

# Magnetic Properties

# Structural, Magnetic, and Computational Correlations of Some Imidazolo-Fused 1,2,4-Benzotriazinyl Radicals

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Dedicated to the memory of Professor Michael Bendikov

**Abstract:** 1,3,7,8-Tetraphenyl-4,8-dihydro-1*H*-imidazolo[4,5*g*]-[1,2,4]benzotriazin-4-yl (**5**), 8-(4-bromophenyl)-1,3,7-triphenyl-4,8-dihydro-1*H*-imidazolo[4,5*g*][1,2,4]benzotriazin-4-yl (**6**), and 8-(4-methoxyphenyl)-1,3,7-triphenyl-4,8-dihydro-1*H*imidazolo[4,5*g*][1,2,4]benzotriazin-4-yl (**7**) were characterized by using X-ray diffraction crystallography, variable-temperature magnetic susceptibility studies, and DFT calculations. Radicals **5**–**7** pack in 1D  $\pi$  stacks made of radical pairs with alternate short and long interplanar distances. The magnetic susceptibility ( $\chi$  vs. *T*) of radicals **5** and **6** exhibit broad maxima at (50±2) and (50±4) K, respectively, and are interpreted in terms of an alternating antiferromagnetic Heisenberg linear chain model with average exchange-interaction

Introduction

Multifunctional materials are under intensive study as components in electronic devices owing to their potential to reduce the size, weight, cost, and power consumption of these devices, while simultaneously improving their efficiency and upgrading their capabilities.<sup>[11]</sup> Organic molecules have an important role as building blocks for such materials because they can be tailor-made to exhibit desired properties. Persistent

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values of J = -31.3 and  $-35.4 \text{ cm}^{-1}$  ( $g_{\text{solid}} = 2.0030$  and 2.0028) and an alternation parameter a = 0.15 and 0.38 for **5** and **6**, respectively. However, radical **7** forms 1D columns of radical pairs with alternating distances; one of the interplanar distances is significantly longer than the other, which decreases the magnetic dimensionality and leads to discrete dimers with a ferromagnetic exchange interaction between the radicals ( $2J = 23.6 \text{ cm}^{-1}$ ,  $2zJ' = -2.8 \text{ cm}^{-1}$ ,  $g_{\text{solid}} = 2.0028$ ). Magnetic exchange-coupling interactions in 1,2,4-benzotriazinyl radicals are sensitive to the degree of slippage and inter-radical separation, and such subtle changes in structure alter the fine balance between ferro- and antiferromagnetic interactions.

open-shell organic molecules hold promise as multifunctional materials because of their unique physical properties.<sup>[2]</sup> The presence of unpaired electrons can give rise to materials with new functionalities that combine magnetic, optical, and transport properties. However, the observed physical properties greatly depend on the solid-state packing, which is difficult to predict and control. Crystal engineering of organic radicals is challenging and breakthroughs achieved to date have been serendipitous.<sup>[3]</sup> Interesting properties, such as bulk ferromagnetism or metallic conductivity are a rarity for organic radicals because intermolecular forces are weak and short range, which leads to low-dimensional magnetic exchange interactions.<sup>[4]</sup> Nevertheless, systematic structure–property studies can identify design rules for the preparation of materials with useful properties.

Numerous families of persistent organic radicals have been extensively studied.<sup>[2]</sup> The 1,2,4-benzotriazin-4-yls (e.g., parent radical **1**, Figure 1), which were first prepared in the late 1960s by Blatter et al.,<sup>[5]</sup> have recently attracted interest owing to their air and moisture stability.<sup>[6]</sup> Although persistent organic  $\pi$  radicals have a tendency to dimerize in the solid state, to date there has been no evidence for dimerization in 1,2,4-benzotriazinyls. In addition, a range of low-dimensional magnetic properties have been reported.<sup>[6]</sup>

Increasing the dimensionality of the magnetic interactions requires strong exchange-coupling interactions that propagate

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**Figure 1.** 1,3-Diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (1) and structures of imidazolo-, oxazolo-, and thiazolo-fused benzotriazinyls **2–7** with IUPAC numbering of the ring systems.

throughout the bulk of the material. Thus, we designed and prepared a range of imidazolo-, oxazolo-, and thiazolo-fused 1,2,4-benzotriazinyls (**2**, **3**, and **4** in Figure 1).<sup>[7]</sup> We anticipated that the extension of the  $\pi$ -acene core of these radicals could provide an effective pathway for stronger exchange interactions because 1,2,4-benzotriazinyls tend to form  $\pi$ -slipped stacked columns. Moreover, the introduction of substituents that can promote intermolecular contacts could increase the dimensionality of the magnetic interactions.

Herein we present the solid-state characterization of 1,3,7,8-tetraphenyl-4,8-dihydro-1*H*-imidazolo[4,5*g*][1,2,4]benzotriazin-4-yl (**5**), 8-(4-bromophenyl)-1,3,7-triphenyl-4,8-dihydro-1*H*-imidazolo[4,5*g*][1,2,4]benzotriazin-4-yl (**6**), and 8-(4-methoxy-phenyl)-1,3,7-triphenyl-4,8-dihydro-1*H*-imidazolo[4,5*g*]-

[1,2,4]benzotriazin-4-yl (7) and provide magnetostructural correlations based on variable-temperature (VT) magnetic susceptibility data, single-crystal X-ray diffraction studies, and DFT calculations.

## Results

#### Synthesis and characterization

Within the context of our ongoing studies on this family of radicals, we have developed high-yielding synthetic routes to several 7-substituted benzotriazinyls and investigated their chemistry.<sup>[8]</sup> Interestingly, 1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (**8**), the oxidation product of Blatter radical **1**, was a useful scaffold for the preparation of imidazolo-, oxazolo-, and thiazolo-fused benzotriazinyls.<sup>[7]</sup> Benzotriazinone **8** undergoes regiospecific nucleophilic substitution at C6, electrophilic substitution at C8, and a range of cyclization reactions to give linear and angular fused benzotriazinones, some of which were unusual zwitterionic compounds.<sup>[8]</sup>

Thiazolo[5',4':4,5]benzo[1,2-*e*][1,2,4]triazin-4-yls **4** were prepared in three steps by C6 amination of benzotriazinone **8** followed by acylation and aroylation to give *N*-(benzotriazin-6-yl)-carboxamides that undergo ring closure on treatment with  $P_2S_5$  to give the thiazolo-fused benzotriazinyls.<sup>[7a]</sup> Following a similar synthetic strategy, reaction of benzotriazinone **8** with *N'*-arylbenzamidines in PhMe at approximately 100 °C in the presence of *N*,*N*-diisopropylethylamine (Hünig's base) gave 6-benzimidamidobenzotriazines **9** in 79 to 95% yield, which cyclodehydrate upon treatment with neat AcOH at approximately 120 °C to give 8-substituted 1,3,7-triphenyl-4,8-dihydro-1*H*-imidazo[4,5*g*][1,2,4]benzotriazin-4-yls **2** in 70 to 81% yield (Scheme 1).<sup>[7b]</sup> In this manner, radicals **5**, **6**, and **7** were prepared in overall yields of 77, 55, and 61%, respectively.<sup>[7b]</sup>

### Cyclic voltammetry and EPR spectroscopy

The redox behavior of imidazolo-fused radicals **5–7** was previously shown to differ from the typical redox behavior of nonfused 1,2,4-benzotriazinyls<sup>[6]</sup> in that their reductions were quasi-reversible. However, we have now attributed this quasireversible behavior to the wet electrolyte. With dry electrolyte both the oxidation (0/+1) and reduction (–1/0) processes of radicals **5–7** were fully reversible (Figures S1–S3 in the Supporting Information). The half-way reduction potentials are  $E_{1/2}^{-0/+1} = 0.09, 0.07, 0.05$  V and half-way reduction potentials are  $E_{1/2}^{-1/0} = -1.03, -0.96, -0.98$  V for **5**, **6**, and **7**, respectively, versus the ferrocene/ferrocinium (Fc/Fc<sup>+</sup>) couple as +0.352 V (1 mm in CH<sub>2</sub>Cl<sub>2</sub> with *n*Bu<sub>4</sub>NBF<sub>4</sub> as the supporting electrolyte).

Solid-state EPR spectra of radicals 5-7 (Figures S4-S6 in the Supporting Information) are essentially isotropic singlets (g<sub>solid</sub>=2.0030, 2.0028, 2.0028 for **5**, **6**, and **7**, respectively) that are consistent with organic radicals with little spin-orbit coupling. The solution EPR spectra (Figures S7-S9 in the Supporting Information) exhibit typical 1,2,4-benzotriazinyls seven-line multiplets, which are consistent with the unpaired electron coupling with the three similar but slightly nonequivalent <sup>14</sup>N nuclei.<sup>[6,9]</sup> Previous EPR and ENDOR studies by Neugebauer on <sup>15</sup>N-labeled benzotriazinyls showed that  $a_{N(1)} \gg a_{N(4)} > a_{N(2)}$ .<sup>[9a]</sup> Simulation of the first-derivative mode gave  $g_{soln} = 2.0025$ , 2.0031, 2.0028 for 5, 6, and 7, respectively. The hyperfine coupling constants (hfcc) were calculated to be  $a_{N(1)} = 7.04$ ,  $a_{N(2)} =$ 4.66, and  $a_{\rm N(4)} =$  4.89 G for radical **5**,  $a_{\rm N(1)} =$  7.06,  $a_{\rm N(2)} =$  4.73, and  $a_{N(4)} = 4.77$  G for radical 6, and  $a_{N(1)} = 7.04$ ,  $a_{N(2)} = 4.92$ , and  $a_{N(4)} = 4.94$  G for radical 7. Spin densities estimated based on hfcc by using McConnell's equation<sup>[10,11]</sup> are  $\rho_{N1}$ =0.282,  $\rho_{N2}$ = 0.220, and  $\rho_{\rm N4}$  = 0.231 for radical **5**,  $\rho_{\rm N1}$  = 0.282,  $\rho_{\rm N2}$  = 0.223, and  $\rho_{\rm N4}\!=\!0.225$  for radical **6**, and



Scheme 1. Synthetic route to 1,3,7-triphenylimidazolobenzotriazinyls 2. Radicals 5 (2:  $R^1 = R^2 = Ph$ ), 6 (2:  $R^1 = Ph$ ,

 $R^2 = 4$ -BrC<sub>6</sub>H<sub>4</sub>), and **7** (**2**:  $R^1 = Ph$ ,  $R^2 = 4$ -MeOC<sub>6</sub>H<sub>4</sub>) were prepared in overall yields of 77, 55, and 61%, respectively.

 $ho_{\rm N1} = 0.282, 
ho_{\rm N2} = 0.232, 
m and 
ho_{\rm N4} = 0.233$  for radical **7**.

## X-Ray diffraction studies

The crystallographic rather than the IUPAC numbering system is used in discussion only for this section. Suitable single crystals

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Reagents and conditions: i) iPr<sub>3</sub>EtN, PhMe, 100 °C, 1-4 d, 79-95%; ii) AcOH, 120 °C, 1 h, 70-81%.

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of radicals **5–7** for X-ray diffraction studies were obtained by slow diffusion of *n*-pentane into a solution of each radical in benzene. The radicals crystallized in the monoclinic space group  $P\bar{1}$  with one molecule in the asymmetric unit. The intra-molecular geometrical parameters (Table 1) of the triazinyl ring

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are similar to previously studied nonfused benzotriazinyl radicals.<sup>[6]</sup> The 1,2,4-amidrazonyl moiety is essentially planar as defined by the angle between the plane of N1, N2, C1, N3 atoms and the plane of the fused benzimidazole (3.45, 5.08,  $3.45^{\circ}$  for 5, 6, and 7, respectively). The C-N bond lengths [C1-N2, 1.340(2)-1.345(9) Å; C1-N3, 1.314(9)-1.342(4) Å], which are intermediate between typical single and double C-N bonds, and the C1-N2-N1 [114.7(5)-115.9(1)°) and C1-N3-C2 (115.5(6)-116.7(1)°] angles, which are typical for sp<sup>2</sup>-hybridized nitrogen atoms, support strong delocalization of the unpaired electron over the amidrazonyl nitrogen atoms. The imidazole ring in radicals 5-7 is planar with typical interatomic lengths and angles: N4–C6 [1.385(2)–1.399(4) Å], N5–C5 [1.310(4)– 1.323(2) Å], C4–C6 [1.401(4)–1.416(2) Å]; C5-N4-C6 [106.1(2)– 106.7(5)°], C5-N5-C4 [105.3(2)–105.9(1)°]. The C5–Ph substituent is out of plane [20.0(1)-27.2(4)°] as a result of the steric interaction between ortho hydrogen atoms H22 and H32. A large torsion angle is observed for the imidazolo N4-Ph [58.1(3)-60.8(9)°] as a result of steric interactions at both sides of the phenyl, thus the para-phenyl substituents have little effect on the electron density around the molecule; only subtle differences are observed with the redox potentials and the hfcc of radicals 5-7. The torsion angle of the triazinyl N1–Ph was variable [36.3(8)–45.1(3)°], in line with previous observations on nonfused benzotriazinyls in which this phenyl substituent participated in  $\pi$ - $\pi$  face-to-face and edge-to-face interactions.<sup>[6c]</sup>

The C1–Ph substituent consistently adopts a coplanar orientation with the triazinyl ring [9.4(2), 7.8(9), and 0.2(4)° for **5**, **6**, and **7**, respectively] owing to the absence of any steric interactions and possibly two weak intramolecular contacts between the *ortho*-H of the Ph and the N2 and N3 atoms of the amidrazonyl moiety.

Similar intramolecular geometries, unit cell dimensions (Table T1 in the Supporting Information), and space group ( $P\bar{1}$ ) for radicals **5–7** give rise to solid-state packing arrangements that are comparable for the three radicals. The main feature of the crystal packing is the formation of 1D  $\pi$ -slipped stacked columns. To facilitate our analysis the discussion below is divided into 1) the intra-stack interactions along the  $\pi$ -stacking direction and 2) the in-plane interactions perpendicular to the stacking direction.

#### Intra-stack interactions

The  $\pi$ -extended acene core of radicals 5–7 favors  $\pi$  stacking and formation of 1D columns along the *a* axis. The radicals within the columns are related with respect to each other through a center of inversion (-x, -y, -z) that places the N-Ph substituents on opposite sides to avoid the build-up of steric congestion (Figure 2). The degree of slippage and mean interplanar distance between the radicals alternates (Table 2) and gives rise to two distinct centrosymmetric pairs, radicals I-II and II-III (Figure 2). The radicals of pair I-II interact mainly through the fused imidazolo rings. The center of inversion running through the middle of these rings gives rise to a pair of symmetrical weak C-H-N contacts between the imidazolo N5 and an ortho-hydrogen of the imidazolo N4–Ph  $[d_{C28 \dots N5} =$ 3.315(3)–3.376(2) Å, ≩ C–H…N = 140.5(2)–156.24(9)°]. The driving force for the formation of radical pair II-III is the positive overlap between the benzotriazinyl rings. This is further supported by a pair of crystallographically equivalent C-H-N contacts between the triazinyl N3 and an ortho-hydrogen of the imidazolo N4–Ph [d<sub>C32···N3</sub>=3.472(2)–3.492(4) Å, ≩ C32–H···N3= 170.6(9)–175.9(4)°].

Table 2. Slippage angles and interplanar distances of pairs I-II and II-III           for radicals 5-7.								
Radical	Pair	Longitudinal $(\phi_1)$ [ $^{\circ}$ ] <sup>[a]</sup>	Latitudinal ( $\phi_2$ ) [°] <sup>[a]</sup>	Interplanar distance ( <i>d</i> ) [Å]				
5	_	47.3	16.6	3.697				
	_	30.0	10.7	3.685				
6	-	52.6	5.6	3.692				
	-	34.5	16.2	3.578				
7	-	49.1	19.7	4.124				
	-	34.2	12.0	3.528				
[a] See Figures S10 and S11 in the Supporting Information for parameters used to define the degree of longitudinal and latitudinal slippage.								

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**Figure 2.** Packing diagrams of radicals a) **5**, b) **6**, and c) **7** along the *a* axis showing the shortest intermolecular contacts. Thermal ellipsoids are drawn at 50% probability (hydrogen atoms are omitted for clarity). a) Pair I–II:  $d_{C1-C22} = 3.378(2)$  Å  $(-x, 1-y, 1-z), d_{C2-C22} = 3.304(2)$  Å  $(-x, 1-y, 1-z), d_{C28-N5} = 3.576(2)$  Å,  $\Leftrightarrow$  C28–H···N5 = 156.24(9)° (-x, 1-y, 1-z); pair II–III:  $d_{C1-C26} = 3.318(2)$  Å  $(1-x, 1-y, 1-z), d_{C32-N3} = 3.472(2)$  Å,  $\diamondsuit$  C32–H···N3 = 170.62(9)° (1-x, 1-y, 1-z). b) Pair I–II:  $d_{C2-C23} = 3.375(9)$  Å  $(1-x, -y, 1-z), d_{C28-N5} = 3.529(8)$  Å,  $\diamondsuit$  C28–H···N5 = 140.5(4)° (1-x, -y, 1-z); pair II–III:  $d_{C1-C26} = 3.381(9)$  Å  $(-x, -y, 1-z), d_{C32-N3} = 3.483(9)$  Å,  $\diamondsuit$  C32–H···N3 = 175.9(4)° (-x, -y, 1-z). c) Pair I–II:  $d_{C8-C22} = 3.392(3)$  Å  $(1-x, -y, 1-z), d_{C28-N5} = 3.315(3)$  Å,  $\diamondsuit$  C28–H···N5 = 140.5(2)° (1-x, -y, 1-z); pair II–III:  $d_{C1-C26} = 3.382(4)$  Å  $(-x, -y, 1-z), d_{C32-N3} = 3.492(4)$  Å,  $\diamondsuit$  C32–H···N3 = 175.3(4)° (-x, -y, 1-z).

The interplanar distance between radicals I–II is significantly longer for 8-(4-bromophenyl) radical **7** ( $d_{I-II}$ =4.124 Å) compared with that of 8-phenyl- and 8-(4-methoxyphenyl)-substituted radicals **5** and **6** ( $d_{I-II}$ =3.697 and 3.692 Å, respectively), which indicates a more pronounced separation between radicals I and II in radical **7** and a drop in dimensionality from a 1D chain to remote dimers. However, the interplanar distance of pair II–III for radical **7** is shorter ( $d_{I-III}$ =3.528 Å vs. 3.685 and 3.578 Å for radicals **5** and **6**, respectively), which denotes a stronger interaction between the radicals. It is anticipated that exchange interactions in pair II–III will be stronger as the radicals overlap mainly through the spin-bearing benzotriazinyls. Exchange interactions in pair I–II are expected to be weaker because the interplanar distances are longer (3.692– 4.124 Å) and longitudinal angles larger (47.3– $52.6^{\circ}$ ).

### Inter-stack interactions

The in-plane inter-stack interactions in imidazolo-fused benzotriazinyls 5-7 are dominated by weak hydrogen bonds. In all three radicals, the imidazolo N5 participates in C-H-N interactions with the para-hydrogen of N-Ph  $[d_{C12\dots N5}=3.410(4)-$ 3.416(1) Å, ≩ C12–H…N5=157.1(1)–166.0(2)°], which connect neighboring molecules into a head-to-tail arrangement to form chains that run parallel to the b axis (Figure S12 in the Supporting Information). Hydrogen-bond acceptors at the para position of the imidazolo N4-Ph in radicals 6 and 7 enable these inter-stack interactions. The MeO group in radical 7 acts as a hydrogen-bond acceptor from the meta hydrogen of C5–Ph  $[d_{C25-O1} = 3.427(4) \text{ Å}, \gtrless C25-H-O1 = 148.3(2)^{\circ}]$  and helps to stabilize the formation of the chain along the b axis (Figure S12b in the Supporting Information). In radical 6, a pair of crystallographically equivalent weak C-H-Br interactions connect antiparallel chains to form 2D sheets in the bc plane (Figure S12c in the Supporting Information). In all three radicals a tight packing with no voids is completed with edge-toface  $\pi$  contacts between the N1- and N4-phenyls and the C1/C5-Ph substituents.

#### **Magnetic properties**

Magnetic exchange coupling interactions were probed by using variable-temperature magnetic-susceptibility measurements by using a SQUID magnetometer in the temperature range of 5 to 300 K and in an applied field of 0.4 T. Data were collected in both warming and cooling modes with no significant differences in sample susceptibility. The data were corrected for both sample diamagnetism (Pascal's constants) and the diamagnetism of the sample holder. Plots of  $\chi$  versus *T* for radicals **5** and **6** and  $\chi T$  versus *T* for radical **7** are presented in Figure 3.

The *g* values of radicals **5–7** determined in the solid state  $(g_{solid} = 2.0030, 2.0028, and 2.0028 for$ **5**,**6**, and**7**, respectively) are very close to that of a free electron, which denotes a small spin-orbit interaction. Isotropic magnetic exchange interactions are, therefore, responsible for the observed magnetic properties of imidazolo-fused benzotriazinyl radicals**5–7** $. The extended <math>\pi$ -based nature of these radicals coupled with their propensity to form 1D  $\pi$ -slipped columns suggests that radicals **5–7** will exhibit strong unidimensional magnetic interactions propagating parallel to the stacking direction, along which the orbital overlap between the singly-occupied molecular orbitals (SOMOs) is maximized.

Upon cooling from 300 K, the molar susceptibility ( $\chi$ ) increases gradually and reaches a broad maximum at  $T_{max} = (50 \pm 2)$  and  $(50 \pm 4)$  K for radicals **5** and **6**, respectively, which indicates strong antiferromagnetic interactions (Figure 3a and

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**Figure 3.** Temperature dependence of  $\chi$  for radicals a) **5** and b) **6**; c) temperature dependence of  $\chi$ T and  $1/\chi$  (inset) for radical **7**. a) The solid line represents the best fit to the 1D alternating AF linear chain model for  $S = \frac{1}{2}$  spin;  $J = -31.3 \text{ cm}^{-1}$ ,  $\alpha = 0.15$ ,  $\rho = 0.94$ ,  $g_{\text{solid}} = 2.0030$ ,  $R = 5.82 \times 10^{-4}$  (correlation factor  $R = \Sigma[\chi_{\text{obsd}} - \chi_{\text{calcd}}]^2 / \Sigma[\chi_{\text{obsd}}]^2$ ). b) The solid line represents the best fit to the 1D alternating AF linear chain model for  $S = \frac{1}{2}$  spin;  $J = -35.4 \text{ cm}^{-1}$ ,  $\alpha = 0.38$ ,  $\rho = 0.91$ ,  $g_{\text{solid}} = 2.0028$ ,  $R = 7.58 \times 10^{-4}$  (correlation factor  $R = \Sigma[\chi_{\text{obsd}} - \chi_{\text{calcd}}]^2 / \Sigma[\chi_{\text{obsd}}]^2$ ). c) The solid line represents the best fit to the Bleaney-Bowers model for a pair of interacting  $S = \frac{1}{2}$  spins with  $2J = 23.6 \text{ cm}^{-1}$ ,  $2zJ' = -2.8 \text{ cm}^{-1}$ ,  $g_{\text{solid}} = 2.0028$ ,  $R = 6.55 \times 10^{-4}$  (correlation factor  $R = \Sigma[(\chi_{\text{D}_{obs}} - (\chi_{\text{T}_{calcd}}]^2 / \Sigma[(\chi_{\text{T}_{Obs}}]^2)$ ). Inset: Curie–Weiss behavior in the 5–300 K region,  $C = 0.338 \text{ emu Kmol}^{-1}$  and  $\theta = 1.83 \text{ K}$ .

b). Below the maximum at 50 K,  $\chi$  falls off gradually down to 15 K for radical **5** and 20 K for radical **6** before it increases again at lower temperatures. This increase in  $\chi$  at low temperatures is attributed to uncoupled radicals at defect sites in the lattice. The alternating interplanar distances along the stacking direction (Table 2) indicate that the appropriate model to fit the magnetic data is Hatfield's expression for the magnetic susceptibility of isotropic Heisenberg alternating antiferromagnetic (AF) chains of  $S = \frac{1}{2}$  spins.<sup>[12]</sup> The corresponding spin Hamiltonian is given by

$$H = -2J \sum_{i=1}^{n/2} \left[ S_{2i} S_{2i-1} + \alpha S_{2i} S_{2i+1} \right]$$

in which  $2J \ (=J_1)$  and  $2\alpha J \ (=J_2)$  are the exchange integrals along the stacking direction and  $\alpha \ (=J_2/J_1)$  is a parameter that indicates the degree of alternation. At the extremes, when  $\alpha =$ 0 the model corresponds to an isolated dimer system and when  $\alpha = 1$  the model reduces to the linear-chain model.

The best fit to the magnetic susceptibility data was obtained by using a set of polynomial parameters for  $0 \le \alpha \le 0.4$ . A parameter  $\rho$  was included to account for the susceptibility arising from uncoupled radicals at the lattice defect sites. The fit reproduces well both the position and the maximum in  $\chi$  when J=-31.3 cm<sup>-1</sup>,  $\alpha=0.15$ ,  $\rho=0.94$ ,  $g_{solid}=2.0030$  for radical **5** and J=-35.4 cm<sup>-1</sup>,  $\alpha=0.38$ ,  $\rho=0.91$ ,  $g_{solid}=2.0028$  for radical **6** (Figure 3). By applying the ratio of  $\alpha=J_2/J_1$ , in which  $J_1=2J$ and  $J_2=2\alpha J$ , the estimated values along the chain direction are 2J=-62.6 cm<sup>-1</sup>,  $2\alpha J=-9.4$  cm<sup>-1</sup> for radical **5** and 2J=-70.8 cm<sup>-1</sup>,  $2\alpha J=-26.9$  cm<sup>-1</sup> for radical **6**.

A different magnetic behavior was observed for radical 7; it follows Curie-Weiss behavior in the temperature range of 5 to 300 K with C = 0.338 emu Kmol<sup>-1</sup> close to the value expected for  $S = \frac{1}{2}$  spin (Figure 3c, inset). The positive Weiss constant ( $\theta$  = 1.83 K) indicates the presence of local ferromagnetic interactions between the radicals. When the temperature is lowered from 300 K,  $\chi T$  increases gradually and reaches a maximum at  $T_{max}$  = (30 ± 4) K (Figure 3c). Below this temperature,  $\chi T$  falls off sharply, which indicates the presence of antiferromagnetic interactions at low temperatures. The interplanar distance between radicals I-II is significantly longer for radical 7  $(d_{I-II} = 4.124 \text{ Å})$  and leads to more discrete pairs of radicals II–III  $(d_{\parallel - \parallel \parallel} = 3.528 \text{ Å})$  and, therefore, the appropriate model to fit the magnetic data is the Bleaney-Bowers expression for the magnetic susceptibility of interacting pairs of  $S = \frac{1}{2}$  spins (based on the Hamiltonian  $H = -2J_{AB} \sum \hat{S}_{A} \hat{S}_{B}$ .<sup>[13]</sup> The Bleaney–Bowers model was extended to cover the low-temperature down curve of  $\chi T$ ; inclusion of a mean field term (2zJ') to account for the antiferromagnetic inter-dimer interactions provided a much improved fit with  $2J = 23.6 \text{ cm}^{-1}$ ,  $2zJ' = -2.8 \text{ cm}^{-1}$ ,  $g_{\rm solid} = 2.0028.$ 

#### Computational modeling

Quantum chemistry methods can provide estimates for the magnetic exchange coupling interactions within radical pairs.

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Although the macroscopic magnetic behavior is the cumulative outcome of all existing magnetic interactions, for radicals with low dimensional magnetic topology, for example, imidazolo-fused benzotriazinyls **5–7**, the computed exchange interactions correlate qualitatively with experimentally determined exchange couplings.<sup>[14]</sup>

The calculated spin–spin exchange interactions of radical pairs I–II ( $J_{I-II}$ ) and II–III ( $J_{I-III}$ ) were determined by using the unprojected equation  $2J_{DFT} = 2(E_{BS} - E_T)/2$ .<sup>[15]</sup> The energies of the triplet ( $E_T$ ) and broken symmetry singlet ( $E_{BS}$ ) states were determined by single-point calculations on crystallographically determined geometries of radical pairs I–II and II–III (Table T2 in the Supporting Information). Although advanced and computationally expensive quantum chemical methods, such as CASSCF and CASPT2, provide good results, DFT functionals, such as B3LYP, perform well in the computation of exchange interactions.<sup>[14]</sup> The latter method was employed for the calculations of the  $J_{I-III}$  and  $J_{II-III}$  values by using the 6-311 + + G(d,p) basis set (Table 3).

<b>Table 3.</b> Calculated exchange interactions of pair I–II ( $J_{I-II}$ ) and pair II–III ( $J_{II-III}$ ) for their X-ray determined geometries by using the UB3LYP level of theory.							
Radical	$J_{\rm I-II}$ [cm <sup>-1</sup> ]	$J_{\text{II-III}}$ [cm <sup>-1</sup> ]	$J_2 [{\rm cm}^{-1}]$	$J_1  [\rm cm^{-1}]$			
5	-4.4 <sup>[a]</sup>	-18.1 <sup>[a]</sup>	-9.4	-62.6			
6	-38.0 <sup>[a]</sup>	18.7 <sup>[a]</sup>	-26.9	-70.8			
	-45.8 <sup>[b]</sup>	-56.0 <sup>[b]</sup>	-	-			
7	-3.8 <sup>[a]</sup>	26.0 <sup>[a]</sup>	-2.8 <sup>[c]</sup>	23.6 <sup>[c]</sup>			
[a] 6-311 + +G(d,p). [b] 6-311 + +G(2d,p). [c] For radical <b>7</b> : $J_2 = 2zJ'$ and $J_1 = 2J$ .							

The computed exchange interactions for radical pairs II-III are stronger than those of pairs I-II. The sign of these interactions  $(J_{||-|||})$  depend mainly on the interplanar distance between the radicals within the dimer because changes in the slippage angles  $(\Pi \to \Pi \phi_1)$  and  $\Pi \to \Pi \phi_2$ ) are only subtle (Table 2). On going from an interplanar distance of  $d_{II-III} = 3.685$  to 3.528 Å, the exchange interactions flip from antiferromagnetic  $(J_{\parallel-\parallel})$  $-18.1 \text{ cm}^{-1}$  in **5**) to ferromagnetic ( $J_{\parallel-\parallel\parallel} = 26.0 \text{ cm}^{-1}$  in **7**). Conversely, the exchange interactions for radical pair I-II are weaker and merely antiferromagnetic in nature, however, in this case their magnitudes depend predominantly on the slippage angles. Surprisingly, a significantly larger interplanar distance for radical **7**  $(d_{I-II} = 4.124 \text{ Å}, J_{I-II} = -3.8 \text{ cm}^{-1})$  does not alter the exchange interaction ( $d_{I-II} = 3.697$  Å,  $J_{I-II} = -4.4$  cm<sup>-1</sup> for radical 5). However, although the longitudinal angles for radicals **5–7** are comparable ( $^{I-II}\phi_1 = 47.3 - 52.6^\circ$ ) the latitudinal angle for radical **6** is considerably smaller ( $^{I-II}\phi_2 = 5.6^\circ$ ) compared with that of radicals **5** and **7** ( $^{I-II}\phi_2 = 16.6$  and 19.7°, respectively), which explains the bigger exchange interaction observed for pair I–II of radical 6 ( $J_{I-II} = -38.0 \text{ cm}^{-1}$ ). Note that the 6-311++G(d,p) basis set predicted a ferromagnetic interaction  $(J_{\parallel-\parallel\parallel} = 18.7 \text{ cm}^{-1})$  for pair II–III of radical **6** whereas experimentally an antiferromagnetic interaction ( $J_1 = -70.8 \text{ cm}^{-1}$ ) was observed (Figure 3b). Nevertheless, the addition of 2d functions to the basis set, that is, 6-311 + G(2d,p), to take in account the heavy Br atom, flips  $J_{II-III}$  from 18.7 to  $-56.0 \text{ cm}^{-1}$ .

## Discussion

The magnetic behavior of radicals **5–7** can be rationalized by using the molecular orbital (MO) model.<sup>[16]</sup> In the MO model, the exchange coupling interaction  $(J_{AB} = 2K_{ij} + 4c_{ij}S_{ij}^{2})$  is proportional to the size of the overlap between SOMO orbitals  $(S_{ij})$ , which depends on the distance and orientation of the interacting radicals. The longitudinal and latitudinal slippage angles and the interplanar distances between the radicals determine the nature of the magnetic exchange along the  $\pi$ -stacking direction. In related  $\pi$  systems, Oakley et al. demonstrated that there is a fine balance between ferro- and antiferromagnetic interactions by adjusting the degree of slippage through chemical pressure (introduction of small perturbations by synthetic means) or with application of physical pressure.<sup>[17]</sup>

Exchange coupling within radical pair II-III is expected to be stronger than that of pair I-II because the radicals overlap predominantly over the spin-bearing triazinyl moieties, which maximizes the SOMO-SOMO interaction. Conversely, the molecular arrangement in radical pair I-II places the 7-Ph substituent, which hosts little spin density, on top of the adjacent triazinyl ring. Therefore, in the absence of other dominating exchange-coupling interactions,  $J_1$  and the weaker  $J_2$  could be assigned to the interactions within radical pairs II-III and I-II, respectively. Calculations confirm the qualitative assignment of  $J_1$ to pair II–III and  $J_2$  to pair I–II because  $|J_{I-III}| > |J_{I-II}|$  and  $|J_1| > |$  $J_2$ . This is in line with the observed geometrical parameters of pairs I–II and II–III; both the longitudinal (average  $^{\parallel-\parallel\parallel}\phi_1 = 32.9^{\circ}$ ) and latitudinal (average  $^{\rm II-III}\phi_2\!=\!13.0^\circ)$  angles of pair II–III are smaller than those of radical pair I–II (average  $^{I-II}\phi_1 = 49.6^\circ$ ,  $^{I-II}\phi_2 = 14.0^{\circ}$ ). Furthermore, the interplanar distances of pair II–III are shorter than those of pair I–II (average  $d_{II-III} = 3.597$  Å vs. average  $d_{I-II} = 3.838$  Å).

The proximity of  $d_{I-II}$  to  $d_{II-III}$  for radicals **5** and **6** (Table 2) leads to a 1D magnetic topology, but the subtle inequality between them results in an alternation in the exchange-coupling interactions along the chain. Conversely, for radical **7** the significantly larger interplanar distance between the radicals of pair I–II ( $d_{I-II} \gg d_{II-III}$ ) transforms the magnetic topology from 1D to 0D with discrete dimers that interact with each other through a weak antiferromagnetic exchange coupling. A careful examination of the crystal packing of radical **7** did not reveal any apparent reason for the observed change in  $d_{I-II}$ .

The magnitude of the exchange interactions of imidazolofused benzotriazinyls **5** and **6** ( $J_1 = -9.4$  to -26.9 cm<sup>-1</sup> and  $J_2 =$ -62.6 to -70.8 cm<sup>-1</sup>) is considerably bigger than the exchange interactions of nonfused benzotriazinyls, such as the 1 D regular chains of the 1,3-diphenyl-7-phenyl- and 7-(4-fluorophenyl)-1,4-dihydro-1,2,4-benzotriazin-4-yls with 2J = -25.8and -23.6 cm<sup>-1.[6c]</sup> The  $\pi$ -extended acene core of imidazolofused radicals leads to the enhanced orbital overlap and, therefore, to stronger exchange interactions. However, although the selected substituents (e.g., Br and MeO in radicals **6** and **7**) give side-on interactions between 1D chains, they fail to in-

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crease the dimensionality of the exchange interactions. Structural tailoring of radicals through strategic substitution to exploit favorable supramolecular interactions might lead to materials with bulk magnetic properties.

## Conclusion

The crystal structures and magnetic properties of three organic 1,3,7,8-tetraphenyl-4,8-dihydro-1H-imidazolo[4,5g]radicals, [1,2,4]benzotriazin-4-yl (5), 8-(4-bromophenyl)-1,3,7-triphenyl-4,8-dihydro-1*H*-imidazolo[4,5*q*][1,2,4]benzotriazin-4-yl (6), and 8-(4-methoxyphenyl)-1,3,7-triphenyl-4,8-dihydro-1H-imidazolo-[4,5g][1,2,4]benzotriazin-4-yl (7) have been investigated. The radicals  $\pi$  stack in 1D columns along the *a* axis and are comprised of slipped radical pairs (I-II and II-III) with alternating short and long interplanar distances. Magnetic susceptibility measurements reveal the presence of antiferromagnetic interactions within the 1D  $\pi$  stacks of radicals  ${\bf 5}$  and  ${\bf 6}$  and ferromagnetic interactions within the  $\pi$  stacks of radical 7. Spindensity distributions determined by using EPR spectroscopy, DFT calculations, and a magnetostructural model have allowed us to correlate the estimated exchange-coupling interactions to the two different pairs within the distorted  $\pi$  stack;  $J_1 =$ -62.6, -70.8, and  $23.6 \text{ cm}^{-1}$  and  $J_2 = -9.4$ , -26.9, and  $-2.8 \text{ cm}^{-1}$  (for 5, 6, and 7, respectively) correspond to pairs II-III and I-II, respectively. The slippage of radicals down the stacking direction coupled with the changes in interplanar distance between them lead to alterations in the SOMO orbital overlap that dictate the nature of exchange-coupling interactions. Although the  $\pi$ -extended acene core of imidazolo-fused benzotriazinyls 5-7 promotes strong exchange-coupling interactions, the low dimensionality of the magnetic topology can be explained by the presence of phenyl groups around the periphery that isolate the spin-bearing units and prohibit interactions over the other two dimensions. If long-range ordering is to be realized then fine tuning of the substituents' steric effects is required to make the 1,2,4-benzotriazinyl core more available to the surrounding environment. Further modifications to the benzotriazinyl framework are underway.

## **Experimental Section**

## Synthetic procedure

The synthesis of imidazolo-fused radicals **5–7** was published previously.<sup>[7b]</sup>

#### Spectral analyses

#### 1,3,7,8-Tetraphenyl-4,8-dihydro-1H-imidazo[4,5g]-

**[1,2,4]benzotriazin-4-yl (5)**:<sup>[7b]</sup> Black needles recrystallized from PhH (78 mg, 81%). M.p. (DSC): 308.6 (decomp. onset), 312.4 °C (peak max);  $R_{\rm f}$  (Et<sub>2</sub>O): 0.64; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\rm max}$  (log  $\varepsilon$ ) = 239 (3.30), 272 inf. (3.54), 291 (3.61), 330 inf. (3.02), 403 inf. (3.26), 419 (3.35), 465 inf. (2.63), 540 (2.50), 624 nm inf. (2.16); IR (ATR, Ge):  $\tilde{v}_{\rm max}$  = 1595 (m), 1503 (m), 1489 (s), 1470 (s), 1452 (m), 1435 (s), 1402 (s), 1389 (s), 1350 (s), 1287 (m), 1180 (m), 1026 (m), 895 (m), 854 (s), 831 (m), 777 (s), 770 (s), 762 cm<sup>-1</sup> (s); MS (EI): m/z (%): 476 [M]<sup>+</sup>

(100); elemental analysis calcd (%) for  $C_{32}H_{22}N_5\colon$  C 80.65, H 4.65, N 14.70; found: C 80.52, H 4.56, N 14.82.

**8-(4-Bromophenyl)-1,3,7-triphenyl-4,8-dihydro-1***H***-imidazo[4,5***g***]-[1,2,4]benzotriazin-4-yl (6):<sup>[7b]</sup> Black needles recrystallized from PhMe (79 mg, 70%). M.p. (DSC): 318.6 (onset), 323.6 (peak max), 325.8 (decomp. onset), 328.5 °C (peak max); R\_{\rm f} (Al<sub>2</sub>O<sub>3</sub> neutral/CH<sub>2</sub>Cl<sub>2</sub>): 0.45; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): \lambda\_{\rm max} (log \varepsilon) = 235 (3.49), 277 inf. (3.73), 292 (3.76), 331 (3.10), 396 inf. (3.28), 417 (3.44), 538 (2.61), 623 nm inf. (2.29); IR (ATR, Ge): \tilde{\nu}\_{\rm max} = 1487 (s), 1470 (s), 1452 (m), 1437 (s), 1402 (s), 1389 (s), 1348 (m), 1288 (m), 1196 (m), 1180 (m), 1169 (m), 1070 (m), 1015 (m), 972 (m), 897 (m), 855 (m), 845 (m), 829 (m), 775 (s), 766 (m), 758 cm<sup>-1</sup> (m); MS (MALDI-TOF):** *m/z* **(%): 558 [***M***+H+3]<sup>+</sup> (23), 557 [***M***+H+2]<sup>+</sup> (64), 556 [M+H+1]<sup>+</sup> (23), 555 [***M***+H]<sup>+</sup> (100); elemental analysis calcd (%) for C<sub>32</sub>H<sub>21</sub>BrN<sub>5</sub>: C 69.20, H 3.81, N 12.61; found: C 69.20, H 3.97, N 12.52.** 

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**[4,5g]**[**1,2,4]benzotriazin-4-yl** (**7**):<sup>[7b]</sup> Black needles recrystallized from PhH (73 mg, 71%). M.p. (DSC): 305.0 (onset), 307.6 °C (peak max);  $R_{\rm f}$  (Al<sub>2</sub>O<sub>3</sub> neutral/CH<sub>2</sub>Cl<sub>2</sub>): 0.25; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\rm max}$  (log  $\varepsilon$  = 233 (3.49), 260 inf. (3.59), 285 (3.76), 332 inf. (3.02), 397 inf. (3.27), 421 (3.45), 532 (2.57), 633 nm inf. (2.19); IR (ATR, Ge):  $\tilde{v}_{\rm max}$  1514 (s), 1489 (m), 1470 (s), 1452 (m), 1439 (s), 1402 (m), 1389 (s), 1350 (m), 1304 (m), 1287 (m), 1254 (s), 1179 (m), 1169 (m), 1040 (m), 899 (m), 858 (m), 839 (s), 775 (s), 768 cm<sup>-1</sup> (s); MS (MALDI-TOF): *m/z* (%): 509 [*M*+H+2]<sup>+</sup> (2), 508 [*M*+H+1]<sup>+</sup> (24), 507 [*M*+H]<sup>+</sup> (100); elemental analysis calcd (%) for C<sub>33</sub>H<sub>24</sub>N<sub>5</sub>O: C 78.24, H 4.78, N 13.82; found: C 78.10, H 4.84, N 13.73.

#### Instrumental analyses

Melting points were determined by using a TA Instruments DSC Q1000 with samples sealed in aluminum pans under an argon atmosphere, with heating rates of 5 K min<sup>-1</sup>. UV/Vis spectra were obtained by using a Perkin-Elmer Lambda-25 UV/Vis spectrophotometer and inflections are identified by the abbreviation inf. IR spectra were recorded by using a Shimidazu FTIR-NIR Prestige-21 spectrometer equipped with a Pike Miracle Ge ATR accessory; strong and medium peaks are indicated by s and m, respectively. Low-resolution (EI) mass spectra were recorded by using a Shimadzu Q2010 GCMS instrument with direct inlet probe. MALDI-TOF MS were conducted by using a Bruker BIFLEX III time-of-flight (TOF) mass spectrometer. Cyclic voltammetry (CV) measurements were performed by using a Princeton Applied Research Potentiostat/Galvanostat 263A apparatus. The concentration of the benzotriazinyl radical used was 1 mm in CH<sub>2</sub>Cl<sub>2</sub>. A solution of tetrabutylammonium tetrafluoroborate (*n*Bu<sub>4</sub>NBF<sub>4</sub>; 0.1 м) in CH<sub>2</sub>Cl<sub>2</sub> was used as the electrolyte. The electrolyte was dried for 4 d in the vacuum oven at 100°C prior to the use. The reference electrode was Ag/AgCl and the scan rate was 50 mV s<sup>-1</sup>. Ferrocene was used as an internal reference; the  $E_{1/2}(ox)$  of ferrocene in this system was 0.352 V.<sup>[18]</sup> EPR spectra were recorded by using a Bruker EMXplus X-band EPR spectrometer at RT on solid-state samples of the imidazolo-fused 1,2,4-benzotriazinyls and on dilute solutions in CH<sub>2</sub>Cl<sub>2</sub>. For the dilute solution spectra, the microwave power was in the region of 5-70 mW with modulation frequencies of 50 or 100 kHz and modulation amplitudes of 0.5–1.0 G<sub>pp</sub>. Simulations of the solution spectra were made by using Winsim.<sup>[19]</sup> The near-isotropic nature of most benzotriazinyl radical samples meant that the majority of solid-state samples could be initially modeled as an isotropic spectrum by using Winsim, but those revealing slight line asymmetry were simulated by using PIP run through the GUI "PIP for Windows".  $^{\ensuremath{\text{[20]}}}$  Magnetic properties were studied by using a Quantum Design SQUID MPMS<sub>2</sub> field-shielded magnetometer. The DC (direct

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current) magnetic moments were measured for 42.2, 36.4, and 50.3 mg samples of radicals 5-7, respectively, which were placed in gelatin capsules held by a polyethylene straw. The magnetic susceptibilities were measured in the temperature range of 5-300 K in an applied field of 0.4 T. Data were collected in both warming and cooling modes with no significant differences in sample susceptibility. Data were corrected by using diamagnetic contributions of  $\chi_{dia}\!=\!-350,$  -370, and -700 (two radicals per dimer)imes $10^{-3}$  emumol<sup>-1</sup> for radicals 5–7, respectively. X-Ray data for radicals 5-7 were collected by using an Oxford Diffraction Supernova diffractometer equipped with a CCD area detector with  $Cu_{K\alpha}$  radiation ( $\lambda = 1.5418$  Å) for **5** and **6** and Mo<sub>Ka</sub> radiation ( $\lambda = 0.71073$  Å) for 7. A suitable crystal was attached to a glass fiber by using paratone-N oil, transferred to a goniostat, and cooled before data collection. Unit cell dimensions were determined and refined by using 3520 ( $3.34 \le \theta \le 72.47^{\circ}$ ) reflections for **5**, 3007 ( $5.65 \le \theta \le 68.22^{\circ}$ ) reflections for **6**, and 3054 ( $3.08 \le \theta \le 28.96^{\circ}$ ) reflections for **7**. Empirical absorption corrections (multiscan based on symmetry-related measurements) were applied by using CrysAlis RED software.<sup>[21]</sup> The structures were solved by direct method and refined on  $F^2$  by using full-matrix least squares using SHELXL97.[22] Software packages used: CrysAlis CCD<sup>[21]</sup> for data collection, CrysAlis RED<sup>[21]</sup> for cell refinement and data reduction, WINGX for geometric calculations,<sup>[23]</sup> and Mercury 3.1<sup>[24]</sup> for molecular graphics. The non-hydrogen atoms were treated anisotropically. The hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms.

Crystal refinement data for 5:  $C_{32}H_{22}N_5$ ;  $M_r = 476.55$ ; triclinic; space group  $P\bar{1}$ ; a = 7.8924(8), b = 11.3721(9), c = 13.2802(12) Å; a =96.019(7),  $\beta = 90.262(8)$ ,  $\gamma = 96.237(8)^{\circ}$ ;  $V = 1178.20(19) \text{ Å}^3$ ; Z = 2; T = 100(2) K;  $\rho_{calcd} =$  1.343 g cm<sup>-3</sup>; 2 $\theta_{max} =$  67. Refinement of 334 parameters on 4186 independent reflections out of 7408 measured reflections ( $R_{int} = 0.0284$ ) gave  $R_1 = 0.0452$  [ $l > 2\sigma(l)$ ],  $wR_2 = 0.1356$ (all data), and S = 1.044 with the largest difference peak and hole of 0.220 and  $-0.315 e^{-3}$ , respectively.

Crystal refinement data for 6:  $C_{32}H_{21}N_5Br$ ;  $M_r = 566.00$ ; triclinic; space group  $P\bar{1}$ ; a = 7.8374(12), b = 11.7232(16), c = 13.2724(10) Å;  $\alpha = 87.875(8), \beta = 88.185(9), \gamma = 87.875(11)^{\circ}; V = 1076.2(3) \text{ Å}^3; Z = 2;$ T = 100(2) K;  $\rho_{calcd} = 1.515$  g cm<sup>-3</sup>;  $2\theta_{max} = 67$ . Refinement of 343 parameters on 4250 independent reflections out of 8137 measured reflections ( $R_{int} = 0.0944$ ) gave  $R_1 = 0.0863$  [ $l > 2\sigma(l)$ ],  $wR_2 = 0.2801$ (all data), and S = 1.028 with the largest difference peak and hole of 2.146 and  $-1.120 e^{-3}$ , respectively.

Crystal refinement data for 7:  $C_{33}H_{24}N_5O$ ;  $M_r = 506.57$ ; triclinic; space group  $P\bar{1}$ ; a = 8.2696(10), b = 11.457(3), c = 13.8478(17) Å; a =83.013(15),  $\beta = 87.393(10)$ ,  $\gamma = 81.254(14)^{\circ}$ ; V = 1286.6(4) Å<sup>3</sup>; Z = 2; T = 100(2) K;  $\rho_{calcd} = 1.308$  g cm<sup>-3</sup>,  $2\theta_{max} = 25$ . Refinement of 353 parameters on 4525 independent reflections out of 8256 measured reflections ( $R_{int} = 0.0353$ ) gave  $R_1 = 0.0591$  [ $l > 2\sigma(l)$ ],  $wR_2 = 0.1720$ (all data), and S = 1.082 with the largest difference peak and hole of 0.275 and  $-0.243 e^{-3}$ , respectively.

CCDC-940089 (5), -972401 (6), and -972402 (7) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

### **Computational methods**

Single-point calculations were carried out on the X-ray crystallographically determined geometries of radical pair I-II and II-III of 5-7 at the UB3LYP/6-311++G(d,p) level of theory to calculate the energies of the triplet ( $E_{\rm T}$ ) and broken-symmetry singlet ( $E_{\rm BS}$ ) states. For radical **6**, additional calculations with the 6-311++G(2d,p) basis set were needed to take the Br atom into account. All the calculations were performed by using the Gaussian 03 suite of programs.<sup>[25]</sup>

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- [1] I. Ratera, J. Veciana, Chem. Soc. Rev. 2012, 41, 303-349.
- [2] a) D. A. Haynes, CrystEngComm 2011, 13, 4793-4805; b) O. A. Rakitin, Russ. Chem. Rev. 2011, 80, 647-659; c) R. G. Hicks, Org. Biomol. Chem. 2007, 5, 1321-1338; d) S. Nakatsuji, H. Anzai, J. Mater. Chem. 1997, 7, 2161-2174; e) J. M. Rawson, A. Alberola, A. Whalley, J. Mater. Chem. 2006, 16, 2560-2575; f) H. Iwamura, Polyhedron 2013, 66, 3-14.
- [3] a) Magnetic Properties of Organic Materials (Ed.: P. M. Lahti), Marcel-Dekker Inc., New York, 1999; b) Molecular Magnetism: New Magnetic Materials (Eds.: K. Itoh, M. Kinoshita), Kodansha and Gordon & Breach, Tokyo and Amsterdam, 2000.
- [4] a) J. A. Crayston, J. N. Devine, J. C. Walton, Tetrahedron 2000, 56, 7829-7857; b) S. J. Blundell, F. L. Pratt, J. Phys. Condens. Matter 2004, 16, R771 – R828.
- [5] H. M. Blatter, H. Lukaszewski, Tetrahedron Lett. 1968, 9, 2701-2705.
- [6] a) C. P. Constantinides, P. A. Koutentis, H. Krassos, J. M. Rawson, A. J. Tasiopoulos, J. Org. Chem. 2011, 76, 2798-2806; b) C. P. Constantinides, P. A. Koutentis, J. M. Rawson, Chem. Eur. J. 2012, 18, 7109-7116; c) C. P. Constantinides, P. A. Koutenis, J. M. Rawson, Chem. Eur. J. 2012, 18, 15433–15438: d) C. P. Constantinides, E. Carter, D. M. Murphy, M. Manoli, G. M. Leitus, M. Bendikov, J. M. Rawson, P. A. Koutentis, Chem. Commun. 2013, 49, 8662-8664; e) C. P. Constantinides, A. A. Berezin, M. Manoli, G. M. Leitus, M. Bendikov, J. M. Rawson, P. A. Koutentis, New J. Chem. 2014, 38, 949-954; f) B. Yan, J. Cramer, R. McDonald, N. L. Frank, Chem. Commun. 2011, 47, 3201-3203.
- [7] a) A. A. Berezin, C. P. Constantinides, C. Drouza, M. Manoli, P. A. Koutentis, Org. Lett. 2012, 14, 5586-5589; b) A. A. Berezin, C. P. Constantinides, S. I. Mirallai, M. Manoli, L. L. Cao, J. M. Rawson, P. A. Koutentis, Org. Biomol. Chem. 2013, 11, 6780-6795.
- [8] a) P. A. Koutentis, D. Lo Re, Synthesis 2010, 2075-2079; b) C. P. Constantinides, P. A. Koutentis, G. Loizou, Org. Biomol. Chem. 2011, 9, 3122-3125; c) T. A. Ioannou, P. A. Koutentis, H. Krassos, G. Loizou, D. Lo Re, Org. Biomol. Chem. 2012, 10, 1339-1348; d) P. A. Koutentis, H. Krassos, D. Lo Re, Org. Biomol. Chem. 2011, 9, 5228-5237; e) P. A. Koutentis, G. Loizou, D. Lo Re, J. Org. Chem. 2011, 76, 5793-5802; f) M. Demetriou, A. A. Berezin, P. A. Koutentis, T. Krasia-Christoforou, Polym. Int. 2013, 63, 674-679:
- [9] a) F. A. Neugebauer, G. Rimmler, Magn. Reson. Chem. 1988, 26, 595-600; b) F. A. Neugebauer, I. Umminger, Chem. Ber. 1980, 113, 1205-1225; c) F. A. Neugebauer, I. Umminger, Chem. Ber. 1981, 114, 2423-2430.
- [10]  $a_N = Q_N \rho_N$ , in which  $a_N$  is the hfcc in Gauss;  $Q_N = 21.2$  G (for N2 and N4), and  $Q_N = 25$  G (for N1).
- [11] H. M. McConnell, J. Chem. Phys. 1958, 28, 1188-1192.

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- [12] J. W. Hall, W. E. Marsh, R. R. Weller, W. E. Hatfield, Inorg. Chem. 1981, 20, 1033-1037.
- [13] B. Bleaney, K. D. Bowers, Proc. R. Soc. London Ser. A 1952, 214, 451-465.
- [14] J. J. Novoa, M. Deumal, J. Jornet-Somoza, *Chem. Soc. Rev.* 2011, 40, 3182–3212.
- [15] L. Noodleman, J. Chem. Phys. 1981, 74, 5737-5743.
- [16] M. Deumal, J. J. Novoa, M. J. Bearpark, P. Celani, M. Olivucci, M. A. Robb, J. Phys. Chem. A 1998, 102, 8404–8412.
- [17] M. Mito, Y. Komorida, H. Tsuruda, J. S. Tse, S. Desgreniers, Y. Ohishi, A. A. Leitch, K. Cvrkalj, C. M. Robertson, R. T. Oakley, J. Am. Chem. Soc. 2009, 131, 16012–16013.
- [18] M. Dietrich, J. Heinze, J. Am. Chem. Soc. 1990, 112, 5142-5145.
- [19] D. A. O'Brien, D. R. Duling, Y. C. Fann, Winsim v0.98, EPR spectral simulation for MS-Windows, Public EPR Software Tools NIEHS.
- [20] M. Nilges, Illinois EPR Research Centre; PIP for Windows (v.2.1), J. M. Rawson, University of Windsor (2011).
- [21] Oxford Diffraction (2008). CrysAlis CCD and CrysAlis RED, version 1.171.32.15, Oxford Diffraction Ltd, Abingdon, Oxford, England.
- [22] G. M. Sheldrick, "SHELXL97 A program for the refinement of crystal structure", University of Göttingen, Germany.
- [23] L. J. Farrugia, J. Appl. Crystallogr. 1999, 32, 837-838.

- [24] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van de Streek, J. Appl. Crystallogr. 2006, 39, 453– 457.
- [25] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

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# **FULL PAPER**

## Magnetic Properties

C. P. Constantinides, A. A. Berezin, M. Manoli, G. M. Leitus, G.A. Zissimou, M. Bendikov, J. M. Rawson, P. A. Koutentis\*

Structural, Magnetic, and Computational Correlations of Some Imidazolo-Fused 1,2,4-Benzotriazinyl Radicals

 $R^1 = C_6H_5$  or  $4-BrC_6H_4$ 

 $0>J_2>J_1$ 

**Bigger is stronger**:  $\pi$ -Extension of 1,2,4benzotriazin-4-yl radicals leads to an enhanced overlap between SOMO orbitals and, therefore, to a strong effective exchange coupling within alternating 1 D chains of imidazolo-benzotriazinyls. However, subtle changes in interplanar distances and slippage angles switch the observed magnetic properties (see figure).

 $R^1 = 4$ -MeOC<sub>6</sub>H<sub>4</sub>

 $J_1 > 0 > J_2$ 

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