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Evaluating the high-pressure structural response and crystal lattice interactions of the magnetically-bistable organic radical TTTA

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Magnetic bistability has previously been observed and evaluated in an organic thiazyl radical 1,3,5-triathia-2,4,6-triazapentalenyl (TTTA). Herein, the structure-pressure response of TTTA has been evaluated by X-ray diffraction, where a lack of a structural phase transition up to 4.6 GPa certifies that the paramagnetic suppression is caused by a steady decrease in the separation between the moieties containing the radical electron along the π-stacking chains. The intermolecular interactions throughout the crystal lattice have also been calculated using the PIXEL method, and highlight the relative strength of the inter-column interactions in the two known polymorphs of TTTA, which provides extra justification for the cause of the wide magnetic hysteresis and its response to pressure.

Introduction

Magnetism is a property of materials that can be exploited for its response to the application of external stimuli. There is considerable interest in materials that exhibit magnetic bistability, namely the co-existence of two magnetic phases under a range of conditions, for potential application in memory or sensory devices.1-4 The field of magnetic materials has also expanded to include organic molecular magnets,5, 6 consisting of neutral molecular radicals synthesised with sufficient steric and electronic hindrance that the unpaired spins remain on individual molecules. The change in magnetic state then occurs through the ordering or disordering of the unpaired spins throughout the crystal lattice in response to an external stimulus.

One class of organic molecule magnets of significant interest are the heterocyclic thiazyl π-type radicals that contain the 1,3,2-dithiazolyl functional group, which have been shown to exhibit a variety of gradual, abrupt, hysteretic and non-hysteretic spin transition behaviours.7-14 The subject of this paper is TTTA, a planar molecular system consisting of two interconnected 5-membered aromatic rings of C, N and S atoms (Fig 1A).15 The radical electron is formally designated onto the N atom on the –S–N–S– moiety, but has been shown to be mainly delocalised across all three atoms.16-18 TTTA has been the subject of multiple publications investigating its magnetic properties at various experimental conditions. It has been shown to display an abrupt and wide hysteretic magnetic phase transition between a high temperature (HT) paramagnetic (weakly antiferromagnetic) phase and low temperature (LT) diamagnetic phase (T < 230 K and T > 305 K).16, 17, 19, 20 The magnetic phase transition has an associated structural phase transition, between a P21/c polymorph at HT (Fig 1B) and a P1̅ polymorph at LT (Fig 1C), with a minimal volume change between the two polymorphs.16, 17 The crystal lattices of both structures are visually dominated by the presence of columns of π-stacking interactions, with regular π-stacks (···A···A···A···A···)n in the P21/c polymorph (Fig 1B) and distorted π-stacks which include fully-eclipsed π-dimers (···A···A···A···) in the P1̅ polymorph (Fig 1C). Slightly shorter distances occur between the overlapping –S–N–S– moieties in the eclipsed dimer form, which are attributed to the interactions between the unpaired electrons on each molecule (Fig 1D).20 Furthermore, the regular π-stacking in the P21/c polymorph is not static: pair exchange dynamic (PED) behaviour has been observed in which dimerisation along the stacks occurs on the picosecond timescale.21 The structure presented in Fig 1B is therefore a time-average representation.

The large hysteresis loop exhibited between the two magnetic phases has previously been attributed to the strength of the inter-column interactions in both polymorphs,16 but this has never been formally quantified in terms of interaction energies. Clarke et al. and Vela et al. have evaluated the hierarchy of magnetic coupling constants between neighbouring molecules.
Figure 1 Molecular structure of 1,3,5-triathia-2,4,6-triazapentalenyl (TTTA) (A), the crystal packing and intermolecular stacking observed in the room-temperature $P2_1/c$ (B) and $P\overline{1}$ (C) polymorphs, and the intermolecular separation between different moieties in the eclipsed dimer in the $P\overline{1}$ polymorph (D).

Article

throughout the crystal lattices of both polymorphs, and shown that the coupling constants for the intra-column $\pi$-stacking interactions ( $-436 \pm 40$ cm$^{-1}$ for the $P2_1/c$ phase and $-2018 \pm 35$ cm$^{-1}$ for the eclipsed dimer in the $P\overline{1}$ phase) significantly outweighed the inter-column interactions.$^{18,22,23}$ Moreover, the magnetic behaviour of TTTA has been evaluated at various temperatures under the application of pressure.$^{24}$ In these experiments, the transition temperatures $T_\uparrow$ and $T_\downarrow$ shift to higher temperatures with pressure, reaching close to room temperature values (of 275 K and 330 K, respectively) by 1.5 GPa. Across this pressure range, the paramagnetism associated with the $P2_1/c$ phase was gradually suppressed, decreasing by ca. 50% between ambient and 1.5 GPa. No structural characterisation of TTTA under pressure has been published, and thus it is not currently known what is responsible for the paramagnetic suppression.

This current work therefore sets out to explore the high-pressure structural response of TTTA using single-crystal X-ray diffraction, and to quantify the strength of intermolecular interactions in the crystal lattice using the semi-classical density sums PIXEL method. These calculations permit the contribution of the inter-column interaction energies towards the overall crystal lattice stabilisation to be evaluated and monitored as the structure adapts upon crystal compression. Furthermore, the calculations allow for comparison between the intermolecular interaction hierarchies of the known ambient pressure LT ($P\overline{1}$) and HT ($P2_1/c$) phases.

**Methods**

**Synthesis**

TTTA was prepared by a modified version of the method outlined in the literature.$^{15}$

**Crystallography**

Ambient pressure diffraction data was obtained at room temperature from a full sphere collection on a single crystal of TTTA, utilising a series of $\omega$ scans, on a Bruker SMART APEX II in-house laboratory diffractometer with monochromated Mo-Kα X-ray radiation ($\lambda=0.71073$ Å, 17.4 eV). Data sets were then integrated using the program SAINT, with the SADABS absorption correction.$^{25,26}$ Sir92 was utilised for the structure solutions within CRYSTALS, with all data refined against $F^2$. All atoms were refined anisotropically.

High-pressure diffraction experiments were undertaken on a single crystal of TTTA, loaded in a modified Merrill-Bassett diamond anvil cell alongside a ruby crystal (acting as the in-situ pressure calibrant) and the hydrostatic pressure transmitting medium Daphne 7474 (a mixture of silicone oil and 2,2,8,8-tetra-alkylsilane).$^{29-34}$ The high-pressure diffraction data were obtained at the Diamond Light Source I19-EH2 beamline,$^{35}$ utilising the Newport 4-circle $\kappa$-geometry diffractometer, installed with a Pilatus 300 K detector, and tuneable monochromatic X-ray radiation set to 0.4859 Å (25.5 keV) at various pressures up to 4.56 GPa. Data were collected in a series of $\omega$ scans, adapted to avoid shading of the detector from the cell body, with a step size and exposure time of 0.2° and 0.2 s respectively. The data reduction (integration and absorption correction) was undertaken within the CrysAlisPro software.$^{36}$ The structure solutions for the high-pressure data were carried out using CRYSTALS.$^{28}$ The ambient pressure-structure was used as the input model, with the structure allowed to refine against each high-pressure data set and adjust to the updated unit cell parameters. All 1,2 and 1,3 distances were restrained, alongside planar, vibrational and thermal similarity restraints which were applied across the TTTA molecule. The data was refined against $F^2$ with all atoms refined anisotropically (Table S1, Fig. S1 and S2). All crystallographic data have been deposited with the CCDC (CCDC 2080534-2080543) and can be obtained free of charge.
PIXEL Calculations
PIXEL calculations were undertaken on the ambient pressure structures of both polymorphs of TTTA; the structure of the \( P_{2_{1}}/c \) polymorph was that obtained at room temperature from the diffraction experiments undertaken in this current work, alongside an already-published structure of the triclinic \( P\bar{1} \) polymorph (SAXPWO6).\textsuperscript{16} It should be noted the interaction energies calculated refer to the time-averaged structure as obtained by X-ray diffraction and therefore do not take into account the picosecond timescale PED dimerisation effect in the \( \pi \)-stacking columns as identified in previous work.\textsuperscript{21} PIXEL calculations were also undertaken on all the structures obtained from the high-pressure diffraction experiments up to 4.56 GPa.

The molecular electron density of TTTA was calculated using the GAUSSIAN09 program using the literature-established MP2/6-31G** level of theory and basis set combination.\textsuperscript{40, 41} The electron density model for each individual structure was then applied to the PIXEL-C component of the CLP-PIXEL suite,\textsuperscript{38, 42} to calculate the dimer and lattice energies. For all the structures investigated, the entire process was streamlined using the MrPIXEL tool.\textsuperscript{43} Interactions were only considered for molecules that had a centroid position at a distance of up to 15 Å from the central reference molecule. The molecular electron density on each molecule was split into cubed pixels, with dimensions of 0.08 Å, which were then combined into blocks of \( 3 \times 3 \times 3 \) superpixels, a process in line with literature precedents (Table S2-S14, Fig. S3-S6).\textsuperscript{39}

Results and Discussion
Crystallography
The data from the room-temperature ambient-pressure X-ray diffraction experiment confirmed the expected crystallisation of TTTA in the \( P_{2_{1}}/c \) polymorph; the diffuse scattering along the \( b^* \) direction, the indicator of the PED behaviour along the \( \pi \)-stacking direction, was also observed (ESI). Upon application of pressure to 4.56 GPa, TTTA was observed to undergo gradual anisotropic compression, with the majority of compression observed along the \( b \)-axis direction (Fig 2), corresponding to the direction of the \( \pi \)-stacking columns. No indication of any structural phase transition was observed up to 4.56 GPa, despite exceeding the pressure expected to result in the complete suppression of the paramagnetism.\textsuperscript{24} An overall volumetric compression of ca. 19 % was observed at 4.65 GPa, which equates to a bulk modulus of 9.0(4) GPa as determined by the 3\textsuperscript{rd}-order Birch-Murnaghan equation of state (ESI).\textsuperscript{44} This is comparable to other spin-crossover molecular-based materials.\textsuperscript{45, 46}

The average intermolecular separation along the \( \pi \)-stacking direction decreased from 3.7100(2) Å to 3.2672(6) Å throughout the pressure series. This smooth gradual decrease, along with the pressure-induced contraction of unit cell parameters of the \( P_{2_{1}}/c \) polymorph of TTTA, as a comparison to those determined at ambient pressure. Error bars are smaller than symbols used.

PIXEL Calculations
In the \( P_{2_{1}}/c \) polymorph, seventy unique interactions were identified within the cluster radius of 15 Å around the central reference molecule, nine of which exceeded a total interaction energy of 2.5 kJ mol\(^{-1}\) (Fig S3). The strongest interaction, \( 1 \) (light blue, Fig 3), is dominated by dispersion energy, and represents the \( \pi \)-stacking intra-column interaction along the \( b \)-axis direction (Table 1). Interactions 2 and 3 (orange and grey respectively, Fig 3), which have a broadly similar total interaction energy to 1 (Table 1), have greater contribution from the Coulombic energy term and relate to inter-column lateral interactions with short N···S contacts. As shown in Fig 3, the combination of these three strongest interactions are responsible for connecting the majority of the crystal lattice. The only exception is the lack of inter-column connectivity along the \( c \)-axis direction, which is accounted for by interaction 5. All other interactions simply account for additional connections.
between columns (see ESI for complete listing).

A similar trend is observed for the $P\bar{1}$ polymorph, with a minimal energy difference between the strongest $\pi$-stacking interaction (representing the staggered dimer interaction) and the two strongest lateral inter-column interactions. Energies and contribution energy terms are very similar to those calculated for the $P2_1/c$ polymorph (see Table 1). The eclipsed dimer (interaction 18), which was previously determined to exhibit the strongest antiferromagnetic coupling constant in the $P\bar{1}$ polymorph due to direct overlap of unpaired spins,\textsuperscript{18, 23} provides a much lower contribution to its lattice energy in the $P2_1/c$ polymorph. With a total interaction energy of just -2.2 kJ mol$^{-1}$, this masks large stabilising dispersion (-61.7 kJ mol$^{-1}$) and large destabilising repulsion (+108.5 kJ mol$^{-1}$) energy terms, the latter arising due to the close contact of $\pi$-electron clouds of neighbouring molecules.

These results have provided a much clearer picture of the construction of the crystal lattices of both polymorphs, in terms of the relative importance of the intra-column $\pi$-stacking interactions and lateral inter-column interactions. Previous publications on TTTA have eluded to the presence of strong inter-column interactions as the source of crystal lattice stability, and thus the large magnetic hysteresis loop,\textsuperscript{16} and this has been substantiated by these calculations; the importance of inter-column interactions towards stabilising the crystal lattice.
has been clearly highlighted here, with the strongest inter-column interactions, 2 and 3 for both polymorphs, calculated to be of similar net interaction energy to that calculated for the strongest π-stacking interactions.

The PIXEL method was also applied to all the high-pressure structures of the P2₁/c polymorph; Figure 4 shows the change in each of the component terms of the lattice energy (the summation of all interactions found within the 15 Å spherical cluster around the reference molecules) with increasing pressure to 4.6 GPa. Across the pressure series, a strengthening of attractive energy terms (coulombic, polarisation and dispersion) is readily apparent, but this is outweighed by a strengthening of the repulsion term due to the greater propensity for overlapping electron clouds as the intermolecular separation decreases, thus resulting in a gradual weakening of the total lattice energy. However, by 4.6 GPa, the total lattice energy has remained negative, and thus the combination of all of the intermolecular interactions still act to stabilise the crystal lattice.

Figure 5 shows the change in the total interaction energy of 1, 2 and 3 across the pressure series as a function of decreasing intermolecular separation (i.e. the longest distances represent the ambient pressure structure); details of the change of all nine of the strongest interactions are reported in the ESI. As expected, reflecting the trend in the lattice energies, the strongest interactions generally weakened across the pressure series, with the growth in the repulsion term outweighing that of the other component energy terms. For the three strongest interactions highlighted in Figure 3, all three showed considerable weakening with the decrease in intermolecular separation (see Figure 5); 1, in particular, which corresponds to the π-stacking interaction along the b-axis, was calculated to turn net-repulsive by the final two pressure points. Given that the volumetric pressure response of TTTA is dominated by b-axis compression, it is unsurprising that this large geometric response relates to a significant change in interaction energy. The inter-column interactions with the shortest N···S contacts (2 and 3) remain net stabilising by the highest pressure point. In other magnetic bistable radical species, such as 1,2,5-thiadiazolo[3,4-b]-1,3,2-dithiazolo[3,4-b]pyrazin-2-yl (TDP-DTA) and naphtho-1,3,2-dithiazolyl NDTA, radical to dimer phase transitions do occur on decreasing temperature, with the transitions in both species involving very little structural changes in order to accommodate the transitions. Considering the interactions in the P2₁/c polymorph in TTTA are still attractive at 4.5 GPa, and the transition to the P -1 polymorph at pressure would require a large re-orientation of the molecules. Collapse or structural phase transitions in the P2₁/c polymorph of TTTA at increasing pressure, further highlight the stabilising importance of these highlighted intermolecular interactions in the crystal lattice construction.

Conclusions

This current investigation sought to determine if a structural transition was responsible for the suppression of paramagnetism seen in the high-temperature monoclinic phase of TTTA under the application of pressure, similar to that observed for the diamagnetic triclinic phase upon cooling. The series of high-pressure X-ray diffraction experiments revealed that no structural phase transition from the P2₁/c polymorph, to the P1 polymorph or otherwise, took place. Instead, compression of the structure can be characterised by anisotropic compression of the unit cell, with the π-stacking (b-axis) direction accounting for most of the volume compression. The suppression of paramagnetism reported for the P2₁/c polymorph under the application of pressure can simply be attributed to the gradual decrease in separation between neighbouring N–S– moieties, thereby facilitating stronger antiferromagnetic coupling. Through the use of PIXEL calculations, the intermolecular interaction energy hierarchy in both polymorphs of TTTA was evaluated. These calculations...
revealed the strength of the slipped intra-column π-stacking interactions are comparable to the closest inter-column lateral interactions. This justifies previous claims concerning the source of the wide magnetic hysteresis loop in this material and, as observed in this investigation, stabilising the crystal lattice from undergoing a structural phase transition as a response to pressure. The energy hierarchy of intermolecular interactions provides an alternative, yet complementary, view to the order of magnetic coupling constants throughout the crystal lattice. Overall this illustrates the importance of other interactions in the construction of the crystal lattice that are separate to the primary directions of magnetic interaction, and thus provides further understanding which can aid the crystal engineering of such materials.

Conflicts of interest

There are no conflicts to declare.

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