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Polymorphism in a π stacked Blatter radical: structures and magnetic properties of 3-(phenyl)-1-(pyrid-2-yl)-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl†

Christos P. Constantinides, a* Daniel B. Lawson, a Georgia A. Zissimou, b Andrey A. Berezin, b Aaron Mailman, c Maria Manoli, b Andreas Kourtellaris, b Gregory M. Leitus, d Rodolphe Clérac, e Heikki M. Tuononen c and Panayiotis A. Koutentis b

3-(Phenyl)-1-(pyrid-2-yl)-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl (2) demonstrates the first example of polymorphism in the family of Blatter radicals. Two polymorphs, 2α and 2β, have been identified and characterized by single crystal X-ray diffractometry and magnetic susceptibility measurements to investigate their magnetism–structure correlations. Both polymorphs form one-dimensional (1D) π stacks of evenly spaced radicals with distinctly different π–π overlap modes. Within the 1D π stacks, radicals are located at evenly interplanar distances, 3.461 Å for 2α and 3.430 Å for 2β. Magnetic susceptibility studies indicate that both polymorphs exhibit antiferromagnetic interactions inside their 1D π stacks. The magnetic susceptibility data are best interpreted in terms of a regular chain model of antiferromagnetically coupled quantum spins

\[ H = -2J \sum_i S_i \cdot S_{i+1} \]

with exchange-interactions of \(J/k_B = -36.7(3) \text{ K}(-25.5(2) \text{ cm}^{-1})\) for 2α and \(J/k_B = -72(3) \text{ K}(-50(2) \text{ cm}^{-1})\) for 2β. For polymorph 2β, a crossover on the magnetic susceptibility around 20 K suggests the presence of a phase transition, which might be related to dimerization of the radicals along the chain. DFT calculations support the experimental structure–magnetism results and the antiferromagnetic nature of the local interactions between radicals within the 1D π stacks.

1. Introduction

1,3-Diphenyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl (1) aka Blatter radical (Fig. 1) was first prepared in 19687 and did not receive much attention2–6 until 1996 when F. Wudl showed that it forms a pressure sensitive semiconductor with tetracyanoquinodimethane (TCNQ).7 Blatter radical 1 is stable to oxygen and moisture,8 and can readily be sublimed without degradation.9,10 Owing to these exceptional physical properties, we have systematically developed new synthetic procedures11–17 to broaden access and significantly expand the structural diversity of Blatter radicals.18–20 These efforts have led to Blatter-type radicals with new physical properties and applications.10,21–34 Various one-dimensional (1D) magnetic properties21–24,28,30–34 and two systems with a first order structural phase transition inducing magnetic bistability25,26 have been reported. Blatter radicals have also been used in chemical synthesis. For example, they can act as

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† Electronic supplementary information (ESI) available. CCDC 1955680 and 1955684. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0ce00789g

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Fig. 1 Molecular structures of benzotriadazins 1 and 2 showing atom numbering.
radicals exhibit antiferromagnetic exchange interactions despite the distinctly different crystal packing.

Polymorphism in organic radicals is a common phenomenon. It occurs as a result of different crystal packings with typically small differences in their lattice energy. Polymorphism is well documented for thiaryl radicals. However, for hydrazyls only one example of a verdazyl radical was recently reported. The 1,5-diisopropyl-3-(4-carboxyphenyl)-6-oxoverdazyl crystallizes as two polymorphs with markedly different crystal packings and magnetic properties. Polymorphism in Blatter-type radicals could potentially be more prevalent owing to the extended spin delocalization and the large SOMO surface of the benzotriazinyl core. This characteristic leads to many potential sites for intramolecular interactions in the crystal packing and thus opportunities for polymorphism. In the present work, 3-(phenyl)-1-(pyrid-2-yl)-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl (2) (Fig. 1) is shown to crystallize in two polymorphs, α and β, consisting of supramolecular chains of equidistant radicals exhibit antiferromagnetic exchange interactions despite the distinctly different crystal packing.

2. Experimental

2.1 Synthesis

As we have previously reported, the synthesis of the 3-(phenyl)-1-(pyrid-2-yl)-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl radical 2 involves the preparation of N′-(2-nitrophenyl)-N′-(pyrid-2-yl)benzohydrazide (3) which upon an acid-catalysed, tin-mediated reductive cyclodehydration and subsequent air oxidation affords 2 (Scheme 1).

2.2 EPR and cyclic voltammetry

The solid-state and solution EPR spectra (CH$_2$Cl$_2$, ca. 20 °C) of radical 2 have been previously reported, and we summarize the data here. The solution EPR spectrum of radical 2 is typical of benzotriazinyls with the largest $^{14}$N hyperfine coupling constant (hfcc) located at N1 followed by N4 and N2 ($a_{\text{N1}} \gg a_{\text{N4}} > a_{\text{N2}}$). The experimentally determined hyperfine coupling constants for radical 2 are $a_{\text{N1}}$ (6.74 G), $a_{\text{N2}}$ (4.88 G), $a_{\text{N4}}$ (4.9, G) with $g_{\text{solution}} = 2.0040$ and $g_{\text{solid}} = 2.0046$ which compare well with the values deduced from the modelling of the magnetic susceptibility data (vide infra). Cyclic voltammetry (CV) measurements of radical 2 (1 mM in CH$_2$Cl$_2$ containing n-Bu$_4$NBF$_4$ (0.1 M) as electrolyte, Ag/AgCl as reference electrode, 50 mV s$^{-1}$ scan rate, ca. 20 °C, Fe/Fe$^+$ as internal reference), show two fully reversible oxidation $E_{1/2}$ (ox) = 0.24 V and reduction waves $E_{1/2}$ (red) = −0.82 V and $E_{1/2}^{ceh}$ = 1.06 V.

2.3 Single crystal and powder X-ray diffractometry

Single crystal X-ray diffraction data were collected on an Agilent SuperNova diffractometer, equipped with an Atlas detector and Cu Kα radiation source ($\lambda = 1.5418$ Å). Suitable crystals were attached to MiTeGen micro-mounts with Fomblin® Y oil and transferred to a goniostat where they were cooled for data collection. Unit cell dimensions were determined and refined by using 2674 reflections ($4.75 \leq \theta \leq 74.49^\circ$) for polymorph α and 2797 ($4.50 \leq \theta \leq 76.65^\circ$) for polymorph β. Data acquisitions, reductions and empirical absorption corrections were applied using Crysalis PRO software. The structures were solved by direct methods and refined on $F^2$ using full-matrix least squares using SHELXL. The non-H atoms were treated anisotropically. The hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms. Crystallography figures were generated using Mercury. Powder X-ray diffraction (PXRD) patterns for samples α and β were recorded on a Shimadzu 6000 Series X-ray diffractometer at room temperature (Cu Kα radiation, $\lambda = 1.5418$ Å).
Crystal refinement data of 3-(phenyl)-1-(pyrid-2-yl)-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl (2α) (CCDC 1955680): C_{19}H_{14}N_4. MW = 285.32 g mol\(^{-1}\), orthorhombic space group P2\(_1\)2\(_1\)2\(_1\), a = 7.1656(3), b = 10.9705(4), c = 17.5843(6) Å, V = 1382.31(9) Å\(^3\), Z = 4, T = 120.0(10) K, \(\rho_{c,d} = 1.371\) g cm\(^{-3}\), 2\(\theta\)max = 77.49. Refinement of 199 parameters on 2674 independent reflections out of 5012 measured reflections (R\(\text{ref}\) = 0.0281) led to R\(_1\) = 0.0388 [I > 2\(\sigma(I)\)], wR\(_2\) = 0.1001 (all data), and S = 1.040 with the largest difference peak and hole of 0.163 and −0.177 e\(^{-3}\), respectively.

Crystal refinement data of 3-(phenyl)-1-(pyrid-2-yl)-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl (2β) (CCDC 1955684): C\(_{19}\)H\(_{14}\)N\(_4\), MW = 285.32 g mol\(^{-1}\), monoclinic space group P2\(_1\)/c, a = 19.7893(9), b = 3.76820(10), c = 19.7322(8) Å, V = 1337.94(10) Å\(^3\), Z = 4, T = 120.00(10) K, \(\rho_{c,d} = 1.416\) g cm\(^{-3}\), 2\(\theta\)max = 76.65. Refinement of 199 parameters on 2797 independent reflections out of 9981 measured reflections (R\(\text{ref}\) = 0.0267) led to R\(_1\) = 0.0418 [I > 2\(\sigma(I)\)], wR\(_2\) = 0.1196 (all data), and S = 1.030 with the largest difference peak and hole of 0.222 and −0.266 e\(^{-3}\), respectively.

### 2.4 Magnetic susceptibility measurements

Magnetic measurements were performed on a Quantum Design SQUID magnetometer MPMS-XL (Quantum Design, San Diego, CA, USA) and MPMS3-VSM at temperatures between 1.8 and 300 K, and dc magnetic fields ranging from −7 to +7 T. The measurements were carried out on polycrystalline samples (22.21, 21.13 and 21.6 mg for 2α, and 21.35, 15.6, 14.5 and 15.1 mg for 2β) introduced in a sealed polyethylene bag (3 × 0.5 × 0.02 cm; typically, 18–22 mg) or gelatin capsules. Prior to the main experiments, the field-dependent magnetization was measured at 100 K on each sample to detect the possible presence of any bulk ferromagnetic impurities. Paramagnetic materials should exhibit a perfect linear dependence of magnetic susceptibility with the large def2-TZVPP basis sets. B3LYP is the classic three-parameter hybrid functional consisting of Becke's 88 exchange functional and the correlation functional of Lee, Yang and Parr, whereas X3LYP replaces Becke's 88 exchange with an improved functional developed to provide a better description of non-bonded interactions, spin states and thermochemical properties. CAM-B3LYP is a hybrid functional which combines B3LYP with a long-range correction based on the Coulomb-attenuating method. LC-oB97X\(^{80}\) is a long-range corrected functional based on Becke’s work, whereas LC-oB88\(^{81}\) is Henderson’s version of the long-range-corrected LC-oPBE functional of Vydrov.\(^{82–84}\) M06-2X\(^{85,86}\) is a global hybrid with 54% HF exchange and empirically parameterized only for nonmetals. MN15\(^{87,88}\) is a newer version of M06 with 44% HF exchange and parameterized for multi-reference systems and noncovalent interactions. All calculations were performed with Gaussian16\(^{89}\) using XSEDE\(^{90}\) resources and services.

### 3. Results and discussion

#### 3.1 Crystal structures

Radical 2 crystallizes in two polymorphs 2α (CCDC 1955680) and 2β (CCDC 1955684). Single crystals suitable for X-ray diffraction studies were obtained by slow cooling of a dilute and concentrated n-hexane solution for 2α and 2β, respectively. Careful recrystallization is required to avoid crystallization of both polymorphs as mixtures. Polymorph 2β comes out rapidly from a hot super saturated solution as it cools down to room temperature and is, tentatively, the thermodynamic polymorph or a metastable kinetic polymorph. Polymorph 2α comes out of solution slowly once at room temperature and is, tentatively, the thermodynamic polymorph. Both crystal structures were collected at 100(2) K. Polymorph 2α crystallizes in the orthorhombic space group P2\(_1\)2\(_1\)2\(_1\), and polymorph 2β in the monoclinic space group P2\(_1\)/c. Both polymorphs contain one molecule in the asymmetric unit. The intramolecular bond angles and bond lengths are similar to that of other benzotriazinyls,\(^{21–27}\) however, there is a significant difference in the geometry of the amidrazonyl moiety. In polymorph 2α, the 1,2,4-amidrazonyl moiety adopts a shallow boat conformation with deviations of the N1 and N3 atoms from the mean plane of C2, C3, N2, C1 of 0.09 and 0.06 Å, respectively (Fig. 2, top). A similar amidrazonyl structure was observed in 1,3-diphenyl-7-trifluoromethyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl.\(^{10}\)

The 1,2,4-amidrazonyl moiety of polymorph 2β is closer to planarity with deviation of the N1 and N3 atoms from the mean plane of C2, C3, N2, C1 of 0.06 and 0.03 Å, respectively (Fig. 2, bottom). The torsion angle (C3, N1, C14, N4) of the N1–(pyrid-2-yl) group with respect to the plane of benzotriazine is similar for both polymorphs [38(9.3) and 36.4(2)° for 2α for 2β, respectively] and significantly less than the average of 59 ± 13° reported thus far.\(^{19}\) This torsion angle is the result of steric repulsion between the H4 and the lone pair of N4. The torsion angle (N3, C1, C8, C9) between the C3-phenyl and the amidrazonyl plane is 15.3(3)° and 0.8(2)° for 2α and 2β, respectively. Despite subtle differences in the intramolecular geometrical parameters of the radicals in...
these two polymorphs, their solid-state packing presents some striking distinctions in the way these radicals associate and π stack.

Most benzoetriazinyls form 1D supramolecular arrangements wherein the radicals π stack to obtain efficient SOMO–SOMO overlap. This is also the case for both polymorphs 2α and 2β, and is attributed to the presence of the spin density primarily on the amidrazonyl unit (ca. 70%) and to a lesser degree on the fused benzene ring and the N1-(pyrid-2-yl) substituent (vide infra).

**Solid-state packing of polymorph 2α.** Polymorph 2α π stacks along the a-axis and forms supramolecular chains of evenly spaced radicals (Fig. 3, left). A 2-fold screw axis in the [1, 0, 0] direction at x, 1/4, 0 and screw component [1/2, 0, 0] places the N1-(pyrid-2-yl) substituent directly on top of a triazine ring (eclipsed conformation) of a subsequent radical inside the π stack to form a “head-to-tails” dimer (Fig. 3, left). This packing is unique as most benzoetriazinyls overlap in either a centrosymmetric manner or via translation parallel to the stacking direction. The centroid distance between these two N1-[pyrid-2-yl] and 1,2,4-triazine rings is 3.48 Å. There are three pairs of close intermolecular contacts between radicals inside the π stack, C16⋯C2 [d = 3.388(3) Å], C15⋯C4 [d = 3.390(3) Å] and C9⋯C17 [d = 3.323(4) Å]. These contacts are significantly shorter than the sum of the van der Waals radii, reflecting strong interactions between spin density sites. Neighbouring π stacks are related via two 2-fold axes. One along the b-axis at 0, y, 1/4 with screw component [0, 1/2, 0] and one along the c-axis at 1/4, 0, z with screw component [0, 0, 1/2]. These neighbouring stacks are connected via a rich network of close intermolecular contacts and proximity interactions to form tight packing without
significant voids. These include two weak hydrogen bonds C10–H10⋯N4 (d = 2.650 Å) [C10⋯N4, d = 3.571(3) Å, C10–H10⋯N4 = 171.0°], C12–H12⋯N3 (d = 2.714 Å) [C12⋯N3, d = 3.556(3) Å, C12–H12⋯N3 = 150.9°] and a short non-stabilizing interaction C7–H7⋯H16 (d = 2.367 Å) [C7⋯C16, d = 3.914(3) Å, C7–H7⋯H16 = 128.0°].

Solid-state packing of polymorph 2β. Radicals in polymorph 2β π stack along the b-axis to form supramolecular chains of evenly spaced radicals (Fig. 3, right). The molecules inside the stack are related via a glide plane perpendicular to [0, 1, 0] with glide component [0, 0, 1/2] packing in a “head-to-head” orientation. This results in a slipped π stack wherein the radicals are not eclipsed but overlap with slippage angles of 76.45° (longitudinal) and 70.75° (latitudinal). The interplanar distance along the supramolecular chains (defined as the distance between subsequent planes of benzotriazinyl rings) is 3.432 Å (Fig. 3, right). The shortest contact inside the π stack is between carbons of the N1-(pyrid-2-yl) substituent C14⋯C15 (d = 3.392(2) Å). Neighbouring π stacks are connected via two weak hydrogen bonds, C5–H5⋯N4 (d = 2.648 Å) [C5⋯N4, d = 3.540(2) Å, C5–H5⋯N4 = 160.9°], C17–H17⋯N3 (d = 2.600 Å) [C17⋯N3, d = 3.507(2) Å, C17–H17⋯N3 = 165.3°] and a non-stabilizing interaction C9–H9⋯C17 (d = 2.899 Å).
patterns for polymorphs demonstrates their phase purity. Additionally, the comparison of powder X-ray diffraction calculated from single crystal X-ray structures at 100 K. samples at 300 K for chemical purity and as well as their powder X-ray diffraction. 3.540(2) Å, hydrogen bonds C5

run along the and screw component [0, 1/2, 0]. These antiparallel chains 0, 0] and a 2-fold screw axis with direction [0, 1, 0] at 0, y, 1/4 and screw component [0, 1/2, 0]. These antiparallel chains run along the α-axis (Fig. 4) and are connected by weak hydrogen bonds C5–H5⋯N4 (d = 2.648 Å) [C5⋯N4, d = 3.540(2) Å, αC5–H5⋯N4 = 160.9°].

Before measuring the magnetic properties of polymorphs 2α and 2β, analytical data were collected to confirm their chemical purity and as well as their powder X-ray diffraction patterns (Fig. 5).

The experimental diffraction signatures of polycrystalline samples at 300 K for 2α and 2β match well the patterns calculated from single crystal X-ray structures at 100 K. Additionally, the comparison of powder X-ray diffraction patterns for polymorphs demonstrates their phase purity. However, the presence of small amounts of amorphous paramagnetic impurities cannot be fully excluded.

3.2 Magnetic properties

The temperature dependence of the magnetic susceptibility (χ) was collected on polycrystalline samples of 2α and 2β in the 2–300 K temperature region. The representative data are shown as χ vs. T and χ/T vs. T plots in Fig. 6. The χ/T product at 300 K is 0.34 and 0.29 cm³ K mol⁻¹ for 2α and 2β, respectively. These values are significantly smaller than the expected Curie constant of 0.375 cm³ K mol⁻¹ K expected for an S = 1/2 radical species with a g factor of 2. This apparent discrepancy is induced by the presence of significant antiferromagnetic interactions between radical molecules as confirmed by the marked decrease of the χ/T product (or the broad maximum of the magnetic susceptibility at 47 and 100 K, respectively) when decreasing the temperature. At 2 K, if one considers that the χ/T product should be null when all the radical spins are fully antiferromagnetically coupled, the observed residual paramagnetism of 0.004 and 0.006 cm³ K mol⁻¹, respectively, corresponds to about 1 and 2% of an S = 1/2 Curie impurity. Based on the crystal structures shown above, the strongest antiferromagnetic interactions should be present along the regular chain of radicals in both polymorphs (Fig. 3). The magnetic susceptibility data were thus modeled using a regular chain of S = 1/2 quantum spins with a single magnetic interaction, J, between radical centers

\[ H = -2J\sum_{i} \mathbf{S}_{i}\cdot\mathbf{S}_{i+1} \]

The analytical expression of the susceptibility established by Bonner and Fischer in 1964, was used to fit both χ vs. T and χ/T vs. T plots shown in Fig. 6 (solid red line). For both polymorphs, the regular chain model is able to reproduce well the experimental data with an estimated intrachain exchange coupling, J/kB = −36.7(3) K (−25.5(2) cm⁻¹; between 300 and 15 K) for 2α and J/kB = −72(3) K (−50(2) cm⁻¹; between 300 and 20 K) for 2β (with g factor of 2.05(5) for both compounds). It should be mentioned that the magnetic properties for 2α and 2β have been measured on different samples (three and four, respectively; see Fig. S2†) with a good reproducibility of data shown in Fig. 6 (the above J values are those of sample 1 in Fig. S2;† the values for the other samples are given in the Fig. S2† caption).

While the regular chain model is perfect for the magnetic data of 2α, the theory/experiment agreement for 2β is obviously less performant. Hence, alternative spin chain models with two different magnetic interactions have also been considered without being able to significantly improve the agreement. It is thus suspected that interchain magnetic interactions are indeed effective in polymorph 2β. Below 20 K (Fig. 6, inset), a clear anomaly is observed on the susceptibility of polymorph 2β, indicating a possible phase

![Fig. 5 Powder X-ray diffraction patterns of samples used for magnetic measurements: (top) 2α collected at 300 K (red line) and calculated from the single crystal X-ray structure at 100 K (blue line), (middle) 2β collected at 300 K (red line) and calculated from the single crystal X-ray structure at 100 K (blue line) and (bottom) comparison of the experimental powder X-ray diffraction patterns at 300 K for the two polymorphs 2α (blue line) and 2β (red line).](image-url)
transition. Attempts to collect the crystal structure of polymorph 2β at 3 K led to diffraction degradation in one direction which appeared to be reversible. The magnetic and X-ray diffraction experimental data suggested a phase transition below 17 K that most likely involves a dimerization of the radicals along the chain as observed in many related 1D spin systems.

3.3 DFT and ab initio calculations

Magnetism–structure correlations can be further supported by means of quantum chemical methods. This is typically done either at post-HF levels or using BS-DFT of which the latter is a computationally efficient but theoretically less-rigorous approach that is typically employed for systems containing several tens, even hundreds, of atoms.

Table 1 lists the exchange-coupling constants calculated for polymorphs 2α and 2β using different density functionals. The data can be compared to the experimentally determined radical···radical interactions, -25.5 and -50 cm⁻¹ for polymorph 2α and 2β, respectively. In general, all functionals predict the coupling in 2α to be antiferromagnetic but the coupling strength varies greatly between different functionals. Most notably, functionals with improved long-range corrections, namely CAM-B3LYP, ωB97x and LC-ωHPBE, predict significantly weaker antiferromagnetic coupling compared to others, which, surprisingly, show only small variation and are in good agreement with the experimentally derived exchange coupling. The results for 2β are, however, more varied with some of the theoretically more just long-range corrected functionals even predicting the coupling to be ferromagnetic and, thus, at variance with experimental observations. It is also notable that even the best-performing functionals give Jcomp for 2β that is almost half (in magnitude) of the experimentally derived intrachain exchange coupling J. The reason for this discrepancy is unclear, though it can be related to problems in treating the singlet state via BS-DFT and it also parallels the problems observed in modelling the magnetic data of 2β with the regular chain model. It should also be noted that by simple examination of the SOMO and the associated spin density of radical 2β (Fig. 7), it is evident that the benzo triazinyl ring contains most of the spin density and overlap through this region, like that in polymorph 2β, should lead to strong antiferromagnetic exchange interaction unless prevented by appropriate stack slippage. However, if the radicals pack so that the interactions involve the N1-(pyrid-2-yl) substituents, such as in polymorph 2α, the antiferromagnetic interaction is expected to be weaker even in case of perfect stacking due to less efficient overlap.

4. Conclusions

3-(Phenyl)-1-(pyrid-2-yl)-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl (2) is the first example of a polymorphic Blatter-type radical.
Two polymorphs, $\alpha$ and $\beta$, were identified, isolated and characterized by means of single crystal X-ray diffractometry and magnetic susceptibility measurements. Polymorph $\alpha$ shows a unique mode of overlap along the 1D stacking direction where the N1-(pyrid-2-yl) substituent interacts face-to-face (eclipsed conformation) with a 1,2,4-triazinyl ring of a subsequent radical. Polymorph $\beta$ forms a slipped 1D π-stack wherein the radicals overlap extensively over the benzotriazinyl rings.

Magnetic susceptibility studies reveal that in both cases the radical⋯radical interactions are antiferromagnetic. The intra-chain magnetic exchange interaction of polymorph $\beta$ ($-50 \text{ cm}^{-1}$) was found to be double that of polymorph $\alpha$ ($-25.5 \text{ cm}^{-1}$), possibly due to more effective SOMO⋯SOMO overlap. The two low dimensional polymorphs of radical 2 demonstrate weak antiferromagnetic interactions often observed in organic open-shell molecules. While recent advances in the chemistry of organic radicals led to some materials exhibiting substantial magnetic hysteresis (primarily in thiazyl radicals), this class of Blatter radicals have yet to demonstrate their efficiency to generate large magnetic couplings and thus magnetic order at high temperature as observed often in purely inorganic systems and in a few metal-organic materials.

Polymorphism in Blatter-type radicals could be more prevalent than heretofore recognized and requires careful examination of the harvested crystals. We are currently working on other examples of a Blatter-type radicals that demonstrate polymorphism.

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Fig. 7 Figures of the (left) SOMO and (right) spin density of radical 2 at the B3LYP/def2-TZVPP level of theory using isodensity values ±0.03 and ±0.0004, respectively.
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Polymorphism in a π Stacked Blatter Radical: Structures and Magnetic Properties of 3-(Phenyl)-1-(pyrid-2-yl)-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl

Christos P. Constantinides,*a Daniel B. Lawson,a Georgia A. Zissimou,b Andrey A. Berezin,b Aaron Mailman,c Maria Manoli,b Andreas Kourtellaris,b Gregory M. Leitus,d Rodolphe Clérac,e Heikki M. Tuononen,e and Panayiotis A. Koutentisb

a Department of Natural Sciences, University of Michigan-Dearborn, 4914 Evergreen Road, Dearborn, MI 48128-1491, United States. E-mail: cconst@umich.edu Fax: +01 3135934937 Tel: +01 3135836728

b Department of Chemistry, University of Cyprus, P.O. Box 20537, 1678 Nicosia, Cyprus
c Department of Chemistry, NanoScience Center, University of Jyväskylä, P. O. Box 35, FI-40014 Jyväskylä, Finland
d Chemical Research Support Unit, Weizmann Institute of Science, 7610001 Rehovot, Israel
e Univ. Bordeaux, CNRS, Centre de Recherche Paul Pascal, UMR 5031, 33600 Pessac, France

Supplemental Information

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Table 1. Crystallographic data for polymorphs 2α and 2β.
|     | $2\alpha$                      | $2\beta$     |
|-----|--------------------------------|--------------|
|     | **Crystal Data**               | **Crystal Data** |
| Formula | C$_{18}$H$_{13}$N$_4$           | C$_{18}$H$_{13}$N$_4$ |
| Formula weight, g.mol$^{-1}$ | 285.32        | 285.32       |
| Crystal system | Orthorhombic                | Monoclinic    |
| Space group   | $P 2_1 2_1 2_1$ | $P-1 2_1/c_1$ |
| $a$, $b$, $c$, Å  | 7.1656(3), 10.9705(4), 17.5843(6) | 19.7893(9), 3.76820(10), 19.7322(8) |
| $\alpha$, $\beta$, $\gamma$, ° | 90, 90, 90 | 90, 114.594(5), 90 |
| $V$, Å$^3$  | 1382.31(9) | 1337.94(10) |
| $Z$  | 4 | 4 |
| $\rho_{\text{calc}}$, g.cm$^{-3}$ | 1.371 | 1.416 |
| $\mu$(Mo Ka), mm$^{-1}$ | 0.671 | 0.693 |
| $F(000)$ | 596 | 596 |
| Crystal size, mm$^3$ | $0.224 \times 0.053 \times 0.035$ | $0.193 \times 0.085 \times 0.026$ |
|     | **Data Collection**            | **Data Collection** |
| $T$, K  | 120.01(10) | 120.00(10) |
| $\lambda$, Å | 1.54184 | 1.54184 |
| $\theta$ (min, max), ° | 4.751, 74.490 | 4.500, 76.649 |
| Dataset (-$h$, $h$; -$k$, $k$; -$l$, $l$) | -8, 7; -12, 13; -20, 21 | -24, 23; -4, 2; -24, 24 |
| Meas./ indep. refl. (R$_{\text{int}}$) | 5012 / 2674 (0.0281) | 9981 / 2797 (0.0267) |
| Obs. refl. [I>2σ(I)] | 199 | 199 |
|     | **Refinement**                 | **Refinement** |
| $R_1$ | 0.0388                      | 0.0418     |
| $wR_2$ a | 0.1001                      | 0.1196 |
| Goodness of fit on $F^2$ | 1.040 | 1.030 |
| Min, max resd density, e.Å$^{-3}$ | -0.177/0.163 | -0.266/0.222 |

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*Graphite monochromator.

$R_1 = \sum |F_o| - |F_c| / \sum |F_o|.

$wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [wF_o^2]^2]^{1/2}, w = 1/[\sigma(F_o^2) + (m \cdot p)^2 + n \cdot p], p = [\max(F_o^2, 0) + 2F_c^2] / 3.$

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**Fig. S1** Structure overlay of polymorphs $2\alpha$ and $2\beta$ (polymorph $2\alpha$ with red capped sticks and polymorph $2\beta$ with blue capped sticks).
Fig. S2 Temperature dependence of (bottom) the magnetic susceptibility and (top) the $\chi T$ product for polymorphs (left; at 0.5 T for sample 1 and 0.1 T for sample 2) 2$\alpha$ and (right; at 0.1 T for sample 1; at 0.5 T for samples 2, 3 and 4) 2$\beta$ ($\chi$ is defined as $M/H$ per mole of radical 2). The best fit of the experimental data to the regular chain model of antiferromagnetically coupled quantum spins (see main text) leads for 2$\alpha$ to $J/k_B = -36.7(3)$ K ($-25.5(2)$ cm$^{-1}$; between 300 and 15 K) for sample 1, $J/k_B = -35.6(3)$ K ($-24.7(2)$ cm$^{-1}$; between 300 and 14 K) for sample 2, $J/k_B = -36.9(3)$ K ($-25.6(2)$ cm$^{-1}$; between 300 and 16 K) for sample 3; and for 2$\beta$ to $J/k_B = -72(3)$ K ($-50(2)$ cm$^{-1}$; between 300 and 20 K) for sample 1, $J/k_B = -70(3)$ K ($-49(2)$ cm$^{-1}$; between 300 and 20 K) for sample 2, $J/k_B = -72(3)$ K ($-50(2)$ cm$^{-1}$; between 300 and 20 K) for sample 3 and $J/k_B = -73(3)$ K ($-51(2)$ cm$^{-1}$; between 300 and 20 K) for sample 4 (with a fixed g factor of 2.05(5))