

Communication

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A Magneto-structural Investigation of an Abrupt Spin-Transition for 1-Phenyl-3-trifluoromethyl-1,4-dihydro-benzo[*e*][1,2,4]triazin-4-yl

Christos P. Constantinides,[†] Andrey A. Berezin,[†] Georgia A. Zissimou,[†] Maria Manoli,[†] Gregory M. Leitus,[‡] Michael Bendikov,[‡] Michael R. Probert,[§] Jeremy M. Rawson,[#] and Panayiotis A. Koutentis^{*,†}

⁺Department of Chemistry, University of Cyprus, P. O. Box 20537, 1678 Nicosia, Cyprus

[‡]Department of Organic Chemistry, Weizmann Institute of Science, 76100 Rehovot, Israel

⁸School of Chemistry, Newcastle University, Newcastle upon Tyne, NE₁ 7RU, United Kingdom

[#]Department of Chemistry & Biochemistry, University of Windsor, 401 Sunset Avenue, Windsor, ON, N9B 3P4, Canada

Supporting Information Placeholder

ABSTRACT: 1-Phenyl-3-trifluoromethyl-1,4-dihydro-benzo-[*e*][1,2,4]triazin-4-yl (**3TB**) is the first example of a hydrazyl radical which shows a reversible sharp spin-transition fully completed within 5(1) K. The nominally first-order transition takes place at *ca*. 58(2) K and proceeds *via* subtle changes of intra- and inter-stack interactions between two similar structural phases. The low temperature phase (5-60 K) is diamagnetic and has a singlet ground state ($2J_{exp} = -166.8 \text{ cm}^{-1}$, g_{solid} = 2.0042, $\rho = 0.2\%$) stemming from a multicentre 2e⁻ interaction. The high temperature phase (60-300 K) is paramagnetic owing to non-interacting S = 1/2 spins arising from weakly bound dimers.

The potential of organic persistent radicals to be used as multifunctional materials in electronic devices is becoming attractive and promising.¹ The presence of unpaired electrons provides the opportunity to combine magnetic, optical and transport properties in a single material. External stimuli such as heat, light or pressure can be used to tune these unique physical properties, although to date, only a few examples have been reported.^{2,3} The response to these external stimuli is directly associated with the ability to switch between spin states.

A prerequisite for organic radicals to demonstrate spintransition behavior is a low dimerization enthalpy ($\Delta H_{\rm dim} \sim$ o) and the presence of two similar structural phases related by small atomic displacements; one enthalpy-favored low spin configuration and one entropy-favored high spin configuration. Many classes of organic radicals have low dimerization enthalpies but so far, the structural reorganization required for spin-transition, has mainly been observed in 1,3,2-dithiazolyls (DTAs).^{3,4} Nevertheless, three more examples of spin-transition radicals have been reported (a spirophenalenyl,^{5a} a phenoxyl^{5b} and a nitroxide^{5c}) indicating that this behavior can exist in other classes of organic radicals with $\Delta H_{\rm dim} \sim$ o.

Chart 1. Structures of 1,2,4-Benzotriazinyls



Hydrazyls have been long known to have low dimerization enthalpies.⁶ To date, no spin-transition has been observed for any member of this class of radicals. 1,2,4-Benzotriazinyls, a subclass of hydrazyls, have recently attracted attention owing to their enhanced air and moisture stability.⁷ Although first prepared by Blatter in the late 1960's, only sporadic work on this radical class has been reported in stark contrast to the closely related verdazyl radicals.⁸ Within the context of our ongoing project on the chemistry of 1,2,4-benzotriazine, we have reported a number of high-yielding synthetic routes to a variety of 1,2,4-benzotriazinyls.9 The majority of these radicals are stable in terms of solid-state σ - or π -dimerization; only 1,3-diphenyl-7-(fur-2-yl)-1,4-dihydro-benzo[e]-[1,24]triazin-4-yl (7FB) has a singlet ground state, arising from a π - π interaction rather than a true bond, with a thermally excited triplet state.7d As part of our magnetostructural studies of 1,2,4-benzotriazinyls, herein we report the first example of a hydrazyl radical, 1-phenyl-3-trifluoromethyl-1,4-dihydro-benzo[*e*][1,2,4]triazin-4-yl (3**TB**), that demonstrates spin-transition behavior between a paramagnetic and a diamagnetic phase at $T_{sp} \sim 58(2)$ K.

The recently reported synthesis of 3-trifluoromethylbenzotriazinyl **3TB** involved a multistep route that gave the radical in an overall yield of 37% (Scheme S1 in SI),^{9e} nevertheless, by applying Ma's copper catalyzed C-N coupling protocol¹⁰ we were able to shorten the synthesis and improve the overall yield to 80% (Scheme S2 in SI).



Figure 1. Temperature dependence of χT upon cooling (blue circles) and heating (red circles) of radical **3TB** between 5 and 300 K; inset: $d(\chi T)/dT vs$. T graph shows full completion of spin-transition within 5(1) K and transition temperatures of 58 K (cooling) and 60 K (heating).

Radical **3TB** was purified by column chromatography (basic alumina, DCM) and was crystallized from a hot concentrated solution of *n*-pentane as dark-red needles. The intramolecular geometry, EPR spectral parameters and cyclic voltammetry data for **3TB** are typical of other 1,2,4-benzotriazinyls (see SI).

The magnetic properties of radical **3TB** were probed by using a SQUID magnetometer. Variable-temperature magneticsusceptibility measurements were carried out on a phase pure polycrystalline sample of radical **3TB** (34.7 mg) in the temperature region 5-300 K at two different applied fields (0.1 and 0.4 T). Data were collected in both warming and cooling modes with heating and cooling rates of 5 K min⁻¹. No significant differences in sample susceptibility were observed between the applied fields or the temperature collecting modes. Data were corrected for both sample diamagnetism (χ_{dia} = -146.5 × 10⁻³ emu mol⁻¹) and the diamagnetic contribution of the sample holder. Upon cooling from 300 K down to 60 K, molar susceptibility (χ) increases following the Curie-Weiss law, with C = 0.377 emu K mol⁻¹ and $\theta = -1.10$ K $(\chi^{-1} vs. T, Figure S5)$, and reaches a maximum at *ca*. 60 K (χ vs. T, Figure S6). Within this temperature region radical 3TB behaves as a paramagnet with a stable χT value of *ca*. 0.374 emu K mol⁻¹ close to that expected for an S = 1/2 paramagnet (Figure 1). Below 60 K the sample undergoes a relatively sharp transition to a diamagnetic state with a small Curie tail at low temperatures attributable to 0.2% of S = 1/2 lattice defect sites. The low temperature magnetic data (5-60 K), fitted to the Bleaney-Bowers modelⁿ for the magnetic susceptibility of interacting pairs of S = 1/2 spins $(H = -2J_{12}\sum S_1S_2)$, provided an estimated $2J_{exp} = -166.8 \text{ cm}^{-1}$, $g_{solid} = 2.0042$, $\rho =$ 0.2% (Figure S7 in SI). This sharp discontinuity in the magnetic susceptibility occurred at $T_{sp} \sim 58(2)$ K and was not affected by the magnitude of the applied magnetic field. The transition was fully reversible upon both warming and cooling modes, showed no thermal hysteresis and was completed within a narrow temperature range of 5(1) K (Figure 1, inset). The observed sudden change in the magnetic response of the sample denoted a first order solid-state transition between two energetically similar structural phases.



Figure 2. % Change of unit cell parameters (left: cell dimensions; right: cell angles) as a function of temperature for radical **3TB** between 50 and 60 K.

To interpret the magnetic data and get a clear structural picture we carried out a variable temperature X-ray diffraction crystallographic study on a single crystal of radical **3TB**. Unit cell parameters were collected between 35-55 K at 5 K intervals and between 55-60 K at 1 K intervals on warming mode (Tables T₂ and T₃ in SI). Full structural determinations were performed before and after the transition at 4 and 75 K (Table T₄ in SI). No degradation in diffraction quality was observed despite cycling the single crystal of radical **3TB** through the transition multiple times.

Throughout the temperature region of 4-300 K the triclinic space group *P*-*i* was retained indicating the transition occurred without a major disruption of the intramolecular contacts and therefore without hysteresis. Unit cell parameters (Figure 2, Tables T2 and T3) show that, on warming up from 4 to 75 K, the nominally first-order transition is associated with a dramatic decrease in γ angle by *ca*. 3.5° (4%), a decrease of *b* axis by *ca*. 0.07 Å (0.8%) and an increase of *a* axis by *ca*. 0.1 Å (1.3%) without a significant change in the cell volume (Table T4). The sharp structural transition occurred at *ca*. 59 K and confirmed the spin-transition of the magnetic susceptibility at $T_{\rm sp} \sim 58(2)$ K. The observed changes in the three critical unit cell parameters are directly related to the solid-state packing arrangement.

Radicals of **3TB** π -stack to form 1D columns along the *b* axis (Figure 3). Within these columns, the radicals are related with respect to each other through a centre of inversion (-x, y, -z) that places the N1-Ph groups on opposite sides, avoiding the build-up of steric congestion. The mean interplanar distance and the degree of slippage alternate along the stacking direction (Table 1). This gives rise to two distinct centrosymmetric pairs comprised of radicals I-II and II-III (Figure 3). At 75 K the radicals of pair I-II are connected via a pair of weak symmetrical C-H···N interactions between the N3 and an ortho-hydrogen of the N1-Ph $[d_{C_9\cdots N_3} = 3.572(2) \text{ Å}, \angle C$ -H···N = $147.9(1)^{\circ}$; (-x, 2-y, 1-z)]. These interactions are absent in the 4 K structure as a smaller slippage angle ${}^{1-11}\phi_1$ between radicals I and II (13.8° at 4 K vs. 21.2° at 75 K) increases the distance between the atoms. Radicals of pair II-III are connected via short edge-to-face contacts.



Figure 3. Unit cell of **3TB** viewed down the stacking direction *b* axis (left). π -Stacks of **3TB** at 4 K (middle) and 75 K (right) showing the shortest intermolecular contacts and the interplanar distances in pairs I-II and II-III (hydrogen atoms are omitted for clarity).

One set of contacts is common to both structures $[d_{C_5\cdots C_{13}}]$ = 3.788(2) Å at 75 K and 3.763(2) Å at 4 K; (-x, 1-y, 1-z)] and the other appears only at the high temperature phase $[d_{C_4...C_{13}} = 3.600(2)$ Å; (-x, 1-y, 1-z)]. Radicals of neighboring stacks are connected in a head-to-tail orientation, via an edge-to-face C-H··· π contact between the fused benzene and the N1-Ph $[d_{C_5\cdots C_{13}} = 3.745(3) \text{ Å at } 75 \text{ K and } 3.707(3) \text{ Å at } 4 \text{ K}],$ to form chains that run parallel to a axis (Figure S8 in SI). Neighboring chains are connected in an antiparallel mode, *via* a net of trans type-II C-F···F interactions $[d_{F_3...F_3} = 2.730(2)]$ Å, $\theta_1 = \theta_2 = 126.5(1)^\circ$ and $d_{F_1\cdots F_1} = 2.690(1)$ Å, $\theta_1 = \theta_2 = 163.9(1)^\circ$ at 75 K; $d_{F_3\cdots F_3} = 2.677(1)$ Å, $\theta_1 = \theta_2 = 135.0(1)^\circ$ and $d_{F_1\cdots F_1} =$ 2.635(1) Å, $\theta_1 = \theta_2 = 157.7(1)^\circ$ at 4 K] of the CF3 group, to form ribbons in the ac plane (Figure S8). Similar C-F...F interactions link neighboring stacks in the crystal packing of **7TB**.^{7a} While the two sets of C-F...F interactions and the short edgeto-face C···C contact appear in both 4 and 75 K structures, a C-H···F interaction $[d_{C_3...F_2} = 3.364(2) \text{ Å}, \angle \text{C-H···F} = 134.4(1)^\circ;$ (1+x, y, z)] is only present at the low temperature phase; on warming up from 4 to 75 K, the CF3 group rotates from a torsion angle (N3, C1, C14, F3) of 15° to 21° causing the C-H···F interactions to break (Figure S8 in SI).

The aforementioned intermolecular interactions are too weak to drive the interconversion between the two structural phases. Moreover, no significant differences were observed in the overall number of these interactions between the phases. Therefore the lattice energy is mainly dominated by the SOMO-SOMO bonding overlap (Figure 4). This is reflected in the transformation of the mean interplanar distance and the degree of slippage between radicals along the stacking direction (Table 1). A computational study by Robert *et al.*,^{12a} showed that spin-transition for the closely related verdazyl radicals^{12b} was possible with a 0.4 Å increase of the intradimer equilibrium distance along with either a relative slippage (*ca.* 1.2 Å) or orientation (*ca.* 42°) of the verdazyl rings.

The phase transition of **3TB** occurred mainly *via* three significant structural changes taking place in the radical pair I-II: on warming up from 4 to 75 K the interplanar distance (d_{I-II}) and longitudinal slippage angle ($^{I-II}\phi_I$) increased by *ca*. 0.14 Å and 7.4°, respectively and the latitudinal slippage angle ($^{I-II}\phi_2$) decreased by *ca*. 6.3°. These changes are critical to the observed magnetic properties as radicals of pair I-II interact mainly through the spin-bearing 1,2,4-amidrazonyl unit.

Table 1. Slippage Angles and Interplanar Distances in Pairs I-II and II-III for Radical 3TB at 4 and 75 K

Temperature/K	Pair	$\phi_1^{\ a}/^{\mathrm{o}}$	$\phi_2^{\ a}/^{\mathrm{o}}$	d/Å
4	I-II	13.8	14.1	3.373
	II-III	11.5	35.7	4.304
75	I-II	21.2	7.8	3.513
	II-III	9.2	33.1	4.383

^{*a*} See Figures S9-10 in SI for parameters used to define the degree of longitudinal and latitudinal slippage.

With a significantly smaller slippage angle $(^{I-II}\phi_2 < ^{II-III}\phi_2)$ and shorter interplanar distance $(d_{I-II} < d_{II-III})$ it is anticipated that radical pair I-II will have stronger exchange coupling interaction than radical pair II-III ($|2J_{I-II}| > |2J_{II-III}|$). Therefore, in the absence of other dominating exchange interactions, $2J_{I-II}$ can be assigned to the exchange interaction determined by SQUID magnetometry ($2J_{exp} = -166.8 \text{ cm}^{-1}$ between 5-60 K).

Direct estimates of the spin-spin exchange interactions within the radical pairs were provided by DFT single-point calculations on the crystallographically determined geometries. We previously showed that for 1,2,4-benzotriazinyls the B₃LYP functional combined with the unprojected equation¹³ $J'_{12} = 2J_{12} = 2(E_{BS} - E_T)/2$ (based on $H = -J'_{12}\sum S_1S_2$ where $J'_{12} =$ $_{2J_{12}}$ to be equivalent to the spin Hamiltonian of Bleaney-Bowers model) performed well in the computation of exchange interactions.^{7e} The energies of the triplet $(E_{\rm T})$ and broken symmetry singlet (E_{BS}) states were determined at the UB₃LYP/6-₃₁₁++G(d,p) level of theory (Table T₅). A reasonable agreement between the calculated $2J_{I-II}^{DFT} = -184.8 \text{ cm}^{-1}$ (4 K) and the experimental $2J_{exp} = -166.8 \text{ cm}^{-1}$ (5-60 K) confirmed the dominating role of pair I-II (Table 2). At 4 K, radical pair I-II adopted a more "superimposed" and shorter structure ($^{I-II}\phi_1 = 13.8^\circ$, $^{I-II}\phi_2 = 14.1^\circ$, $d_{I-II} = 3.373$ Å) which gave rise to a multicentred 2e interaction that guenched paramagnetism (i.e. enhanced overlap in *a*-SOMO1 at 4 K vs. *a*-SOMO1 at 75 K in Figure 4). The exchange interactions of 3TB are of the same magnitude as the ones previously reported for 7FB ($2J_{DFT} = -244$ cm⁻¹ and $2J_{exp} = -172$ cm⁻¹ at 100 K) which has a singlet ground state dimer with a thermally accessible triplet state evident even at cryogenic temperatures ($|D| = 0.018 \text{ cm}^{-1}$, $|E| = 0.001 \text{ cm}^{-1}$ at 5 K).⁷



Figure 4. α -SOMO orbitals of pair I-II generated *via* singlepoint calculations (triplet states) on the crystal structures determined at 4 and 75 K employing the UB3LYP/6-311++G(d,p) level of theory (visualized with an isovalue of 0.02).

The rise of paramagnetism above 70 K for 7FB, was attributed to the population of the triplet state. A smooth second-order increase of intradimer distance by ca. 0.076 Å, leads to a relatively weakened exchange interaction and to a triplet exciton. However, even at 300 K the exchange interaction of **7FB** remained strongly antiferromagnetic $(2J_{300K} = -191)$ cm⁻¹) denoting a persistent spin-pairing. Our results on 7FB indicate that pair I-II at the low temperature phase of 3TB has a singlet ground state with a thermally accessible triplet state. With the rise of temperature the thermally excited triplet state becomes populated leading to an increased net non-bonding interaction between the radicals. A large population of the triplet may cause the spin-paired dimer structure to collapse, via an increased interplanar distance, and consequently destabilize the lattice. While the gain in vibrational entropy is most likely driving the transition from the low to the high temperature phase, the aforementioned intra-stack mechanism of magnetism potentially assists the process. The calculated exchange interactions of the high temperature phase have negligible magnitudes $(2J_{I-II})^{DFT} = 4$ cm^{-1} and $2J_{\text{II-III}} = 7 \text{ cm}^{-1}$ at 75 K in Table 2) indicating that the sudden rise of paramagnetism above 58 K is stemming from non-interacting S = 1/2 spins within the weakly bound pairs of I-II and II-III.

Table 2. Calculated Exchange Interactions^{*a*} of Pair I-II (2 J_{I-II}^{DFT}) and Pair II-II (2 J_{II-III}^{DFT}) on their X-Ray Determined Geometries at 4 and 75 K employing the UB3LYP/6-311++G(d,p) Level of Theory

Temperature/K	$2J_{\rm I-II}^{\rm DFT}$	$2J_{\rm II-III}^{\rm DFT}$	$2J_{exp}^{a}$
4	-184.8	-8.3	-166.8
75	4.1	7.0	

^{*a*} Exchange interactions are given in cm⁻¹.

In summary, we have identified and investigated a rare spin-transition of a low molecular weight radical composed exclusively by light atoms (C/N/F/H). 1-Phenyl-3-trifluoro-

methyl-1,4-dihydro-benzo[*e*][1,2,4]triazin-4-yl (**3TB**) is the first example of a hydrazyl radical that undergoes such a first-order transition and one of the few air and moisture stable radicals that demonstrate this behavior. The spin transition of **3TB** involves a low temperature diamagnetic (S = o) to a high temperature paramagnetic ($S = \frac{1}{2}$) phase, it occurs at *ca*. 58(2) K, is fully reversible and compared to other examples is relatively sharp and completed within a narrow temperature range 5(1) K. We are currently investigating the observed behavior under different external stimuli.

ASSOCIATED CONTENT

Supporting Information

Crystallographic, magnetic, EPR, CV, DSC data for radical **3TB** along with details of the latest synthetic route to **3TB**, instrumental analyses, computational methodology and coordinates of atoms in pairs I-II and II-III used in computations. This material is available free of charge *via* the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

koutenti@ucy.ac.cy

Notes

The authors declare no competing financial interests.

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