uchida, *Org. Chem*., 1995, **60**, 8305.

24 K. Uchida, Y. Nakayama and M. Irie, *Bull. Chem. Soc. Jpn*., 1990, **63**, 1311.

25 V. Ramamurthy and K. Venkatesan, *Chem. Rev*., 1987, **87**, 433.

26 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford CT, 2009.

27 F. Hu, M. Hu, W. Liu, J. Yin, G.-A. Yu and S. H. Liu, *Tetrahedron Lett*., 2015, **56**, 452.

Received: 8th July 2015; Com. 15/4674