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New cyano-substituted 3-*tert*-butylbenzotriazinyls, **7CN** and **6CN**, were synthesized and their spectroscopic property and magneto-structural correlation were investigated. The radical **7CN** formed a 1D columnar structure and displayed an antiferromagnetic interaction along the column ($J = -15.8 \text{ cm}^{-1}$). The 6-cyano substituted radical **6CN** also formed a 1D columnar structure and exhibited a reversible spin transition at *ca*. 284 K in the range of 6 K. The molecular arrangements in the high-temperature phase (300 K) and low-temperature phase (263 K) were evaluated by an X-ray crystallographic analysis and the molecules slightly rotated while remaining in the 1D columnar structure, resulting in a phase transition. The spin transition behavior was caused by the structural phase transition, which was consistent with the DSC and the computational studies.

Introduction

Organic radicals have been investigated for developing molecule-based multifunctional materials for electronics, spintronics, as well as molecule-based magnets.¹ If their physicochemical properties are changed in response to external stimuli, such as light, heat, and pressure, the material can be used as a switching device by controlling their spin state and molecular arrangement. In the field of magnetism, many metal complexes exhibit a spin crossover (SCO) behaviour induced by thermal or light stimulus to control the spin state of the metal ion.² On the other hand, in organic radical systems, the magnetic property of the organic radicals significantly depends on their molecular arrangement.³ and their structural phase transition is one of the triggers to exhibit a spin transition like SCO phenomena. Several radical derivatives showing a phase transition by changing their molecular assembly in a solid have been reported,⁴ whereas almost all radicals do not demonstrate a spin transition. However, these compounds have been fortuitously discovered in the study of the magnetic property for organic radicals. In general, it is difficult to design a group of radical substances exhibiting a structural phase transition involving a spin transition like the SCO. Therefore, in the investigation of the physicochemical properties, such as the magneto-structural correlation for the analogues of external stimuli-response organic radical systems, is important to discover the molecules

Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan. Email: yoshioka@applc.keio.ac.jp Electronic Supplementary Information (ESI) available: Magnetic data; Crystallographic data; the summery of DFT calculations; EPR, UV-Vis, CV data. CCDC 1524669-1524671. See DOI: 10.1039/x0xx00000x displaying those kinds of interesting properties.

The 1,2,4-benzotriazin-4-yl radical analogue, which was first reported by Blatter and Lukaszewski,⁵ has drawn attention over the past two decades due to its enhanced stability against air and moisture, the facile transformation of the functional group⁶ and interesting physicochemical properties.⁷ In addition, not only a computational study⁸ but also many kinds of facile synthetic routes⁹ have been reported and various derivatives have been prepared. Focusing on the benzotriazinyl analogues, the planar benzotriazinyl radical derivatives, which have a greater spin delocalization, exhibited a ferromagnetic interaction in the 1D columnar structure, providing a new basic skeleton for supramolecular chemistry.¹⁰ Therefore, the benzotriazinyls are promising spin centres for multifunctional materials. Notably, 3CF3 showed a reversible spin transition at ca. 58 K fully completed within 5 K caused by the structural phase transition.¹¹ To the best of our knowledge, it is the only example of a benzotriazinyl exhibiting a spin transition between the paramagnetic and diamagnetic phases. Regarding the hydrazyl radical, 3-(4-cyanophenyl)-1,5dimethyl-6-oxoverdazyl radical exhibited a Spin-Peierls transition at 16 K.¹²



Fig. 1 Molecular structures of 1,2,4-benzotriazine-4-yl derivatives.



Scheme 1 Synthetic route of 3-tert-butyl benzotriazinyls

In the examples where an organic radical exhibited spin transition behaviour caused by a structural phase transition, this was accompanied by packing motif changes between the dimer and columnar structure. Therefore, the construction of a columnar structure using a dimer with a weak π - π interaction may be one of the methodologies to design an organic radical exhibiting the spin transition behaviour. Keeping the size of molecule small may also be beneficial. Based on this view point, it is one of the good approaches to generate a dipole moment by introducing electron donating or withdrawing substituents for the formation of the π -dimer. For cancelling the dipole moment between the molecules, dimerization of the π -radicals can be promoted. In addition, the magnitude of the π - π interaction can be controlled by chemical modification of the bulky group into the radical for formation of the dimer and columnar structure. Recently, we investigated the magneto-structural correlation of the 3-tertbutylbenzotriazinyls carrying an electron withdrawing group and reported that 7CF3 forms an ideal 1D ferromagnetic chain.¹³ As part of our investigation, in the present paper, the synthesis, EPR spectroscopic study and magneto-structural correlation in connection with the computational study of the 3-tert-butylbenzotriazinyls carrying a cyano group at the 7- or 6-position are described, and a reversible spin transition of 6CN at ambient temperature is demonstrated (Figure 1).

Results and discussion

Synthesis

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We first tried to synthesize the 7-cyano benzotriazinyl radical 7CN by applying the Cu-catalyzed C-N coupling and condensation in AcOH according to the literature methods,^{11,13} however, the radical 7CN was obtained in only 8% yield due to the instability of the intermediate aniline. Thus, the cyanosubstituted benzotriazinyls were prepared according to Scheme 1. The chlorination of pivalohydrazide proceeded in a 90% yield. Condensation between compound 3 and the corresponding aniline gave the hydrazonamides 4 (4a:82%, 4b:38%, 4c:61%). The radical precursor 4c was air-sensitive and its appearance was changed from a yellow solid to orange oil in the air. The palladium-catalysed oxidative cyclization^{9a} then afforded the benzotriazinyls (1:87%, 7CN:78%, 6CN:15%). The overall yield of the radicals using 2 as the starting material (1:64%, 7CN:27%, 6CN:8%) was improved compared to that of our previous report¹³ (**1**:34%).



Fig. 2 Temperature dependence of $\chi_m T$ for **GCN**; (a) The temperature range of 1.8-320 K under the applied field of 50 kOe. The two arrows indicate the temperature's changing sign of the observed magnetization in the raw data. The solid line represents the best fit to the Bleaney-Bowers model in the range of 284-320 K (2*J* = -122.8 cm⁻¹, ϑ = -0.69 K, correlation factor $R = \Sigma [\chi_m T_{obs} - \chi_m T_{calcd}]^2 [\Sigma [\chi_m T_{obs}]^2 = 4.58 \times 10^{-5})$ including a 2.6% uncoupled doublet species. (b) Temperature range of 260-290 K under the applied field of 50 kOe. The measurement was carried out for the sample wrapped in paramagnetic Al foil to avoid any discontinuity of the magnetization in the range of 3-250 K. The red circle and blue triangle represent the heating and cooling processes, respectively.



Magnetic property

The thermal behaviour of the magnetic susceptibility for the polycrystalline sample of **7CN** in the temperature range of **1.8** – 300 K is shown in Figure S1. The $\chi_m T$ value gradually decreased with the decreasing temperature, which suggested that the intermolecular antiferromagnetic interaction was

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dominant in the solid state. This observed behaviour was well described by the Bonner-Fisher equation¹⁴ taking into account the molecular field and the best-fit result of $J = -15.8 \text{ cm}^{-1}$ and mean field term $\vartheta = -1.3 \text{ K}$. The crystallographic analysis also supported the result; the radical **7CN** is in close contact for the intermolecular magnetic interaction along the column (See below).

The temperature dependence of the $\chi_m T$ value for **6CN** in the temperature range of 1.8 - 320 K is shown Figure 2. The $\chi_{\rm m} T$ value at 300 K was 0.313 emu K mol⁻¹, which was a lower value than that of the estimated value of the isolated S = 1/2spin (0.375 emu K mol⁻¹). It implied the existence of the intermolecular antiferromagnetic interaction. No change in $\chi_{\rm m} T$ occurred during cooling until 284 K, then an abrupt decrease occurred and plateaued below 280 K. When heating, the $\chi_m T$ exhibited a behaviour similar to the cooling process and a sharp increase took place near 278 K. As shown in the inset of Figure 2, the radical 6CN exhibited a fully reversible transition during the heating and cooling processes in the range of 6 K and the transition was completed in a small thermal range around 280 K. The thermal behaviour of the $\chi_m T$ in the range of 284-320 K can be reproduced by the Bleaney-Bowers dimer model¹⁵ (equation 1) with $2J = -122.8 \text{ cm}^{-1}$ and ϑ = -0.71 K. The thermal behaviour of the $\chi_{\rm m} T$ below 280 K can be roughly reproduced by the Bleaney-Bowers model with -485 cm⁻¹ (Figure S2).

$$\chi_{\rm m} = \frac{N_{\rm A}g^2\mu_{\rm B}^2}{k_{\rm B}} \cdot \frac{1}{T-\theta} \cdot \frac{1}{3+\exp\left(-\frac{2J}{k_{\rm B}T}\right)} \quad (1)$$

To confirm the change in the molecular packing, the DSC measurement was carried out in the range of 250 - 320 K (Figure 3). The DSC curve exhibited an endothermic peak at 283.9 K, which is the corresponding temperature of the spin transition.

X-ray crystallographic analysis

Single crystals of 7CN and 6CN suitable for a crystallographic analysis were obtained by slow evaporation from the mix solvents of CH₂Cl₂ and *n*-hexane. As already described, 6CN exhibited the spin transition at ca. 284 K. The DSC measurement revealed the possibility of a structural phase transition at the corresponding temperature. Thus, Xray crystallographic measurements were carried out at 263 and 300 K. It revealed that 6CN can form two polymorphs in response to the temperature and these polymorphs are referred to as the low-temperature (LT) and high-temperature (HT) phases. Because of the rapid conversion from the HT/LT phase to the LT/HT phase, the reflection data were obtained using the same single crystal at 263 K (LT phase) and 300 K (HT phase). The crystallographic data are shown in Table S1. The ORTEP drawing of 7CN and 6CN are shown in Figure 4 and S3. The bond lengths of the amidrazonyl ring (Table S2) are similar to that of other benzotriazinyls, which suggest that an unpaired electron is delocalized over the benzotriazinyl ring. The dihedral angle between the phenyl ring and π -conjugated system of 7CN is relatively smaller (45.236(80)°) than that of **6CN**, **1** (73.85(6)°) and **7CF3** (82.18(17)°)¹³ due to the crystal packing effect. The crystal of **7CN** belongs to the monoclinic I2/a space group. In the









Fig. 5 Molecular arrangement of (a) HT and (b) LT phases of 6CN. Hydrogen atoms and some *tert*-butyl groups are omitted for clarity.



Fig. 6 Proposed mechanism of phase transition from HT phase to LT phase for 6CN.

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crystal, **7CN** formed a 1D columnar structure due to the π - π interaction between the phenyl ring and π -conjugated system with an ca. 3.6 separation (Figure S4). In the column, the molecules formed an antiparallel stacked arrangement to cancel the dipole moment. On the other hand, the crystal of the HT phase of 6CN belongs to the monoclinic I2/a space group and formed a 1D columnar structure along the b axis due to the weak π - π interaction between the functionalized separation. There is an benzo rings with an ca. 3.3 antiparallel stacked structure in the column to cancel the dipole moment. There was a negligible intermolecular contact without a columnar direction. In contrast, the LT phase belongs to the triclinic P-1 space group and exhibits crystal twinning. The observed data were analysed by the TWINABS $program^{16}$ with the volume fraction parameter = 0483. The bond lengths and dihedral angle are almost the same values as those of the HT phase. Regarding the contacts of the molecules, the intermolecular distance between the π conjugated systems is *ca.* 3.3 , which is slightly shorter than that of the HT phase (Figure 5). The molecules were slightly slipped while maintaining the columnar structure due to the rotation of the molecules arising from the weak π - π interaction (The longitudinal slippage ϕ_1 and latitudinal slippage ϕ_2 are shown in Table S3; these slippages are defined according to the literature¹¹). The ϕ_2 slightly changed with the structural phase transition, however, the ϕ_1 increased 6.4° for the Pair I-II and decreased 4.0° for the Pair II-I'. Therefore, a structural phase transition of **6CN** was induced by the small rotation of the molecules (Figure 6).

Computational study

The DFT calculations using crystallographic geometry were performed at the UB3LYP/6-31G(d) level of theory to estimate the distributions of the singly-occupied molecular orbitals (SOMO) and spin density. The SOMO and spin density distributions for 7CN and 6CN are shown in Figure 7. The SOMO and spin density mainly distributed over the molecules include the substituent and the spin density slightly distributed on the tert-butyl group. For 6CN, there are negligible differences in the SOMO and spin density distributions between the HT and LT phases. To evaluate the contribution of the intermolecular magnetic interaction, the magnitude of interaction J was estimated at the UB3LYP and UBLYP levels and 6-31G(d) basis set. The J value was calculated using equation $J = (E_{BS}-E_T)/(\langle S^2 \rangle_T - \langle S^2 \rangle_{BS})$, where E and S^2 are the total energy and total spin angular momentum, respectively, reported by Yamaguchi and co-workers.¹⁷ For **7CN**, the estimated J values within the column using both the UB3LYP (J = -3.4 cm⁻¹) and UBLYP (J = -8.7 cm⁻¹) functions were negative, suggesting that there was an antiferromagnetic interaction in the column (Table S4). It is consistent with the experimental result. Focusing on the contact of the SOMO, there were large overlaps of the SOMO and overlap integral, leading to the antiferromagnetic behaviour (Figure S5(a)). The magnitude of the J value of the intermolecular magnetic interaction within and between columns was well reproduced by the UBLYP implied that function. The computation also the

antiferromagnetic interaction was mainly derived from the π - π interaction along the column.

Regarding the radical **6CN**, there were two kinds of contacts in both the HT and LT phases and the *J* values were also



Fig. 7 (a) SOMO and (b) spin density distributions of **7CN**(left) and **6CN** (HT: middle, LT: right) at UB3LYP/6-31G(d) level of theory.

Table 1 The calculation results of **6CN** at U3LYP/6-31G(d) level. BS and T represent broken symmetry singlet and triplet state.

Pair (Phase)	Spin state	Energy / a.u.	<s<sup>2></s<sup>	2 <i>J</i> / cm ⁻¹
I-II(HT)	BS	-1828.7783900	0.996173	-40.9
	Т	-1828.7782979	2.008510	
I-II(LT)	BS	-1828.7934835	0.737716	-1600
	Т	-1828.7906151	2.008629	
II-I'(HT)	BS	-1828.7760002	1.003631	-4.8
	Т	-1828.7759894	2.008553	
II-I'(LT)	BS	-1828.7940379	0.934801	-358.9
	Т	-1828.7932765	2.008723	

estimated (Table 1, S5). The magnetic property of the HT and LT phases was reproduced by the UBLYP function. The magnitude of the 2J values of the LT phase is much larger than those of the HT phase, indicating that the strong antiferromagnetic interaction was dominant in the pair I-II and pair II-I' of the LT phase, whereas there was a weak antiferromagnetic interaction in the HT phase. Focusing on the molecular arrangement, there are small structural changes in the overlaps of the molecules between the HT and LT phases, however, the contact and overlap of the SOMOs significantly changed (Figure S5(b, c)). The existence of large overlaps of the SOMO in the LT phase lead to an increase in the bonding character and diamagnetic behaviour.

EPR spectroscopic study

The EPR spectra of **7CN** and **6CN** in toluene are shown in Figure S6 and exhibited complex patterns derived from the non-equivalent nitrogen and hydrogen nuclei. The spectra showed a seven-line hyperfine splitting attributed to the three nitrogen nuclei of the benzotriazinyl ring, and the hyperfine splitting of the hydrogen nuclei and nitrogen nucleus of the cyano group were also observed. However, the hyperfine coupling constants (hfccs) derived from the hydrogen nuclei of the tert-butyl group cannot be assigned. The spin density can be estimated by comparing the hfcc, which is proportional to the spin density. The hfcc values were determined by the Winsim program¹⁸ and assigned according to the result of the ENDOR measurement¹⁹ (Table S6). This result indicated that the spin density is distributed over the molecule without the tert-butyl group, which was consistent with the computational study. Comparing the hfccs of the nitrogen nuclei on the benzotriazinyl ring, the hfccs of N2 and N3 for 7CN, and N1 for 6CN were smaller than that of the corresponding nitrogen nuclei for radical 1. This implied that the electron withdrawing cyano group on the 7-position affected the spin density of N2 and N3, which is similar to the 7CF3 system. On the other hand, the substituent on the 6-position mainly affected the spin density of N1, which was smaller than that of 1. Therefore, the spin density of the nitrogen nuclei can be modulated by introducing a substituent on the para-position of the nitrogen nuclei.

Conclusions

The 3-tert-butyl benzotriazinyls carrying the cyano group at the 7- or 6-position were prepared and their physicochemical discussed. The magnetic susceptibility properties measurement revealed that 7CN forms a 1D antiferromagnetic chain with J = -15.8 cm⁻¹ and mean field term of ϑ = -1.3 K, which was derived from the overlap between the SOMOs. The crystallographic study revealed that 7CN formed a 1D columnar structure due to the π - π interaction. The computations supported the experimental results. Surprisingly, in contrast, 6CN exhibited a spin transition at ca. 284 K in the range of 6 K between the paramagnetic HT and diamagnetic LT phases. The spin transition was fully reversible. The DSC measurement implied a structural phase transition at ca. 284 K. The crystallographic analysis revealed that 6CN exhibited a structural phase transition at ambient temperature due to the small rotation of the molecules. The computation using the UBLYP/6-31G(d) level reproduced the observed spin transition behaviour and implied that the phenomena were derived from a transformation of the overlap between the SOMOs and spin density of 6CN due to the structural phase transition. The EPR study and the computations showed delocalization of the spin density over the molecule.

Experimental

General information

Acetonitrile and dichloromethane were distilled from calcium hydride. *N*-phenylpivalohydrazonoyl chloride (3) was prepared according to the literature.²⁰ The other chemicals were purchased from Wako, TCI Chemicals, Junsei Chemical and Sigma-Aldrich and used as received. The ¹H and ¹³C NMR

spectra were recorded by a JEOL JNM-LA 300 spectrometer using tetramethylsilane as the internal reference in CDCl₃. The chemical shifts and coupling constants were expressed in ppm and Hz, respectively. The mass spectroscopy was carried out using a Bruker Ultraflex II(MALDI-TOF, sinapic acid was used as the matrix) and JEOL GC-mate(EI). The IR spectra were recorded using a JASCO FT/IR-4100 (KBr method) and Bruker ALPHA FTIR spectrometer (ATR method). The crystal data were collected using a Bruker D8 Venture with MoKa (0.71073 Å) radiation. For the radical 7CN, the structures were solved by the direct method using SHELXT-2013 and refined by the F^2 full matrix least squares using SHELXL-2013 in the Bruker APEX-II program package. For the radical GCN, the structures were solved by the Intrinsic Phasing method using SHELXT-2013 and refined by the F^2 full matrix least squares using SHELXL-2014 in the Bruker APEX-III program package.²¹ The magnetic susceptibility measurements were performed using a Quantum Design MPMP-XL SQUID magnetometer. The diamagnetic contribution from the sample holder and samples estimated using the Pacault method²² (-1.82×10⁻⁴ emu mol⁻¹) were corrected. The X-band EPR spectra were recorded using a Bruker E500 spectrometer. The signal positions were calibrated by a Bruker ER035M teslameter. The samples were degassed by the freeze-pump-thaw method. The elemental analyses were carried out at the Central Laboratory of the Faculty of Science and Technology, Keio University. Computational studies were carried out using the Gaussian 09

Preparation of N, N'-diphenylpivalohydrazonamide (4a)

program package.²³

A mixture of N-phenylpivalohydrazonoyl chloride (277 mg, 1.31 mmol), aniline (0.120 mL, 1.31 mmol) and triethylamine (0.201 mL, 1.44 mmol) in EtOH(2.0 mL) was stirred for 16 h at room temperature under a nitrogen atmosphere. The reaction mixture was extracted with CH₂Cl₂, washed with water, dried over Na₂SO₄ and evaporated under reduced pressure. The residue was purified by column chromatography on SiO₂ $(CH_2Cl_2 / n-hexane = 2 / 3 as eluent)$ to afford a colourless solid. Yield: 287 mg, 1.07 mmol, 82%; mp: 76-78 °C; ¹H NMR(CDCl₃, 300 MHz) δ: 7.25-7.16(m, 4H), 6.96-6.94(m, 3H), 6.88(t, 1H, J = 7.2 Hz), 6.77(t, 1H, J = 7.2 Hz) 6.62(d, 2H, J = 7.8 Hz), 5.34(s, 1H), 1.26(s, 9H); 13 C NMR(CDCl₃, 75 MHz) δ : 145.57, 143.14, 141.12, 129.20, 129.00, 120.33, 119.14, 115.67, 112.70, 37.90, 27.77; HRMS(EI): Calcd. for $C_{17}H_{21}N_3[M]^+$: m/z = 267.1735, Found 267.1735; IR(KBr pellet, cm⁻¹): 3378, 3338, 3050, 2966, 1598.

Preparation of 3-*tert*-Butyl-1,4-dihydro-1-phenyl-1,2,4-benzotriazin-4-yl (1)

To a solution of *N*, *N*'-diphenylpivalohydrazonamide (325 mg, 1.22 mmol) and a catalytic amount of 10% Pd/C in $CH_2Cl_2(4.5 mL)$ was added DBU (0.182 mL, 1.22 mmol) and stirred for 16 h at room temperature. The reaction mixture was concentrated and the residue was purified by column chromatography on neutral alumina (CH_2Cl_2 / *n*-hexane = 1 / 3 as eluent) and recrystallized from *n*-hexane to afford a reddish-black crystal.

Yield: 280 mg, 1.06 mmol, 87%; mp: 107-109 °C (lit.¹³ 106-108 °C), identical to the authentic sample.

Preparation of *N*-(4-cyanophenyl)-*N*'-phenylpivalohydrazonamide (4b)

A mixture of N-phenylpivalohydrazonoyl chloride (297 mg, 1.41 mmol), 4-aminobenzonitrile (167 mg, 1.41 mmol) and triethylamine (0.216 mL, 1.55 mmol) in EtOH(2.0 mL) was stirred for 1 d at room temperature under a nitrogen atmosphere. The reaction mixture was extracted with CH₂Cl₂, washed with water, dried over Na₂SO₄ and evaporated under reduced pressure. The residue was purified by column chromatography on SiO₂ (CH₂Cl₂ / n-hexane = 2 / 1 as eluent) to afford an orange solid. Yield: 158 mg, 0.540 mmol, 38%; mp: 54-57 °C; ¹H NMR(CDCl₃, 300 MHz) δ : 7.50(d, 2H, J = 8.7 Hz), 7.22(t, 2H, J = 7.8 Hz) 6.97(d, 2H, J = 7.8 Hz), 6.93(s, 1H), 6.83(t, 1H, J = 7.5 Hz), 6.61(d, 2H, J = 8.7 Hz), 1.25(s, 9H); ¹³C NMR(CDCl₃, 75 MHz) δ: 145.22, 145.00, 141.31, 133.67, 129.16, 120.00, 119.47, 115.25, 112.95, 102.67, 38.11, 27.67; HRMS(EI): Calcd. for $C_{18}H_{20}N_4[M]^+$: m/z = 292.1688, Found 292.1686; IR(KBr pellet, cm⁻¹): 3330, 2966, 2363, 2219, 1601.

Preparation of 3-*tert*-Butyl-7-cyano-1,4-dihydro-1-phenyl-1,2,4benzotriazin-4-yl (7CN)

То а solution of N-(4-cyanophenyl)-N'phenylpivalohydrazonamide (90 mg, 0.308 mmol) and a catalytic amount of 10% Pd/C in CH₂Cl₂(2.0 mL) was added DBU (0.046 mL, 0.308 mmol) and stirred for 16 h at room temperature. The reaction mixture was concentrated and the residue was purified by column chromatography on neutral alumina (CH₂Cl₂ / n-hexane = 1 / 3 as eluent) and recrystallized from CH_2Cl_2 / *n*-hexane to afford a greenish-black crystal. Yield: 69 mg, 0.238 mmol, 78%; mp: 117-119 °C; LRMS(MALDI): Calcd. for $C_{18}H_{17}N_4[M]^+$: m/z = 289.2, Found: 289; IR(ATR, cm⁻) ¹): 2956, 2222, 1581; Elem. Anal.: Calcd. for C₁₈H₁₇N₄: C 74.72, H 5.92, N 19.36, Found: C 74.87, H 5.95, N 18.98; CCDC number: 1524670.

Preparation of *N*-(3-cyanophenyl)-*N*'-phenylpivalohydrazonamide (4c)

A mixture of N-phenylpivalohydrazonoyl chloride (526 mg, 2.50 mmol), 3-aminobenzonitrile (296 mg, 2.51 mmol) and triethylamine (0.383 mL, 2.75 mmol) in EtOH (2.5 mL) was stirred for 24 h at room temperature under a nitrogen atmosphere. The reaction mixture was extracted with CH₂Cl₂, washed with water, dried over Na2SO4 and evaporated under reduced pressure. The residue was purified by column chromatography on SiO₂ (EtOAc / n-hexane = 1 / 4 as eluent) to afford a yellow solid which turn orange oil in the air. Yield: 446 mg, 61%; ¹H NMR(CDCl₃, 300 MHz) δ : 7.30(t, 1H, J = 7.8 Hz), 7.24-7.14(m, 3H), 6.97(d, 2H, J = 8.1 Hz), 6.90(m, 2H), 6.83(t, 1H, J = 7.3 Hz), 6.75(dd, 1H, J = 8.1 Hz, 2.7 Hz), 5.49(s, 1H), 1.26(s, 9H); ¹³C NMR(CDCl₃, 75 MHz) δ: 145.27, 142.18, 141.84, 130.050, 129.09, 123.69, 119.84, 119.64, 118.87, 118.36, 113.01, 112.93, 38.00, 27.66; HRMS(EI): Calcd. for $C_{18}H_{20}N_4[M]^+$: m/z = 292.1688, Found 292.1672; IR (KBr pellet, cm⁻¹): 3350, 2965, 2229, 1600.

Preparation of 3-*tert*-Butyl-6-cyano-1,4-dihydro-1-phenyl-1,2,4benzotriazin-4-yl (6CN)

То N-(3-cyanophenyl)-N'а solution of phenylpivalohydrazonamide (393 mg, 1.34 mmol) and a catalytic amount of 10% Pd/C in CH₂Cl₂ (5.0 mL) was added DBU (0.250 mL, 1.37 mmol) and stirred for 23 h at room temperature. The reaction mixture was concentrated and the residue was purified by column chromatography on SiO₂ (EtOAc / n-hexane = 1 / 10 as eluent) and recrystallized from CH₂Cl₂ / n-hexane to afford a black crystal. Yield: 57 mg, 15%; mp: 180-181 °C; LRMS(MALDI): Calcd. for $C_{18}H_{17}N_4[M]^+$: m/z =289.2, Found: 289; IR (ATR, cm⁻¹): 2958, 2217, 1590; Elem. Anal.: Calcd. for C₁₈H₁₇N₄: C 74.72, H 5.92, N 19.36, Found: C 74.65, H 5.89, N 19.05; CCDC number: 1524671(300 K), 1524669(263 K).

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- (a) P. M. Lahti, Magnetic Properties of Organic Materials, Marcel Dekker, New York, 1999; (b) J. S. Miller and M. Drillon, Magnetism: Molecules to Materials II, Molecule-Based Materials, Wiley-VCH, New York, 2001; (c) ed. R. G. Hicks, Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds, Wiley, Chichester, UK, 2010; (d) I. Ratera and J. Veciana, Chem. Soc. Rev., 2012, 41, 303-349; (e) C. P. Constantinides and P. A. Koutentis, Adv. Heterocycl. Chem., 2016, 119, 173-207.
- (a) O. Kahn and C. J. Martinez, *Science*, 1998, **279**, 44-48; (b)
 C. Janiak, *Dalton Trans.*, 2003, 2781-2804.
- 3 (a) P. M. Allemand, G. Srdanov and F. Wudl, J. Am. Chem. Soc., 1990, 112, 9391-9392; (b) M. Yao, S. Asakura, M. Abe, H. Inoue and N. Yoshioka, Cryst. Growth Des., 2005, 5, 413-417; (c) M. Yao, H. Inoue and N. Yoshioka, Chem. Phys. Lett., 2005, 402, 11-16; (d) N. Yoshioka, in Advances in Organic Crystal Chemistry: Comprehensive Reviews 2015, ed. R. Tamura and M. Miyata, Springer Japan, Tokyo, Japan, 2015, ch. 34, pp. 669-688.
- 4 (a) K. Mukai, Bull. Chem. Soc. Jpn., 1969, 42, 40-46; (b) K. Awaga, T. Sugano and M. Kinoshita, Solid State Commun., 1986, 57, 453-456; (c) W. Fujita and K. Awaga, Science, 1999, 286, 261-262; (d) J. L. Brusso, O. P. Clements, R. C. Haddon, M. E. Itkis, A. A. Leitch, R. T. Oakley, R. W. Reed and J. F. Richardson, J. Am. Chem. Soc., 2004, 126, 8256-8265; (e) W. Fujita, K. Awaga, R. Kondo and S. Kagoshima, J. Am. Chem. Soc., 2006, 128, 6016-6017; (f) B. D. Koivisto, A. S. Ichimura, R. McDonald, M. T. Lemaire, T L. K. hompson and R. G.Hicks,

Journal Name

J. Am. Chem. Soc., 2006, **128**, 690-691; (g) Y. Morita, S. Suzuki, K. Fukui, S. Nakazawa, H. Kitagawa, H. Kishida, H. Okamoto, A. Naito, A. Sekine, Y. Ohashi, M. Shiro, K. Sasaki, D. Shiomi, K. Sato, T. Takui and K. Nakasuji, *Nat. Mater.*, 2008, **7**, 48-51; (h) A. Alberola, D. J. Eisler, L. Harvey and J. M. Rawson, *CrystEngComm*, 2011, **13**, 1794-1796; (i) S. Matsumoto, T. Higashiyama, H. Akutsu, S. Nakatsuji, *Angew. Chem. Int. Ed.*, 2011, **50**, 10879-10883.

- 5 H. M. Blatter and H. Lukaszewski, *Tetrahedron Lett.*, 1968, **9**, 2701-2705.
- 6 (a) C. P. Constantinides, P. A. Koutentis and G. Loizou, Org. Biomol. Chem., 2011, 9, 3122-3125; (b) Y. Takahashi, Y. Miura and N. Yoshioka, Chem. Lett., 2014, 43, 1236-1238; (c) A. Bodzioch, M. Zheng, P. Kaszyński and G. Utecht, J. Org. Chem., 2014, 79, 7294-7310.
- 7 (a) B. Yan, J. Cramer, R. McDonald and N. L. Frank, *Chem. Commun.* 2011, **47**, 3201-3203; (b) C. P. Constantinides, E. Carter, D. M. Murphy, M. Manoli, G. M.Leitus, M. Bendikov, J. M. Rawson and P. A. Koutentis, *Chem. Commun.* 2013, **49**, 8662-8664; (c) C. P. Constantinides, A. A. Berezin, M. Manoli, G. M. Leitus, G. A. Zissimou, M. Bendikov, J. M. Rawson and P. A. Koutentis, *Chem. Eur. J.*, 2014, **20**, 5388-5396; (d) Y. Miura and N. Yoshioka, *Chem. Phys. Lett.*, 2015, **626**, 11-14; (e) M. Jasiński, J. Szczytko, D. Pociecha, H. Monobe and P. Kaszyński, *J. Am. Chem. Soc.*, 2016, **138**, 9421-9424; (f) F. Ciccullo, N. M. Gallagher, O. Geladari, T. Chasse, A. Rajca and M. B. Casu, *ACS Appl. Mater. Interfaces*, 2016, **8**, 1805-1812.
- 8 (a) M. Fumanal, S. Vela, J. Ribas-Arino and J. J. Novoa, *Chem. Asian J.*, 2014, 9, 3612-3622; (b) M. Fumanal, S. Vela, J. J.
 Novoa and J. Ribas-Arino, *Chem. Commun.*, 2015, 51, 15776-15779.
- 9 (a) P. A. Koutentis and D. Lo Re, Synthesis 2010, 2075-2079; (b) C. P. Constantinides, E. Obijalska and P. Kaszyński, Org. Lett., 2016, 18, 916-919. (c) J. A. Grant, Z. Lu, D. E. Tucker, B. M. Hockin., D. S. Yufit, M. A. Fox, R. Kataky, V. Chechik and A. C. O'Donoghue, Nat. Commun., 2017, 8, 15088; (d) A. C. Savva, S. I. Mirallai, G. A. Zissimou, A. A. Berezin, M. Demetriades, A. Kourtellaris, C. P. Constantinides, C. Nicolaides, T. Trypiniotis and P. A. Koutentis, J. Org. Chem., 2017, 82, 7564-7575.
- 10 P. Kaszyński, C. P. Constantinides and V. G. Young Jr., Angew. Chem. Int. Ed., 2016, **55**, 11149-11152.
- C. P. Constantinides, A. A. Berezin, G. A. Zissimou, M. Manoli, G. M. Leitus, M. Bendikov, M. R. Probert, J. M. Rawson and P. A. Koutentis, *J. Am. Chem. Soc.*, 2014, **136**, 11906-11909.
- (a) K. Mukai, N. Wada, J. B. Jamali, N. Achiwa, Y. Narumi, K. Kindo, T. Kobayashi and K. Amaya, *Chem. Phys. Lett.*, 1996, 257, 538-544; (b) K. Mukai, Y. Shimobe, T. Hamamoto and K. Kindo, *Physica B*, 2000, 284-288, 1647-1648.
- 13 Y. Takahashi, Y. Miura and N. Yoshioka, *New J. Chem.*, 2015, **39**, 4783-4789.
- 14 J. C. Bonner and M. E. Fisher, *Phys. Rev.* 1964, **135**, A640-A658.
- 15 B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, 1952, **214**, 451-465.
- 16 *TWINABS Ver. 2012/1*, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
- 17 K. Yamaguchi, H. Fukui and T. Fueno, Chem. Lett., 1986, 625.
- 18 Public EPR Software Tools: Winsim Spectral Simulation for MS Windows 9x, NT v0.98; D. A. O'Brien, D. R. Duling and Y. C. Fann, NIEHS, National Institute of Health, Bethesda, MD.
- 19 F. A. Neugebauer and G. Rimmler, *Magn. Reson. Chem.* 1988, **26**, 595-600.
- 20 Y. Takahashi, R. Matsuhashi, Y. Miura and N. Yoshioka, Chem. Eur. J., 2018, accepted. (The authors would like to cite accepted article and reference will be corrected when doi number is given.)

- 21 APEX-II, APEX-III, Bruker AXS Inc., Madison, Wisconsin, USA, 2012.
- R. R. Gupta, in Landolt-Börnstein New Series Group II, ed. K. H. Hellwege and A. M. Hellwege, Springer, Berlin, Germany, 1986, Vol. 16, ch. 1.2, pp. 4-5.
- 23 Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

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