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Cooperative Magnetism in Crystalline *N*-Aryl-substituted Verdazyl Radicals: First-Principles Predictions and Experimental Results

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Abstract

We report on a series of eight diaryl-6-oxo-verdazyl radicals containing a tert-butyl group at the C(3) position regarding their crystal structure and magnetic properties by means of magnetic susceptibility measurements in combination with quantum chemical calculations using the firstprinciples bottom-up approach. The latter method allows for a qualitative prediction and detailed analysis of the correlation between solid state architecture and magnetic properties. Although the perturbation in the molecular structure by varying the substituent of the N-aryl-ring may appear small, the effects upon the structural parameters controlling intermolecular magnetic coupling interactions are strong, resulting in a wide spectrum of cooperative magnetic behavior. The nonsubstituted 1,5-diphenyl-t.butyl-6-oxo-verdazyl radical features a ferromagnetic one-dimensional spin ladder type magnetic network, an extremely rarely observed phenomenon for verdazyl radicals. By varying substituents at the phenyl group, different non-isostructural compounds were obtained with widely different magnetic motifs ranging from linear and zig-zag one-dimensional chains to potentially two-dimensional networks, from which we predict magnetic susceptibility data that are in qualitative agreement with experiments and reveal a large sensitivity to packing effects of the molecules. The present study advances the fundamental understanding between solid state structure and magnetism in organically based radical systems.

Introduction

Spin alignment in the solid state of organic radicals is an important structural feature affecting molecular charge transfer^[1] and magnetic exchange coupling instrumental for the design of organic magnetic materials.^[2] One key element is an organic spin-carrying building block, which is stable enough to be purified under ambient atmospheric conditions and to be stored in a crystalline form over several months to years without the loss of integrity.^[3] With this objective and prospect, carbon centered radicals such as polychlorinated triphenylmethyl radicals and nitrogen/oxygen centered radicals, especially nitronyl and imino nitroxides, have been studied most commonly, since they do not show any disproportionation or hydrogen abstraction between two spin centers), the geometry of the mutual orientations of the spin sites is of critical importance. There are different approaches for controlling these interactions within organic magnetic materials. Whereas the "through bond" approach uses di- or polyradicals to achieve intramolecular spin communication through a π -conjugated network^[5], metal ions have also been

used to coordinate to the radical moiety to give rise to metal-organic radical frameworks.^[6] Overall, the control of the intermolecular "through space" interactions in organic radical crystals is of fundamental interest for understanding, manipulating, and designing the magnetic properties of these materials in the solid state. Following this approach, in the early 1990's the first fully organic ferromagnetic material – the *para*-nitrophenyl nitronyl nitroxide^[7] – was characterized with a Curie temperature of $T_{\rm C} = 0.6$ K and further materials have been discovered since then.^[8] However, in nitroxide radicals, the presence of bulky alkyl groups in the α -position tends to attenuate such intermolecular magnetic interactions, owing to steric hindrance. Alternatively, 6-oxo-verdazyl radicals, well known for their uses as mediators in polymerizations^[9], as substrates in organic synthesis^[10] and as profluorescent spin probes^[11], may be considered as suitable magnetic building blocks. As they show an almost planar radical heterocycle and no bulky substituents near the radical center, they appear to be rather promising building blocks for the design of cooperative magnetic materials.^[12] Following their discovery by Kuhn^[13] (saturated carbon at C(6)) and Neugebauer (carbonyl or thiocarbonyl group at C(6))^[14], there have been only few studies focusing on the magnetic properties of structurally characterized verdazyl radicals (Figure 1).^[15]



Figure 1. Chemical structures of the two verdazyl radical classes.

At the same time, there are many reports about different magnetic phenomena of not fully structurally characterized radicals.^[12] However, for revealing structure-property relationships and for designing new systems based on cooperative magnetic interactions crystal structure information is indispensable.^[12] Ferromagnetic interactions – the parallel alignment of spins in the solid state – are of special interest and to the best of our knowledge only two examples based on structurally characterized verdazyl radicals are known in the literature.^[16] In this contribution we present the results of a collaborative effort, combining synthesis, physical property analysis and quantum chemical modelling of magnetic topologies, to uncover new structure-property relationships for a series of crystalline *tert*-butyl substituted 1,5-diaryl-6-oxo verdazyl radicals. The

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results will be important for designing promising candidates with unique solid state architectures and enhanced intermolecular magnetic interactions.

Results and Discussion

Structure and Ferromagnetic Interactions in a 1,5-diphenyl-6-oxo-verdazyl radical

Although verdazyls are generally considered to be hard to obtain in the form of single crystals^[12] we were able to solve and refine the structure of a 1,5-diphenyl-6-oxo-verdazyl radical bearing a tert-butyl group at the C(3) position. Verdazyl radical **3a**^[11b] (for the synthesis, see Scheme 1) crystallizes in the monoclinic crystal system with space group $P2_1/c$ and unit cell parameters a =15.8770(9), b = 5.9373(3), c = 17.0945(5) Å and four molecules within the unit cell (for more detailed crystallographic data, see Table S1, Supporting Information (SI)). As can be seen from the CNNC dihedral angle of 2.8° the verdazyl heterocycle adopts an almost planar 7π -system (Figure 2). As also found for other verdazyl radicals^[11a, 17], the *N*-phenyl rings appear twisted with respect to the central heterocycle with CCNN torsion angles of around 28.6° (-28.9°). A characteristic of the solid state structure of this system is an arrangement of the molecules to chains along the *c*-axis, which are interconnected in a head-to-tail structure by C=O···H-C (tertbutyl group) interactions. Neighboring chains are oriented antiparallel to each other, as can be seen by the view on the ac-plane (Figure 3, right). Along the b-axis, linear chains are formed with the same orientation of the verdazyl radical through π - π interactions involving the N-phenyl rings. The shortest distance between the verdazyl ring and the neighboring phenyl ring C1...C15 is 3.367 A in this direction (Figure 3, left). We also note that the orientation of two neighboring verdazy rings is almost parallel with an angle between the two planes of 4.5°. However, the bulky tertbutyl C(3) substituent prevents an efficient intermolecular π - π stacking of the verdazyl heterocycles, as indicated by the translation vector b of 5.937 Å



Figure 2. Molecular entity in the crystal structure of verdazyl radical **3a** (displacement ellipsoids are shown with 30% probability).



Figure 3. Solid state structure of verdazyl radical **3a**. Left: $\pi - \pi$ interaction between two verdazyl radicals responsible for J_1 (the shortest distance between the verdazyl ring and the neighboring phenyl ring, C1... ·C15, is 3.367 Å); right: formation of linear chains along the *b*-axis.

Next, we investigated the magnetic properties of a polycrystalline sample of **3a**. The temperature dependent magnetic susceptibilities χ , measured in an external magnetic field of 10 kOe (Figure S29, SI), increase with decreasing temperature. The χ^{-1} data can be fitted using the Curie-Weiss law, with a Curie constant of C = 0.376(1) K ($\mu_{eff} = 1.73(1) \mu_B$), which corresponds to the theoretical value for a one electron system. In addition, a positive Weiss constant $\theta_p = 0.7(1)$ K indicates weak ferromagnetic interactions in the paramagnetic region. These are also revealed by an increase of χT with decreasing temperature (see Figure 4).

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Figure 4. Experimental (black crosses) and calculated temperature-dependent magnetic susceptibility of **3a**, plotted as molar susceptibility times temperature (left) and molar susceptibility (right) *versus* temperature, shown for magnetic models of various size (solid lines).

The experimental magnetization isotherms, measured at 2 and 5 K using an external magnetic field ranging from 0 to 50 kOe are shown in S29, SI (bottom). Whereas the magnetization M(H) shows a linear dependence at 5 K, the corresponding magnetization isotherm at 2 K is curved, both typical behavior of paramagnetic compounds. As the external magnetic field is increased at 2 K, an increase of the magnetization is observed, in agreement with a preferential parallel alignment of the spins. A saturation magnetization of $\mu_{sat} = 0.24(1) \mu_B$ was observed at 2 K and 50 kOe.

In order to explain the ferromagnetic interactions, we applied a systematic computational procedure,^[18] which implements the first-principles bottom-up approach by Deumal *et al.*.^[19] Analyzing the solid state structure of **3a**, we calculated three relevant coupling constants of $J_1 = +0.54 \text{ cm}^{-1}$, $J_2 = +0.45 \text{ cm}^{-1}$ and $J_3 = +0.09 \text{ cm}^{-1}$, representing ferromagnetic interactions between neighboring sites in all cases. The strongest magnetic interaction J_1 is caused by the linear chain structure and parallel orientation of the verdazyl radicals along the *b*-axis (see Figure 3, left). The less pronounced ferromagnetic coupling described by J_2 is perpetuated in a zig-zag manner between two antiparallel oriented staples along the *b*-axis (Figure 5). In this case, the shortest distance between two neighboring phenyl rings is found to be 3.497 Å (between C21 and C25'). The combination of J_1 and J_2 results in a one-dimensional ladder type structure along the *b*-axis (illustrated by the blue and red lines in Figure 5, bottom). A much weaker interaction to the other neighboring staples along the *a*-axis is described by a third coupling constant $J_3 = +0.09 \text{ cm}^{-1}$, which induces a two dimensional magnetic model at lower temperatures (purple lines in Figure 5, bottom). In total, the system can be described as a ferromagnetically coupled 2D system of weakly interacting 1D spin ladders with zig-zag rungs.

The magnetic models for which the magnetic susceptibility has been simulated implement this motif. The results are shown in Figure 4. Note, that the crystallographic axes do not necessarily represent the best choice for the directions, into which a minimal magnetic model is enlarged.^[18-19] Thus, in our procedure a better suited set of axes is automatically chosen. These axes are at the same time ordered by their expected relevance for the total system, so that the first of the new axes represents the direction, in which the strongest interactions occur. For **3a**, the new axes are shown in the bottom panel of Figure 5. The labels for the model size given in Figure 4 and analogous plots for the other compounds (see further below) are to be understood in terms of axes chosen in this way.



Figure 5. View along the *c*-axis onto the solid state structure (top) and the magnetic model (bottom) of verdazyl radical **3a**. Top: The shortest contacts responsible for J_2 (C21···C25', 3.497 Å) and J_3 (C13···C15, 3.723 Å) are indicated; bottom: Interactions within the unit cell (solid lines), entering or leaving the unit cell (dashed lines) and outside the unit cell (dotted lines), are shown with a line thickness qualitatively reflecting the strength of the coupling constant indicated with the corresponding color. The directions into which the model is extended are indicated as the *x*- and *y*-axes. The origin of the unit cell has been shifted to enable a more convenient representation.

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All couplings calculated for **3a** have a rather small strength, which can be explained by the large distance and by unfavorable slips and tilt angles between the interacting aromatic rings. Interestingly, no relevant magnetic interactions were found for the head-to-tail structural motif along the *c*-axis involving the discussed hydrogen bonds. In summary, for these specific 1,5-diaryl-6-oxo verdazyl radicals such ferromagnetic interactions are revealed for the first time.

Synthesis and Characterization of substituted 1,5-diphenyl-6-oxo-verdazyl radicals

Encouraged by these initial results we decided to systematically investigate the effect of various substituents at the *N*-bonded phenyl ring of the verdazyl radical on the relation between crystal structure and magnetic properties. We aimed at similar ferromagnetic networks such as in **3a** by replacing the H atom in the *para*-position by other substituents (compounds **3b–3g**). The preparation of these verdazyl radicals (Scheme 1) starts with a diaryl substituted carbonohydrazide **1a–1h**, readily prepared by Ullmann coupling (for more experimental details, see the SI). A treatment with pivalaldehyde afforded the corresponding tetrazinan-3-ones **2a–2h** in moderate to good yields by simple filtration of the alcoholic reaction mixture. Improved yields were obtained by recrystallization of the filtrate in MeOH. We also noticed that the electron rich compound **2f** is easily oxidized to the verdazyl radical upon simple exposure to air, as indicated by a color change from colorless to red in the solid state. All the other derivatives did not show this behavior. In order to quantitatively oxidize these precursors, they were reacted with 1,4-benzoquinone to afford the verdazyl radicals **3b–3h** in good yields as crystalline red solids.

	O N NH2 NH2	^a) R			R	b)	R		R
				\wedge	vield:			\frown	vield:
1a	R ⁼ H	2	а	r ⁼ H	86% ^a		за	R ⁼ H	55% ^a
1b	R = p F	2	b	R = p F	76%		3b	R ⁼ <i>p</i> F	50%
1 ^C	R = pCI	2	С	R ⁼ pCl	48%		3C	R ⁼ <i>p</i> ⁻ Cl	49%
1d	R = pBr	20	d	R = pBr	52%		3d	$R = pB^{T}$	37%
1e	R ⁼ p ⁻ M ^e	29	е	R ⁼ p ⁻ M ^e	72%		зе	R ⁼ p ⁻ M ^e	57%
1f	R ⁼ pOMe	21	f	R = pOMe	56%		3f	R ⁼ <i>p</i> ⁻ OM ^e	64%
1g	R = m Br	2	g	R = <i>m</i> Br	67%		3g	R = <i>m</i> _Br	49%
1h	$R = m m Me_2$	2	h	$R = m m Me_2$	51%		3h	$R = m_{p}m_{M}e_{2}$	68%

Scheme 1. General reaction scheme for the preparation of *tert*-butyl substituted verdazyl radicals **3a–3h**. a) Pivalaldehyde (1.0 eq.), MeOH, 40–60 °C, 2–3 h; b) 1,4-benzoquinone (1.7 eq.), CH₂Cl₂, sealed tube, 60 °C, 3–4 h. ^a See ref 11b.

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All the verdazyl radicals of the present study were characterized by electron spin resonance (ESR) in CH₂Cl₂ (1 mM) and the optical and redox properties were determined through UV/Vis absorption spectroscopy and cyclic voltammetry measurements. Figure 6 shows the experimental ESR spectra, together with best-fit simulations (dashed lines). The spectra can be explained in terms of isotropic hyperfine coupling with two sets of two ¹⁴N nuclei, corresponding to N₁,N₅, and N₂,N₄, respectively. In addition, the spectra are influenced by weak hyperfine coupling with the ¹H nuclei through σ - π spin polarization, which were considered with their appropriate multiplicities. In compound **3b**, a moderately strong hyperfine coupling to the two ¹⁹F nuclei was detected, whereas hyperfine coupling with the chlorine and bromine nuclear magnetic moments in compounds **3c**, **3d**, and **3g** was found to be negligible. The complete set of g-factors and hyperfine coupling parameters is summarized in Table 1. These were obtained, using theoretically calculated values from quantum mechanical (QM) calculations as starting values in the fitting procedure (see SI for a brief description of the procedure used). The complicated spectra caused by the large number of couplings lead to difficulties in their interpretation. Already the information which nuclei have a significant coupling is hard to obtain directly from the experimental data. Furthermore, a fitting procedure can quickly lead to ambiguous results, if the starting values are not chosen very carefully. While a straightforward computation of ESR parameters for an optimized structure^[20] leads to unsatisfactory spectra, inclusion of vibrational effects as in our current approach^[21] (see the SI for details) yields much more accurate results. A rough agreement for the shape of the spectra can already be obtained without recourse to fitted hyperfine coupling constants and g-factors (see red curves in Figure 6). This fact and the small deviations to the values optimized after fitting to the experimental data give a lot of confidence in the quality of the final results.



Figure 6. Experimentally measured, QM calculated and fitted ESR spectra of the verdazyl radicals **3a-3h** in degassed CH₂Cl₂.

Table 1. QM calculated and fitted ESR-parameters for the verdazyl radicals **3a–3h**. Coupling constants with | A | < 1 MHz are indicated as *small*. ¹The coupling constants for the methyl hydrogens are on average 1.6230 MHz (QM) and 1.8350 MHz (fitted). ²The coupling constants of the methyl hydrogen atoms were calculated to be *small* for these compounds. ³The coupling constant of the bromine atom in *meta*-position was calculated to be *small*.

	R		g-factor	A(N₁,₅) MHz	A(N _{2,4}) MHz	A(H _{ortho}) MHz	A(H _{meta}) MHz	A(H _{para}) MHz	A(X _{para}) MHz
20	Ц	QM	2.0041	11.924	17.477	-1.904	1.446	-1.667	-
3a	П	Fitted	2.0038	12.387	18.155	-1.833	1.356	-1.572	-
2 L	<i>т</i> Г	QM	2.0041	13.025	18.084	-2.055	1.448	-	3.933
30	<i>р</i> -г	Fitted	2.0038	12.386	18.466	-2.050	1.474	-	3.935
2-		QM	2.0042	12.123	17.559	-2.299	1.647	-	small
3C	<i>ρ</i> -Ci	Fitted	2.0041	12.113	18.501	-2.130	1.719	-	-
24		QM	2.0046	11.412	17.032	-2.458	1.765	-	small
30	<i>р</i> -вг	Fitted	2.0042	11.964	18.447	-2.275	1.700	-	-
20	1 n Mo	QM	2.0041	12.898	17.574	-1.822	1.420	-	-
3e	<i>p</i> -ivie	Fitted	2.0038	12.558	18.285	-1.839	1.428	-	-
24	² 	QM	2.0041	12.901	17.293	-1.918	1.335	-	-
31	p-Oivie	Fitted	2.0038	12.816	18.151	-1.705	1.192	-	-
3g	3m Dr	QM	2.0039	12.381	17.911	-1.989	small	-1.702	-
	°///-DI	Fitted	2.0037	11.909	18.602	-2.1400	small	-1.676	-
2 h	² m,m-	QM	2.0041	12.444	17.458	-1.883	-	-1.675	-
3n	Me ₂	Fitted	2.0038	12.621	18.450	-1.689	-	-1.575	-

For a further analysis of the optical properties of these radicals, we looked at the absorption maxima in dichloromethane solution at room temperature. In the VIS spectral region we note a characteristic band appearing from 490 nm to 516 nm, which is due to the nature of the substituent and explains the color of the verdazyl radical (Figure 7, for full spectra, see Figure S26, SI). The red shift of these derivatives can be understood in terms of more effective π conjugation of the *N*-aryl substituent to the verdazyl heterocycle. Therefore, the electron rich methyl- (**3e**: $\lambda_{max} = 501$ nm) and methoxy-substituted radicals (**3f**: $\lambda_{max} = 516$ nm) show a more bathochromic shift of the absorption maximum compared to radicals featuring electron withdrawing groups. For example, in the series of the *para*-halogen substituted derivatives the wavelength of the absorption maximum increases from fluorine (**3b**: $\lambda_{max} = 495$ nm) to chlorine (**3c**: $\lambda_{max} = 504$ nm) to bromine (**3d**: $\lambda_{max} = 505$ nm) in accordance with the decrease of electronegativity of the substituent. Interestingly, the non-substituted compound **3a** ($\lambda_{max} = 490$ nm) shows a clear hypsochromic shift, which is also found for the *meta*-substituted derivatives **3g** and **3h**. For the latter two compounds

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this may be due to steric effects, thereby prohibiting an efficient delocalization of the *N*-aryl substituent to the heterocycle. For instance, the 3,5-dimethyl verdazyl radical **3h** shows a larger CCNN torsion angle $(42.2^{\circ}/42.1^{\circ})$ than the *para*-methyl substituted one (**3e**: $-31.9^{\circ}/25.3^{\circ}$). Assuming that the geometries in solution and the solid state are comparable this may explain the slight shifts in the absorption maxima for these different compounds.



Figure 7. Normalized absorption spectra of the verdazyl radicals 3a-3h in degassed CH₂Cl₂.

The different electronic properties of the derivatives are also evident in cyclic voltammetry measurements. In general, for all derivatives reversible oxidation and reduction waves are found, when measured against ferrocene^[22] as an internal standard (Figure 8; for more information, see Table or Figures S27 and S28, SI). Electron donating groups like methyl in **3e** ($E_{ox} = +0.31$ V), methoxy in **3f** ($E_{ox} = +0.23$ V) or the 3,5-dimethyl group in **3h** ($E_{ox} = +0.32$ V) effect lower oxidation potentials than derivatives with electron withdrawing groups like fluorine (**3b**: $E_{ox} = +0.41$ V), chlorine (**3c**: $E_{ox} = +0.44$ V), bromine (**3d**: $E_{ox} = +0.45$ V) or *meta*-bromine (**3g**: $E_{ox} = +0.49$ V). Not surprisingly, the reduction potentials show the same trend *vice versa*, since the ΔE_{cell} potentials (1.40–1.44 V) are comparable.^[23]



Figure 8. Cyclic voltammetry curves for selected verdazyl radicals **3a**, **3f** and **3g** (0.1 M TBATFB in MeCN vs. Fc⁺/Fc); the red dashed line belongs to **3a** measured with ferrocene as an internal standard.

	R	λ _{max} (nm)	Eox(V)	E _{Red} (V)	<i>∆E</i> cell (V)	
3a	Н	490	0.36	-1.08	1.44	
3b	<i>p</i> -F	495	0.41	-1.02	1.43	
3c	<i>p</i> -Cl	504	0.44	-0.97	1.41	
3d	<i>p</i> -Br	505	0.45	-0.95	1.40	
3e	<i>p</i> -Me	501	0.31	-1.12	1.43	
3f	<i>p</i> -OMe	516	0.23	-1.17	1.40	
3g	<i>m</i> -Br	496	0.49	-0.92	1.41	
3h	<i>m</i> , <i>m</i> -Me ₂	494	0.32	-1.11	1.43	

Table 2. Summary of analytical data for the verdazyl radicals 3a–3h . Optical properties (λ_{max}) and
oxidation and reduction potentials E_{ox} and E_{red} , measured against Fc ⁺ /Fc.

Crystal Structures and Magnetic Interactions in substituted 1,5-diphenyl-6-oxo-verdazyl radicals

For all the derivatives, the solid state structures could be solved and refined by single crystal X-Ray diffractometry. Suitable crystals of **3b–3h** were obtained by slow evaporation of a CHCl₃ or EtOAc solution of the sample at room temperature. In this section the magnetic properties of these derivatives are described and discussed in the context of their crystal structures. As in the case of **3a**, the magnetic couplings are most conveniently discussed within a different coordinate system than that given by the crystallographic axes. Table 1 summarizes the choice of axes in the magnetic models in terms of the crystallographic axes for all magnetic models constructed in this work.

Table 3. Information about the magnetic models used in simulations for the magnetic susceptibility. The
sizes of the magnetic models in the corresponding figures are in terms of the axes x, y and z as denoted
here. Axis definitions given in round brackets do not feature periodic magnetic interactions, i.e. magnetic
models do not need to be extended into that direction.

Compound	Couplings	Axes of the magnetic cells		Molecules per	Madal	
	Considered	X	У	Z	magnetic cell	Woder
3a	J_1, J_2, J_3	b	а	(<i>c</i>)	2	Net (weakly coupled
						spin ladders)
	J_1	а	(b)	(<i>C</i>)	2	Chain
3b	J_1, J_2, J_3	а	b	a+b-c	4	Network (weakly
						interacting chains)
	J_1	(<i>a</i>)	(b)	(<i>C</i>)	2	Dimer
3с	J_2	(<i>a</i>)	(b)	(<i>C</i>)	2	Dimer
	J 1- J 4	a - b	b	(<i>C</i>)	8	Net
3d -α	J_1, J_2	а	С	(<i>b</i>)	2	Net
	J_1	(<i>a</i>)	(b)	(<i>C</i>)	2	Dimer
3d -β	J_2	(<i>a</i>)	(b)	(<i>C</i>)	2	Dimer
	J_1, J_2, J_3	a+b	(a)	(<i>C</i>)	8	Chain
	J_1	b	(a)	(<i>C</i>)	2	Chain
	J_2	b	(a)	(<i>C</i>)	2	Chain
30	J_1, J_2, J_3	b	а	(<i>C</i>)	4	Net (weakly coupled
•9						chains)
	J ₁ - J ₄	b	а	b + c	8	Network (weakly
						interacting chains)

Interestingly, the verdazyl radicals **3b**–**3h** do not crystallize isostructurally to **3a**. Despite the comparable sizes of fluorine and hydrogen,^[24] the crystal structures of **3a** and **3b** are completely different, probably because of the unique electronic effects of the fluorine atom. **3b** (Figure S2, SI) crystallizes in the orthorhombic crystal system with space group *Pnma* and unit cell parameters of *a* = 6.8786(2), *b* = 19.0272(5), and *c* = 12.6718(4) Å with four molecules in a unit cell (see Table S1, SI). In detail, two neighboring molecules are oriented almost perpendicular to each other with an angle between the two planes of 77°. In that way the carbonyl group is pointing towards the heterocycle of a neighboring molecule with a distance of 3.042 Å between O1 and C1' (Figure 9, left and Figure S3, SI). Through this C=O···*π* interaction, linear chains are formed along the *a*-axis (Figure 10). Consequently, the two neighboring *N*-phenyl substituents are arranged in an eclipsed manner with distances of around 3.388 Å, which leads to a staple-like structure along the *a*-axis, built through π - π interactions of the *N*-phenyl rings.



Figure 9. Left: Solid state structure of verdazyl radical **3b**. The C=O··· π interaction between two verdazyl radicals corresponding to J_1 =-4.34 cm⁻¹ is a result of linear chains along the *a*-axis with verdazyl radicals oriented almost perpendicular to each other (shortest distance between two verdazyl radicals: O1···C1 = 3.042 Å); right: the magnetic model of **3b** implementing this interaction. Interactions within the unit cell (solid line), entering or leaving the unit cell (dashed lines) and outside the unit cell (dotted lines), are shown. The direction into which the model is extended is labeled as the *x*-axis.



Figure 10. View along the a-axis of verdazyl radical **3b** emphasizing the formation of linear chains involving verdazyl radicals orientated almost perpendicular to each other.

Because of the different solid state architecture of 3a and 3b significantly different magnetic interactions are expected. Indeed, the experimental results show antiferromagnetic interactions with a Neél temperature of $T_{\rm N} = 7.2(1)$ K for **3b**. From the paramagnetic region of compound **3b** a Curie constant of C = 0.352(1) ($\mu_{eff} = 1.68(1) \mu_B$), which is close to the theoretical value ($\mu_{calc} =$ 1.73 $\mu_{\rm B}$) and a Weiss constant of $\theta_{\rm p} = -2.6(1)$ K could be extracted (Figure S30, SI). In good agreement with the experiment (Figure 11, comparison of theoretical and experimental values) the calculations delivered also one antiferromagnetic coupling constant $J_1 = -4.34$ cm⁻¹, which corresponds to the chain arrangement along the a-axis. Further calculated coupling constants of $J_2 = -0.09 \text{ cm}^{-1}$ and $J_3 = -0.07 \text{ cm}^{-1}$ were found to be negligible in this case and are thus not depicted. Figure 11 also shows an approximation of the magnetic susceptibility data by the Bleaney-Bowers equation^[25] (blue curve), which is based on a simple singlet-triplet transition model for an isolated dimeric system. This model predicts a magnetic susceptibility maximum at 7.2 K based on an assumed magnetic coupling constant J = -3.95 cm⁻¹, which agrees reasonably well with J_1 . However, the shape of the curve is incompatible with the experimental data. A chain model according to the Bonner-Fisher equation^[26], which corresponds to the magnetic topology suggested by our implementation of the first-principles bottom-up approach, yields an excellent description of the measured susceptibility with an assumed magnetic coupling constant J = -3.25cm⁻¹.



Figure 11. Experimental (black crosses) and calculated temperature-dependent molar magnetic susceptibility of **3b** for magnetic models of various size (solid red and green lines). Enclosed is also a comparison with susceptibility curves calculated from the Bleaney-Bowers model,^[25] assuming J = -3.95 cm⁻¹ (blue curve), and from the Bonner-Fisher model^[26], assuming J = -3.25 cm⁻¹ (purple curve).

Antiferromagnetic behavior is also observed in the *para*-chlorine substituted verdazyl radical **3c** (Figure S4, SI), which crystallizes in a different crystal system (monoclinic with space group *C*2/*c*) than verdazyl radical **3b**. A Neél temperature of $T_N = 5.9(1)$ K was observed with elevated values for the Curie constant (*C* = 0.466), the effective magnetic moment $\mu_{eff} = 1.93(1) \mu_B$ and a Weiss constant $\theta_p = -27.9(2)$ K (see Figure S31, SI). The solid state structure is depicted in Figures 12 and 13.



Figure 12. Formation of tetrameric units within the solid state structure of verdazyl radical **3c** involving $C=O\cdots\pi$ interactions (O1A···C1B = 2.889 Å; O1B···C15A = 2.941 Å).

Tetrameric units are formed through the existence of C=O $\cdot\cdot\cdot\pi$ - π interactions between O1A and C1B (2.889 Å) and O1B and C15A (2.941 Å) (see Figure 12 and Figure S5, SI). The angle between the planes of the verdazyl rings is 58°. These tetramers are connected to each other via π - π interactions with shortest distances between two neighboring phenyl rings of C26...C26 = 3.299 Å building linear chains along the *b*-axis. Quantum chemical calculations revealed a negative magnetic coupling constant of $J_1 = -7.26$ cm⁻¹ for this interaction. The tetramers are further connected by π - π interactions with shortest distances between neighboring phenyl and verdazyl rings of C1...C15 = 3.280 Å and a coupling constant of $J_2 = -4.56$ cm⁻¹ leading to a net structure in the *ab*-plane (Figure 13). The coupling constants inside the tetramer are $J_3 = -1.54$ cm⁻¹ and $J_4 = -0.37$ cm⁻¹. Further couplings were found to be negligible. The relative strength of the couplings can be easily explained by the tilt angle between the aromatic systems. The predicted magnetic susceptibility for this compound is depicted along with the experimental curve in Figure 14. Neglecting the interactions inside the tetramers, J_1 and J_2 lead to isolated interactions only (red curve) and the result becomes independent of the number of cells used in the simulation. This changes if further interactions are included (J_1-J_3) : green curve, J_1-J_4 : blue curve). In that case, however, only the minimal magnetic model can be simulated with the procedure used by us. The effect of including J_3 and in particular J_4 in the simulation is comparatively small and does not change the good qualitative agreement with experiment. This good agreement supports the assumption that considering multiple cells with all couplings J_1 - J_4 will not significantly change this picture. The susceptibility maximum is predicted at higher temperatures than measured, suggesting that the calculation tends to over-estimate the dominant J-values in this case.



Figure 13. View along the *c*-axis onto the solid state structure (top) and the magnetic model (bottom) of verdazyl radical **3c**. Top: Tetramers are connected to each other through classical π - π interactions along the *b*-axis (shortest distance between the phenyl rings: C26···C26 = 3.299 Å, J₁) and along the *ab*-

diagonal (C1···C15 = 3.279 Å, J_2) (H atoms were omitted for clarity); bottom: Interactions within the unit cell (solid lines), entering or leaving the unit cell (dashed lines) and outside the unit cell (dotted lines), are shown with a line thickness qualitatively reflecting the strength of the coupling constant indicated with the corresponding color. The directions into which the model shows periodic interactions are indicated as the *x*- and *y*-axes. Molecules outside the unit cell are shown in grey.



Figure 14. Experimental (black crosses) and calculated temperature-dependent molar magnetic susceptibility of **3c** for the magnetic models of isolated dimers (red line) and the minimal magnetic models including J_1 - J_3 (green line) and J_1 - J_4 (blue line). Enclosed is also a comparison with a susceptibility curve calculated from the Bleaney-Bowers model,^[25] assuming J = -3.22 cm⁻¹ (purple curve), and from the Bonner-Fisher model^[26], assuming J = -3.22 cm⁻¹ (turquoise curve).

For comparison, Figure 14 includes an approximation by the Bleaney-Bowers equation and one according to Bonner and Fisher, which reproduce the experimental susceptibility maximum for an assumed J- value of -3.22 cm⁻¹ On the other hand, the curvature of the susceptibility data is much better predicted by the QM-based approach than by the model equations, indicating the necessity to consider more than a single coupling for the description of **3c**.

With these two antiferromagnetic networks in hand, we expected interesting magnetic properties also for the *para*-bromine system **3d**. In contrast to all other discussed solid state structures, we observed dimorphism under the same crystallization conditions. Whereas the orthorhombic phase (**3d**- α) (Figure S6, SI) crystallizes with the same space group type *Pnma* (crystal parameters: *a* = 7.4879(4), *b* = 23.0270(11), *c* = 10.4930(5) Å and with four molecules in a unit cell) as **3b**, also a second polymorph, a monoclinic (**3d**- β) (Figure S9, SI) phase is found. The latter crystallizes like **3c** in the monoclinic group *C*2/*c* with cell parameters *a* = 22.1850(14), *b* = 15.5200(10) and *c* = 21.7749(14) Å and with 16 molecules in a unit cell (for a comparison of crystallographic data, see Table S1, SI). Interestingly, the **3d**- β phase was calculated to show mainly antiferromagnetic interactions with *J*₁ = -6.66 cm⁻¹, *J*₂ = +1,34 cm⁻¹ and *J*₃ = -1.18 cm⁻¹. The solid state of **3d**- β is built from C=O··· π interactions between two verdazyl radicals with a shortest distance between O1A and C1B of 2.830 Å, resulting in an angle between the two verdazyl heterocycles' planes of 62° (Figure S10, SI). Furthermore, a linear chain of radical pairs (AB) in the order BA-AB-BA-AB is formed through the presence of π - π interactions of neighboring *N*-phenyl substituents with alternating radical pair distances of up to 3.415 A (between BA-AB) and 3.370 Å (between AB-

BA) along the *ab*-diagonal (Figure 15, left). The corresponding one-dimensional magnetic model is shown in the right panel of Figure 15.



Figure 15. Solid state structure (left) and magnetic model (right) of verdazyl radical 3d-β (A representing the molecule "A" and B representing the molecule "B"). Left: Formation of linear chains involving π-π interactions between the *N*-phenyl rings of two neighboring verdazyl radicals in the order BA-AB-BA-AB (H atoms were omitted for clarity). Several intermolecular distances are displayed. [C26B···C23A 3.394 Å (*J*₃); C21B···C22A 3.376 Å (*J*₃); C23A···C22A 3.415 Å (*J*₁); C26B···C21B 3.370 Å (*J*₂)]; right: Interactions within the unit cell (solid lines) and entering or leaving the unit cell (dashed lines), are shown with a line thickness qualitatively reflecting the strength of the coupling constant indicated with the corresponding color. The direction into which the model shows periodic interactions is indicated as the *x*-axis. Molecules outside the unit cell are shown in grey. The origin of the unit cell has been shifted to enable a more convenient representation.

In the experimental data (see Figure S32, SI), however, we could not observe any clear cooperative effects. One might explain the paramagnetic character of **3d** in terms of a dominant contribution from the **3d**- α phase, which has rather weak interactions (calculated coupling constants: $J_1 = +0.6 \text{ cm}^{-1}$ and $J_2 = -0.17 \text{ cm}^{-1}$) compared to the ones of **3a**, **3b** and **3c**. In the solid state of **3d**- α zig-zag chains along the *a*-axis are formed through the presence of C=O··· π interactions (J_1) between the verdazyl radicals (Figure S7, SI). We note shortest distances between the two verdazyl rings of 3.175 Å (O1A···C1) or 3.143 Å (O1A···C2), while the angle of the two heterocycle planes is 71°. Although the solid-state structure is similar to that of the *para*-

fluorine system **3b**, no antiferromagnetic behavior is found in the experiments or calculations. A careful analysis of the crystallographic data revealed that the shortest distances, resulting from the C=O··· π interaction (*i. e.* C1···O1) of two neighboring verdazyl rings are a little bit longer for the *para*-bromine system (**3d**- α : 3.143 Å vs. **3b**: 3.042 Å; for a comparison, see also Table 4). Along these lines, further effects should be considered as well: a) different angles of two neighboring verdazyl heterocycle planes (**3d**- α : 71° vs. **3b**: 77°), b) different angles between the planes of two neighboring phenyl rings (**3d**- α : 47° vs. **3b**: 27°). All of this indicates that the intermolecular magnetic interactions for **3d**- α are weaker than for the antiferromagnetically coupled *para*-fluorine system **3b**, thus explaining the Curie-type paramagnetism over the whole studied temperature range. Hence, these data demonstrate that the observed magnetic behavior is complex and shows a strong dependence on packing effects. The magnetic model and a packing diagram of the compound are shown in Figure 16.



Figure 16. Solid state structure (left) and magnetic model (right) of verdazyl radical 3d-α (view along the *b*-axis. Left: The shortest intermolecular distances responsible for J₁ (O1A···C2 3.143 Å) and J₂ (C5···C5 3.802 Å) are indicated (H atoms were omitted for clarity); right: Interactions within the unit cell (solid lines), entering or leaving the unit cell (dashed lines) and outside the unit cell (dotted lines), are shown with a line thickness qualitatively reflecting the strength of the coupling constant indicated with the corresponding color. The directions into which the model is extended are indicated as the *x*- and *y*-axis. Molecules outside the unit cell are shown in grey. The origin of the unit cell has been shifted to enable a more convenient representation.

In Figure 17, the magnetic susceptibility of the investigated sample **3d** is depicted. As seen from comparison with the calculations the expected superposition of the magnetic behavior of **3d**- α and **3d**- β is observed. Additional information about the magnetic models used is given in the SI.



Figure 17. The temperature-dependent magnetic susceptibility of **3d**, calculated for the structures of the α (red) and the β (green) phases. The experimental results (black crosses) remain almost constant in this plot (indicating paramagnetism) and are in-between the results calculated for the different phases.

Next, we studied the effect of the position of the bromine on the structure-property relation, starting with the solid state structure of verdazyl radical **3g** bearing the bromine in the *meta* positions of the *N*-phenyl rings. The solid-state structure shows π - π interactions between two verdazyl radicals. The verdazyl rings present a parallel shifted orientation into opposite directions, so that the shortest distances are formed between the verdazyl ring and the phenyl ring of 3.256 Å (between C1A and C16B) and 3.267 Å (between C1B and C15A; Figure S18, SI). Along the *b*-axis additional π - π interactions are present between the verdazyl ring and the phenyl ring of a neighboring molecule (N1B···C25B = 3.311 Å), forming an antiferromagnetically coupled zig-zag Heisenberg chain (Figure 18) with a coupling constant of $J_1 = -3.27$ cm⁻¹. A secondary structure comprises a

chain parallel to the first one, characterized by a smaller coupling constant of $J_2 = -1.18$ cm⁻¹. The resulting antiferromagnetic behavior is barely visible in the experimental temperature range (Figure 19). A third, ferromagnetic coupling ($J_3 = +0.39$ cm⁻¹, Figure S18, SI), which connects the different chains and thus would promote the magnetic topology to a net, and an even weaker antiferromagnetic coupling ($J_4 = -0.15$ cm⁻¹, Figure S19, SI) are present in the system. However, a comparison of the green and blue curves in Figure 19 as well as the plots shown in Figure S25 in the SI clearly demonstrate that these couplings have a negligible influence on the macroscopic magnetic behavior. Considering only J_1 and J_2 , the total system can be described by an equal number of parallel zig-zag chains for the two different coupling strengths of the same order of magnitude. Additional information about the simulations is given in the SI.



Figure 18. Solid state structure (left) and magnetic model (right) of verdazyl radical **3g**. Left: Formation of chains along the *b*-axis involving additionally π - π interactions between the verdazyl ring and phenyl ring of the molecule "B" (N1B···C25B 3.311 Å, *J*₁) and between the phenyl rings of molecule "A" (C12A···C21A 3.426 Å, *J*₂). Another contact visible in this view (C1A···C16B 3.256 Å, *J*₃) leads to a negligible coupling. H atoms were omitted for clarity; right: Interactions within the unit cell (solid lines), entering or leaving the unit cell (dashed lines) and outside the unit cell (dotted lines), are shown with a line thickness qualitatively reflecting the strength of the coupling constant indicated with the corresponding color. The direction into which the model is extended is indicated as the *x*-axis. Molecules outside the unit cell are shown in grey.



Figure 19. Experimental (black crosses) and calculated temperature-dependent molar magnetic susceptibility of **3g** for magnetic models of various size (solid lines). J_4 is neglected in all curves.

Similar to **3g** also in the solid state structures of **3e** (R = *p*-Me) and **3f** (R = *p*-OMe) the verdazyl radicals are parallel shifted, *i.e.* at an angle between the verdazyl planes of 0°. For **3e** and **3f** π - π interactions between the verdazyl heterocycle and the phenyl rings are dominant, which leads to the formation of linear chains (found for **3f**, see Figure S16, SI) or linear chains of dimeric units (found for **3e**, see Figure S13 and S14, SI). However, for both verdazyl radicals we calculated rather small magnetic coupling constants, which are also summarized in Table 4. Furthermore, magnetic susceptibility measurements indicate simple paramagnetic behavior of these species over the whole studied temperature range from 3–300 K. (see Figure S33 and S34, SI). For a more detailed discussion of the structure property relation of these species, see the SI. Also in the case of the dimethylated verdazyl radical **3h** linear chains along the *a*-axis are formed through CH… π interactions, in which the verdazyl rings are oriented antiparallel but stacked on top of each other (Figure 20 and S21, SI). However, no relevant π - π interactions between the verdazyl rings

or/and the *N*-phenyl rings are present, thus leading to large intermolecular distances around 4.4 Å between the radical heterocycles. Not surprisingly, the large radical-radical distances manifest themself in comparatively small coupling constants of $J_1 = -0.66 \text{ cm}^{-1}$, $J_2 = -0.11 \text{ cm}^{-1}$ and $J_3 = -0.10 \text{ cm}^{-1}$, which explains the experimental paramagnetic behavior (Figure S36, SI).



Figure 20. Solid state structure of verdazyl radical **3h**. Formation of linear chains along the *a*-axis of alternating verdazyl radicals built through CH… π interactions. No relevant π - π interactions between the verdazyl rings or/and phenyl rings were observed. The angle between the two planes corresponding to the phenyl rings is 80°. The verdazyl rings present an antiparallel orientation with large distances about 4.4 Å.

Table 4. Summary of the solid state characteristics along with the most relevant calculated magnetic exchange coupling constants J_n (in cm⁻¹) and the experimentally observed macroscopic behavior. VV angle, i.e. the angle between the planes of two neighboring verdazyl heterocycles; FM = ferromagnetic interactions, AFM = antiferromagnetic interactions; PM = paramagnetism; ^a the paramagnetic behavior was observed for **3d**, being a mixture of the two phases **3d**- α and **3d**- β ; ^b same orientation of the two verdazyl rings with d ~ 4.50 Å; ^c opposite orientation of the two verdazyl rings; ^d opposite orientation of the two verdazyl rings.

compound	solid state characteristics			co K	omputational parameters	macroscopic behavior /
	interaction type	packing type	VV angle / °	<i>J</i> _n / cm⁻¹	shortest distances/ Å	magnetic topology
3a R = H	π-π verdazyl- phenyl	linear chains	р О о	+0.54 +0.45 +0.09	3.367 (C1-C15) 3.497 (C21-C25) 3.723 (C13-C15)	FM 2D: weakly interacting 1D-spin ladders with zig- zag rungs
3b R = <i>p</i> -F	C=O···π verdazyl- verdazyl	zig-zag chains	77°	-4.34	3.042 (C1-O1)	AFM $T_N = 7.2(1)$ K 1D-zig-zag chains

3c R = <i>p</i> -Cl	C=O···π verdazyl- verdazyl	linear chains of tetrameric units	58°	-7.26 -4.56 -1.54 -0.37	3.299 (C26-C26) 3.280 (C1-C15) 2.889 (C1-O1) 2.941 (C15-O1)	AFM $T_N = 5.9(1)$ K 2D: isolated dimers weakly coupled to a net
3d- α R = <i>p</i> -B r	C=O […] π verdazyl- verdazyl	zig-zag chains	71°	+0.60 -0.17	3.143 (O1-C2) 3.802 (C5-C5)	PMª 2D: weakly interacting net
3d- β R = <i>p</i> -Br	C=O···π verdazyl- verdazyl	linear chains with ABBA- pattern	62°	-6.66 +1.34 -1.18	3.415 (C22-C23) 3.370 (C21-C26) 2.830 (C1-O1)	PM ^a 1D: linear chain with ABBA-pattern
3e R = <i>p</i> -Me	π-π verdazyl- phenyl	linear chains of dimeric units	с О о	−1.50 +0.44	3.604 3.266 (C1-C26)	РМ
3 f R = <i>p</i> -OMe	π-π verdazyl- phenyl	linear chains	с 0 о	+0.28 -0.16	3.389 3.754	РМ
3g R = <i>m</i> -B r	π-π verdazyl- phenyl	linear chains of dimeric units	c 0°	-3.27 -1.18	3.311 (N1-C25) 3.426 (C12-C21)	AFM T _N ≈ 3.0 K parallel zig-zag chains
3h R = <i>m</i> , <i>m</i> -Me ₂	CH···π	linear chains	q 0 0	-0.66 -0.11 -0.10	3.572 3.809 3.810	РМ

Conclusion

Ferromagnetic interactions between spin centers have been observed in a phenyl substituted verdazyl radical, a behavior rarely observed for this kind of radical compounds. The magnetic coupling network has been analyzed using our previously developed first-principles bottom up approach based on crystallographic input. The magnetic network consists of weakly interacting one-dimensional spin ladders with zig-zag rungs and calculated magnetic exchange coupling constants of comparable magnitude ($J_1 = +0.54 \text{ cm}^{-1}$, $J_2 = +0.45 \text{ cm}^{-1}$) as well as a third weaker interaction characterized $J_3 = +0.09 \text{ cm}^{-1}$. In particular, the linear chain of parallel oriented verdazyl radicals caused by the π - π interaction of the verdazyl ring and the phenyl ring may be held responsible for the stronger ferromagnetic interaction.

By varying substituents at the phenyl group, a series of seven additional verdazyl radicals were prepared, characterized, and their bulk magnetic properties measured and analyzed in terms of their magnetic coupling networks. Table 4 gives a summary of the crystal structural characteristics,

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the most relevant calculated magnetic exchange coupling constants J_n and the experimentally observed macroscopic magnetic behavior. The cooperative magnetic properties found in the present series of molecular verdazyl radicals are the result of complex interaction networks whose topology is strongly dependent on the solid state structure. Along these lines, the angles, distances and translational displacements describing the relative orientation of neighboring molecules with respect to each other are crucial in controlling the relevant magnetic coupling interactions. Our recent black box implementation of the first-principles bottom up approach allows for accurate qualitative prediction and detailed analysis of the correlation between solid state architecture and magnetic properties. Although the perturbation in the molecular structure by varying the substituent of the N-aryl-ring may appear small, the effects upon the structural parameters controlling intermolecular magnetic coupling interactions are strong, resulting in a wide spectrum of cooperative magnetic behavior. They include dimorphism (3d), and can range from simple paramagnetic behavior (3d, 3e, 3f and 3h) to pronounced antiferromagnetic (3b and 3c) and even ferromagnetic interactions (3a). For 3b, featuring a para-fluorine substituent, C=O. $\cdot\pi$ interactions between neighboring radicals lead to a formation of one-dimensional zig-zag chains, in which the molecules are coupled antiferromagnetically to each other, observable in the χ (T)-plot with a maximum of the magnetic susceptibility at around $T_N = 7$ K. The substitution of fluorine with chlorine in 3c resulted in a two-dimensional network, in which dimeric units are connected to a weakly coupling net. Besides a weaker C=O $\cdots\pi$ interaction, an additional π - π interaction between the aryl substituents leads to a macroscopic antiferromagnetic state with $T_{\rm N}$ = 6 K. In **3g**, the dominant structural motif is a π - π interaction between a verdazyl heterocycle and an N-Aryl-ring, which is responsible for the dominant antiferromagnetic coupling extending through a parallel zig-zag chain.

The important role played by the intermolecular π - π interactions between the verdazyl ring and the phenyl substituent groups of adjacent molecules in establishing the magnetic coupling topology is a quite general result of the present study. Based on this finding, the incorporation of additional planar substituents into the radical's molecular architecture appears to be a promising approach for exercising further structural control of magnetic interactions in these materials.

Experimental Section

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All reactions involving air or moisture sensitive reagents or intermediates were carried out under argon atmosphere. All glassware was dried by the use of a heat gun under high vacuum prior to use. Concentration of the reaction mixture was performed under reduced pressure at 40 °C at the appropriate pressure. Purified compounds were further dried under high vacuum.

General procedure for the synthesis of diaryl substituted carbonohydrazides 1a-1h (GP1):

According to literature procedures^[11a, 27] in a Schlenk tube Cul (5 mol%), 1,10-phenanthroline (10 mol%), K₃PO₄ (3.05 equiv.) and carbohydrazide (1.0 equiv.) were added, evacuated and backfilled with argon two consecutive times. Aryl iodide (2.2 - 2.3 equiv.) and DMF (2 mL/mmol carbohydrazide) were added and the mixture was heated to 90 °C in the dark and stirred for 48 h at this temperature. After the reaction mixture was allowed to cool to room temperature it was filtered through a short pad of silica and eluted with EtOAc. Water was added and the two layers were separated. The aqueous layer was extracted with EtOAc twice and the combined organic layers were washed with brine and dried over MgSO₄. Filtration, evaporation of the solvent *in vacuo* and FC afforded the diaryl-substituted carbohydrazides.

General procedure for the synthesis of tetrazinan-3-ones 2a–2h (GP2): In a two-necked flask with condenser carbonohydrazide 1 (1.0 eq.) was dissolved in MeOH and stirred at 45 °C for 5 min. A methanolic solution of pivalaldehyde (1.0 eq.) was added dropwise using a syringe pump within 30 min. After addition the mixture was refluxed for 3–4 h. Stirring was stopped and the mixture was allowed to cool to rt. The precipitate was filtered off and carefully washed with little amounts of cold MeOH. The filtrate was cooled to -14 °C overnight and the achieved precipitate filtered off again and washed with cold MeOH. The combined solids were dried *in vacuo* to afford the tetrazinan-3-one without the need of a further purification step.

General procedure for the synthesis of 6-oxo-verdazyl radicals 3a–3h (GP3): In a Schlenk tube tetrazinan-3-one **2** (1.0 eq.) and 1,4-benzoquinone (1.7 eq.) were added and dissolved in CH₂Cl₂. The mixture was heated to 60 °C for an appropriate time. After full conversion of the starting material (monitored by TLC) the mixture was cooled to rt and filtered. The solvent was removed *in vacuo* and the residue subjected to FC to afford the 6-oxo-verdazyl radical as a red crystalline solid.

For detailed analytical data and yields of the precursor compounds **1a–1h**, **2a–2h** and the radicals **3a–3h** (including crystal structures, CCDC 1508710-1508718), see SI.

Magnetic Properties: Powdered samples of compounds **3a–3h** were filled in PE capsules and attached to the sample holder rod of a Vibrating Sample Magnetometer (VSM) unit for measuring the magnetization M(T,H) in a Quantum Design Physical-Property-Measurement-System (PPMS). The samples were investigated in the temperature range of 2.5–300 K and with magnetic flux densities up to 80 kOe.

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Text for the table of contents

Cooperative magnetic effects: The preparation of a series of eight *tert*-butyl substituted 1,5-diaryl-6-oxo verdazyl radicals and the characterization of the magnetic susceptibilities are presented. Quantum chemical calculations revealed different complex magnetic networks including ferromagnetic and antiferromagnetic one- and two-dimensional networks. This study highlights the relationship between crystal structure and magnetic properties.



Keywords: Verdazyl Radicals • Organic Magnetism • Cooperative Effects • Ferromagnetic Interactions • Structure Property Relations • Electron Spin Resonance