Spin-dimer networks: engineering tools to adjust the magnetic interactions in biradicals†

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Magneto-structural correlations in stable organic biradicals have been studied on the example of weakly exchange coupled models with nitronyl nitroxide and imino nitroxide spin-carrying entities. Here, heteroatom substituted 2,2′-diaza- and 3,3′-diaza-tolane bridged biradicals were compared with the hydrocarbon analogue, while a bipheryl model with its 2,2′-bipyridine counterpart. For a 3,3′-diazatolane bridge the torsional angle between the nitronyl nitroxides and the pyrrolid rings increased heavily (~52–54°) leading to a smaller theoretical intra-dimer exchange coupling value. However, a very large antiferromagnetic coupling was obtained experimentally. This could be appropriately explained by the presence of dominating inter-dimer exchange between the molecules. For the bis(imino nitroxide) with tolane bridge a field induced ordered state between 1.8 to 4.3 T in AC-susceptibility measurements was observed. In terms of a Bose Einstein condensate (BEC) of tripons this phenomenon could be described as a magnetic field induced ordered phase with 3D character.

In general, organic magnetic materials possess properties not shown by traditional inorganic compounds.5–9 Plasticity, flexibility and solubility in common organic solvents define the ease of various device fabrication. Advanced chemistry techniques permit small structural modifications in already achieved model systems in order to fine-tune their physical properties. In addition, organic-based magnetic materials offer a number of convenient tools extremely helpful in controlling the intra- and inter-dimer exchange coupling, such as π–π interactions, hydrogen bonding, etc. Nitronyl nitroxide (NN) radicals are well-known for their stability and bidentate character.5,10 NN radicals are among the most popular spin carriers used to construct molecule-based magnets.10

Importantly, in these radicals the spin density of the unpaired electron is delocalized over two semi-equivalent sites of coordination. This in turn allows the arrangement of the NN-molecules into a supramolecular network of interacting spins.11 Theoretical studies emphasized the importance of the mutual orientation and the relative distances in the crystal packing for promoting an efficient magnetic coupling.11,12 As was mentioned by Lahti,13 minor changes in the crystal packing of biradicals could result in significant alterations of the magnetic behavior in the bulk material. In this regard the influence of the π-bridges on the intra- and intermolecular exchange interactions in conjugated biradical networks was studied on the example of the diazatolane dinitroxide models (Fig. 1). It was anticipated that heteroatom substitution could offer a particularly effective pathway for transmitting the magnetic interactions.14

Introduction

Magnetic dimers formed by weakly interacting antiferromagnetically coupled spin S = 1/2 centres are recognized as suitable candidates for exploring critical phenomena under well-controlled conditions.1 When these systems are placed in a magnetic field strong enough to close the dimer gap, a gas of triplet excitations (trippons) is formed.1 Depending on the topology of the dimer–dimer couplings, various scenarios can be observed. Prominent examples include the Bose-Einstein condensation (BEC) of tripons in three-dimensionally-coupled dimer systems, as described by Tchernyshyov et al.,2 and the Luttinger-liquid behavior revealed in a one-dimensional spin-ladder system by Krämer and co-workers.3 More recently, a Berezinskii–Kosterlitz–Thouless scenario was observed by Tutsch et al. in a two-dimensional coordinated copper polymer with large interlayer spacing.4

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Typically, imino nitroxides (INs) reveal a reduced $J_{dimer}$ value when compared to the corresponding NN biradicals. Taking this fact into consideration, already known bridges could be used, where otherwise a strong intramolecular exchange coupling was observed.\textsuperscript{11} Following this strategy, three bisimino nitroxides \textit{3d, 4d, 5d} were prepared (Fig. 1).\textsuperscript{15}

In the current work we report the synthesis of a series of new nitroxide biradicals (Fig. 1), their characterization, including X-ray structural analysis and their magnetic properties, which are discussed with respect to the quantum chemical calculations based on the DFT approach.

Results and discussion

Synthesis of nitroxide biradicals

Access to the family of diazatolane biradicals \textit{1c and 2c} required the synthesis of key precursors \textit{1a and 2a}, which were prepared following Sonogashira–Hagihara methodology.\textsuperscript{16} Interestingly, both structural isomers \textit{1a and 2a} could be achieved starting from the same precursor, \textit{i.e.} commercially available 2,5-dibromo-pyridine \textit{6} (Scheme 1). Depending on the reaction conditions (such as solvent, base) compound \textit{6} could be selectively monolithiated.\textsuperscript{17–21} More precisely, reaction times and solvents played a crucial role in the course of electrophilic substitution, leading to predominant formation of the organolithium intermediate at the 2 or 5 position.\textsuperscript{22,23} In order to drive the reaction in the course of kinetically more favorable 2-bromo-5-carbaldehyde-pyridine \textit{7}, it was carried out in dry ethyl ether at $-78 \, ^{\circ}\mathrm{C}$, and DMF was added to the mixture 20 min after the addition of \textit{n-BuLi} was complete (Scheme 1).

According to the preliminary results obtained by our group, 2-ethylvinyl-5-formyl-pyridine was unstable. Therefore, at first aldehyde \textit{7} was transformed into 2-bromo-5-[1,3]dioxolan-2-yl-pyridine \textit{8} following the standard protocol.\textsuperscript{24} Compound \textit{8} was involved in Pd-catalyzed Sonogashira–Hagihara coupling with trimethylsilyl acetylene (TMSA) giving rise to derivative \textit{9}. Hydrolysis of the trimethylsilyl group using 1 N NaOH solution in a deaerated THF-water mixture (1:1) granted the NMR-pure ethynyl derivative \textit{10}, which was used further without additional purification.

Sonogashira–Hagihara coupling reactions can be successfully carried out under various conditions.\textsuperscript{16} For our systems it was found that by decreasing the reaction temperature from 80 °C (DMF/Et$_3$N, 1:1) to $\sim 22 \, ^{\circ}\mathrm{C}$ (CH$_3$CN/Et$_3$N, 1:1) the formation of several side-products was prevented. Therefore, the attachment of bromo derivative \textit{8} to the pre-organized ethynyl-pyridine \textit{10} was carried out at room temperature in the CH$_3$CN/Et$_3$N solvent mixture, which led to the corresponding product in a reasonable yield (72%). Notably, our attempts to remove dioxolane protective groups in the presence of dilute HCl (3%) resulted in precipitation of the acid by the triple bond. Thus, the final step towards \textit{1a} was performed under milder conditions. To a solution of the dioxolane precursor in an acetone–water mixture \textit{(7:1)} a catalytic amount of p-TsOH acid (2 mol%) was added.\textsuperscript{24} Upon stirring the reaction mixture for 3 days at room temperature the target \textit{2,2'-diazatolane dialdehyde 4,4'} was obtained in nearly quantitative yield (81%).

The isomeric \textit{3,3'-diazatolane dialdehyde 2a} was obtained in a similar way (Scheme 1). Here, 2,5-dibromo-pyridine \textit{6} was selectively monolithiated in position 2 in toluene media. Time of the exchange reaction with \textit{n-BuLi} was increased to 90 min to ensure the desired organolithium intermediate formation, and precursor \textit{11} was obtained in 49% yield.\textsuperscript{25} Next, standard Sonogashira–Hagihara methodology\textsuperscript{16} was employed. Final separation on a silica gel column with a hexane/EtOAc eluent mixture \textit{(3:2)} yielded \textit{5,5'-ehyn-1,2,4-diyldis(pyridine-2-carbaldehyde) 2a} in decent yield (69%).

Several synthetic procedures towards compound \textit{3a} were reported in the literature.\textsuperscript{15} Inspired by the efficiency and simplicity of the approach sketched in Scheme 2, commercially available 4,4'-dibromobiphenyl \textit{14} was treated with \textit{n-BuLi} in the presence of a catalytic amount of TMEDA. After addition of dry DMF, typical work-up and purification, biphenyl dialdehyde \textit{3a} was isolated in 58% yield.

Bipyridine-4,4'-dicarbaldehyde \textit{4a} was achieved upon formation of 5,5'-bis(bromo-methyl)-2,2'-bipyridine \textit{16} from the corresponding dimethyl-bipyridine precursor \textit{15} following the procedure described by Vögtle.\textsuperscript{25} Then nucleophilic substitution under Sommelet

![Diagram](image-url)
conditions led to 4a.26 Synthesis of tolane dialdehyde 5a was described elsewhere.11

Final steps in the synthesis of nitroxides included condensation between 2,3-bis(hydroxyamino)-2,3-dimethylbutane (BSA) with an aldehyde, followed by the oxidation of the condensation products (i.e. imidazolidine derivatives 1-5b).11,15 Typically, the first reaction was performed under strictly anaerobic conditions in refluxing toluene (Scheme 3). Here, the corresponding N,N'-dihydroxylimidazolines 1b, 3b, 4b, and 5b were obtained in quantitative yields. As an exception synthesis of diazotolane imidazolidine 2b was realized in absolute degassed methanol at room temperature.

In order to avoid further oxidation, and, therefore, to diminish the loss of the radical units, oxidation of 1d-5d in methanol was carried out at ~0–5 °C using an ice bath.27 The progress of the reaction could be conveniently monitored by TLC analysis of the reaction mixture aliquots. Synthesis of derivative 2c was achieved using an excess of MnO₂ in methanol. Imino biradicals 1d, 3d, and 4d were obtained following the procedure described by Tretyakov et al.28,29 This method helped to avoid the harmful usage of acids and to synthesize the target molecules in better yields. As an illustration, transformation of imidazolidine 1b into the corresponding imino biradical 1d with an excess of MnO₂ in CH₃NO₂ media is depicted in Scheme 3. To aid the interpretation of magnetic properties of the isomeric NN 1c and 2c related IN biradical 1d was also prepared.

The UV-Vis absorption spectra of 1c and 2c with maxima around 600 nm were typical for the nitronyl nitroxides, while the red bisiminonitroxides absorbed around 460 nm (Table S2, ESIF). The EPR spectra of bisinitronylnitroxides exhibited nine lines with A₁/2 spacing for four equivalent nitrogens with two strongly coupled radicals. The bisiminonitroxides (1d, 3b, 4b, 5d) featured 13 lines, corresponding to the inequivalent nitrogens of the imidazole ring (as presented in the Graphical abstract and Table S2, ESIF†).

Crystal structure analysis

Crystals were obtained by slow diffusion of hexane in dichloromethane solutions of the nitroxide biradicals at room temperature. Deep-blue needle crystals of nitronyl nitroxides 1c and 2c and red blocks of imino nitroxides 1d, 3d, 4d, and 5d were then characterized using X-ray diffraction analysis. Selected torsion angles are reported in Table 1 (with some additional structural data given in the ESIF†).

Not surprisingly, similar torsion angles θ of about ~24° result in a nearly identical degree of conjugation.11,15 Consequently, a comparable spin polarization and close values of the exchange integrals were expected for most of the obtained biradical models (see for comparison Table 1). In contrast to the described situation, the radical units in nitronyl nitroxide 2c were far more twisted (>50°). From this crystal structure analysis it was assumed that nitronyl biradical 2c would exhibit a unique behavior among the compounds investigated here.

Biradical 1c adopts a triclinic space group with an inversion centre residing in the middle of the acetylone bridge (Fig. 2). Remarkably, in the asymmetric unit there are two crystallographically independent molecules with a nearly equal geometry. The dihedral angles of the mean plane of the imidazolidine ring and the two coplanar pyridine rings were found to be ±25° for O1N2C7 (O2N3C7) towards C5 and 22° for O3N5C20 (O4N6C20) towards C18 (see Table 1). Here, the N(2)–O(1) 1.280(1), N(3)–O(2) 1.278(2), N(5)–O(3) 1.279(1), and N(6)–O(4) 1.272(2) Å bond lengths occur in the typical range for the nitroxide11,14,15 The N(2)–C(7) 1.355(2), N(2)–C(11) 1.503(1), N(3)–C(20) 1.351(2), N(5)–C(20) 1.358(2), N(6)–C(20) 1.354(2), and N(6)–C(21) 1.354(2) Å bond lengths occur in the typical range for the nitroxide11,14,15 bond lengths occur in the typical range for the nitroxide11,14,15

Table 1 Selected bond lengths and dihedral angles for the synthesized biradicals

| Biradical | d, Å | θ, deg |
|----------|------|--------|
| 1c       | 1.4513(15) on C18 | 21.62(9) |
| 1c       | 1.4564(15) on C5 | 24.84(10) |
| 2c       | 1.472(18) | 53.72(11) |
| 1d       | 1.474(12) on C25 | 23.16(12) |
| 3d       | 1.471(2) on C5 | 24.85(9) |
| 4d       | 1.473(2) | 20.2(2) |
| 5d       | 1.475(17) at O2 | 15.3(5) | 15.37(19) | 5.97(12) |
The intermolecular contacts between NO groups of the first molecule with the pyridine rings (O4···C1’ 3.036, O4···C2’ 3.135 Å) of the neighboring biradical lead to V-shaped alignment of dimers (Fig. 2 and Fig. S1, ESI†).

Biradical 2c crystallizes in the P21/c space group and its molecular structure is shown in Fig. 3. Compound 2c features a transoid arrangement with an inversion center of symmetry located in the C1–C1’ bond, which is typical for the derivatives containing acetylene bridges (Fig. 3). In general, the structural data of 2c are rather similar to those described for the other nitronyl nitroxide biradicals in the literature (Table 1 and Table S1, ESI†).11,14 A remarkable difference is found in the largely increased torsion between the pyridyl ring and the imidazolidine fragment O1–N2–C7 (O2–N3–C7) with a dihedral angle of 53.72(11) (Fig. 3).

The crystal packing of 2c presents a beautiful example where the bidentate character of the nitronyl nitroxide fragment plays a major role in the spatial arrangement of the biradical chains. Here, the molecules of 2c form infinite zig-zag ribbons along the b axes (Fig. 3 and Fig. S3, ESI†). Notably, the neighboring molecules are organized in an alternate fashion, placing NN groups next to the pyridine plane and, thereby, stabilizing the crystal packing (Fig. S3, ESI†).

Imino biradical 1d crystallizes in the triclinic space group P1. There are two independent centrosymmetric half molecules in the asymmetric unit cell (Fig. 4). The main structural characteristics are similar to those described for the corresponding nitronyl nitroxide derivative 1c. Thus, the pyridine rings form angles of ≈23° and ≈25° with the imidazolidine plane (Table 1). The N(2)–O(1) 1.269(1), N(221)–O(211) 1.277(2), and N(222)–O(212) 1.257(5) Å bond distances featured minor differences.

The packing arrangement of radical dimers 1d is shown in Fig. 4, and can be described as a ladder-like structure with biradicals of the first kind forming a stair, and nitroxides of the second type extending from both sides of each step (Fig. S4, ESI†). The structure is supported by numerous hydrogen bonds.
arising from the pyridine π-bridges and the imino nitroxide chelating units. The short contacts of the NO groups and the hydrogen atoms of the pyridine core O211⋅⋅⋅H261’ = 2.456, O212⋅⋅⋅H261” = 2.538 Å (Fig. 4) seems to be the most important. The shortest interchain distances of 3.352 Å (C6⋅⋅⋅C25’) are found between the two neighboring diazatolane bridges (Fig. 4). The closest intermolecular contacts between NO groups and a pyridine ring are slightly larger, and are within the range of ~2.4–2.7 (O1⋅⋅⋅H41’, O1⋅⋅⋅H31’, respectively) and ~3.1 Å (O1⋅⋅⋅C4’).

Imino biradicals 3d and 4d feature isomorphic crystal structures. Thus, they possess the P21/n space group with a center of symmetry located in the middle of the aromatic C–C' bond (Fig. 5 and Fig. S4, ESI†). The biphenyl bridge in 3d is surprisingly planar, and the dihedral angle between the mean plane of the benzene ring and the imidazolidine moiety is only 20.2°. 3d is slightly disordered, since the five membered ring can flip around 180° such that the two NO groups could be oriented ‘E’ or ‘Z’ with 50% probability. The N(1)–O(1) 1.226(3) Å and N(2)–O(2) 1.213(3) Å bond lengths are in the standard range.15

Naturally, for the isomorphic imino nitroxide derivatives 3d and 4d the main structural characteristics are very similar.14,27 Thus, in 4d the O–N–C–N–O moiety is planar, with the N(3)–O(2) bond being slightly shorter than N(2)–O(1) 1.167(4) and 1.215(3) Å, respectively (Fig. S4, ESI†). Furthermore, in the asymmetric unit of 4d there are two crystallographically independent forms with the ratio of ~2:3 belonging to different biradical chains (Fig. S4, ESI†).

An important feature already mentioned for the other biradicals of the current series is the abundance of close intermolecular contacts between the N–O entities and the aromatic moieties in the asymmetric unit. In particular, the hydrogen bonding O1⋅⋅⋅H31’ 2.580, O1⋅⋅H123’ 2.696, and O1⋅⋅⋅C3’ 3.177 Å between the neighboring oxygen atoms and phenyl rings in 3d defines the formation of ribbon-like structures which are further organized in a zig-zag pattern. Likewise, multiple oxygen contacts (i.e. O1⋅⋅⋅H91’ 2.302, O2⋅⋅⋅H51’ 2.473, O2⋅⋅⋅H93’ 2.600, O1⋅⋅⋅C9’ 3.199 and O2⋅⋅⋅C5’ 3.085 Å) accompany the molecular ordering in the case of imino derivative 4d (Fig. S4, ESI†). Notably, the neighboring chains in 4d are connected with close O2⋅⋅O2’ 2.801 Å contacts.

Imino nitroxide biradical 5d crystallizes in a monoclinic space group with P21/n symmetry. The structure of compound 5d is shown in Fig. 6. In contrast to the previously described biradicals compound 5d has surprisingly small torsion angles between the radical unit and the adjacent phenyl ring of only about 6°.20 The overall tolane backbone is fairly planar. The N(2)–O(1) 1.271(1) Å bond distances are similar for this type of compound.

The oxo atoms in 5d act as bridging ligands (O1⋅⋅⋅H141’ 2.622, O1⋅⋅⋅H131’ 2.654 Å) connecting the neighboring biradical molecules into 1D zig-zag shaped chain structures in the crystal cell. These radical ribbons are then piled up along the b crystallographic axis (Fig. S5, ESI†), using C7⋅⋅C10’ 3.381 Å close contacts to stabilize the packing (Fig. 6 and Fig. S7, ESI†).

**Magnetic characterization**

To gain a more complete picture of the influence of a given π-spacer on the electronic properties, and especially on the intra- and inter-dimer exchange couplings, DFT calculations were performed. To get a first idea on the sizeable changes of the exchange interaction in the studied biradical models, geometry optimization with the B3LYP hybrid function and the 6-31G* basis set was carried out.31 Then the broken symmetry approach (BS) for the singlet and triplet states with the BLYP functional (to avoid Hartree–Fock contamination) and the same basis set were applied.12 Therefore, the direct exchange interaction for a weakly coupled spin dimer can be described as $J/k_B = E(\text{BS}) - E(\text{T})$, since the spin expectation.

Fig. 5 Molecular structure (top) and crystal packing (bottom) of biradical 3d.

Fig. 6 Molecular structure (top) and crystal packing (bottom) of biradical 5d.
values ($\langle S^2 \rangle_{\text{BS}}$) and $\langle S^2 (T) \rangle$ for the broken symmetry configuration are close to 1 and for the triplet configuration they are close to 2 such that their difference is close to unity.\textsuperscript{32} Notably, in the case of antiferromagnetic interactions $J$ takes negative values. The calculations were then re-done in accordance with the X-ray geometries, as listed in Table 2.

Applying a Quantum Design SQUID magnetometer the temperature dependence of the molar magnetic susceptibilities $\chi_{\text{mol}}(T)$ of microcrystalline samples 1c, 2c, 1d, 3d, 4d, and 5d was determined in the range of $2 \, \text{K} \leq T \leq 270 \, \text{K}$ in a magnetic field $B = 1 \, \text{T}$. The obtained data were corrected for the temperature-independent diamagnetic core contribution of the constituents.\textsuperscript{33} The magnetic contribution of the sample holder was determined in an independent experiment without a sample. The results are graphically displayed in the form of $\chi_{\text{mol}}(T)$ vs. $T$ in the main panel, and $\chi_{\text{mol}}$ vs. $T$ in the insets of Fig. 7 and 8 and in the ESI\textsuperscript{†} (Fig. S8). AC-susceptibility measurements ($\chi_{\text{ac}}$) were performed only on 5d as a function of the magnetic field at $T = 0.028 \, \text{K}$ using an ultra-high resolution AC-susceptometer adapted to a $^3\text{He}$-$^4\text{He}$ top-loading dilution refrigerator. The compensated-coil susceptometer was optimized for measuring small single crystals in the mg range.

Generally, all the biradicals under investigation (1c, 2c, 1d, 3d, 4d, 5d) featured a similar magnetic behavior in the studied temperature range. The observed $\chi_{\text{mol}}(T)$ values at $300 \, \text{K}$ of the nitroxides are around $0.7 \, \text{cm}^3 \, \text{mol}^{-1}$. Importantly, experimental data are rather close to the theoretical value of $0.75 \, \text{cm}^3 \, \text{mol}^{-1}$, which is expected for the two uncoupled spin $S = 1/2$ units (indicated by the broken line in Fig. 7). This indicates the high quality of the studied single crystals.

As a typical example, $\chi_{\text{mol}}(T)$ of NN-biradical 1c is shown in Fig. 7. Upon decreasing the temperature $\chi_{\text{mol}}(T)$ features an approximately linear moderate decrease down to $\sim 120 \, \text{K}$ followed by a more pronounced drop below $\sim 50 \, \text{K}$. This overall behavior reflects the dominant antiferromagnetic intra-dimer coupling $J_{\text{intra}}$. The inset of Fig. 7 shows the molar magnetic susceptibility as a function of temperature. The Bleany–Bowers equation\textsuperscript{34} for a model of an isolated dimer $\chi_{\text{iso}}$ with a mean-field correction was applied to fit the experimental data (solid line in the inset of Fig. 7). Using this fitting the sizes of the intra-dimer $J_{\text{intra}}$ and inter-dimer $zJ'_{\text{inter}}$ (where $z$ is the number of the nearest neighbors) coupling constants were extracted:

$$
\chi_{\text{mol}} = \chi_{\text{iso}} \left[1 - (zJ'_{\text{iso}}/Ng^2\mu_B^2)\right]
$$

Thus, for 1c an experimental intra-dimer coupling constant $J_{\text{intra}}/k_B = -5.4 \pm 0.2 \, \text{K}$ was obtained. This value is in tangible agreement with the coupling constant acquired from the broken-symmetry approach (Table 2). It should be mentioned that the experimental and theoretical $J_{\text{intra}}$ values of 1c are very similar to the ones reported for tolane NN ($J_{\text{intra}}/k_B = -4.8 \, \text{K}$).\textsuperscript{11}

| Table 2 | Calculated $J_{\text{intra}}$ and experimentally obtained $J_{\text{intra}}^{\text{exp}}$ intra-dimer exchange coupling constants. $J_{\text{intra}}^{\text{calc}}$ describes the inter-dimer coupling. where $z$ is the number of the nearest neighbors. $\chi_{\text{mol}}$ corresponds to the maximum in the $\chi_{\text{mol}}(T)$ plot |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Biradical | $T_{\text{max}}$ [K] | $J_{\text{intra}}^{\text{calc}}$ [kJ] | $J_{\text{intra}}^{\text{exp}}$ [kJ] | $zJ_{\text{intra}}^{\text{exp}}$ [kJ] |
| 1c | 6.8 | -19.6 | -9.8 | -5.4 $\pm$ 0.2 | -1.4 $\pm$ 0.4 |
| 2c | 53 | -2.4 | -3.1 | -12.0 $\pm$ 3.0\textsuperscript{a} | -42.4 $\pm$ 1.7\textsuperscript{a} |
| 1d | - | -2.4 | -1.1 | < -1.5 |
| 3d | 4.2 | -4.7 | -5.0 | -3.3 $\pm$ 0.1 | -2.0 $\pm$ 0.5 |
| 4d | 3.2 | 3.2 | -3.6 | -2.5 $\pm$ 0.1 | -5.8 $\pm$ 1.4 |
| 5d | 2.8 | -2.6 | -1.6 | -2.2 $\pm$ 0.1 | -0.5 $\pm$ 0.1 |
In light of this it is reasonable to assume that a mere substitution of N for C in position X (as indicated in Fig. 1), if it does not severely affect the geometry of a given crystal structure, has no practical influence on the magnetic interactions.

An unexpected result was acquired for NN derivative 2c where N was substituted with C in the Y position (Fig. 1). For this system the DFT calculations predict $J_{\text{intra}}$ values of a few Kelvin, i.e. similar to those found for the other materials under investigation. The magnetic properties of 2c determined experimentally are shown in Fig. 8. The $\chi_{\text{mol}} T$ data decreased gradually and leveled off around 20 K at a small value of approximately 0.02 cm$^3$ K mol$^{-1}$. In the inset of Fig. 8 a broad maximum in $\chi_{\text{mol}}$ at 53 K is clearly visible. From a theoretical fit corrected with a Curie term for uncoupled $S = 1/2$ entities (solid red line in the inset of Fig. 8), an inter-dimer coupling constant of $J_{\text{intra}}/k_B = -42.4$ K was obtained. This is significantly larger than $J_{\text{intra}}$ of 1c and tolane NN in ref. 11.

This observation is conceivable in terms of the crystal structure peculiarities. As described above, the radical units in nitronyl nitroxide 2c are far more twisted ($\sim 53^\circ$) in comparison to other biradical models described here. The further analysis of the X-ray data revealed exceptionally short contacts of $\sim 3.51$ Å between two neighboring NO fragments in 3,3'-diazotiane nitronyl nitroxide 2c (Fig. S7, ESI†). Apparently, these short contacts are responsible for the unpredicted strong antiferromagnetic exchange interactions found in the solid. Taking only these intermolecular interactions into account and replacing the second radical unit by hydrogen, the value $J_{\text{intra}}/k_B = -45.6$ K was calculated, which was very close to the experimentally obtained value of $-42.4 \pm 1.7$ K (Table 2). Such short inter-dimer distances between spin centers could not be found in the other biradicals.

In accordance with the theoretical predictions and crystal structure analysis IN biradicals 1d, 3d, 4d and 5d featured weak antiferromagnetic intramolecular coupling. Their intra-dimer exchange constants are listed in Table 2 (see also Fig. S8, ESI†). Interestingly, in the case of IN-biradicals 3d and 4d the N-heteroatomic substitution has barely affected their magnetic properties in accordance to the previous statement. From the experimental data recorded for imino biradical 1d no clear maximum could be resolved, indicating an extremely weak intra-dimer coupling constant $\sim -1.5$ K.

Remarkably, a closer examination of the low-temperature ($T < J_{\text{intra}}/k_B$) susceptibility data for IN-biradical 5d revealed a significant deviation from the isolated-dimer model. Typically, magnetization of the isolated-dimer systems changes in a quasi-2D system. More likely, the inter-dimer coupling in 5d has a 3D character, and therefore, this field-induced ordered phase can be described in terms of a BEC of triplons.

**Experimental section**

**Materials and methods**

All chemicals and reagents were used as received from commercial sources (Acros Organics, Aldrich, Fluka, Lancaster, Merck and Strem) without additional purification. Solvents for synthesis were used as received, unless otherwise mentioned. ESR spectra were recorded in dilute, oxygen-free solutions in toluene, concentrations $\sim 10^{-4}$ mol L$^{-1}$, using a Bruker ESP300 E X-band spectrometer equipped with an NMR gaussmeter (Bruker ER35), a frequency counter (Bruker ER340XK) and a variable temperature control continuous flow N$_2$ cryostat (Bruker B-VT 2000). The g-factor corrections were obtained using DPPH ($g = 2.0037$) as the standard. UV-Vis spectra were recorded in toluene solutions with a PerkinElmer spectrometer (UV/Vis/NIR Lambda 900) using a 1 cm optical path quartz cell at room temperature,
unless otherwise specified. ¹H and ¹³C NMR spectra were recorded on a Bruker DPX 250, Bruker DMX 300 spectrometer. Solid powders were pressed and IR spectra of the samples were recorded as they were (Nicolet 730 FT-IR spectrometer). Mass spectra (FDMS) were obtained on a VG Instruments ZAB-2 mass spectrometer. Elemental analyses were performed at the University of Mainz, Faculty of Chemistry and Pharmacy on a Foss Heraeus Vario EL. The melting points were measured on a Büchi B-545 apparatus (uncorrected) by using open-ended capillaries. Crystallographic data for the reported structures of the biradicals have been deposited at the Cambridge Crystallographic Data Centre.© The Royal Society of Chemistry 2017. This journal is

A1. General procedure for Sonogashira–Hagihara coupling reaction. An aryl bromide (21.7 mmol, 1 eq.) was transferred into a flame-dried flask in an argon stream. A mixture of dry DMF/NET₃ (50 mL, 1:1) solvents was added through the rubber septum. The solution was carefully deaerated by purging with argon for 20–25 min, and a catalytic mixture of Pd(PPh₃)₂Cl₂ (1.1 mmol, 0.05 eq.), PPh₃ (2.2 mmol, 0.1 eq.), and CuI (1.1 mmol, 0.05 eq.) was added at once. The resulting mixture was slightly heated (to 45 °C) and ethynyltrimethylsilane (32.6 mmol, 1.5 eq.) was added through the septum. After that the heating was increased to 80 °C. A white precipitate began to form after ~15 min of heating. After the reported time (4 to 16 h), the mixture was cooled to ambient temperature, and the crystalline white solid of triethylamine hydrobromide was isolated by filtration. The orange-brown filtrate was concentrated, mixed with NH₄Cl saturated aqueous solution (50 mL), and extracted with dichloromethane or diethyl ether (3 × 40 mL). The organic fractions were combined, dried over magnesium sulfate, and concentrated with silica gel in vacuo. The residue was purified using column chromatography.

A2. Using the same set-up and the catalyst/reagent ratio a mixture of dry NET₃/CH₃CN (1:1) as the solvent media was preferred. Here, after 5 minutes of stirring at room temperature formation of triethylamine hydrobromide salt was observed. The light yellow reaction mixture was stirred at room temperature for 17–19 h. The work-up was done in accordance with protocol A1. Purification on a silica gel column with dichloromethane was obtained as a yellowish oil in 85% yield (5.4 g), and was used further without additional purification. ¹H-NMR (CDCl₃, 250 MHz, 298 K, 256 scan), δ ppm: 3.92 (m, 4H, –CH₂), 5.71 (s, 1H, H-7), 7.34 (d, 1H, J = 8 Hz, H-3), 7.62 (dd, 1H, J = 8 Hz, H-4). ¹³C-NMR (CDCl₃, 63 MHz, 298 K, 256 scan), δ ppm: 129.3 (C-3), 132.7 (C-2), 152.9 (C-6), 189.8 (–CHO). MS-FD (70 eV, CH₂Cl₂) m/z: 187.3 (M⁺), MW calculated C₆H₄BrNO (MW⁺) 186.01.

2-Bromo-5-[1,3]-dioxolan-2-yl-pyridine (8). Starting compound 7 (5 g, 26.85 mmol) was charged into a flask together with benzene (100 mL), ethylene glycol (2.7 mL, 48.5 mmol) and a catalytic amount of para-toluene-sulfonic acid (0.4 g, 2.1 mmol). The solution was heated to reflux with Deane-Stark for 20 h. Then the reaction mixture was cooled down to rt, and neutralized with NaHCO₃ aqueous solution, and the phases were separated. The aqueous layer was extracted with small portions of benzene (3 × 15 mL). Benzene extracts were collected, dried over MgSO₄ and filtered. The solvent was evaporated under reduced pressure. Compound 8 was obtained as a yellowish oil in 85% yield (5.4 g), and was used further without additional purification. ¹H-NMR (CDCl₃, 250 MHz, 298 K, 16 scan), δ ppm: 3.92 (m, 4H, –CH₂), 5.71 (s, 1H, H-7), 7.34 (d, 1H, J = 8 Hz, H-3), 7.62 (dd, 1H, J = 8 Hz, H-4), 8.47 (s, 1H, H-6). ¹³C-NMR (CDCl₃, 63 MHz, 298 K, 256 scan), δ ppm: 64.5 (–CH₃), 100.2 (C-7), 126.9 (C-3), 132.4 (C-5), 135.9 (C-4), 142 (C-2), 147.9 (C-6). MS-FD (70 eV, CH₂Cl₂) m/z: 231.2 (M⁺), MW calculated C₆H₄BrNO (MW⁺) 230.06.

2-Ethynyl-trimethyl-silyl-5-[1,3]-dioxolan-2-yl-pyridine (9). Derivative 9 was synthesized according to the synthetic procedure A1. Purification on a silica gel column with dichloromethane/hexane as the eluent (3:2) afforded precursor 9 in 89% yield. ¹H-NMR (CDCl₃, 250 MHz, 298 K, 16 scan), δ ppm: 0.28 (s, 9H, –CH₃), 4.09 (m, 4H, –CH₂), 5.85 (s, 1H, H-7), 7.47 (d, 1H, J = 8 Hz, H-3), 7.74 (dd, 1H, J = 8 Hz, H-4), 8.65 (s, 1H, H-6). ¹³C-NMR (CDCl₃, 63 MHz, 298 K, 256 scan), δ ppm: 0 (–CH₃), 67.1 (–CH₂), 94.8 (C-9), 102.2 (C-7), 104.1 (C-8), 126.7 (C-3), 132.6 (C-5), 134.9 (C-4), 143.4 (C-2), 148.6 (C-6). MS-FD (70 eV, CH₂Cl₂) m/z: 247.1 (M⁺), MW calculated C₆H₄BrNO (MW⁺) 247.37.

2-Ethynyl-5-[1,3]-dioxolan-2-yl-pyridine (10). A solution of 2-ethynyl-trimethyl-silyl-5-[1,3]-dioxolan-2-yl-pyridine 10 (0.33 g, 1.3 mmol) in THF (25 mL) was treated with 1 N NaOH (50 mL) under argon at 5 °C (ice/water bath). After 35 min the reaction was complete (according to the TLC analysis of the reaction mixture aliquots). The solvent was evaporated under reduced pressure, and brine (50 mL) was added to the residue. The aqueous layer was extracted with dichloromethane (3 × 60 mL). The combined organic fractions were dried over MgSO₄ and concentrated in vacuo. The so-obtained compound 10 (89% yield)
was used for the next step without additional purification. 

\( ^{1} \text{H}-\text{NMR (CDCl}_3, 250 \text{ MHz, 298 K, 16 scan), } \delta \text{ ppm: 3.2 [s, 1H, H-9], 4.11 [m, 4H, -CH}_2, 5.88 [s, 1H, H-7], 7.51 [d, 1H, } \int^J = 8 \text{ Hz, H-3], 7.78 [dd, 1H, } \int^J = 8 \text{ Hz, H-4], 8.69 [s, 1H, H-6].} \)

\( ^{13} \text{C}-\text{NMR (CDCl}_3, 63 \text{ MHz, 298 K, 256 scan), } \delta \text{ ppm: 65.4 [ -CH}_2, 72.8 [C-9), 81.4 [C-8], 101.8 [C-7], 134.2 [C-3], 142.5 [C-2], 149.4 [C-6].} \)

Next, to the solution of the corresponding dialdehyde precursor (0.38 g, 1.35 mmol) in an acetone–water mixture (7: 1, 40 mL) para-toluene-sulfonic acid (52 mg, 0.227 mmol, 2 mol%) was added. The progress of the reaction was monitored by TLC (SiO\(_2\), dichloromethane). 1H-NMR (CDCl\(_3\), 250 MHz, 298 K, 16 scan), \( \delta \) ppm: 4.01 (m, 8H, -CH\(_2\)), 5.8 (s, 2H, H-7), 7.56 (d, 2H, \( \int^J = 8 \text{ Hz, H-3}], 7.72 (dd, 2H, \int^J = 8 \text{ Hz, H-4], 8.65 (s, 2H, H-6).} \)

\( ^{13} \text{C}-\text{NMR (CDCl}_3, 63 \text{ MHz, 298 K, 256 scan), } \delta \text{ ppm: 65.8 [ -CH}_2, 88.5 [C-8], 101.9 [C-7], 127.8 [C-3], 133.9 [C-5), 134.9 [C-4), 143.5 [C-2], 149.1 [C-6].} \)

Next, to the solution of the corresponding dialdehyde precursor (0.38 g, 1.35 mmol) in an acetone–water mixture (7: 1, 40 mL) para-toluene-sulfonic acid (52 mg, 0.227 mmol, 2 mol%) was added. The progress of the reaction was monitored by TLC (SiO\(_2\), dichloromethane). 1H-NMR (CDCl\(_3\), 250 MHz, 298 K, 16 scan), \( \delta \) ppm: 3.36 (s, 1H, H-8), 4.78 (d, 2H, \( \int^J = 8 \text{ Hz, H-3}], 8.79 (t, 1H, \int^J = 8 \text{ Hz, H-6], 10.0 (s, 1H, } \int^J = 2 \text{ Hz, H-4).} \)

\( ^{13} \text{C}-\text{NMR (CDCl}_3, 63 \text{ MHz, 298 K, 256 scan), } \delta \) ppm: 78.7 (C-7), 83.6 (C-6), 119.9 (C-3), 122.7 (C-5), 139.2 (C-4), 150.4 (C-2), 152.0 (C-6), 191.4 (–CHO). MS-FD (70 eV, CH\(_2\)Cl\(_2\) m/z: 130.3 (M\(^+\)), MW calculated C\(_6\)H\(_5\)NO (MW\(^+\)) 131.13.

5′-Ethynyl-1,2-dibis(pyridine-5-carbaldehyde) (2a). Compound 2a was synthesized applying Sonogashira–Hagihara coupling methodology A1 towards precursors 11 and 13. After evaporation of the solvent, the residue was diluted with chloroform (40 mL), and washed with NaHCO\(_3\) saturated aqueous solution. The solvent was evaporated in vacuo. The product was isolated from the reaction mixture after flash chromatography (SiO\(_2\), hexane/toluene (2: 1) and recrystallized from ethanol (6: 1). 1H-NMR (CDCl\(_3\), 250 MHz, 298 K, 16 scan), \( \delta \) ppm: 7.8 (d, 1H, H-6), 7.9 (dd, 1H, \( \int^J = 8 \text{ Hz, H-4], 8.78 (d, 1H, H-3], 9.97 (s, 1H, } \int^J = 2 \text{ Hz, H-2).} \)

\( ^{13} \text{C}-\text{NMR (CDCl}_3, 63 \text{ MHz, 298 K, 256 scan), } \delta \) ppm: 122.7 (C-5), 126.2 (C-3), 129.0 (C-4), 138.8 (C-5), 142.5 (C-2), 149.4 (–CHO). MS-FD (70 eV, CH\(_2\)Cl\(_2\) m/z: 236.0 (M\(^+\)), MW calculated C\(_6\)H\(_5\)NO (MW\(^+\)) 236.23.

Biphenyl-4,4′-dicarbaldehyde (3a). n-BuLi (10 mL, 1.6 M solution in hexane, 16 mmol) was charged into a flame-dried flask filled with argon through a septum. The mixture was stirred at -78 °C for 8 h. Dried TMEDA (2 mL, 0.013 mmol) was added. After stirring at room temperature for 15 minutes the mixture was cooled to -78 °C (dry ice/i-PrOH) and a solution of 4,4′-dibromo-biphenyl (14 g, 6.4 mmol) in dry THF (20 mL) was added slowly dropwise within 30 min. The temperature was gradually increased to -50 °C, due to a dramatic decrease in the solubility of the starting substrate at a lower temperature, and kept at this level for 25 minutes. After that the

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temperature was lowered again to −78 °C, and dry dimethylformamide (1.25 mL, d = 0.94 g mL⁻¹, 16.1 mmol) was added. The temperature was kept constant for 1 h, and then it was allowed to increase slowly. The obtained dense mixture was decomposed with NH₂Cl saturated aqueous solution and extracted with diethyl ether (3 × 50 mL). The combined organic extracts were dried over MgSO₄, and the solvents were evaporated under reduced pressure. The orange residue was recrystallized from dimethylformamide/water (1:2), yielding 0.78 g (58%) of light-yellow dialdehyde 3a. ¹H NMR (CDCl₃, 250.13 MHz), δ ppm: 7.71−7.75 (d, 4H, J = 8.0 Hz, H-2), 7.92−7.95 (dd, 4H, J₁ = 8.0 Hz, H-3), 10.02 (s, 2H, −CHO). ¹³C-NMR (CDCl₃, 63 MHz, 298 K, 206 scan), δ ppm: 128.1 (C-1), 130.4 (C-2), 136 (C-3), 145.6 (C-4), 191.7 (−CHO). MS-FD (70 eV, CH₂Cl₂) m/z: 210.1 (M⁺), MW calculated C₁₄H₁₀O₂ (MW+) 210.1.

**Bipyridine-2,2’-dicarbaldehyde (4a).** A solution of dimethyl bipyridine 15 (1 g, 5.38 mmol, 1 eq.), NBS (2.49 g, 14 mmol, 2.6 eq.), and benzoyl peroxide (0.29 g, 1.2 mmol, 0.22 eq.) in CCl₄ (50 mL) was refluxed under argon for 14 h. The precipitated succinimide was removed from the hot mixture by filtration. The precipitate was washed with CCl₄ (10 mL) and the combined CCl₄ extracts were evaporated in vacuo. The resulting yellowish solid containing 5,5’-bis(bromomethyl)-2,2’-bipyridine 1b (1 g, 2.95 mmol, 1 eq.) was refluxed with hexamethylenetetramine (2.95 mmol, 1 eq.) was refluxed with hexamethylenetetramine (2.95 mmol, 1 eq.). The mixture was heated under argon near reflux for 2−18 h. The precipitate (white or yellowish) was filtered off, washed with toluene (2−5 × 10 mL) and heptane (1 × 10 mL), and dried in air. The so-obtained derivatives were used further without additional purification.

**General synthesis of the 4,4,5,5-tetramethylimidazolidine-1,3-diol precursors 1-5b.** A suspension of BHA (1.1 eq. for each aldehyde group) and an aldehyde (1.0 eq.) in toluene (5 mL/1 mmol) was carefully deaerated by purging with argon for ~20−25 minutes. The flask was provided with a condenser equipped with an aldehyde group, and placed in an oil bath. The mixture was heated under argon near reflux for 2−18 h. The progress of the reaction was monitored by TLC (SiO₂, hexane/ethyl acetate or dichloromethane with 5% of methanol). After the process was complete and the flask was cooled down to room temperature, the precipitate (white or yellowish) was filtered off, washed with toluene (2 × 10 mL) and heptane (1 × 10 mL), and dried in air. The so-obtained derivatives were used further without additional purification.

**Bipyrine-1,1’-diyl bis[4,4,5,5-tetramethylimidazolidine-1,3-diol](3b).** Compound 3b was synthesized in accordance with general procedure B1 from biphenyl-4,4’-dicarbaldehyde 3a (0.305 g, 1.5 mmol) and BHA (0.64 g, 4.3 mmol) in quantitative yield (0.65 g, 95%). ¹H NMR ([CD₃]SO, 250.13 MHz, δ ppm: 7.00−7.06 (d, 2H, J = 8 Hz, H-4), 7.94−7.98 (dd, 2H, J₁ = 8.2 Hz, H-6), 8.76 (d, 2H, J = 1.6 Hz, H-3), 10.02 (s, 2H, −CHO). ¹³C-NMR ([THF-d₈], 63 MHz, 298 K, 338 scan), δ ppm: 121.3 (C-1), 127.6 (C-2), 129.4 (C-4), 131.9 (C-6), 136.4 (C-2), 189.7 (−CHO). MS-FD (70 eV, CH₂Cl₂) m/z: 211.6 (M⁺), MW calculated C₁₄H₁₀O₂ (MW+) 212.1.

**Bipyrine-1,1’-diyl bis[4,4,5,5-tetramethylimidazolidine-1,3-diol](4b).** Bipyrine imidazolidine 4b was synthesized following methodology B1. Thus, 4b was obtained from the reaction between bipyrine-2,2’-dicarbaldehyde 4a (0.15 g, 0.71 mmol) and BHA (0.28 g, 1.83 mmol) in 88% yield (0.30 g).

The 13C-NMR spectrum of §2b was not obtained, as the sample appeared to be unstable in DMSO and began to oxidize in the NMR tube upon measurement.
A suspension of 4,4,5,5-tetramethylimidazoline-1,3-diol in nitromethane (12 mL) was cooled down to 0–5 °C using an ice bath. To that mixture a 5% aqueous solution of NaIO4 (0.8 eq.) was added dropwise. The progress of the reaction was monitored by TLC (SiO2, hexane/ethyl acetate with 5% methanol). After the reaction was complete (0.5–3 h), a dark-blue organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 25 mL). The combined organic extracts were additionally washed with water (2 × 30 mL), brine (1 × 50 mL), and dried over MgSO4 (in some cases − Na2SO4). The residue after filtration was reduced to a volume of 2 mL, and purified on a chromatographic column (SiO2, hexane/ethyl acetate or CH2Cl2/MeOH).

**General procedure for the oxidation of 4,4,5,5-tetramethylimidazoline-1,3-diol derivatives to nitronyl nitroxides.**

To a magnetically stirred solution of imidazolidine (1 mmol) (0.27 g, 0.55 mmol) employing an excess of MnO2 (0.7 g, 9.5 mmol) in 61% yield (250 mg). M.p.: compound decomposed at 193 °C. UV-Vis (toluene) λ/nm (ε, mol−1 cm−1): 467 (944), 326 (35207). FT-IR (powder, ν/cm−1): 3067, 2969, 2924 (s, Py−C−H stretching), 2136 (w, C≡C), 1591 (s, Py−C=C stretching), 1555 (s, C=Nimid), 1368 (m, N−O). Elemental analysis: C 67.6; H 6.43; N 18.07; calculated for C26H30N6O4: C 63.66; H 6.16; N 17.13.

**Conclusion**

We have demonstrated that the synthesis and study of structurally similar compounds exhibiting different magnetic behaviors provide a reasonable approach for understanding the relationship between the substituents in the aromatic ring and the intramolecular exchange constant Jinterr. Unfortunately, the magnetic interactions based on structural peculiarities are difficult to predict as their strength strongly depends on the relative orientation.
between the interacting magnetic orbitals. Here, the torsion angles $\theta$ have crucial impacts on the overall $\pi$-conjugation in the nitroxide biradical systems. The latter in turn is responsible for the efficient communication between the nitroxide fragments. The crystal structure analysis shows that the synthesized biradicals are planar with relatively small torsions between the radical fragments and the aromatic bridges (with an exception in the case of derivative 2c). These are the essential prerequisites for obtaining a weak intramolecular coupling. A rapid increase of the torsion hinders the conjugation within the biradical system 2c, decreasing the intramolecular exchange interactions within the molecule. This structural feature causes an enhancement of the intermolecular coupling within 2c. As a result, an unprecedentedly high value of the coupling constant is observed in NN biradical 2c. This work illustrates the difficulties in the design and prediction of a target structure, and the need for an experimental proof.

Magnetic measurements, carried out on single-crystalline samples, confirmed that for biradicals 1c, 1d, 3d, 4d and 5d, weak antiferromagnetic intramolecular interactions are predo-
minant. According to the magnetic characterization studied $\pi$-bridged nitroxides possess a moderate intra-dimer coupling in the range $-2$ to $-6$ K as derived from the fits based on an isolated dimer model. Furthermore, magnetic measurements and their interpretation revealed that NN biradical 2c exhibits surprisingly strong antiferromagnetic interactions, owing to the short ($\sim 3.5$ Å) interdimer interaction. IN biradical 5d features a field-induced ordered phase assigned to 3D inter-dimer couplings, which accounts for a description in terms of a BEC of triplons.

In summary, we have found promising candidates in the quest for purely organic molecular magnets and crystalline networks with higher ordering.

**Conflicts of interest**

There are no conflicts to declare.

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