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Luminescence of the nitronyl nitroxide radical group in a spin-labelled pyrazolylquinoline

Evgeny V. Tretyakov [a], Victor F. Plyusnin [b,*], Anastasiya O. Suvorova [a], Stanislav V. Larionov [c], Sergey A. Popov [d], Olga V. Antonova [c], Ekaterina M. Zueva [e], Dmitry V. Stass [b], Artem S. Bogomyakov [a], Galina V. Romanenko [a], Victor I. Ovcharenko [a]

[a] International Tomography Center SB RAS, 3a Institutskaya Str., 630090 Novosibirsk, Russian Federation
[b] Institute of Chemical Kinetics and Combustion SB RAS, 3, Institutskaya Str., 630090 Novosibirsk, Russian Federation
[c] Nikolaev Institute of Inorganic Chemistry SB RAS, 3 Lavrentieva Ave., 630090 Novosibirsk, Russian Federation
[d] Vorozhtsov Institute of Organic Chemistry SB RAS, 9 Lavrentieva Ave., 630090 Novosibirsk, Russian Federation
[e] Department of Inorganic Chemistry, Kazan National Research Technological University, 68 K. Marx Str., 420015 Kazan, Russian Federation

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ABSTRACT

The synthesis, structure and photoluminescence of a group of substituted 2-pyrazolylquinolines, including a spin-labelled derivative, are described. A comparative study of photoluminescence from the synthesized compounds demonstrates that introduction of a nitronyl nitroxide radical group results not only in the expected reduction in photoluminescence from the pyrazolylquinoline moiety, but also gives rise to a new red photoluminescence band (maximum at 692 nm in acetonitrile) from the radical fragment.

1. Introduction

An important trend in modern chemistry is the synthesis of polyfunctional luminescing organic compounds containing heterocyclic nitrogen nuclei and luminescing metal complexes from such ligands [1–7] due to potential applications of these compounds in luminescing devices and sensors [8–11]. Luminescing nitrogen heterocycles include quinoline derivatives [12–15], e.g., recently photoluminescence (PL) was reported from 2-(3,5-dimethylpyrazol-1-yl)-4-methylquinoline [16] and a chiral pyrazolylquinoline, a derivative of natural terpene (+)-3-carene [17].

Apart from a broad interest in the luminescence of diamagnetic heterocyclic species, the luminescence properties and photophysical processes in series of aromatic compounds spin-labelled with an imino and/or nitronyl nitroxide are being actively studied today [18–25]. It was found that the nitronyl nitroxide moiety *per se* as a fluorophore shows a weak PL in the solid phase at low temperature in the range of 650–900 nm [26–29]. However, the level of accumulated knowledge is still far from being sufficient to predict the PL properties of a nitronyl nitroxide moiety linked with a given heterocycle.

In the present work, we report the first luminescence spectroscopy studies of an organic paramagnetic **1** compound combining a good fluorophore moiety, pyrazolylquinoline, and a nitronyl nitroxide radical group in the same molecule. We found that the addition of a nitronyl nitroxide group to the pyrazolylquinoline system (Scheme 1) results not only in the expected reduction in PL from the pyrazolylquinoline moiety, but also gives rise to a near-infrared luminescence centered on the radical ligand.

2. Experimental section

2.1. Spectroscopic instrumentation

Excitation and PL spectra of compounds **1**, **3** and **4** in the solid phase and in acetonitrile were taken at room temperature with a FLS920 spectrofluorimeter (Edinburg Instruments). The PL spectra and kinetics of the solids were taken in a thin layer of powder produced by grinding crystals between two quartz glasses that were then set at an angle of 45° to the excitation beam. To measure the spectra in acetonitrile, a standard 1 cm quartz cuvette was used. Solutions were prepared by means of spectrally pure acetonitrile.

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* Corresponding author. Tel.: +7 383 3332385; fax: +7 383 3307350.
E-mail addresses: tev@tomo.nsc.ru (E.V. Tretyakov), plyusnin@kinetics.nsc.ru (V.F. Plyusnin).

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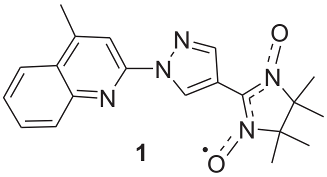
When necessary, oxygen was removed by blowing argon through the solution for 30 min. As excitation sources a Xe900 xenon lamp and EPLED laser diodes (280, 300, 320 nm, pulse length 600 ps) or an EPL-375 diode laser (375 nm, pulse length 60 ps) were used. Electronic absorption spectra were taken with an HP 8453 spectrometer (Agilent Technologies).

2.2. 4,4,5,5-Tetramethyl-2-(1-(4-methylquinolin-2-yl)-1H-pyrazol-4-yl)-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl (1)

To a stirred solution of **6** (0.25 g, 0.68 mmol), CH_2Cl_2 (20 mL) and water (10 mL) were added along with $NaIO_4$ (0.218 g, 1.019 mmol). The reaction was stirred at room temperature for 40 min. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (15 mL). The combined organic solutions were dried with Na_2SO_4 and concentrated. The product was purified using column chromatography followed by multiple recrystallizations from a CH_2Cl_2–heptane mixture (v/v=1:2). Yield 0.178 g (72%), blue crystals, m.p. 142–145 °C. $\mu_{eff}=1.73\ \mu_B$ (in temperature range 50–300 K). ESR: $g_{iso}=2.0065$, $a_{N(N-O)}(2\ N)=0.749$ mT, $a_{H(Me)}$ (12 H)$=0.022$ mT, $a_H(1\ H)=0.065$ mT, $a_H(1\ H)=0.029$ mT. IR, ν/cm^{-1}: 3425, 3171, 3064, 2987, 1597, 1513, 1494, 1471, 1455, 1429, 1408, 1361, 1330, 1295, 1218, 1180, 1125, 1062, 1011, 968, 893, 848, 754. Found (%): C, 65.8; H, 5.9; N, 18.9. $C_{20}H_{22}N_5O_2$. Calculated (%): C, 65.9; H, 6.1; N, 19.2.

2.3. X-ray diffraction study

Reflection arrays were collected on a SMART APEX II CCD diffractometer (Bruker AXS) (Mo Kα, $\lambda=0.71073$ Å; absorption was taken into account using Bruker SADABS software, ver. 2.10). The structures were solved by direct methods and refined using full-matrix LS techniques in anisotropic approximation for all non-hydrogen atoms. The H atoms were calculated geometrically and included as riding groups in the refinement. All calculations for structure solving and refining were performed using the Bruker Shelxtl software suite, ver. 6.14. It should be noted that crystals of **3** and **4** had the form of thin plates (about 0.01–0.02 mm thick), while the crystals of **6** were fine needles ($0.02 \times 0.02 \times 0.28$ mm^3), so they reflected very poorly. Our numerous attempts to crystallize compounds from different solvents in order to obtain crystals in another form were unsuccessful.



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Scheme 1. Structure of radical **1** combining pyrazolylquinoline and nitronyl nitroxide radical group.

2.4. Computational details

DFT calculations were performed for isomers A and B of **1** with the GAUSSIAN03 program [34] using the B3LYP functional in conjunction with the 6−31+G(d,p) basis set. The ground state and the first excited state geometries were optimized using the DFT and TD-DFT methods, respectively. In all calculations (geometry optimizations and single point TD-DFT calculations), solvent effects were included within the SCRF method (solvent=acetonitrile).

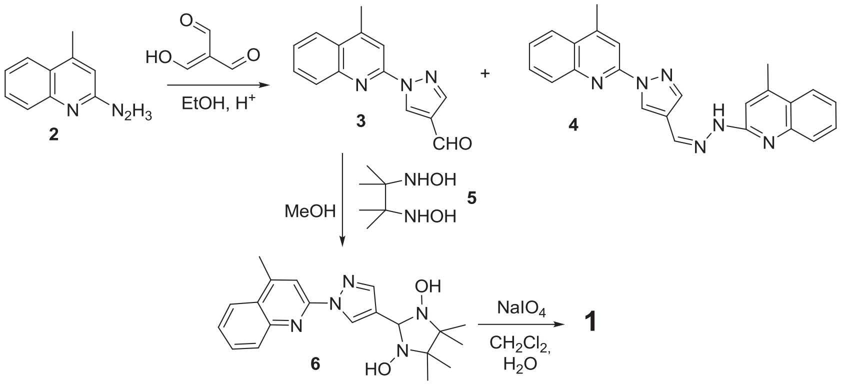
3. Results and discussion

To obtain **1**, a substituted hydrazine **2** was condensed with triformylmethane (TFM) in EtOH in the presence of HCl to give formylpyrazolylquinoline **3**. To avoid the formation of substantial amounts of hydrazone **4** as a byproduct, a hot solution of **2** in ethanol was added to an ethanol solution of a double excess of TFM at 70 °C. In this synthetic scenario the yields of aldehyde **3** reached 59% (Scheme 2). On the other hand, gradual reaction of **2** with TFM (0.5 h) and performance of the process at room temperature resulted in the formation of hydrazone **4** as the main product (57%). Condensation of the obtained aldehyde **3** with dihydroxyamine **5** produced imidazoline **6**, which was subsequently oxidized with $NaIO_4$ in a biphasic CH_2Cl_2–H_2O system into the target nitronyl nitroxide **1**.

3.1. Structure of synthesized compounds

The molecular and crystal structures of all obtained compounds were established using X-ray diffraction analysis (XRD). The purity of the products was confirmed by spectral methods and elemental analysis, further supported in the case of the nitroxyl radical **1** with the results from magnetochemical measurements and ESR spectroscopy (Supplementary material).

The structure of the nitroxyl radical **1** is formed by two crystallographically independent molecules A and B (Fig. 1) that differ mainly in the angle between the planes of the quinoline and nitronyl nitroxide (CN_2O_2) fragments, which is equal to 10.3° in molecule A and 28.7° in molecule B. Each molecule forms its own centrosymmetric dimer (Fig. 2 A and B): in {A…A} pyrazolylquinoline the fragments overlap with minimal interplane distances of ~3.6 Å, while in {B…B} dimers the only overlapping is by quinoline fragments with interplane distances of ~3.3 Å.



Scheme 2. The scheme for synthesis of the radical **1** through the successive synthesis of **2, 3, 6** compounds.