Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2019, **29**, 229–231

Mendeleev
Communications

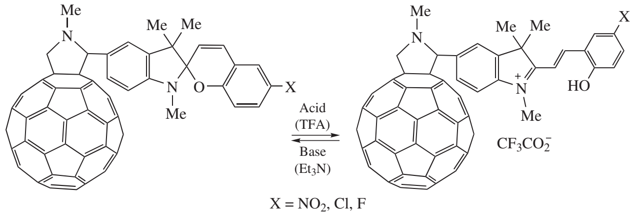
Acid-base isomerization of hybrid molecules based on fullerene C_{60} and spiropyrans

Airat R. Tuktarov,* Artur A. Khuzin 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.2019.03.039

The reversible acid-base isomerization of fullerene C_{60} hybrid compounds with spiropyrans has been performed for the first time. It has been found that irradiation induces isomerization only for hybrid bearing NO_2 group in the photochromic spiropyran part, while the treatment with trifluoroacetic acid induces isomerization for compounds containing NO_2, Cl or F, *i.e.* irrespective of the nature of substituent in the spiropyran moiety.



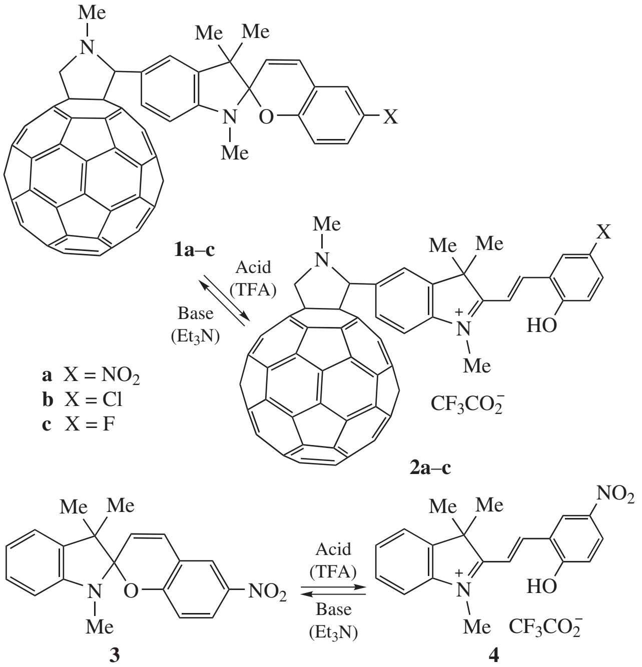
The ability of organic molecules to undergo reversible structural changes as a result of external factors is of great importance for the design of field effect transistors, sensors and optical memory elements, as well as photochemically and electrochemically switchable catalytic, enzymatic, bio- and chemosensing systems. Among organic compounds of this reversible structure type, spiropyrans deserve special attention due to the large amount of possible ways of initiating their isomerization. For example, colorless spiropyrans can be converted to the corresponding colored isomeric merocyanines under the action of ultraviolet light,[1–3] electric voltage,[4,5] some solvents,[6,7] metal ions,[8] carbon dioxide,[9,10] tensile force applied to polymers with spiropyran moieties,[11] heating[12] and acids or bases.[13,14]

The combination of spiropyrans possessing high sensitivity to various types of external action with nano-sized carbon clusters, namely fullerenes, carbon nanotubes or graphene, may result in multifunctional materials for cell imaging, memory and recording devices, colorimetric sensors and other prospective applications.[7,15–22]

Despite the advances in the synthesis of new nanomaterials, little data[7,23] is available on the chemical binding of fullerenes to spiropyrans. Meantime, such fullerene–spiropyran hybrid materials may have not only the increased sensitivity to external influence, but also high quantum yield of photoinitiated isomerization, along with the highest two-photon absorption coefficients, among the known photochromic systems, inherent in both interconverting isomers.[24]

Recently,[23] we synthesized fullerene C_{60}–spiropyran compounds **1a–c** by 1,3-dipolar cycloaddition of azomethine ylides, generated *in situ* from spiro photochromes, to fullerene C_{60} (Prato reaction). The physicochemical investigations of the obtained hybrids **1a–c** indicated that the reversible phototransformation took place only for compound **1a** with an NO_2 group in the pyran moiety, whereas Cl- and F-substituted compounds **1b** and **1c**, respectively, did not undergo the transformation upon continuous or pulsed photoexcitation. We assumed[23,25] that the lack of photochromism for the hybrids **1b**,**c** could be caused by reabsorption of the activating radiation by the fullerene core, since the absorption bands of spiropyran moieties for the corresponding starting compounds overlapped with the bands of fullerene C_{60}.

As a continuation of our work,[23,25–29] we investigated the possibility of isomerization of hybrid compounds **1a–c** upon acid or base treatment.[†]



Scheme 1 Acid-base isomerization of spiropyrans to protonated merocyanines.

[†] *General procedure for the acid-base isomerization of compounds* **1a–c**. Trifluoroacetic acid (13.9 µmol) was added to a solution of the corresponding hybrid compound **1a–c** (13.9 µmol) in toluene (10 ml). For neutralization of acid the equimolar quantity of triethylamine was added. Spectrophotometric measurements for solutions were carried out on an Agilent Cary 60 Bio spectrophotometer in a KU-1 quartz cell with optical path length of 2 mm. The isomerization was investigated at room temperature for 0.2 mM solutions of **1a–c**.

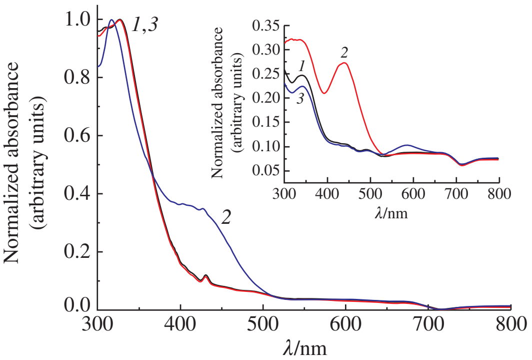


Figure 1 Normalized absorption spectra for compound **1a** in toluene: (*1*) initial solution, (*2*) after TFA-induced isomerization and (*3*) after further treatment with Et_3N. Inset: the corresponding absorption spectra for the model spiropyran **3**.

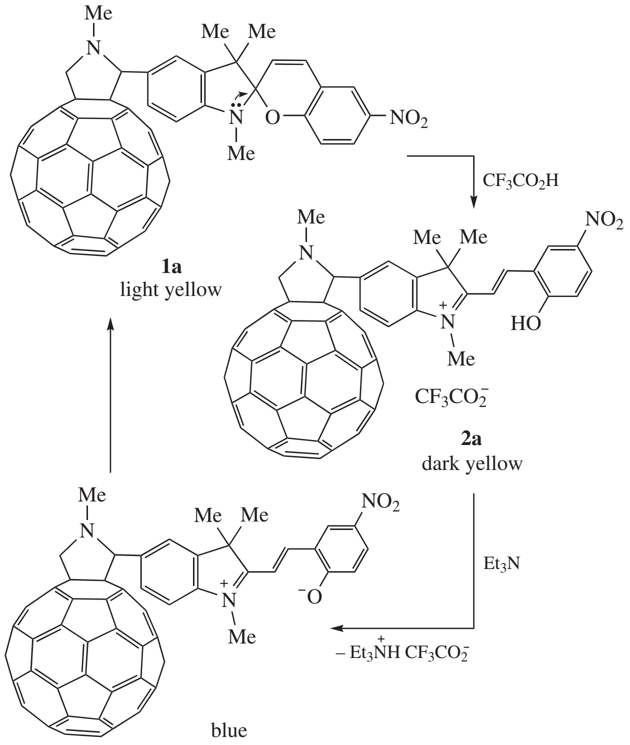
After addition of trifluoroacetic acid (TFA), the isomerization of spiropyran moieties in hybrids **1a–c** results in protonated merocyanine compounds **2a–c** (Scheme 1). As a model for comparison, we chose the spiropyran **3** (Scheme 1), which did undergo pyran ring opening both under photoexcitation and on treatment with TFA.

Similar to the model spiropyran **3**, the hybrid compound **1a** was converted, on treatment with TFA, to the protonated merocyanine **2a**, which showed a new band at 415 nm in the absorption spectrum (Figure 1). Merocyanine **4**, obtained by the similar treatment of spiropyran **3**, gave rise to an absorption peak at 440 nm (inset in Figure 1). Treatment of protonated merocyanines **2a** and **4** solutions with triethylamine afforded the starting spiropyrans **1a** and **3**, respectively. According to the published data,[14] the conversion of merocyanine **4** to spiropyran **3** proceeds *via* the formation of another intermediate merocyanine structure as a result of deprotonation of phenolic hydroxyl group. The formation of intermediate merocyanine after treatment of compound **4** with triethylamine was evidenced by an absorption peak at 580 nm (inset in Figure 1, curve *3*).

Spiropyran ring opening in the hybrid molecule **1a**, like that for the model spiropyran **3**, was confirmed by NMR data. The TFA-induced isomerization for compound **3** was detected by a downfield shift (from 2.4 to 4.0 ppm) of the signal for the methyl group at the indole nitrogen atom (Figure S1, see Online Supplementary Materials). The ^{1}H NMR spectrum of the hybrid compound **1a** (Figure S2) exhibited not only the TFA-induced downfield shift for methyl group at the indole nitrogen (from 2.6 to 3.6 ppm), but also broadening of the signal of the methyl group at the pyrrolidine ring fused to the fullerene core (~2.9 ppm), which was apparently caused by the formation of a quaternary salt at the pyrrolidine moiety. Upon neutralization of TFA with Et_3N, the initial ^{1}H NMR spectra were restored (Figures S1 and S2).

After treatment of compounds **3** and **1a** with TFA, the corresponding protonated merocyanines **4** and **2a** are formed in quantitative yield, whereas the photoinitiated transformation of spiropyranes to merocyanines proceeds in not more than 20% yield.[14] Presumably, the TFA-induced pyran ring opening in molecules of **3** and **1a** occurs as a result of deactivation of the nucleophilic phenol oxygen atom upon protonation.[14,30] Neutralization of TFA with an equimolar amount of Et_3N liberates the nucleophilic phenoxide anion and, as a consequence, gives the starting spiropyran (Scheme 2).

Similar results have been obtained for hybrid compounds **1b** and **1c** with Cl and F atoms, respectively, in the spiropyran moiety instead of the NO_2 group. Although hybrids **1b** and **1c** did not undergo photoinduced isomerization, treatment of their solutions with TFA resulted in stable protonated merocyanines **2b** and **2c** (see Online Supplementary Materials).



Scheme 2

Since TFA-induced isomerization of the spiropyran moieties in the hybrids **1a–c** and the photoinduced isomerization of compound **1a** are reversible processes and the synthesized compounds are stable against photodegradation, these hybrid derivatives of nanosized carbon clusters, in our opinion, are promising active components for multi-resistor electric switches.

This work was supported by the Grants of the President of the Russian Federation (nos. MK-3058.2018.3 and NSh- 5240.2018.3) and Budget theme (AAAA-A17-117012610065-2). The structural investigations were performed with assistance of Collective Usage Centre ‘Agidel’ at the Institute of Petrochemistry and Catalysis of the Russian Academy of Sciences.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.03.039.

References

1 A. R. Tuktarov, A. A. Khuzin and U. M. Dzhemilev, *Russ. Chem. Rev*., 2017, **86**, 474.
2 V. A. Barachevsky, *Org. Photonics Photovolt*., 2015, **3**, 8.
3 R. Klajn, *Chem. Soc. Rev*., 2014, **43**, 148.
4 J.-F. Zhi, R. Baba, K. Hashimoto and A. Fujishima, *Chem. Lett*., 1994, **23**, 1521.
5 J. F. Zhi, R. Baba, K. Hashimoto and A. Fujishima, *J. Photochem. Photobiol., A*, 1995, **92**, 91.
6 X. Song, J. Zhou, Y. Li and Y. Tang, *J. Photochem. Photobiol., A*, 1995, **92**, 99.
7 J.-H. Xu, Y.-L. Li and D.-B. Zhu, *Synth. Commun*., 2002, **32**, 1647.
8 S. Yagi, S. Nakamura, D. Watanabe and H. Nakazumi, *Dyes Pigm*., 2009, **80**, 98.
9 T. A. Darwish, R. A. Evans, M. James, N. Malic, G. Triani and T. L. Hanley, *J. Am. Chem. Soc*., 2010, **132**, 10748.
10 T. A. Darwish, R. A. Evans, M. James and T. L. Hanley, *Chem. Eur. J*., 2011, **17**, 11399.
11 D. A. Davis, A. Hamilton, J. Yang, L. D. Cremar, D. Van Gough, S. L. Potisek, M. T. Ong, P. V. Braun, T. J. Martínez, S. R. White, J. S. Moore and N. R. Sottos, *Nature*, 2009, **459**, 68.
12 Y. Shiraishi, M. Itoh and T. Hirai, *Phys. Chem. Chem. Phys*., 2010, **12**, 13737.

13 J. T. C. Wojtyk, A. Wasey, N.-N. Xiao, P. M. Kazmaier, S. Hoz, C. Yu, R. P. Lemieux and E. Buncel, *J. Phys. Chem. A*, 2007, **111**, 2511.

14 N. Darwish, A. C. Aragonès, T. Darwish, S. Ciampi and I. Díez-Pérez, *Nano Lett*., 2014, **14**, 7064.

15 X. Guo, L. Huang, S. O'Brien, P. Kim and C. Nuckolls, *J. Am. Chem. Soc*., 2005, **127**, 15045.

16 E. Del Canto, K. Flavin, M. Natali, T. Perova and S. Giordani, *Carbon*, 2010, **48**, 2815.

17 A. Perry, S. J. Green, D. W. Horsell, S. M. Hornett and M. E. Wood, *Tetrahedron*, 2015, **71**, 6776.

18 Y. Li, Y. Duan, J. Zheng, J. Li, W. Zhao, S. Yang and R. Yang, *Anal. Chem*., 2013, **85**, 11456.

19 P. Joo, B. J. Kim, E. K. Jeon, J. H. Cho and B.-S. Kim, *Chem. Commun*., 2012, **48**, 10978.

20 A.-R. Jang, E. K. Jeon, D. Kang, G. Kim, B.-S. Kim, D. J. Kang and H. S. Shin, *ACS Nano*, 2012, **6**, 9207.

21 A.-A. Nahain, J.-E. Lee, J. H. Jeong and S. Y. Park, *Biomacromolecules*, 2013, **14**, 4082.

22 S. M. Sharker, C. J. Jeong, S. M. Kim, J.-E. Lee, J. H. Jeong, I. In, H. Lee and S. Y. Park, *Chem. Asian J*., 2014, **9**, 2921.

23 A. R. Tuktarov, A. A. Khuzin, A. R. Tulyabaev, O. V. Venidictova, T. M. Valova, V. A. Barachevsky, L. M. Khalilov and U. M. Dzhemilev, *RSC Adv*., 2016, **6**, 71151.

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

25 V. A. Pomogaev, V. A. Barachevsky, A. R. Tuktarov, P. V. Avramov and V. Ya. Artyukhov, *J. Phys. Chem. A*, 2018, **122**, 505.

26 A. R. Tuktarov, A. A. Khuzin, L. M. Khalilov, A. R. Tulyabaev, A. R. Akhmetov and U. M. Dzhemilev, *Mendeleev Commun*., 2015, **25**, 470.

27 A. R. Tuktarov, A. A. Khuzin, A. R. Akhmetov, V. A. Barachevsky, O. V. Venidiktova and U. M. Dzhemilev, *Tetrahedron Lett*., 2015, **56**, 7154.

28 A. R. Tuktarov, A. A. Khuzin, A. R. Akhmetov, L. M. Khalilov, A. R. Tulyabaev, V. A. Barachevsky, O. V. Venidiktova and U. M. Dzhemilev, *Mendeleev Commun*., 2016, **26**, 143.

29 A. R. Tuktarov, A. R. Akhmetov, A. A. Khuzin, O. V. Venidiktova, V. A. Barachevskii and U. M. Dzhemilev, *Russ. J. Org. Chem*., 2017, **53**, 891 (*Zh. Org. Khim*., 2017, **53**, 874).

30 J. T. C. Wojtyk, A. Wasey, N.-N. Xiao, P. M. Kazmaier, S. Hoz, C. Yu, R. P. Lemieux and E. Buncel, *J. Phys. Chem. A*, 2007, **111**, 2511.

Received: 29th June 2018; Com. 18/5624