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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 the first triazinyl radical undergoing a spin transition (1-phenyl-3-trifluoromethyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl) 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.[1-4] In the quest for new organic radicals, 1,2,4-benzotriazinyl-based radicals have lately emerged as promising building blocks for new functional materials.[5-10] 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. 1) 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_I= −185 cm^{-1}), and the latter with small ferromagnetic (FM) exchange interactions (J_I= +4.1 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 with improved properties. Yet the rational design of benzotriazinyl-based compounds 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 the phase transition in **1** on the basis of a comparison between this compound and 1,3-diphenyl-7-(fur-2-yl)-1,4-dihydro-1,2,4-benzotrizin-4-yl (**2**), which does not feature any spin transition but only a gradual increase of its magnetic response.

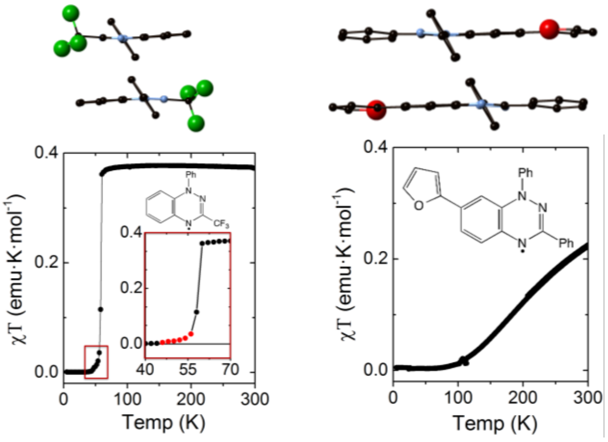

Fig. 1. Chemical structure and magnetic properties of radicals **1** (left) and **2** (right). The inset shows the region around $T_{1/2}$, where we have highlighted the points with *χT≠0* before the phase transition.

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$_{\text{X-ray}}$ and **1**-HT$_{\text{X-ray}}$, respectively. In turn, the X-ray structure of compound **2**, resolved at 100 K, has been labelled as **2**$_{\text{X–Ray}}$. Similarly, the minimum energy structures found when analysing the PES of **1** have been labelled according this scheme: **1**-Phase$^{\text{SpinState}}$, where we specify the spin state of the dimers (HS, 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. Accordingly, the four possible minima have been named: **1**-HT$^{\text{HS}}$, **1**-HT$^{\text{LS}}$, **1**-LT$^{\text{HS}}$ and **1**-LT$^{\text{LS}}$. Since compound **2** has only one phase, the two minima have been labelled **2**$^{\text{LS}}$ and **2**$^{\text{HS}}$.‡ All the calculations in the crystalline phase were carried out using supercells containing 8 molecules and

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x in 3D periodic boundary conditions using the Quantum Espresso code,[11] the PBE functional,[12] and the DFT-D2 parametrization of the Grimme's dispersion correction[13] (see Section S2).[§]

In order to investigate the different magnetic behaviour of compounds **1** and **2**, we have explored the potential energy surfaces (PES) of their LS and HS states. 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 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 qualitative description of the PES of compounds **1** and **2** has been depicted in Fig. 2.

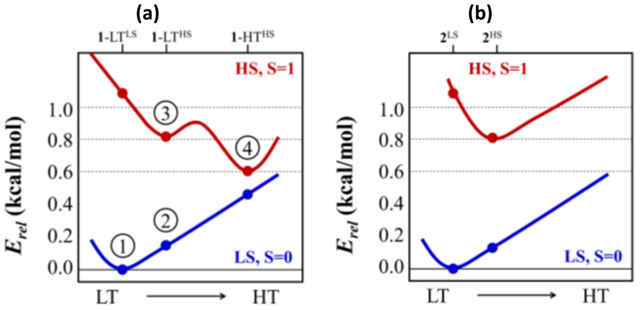

Fig. 2. HS- and LS-PES of compounds (a) **1** and (b) **2** along the coordinate connecting the different minima. The position of the points has been evaluated computationally in the solid state whereas the shape of the lines connecting those points is approximate. The numbered circles correspond to 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 the diamagnetic **1**-LT^{LS} and the 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, 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. 1 inset). 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 (0.035 emu·K^{-1}·mol^{-1} at 56 K), reached after the phase transition (0.375 emu·K^{-1}·mol^{-1}). This indicates that the population of the triplet HS state must also be around 10% at this temperature. Such HS population cannot be explained by the computed *J* values at **1**-LT$_{X\text{-}Ray}$ (−185 cm^{-1}), 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 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. 2a). This step would be assisted by the population of higher vibrational levels, responsible to create geometrical arrangements (from ① to ②) where the *J* value or, in other words, the line connecting ② and ③, is smaller than in the **1**-LT^{LS} minimum. Shortly after, at $T_{1/2}$, once a certain amount of nucleation centres is reached (*ca.* 10%, according to the magnetic response observed before the χT jump), the system would have enough energy to continue the structural transformation up to **1**-HT^{HS} (from ③ to ④). If such scenario is certain, the strength of magnetic exchange coupling (*J*) between dimers in **1**-LT^{HS} determines at which temperature the crystal achieves the nucleation centres required for the second transition, thereby playing a prime role in defining the transition temperature observed for compound **1**. Finally, it must be mentioned that, although the spin state switching is essential, the largest contribution to the stability of the HT phase as the temperature increases is the vibrational entropy (see Section S5), which must be thus regarded as the main driving force for the transition.[14]

Once we have addressed the mechanism of the spin transition of compound **1**, we shall now understand why it is the only benzotriazinyl-based compound for which a phase transition has been reported. The fact that **1**-LT^{HS} is a metastable minima, indicates that it exists an energy barrier at 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** (see Fig. 2b), 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** (hereafter referred to as **2**-HT^{HS}). Overall, the absence of a reported phase transition in compound **2** could be explained by three possible mechanisms. The first possibility would involve the existence of a large energy barrier between **2**^{HS} and **2**-HT^{HS}. If so, the phase transition would be kinetically impeded. The second possible scenario would imply that the **2**^{HS} structure is already the absolute minimum in the PES of the HS state, much more stable than **2**-HT^{HS}. In that case, the phase transition would not be thermodynamically favoured. Finally, the third option would be that the absence of a phase transition is originated by the lack of the second minima (*ie.* **2**-HT^{HS} does not exist). To answer this question, geometry optimizations of compound **2** dimers in its HS and LS states were performed in gas phase (see Table 1 and Section S6). The results confirm that **2**^{HS} is, indeed, the only minimum energy structure in the HS-PES and, thus, allow us to rule out the first two hypotheses. 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. Furthermore, it must be noted that the optimized dimer structures of **1** and **2** are very similar irrespectively of being obtained in isolated conditions or within the crystal, 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 the IMPT partitioning (see Section S7).[15] 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** ($\Delta E_{int}/\Delta\phi_1$= −0.28 vs. −0.11, 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**.

Table 1. Distance (*d*), longitudinal angle (ϕ_1) and latitudinal angle (ϕ_2) of the dimers in the minimum energy structures obtained at gas phase for compounds **1**, **2** and **3**, together with calculated intermolecular interaction energies E_{int} (in kcal·mol^{-1}) and its evolution along a representative coordinate that connects the LS- and HS- minima, in this case ϕ_1.

		d (Å)	ϕ_1 (º)	ϕ_2 (º)	E_{int}	$\frac{\Delta E_{int}}{\Delta\phi_1}$
1	LS	3.18	81.1	76.7	−23.3	−0.11
	HS	3.49 (+10%)	74.3 (−8%)	82.7 (+8%)	−22.5	
2	LS	3.19	81.8	75.7	−27.2	−0.28
	HS	3.40 (+6%)	79.0 (−3%)	75.9 (0%)	−26.4	
3	LS	3.21	80.3	81.4	−22.0	−0.04
	HS	3.48 (+8%)	72.5 (−9%)	85.2 (+5%)	−21.7	

The analysis presented above demonstrates that $\Delta E_{int}/\Delta\phi_1$ is an indication of the shape of the E_{int} well. It thus follows that smaller values of E_{int} lead to smaller gradients ($\Delta E_{int}/\Delta\phi_1$) near the minima. The applicability of this idea has been empirically tested in the hypothetical compound **3**, in which we have removed (substituted by an H atom) the fur-2-yl ring from the chemical structure of **2** (see Fig. 1), with the aim of diminishing the strength of the E_{disp} term, which is the largest contribution to E_{int}. In so doing, we have effectively reduce the strength of E_{int} up to a similar level to that of compound **1** (−21.7 vs. −22.5 kcal·mol^{-1}, HS minima). In parallel, $\Delta E_{int}/\Delta\phi_1$has also decreased (from −0.28 to −0.04 kcal·mol^{-1}·degree^{-1}) and, more important, we have achieved a more slipped HS minimum energy structure, such as in compound **1** (ϕ_1 is decreased by 9% and 8%, respectively)§. The general applicability of this strategy will be further tested in future work, but might be an important first step towards the rational design of benzotriazinyl-based compounds displaying a thermally-driven phase transition.

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 a phase transition in compound **2** to the lack of significant structural differences between its HS- and LS- minima, in contrast to what is observed for **1**. This has been further rationalized by studying isolated dimers of both materials, and has ultimately led to the rational design of compound **3**, for which we have predicted that it might present notably different HS- and LS- minima and, thus, is a candidate to present a phase transition if it would present the adequate crystal packing.[10] Overall, these findings enable the study of isolated pi-dimers in a first screening to identify potentially functional triazinyl derivatives, thus paving the way to the rational design of new switchable materials of this family.

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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