

## Synthesis and crystal structure of novel fluorescent 1,3,4-oxadiazole-containing carboxylate ligands

Igor E. Mikhailov<sup>a, b</sup>, Leonid D. Popov<sup>c</sup>, Valery V. Tkachev<sup>d</sup>, Sergey M. Aldoshin<sup>d</sup>, Galina A. Dushenko<sup>a, \*</sup>, Yurii V. Revinskii<sup>b</sup>, Vladimir I. Minkin<sup>a</sup>

<sup>a</sup> Institute of Physical and Organic Chemistry, Southern Federal University, 194/2 Stachka Str., 344090 Rostov on Don, Russian Federation

<sup>b</sup> Southern Scientific Center, Russian Academy of Sciences, 41 Chekhov Str., Rostov on Don 344006, Russian Federation

<sup>c</sup> Southern Federal University, Chemistry Department, 7 Zorge Str., Rostov on Don 344090, Russian Federation

<sup>d</sup> Institute of Problems of Chemical Physics of Russian Academy of Sciences, 1 Akad. Semjonov N.N. Ave., 142432 Chernogolovka, Moscow Region, Russian Federation

### ARTICLE INFO

#### Article history:

Received 4 October 2017

Received in revised form

12 December 2017

Accepted 12 December 2017

Available online 14 December 2017

#### Keywords:

1,3,4-Oxadiazoles

Acrylic acids

Luminophors

Intermolecular interactions

### ABSTRACT

Novel chelating ligands, 3-(5-aryl-1,3,4-oxadiazol-2-yl)acrylic acids and their zinc complexes were synthesized and their spectral and luminescent properties studied. The compounds intensively (quantum efficiencies  $\varphi = 0.18-0.76$ ) luminesce in nonpolar solvents in the blue-green region ( $\lambda_{\text{max}}^{\text{PL}} = 458-504$  nm) of the spectrum. Molecular and crystal structures of 3-[5-(4-dimethylaminophenyl)-1,3,4-oxadiazol-2-yl]acrylic acid were established using X-ray crystallography. In crystal, the infinite chains of the molecules lie in the parallel planes and are arranged by the “head to tail” type to provide for strong  $\pi-\pi$  stacking interactions between the layers facilitating appearance of high electron transport properties and formation of excimers.

© 2017 Elsevier B.V. All rights reserved.

### 1. Introduction

1,3,4-Oxadiazoles and their derivatives exhibit high and diverse biological activity [1] and are widely used as organic scintillators, photostabilizers of polymers, electron transport materials, components of active media of dye lasers, organic semiconductors and other materials for modern optoelectronics [2]. A special and rapidly developing area of application of 1,3,4-oxadiazoles stipulated by their appealing spectral and luminescent properties is the design on their basis of a series of efficient fluorescent and phosphorescent luminophores [3] and highly emissive materials with low self-absorption [4]. Functionalization of the oxadiazoles with an *ortho*-hydroxyphenyl substituent in either 2nd or 5th position of the ring gives rise to the compounds with a six-membered N,O-chelate unit which serve as the powerful bidentate ligands of highly emissive metal-complexes and components of electron transport materials for organic light-emitting diodes (OLEDs) [5]. Other 1,3,4-oxadiazoles with the substituents capable of the formation of a chelate ring abridged by one of the cyclic nitrogens and suitable for

metal coordination are limited by the cases of oxadiazolylacrylic, oxadiazolylpropionic [6] and furanoxadiazolylacrylic [7] acids, of which only the latter has already been implemented for complexation with metal ions as is exemplified by its silver complex. In recent years, metal complexes of the flexible and polymerizable carboxylate ligands derived from unsaturated carboxylic acids received much attention because of interesting electronic, magnetic, optical and thermal properties and wide areas of application of these compounds and their (co)polymers and nanocomposites [8].

In pursuing this trend, the present work was aimed at the synthesis and investigation into the spectral and fluorescent properties of new carboxylate ligands with a 1,3,4-oxadiazole fragment, preparation, structural characterization and study of the luminescent properties of their zinc complexes. Zinc complexes have high thermal stability, low toxicity, are characterized by effective luminescence and high electron mobility necessary for electronic transport layers in OLEDs, i.e. the properties that make them a promising alternative to expensive iridium and osmium complexes [9]. Recently, zinc complexes of heterocyclic ligands have been successfully used as the “hosts” for fluorescent and phosphorescent dopants in OLEDs [10], and their ability to form

\* Corresponding author.

E-mail address: [dushenko@ipoc.sfedu.ru](mailto:dushenko@ipoc.sfedu.ru) (G.A. Dushenko).

exciplexes with hole transport layers ensured the preparation of white OLEDs on their basis [11].

## 2. Experimental

### 2.1. Materials required and general methods

All starting materials and solvents were of reagent quality and were used as received. C, H, N elemental analyses were carried out on a “Carlo Erba Instruments TCM 480”. Melting points were determined on a Kofler table. The IR spectra of the ligands and complexes were recorded in the range 600–4000  $\text{cm}^{-1}$  by means of a Varian Excalibur 3100 FT-IR spectrometer in mineral oil in a thin film. Electronic absorption spectra were recorded on a Varian Cary 100 spectrophotometer. Fluorescence measurements were performed on a Varian Cary Eclipse spectrofluorimeter.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX-250 nuclear magnetic resonance spectrometer operating at 250.13, or 62.9 MHz, using DMSO- $d_6$  as a locking solvent. Quantum-chemical calculations were performed by the density functional theory (DFT) method using the B3LYP three-parameter potential with the 6–311++G(d,p) split-valence basis set for ligands and with the 6–311G(d,p) basis set for zinc complexes in the gas phase and with allowance for solvation using the Gaussian-09 software package [12]. All stationary points were identified by the calculation of the Hessian matrix. Accounting of non-specific solvation (solvent – dimethylsulfoxide) has been performed in the framework of continuum model (IEFPCM) [13].

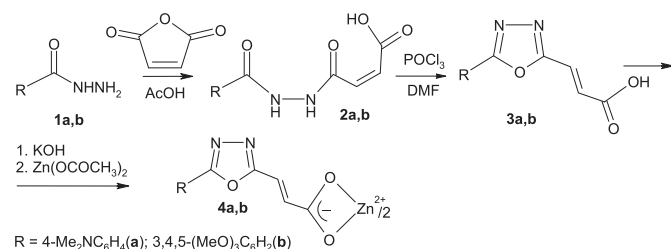
### 2.2. Synthesis

Scheme 1 depicts the synthesis of (Z)-4-(2-aryloxyhydrazinyl)-4-oxo-2-butenoic acids **2a,b**, (E)-3-(5-aryl-1,3,4-oxadiazol-2-yl) acrylic acids **3a,b** and Zinc(II) bis[(E)-3-(5-aryl-1,3,4-oxadiazol-2-yl)]acrylates **4a,b**.

#### 2.2.1. Synthesis of (Z)-4-(2-aryloxyhydrazinyl)-4-oxo-2-butenoic acids **2a,b**

(Z)-4-(2-Aroyloxyhydrazinyl)-4-oxo-2-butenoic acids **2a,b** were prepared by the procedure of [6a]. To a solution of 2.16 g (0.022 mol) of maleic anhydride in 10 mL of glacial acetic acid at room temperature and stirring, a solution of 0.02 mol of the hydrazide of the corresponding benzoic acid in 15 mL of glacial acetic acid was added dropwise. The reaction mixture was stirred for 30 min, the precipitate was filtered off, washed sequentially with glacial acetic acid (5 mL) and water (10 mL). Then the precipitate was air dried, and recrystallized from propan-2-ol.

2.2.1.1. (Z)-4-[2-(4-Dimethylaminobenzoyl)hydrazinyl]-4-oxo-2-butenoic acid **2a**. Yield 93%, yellow crystals, mp 192–193 °C. IR,  $\nu$ ,  $\text{cm}^{-1}$ : 3208 (NH); 2730, 2603 (OH); 1705 (C=O), 1663 (C=O, amide), 1622 (C=C); 1600, 1594 (C=C<sub>arom.</sub>); 1537, 1531 ( $\delta\text{N-H}$ );



Scheme 1. Synthesis of aroyloxyhydrazinyl-oxobutenoic acids **2a,b**, oxadiazolylacrylic acids **3a,b** and oxadiazolylacrylic zinc complexes **4a,b**.

1335, 1215, 1172; 950 ( $\delta\text{OH}$ ), 849 ( $\delta\text{C-H}_{\text{arom.}}$ ).  $^1\text{H}$  NMR (DMSO- $d_6$ , 250 MHz),  $\delta$  (ppm): 3.01 (s, 6H, Me<sub>2</sub>N), 6.36 (d, 1H=CH-2,  $^3J$  10.4 Hz), 6.44 (d, 1H=CH-3,  $^3J$  10.4 Hz), 6.75 (d, 2H<sub>Ar</sub>-3,5,  $^3J$  10.4 Hz), 7.79 (d, 2H<sub>Ar</sub>-2,6,  $^3J$  10.4 Hz), 10.27 (s, 1H, NH), 10.32 (s, 1H, NH), 13.08 (s, 1H, OH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 62.9 MHz),  $\delta$  (ppm): 40.12 (2C, Me<sub>2</sub>N), 111.25 (2C<sub>Ar</sub>-3,5), 118.86 (C<sub>Ar,quart.</sub>-1), 127.53 (C=CH-2), 129.43 (2C<sub>Ar</sub>-2,6), 133.80 (C=CH-3), 153.00 (C<sub>Ar,quart.</sub>-4), 163.91 (C<sub>quart.</sub>, CO), 165.64 (C<sub>quart.</sub>, CO), 167.27 (C<sub>quart.</sub>, CO). Found, (%): C 56.04; H 5.61; N 15.18. C<sub>13</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub>. Calculated, (%): C 56.31; H 5.45; N 15.15.

2.2.1.2. (Z)-4-[2-(3,4,5-Trimethoxybenzoyl)hydrazinyl]-4-oxo-2-butenoic acid **2b**. Yield 91%, colourless crystals, mp 146–147 °C. IR,  $\nu$ ,  $\text{cm}^{-1}$ : 3229 (NH); 2726, 2633 (OH); 1704 (C=O); 1661, 1621 (C=O, amide); 1615 (C=C); 1600, 1591 (C=C<sub>arom.</sub>); 1538, 1523 ( $\delta\text{N-H}$ ); 1504, 1486 (C=C<sub>arom.</sub>); 1416 ( $\delta\text{CH}_3$ ); 1343, 1311 (C-N); 1225, 1034; 969 ( $\delta\text{OH}$ ), 852 ( $\delta\text{C-H}_{\text{arom.}}$ ).  $^1\text{H}$  NMR (DMSO- $d_6$ , 250 MHz),  $\delta$  (ppm): 3.76 (s, 3H, OMe), 3.87 (s, 6H, 2OMe), 6.43 (d, 1H=CH-2,  $^3J$  12.0 Hz), 6.46 (d, 1H=CH-3,  $^3J$  12.0 Hz), 7.27 (c, 2H<sub>Ar</sub>-2,6), 10.60 (s, 1H, NH), 10.64 (s, 1H, NH), 13.87 (s, 1H, OH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 62.9 MHz),  $\delta$  (ppm): 56.47 (2C, 2OMe), 60.57 (C, OMe), 105.50 (2C<sub>Ar</sub>-2,6), 127.48 (C=CH-2), 127.68 (C<sub>Ar,quart.</sub>-1), 133.40 (C=CH-3), 140.97 (C<sub>Ar,quart.</sub>-4), 153.12 (2C<sub>Ar,quart.</sub>-3,5), 163.73 (C<sub>quart.</sub>, CO), 165.10 (C<sub>quart.</sub>, CO), 167.41 (C<sub>quart.</sub>, CO). Found, (%): C 52.03; H 4.82; N 8.75. C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>7</sub>. Calculated, (%): C 51.85; H 4.97; N 8.64.

#### 2.2.2. Synthesis of (E)-3-(5-aryl-1,3,4-oxadiazol-2-yl)acrylic acids **3a,b**

(E)-3-(5-Aryl-1,3,4-oxadiazol-2-yl)acrylic acids **3a,b** were obtained by the procedure of [6a]. Phosphoryl chloride (1.1 mL) was added to a solution of 0.01 mol of (Z)-4-(2-aryloxyhydrazinyl)-4-oxo-2-butenoic acid **2** in 10 mL of DMF under stirring, maintaining the temperature below 40 °C. The reaction mixture was kept at room temperature for 40 min and then poured onto crushed ice (30 g). The precipitate was filtered off, washed with water (2 × 15 mL), air dried and recrystallized from a suitable solvent.

2.2.2.1. (E)-3-[5-(4-Dimethylaminophenyl)-1,3,4-oxadiazol-2-yl]acrylic acid **3a**. Yield 52%, yellow crystals, mp 249–250 °C (from pyridine). IR,  $\nu$ ,  $\text{cm}^{-1}$ : 2671, 2626 (OH); 1710 (C=O), 1615 (C=C), 1574 (C=C<sub>arom.</sub>), 1556, 1514 (C=N); 1435 ( $\delta\text{CH}_3$ ), 1296, 1278, 1227; 1192 (C-O-C), 981 ( $\delta$  *trans*-CH=CH), 910 ( $\delta\text{OH}$ ), 816 ( $\delta\text{C-H}_{\text{arom.}}$ ).  $^1\text{H}$  NMR (DMSO- $d_6$ , 250 MHz),  $\delta$  (ppm): 3.05 (s, 6H, Me<sub>2</sub>N), 6.85 (d, 1H=CH-3,  $^3J$  16.0 Hz), 6.86 (d, 2H<sub>Ar</sub>-3,5,  $^3J$  8.8 Hz), 7.43 (d, 1H=CH-2,  $^3J$  16.0 Hz), 7.91 (d, 2H<sub>Ar</sub>-2,6,  $^3J$  8.8 Hz), 13.14 (s, 1H, OH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 62.9 MHz),  $\delta$  (ppm): 40.07 (2C, Me<sub>2</sub>N), 109.39 (C<sub>Ar,quart.</sub>-1), 112.18 (2C<sub>Ar</sub>-3,5), 124.85 (C=CH-3), 128.34 (C=CH-2), 128.80 (2C<sub>Ar</sub>-2,6), 153.08 (C<sub>Ar,quart.</sub>-4), 161.55 (C<sub>quart.</sub>, Het), 165.67 (C<sub>quart.</sub>, Het), 166.50 (C<sub>quart.</sub>, CO). Found, (%): C 60.05; H 5.17; N 16.32. C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>O<sub>3</sub>. Calculated, (%): C 60.22; H 5.05; N 16.21.

2.2.2.2. (E)-3-[5-(3,4,5-Trimethoxyphenyl)-1,3,4-oxadiazol-2-yl]acrylic acid **3b**. Yield 57%, colourless crystals, mp 205–207 °C (from toluene). IR,  $\nu$ ,  $\text{cm}^{-1}$ : 2631, 2563 (OH); 1716 (C=O), 1657 (C=C), 1594 (C=C<sub>arom.</sub>), 1548, 1537 (C=N); 1494, 1469 (C=C<sub>arom.</sub>); 1456, 1433; 1421 ( $\delta\text{CH}_3$ ), 1289, 1246, 1130; 1043 (C-O-C), 971 ( $\delta$  *trans*-CH=CH), 920 ( $\delta\text{OH}$ ), 841 ( $\delta\text{C-H}_{\text{arom.}}$ ).  $^1\text{H}$  NMR (DMSO- $d_6$ , 250 MHz),  $\delta$  (ppm): 3.78 (s, 3H, OMe), 3.92 (s, 6H, 2OMe), 7.07 (d, 1H=CH-3,  $^3J$  16.0 Hz), 7.43 (c, 2H<sub>Ar</sub>-2,6), 7.47 (d, 1H=CH-2,  $^3J$  16.0 Hz), 13.18 (s, 1H, OH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 62.9 MHz),  $\delta$  (ppm): 56.73 (2C, 2OMe), 60.73 (C, OMe), 104.93 (2C<sub>Ar</sub>-2,6), 118.42 (C<sub>Ar,quart.</sub>-1), 124.57 (C=CH-3), 129.96 (C=CH-2), 141.49 (C<sub>Ar,quart.</sub>-4), 153.97 (2C<sub>Ar,quart.</sub>-3,5), 162.69 (C<sub>quart.</sub>, Het), 164.87 (C<sub>quart.</sub>, Het), 166.44 (C<sub>quart.</sub>, CO). Found, (%): C 55.03; H 4.58; N 9.23. C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>6</sub>. Calculated, (%): C 54.90; H 4.61; N 9.15.

Download English Version:

<https://daneshyari.com/en/article/7808279>

Download Persian Version:

<https://daneshyari.com/article/7808279>

[Daneshyari.com](https://daneshyari.com)