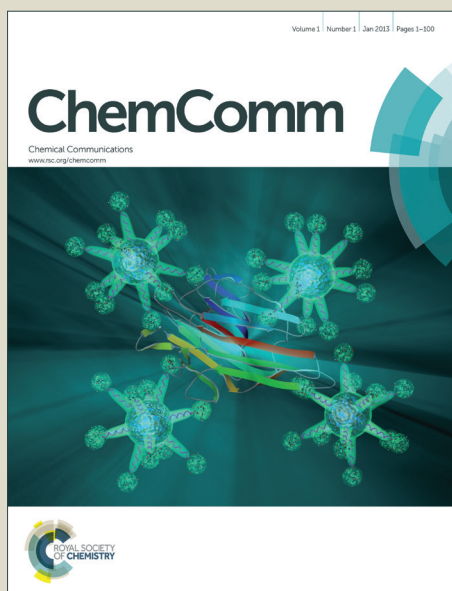


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Towards the tailored design of benzotriazinyl-based organic radicals displaying a spin transition

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The mechanism of the phase transition of 1-phenyl-3-trifluoromethyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl (1), the first reported triazinyl radical to present such feature, is unveiled. In so doing, we identify the key ingredients that are crucial to enable the phase transition in this family of radicals, and how those can be exploited by a rational design of the spin-carrying units.

Research in persistent organic radicals has garnered a great deal of attention in the last few years due to their huge potential in the design of future multifunctional materials and electronic devices.^{1–3} In the quest for new organic radicals, 1,2,4-benzotriazinyl-based radicals have lately emerged as promising building blocks for new functional materials.^{4–10} Most recently, Koutentis and coworkers have reported the first example of a benzotriazinyl radical that undergoes a sharp spin transition.⁹ In particular, it has been shown that 1-phenyl-3-trifluoromethyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl (**1**) (see Fig. 1a, black curve) presents an abrupt first-order phase transition at ca. 58 K between a diamagnetic low temperature (LT) phase and a paramagnetic high temperature (HT) phase, the former associated with a strong antiferromagnetic (AFM) interaction between stacked dimers ($J_f = -185 \text{ cm}^{-1}$), and the latter with small ferromagnetic (FM) exchange interactions ($J_f = +4.1 \text{ cm}^{-1}$).⁹ This phase transition is accompanied by an evident change in the unit cell parameters (most notably a and γ) and in the slippage angle ϕ_1 between dimers (see Section S1). The spin transition discovered in compound **1** suggests that benzotriazinyl radicals can be excellent building blocks for the synthesis of new switchable materials.¹¹ Yet the rational design of other derivatives with higher spin-transition temperatures, possibly accompanied by wide hysteresis loops, is still challenging because the phase transition undergone by **1** is not yet fully understood. Here we present a computational study aimed at

unravelling the driving forces and the mechanism of the phase transition in **1**. We will also identify which structural and electronic factors are crucial in enabling such phase transition, on the basis of a comparison between this compound and 1,3-diphenyl-7-(fur-2-yl)-1,4-dihydro-1,2,4-benzotriazin-4-yl (**2**), which does not feature any phase transition but only a gradual increase of its magnetic response (see Fig. 1a, blue curve).

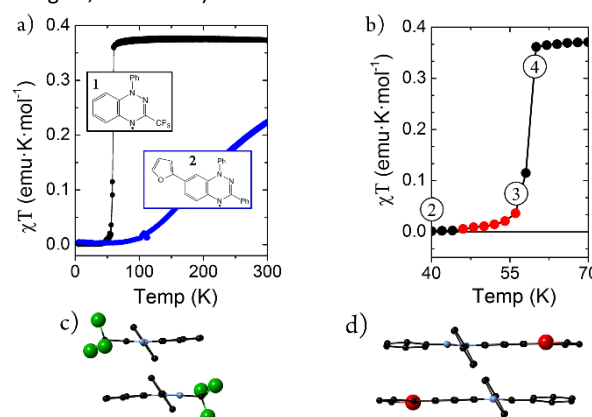


Figure 1. (a) Structure and magnetic properties of radicals **1** (black) and **2** (blue). (b) Inset of the χT values of **1** around $T_{1/2}$. We have highlighted the points with $\chi T \neq 0$ before the jump, and numbered the key steps of the phase transition, as discussed in the main text. Also shown the structure of the dimers of **1** (c) and **2** (d). H atoms are not shown.

Along the manuscript, the two crystalline structures reported for compound **1**, resolved at 4 K (LT-phase) and 75 K (HT-phase) have been referred to as **1-LT_{X-ray}** and **1-HT_{X-ray}**, respectively. In turn, the X-ray structure of compound **2** has been labelled as **2_{X-ray}**. The minimum energy structures found when analysing the potential energy surfaces (PES) of **1** have been labelled as: **1-HT^{HS}**, **1-HT^{LS}**, **1-LT^{HS}** and **1-LT^{LS}**, where we specify the spin state of the dimers (HT or LT) with $S=1$, or LS, with $S=0$), and the phase (HT or LT) that has been used to define the initial coordinates and unit cell parameters. Similarly, since compound **2** has only one phase, the two possible minima have been labelled **2^{LS}** and **2^{HS}**. All the calculations in the crystalline phase were done using supercells and in 3D periodic boundary conditions using the Quantum Espresso code,¹² the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional,¹³ the projector augmented wave (PAW) method,¹⁴ and the plane-wave basis set (PW) with a cutoff energy of 500 eV.

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functional,¹³ and the DFT-D2 parametrization of the Grimme's dispersion correction¹⁴ (see Section S2).⁵

In order to investigate the different magnetic behaviour of compounds **1** and **2**, we have explored their HS- and LS-PES. For compound **1**, calculations performed at the solid-state level revealed two minimum energy structures for the HS configuration (**1-HT^{HS}** and **1-LT^{HS}**), and one for the LS state (**1-LT^{LS}**), which does not feature any minimum close to the structural characteristics of the HT phase (*ie.* there is no **1-HT^{LS}** minimum). For compound **2**, the only reported X-ray crystal structure (**2_{X-Ray}**) was taken as starting structure for an optimization procedure on its LS and HS states, yielding the **2^{LS}** and **2^{HS}** minima, respectively. The resulting cell parameters and main structural variables (distance d , longitudinal ϕ_1 and latitudinal ϕ_2 angles) of the computed minima are in reasonable agreement with those of the corresponding X-ray crystals, and are discussed in Section S3. Additionally, vertical energy gaps have been computed at the different minima, and a semi-quantitative description of the PES of **1** and **2** has been depicted in Fig. 2.

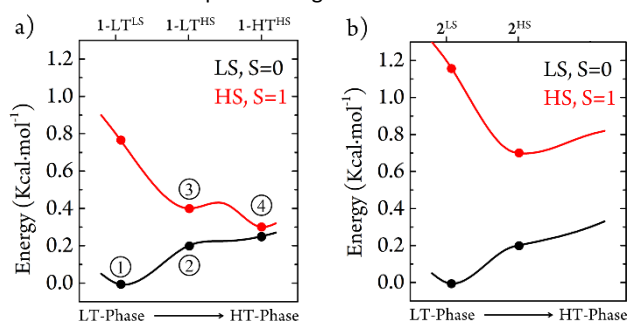


Figure 2. HS- and LS-PES of pair-I dimers of (a) **1** and (b) **2** along the coordinate connecting the different minima. Energies are given per molecule. The energy of the points has been evaluated computationally in the solid state whereas the shape of the lines connecting those points is approximate. The numbered circles correspond to the different steps along the pathway predicted for the phase transition of **1**.

Overall, the results confirm that the phase transition of compound **1** occurs between a diamagnetic **1-LT^{LS}** and a paramagnetic **1-HT^{HS}** phases, whereas the role of the **1-LT^{HS}** polymorph is still unclear. However, since the phase transition requires the population of the triplet HS state (*ie.* the HT phase is only a minimum in the HS-PES), it is intuitive to think that **1-LT^{HS}** phase must be a necessary intermediate step. This hypothesis is further supported by a careful analysis of the magnetic response of **1** (see Fig. 1b). According to the experimentally-reported magnetic measurements, at *ca.* 60 K (before the χT jump) the magnetic response is roughly 10% of the maximum value, reached after the phase transition (0.035 at 56 K vs. 0.375 emu·K⁻¹·mol⁻¹). This 10% corresponds to the population of the triplet HS state at this temperature. Such HS population cannot be explained by the computed J values at **1-LT_{X-Ray}** (−185 cm⁻¹),⁹ which correspond to a population of *ca.* 0.05% at 60 K. Interestingly, we have found that the dominant J value between radicals on **1-LT^{HS}** is −74 cm⁻¹ (see Section S4), which now corresponds to a HS population of *ca.* 8% at 60 K, in much better agreement with the experimental measurements. This fact clarifies the importance of the **1-LT^{HS}** phase, and suggests that the phase transition of **1** is, indeed, a two-step procedure. The first step would happen at temperatures close to $T_{1/2}$, and would imply the jump of some dimers from the LS to the HS state (from **2** to **3**, see Fig. 1a and 2a). This step would be assisted by the population of

higher vibrational levels, responsible to create geometric arrangements (from **1** to **2**) where the J value or, in other words, the vertical line connecting **2** and **3**, is smaller than in the **1-LT^{LS}** minimum, thus allowing the thermal population of the HS state. The second step would occur shortly after, at $T_{1/2}$, and once the 10% of nucleation centres (*ie.* HS dimers) is reached. At this point, the system would have enough energy to abruptly continue the structural transformation up to **1-HT^{HS}** (from **3** to **4**). This proposed mechanism explains all the experimental observations and computational results obtained for **1**, clarifies the role of the **1-LT^{HS}** minimum, and identifies the key parameters that characterize the phase transition of **1**. For instance, the strength of the magnetic exchange coupling (J) between dimers in **1-LT^{HS}** determines at which temperature the crystal achieves the 10% of nucleation centres that is required for the second step of the transition, thereby playing a prime role in defining the observed $T_{1/2}$ for compound **1**. Finally, we would like to stress that, although the spin state switching is essential to reach **1-LT^{HS}** and, eventually, **1-HT^{HS}**, the phase transition is possible (mainly) due to the contribution of vibrational entropy, which is *ca.* two times larger than the electronic entropy change and, thus, must be regarded as the main driving force (see Section S5).

Table 1. Distance (d), longitudinal (ϕ_1) and latitudinal (ϕ_2) angles within dimers in the minima obtained at gas phase for compounds **1**, **2** and **3**. In brackets is shown the change in those variables between the HS and LS state. Also shown the intermolecular interaction energies E_{int} (in kcal·mol⁻¹) and its gradient with respect to a change in d (in kcal·mol⁻¹·Å⁻¹).

		d (Å)	ϕ_1 (°)	ϕ_2 (°)	E_{int}	$\frac{\Delta E_{int}}{\Delta d}$
1	LS	3.18	81.1	76.7	−23.3	2.5
	HS	3.49 (+10%)	74.3 (−8%)	82.7 (+8%)	−22.5	
2	LS	3.19	81.8	75.7	−27.2	3.8
	HS	3.40 (+6%)	79.0 (−3%)	75.9 (+0%)	−26.4	
3	LS	3.21	80.3	81.4	−22.0	1.0
	HS	3.48 (+8%)	72.5 (−9%)	85.2 (+5%)	−21.7	

Once we have addressed the mechanism of the spin transition for compound **1**, we shall now understand why it is the only benzotriazinyl-based compound for which such feature has been reported. The fact that **1-LT^{HS}** is a metastable minimum, indicating that an energy barrier exists in the HS-PES of **1**, between **1-LT^{HS}** and **1-HT^{HS}** (see Fig. 2a), originated in the constraints imposed by the crystal packing (see Section S6), which must be small enough to be overcome at low temperatures. The similarities between the HS- and LS-PES of **1** and **2**, and the fact that the structural differences between the optimized dimers in **2^{LS}** and **2^{HS}** are similar to those observed between the **1-LT^{LS}** and **1-LT^{HS}** polymorphs (see Section S3), prompted us to hypothesize that, indeed, **2^{HS}** might be also (such as **1-LT^{HS}**) a metastable minimum, and that a second minimum, analogous to **1-HT^{HS}**, would exist in the HS-PES of **2**. To answer this question, geometry optimizations of dimers of **2** in their HS and LS states were performed in gas phase (see Table 1 and Section S6), and confirm that **2^{HS}** is, indeed, the only minimum in the HS-PES. Therefore, the absence of a phase transition in **2** can be ascribed to the lack of a HS minima substantially different to the LS minima. It must be also noted that the optimized dimer structures of **1** and **2** are very similar irrespectively of being obtained in isolated conditions

or within the crystal (see Tables 1 and S3), which indicates that their spin transition properties can be rationalized at the molecular level.

We shall now explain the different degrees of distortion undergone by the dimers of **1** and **2** upon spin-state switching. One notable structural difference between them is that the latter has two rings (3-phenyl and fur-2-yl) attached to the central benzotriazinyl unit in an almost-planar fashion, whereas the former does not present any extra ring in the molecular plane. This results in a larger interaction energy (E_{int}) between radicals (see Table 1). Our hypothesis is that such larger E_{int} in **2** precludes a significant structural rearrangement of its dimers upon the spin-state switching. This has been corroborated by means of an evaluation of the changes in E_{int} in response to structural distortions, and by an analysis of its nature via a decomposition of E_{int} into the sum of different energy contributions; dispersion (E_{disp}), electrostatic (E_{el}), Pauli exchange-repulsion (E_{er}) and bonding energy (E_{bond}), following a IMPT-like partitioning (see Section S7).¹⁶ The results obtained show that the HS minimum corresponds to the dimer arrangement for which the sum of E_{disp} , E_{el} and E_{er} is more favourable. In turn, the LS minimum is slightly more stable, and structurally different, essentially as a result of the addition of E_{bond} term, which is proportional to the efficiency of the SOMO-SOMO overlap, and is zero in the HS state. Indeed, since the contribution of E_{bond} is similar for both **1** and **2**, the magnitude of the structural distortion is determined by the evolution of the remaining terms from the HS to the LS minima (see Section S7). Since this evolution is much more pronounced in compound **2** than in **1** ($\Delta E_{int}/\Delta d = 3.8$ vs. 2.5 kcal·mol⁻¹·Å⁻¹, respectively, see Table 1), the loss in bonding energy associated to the population of the HS state can be countered with a smaller structural change, which explains why the HS- and LS- minima are so similar in compound **2**.

The analysis presented above demonstrates that $\Delta E_{int}/\Delta d$ is an indication of the shape of the E_{int} well near the minima, with smaller values of E_{int} leading to smaller gradients ($\Delta E_{int}/\Delta d$). The applicability of this idea has been empirically tested in compound **3**, the original Blatter radical, in which the fur-2-yl ring is removed from compound **2** (ie. substituted by a H atom, see Fig. 1). This compound has been selected because the absence of the fur-2-yl ring must lead to a weaker E_{disp} term, which is the largest contribution to E_{int} . Such change in the chemical structure effectively reduces the strength of E_{disp} and, thus, of E_{int} (from -27.2 in compound **2** to -22.0 kcal·mol⁻¹ in **3**, LS minima). In parallel, $\Delta E_{int}/\Delta d$ has also decreased (from 3.8 to 1.0 kcal·mol⁻¹·Å⁻¹) and, more important, we have achieved a more slipped HS minimum energy structure (ϕ_1 is changed from 3% to 9%). This demonstrates that is possible to rationally modify the degree of structural change between the different spin-state minima in the gas phase. However, it is known that the dimers in the reported crystal structure of **3** present a different crystal packing and no phase transition is observed.¹⁷ This must be the consequence of some interactions originated in the solid state that cannot be captured at the gas-phase level. Nevertheless, these findings encourage the study of isolated pi-dimers in a first screening to identify potentially functional triazinyl derivatives.

In summary, in this work we have identified the mechanism of the phase transition of compound **1**, which occurs between a diamagnetic LT phase in the singlet spin state (polymorph **1-LT^{LS}**) and a paramagnetic HT phase in the triplet state (polymorph **1-HT^{HS}**) and is mediated by polymorph **1-LT^{HS}**. Indeed, we have related the $T_{1/2}$

displayed by **1** to the strength of the magnetic coupling (J) between its dimers in this intermediate structure. Moreover, by comparing the HS- and LS- PES of **1** and **2**, we have ascribed the absence of phase transition in compound **2** to the lack of significant structural differences between its HS- and LS- absolute minima, in contrast to what is observed for **1**. This has been further rationalized by studying isolated dimers of both materials, and has led to the identification of a strategy to modify the shape of the PES of this compounds to achieve larger differences between the spin-states minima. Overall, the findings reported in this manuscript might be an important first step towards the rational design of new benzotriazinyl-based compounds displaying a thermally-driven phase transition.

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Notes and references

‡ This nomenclature refers to structural minima, not the spin state of those structures.

§ An increased slippage implies the reduction of the ϕ_1 angle.

§§ Although the structural change involves several variables, here we have used ϕ_1 in order to quantify the gradient.

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