

2,6-Bis(pyrazolyl)pyridine Functionalised with Two Nitronylnitroxide and Iminonitroxide Radicals

Giorgio Zoppellaro,^[a] Ahmed Geies,^[a] Volker Enkelmann,^[a] and Martin Baumgarten^{*[a]}

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During the last two decades, growing interest in the field of material chemistry has been focused on the synthetic design of organic high-spin molecules for use as novel magnetic materials. Conjugated radicals based on the bis(pyrazolyl)pyridine core are very attractive in principle, since they per se combine optical, chelating and magnetic properties on a single molecular entity. The functionalisation of this core via the bis(4'-formyl) derivatives with Ullman radicals results in novel functional biradicals, which may further be used for supramolecular architectures. In this paper we describe the synthesis, structure and properties of 2,6-bis[4'-(3-oxo-1-oxyl-4,4,5,5-tetramethylimidazolin-2-yl)pyrazol-1'-yl]pyridine (Pz₂PyNN) and 2,6-bis[4-(1-oxyl-4,4,5,5-tetramethylimidazolin-2-yl)pyrazolyl]pyridine (Pz₂PyIN). The two biradicals can clearly be differentiated by UV/Vis, IR and EPR spectroscopy. The optical absorptions of the blue

Pz₂PyNN appear around $\lambda_{\text{max}} = 610 \text{ nm}$ ($\epsilon \approx 1700 \text{ M}^{-1} \text{ cm}^{-1}$) while for Pz₂PyIN the orange-red colour arises from absorptions at $\lambda_{\text{max}} = 468 \text{ nm}$ ($\epsilon \approx 1400 \text{ M}^{-1} \text{ cm}^{-1}$). A triplet ground state for the bis(nitronylnitroxide) Pz₂PyNN with $\Delta E_{\text{S-T}} \approx 11.8 \pm 4.8 \text{ cm}^{-1}$ can be deduced from the EPR studies because of the increase of the double integrated intensity times temperature at very low temperatures, indicating complete population of the triplet state. For the related bis(iminonitroxide) Pz₂PyIN a much smaller (at least one order of magnitude lower) singlet-triplet energy gap with an upper limit of 0.7 cm^{-1} has been derived ($0.7 \geq \Delta E_{\text{S-T}} \geq -0.07 \text{ cm}^{-1}$). The new multifunctional biradicals represent the first example of high-spin molecules in the bis(pyrazolyl)pyridine family.

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1. Introduction

Studies of magneto-structural correlations in organic-based materials have fascinated chemists, physicists and theoretical chemists, because the rich variety of properties and related physical phenomena that these materials exhibit macroscopically provide inspiration for their potential applications in material science.^[1–3] For preparative organic chemists,^[4–6] the challenge in this field consists in tailoring the magnetic properties by modification of the molecular unit, thereby gaining control of the intramolecular interactions among the spin carriers. Several theoretical guidelines^[7–11] for the design of the organic backbone in non-Kekulé^[12–16] hydrocarbons have been described and much debated,^[17–20] and these in turn allow prediction of the ground-state multiplicity of the single magnetic entity. Conceptually, the intramolecular interactions among unpaired spins can be visualised as the fine balance of three physical mechanisms^[1,21–24]: (i) direct coupling, (ii) indirect coupling and (iii) spin polarisation. The design of the molecular backbone (spacer) allows a decrease in the effect of

direct coupling that leads in general to antiferromagnetic interactions, and tuning of the indirect coupling, by choosing the types of bonds involved (connectivity) and molecular topology. Then, the nature of the radicals defines the magnitude of the spin polarisation contribution.^[23,25] In this regard, much of the progress achieved in this field over the last twenty years, and the enormous knowledge gained about the magnetism phenomenologically, has been driven by the chemistry of nitroxides^[26–28] and the discovery of nitronylnitroxide (NN) and iminonitroxide (IN) radicals.^[29–31] Their inherent stability^[31–35] in fact allows experimental probing of all the effects governing the intramolecular interaction among spin units. Finally, the goal as commonly recognised is to arrange each unit into a supramolecular network.^[36–40] One approach is based on intermolecular interactions between pure organic carriers, and this led to the achievement of bulk ferromagnetism where the *p*-nitrophenyl nitronylnitroxide made by Kinoshita's group^[41] and the 1,3,5,7-tetramethyl-2,6-diazaadamantane-*N,N'*-dioxyl made by Rassat et al.^[42] represent just two among many outstanding examples.^[43–48] Another approach relies on the combination between paramagnetic metal ions and pure organic radicals, leading to a new class of hybrid organic-inorganic materials described in the extensive work carried out by several groups.^[49–55] We therefore thought to follow the last approach by building chelating ligands as a core and functionalising them with

^[a] Max Planck Institute for Polymer Research, Ackermannweg 10, 55128, Mainz, Germany
E-mail: baumgart@mpip-mainz.mpg.de
Fax: (internat.) +49-6131-379370

nitronyl- and iminonitroxide radical moieties. In this instance, a clear understanding of the intramolecular exchange interaction (J) between the radical fragments through the coupler is a prerequisite to their possible use as novel building blocks for supramolecular architectures. In our previous work,^[56] we showed how, following design of the molecular backbone, the novel nitronylnitroxide and iminonitroxide biradical systems, attached to a terpyridine spacer, exerted a strong intramolecular ferromagnetic exchange interaction between the radical units. Those represented the first reported example of $S = 1$ coupled Ullman radicals appended on a terpyridine system, and their triplet ground-state spin multiplicity had been predicted on the basis of topological considerations. In order to further extend this work on similar heterosystems, we substituted the pyridines with pyrazolyl moieties^[57] which led to the novel symmetric bis(pyrazolyl)pyridine (**Pz₂Py**) derivative presented in this paper. This unit may be regarded as a terpyridine-analogue, since it reproduces the tridentate nitrogen binding motif of the terpyridine core as schematically shown in Figure 1. On the other hand, it is worth mentioning that in **Pz₂Py** the topological guidelines for intramolecular coupling for π -conjugated radicals cannot be applied because the presence of two pyrazolyl fragments (five-membered ring) renders this system nonalternant. However, besides the unfavourable spin-coupling pathways, the triplet ground state was experimentally found for the bis(nitronyl-nitroxide) radical with an appreciable singlet–triplet energy gap ΔE_{S-T} of 17 K ($\approx 11.8 \pm 4.8 \text{ cm}^{-1}$) while a much smaller gap of $\approx 1 \text{ K}$ ($0.70 \geq \Delta E_{S-T} \geq -0.07 \text{ cm}^{-1}$) has been estimated for the related bis(iminonitroxide) radical. One can recognise that the search for new organomagnetic units in turn stimulates further progress in theoretical considerations.

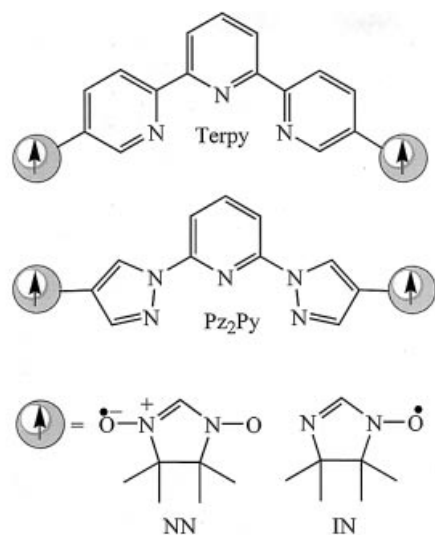


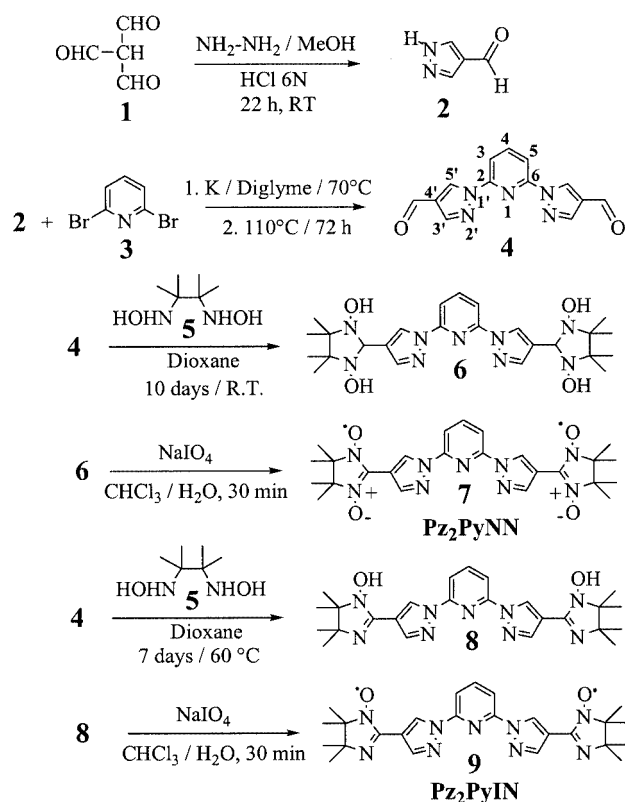
Figure 1. The tridentate nitrogen core in the terpyridine (terpy) and in the bis(pyrazolyl)pyridine (**Pz₂Py**); the position in which the radical units have been appended are indicated with arrows

2. Results and Discussion

2.1. Synthesis of **Pz₂PyNN** and **Pz₂PyIN**

The bis(radical) derivatives **Pz₂PyNN** (2,6-bis[4'-(3-oxo-1-oxyl-4,4,5,5-tetramethylimidazolin-2-yl)pyrazol-1'-yl]pyridine, **7**) and **Pz₂PyIN** (2,6-bis[4-(1-oxyl-4,4,5,5-tetramethylimidazolin-2-yl)pyrazolyl]pyridine, **9**) have been synthesised following the multistep approach outlined in Scheme 1. The condensation of triformylmethane **1**^[58] with hydrazine monohydrate in acidified alcoholic medium, afforded the pyrazol-4-carboxaldehyde **2**.^[59] Then, the 2,6-bis(4-formyl-pyrazolyl)pyridine **4** was synthesized in a one-step reaction by condensation between the nucleophilic potassium salt of **2**^[60] with 2,6-dibromopyridine **3** in diethylene glycol dimethyl ether (diglyme) as reaction solvent (yield 45%). The choice of diglyme was dictated by the observation that while the first bromine group in **3** is replaced relatively easily (70 °C, 48 h), substitution of the strongly inactivated second bromine group requires a higher temperature and prolonged reaction time. Diglyme offers the advantages with respect to other ethereal solvents (e.g. THF, Et₂O) of high boiling point and stability at high temperature. In addition, its ability to chelate cations (the potassium cation in our case) leaves the nucleophile much more active. The subsequent condensation between the diformyl derivative **4** with 2,3-bis(hydroxylamino)-2,3-dimethylbutane (**5**)^[29–31,61] in dioxane occurred while stirring at room temperature under argon over ten days, and afforded the radical precursor **6** (2,6-bis[4-(1,3-dihydroxy-4,4,5,5-tetramethylimidazolidin-2-yl)-pyrazolyl]pyridine) as a yellowish powder (yield 42%). Heating the reaction mixture increased the decomposition of **6** (dehydration) in solution, and led to the formation of compound **8** (2,6-bis[4-(1-hydroxy-4,4,5,5-tetramethylimidazolin-2-yl)pyrazolyl]pyridine). The sodium periodate oxidation of **6** carried under phase-transfer conditions (CHCl₃/H₂O) gave the crude biradical **Pz₂PyNN** in the organic phase. The side products (i.e. mono-nitronyl-nitroxide, mono-iminonitroxide) were easily recognised on TLC and separated by column chromatography (silica gel, acetone/light petroleum ether, b.p. 30–40 °C, 2:8), then highly pure **Pz₂PyNN** was collected ($R_f = 0.34$) and recrystallised from CHCl₃ (blue crystals, yield 27%). Similarly, oxidation of the radical precursor **8** under phase-transfer conditions (CHCl₃/H₂O) afforded the crude biradical **Pz₂PyIN** in the organic phase. Purification of the crude mixture was carried out by column chromatography (silica gel, acetone/light petroleum ether, b.p. 30–40 °C, 2:8, $R_f = 0.46$), then recrystallisation from CH₂Cl₂ gave pure **Pz₂PyIN** (orange powder, yield 51%). As expected, the biradical **Pz₂PyIN** was obtained in larger yield than **Pz₂PyNN**. Once isolated, the biradicals are stable as powder over several months, while in protic solvents (e.g. CH₂Cl₂ or CHCl₃), which may catalyse loss of water molecules, a clear decrease of their stability was observed upon prolonged storage. However, in aprotic solvents such as toluene, both biradicals can safely be kept for a long time, and even heated up to 60 °C for several hours, with no hint of

decomposition, providing that the medium is maintained oxygen free.



Scheme 1

2.2. Optical Properties

In solution the biradical Pz_2PyNN is light blue (toluene, $\lambda_{max} = 610$ nm and $\epsilon \approx 1700$ M⁻¹ cm⁻¹, $n \rightarrow \pi^*$ transitions) while Pz_2PyIN shows the typical orange-red colour (toluene, $\lambda_{max} = 468$ nm and $\epsilon \approx 1400$ M⁻¹ cm⁻¹, $n \rightarrow \pi^*$ transitions). For both biradicals, the broad absorptions in the visible region of the spectra are characterized by several vibronic components (Figure 2, solid line for Pz_2PyNN and dashed-dotted line for Pz_2PyIN , respectively), and their molar extinction ϵ is more than three times greater than in the analogous terpyridine system^[56] (Figure 1), where two nitronylnitroxide or iminonitroxide radicals have been attached in position 5,5'' (toluene, $\lambda_{max} = 605$ nm, $\epsilon = 480$ M⁻¹ cm⁻¹ for the bisnitronyl- and $\lambda_{max} = 459$ nm, $\epsilon = 380$ M⁻¹ cm⁻¹ for the bisiminonitroxide). Their infrared spectra recorded in KBr pellets are shown in Figure 3. In the case of Pz_2PyNN (solid line) a strong absorption originating from the N–O stretching mode is visible around 1359 cm⁻¹ while for Pz_2PyIN (Figure 3, dashed-dotted line) such a signal, much weaker and commonly shifted to higher wavenumber,^[31,60,62] appears to be embedded in the spectrum.

2.3. The Crystal Structure of Pz_2PyNN

Upon slow diffusion of hexane into a $CHCl_3$ solution of radical Pz_2PyNN , blue crystals were obtained and these

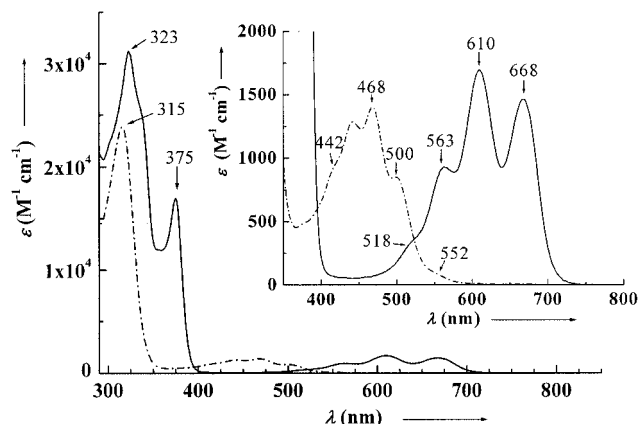


Figure 2. UV/Vis spectra of Pz_2PyNN (solid line) and Pz_2PyIN (dashed-dotted line) recorded in toluene solutions at room temperature; the inset shows magnified their visible region of the spectra

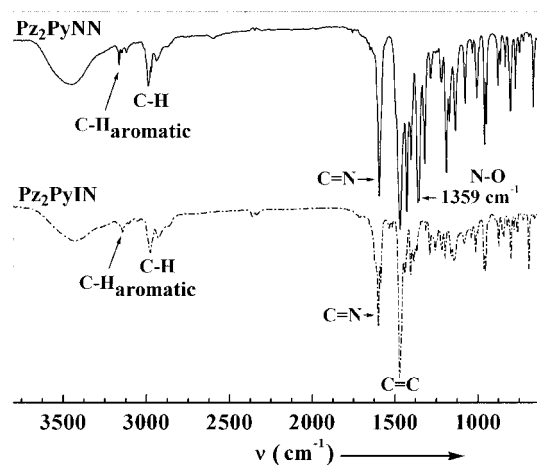


Figure 3. IR spectra of Pz_2PyNN (solid line) and Pz_2PyIN (dashed-dotted line) recorded in KBr pellets at room temperature

were structurally characterized by X-ray diffraction (Figure 4). One of the structural features of the molecule are the torsional angles ϕ_1 and ϕ_2 because they reflect the possibility of free rotation around the single bonds (σ , N2–C1, C7–C5) and hence can be a measure of the effective π -conjugation through the spacer. Since the molecules are located on a twofold rotation axis, angles ϕ_1 and ϕ_2 are identical for each half-molecule. ϕ_1 (C6–N2–C1–N1) is 4.6° and the torsional angle (C6–N2–N3–C4) is 0.29°, so the two pyrazolyl rings and the pyridinyl central core are nearly coplanar. ϕ_2 , between the imidazolidinyl and the pyrazolyl moieties (N5–C7–C5–C6), is very similar at 4.2°. Hence, the overall quasi-planar structure of Pz_2PyNN in the crystals satisfies the geometrical prerequisite for effective π -conjugation between the two radical fragments. The imidazolidinyl rings show relatively high intraring torsion in the periphery, with (C8–C9–N5–C7) being –18.86° and (C9–C8–N4–C7) –22.58°. The intramolecular (O2–O* 2) and the shortest intermolecular through-space distances

(short magnetic contacts) between the imidazolidinyl oxygen atoms are 5.642 and 4.738 Å, respectively. The intramolecular distances between the two ONCNO groups (C7–C*7), where most of the radical-spin densities are located, and that between the pyrazolyl carbon atoms (C5–C*5) are 9.130 and 7.706 Å, respectively. Finally, the N–O bond lengths are in the range of the nitroxide radicals reported in literature (1.283 Å for O2–N5, 1.281 Å for O1–N4).

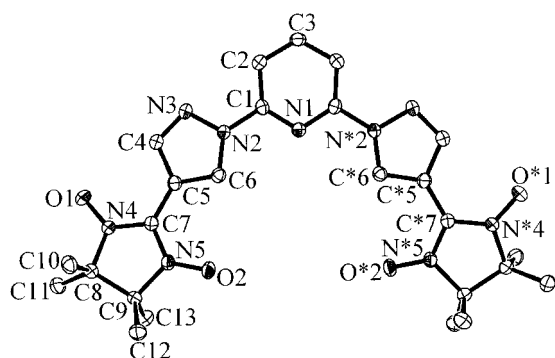


Figure 4. The crystal structure of Pz₂PyNN; the thermal ellipsoids are drawn at 50% probability. The hydrogen atoms are omitted for clarity

2.4. EPR Characterisation of Pz₂PyNN and Pz₂PyIN in Solution and in the Frozen State

In order to disclose the magnitude and sign of the intramolecular exchange interaction between the radical moieties in Pz₂PyNN and Pz₂PyIN, detailed EPR analyses have been carried out. Owing to its high sensitivity, the EPR technique allows working with magnetically diluted samples, thus minimising the effects of intermolecular contributions among the paramagnetic centres. The EPR spectrum of Pz₂PyNN (toluene, 10^{−4} M, 298 K) displayed a resolved nine-line pattern [Figure 5 (A), solid line] at $g_{iso} = 2.0065(1)$, where the observed line-spacing ($a_{N1obs} = 0.38$ mT) corresponds to half of that found for the related mono-nitronitroxide radical (where $a_N = 0.76$ mT). Similarly, a 13-line pattern at $g_{iso} = 2.0060(1)$ is exhibited in Pz₂PyIN [Figure 5 (B), solid line, toluene, 10^{−4} M, 298 K] where again half of the line-spacing ($a_{N1obs} = 0.21$ mT, $a_{N2obs} = 0.45$ mT) is observed, compared with the related mono-iminonitroxide radical (where $a_{NI} = 0.42$ mT and $a_{N2} = 0.91$ mT). Such findings indicate that in these biradicals, the intramolecular exchange interaction (J) between the radical fragments through the spacer bis(pyrazolyl)pyridine is much larger than the hyperfine terms ($|J/a_N| \gg 1$). The total spectral width, shape and number of observed peaks did not change upon changing solvent (CHCl₃, CH₂Cl₂, acetone, THF, MeOH) either for Pz₂PyNN and Pz₂PyIN, so toluene was used for all the measurements since the radicals showed the highest stability in this sol-

vent. The double integrated EPR signal intensities for Pz₂PyNN and Pz₂PyIN in solution accounts for 2.0 ± 0.1 uncorrelated spins, thus a rather small singlet–triplet energy gap (ΔE_{ST}) is present, and contributions arising from thermally accessible spin states are active in the high-temperature regime. In such systems, when the fraction of biradicals under the strong exchange limit ($|J/a_N| \gg 1$) represents the unique or the dominating component in the observed spectrum,^[31,69] the simulation of the entire isotropic solution EPR spectrum by numerical diagonalisation of the spin Hamiltonian [Equation (1)].

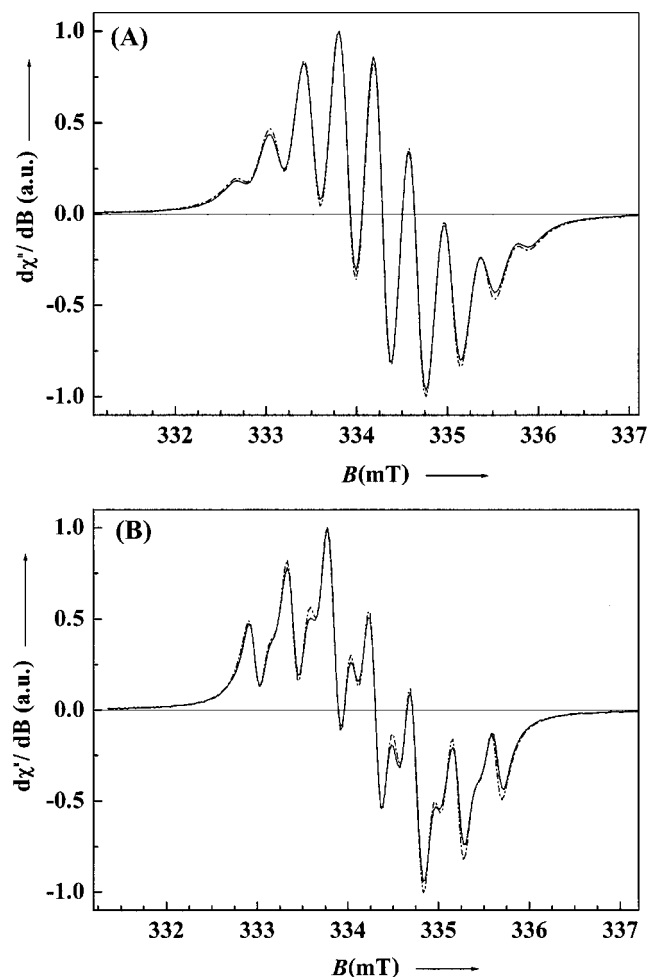


Figure 5. (A) EPR spectrum of Pz₂PyNN (solid line) recorded in dilute and oxygen-free toluene solution at 298 K and its computer simulation (dashed-dotted line, Gaussian line-width: 6.12 MHz, modulation amplitude: 0.84 MHz, $|a_{iso}| = 21.44$ MHz; experimental parameters: 9.4033 GHz, 100 kHz modulation frequency, 4.0 mW power, 0.03 mT modulation amplitude; (B) EPR spectrum of Pz₂PyIN (solid line) recorded in dilute and oxygen-free toluene solution at 298 K and its computer simulation (dashed-dotted line, Lorentzian line-width: 4.78 MHz, modulation amplitude: 0.84 MHz, $|a_{iso}| = 18.67$ MHz where $|a_{iso}| = [|a_{N1}| + |a_{N2}|/2]$ with $|a_{N1}| = 11.62$ MHz and $|a_{N2}| = 25.7211$ MHz, weight factor: 0.73 for the averaged molecular conformations in strong exchange limit, the other factors are kept the same as the experimentally recorded spectrum); experimental parameters: 9.4027 GHz, 100 kHz modulation frequency, 5.0 mW power, 0.03 mT modulation amplitude

$$H = g\beta B(S_a + S_b) - 2JS_aS_b + \sum_i a_{Ni} \times (S_a \hat{I}_{Ni} + S_b \hat{I}_{Ni}) - g_N \beta_N B \hat{I}_N \quad (1)$$

may provide an estimate of the lower limiting value for the exchange interaction, but clearly not its sign (either ferro, $J > 0$, or antiferromagnetic, $J < 0$). The simulation accounts for $|\Delta E_{S-T}| = |2J/k_b| = 0.07 \text{ cm}^{-1}$ (rms = 0.31) in the case of Pz_2PyNN [Figure 5 (A), dashed-dotted line] and for $|2J/k_b| = 0.06 \text{ cm}^{-1}$ (rms = 0.38) in the case of Pz_2PyIN [Figure 5 (B), dashed-dotted line]. In frozen solution, the EPR spectrum of the allowed transitions in Pz_2PyNN ($\Delta M_s = 1$, toluene, 10^{-3} M , 120 K, $g_{av} = 2.0065$) showed a poorly resolved anisotropic pattern. This arises from dipolar interactions characteristic of randomly oriented triplet species and the relatively large distance between the radical centres.

However, the zero-field-splitting parameter D' ($D' = |D|/hc$) has been estimated as 4.8 mT ($\approx 4.50 \times 10^{-3} \text{ cm}^{-1}$). In the point-dipole approximation,^[71–74] the D' value is consistent with the average distance between the centres of the ONCNO groups of about 8.3 Å, and correlates nicely with the average distances between the radical centres observed in the crystal structure.

Similarly, a poorly resolved anisotropic pattern was observed in the case of Pz_2PyIN ($\Delta M_s = 1$, toluene, $1.2 \times 10^{-3} \text{ M}$, 120 K, $g_{av} = 2.0060$); the zero-field-splitting parameter D' ($D' = |D|/hc$) has been estimated as 5.1 mT ($\approx 4.78 \times 10^{-3} \text{ cm}^{-1}$), which is consistent with the shorter distance between the centres of the ONCN groups of about 8.2 Å.

The triplet state nature of Pz_2PyNN was supported by the appearance of the forbidden transition at half-field ($\Delta M_s = 2$, toluene, 10^{-3} M , $T = 120 \text{ K}$, $g_{av} \approx 4.01$, $\Delta B_{pp} \approx 1.05 \text{ mT}$) and its temperature dependence was followed down to cryogenic temperature [Figure 6 (A) in the inset, $T = 4.1 \text{ K}$, $g_{av} \approx 4.01$, $\Delta B_{pp} = 1.04 \text{ mT}$]. The microwave powers applied in the measurements were carefully controlled in such a way that the signal intensities were proportional to the square root of the power. As shown in Figure 6 (A), the double integration (DI) of the $\Delta M_s = 2$ signal increased upon decreasing the temperature (open circles). Furthermore, the quantity $\text{DI} \cdot T$ (closed circles), which is proportional to the population in the triplet state, also increased with decreasing temperature. Such findings indicate that the ground state in Pz_2PyNN is the triplet ($S = 1$), and the singlet ($S = 0$) should be associated with a thermally accessible excited state. Fitting of the data according to the Bleaney–Bowers model for two interacting spin systems as described in Equation (2),^[69] where

$$\text{DI} = \chi_{\text{EPR}} \propto \{ (2Ng^2\beta^2/3k_bT) \times [1/3 + \exp(-2J/k_bT)] \} \quad (2)$$

gave a separation $\Delta E_{S-T} = 2J/k_b$ of $11.8 \pm 4.8 \text{ cm}^{-1}$ between the magnetic ground ($S = 1$) and the excited states ($S = 0$). In the Pz_2PyIN system, the triplet-state nature was also confirmed by the appearance of the forbidden transition at half-field ($\Delta M_s = 2$, toluene, $1.2 \times 10^{-3} \text{ M}$, $T = 120 \text{ K}$, $g_{av} \approx 4.01$, $\Delta B_{pp} = 0.99 \text{ mT}$). Its temperature depen-

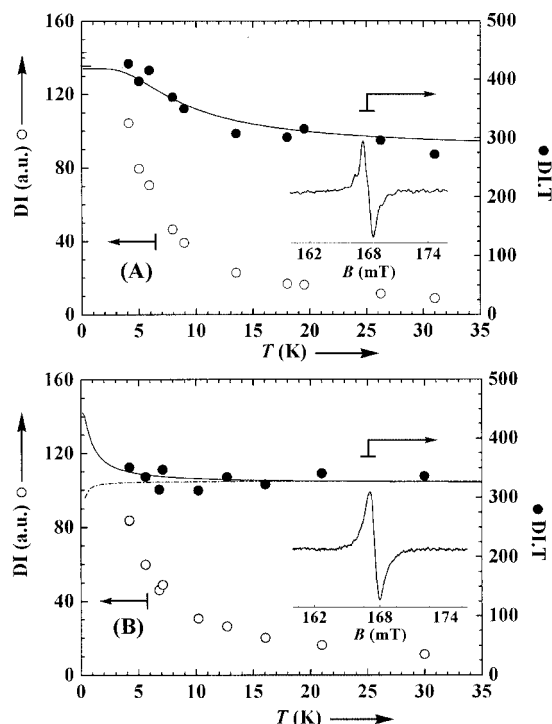


Figure 6. (A) The evolution of the double integrated signal intensities (DI, open circles) and the product $\text{DI} \cdot T$ (closed circles) versus T of the $\Delta M_s = 2$ signal for Pz_2PyNN in the low temperature range ($T < 40 \text{ K}$); the solid lines in $\text{DI} \cdot T$ represent the best fitting of the data with parameters given in the text according to the Bleaney–Bowers model for two interacting $S = 1/2$ systems; the inset shows the half-field transition of Pz_2PyNN recorded in frozen solution at $T = 4.1 \text{ K}$; experimental parameters: 9.4193 GHz, 100 kHz modulation frequency, 0.4 mT modulation amplitude, 0.320 mW power; (B) the evolution of the double integrated signal intensities (DI, open circles) and the product $\text{DI} \cdot T$ (closed circles) versus T of the $\Delta M_s = 2$ signal for Pz_2PyIN in the low temperature range ($T < 40 \text{ K}$); the solid line in $\text{DI} \cdot T$ represents the best fitting of the data for the upper $2J/k_b$ limit ($S = 1$) with parameters given in the text according to the Bleaney–Bowers model; similarly, the dashed-dotted line represents the correspondent fitting for $\text{DI} \cdot T$ assuming the singlet ground state ($S = 0$); the inset shows the half-field transition of Pz_2PyIN recorded in frozen solution at $T = 4.2 \text{ K}$; experimental parameters: 9.4192 GHz, 100 kHz modulation frequency, 0.4 mT modulation amplitude, 0.320 mW power

dence has also been followed down to cryogenic temperature [Figure 6 (B) in the inset, $T = 4.2 \text{ K}$, $g_{av} \approx 4.01$, $\Delta B_{pp} = 0.96 \text{ mT}$].

While the $\Delta M_s = 2$ signal clearly increased upon decreasing the temperature [Figure 6 (B), open circles], the product $\text{DI} \cdot T$ appeared nearly constant (closed circles), with a very small rise at the lowest temperature. In such a case, either the triplet state ($S = 1$) is the lowest-energy state separated from the singlet ($S = 0$) by a substantial gap relative to the thermal energy ($|2J| \gg k_bT$), or the energy difference between triplet ($S = 1$) and singlet ($S = 0$) is extremely small leading to degeneracy of those levels. Therefore, any change in temperature does not shift the thermal equilibrium between the two states, and they remain statistically populated according to the Boltzmann distribution ($N_u/N_0 = [g_u/g_0] \times \exp[-\Delta E/k_bT]$, e.g. 75% of the molecules occupy the triplet state and 25% the singlet state). Since

from the solution EPR studies discussed on Pz_2PyIN , it was clear that the energy gap between singlet and triplet cannot be large, such separation has to be very small, ranging far below the temperature available with our experimental setting (4 K). Fitting the $\text{DI}\cdot T$ data according to the Bleaney–Bowers model for two interacting spin system, gave an upper limit for the singlet–triplet separation $\Delta E_{\text{S-T}} = 2J/k_{\text{B}}$ of 1 K (i.e. about 0.70 cm^{-1}) assuming a triplet ground state. If the singlet ground state ($S = 0$) is considered, the separation $\Delta E_{\text{S-T}}$ is further reduced by a factor of ten ($2J/k_{\text{B}}$ of about -0.07 cm^{-1}), in close agreement with the lower limiting value obtained from the simulation of the solution EPR spectra. Since complete spin reversal of the ground-state multiplicity (from nitronyl- to iminonitroxide) seems improbable but cannot be excluded, we may suggest that in Pz_2PyIN also the ground state is the triplet. These findings are consistent with previous observations where nitronylnitroxide-based biradicals exert a much stronger exchange interaction than the parent bis(iminonitroxide) system.^[31,70]

In conclusion we have described a hitherto novel functionalisation of the bis(pyrazolyl)pyridine core with neutral radical moieties of the NN and IN type. Clear differentiations between their spectroscopic behaviour (UV, IR, EPR spectroscopy) is described, allowing also their use as fingerprints for contaminated samples. While the bis(nitronylnitroxides) are relatively strong ferromagnetic exchange coupled in intramolecular fashion the exchange coupling of the bis(iminonitroxides) must presumably still undergo ferromagnetic exchange but by at least an order of magnitude lower than for the NIT series, making them less favourable in such functionalised building blocks.

3. Experimental Section

3.1. General Remarks: Solvents were distilled before use and kept dry over molecular sieves; all other reagents were used as received. ESR spectra were recorded in dilute, oxygen-free solutions in toluene, concentration $10^{-4} \text{ mol} \times \text{dm}^{-3}$ unless otherwise stated, using a Bruker X-band spectrometer ESP300 E, equipped with an NMR gaussmeter (Bruker ER035), a frequency counter (Bruker ER041XK) and a variable temperature control continuous flow N_2 cryostat (Bruker B-VT 2000) or with an Oxford system (ESR, 910) helium continuous flow cryostat. The g -factor corrections were obtained using the PNT radical ($g = 2.0026$) or DPPH ($g = 2.0037$) as standard. Calculations of the spin concentrations were carried out on dilute solutions (10^{-4} M), where the double integrated signal intensities of 2,6-bis[4'-(3-oxo-1-oxyl-4,4,5,5-tetramethylimidazolin-2-yl)pyrazol-1'-yl]pyridine (**7**) and 2,6-bis[4-(1-oxyl-4,4,5,5-tetramethylimidazolin-2-yl)pyrazolyl]pyridine (**9**) were compared with those of the corresponding nitronylnitroxide and iminonitroxide monoradicals recorded under identical conditions (modulation amplitude, receiver gain, power, sweep time, temperature) using the same EPR tube, and with careful control of the filling factors. UV/Vis spectra were recorded in toluene solutions with a Perkin–Elmer spectrometer (UV/Vis/NIR Lambda 900) using a 1-cm optical path quartz cell at room temperature. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX 250 spectrometer. IR spectra were recorded in KBr pellets (Nicolet 730 FT-IR spec-

trometer) at room temperature. Mass spectra were obtained on FD-MS, VG Instruments ZAB-2 mass spectrometer. Elemental analyses were performed at the University of Mainz, Faculty of Chemistry and Pharmacy on a Foss Heraeus Varico EL. Melting points were measured on a Büchi B-545 apparatus (uncorrected) by using open-ended capillaries. The 4-formylpyrazole **2**^[59] and 2,3-bis(hydroxylamino)-2,3-dimethylbutane (**5**) (free base) were prepared according to literature procedures.^[61]

Triformylmethane (1): Compound was prepared according to a briefly reported procedure,^[58] which is described fully here. POCl_3 (13.8 mL, 0.147 mol) was added dropwise to a cooled solution of DMF ($\text{C}_3\text{H}_7\text{NO}$, 40 mL, 0.518 mol, at about 0°C) over a period of 1 h keeping the temperature below 5°C during the addition. The solution initially appeared greenish but turned pale orange by the end of the addition. Then the ice-bath was removed and the dense mixture was stirred at room temperature for 1 h. Bromoacetic acid (7.15 g, 0.051 mol) was added in portions, and the mixture was heated for 24 h at 70°C . The brownish mixture was decomposed with ice/water (200 mL) and solid Na_2CO_3 was carefully added in large excess until $\text{pH} \approx 8$. Absolute ethanol was added (2 L), and the inorganic salts were filtered off. The organic filtrate was evaporated slowly under a stream of air, and the pale yellowish residue was neutralized with H_2SO_4 (50%, 10 mL), extracted with CHCl_3 ($3 \times 200 \text{ mL}$) and dried over MgSO_4 . After solvent removal, triformylmethane **1** was obtained as yellowish crystals that were further purified by sublimation (2.3 g, yield 45% based on bromoacetic acid). The infrared data and elemental analysis have not been reported previously.^[58,59]

M.p. $102\text{--}103^\circ\text{C}$ (ref. M.p., 101°C). FT-IR (KBr): $\tilde{\nu} = 2828$ (w, $\nu_{\text{C-H}}$), 2731 (m, $\nu_{\text{C-H}}$), 1699 (s, C=O), 1599(s), 1566 (s), 1561 (m), 1207 (s), 1166 (m), 826 (s), 723 (m) cm^{-1} . $\text{C}_4\text{H}_4\text{O}_3$ (100.07): calcd. C 48.01, H 4.03; found C 48.25, H 4.11.

2,6-Bis(4'-formylpyrazol-1'-yl)pyridine (4): Potassium metal (0.4 g, 10 mmol) was added to a solution of 4-formylpyrazole **2** (1 g, 10 mmol) dissolved in dry diglyme (30 mL, b.p. 162°C), then the mixture was heated under argon at 70°C whilst stirring until all of the potassium had reacted to form the pyrazolate derivative. Then, 2,6-dibromopyridine **3** (1.18 g, 5 mmol) was added with a cannula, and the reaction mixture was heated at 110°C for a further 72 h under argon. The mixture was cooled to room temperature and the solid product formed was filtered off, washed first with cold water and then with small portions of ethanol. Finally the residue was air dried. Recrystallisation from toluene afforded **4** (0.6 g, yield 45%) as pale yellowish crystals. M.p. $283\text{--}284^\circ\text{C}$ (from toluene). FT-IR (KBr): $\tilde{\nu} = 3129$ (w, $\nu_{\text{C-H}}$, aromatic), 3097 (w, $\nu_{\text{C-H}}$, aromatic), 2857 (w, $\nu_{\text{C-H}}$), 1682 (s, $\nu_{\text{C=O}}$), 1610 (m), 1583 (m), 1552 (s), 1473 (s), 1409 (m), 1336 (w), 1290 (w), 1217 (m) (pyridinyl and pyrazolyl moieties) cm^{-1} . ^1H NMR (250 MHz, $[\text{D}_6]\text{DMSO}$, 298 K): $\delta = 9.97$ (s, 2 H, 2-CHO), 9.73 (s, 2 H, 2-CH), 8.34 (s, 2 H, 2-CH), 8.25 (t, $J = 7.2 \text{ Hz}$, 1 H, -CH), 7.95 (d, $J = 7.9 \text{ Hz}$, 2 H, 2-CH) ppm. ^{13}C NMR (63 MHz, $[\text{D}_6]\text{DMSO}$, 298 K): $\delta = 185.3$, 149.9, 143.0, 142.4, 133.1, 125.8, 111.3 ppm. FD-MS (8 kV, CH_2Cl_2): m/z (%) = found 266.90 (100%), calcd. for $\text{C}_{13}\text{H}_9\text{N}_5\text{O}_2$ (267.24). $\text{C}_{13}\text{H}_9\text{N}_5\text{O}_2$ (267.24): calcd. C 58.43, H 3.39, N 26.21; found C 58.28, H 3.56, N, 26.10.

2,6-Bis[4'-(1,3-dihydroxy-4,4,5,5-tetramethylimidazolidin-2-yl)pyrazol-1'-yl]pyridine (6): A mixture of 2,6-bis(4'-formylpyrazol-1'-yl)pyridine (**4**) (300 mg, 1.12 mmol) and 2,3-bis(hydroxylamino)-2,3-dimethylbutane (**5**) (600 mg, 4 mmol) in dioxane (40 mL) was stirred under argon for 10 days. The solvent was removed under reduced pressure and the solid product was collected, washed first

with water then with ethanol and air dried to afford 265 mg of crude **6** that was used for the next step without further purification (yield of the crude product 42%). M.p. 253–254 °C (from ethanol). FT-IR (KBr): $\tilde{\nu}$ = 3215 (s, broad, ν_{OH}), 3121 (s, $\nu_{\text{C-H}}$, aromatic), 2977 (s, $\nu_{\text{C-H}}$), 2932 (s, $\nu_{\text{C-H}}$), 1620 (s), 1472 (s), 1405 (s), 1320 (m), 1207 (m) (pyridinyl and pyrazolyl moieties) cm^{-1} . ^1H NMR (250 MHz, $[\text{D}_6]\text{DMSO}$, 298 K): δ = 8.85 (s, 2 H, 2-CH), 8.17 (t, J = 2.8 Hz, 1 H, -CH), 8.0 (s, 4 H, 4-OH), 7.86 (s, 2 H, 2-CH), 7.82 (d, J = 8.2 Hz, 2 H, 2-CH), 4.75 (s, 2 H, 2-CH imidazolidyn), 1.15 (d, J = 8.4 Hz, 24 H, 8- CH_3) ppm. ^{13}C NMR (63 MHz, $[\text{D}_6]\text{DMSO}$, 298 K) δ = 149.8, 143.7, 141.5, 126.7, 108.5, 83.1, 66.2, 24.0, 27.0 ppm. $\text{C}_{25}\text{H}_{37}\text{N}_9\text{O}_4 \times 2\text{H}_2\text{O}$ (563.65): calcd. C 53.27, H 7.33, N 22.37; found C 52.96, H 7.44, N 22.10.

2,6-Bis[4'-(3-oxo-1-oxyl-4,4,5,5-tetramethylimidazolin-2-yl)pyrazol-1'-yl]pyridine (Pz₂PyNN) (7): Compound **6** (200 mg, 0.38 mmol) dissolved in chloroform (30 mL) was oxidised under phase-transfer conditions with NaIO_4 (400 mg, 1.85 mmol), previously dissolved in water (20 mL), during 30 min. The color of the organic phase gradually changed to give finally a deep-blue organic solution. The organic phase was collected and the solvents evaporated under air. The bluish residue was dissolved in acetone (3 mL) and chromatographed on a SiO_2 column using a mixture of acetone/petroleum ether (2:8) as eluent to afford Pz₂PyNN as a blue solid (R_f = 0.34) that was further recrystallised from CHCl_3 (54 mg, yield 27%). M.p. 220–221 °C (from CHCl_3). FT-IR (KBr): $\tilde{\nu}$ = 3164 (w, $\nu_{\text{C-H}}$, aromatic), 2984 (w, $\nu_{\text{C-H}}$), 2936 (w, $\nu_{\text{C-H}}$), 1596 (s), 1470 (s), 1429 (s), 1403 (s), 1359 (s, $\nu_{\text{N-O}}$), 1312 (m), 1190 (m) (pyridinyl and pyrazolyl moieties) cm^{-1} . UV/Vis (toluene): λ_{max} (ϵ , $\text{M}^{-1} \times \text{cm}^{-1}$) = 668 (1460), 610 (1696) 563 (930), 518 (328), 375 (16960), 328 (24850), 323 (31220) nm. FAB-MS (NBA as matrix): m/z (%) = found 521.30 (100%) $[\text{M} + \text{H}]^+$, calculated for $\text{C}_{25}\text{H}_{31}\text{N}_9\text{O}_4$ (521.57). $\text{C}_{25}\text{H}_{31}\text{N}_9\text{O}_4$ (521.57): calcd. C 57.57, H 5.99, N 24.17; found C 57.34, H 5.72, N 23.94.

2,6-Bis[4-(1-hydroxy-4,4,5,5-tetramethylimidazolin-2-yl)pyrazolyl]pyridine (8): A mixture of 2,6-bis(4'-formylpyrazol-1'-yl)pyridine **4** (260 mg, 1 mmol) and 2,3-bis(hydroxylamino)-2,3-dimethylbutane **5** (300 mg, 2.02 mmol) in dioxane (40 mL) was heated at 60 °C under argon for seven days. The solvent was removed under reduced pressure, and the solid product was collected, washed with water then with ethanol and dried under a nitrogen stream to give the highly air-sensitive compound **8** (225 mg, crude yield 46%), which was used in the next step without further purification. FT-IR (KBr): $\tilde{\nu}$ = 3225 (broad, -OH), 3121 (s, $\nu_{\text{C-H}}$, aromatic), 2977 (s, $\nu_{\text{C-H}}$), 2932 (s, $\nu_{\text{C-H}}$), 1620 (s), 1472 (s), 1405 (s), 1320 (s), 1207 (m) (pyridinyl and pyrazolyl moieties) cm^{-1} . $\text{C}_{25}\text{H}_{33}\text{N}_9\text{O}_2$ (491.59): calcd. C 61.08, H 6.77, N 25.64; found C 60.78, H 6.52, N 25.34.

2,6-Bis[4-(1-oxyl-4,4,5,5-tetramethylimidazolin-2-yl)pyrazolyl]pyridine (Pz₂PyIN) (9): Compound **8** (200 mg, 0.41 mmol) was oxidised under phase-transfer conditions ($\text{H}_2\text{O}/\text{CHCl}_3$, 20:40 mL) mixture using NaIO_4 (400 mg, 1.87 mmol) for 30 min; within this period of time, the color of the organic layer gradually turned to deep orange. The organic phase was collected and the solvents evaporated under reduced pressure. The residue was dissolved in acetone (5 mL) and chromatographed on a SiO_2 column using acetone/petroleum ether as eluent (2:8, b.p. 30–40 °C, R_f = 0.46). After solvent removal, pure Pz₂PyIN was collected as an orange hygroscopic solid (105 mg, yield 51%). The solid was recrystallised from CH_2Cl_2 . M.p. 254–255 °C (from CH_2Cl_2). FT-IR (KBr): $\tilde{\nu}$ = 3142 (w, $\nu_{\text{C-H}}$, aromatic), 2976 (m, $\nu_{\text{C-H}}$), 2926 (w, $\nu_{\text{C-H}}$), 1599 (s, $\nu_{\text{C=N}}$), 1585 (m), 1470 (s), 1439 (m), 1405 (m), 1289 (w), 1257 (w), 1198 (w) (pyridinyl and pyrazolyl moieties) cm^{-1} . UV/Vis (tolu-

ene): λ_{max} (ϵ , $\text{M}^{-1} \times \text{cm}^{-1}$) = 552 (90), 500 (850), 468 (1400), 442 (1285), 415 (910), 315 (23850) nm. $\text{C}_{25}\text{H}_{31}\text{N}_9\text{O}_2 \times \text{H}_2\text{O}$ (507.59): calcd. C 59.16, H 6.55, N 24.84; found C 58.96, H 6.66, N 24.68.

3.3. Crystal Structure Determination and Refinements for 2,6-Bis[4'-(3-oxo-1-oxyl-4,4,5,5-tetramethylimidazolin-2-yl)pyrazol-1'-yl]pyridine (Pz₂PyNN) (7): Formula $\text{C}_{25}\text{H}_{31}\text{N}_9\text{O}_4$, M_w = 521.57, monoclinic, space group $C2/c$ ($N^\circ 15$), a = 18.5194(7), b = 9.6934(5), c = 14.4537(6) Å, β = 103.4960(10)°, V = 2522.92(19) Å³, D_c = 1.373 g $\times \text{cm}^{-3}$, Z = 4, T = 120 K. Crystal color, shape and size: dark blue, needles, $0.43 \times 0.26 \times 0.18$ (mm). Dataset: 3057 total, 2889 unique reflections ($4.1 < \theta < 27.5^\circ$) of which 1895 were observed [$I_0 > 2.0 \sigma(I_0)$], N_{ref} = 1895, N_{par} = 175. The structure was solved by direct methods (SHELXS) and refined by a full-matrix least-squares procedure to R_1 value of 0.0385 (wR_2 = 0.0453, all data), GOF = 1.05. The crystallographic data were collected on a Nonius-Kappa CCD (Mo- K_α , μ = 0.71073 Å⁻¹) diffractometer equipped with a graphite monochromator. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-217301. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44- (1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

Calculations: The simulations were performed using the program *BiRad*, written by Priv.-Doz. Dr. Gunnar Jeschke and Mr. Dariush Hinderberger (Prof. Dr. Hans W. Spiess, Polymer Spectroscopy Group, Max Planck Institute for Polymer Research, Mainz). This program is available free to the public upon request (E-mail: jeschke@mpip-mainz.mpg.de).

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