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Synthesis, structure, and magnetic properties of 2,2′-(buta-1,3-diyne-1,4-diyl)-bis(4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole 3-oxide 1-oxyl)

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ABSTRACT

An approach to the synthesis of nitronyl nitroxide 2,2′-(buta-1,3-diyne-1,4-diyl)bis(4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole 3-oxide 1-oxyl) (**4**) was developed. Compound **4** is the first diradical with nitronyl nitroxide groups directly linked through a diacetylene fragment. In solid phase the diradicals are arranged in stacks with parallel $\mathrm{C{\equiv}C}$ fragments, with the distances between the terminal carbon atoms of the neighboring diacetylene groups (T and d) being 6.170 and 4.466 Å, respectively, and the angle between the translation vector and the median line passing through the $\mathrm{C{\equiv}C{-}C{\equiv}C}$ fragment of 45.9°. The values of T and d are outside the range of structural criteria allowing a topochemical reaction. Thus UV irradiation does not initiate solid phase polymerization of **4**. After exposure at 373 K for 1 h the crystals of **4** turn dark-brown, become X-ray amorphous and lose the majority of their paramagnetic centers without significantly changing their mass. Upon further heating up to 400–420 K the product explodes, releasing about 360 kJ/mol of heat. A diluted solution of **4** in 1,4-dioxane produces an EPR spectrum typical of a strong exchange (a multiplet of nine broadened lines with $A_{4N} = 0.35$ mT), indicating the efficiency of the $\mathrm{C{\equiv}C{-}C{\equiv}C}$ fragment as an exchange channel. The character of the experimental $\mu_{\mathrm{eff}}(T)$ dependence for **4** indicates a strong intramolecular antiferromagnetic-type exchange interaction ($J/k_B \sim -104$ K) and the dominating weak intermolecular ferromagnetic exchange.

1. Introduction

The last decades have witnessed an intense development of the molecular methodology for creation of magnetoactive materials [1]. A systematic investigation of charge transfer complexes, mono- and heterospin coordination compounds brought about a large number of crystalline solids that can undergo phase transition into a magnetically ordered state at temperatures exceeding helium boiling point [2]. The discovered magnetostructural correlations formed the basis for the subsequent targeted design of molecular-based magnets [3]. The rather high critical temperatures for a number of such magnets are due to the system of covalent bonds that couple their paramagnetic centers in solid phase providing high energies of the exchange interaction between the unpaired electrons and 3D ordering of the magnetic moments. In principle that high energies of exchange interactions can be provided by constructing conjugated polyradicals or hybrid metal–polyradical systems, which opens a way to plastic magnets. This problem was tackled in both theoretical works [4] and in experimental studies [5].

Two inherently different strategies can be distinguished that are being developed to obtain magnetoactive polymers saturated with the organic component. According to one of them the polyradicals are synthesized from a solution of monomers bearing one or more paramagnetic groups [6], or from high molecular weight diamagnetic precursors [7]. Thus obtained polyradicals are characterized by a certain distribution over the degree of polymerization, conformational inhomogeneity, and the presence of defects, which can lower the spin multiplicity of the ground state [8]. In this respect, at least in view of preparing conformationally ordered polyradicals, an alternative strategy based on topochemical polymerization appears to be rather promising. The thoroughly studied topochemical reactions include photopolymerization of diolefins leading to polymers with cyclobutane rings in the main chain [9], and polymerization of conjugated diacetylenes producing substituted polyenynes [10]. These reactions are peculiar in that in certain cases they yield polymer crystals with very low concentrations of defects, i.e., a topochemical polymerization of the crystals of spin-labeled 1,3-butadienes or 1,3-butadiynes can produce nearly perfect crystals of polyradicals, in which saturated or π-conjugated polymer chains stretched along one of crystallographic directions bear paramagnetic groups that are strictly ordered in a well-defined manner.

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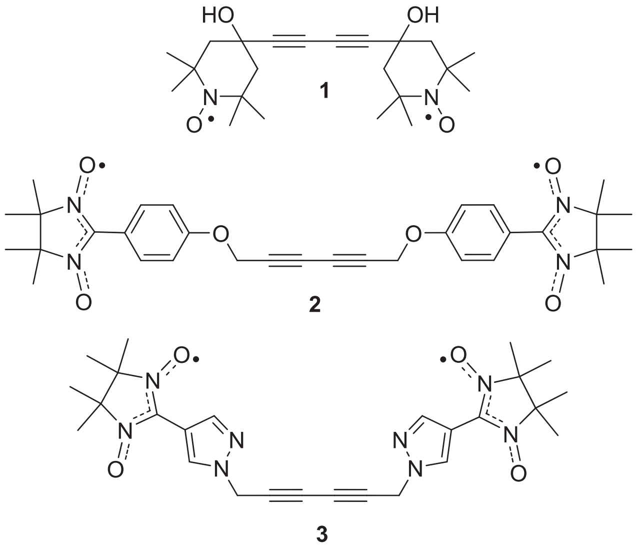
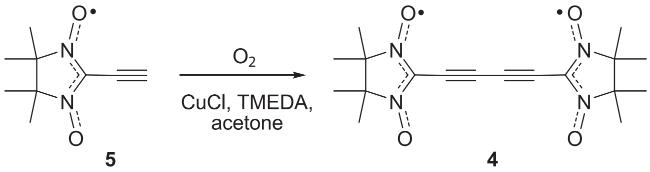


Scheme 1. 1,3-Butadiynes with nitroxide substituents.



Scheme 2. Synthesis of diradical **4**.

Spin-labeled 1,3-butadiynes (Scheme 1) are not widely available compounds, and thus their studies are rather scarce [11]. An example is provided by the works on synthesis and study of the structure and properties of modifications of the piperidine-*N*-oxyl diradical **1** [11a,b], for which is was shown that the geometric parameters for both polymorphs of **1** do not meet the structural criteria for a topochemical reaction of polymerization. Thus UV, fast electron, or γ-irradiation of the crystals of **1** at ambient conditions did not promote in them a topochemical reaction. Thermal treatment caused deep decomposition of **1** yielding a complex mixture of products (mostly diamagnetic), in which no organic ferromagnets were found. According to XRD data, the shortest distances between the diacetylene fragments in diacetylene **2**, equal to 8.285 Å, are also too far beyond the structural criteria making the topochemical polymerization feasible [11c]. As a result **2** did not engage in the reaction of UV-induced polymerization, and upon heating above 90 °C decomposed with explosion accompanied by evolution of NO and a loss of the majority of its paramagnetic centers. An important structural feature of **2** is formation of complementary H-bonds between the oxygens of the NO groups and the hydrogens of the phenyl cycles. In diradical **3** the side groups in solid also tend to form complementary H-bonds between the oxygens of the NO groups and the hydrogens of the pyrazole cycles [11d]. A decrease in the size of the side groups in **3** resulted in a noticeable decrease in the distances between the diacetylene fragments as compared to **2**, but the latter still remained too large (6.887 Å). Thus UV-irradiation of the crystals of **3** did not lead to solid phase polymerization.

In this work we develop a synthesis of diradical 2,2′-(buta-1,3-diyne-1,4-diyl)bis(4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole 3-oxide 1-oxyl) (**4**), which contains solely the diacetylene bridge between its two paramagnetic fragments. We contemplated that by synthesis of **4** a much closer intermolecular positioning of the butadiyne groups can be achieved as compared to the known examples of diradicals [11]. The structural and magnetic properties of the products forming upon thermal treatment of **4** are also discussed.

2. Results and discussion

2.1. Synthesis

Diradical **4** was prepared by oxidative coupling of monosubstituted alkyne **5** (Scheme 2), which was in turn prepared by a method involving the interaction of the corresponding 1,3-dihydroxy derivative of imidazolidine with PbO_2 in EtOH [12]. Several main methods for one-stage oxidative coupling of acetylenes have been described: in (O_2, Cu^I, NH_4Cl)/water system [13], in (O_2, Cu^I)/amine system [14], as well as oxidation in the system of Cu^{II}/amine (or inorganic base) [15]. For oxidative coupling of **5** the system (O_2, Cu^I)/amine was used in two its classical variants [16,17]. In the system (O_2, CuCl)/pyridine nitroxide **5** underwent decomposition into a multitude of products with unidentified structures. On the other hand, in the system (O_2, CuCl, TMEDA)/acetone the reaction of oxidative coupling proceeded smoothly, in the course of reaction the forming **4** precipitated from the reaction mixture as a fine green crystalline powder. According to results of IR spectroscopy and visual inspection using a microscope, after purifying by recrystallization diradical **4** stored at +5 °C remained intact for 2 months .

2.2. Molecular geometry and crystal packing

X-ray diffraction study of **4** was performed at 298 and 35 K. The molecular geometry of **4** in the crystal, as well as the atom labeling for one half of the diradical, are shown in Fig. 1. Selected bond lengths and angles are given in Table 1. An important feature of the molecular structure of **4** is the non-linearity of the diacetylenic moiety; the valence angles at atoms C8 and C9 are equal to 173.6(2)° and 179.5(2)°, respectively. Such distortions have been rather rarely found in the series of non-cyclic diacetylenes, and within the family of diacetylene diradicals have only been reported in solid **3** [9].

The lengths of triple bonds in **4** are typical for conjugated diacetylenes. The length of the single bond in the diacetylene fragment is somewhat increased because of its bending and, as a consequence, a reduction in the degree of conjugation of the triple bonds: d(C8—C9) = 1.191(2) Å, d(C9—C9′) = 1.365(3) Å, d(C7—C8) = 1.403(2) Å. The five-membered rings have the usual slightly distorted planar structure, the atoms C1 and C4 being situated 0.136 Å above and 0.276 Å below, respectively, the mean plane defined by the atoms O1, N1, C7, N2, O2. The bond lengths in the two unique N—O groups are equal within the experimental error and have the values 1.267(2) Å (N1—O1) and 1.263(2) Å (N2—O2). This is also the case with the lengths of the two N—C(sp^2) bonds that have the values 1.338(2) Å (C7—N1) and 1.337(2) Å (C7—N2), which strongly suggests the equivalence of the two unique N—O groups. In general, the geometric parameters of the terminal 2-imidazoline

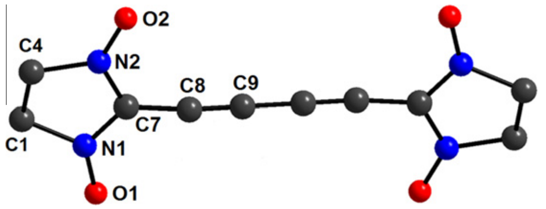


Fig. 1. Molecular structure of **4** and the numbering scheme (methyl groups are omitted).