ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 6, pp. 1214–1215. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © E.V. Antina, M.B. Berezin, A.S. Semeikin, N.A. Dudina, S.L. Yutanova, 2010, published in Zhurnal Obshchei Khimii, 2010, Vol. 80, No. 6, pp. 1046–1047.

LETTERS TO THE EDITOR

Synthesis and Optical Properties of BF_2-Complexes of Alkylated Dipyrrolylmethenes (BODIPY)

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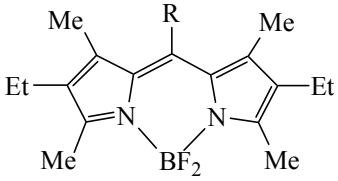
Received December 24, 2009

DOI: 10.1134/S1070363210060320

The first information about fluorophores on the basis of dipyrrolylmethene BF_2 complexes (BODIPY) appeared as early as 1968 [1], but the most active work on the synthesis and the study of BODIPY was carried out the in the last 10–15 years [2]. By now the unique variety of prospects of applying BODIPY as biomolecule markers, fluorescence switches, chemosensors, limiters of rigid laser radiation intensity, photosensitizers for photodynamic therapy, DNA intercalators, etc. has been described.

Aiming at the creation of new promising fluorophores of this group, we developed convenient synthesis procedures of BF_2 complexes of 3,3',5,5'-tetramethyl-4,4'-diethyldipyrrolylmethene **I** and its aryl derivative, *ms*-phenyl-3,3',5,5'-tetramethyl-4,4'-diethylpyrrolylmethene **II**, and examined their optical properties.



R = H (**I**), C_6H_5 (**II**).

3,3',5,5'-Tetramethyl-4,4'-diethyldipyrrolylmethene difluoroborate complex (I). To a solution of 0.4 g of 3,3',5,5'-tetramethyl-4,4'-diethyldipyrrolylmethene hydrobromide in 50 ml of methylene chloride were added 1.6 ml of triethylamine and 1.4 ml of boron trifluoride etherate in one portion at room temperature under stirring. The reaction mixture was stirred for 3.5 h at the same temperature. Then it was twice washed with water, dried with sodium sulfate and subjected to chromatography on silica gel, eluting with methylene chloride. The first intensively fluorescing zone was concentrated, and the complex was precipitated with methanol. Yield 0.33 g (91.2%). EA spectrum, λ_{max}^{abs}, nm (log ε): 526 (4.88) (C_2H_5OH), 530 (–) (C_6H_{12}), 532 (4.90) (C_6H_6), 532 (4.89) (C_6H_5–CH_3). Emission spectrum, λ_{max}^{fl}, nm: 540 (C_2H_5OH), 541 (C_6H_{12}), 544 (C_6H_6), 544 (C_6H_5–CH_3). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.07 t (6H, C*H*$_3$–CH$_2$–), 2.06 s (6H, CH_3), 2.25 q (CH_3–C*H*$_2$–), 2.27 s (6H, CH_3), 6.97 s (1H, –CH=). Found, %: C 66.97; H 7.45; N 9.15. $C_{17}H_{23}N_2BF_2$. Calculated, %: C 67.12; H 7.62; N 9.22.

***ms*-Phenyl-3,3',5,5'-tetramethyl-4,4'-diethyldipyrrolylmethene difluoroborate complex (II).** To a solution of 0.9 g of 2,4-dimethyl-3-ethylpyrrole in 50 ml of methylene chloride was added 0.5 ml of benzoyl chloride. The mixture was stirred at room temperature for 111 h. Then 3.6 ml of triethylamine and 4.4 ml of boron trifluoride etherate were added followed by stirring for 24 h. The mixture was washed with water, with a saturated solution of sodium hydrogen carbonate and again with water. Organic layer was dried with sodium sulfate and concentrated. The residue was dissolved in benzene and subjected to chromatography on silica gel, eluting with benzene. Yield 0.3 g (10.7%). EA spectrum, λ_{max}^{abs}, nm (log ε): 520 (4.80) (C_2H_5OH), 522 (–) (C_6H_{12}), 525 (4.79) (C_6H_6), 524 (4.79) (C_6H_5–CH_3). Emission spectrum, λ_{max}^{fl}, nm: 539 (C_2H_5OH), 538 (C_6H_{12}), 543 (C_6H_6), 545 (C_6H_5–CH_3). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.00 t (6H, C*H*$_3$–CH$_2$–), 1.28 s (6H, CH_3), 2.32 q (CH_3–

CH_2–), 2.56 s (6H, CH_3), 7.31–7.33 m (2H, Ph), 7.47–7.50 m (3H, Ph). Found, %: C 72.27; H 7.06; N 7.24. $C_{17}H_{23}N_2BF_2$. Calculated, %: C 72.64; H 7.16; N 7.37.

The ^{1}H NMR spectra were registered on a Bruker 500 spectrometer in $CDCl_3$. EA and emission spectra were taken on an SF-103 and Cary 100 spectrophotometers and CM 2203 spectrofluorimeter in organic solvents. Solvents were additionally purified by the known procedures [3]. Water content in the solvents did not exceed 0.02% by the results of Fisher method titration.

ACKNOWLEDGMENTS

This work was financially supported by the Program of Basic Research of the Presidium of Russian Academy of Sciences (18-P project-2, 2009), by Analytic Departmental Targeted P*rogram* **"***Development of the Scientific Potential of High School* (2009–2010)" (project no. 2.1.1/827), and Federal Targeted Program "Scientific and Scientific-Pedagogical Potential of Innovative Russia" (2009–2013) (contract no. 02.740.11.0253).

REFERENCES

1. Treibs, A. and Kreuzer, F.H., *Justus Liebigs Ann. Chem*., 1968, vol. 718, no. 1, p. 208.
2. Loudet, A. and Burgess, K., *Chem. Rev*., 2007, vol. 107, p. 4891.
3. Gordon, A.J. and Ford, R.A., *The Chemist's Companion. A Handbook of Practical Data, Techniques and References*, New York: Wiley, 1972.