Antiferromagnetic Interactions in 1D Heisenberg Linear Chains of 7-(4-Fluorophenyl) and 7-Phenyl-Substituted 1,3-Diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl Radicals

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Abstract: 7-(4-Fluorophenyl) and 7phenyl-substituted 1,3-diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl radicals were characterized by X-ray diffraction analysis and variable-temperature magnetic susceptibility studies. The radicals pack in 1D π stacks of equally spaced slipped radicals with interplanar distances of 3.59 and 3.67 Å and longitudinal angles of 40.97 and 43.47°, respectively. Magnetic-susceptibility studies showed that both radicals exhibit antiferromagnetic interactions. Fitting the magnetic data revealed that the behavior is consistent with 1D regular linear antiferromagnetic chain with J=-12.9 cm⁻¹,

Keywords: benzotriazinyls • heterocycles • heterocyclic radicals • magnetic properties • stacking interactions $zJ' = -0.4 \text{ cm}^{-1}$, g = 2.0069 and $J = -11.8 \text{ cm}^{-1}$, $zJ' = -6.5 \text{ cm}^{-1}$, g = 2.0071, respectively. Magnetic-exchange interactions in benzotriazinyl radicals are sensitive to the degree of slippage, and inter-radical separation and subtle changes in structure alter the fine balance between ferro- and antiferromagnetic interactions.

Introduction

The quest for new multifunctional molecular materials based on open-shell molecules has been intensively pursued over the past couple of decades.^[1] Although numerous radical families are known, and a plethora of persistent organic radicals have been synthesized, their magnetic properties, which depend on their crystal packing, are difficult to pre-



Scheme 1. 1,2,4-Benzotriazinyl radicals 1–7 with IUPAC numbering of the ring system.

dict and control.^[2] Research efforts to develop "magnetostructural relationships" aimed to understand the effects of molecular structure on solid-state packing and their resultant magnetic behavior. Ultimately, these efforts can assist in the design of radicals with favorable properties.

1,2,4-Benzotriazinyls, despite their exceptional air and moisture stability, have received little attention (Scheme 1 and Table 1).^[3] As part of our efforts to explore the chemis-

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Table 1. Table for Scheme 1.

Radical	\mathbb{R}^1	\mathbf{R}^2	R ³		
1	Ph	Ph	thien-2-yl		
2	Ph	Ph	CF ₃		
3	Ph	3-vinyl C ₆ H ₄	Н		
4	$4-BrC_6H_4$	3-vinyl C ₆ H ₄	Н		
5	$4-ClC_6H_4$	Ph	Н		
6	Ph	Ph	$4 - FC_6H_4$		
7	Ph	Ph	Ph		

try of 1,2,4-benzotriazine, we developed a short synthetic route to access a range of derivatives functionalized at the C7 position of the benzo-fused ring.^[4]

1,3-Diphenyl-7-(thien-2-yl)-1,4-dihydro-1,2,4-benzotriazin-4-yl (1)^[5] was a 1D alternating ferromagnetic chain $(J_1 = +$ 7.12 cm⁻¹, $J_2 = +1.28$ cm⁻¹, g = 2.0071) and 1,3-diphenyl-7trifluoromethyl-1,4-dihydro-1,2,4-benzotriazin-4-yl $(2)^{[6]}$ a 1D regular ferromagnetic chain $(J = +1.05 \text{ cm}^{-1}, g = 2.0000)$ with weaker antiferromagnetic interchain interactions. Three other radicals 3-5 have also been reported by other groups.^[7,8] Radicals **3** and **4** have similar magnetic behavior as radical 2 (J = +7.38 and 6.90 cm⁻¹, respectively),^[7] whereas radical 5 has strong 1D alternate linear-chain antiferromagnetic interactions $(J_1 = -76.50 \text{ cm}^{-1}, J_2 = -22.90 \text{ cm}^{-1})$.^[8] In all cases, the benzotriazinyl radicals exhibited π -slipped stacked structures, but in some cases, the interactions are ferromagnetic and in others antiferromagnetic. Herein, we present the solid-state characterization of two new benzotriazinyls: 1,3-diphenyl-7-(4-fluorophenyl)-1,4-dihydro-1,2,4benzotriazin-4-yl (6) and 1,3-diphenyl-7-phenyl-1,4-dihydro-1,2,4-benzotriazin-4-vl (7) and provide a magnetostructural correlation for the series 1-7 based on the degree of slippage of the π stacks.

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Results

Synthesis and characterization: Radicals 6 and 7 were prepared by Suzuki–Miyaura reactions of 7-iodo-1,2,4-benzotriazinyl (8, Scheme 2)^[4a] with 4-FC₆H₄B(OH)₂ and



Scheme 2. Synthesis of radicals 6 and 7. a) DBU (0.1 equiv), Pd/C (1.6 mol%), CH₂Cl₂ (1 mL), approximately 20 °C under air atmosphere, 4–9 h (81%); b) 4-FC₆H₄B(OH)₂ or PhB(OH)₂ (3 equiv), [Pd(OAc)₂] (5 mol%), dry DMF (2 mL), approximately 100 °C, under argon, 30 min (47 and 93%, respectively).

PhB(OH)₂ by using Pd(OAc)₂ (5 mol%) in dry toluene (2 mL) at 100 °C under argon with yields of 47 and 93%, respectively (Scheme 2).^[4b]

Cyclic voltammetry and EPR spectroscopy: The redox behavior of radicals 6 and 7 was similar to that of radicals 1- $5^{[5-8]}$ exhibiting two fully reversible waves, which correspond to the -1/0 and 0/+1 processes (Figures S1 and S2 in the Supporting Information). Oxidation potentials in radicals 6and 7 occurred at +0.16 and +0.15 V versus ferrocene/ferrocenium, whereas the corresponding reduction potentials occurred at -0.95 and -0.96 V, respectively. Solution EPR spectra of radicals 6 and 7 have the typical seven-line spectrum consistent with the coupling of the unpaired electron with three similar but slightly inequivalent ¹⁴N nuclei. Radicals 6 and 7 have hyperfine coupling constants (hfcc) similar to radicals 1-5 (Figures S3 and S4 in the Supporting Information).^[5-8] Simulated first- and second-derivative modes gave hfcc $\alpha_N(1) = 7.47$, $\alpha_N(2) = 4.84$, $\alpha_N(3) = 4.70$, and g =2.0069 for radical **6** and $\alpha_N(1) = 7.49$, $\alpha_N(2) = 4.89$, $\alpha_N(3) =$ 4.65, and g = 2.0071 for radical 7.

X-ray diffraction studies: Suitable single crystals of **6** and **7** for X-ray diffraction studies (Table S1 in the Supporting Information) were obtained by slow cooling of concentrated hot hexane solutions. Radicals **6** and **7** crystallize in the monoclinic space groups $P\bar{1}$ and $Pna2_1$, respectively, with one molecule in the asymmetric unit. Intramolecular dimensions of radicals **6** and **7** are similar to those of radicals **1–5** with the 1,2,4-amidrazonyl moiety close to planarity with the *N*-phenyl rotated out of the plane to minimize steric interactions.

1,2,4-Benzotriazinyl radicals tend to form 1D π -slipped stacked columns, and radicals **6** and **7** are no exception. Molecules of the 7-(4-fluorophenyl)benzotriazinyl **6** are related by translation parallel to the crystallographic *a* axis with a longitudinal slippage of 40.97° and an intraplane distance of 3.59 Å (Figure 1, top). This leads to the triazinyl



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Figure 1. Solid-state packing of the 7-(4-fluorophenyl)benzotriazinyl radical 6. Top: 1D π -slipped stacks of radicals along the *a* axis (*N*-phenyls are omitted for clarity). Bottom: lamellar sheets formed along the *bc* diagonal.

ring being located between the phenyl substituent and a C– C bond of neighboring molecules within the stack. The intrastack distance between the centroids of the triazinyl ring and the phenyl ring is 3.624 Å with a closest inter-ring contact of 3.411(2) Å [C(17)···N(3)]. The intrastack distance between the centroids of the triazinyl ring and the C–C bond is 3.769 Å with the closest contact being C(1)···C(6) at 3.705(2) Å. Neighboring stacks, pack along the *c* axis in an antiparallel orientation to form chains, in which the *N*-phenyls of one stack form edge-to-face C–H···π interactions with the 3-phenyls of the neighboring stacks. This causes alternation in the interchain distances of 6.591 and 6.364 Å. In the latter case, centrosymmetric C–H···H–C contacts, with a C···C distance of 3.869(2) Å for C(5)···C(19), causes neighboring chains to form lamellar sheets (Figure 1, bottom).

The 7-phenylbenzotriazinyl **7** packs similarly to radical **6**: The molecules of radical **7** are related by translation parallel to the crystallographic c axis with a longitudinal slippage of 43.47° and an intraplane distance of 3.67 Å (Figure 2, top). The triazinyl ring is again located between the phenyl sub-

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Figure 2. Solid-state packing of **7**. Top: 1D π -slipped stacks of radicals along the *c* axis (*N*-phenyls are omitted for clarity). Bottom: antiparallel chains along the *a* axis form voids (opaque light diamonds). Pinwheel orientation of radicals around the voids.

stituent and a C–C bond of neighboring molecules within the stack. The intrastack distances between the centroids of the triazinyl ring and the phenyl ring is 3.822 Å with a closest inter-ring contact of 3.663(2) Å [C(17)···N(3)]. The intrastack distance between the centroids of the triazinyl ring and the C–C bond is 3.779 Å, and the closest contact is C(2)···C(8) at 3.803(2) Å. In the packing of radical **6**, the longitudinal slippage angle can accommodate the *N*-phenyl substituent without disorder at a torsional angle of 69.52°. In contrast, the smaller longitudinal slippage angle in radical **7** brings the *N*-phenyl substituents closer. Because there is only one molecule in the asymmetric unit, the phenyl ring appears disordered over two sites with torsion angles at 50.48 and 97.71° affording favorable C–H···π (edge-to-face) interactions between the *N*-phenyls.

Neighboring stacks pack along the *a* axis in a head-to-tail orientation to form chains. Neighboring chains run antiparallel in the *ab* plane so that the *N*-phenyls of one stack form edge-to-face C-H··· π interactions with the 7-phenyls of the neighboring stacks. The packing of these chains gives rise to small voids in the structure, which generate pores parallel to the *c* axis (Figure 2, bottom). The centroid···centroid distance for the disordered *N*-phenyl substituent is 8.481 Å, which acts as an upper limit to the pore size. Conversely, if

both rings align perpendicular to the channel this pore closes to approximately 2.4 Å. The pore is too small to be accessible by the solvent molecules (hexane), and there was no evidence of residual electron density in the channel region in the final difference map.

Magnetic properties: The π -based nature of the benzotriazinyl radical coupled with the 1D π -slipped stacked columns of radicals 6 and 7 suggest that both 6 and 7 will exhibit strongly uni-dimensional magnetic interactions propagating parallel to the stacking direction, because overlap between singly-occupied molecular orbitals is maximized parallel to the stacking direction.

Variable-temperature magnetic-susceptibility measurements on radicals **6** and **7** were obtained by using a Quantum Design SQUID magnetometer in the region 5-300 K in an applied field of 0.5 T. The data were corrected for both sample diamagnetism (Pascal's constants) and the diamagnetism of the sample holder.

Radical 6 demonstrated Curie–Weiss behavior above 50 K with $C = 0.374 \text{ emu K mol}^{-1}$, which is close to that expected for an $S = \frac{1}{2}$ radical with g = 2.0069 (C = 0.375 emuKmol⁻¹; Figure 3, upper inset). The Weiss constant ($\theta = -11.3$ K) is consistent with local antiferromagnetic interactions. From the mean-field approach, a first estimate of the intrachain interaction was $J/k = -11.3 \text{ K} (\theta = 2zJS(S+1)/3k)$ [Eq. (1)]. The magnetic data were modeled by using the Bonner-Fisher expression (Figure 3, top) for a linear chain of antiferromagnetically coupled $S = \frac{1}{2}$ spins by using the g value (2.0069) from EPR data.^[9] A close examination of the lowtemperature data revealed a deviation from the simple isolated chain model. Inclusion of a mean field approximation [Eq. (1)] to take into account weak interchain interactions led to a marginally improved fit with $J = -12.9 \text{ cm}^{-1}$, zJ' = -0.4 cm^{-1} , $R = 6.21 \times 10^{-4}$ (correlation factor R = $\Sigma[(\chi T)_{obs} - (\chi T)_{calcd}]^2 / \Sigma[(\chi T)_{obs}]^2)$. This fit reproduces both the position and maximum in χ extremely well, and the magnitude of J in relation to zJ' indicates that radical 6 is well described as a 1D antiferromagnetic linear chain of equally spaced $S = \frac{1}{2}$ radicals.

Radical 7 showed similar magnetic behavior with radical 6: It demonstrated Curie–Weiss behavior above 50 K with $C=0.379 \text{ emu K mol}^{-1}$, which is close to that expected for an $S=\frac{1}{2}$ radical. The Weiss constant ($\theta=-19.2$ K) indicates local antiferromagnetic interactions. Fitting the magnetic data in the Bonner–Fisher model provided $J=-11.8 \text{ cm}^{-1}$, $zJ'=-6.5 \text{ cm}^{-1}$, $R=5.14\times10^{-4}$ (Figure 3, bottom). The magnitude of the interchain interactions indicates that the antiparallel chains along the *a* axis are not well isolated from each other (Figure 2, bottom). Each benzotriazinyl radical generates two crystallographically equivalent contacts to molecules in the neighboring stack; the N atom points between a pair of C–H bonds to one molecule and offers a pair of C–H bonds to another one.



0.002 0.000 0 50 100 150 200 250 300 Temperature / K

Figure 3. Temperature dependence of χ for radical **6** (top) and **7** (bottom). The solid line represents the best fit to the 1D antiferromagnetic regular linear chain model. $J = -12.9 \text{ cm}^{-1}$, $zJ' = -0.4 \text{ cm}^{-1}$, g = 2.0069 for radical **6**; $J = -11.8 \text{ cm}^{-1}$, $zJ' = -6.5 \text{ cm}^{-1}$, g = 2.0071 for radical **7**. Inset: Curie–Weiss behavior in the 50–300 K region, $C = 0.374 \text{ emu K} \text{ mol}^{-1}$, $\theta = -11.3 \text{ K}$ for **6** and $C = 0.379 \text{ emu K} \text{ mol}^{-1}$, $\theta = -19.2 \text{ K}$.

Discussion

The magnetic behavior of radicals **6** and **7** can be rationalized by using the molecular orbital model,^[10] because DFT studies performed on the X-ray geometries of benzotriazinyls did not describe accurately the electronic structure of the ground state and, therefore, the magnitude of the exchange interaction within the radical stacks. Because the size of the overlap between the SOMO orbitals (Figures S5 and S6 in the Supporting Information) is proportional to the exchange coupling interaction, the latitudinal and longitudinal slippage angles as well as the distances between radicals determine the nature of the magnetic exchange along the π -stacking direction. In related π -stacked systems, Oakley has shown that there is a fine balance between ferro- and antiferromagnetic interactions, because the degree of slippage is adjusted through chemical or mechanical pressure.^[2h,11]

The structures of radicals 1 and 5 adopt an alternating π stack, whereas 2 adopts a twisted stack of radicals, and so neither are directly comparable with 6 and 7. Conversely,

radicals **3** and **4** both adopt π -slipped stacks similar to **6** and **7**, yet the interactions in **3** and **4** are both ferromagnetic, whereas those in **6** and **7** are antiferromagnetic. A direct comparison between these four radicals is more complex, because there are three molecules in the asymmetric unit of **4** leading to a more complex set of geometric parameters; nevertheless, the maximum orbital overlap occurs in a perfectly eclipsed geometry, favoring an antiferromagnetic interaction. In this regard, the degree of slippage in **6** and **7** is somewhat less than that observed in **3** and **4**, in qualitative agreement with the observed exchange interaction in **6** and **7** being antiferromagnetic (Table 2, Figure 4).

Table 2. Geometric parameters and exchange interactions in π -slipped stacked benzotriazinyls. Parameters are defined in Figure 4.

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Molecule	Longitudinal [°]	Latitudinal [°]	Distance [Å]	$J [\mathrm{cm}^{-1}]$
3	45.07	77.32	3.44	+7.4
4	46.09	68.71	3.28	+6.9
	59.68	69.90	3.25	
6	40.97	75.84	3.59	-12.9
7	43.47	79.15	3.67	-11.8



Figure 4. Parameters used to define the degree of longitudinal and lateral slippage. Top: the longitudinal slippage α is defined as the plane formed between the central C atoms of two benzotriazinyl rings and the benzotriazinyl ring plane. Bottom: the latitudinal slippage β defined the angle between the plane linking atoms N(2) and C(7) on each of the two neighboring benzotriazinyl radicals and the benzotriazinyl ring plane.

Of particular note in the design of future radicals is the larger interplanar distance in radicals 6 and 7 in relation to 3 and 4, which is likely to lead to reduced magnetic-exchange interactions (either ferro- or antiferromagnetic); both radicals 6 and 7 can be considered as biphenyl derivatives and exhibit twist angles between the two phenyl rings of 31.79 and 26.12°, respectively. This lack of coplanarity

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may lead to larger intermolecular separations along the π stacking direction. Further modifications to the benzotriazinyl framework are in progress to optimize both the intrastack separation and the degree of lateral and longitudinal slippage.

Conclusion

The crystal structures and magnetic properties of 1,3-diphenyl-7-(4-fluorophenyl)-1,4-dihydro-1,2,4-benzotriazin-4yl (6) and 1,3-diphenyl-7-(4-phenyl)-1,4-dihydro-1,2,4-benzotriazin-4-yl (7) have been investigated. The radicals form regular 1D π stacks and magnetic-susceptibility studies showed local 1D antiferromagnetic interactions within the stacks. The reduced slippage of the stacks in both 6 and 7 in relation to 3 and 4 favored a net antiferromagnetic interaction. Clearly subtle fine tuning of the steric effects of the substituents is required to control the degree of slippage and inter-radical separation, which dictate the nature of the resultant magnetic-exchange interaction. Further studies are underway.

Experimental Section

General synthetic procedure: A stirred mixture of 7-iodo-1,3-diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (8),^[4a] arylboronic acid (3 equiv), K₂CO₃ (3 equiv) and Pd(OAc)₂ (5 mol %) was heated to about 100 °C in dry toluene for 1–3 h under argon until all the starting material was consumed (TLC). Dry flash chromatography (Et₂O/hexane 1:3) of the reaction mixture gave the following products:

1,3-Diphenyl-7-(4-fluorophenyl)-1,4-dihydro-1,2,4-benzotriazin-4-yl (6): Black needles; m.p. 194–195 °C (from pentane); $\tilde{v}_{max} = 3066vw$, 3039vw, 1593w, 1487 m, 1450w, 1431w, 1390 (m), 1328 (w), 1315 (w), 1219 (m), 1163 (w), 1066 (w), 1024 (w), 900 (w), 862 (w), 837 (w), 821 (s), 779 (m), 758 cm⁻¹ m; λ_{max} (CH₂Cl₂; log ε) 293 (3.52), 382 (2.81), 513 nm (2.14); MS (EI): m/z (%) 379 [M^+ +1] (32), 378 [M^+] (100), 180 (6), 170 (25), 120 (44), 77 (45), 51 (21); elemental analysis calcd (%) for C₂₅H₁₇FN₃ (378.42): C 79.35, H 4.53, N 11.10; found: C 79.41, H 4.57, N 11.05; g = 2.0069.

1,3-Diphenyl-7-phenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (7): Black needles; m.p. 152–154 °C (cyclohexane); \bar{v}_{max} =3062 (vw), 3032 (vw), 2953 (vw), 2924 (vw), 1595 (w), 1510 (w), 1481 (m), 1448 (w), 1415 (w), 1392 (m), 1317 (w), 1278 (w), 1247 (w), 1199 (w), 1168 (w), 1080 (w), 1066 (w), 1022 (w), 898 (w), 839 (w), 776 cm⁻¹ (m); λ_{max} (CH₂Cl₂; log ε)=293 (3.50), 323 inf (2.88), 385 (2.78), 443 (2.46), 514 (2.20); MS (EI): m/z (%): 361 [M^+ +1] (37), 360 [M^+] (100), 255 (12), 180 (12), 152 (26), 126 (5), 102 (46), 77 (51), 57 (5), 51 (22); elemental analysis calcd (%) for C₂₅H₁₈N₃ (360.43): C 83.31, H 5.03, N 11.66; found: C 83.45, H 5.12, N 11.68; g=2.0071.

Instrumental analyses: Cyclic voltammetry (CV) measurements were performed on a Princeton Applied Research Potentiostat/Galvanostat 263 A apparatus. The concentration of the benzotriazinyl radical used was 1 mm in CH₂Cl₂. A 0.1 M CH₂Cl₂ solution of tetrabutylammonium tetrafluoroborate (TBABF₄) was used as electrolyte. The reference electrode was Ag/AgCl, and the scan rate was 50 mV s⁻¹. Ferrocene was used as an internal reference; the $E_{1/2}(\text{ox})$ of ferrocene in this system was 0.352 V.^[12] EPR measurements were carried out on a Bruker EMX spectrometer by using an X band (9.8 GHz) microwave bridge at 290 K. The EPR spectrum was simulated by using the Winsim Spectral Simulation for MS Windows 9x, NT v0.98^[13] Magnetic-susceptibility measurements were performed on a Quantum Design MPMS-XL SQUID magnetometer in

the temperature region of 5-300 K and in an applied magnetic field of 5000 G. X-ray diffraction data were collected on an Nonius Kappa-CCD diffractometer, equipped with a CCD area detector and graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). A suitable crystal (black plate of dimensions $0.32 \times 0.18 \times 0.10$ mm) was attached to a glass fiber by using paratone-N oil and transferred to a goniometer, in which it was cooled to 180(2) K for data collection by using an Oxford Instruments cryostream. Unit cell dimensions were determined and refined by using 17991 (1.02 < $\theta < 27.48^{\circ}$), reflections. An empirical absorption correction was applied by using multiscan based on symmetry-related measurements by using Sortav.^[14] The structure was solved by direct methods and refined on F² by using full-matrix least squares with SHELXL97.[15] Programs used: HKL Denzo and Scalepack for cell refinement and data reduction^[16a] and MERCURY^[16b] for molecular graphics. The nonhydrogen atoms were treated anisotropically, whereas the hydrogen atoms were placed in calculated, ideal positions and refined by using a riding model.

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