Anomalous Magnetic Behaviour Induced by

a Structural Phase Transition with Anisotropic

Thermal Expansion in a Spirodiradical

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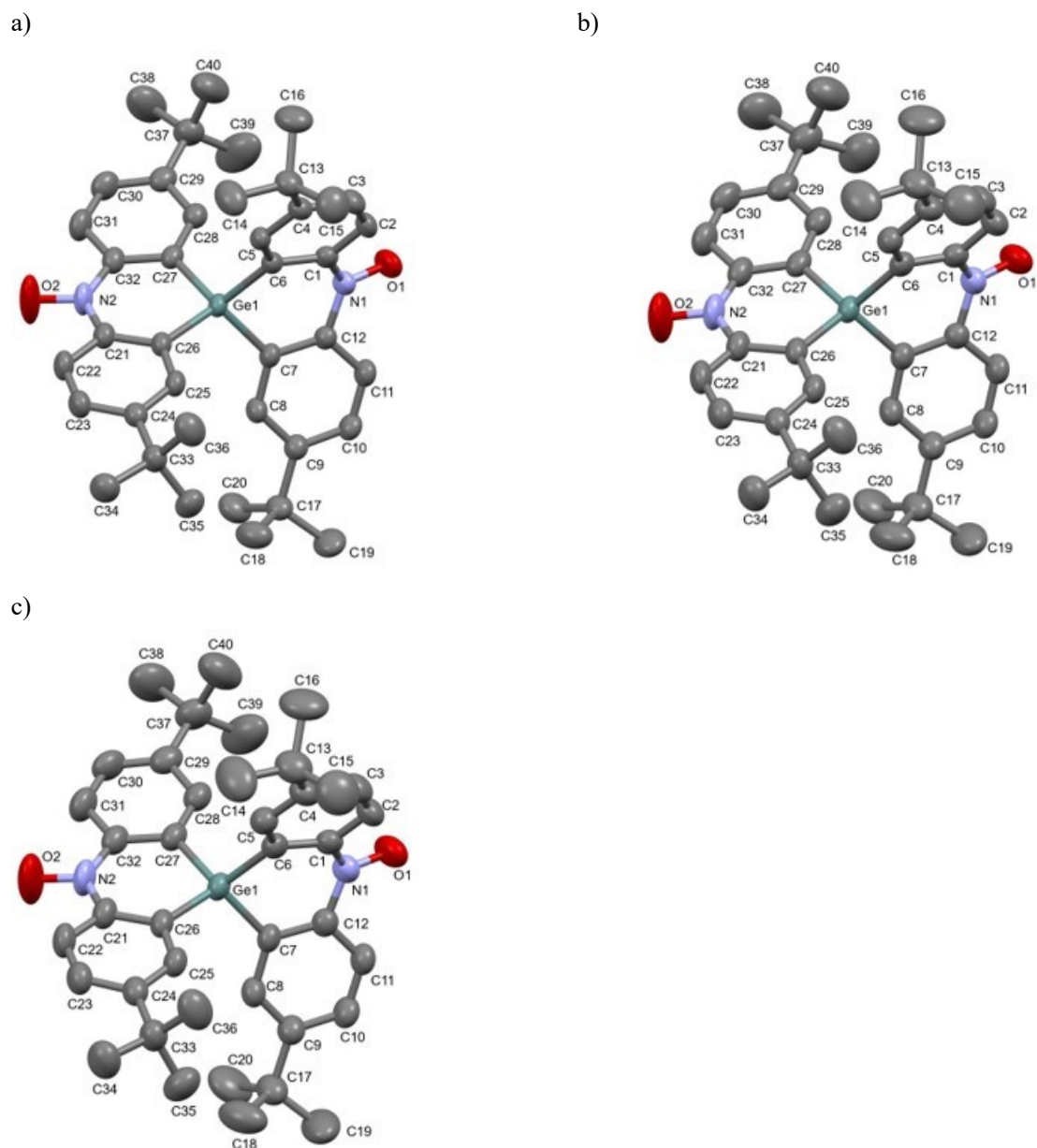Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo, 162-8603, Japan

Fig. S1. Crystal structures for **1-Ge** at (a) 220, (b) 250 and (c) 280 K. Thermal ellipsoids for non-hydrogen atoms are drawn at the 50% probability level. The H atoms are omitted for clarity. (b,c) The major configuration is shown in disordered *tert*-butyl groups (C14/C15/C16 and C39).

Table S1. Cell parameters for **1-Ge** in 90–300 K.

T / K	90	100	110	120	130	140
a/Å	12.404(5)	12.423(5)	12.429(5)	12.450(5)	12.464(5)	12.445(7)
b/Å	25.416(8)	25.431(9)	25.422(10)	25.439(9)	25.442(9)	25.376(14)
c/Å	11.303(5)	11.311(5)	11.316(6)	11.331(5)	11.341(5)	11.316(8)
β/°	105.385(9)	105.378(10)	105.360(10)	105.355(11)	105.359(10)	105.334(14)
V/Å^3	3436(4)	3446(4)	3448(4)	3461(4)	3468(4)	3446(6)
T / K	150	160	170	180	190	200
a/Å	12.481(5)	12.511(5)	12.503(3)	12.526(3)	12.540(3)	12.566(4)
b/Å	25.418(10)	25.445(9)	25.404(6)	25.410(6)	25.388(6)	25.379(6)
c/Å	11.348(6)	11.369(6)	11.349(4)	11.363(3)	11.364(4)	11.378(4)
β/°	105.336(10)	105.324(9)	105.277(7)	105.274(7)	105.275(8)	105.296(7)
V/Å^3	3472(5)	3490(4)	3478(3)	3489(3)	3490(3)	3500(3)
T / K	210	220	230	240	250	255
a/Å	12.588(3)	12.626(3)	12.680(4)	12.744(11)	13.162(5)	13.178(6)
b/Å	25.345(5)	25.316(6)	25.291(8)	25.20(2)	24.563(8)	24.547(11)
c/Å	11.378(3)	11.390(3)	11.410(5)	11.419(13)	11.509(5)	11.510(7)
β/°	105.321(7)	105.322(7)	105.403(8)	105.53(2)	106.643(10)	106.667(13)
V/Å^3	3501(3)	3511(3)	3528(4)	3533(10)	3565(4)	3567(5)
T / K	260	265	270	275	280	285
a/Å	13.18(2)	13.219(15)	13.224(4)	13.213(12)	13.23(2)	13.249(3)
b/Å	24.54(4)	24.58(3)	24.562(8)	24.50(3)	24.48(4)	24.570(6)
c/Å	11.51(2)	11.539(15)	11.547(4)	11.498(12)	11.50(2)	11.570(3)
β/°	106.68(5)	106.66(3)	106.652(8)	106.88(2)	106.69(4)	106.604(5)
V/Å^3	3569(17)	3591(13)	3593(3)	3562(10)	3568(18)	3609(2)
T / K	290	295	300			
a/Å	13.22(5)	13.267(3)	13.269(3)			
b/Å	24.50(10)	24.571(7)	24.572(7)			
c/Å	11.53(5)	11.586(3)	11.591(4)			
β/°	106.92(8)	106.566(6)	106.539(6)			
V/Å^3	3570(40)	3620(3)	3623(3)			

Fig. S2. *T*-dependence of cell parameter β.

Fig. S3. DSC curves for **1-Ge**.

Table S2. Intramolecular structural parameters.

T / K	93 [a]	220	250	280
N1–O1 / Å	1.2868(15)	1.284(3)	1.284(3)	1.281(3)
N2–O2 / Å	1.2846(16)	1.283(4)	1.285(4)	1.292(4)
Ge1–C6 / Å	1.944(1)	1.940(2)	1.942(3)	1.946(3)
Ge1–C7 / Å	1.945(2)	1.943(2)	1.942(3)	1.939(4)
Ge1–C26 / Å	1.934(1)	1.929(2)	1.923(3)	1.926(3)
Ge1–C27 / Å	1.942(2)	1.943(3)	1.941(3)	1.939(3)
ϕ_1 (spiro)[b] / deg	84.99	86.07	87.21	87.54
ϕ_2 (acridine; N1)[c] / deg	40.20	40.24	39.29	39.06
ϕ_2 (acridine; N2)[c] / deg	4.61	4.44	6.14	6.31

[a] Ref. [S1]. [b] The torsion angle ϕ_1 is defined as the angle between two dihydroacridine moieties (each 15 atoms) within the same molecule. [c] The torsion angle ϕ_2 is defined as the angle between two terminal phenyl rings (each 6 atoms) within the same dihydroacridine.
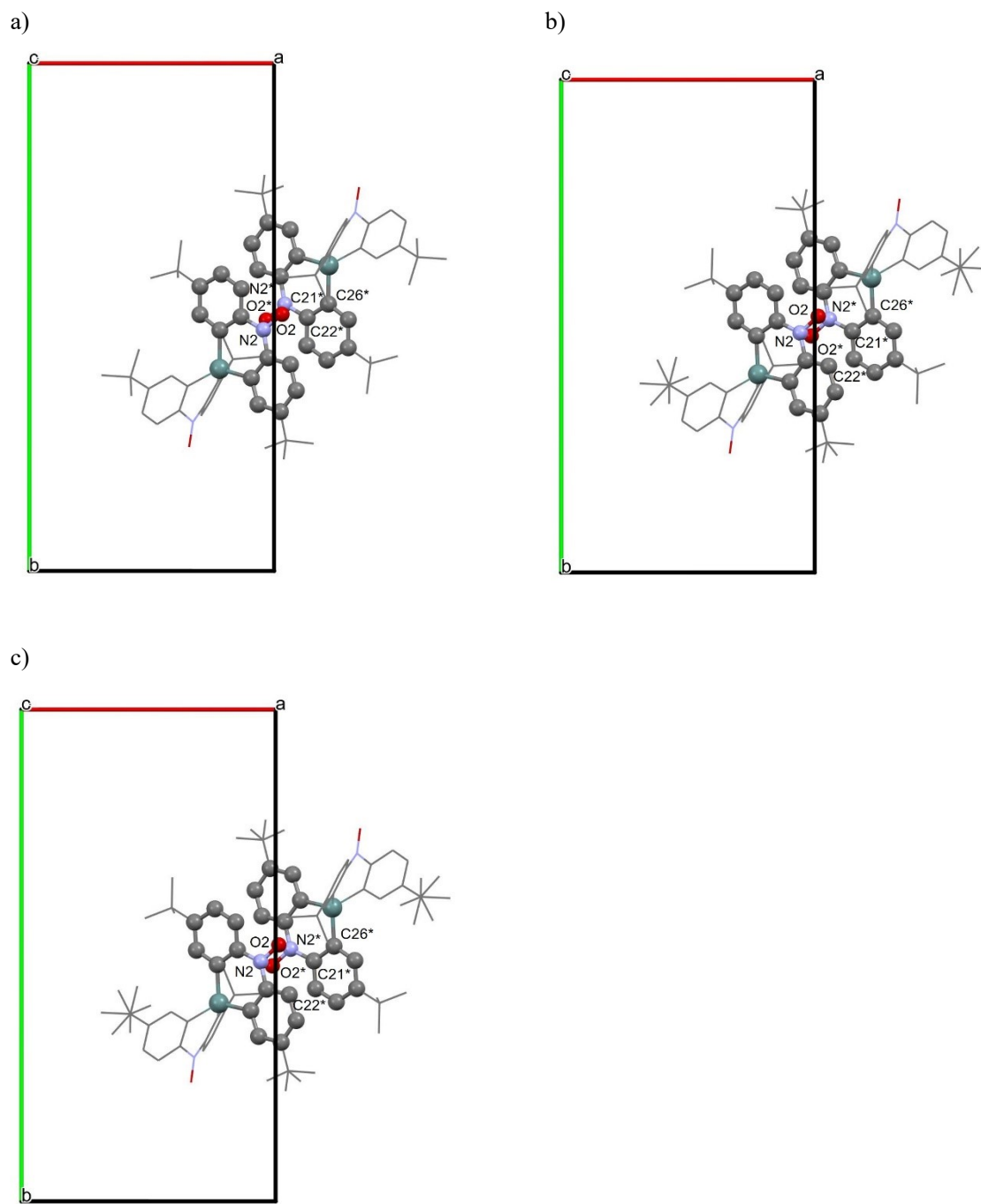
a)

b)

c)

Fig. S4. The structures of the dimer (i) at (a) 220, (b) 250 and (c) 280 K. The symmetric code of * is 2-x, 1-y, 1-z.

Table S3. Intermolecular structural parameters.

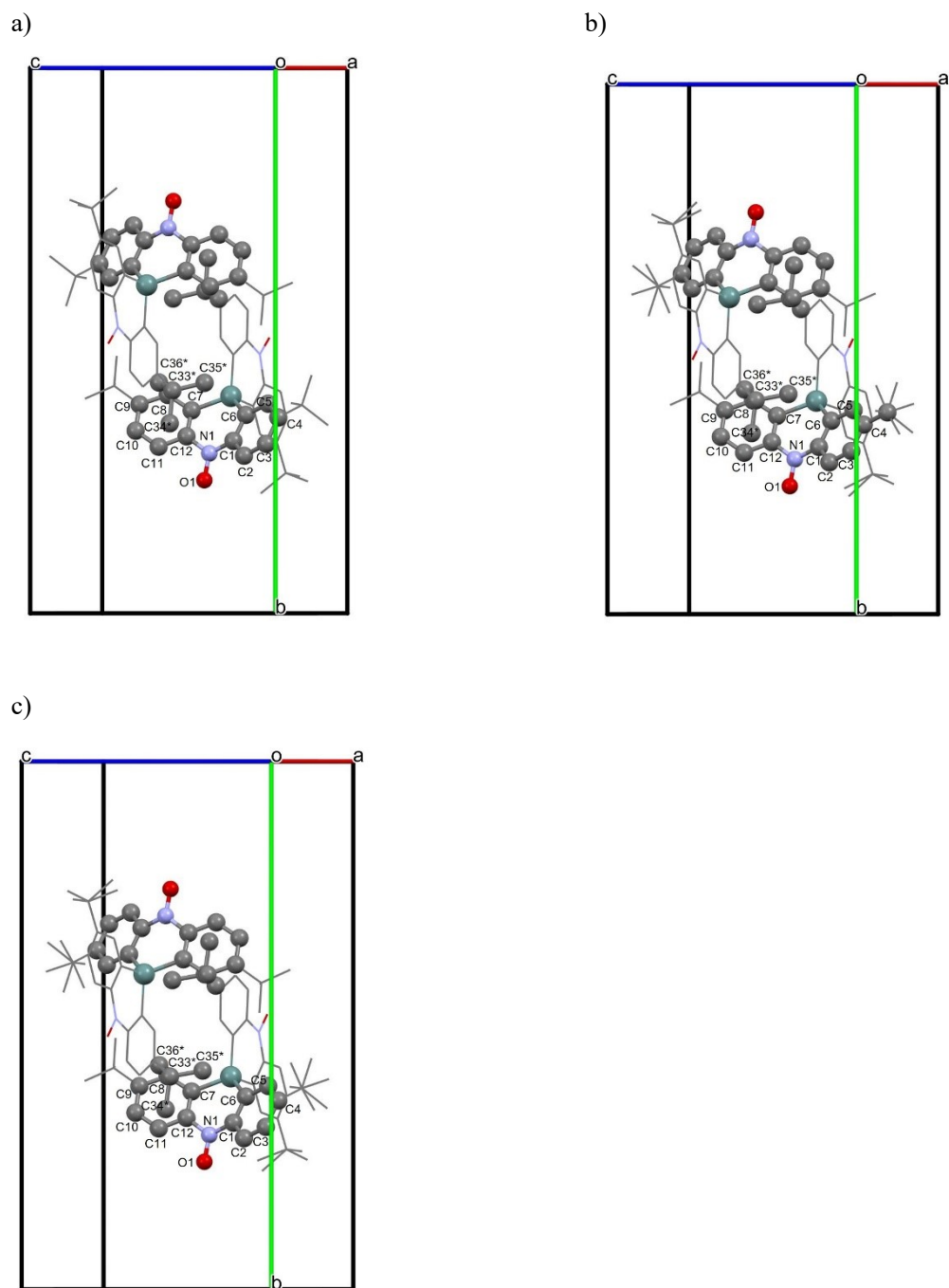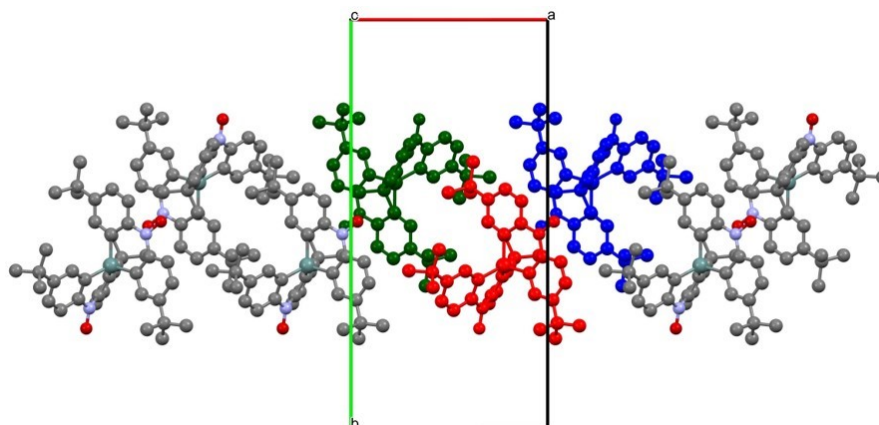| T / K	93 [a]	220	250	280
N2···C21 / Å	3.455(2)	3.484(3)	3.460(4)	3.479(4)
N2···C22 / Å	3.396(2)	3.530(3)	3.781(4)	3.828(4)
N2···C26 / Å	3.985(2)	4.017(3)	4.061(3)	4.076(3)
O2···C21 / Å	3.340(2)	3.349(4)	3.260(4)	3.268(5)
O2···C22 / Å	3.602(2)	3.709(4)	3.892(4)	3.931(5)
O2···C26 / Å	3.395(2)	3.415(3)	3.405(3)	3.411(4)
N2···O2 / Å	3.847(2)	3.732(4)	3.303(5)	3.270(6)
N2···N2 / Å	3.739(2)	3.644(3)	3.273(4)	3.252(4)
O2···O2 / Å	4.349(3)	4.227(5)	3.795(5)	3.761(6)
O2···C8 / Å	3.138(2)	3.132(4)	3.081(4)	3.080(4)

[a] Ref. [S1].

a)

b)

c)

Fig. S5. The structures of the dimer (ii) at (a) 220, (b) 250 and (c) 280 K. The symmetric code of * is 1-*x*, 1-*y*, 1-*z*.
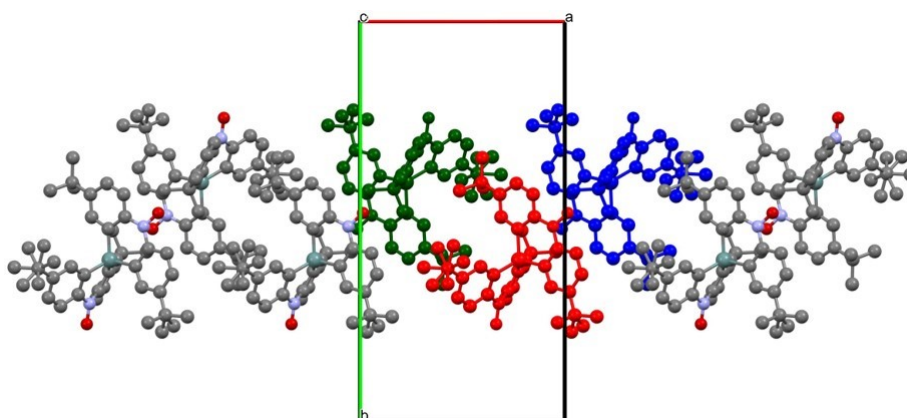
Table S4. Intermolecular structural parameters.

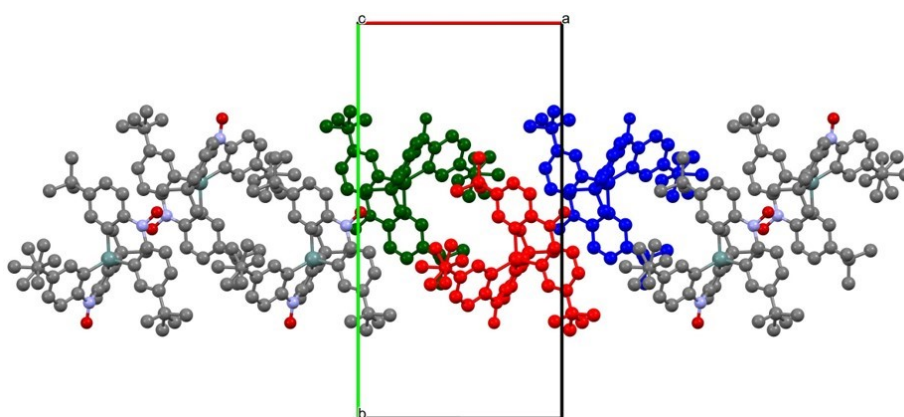| T / K	93 [a]	220	250	280
C19···C27 / Å	3.727(2)	3.823(4)	3.892(4)	3.921(5)
C19···C28 / Å	3.891(2)	4.004(4)	4.001(5)	4.022(5)
C19···C32 / Å	3.737(2)	3.790(4)	3.895(5)	3.918(5)
C20···C31 / Å	3.845(2)	3.943(5)	4.061(5)	4.105(6)
C35···C5 / Å	3.823(3)	3.859(5)	3.925(5)	3.941(7)
C35···C6 / Å	3.861(2)	3.922(5)	3.970(5)	3.984(6)
C36···C7 / Å	3.745(2)	3.783(4)	3.783(5)	3.795(5)
C36···C8 / Å	3.700(2)	3.741(4)	3.769(5)	3.782(5)
C36···C9 / Å	3.686(2)	3.746(3)	3.809(5)	3.829(5)
C36···C10 / Å	3.718(2)	3.783(4)	3.843(5)	3.864(5)
C36···C11 / Å	3.757(2)	3.818(4)	3.849(5)	3.868(5)
C36···C12 / Å	3.737(2)	3.787(4)	3.798(5)	3.814(5)
C39···C9 / Å	3.791(3)	3.975(6)	3.96(2)	4.06(2)
C39···C10 / Å	3.759(3)	3.899(6)	3.84(2)	3.93(2)
C40···C7 / Å	3.669(2)	3.717(5)	3.815(6)	3.837(6)
C40···C11 / Å	3.644(3)	3.606(5)	3.592(6)	3.587(7)
C40···C12 / Å	3.390(2)	3.445(4)	3.492(6)	3.512(6)
C40···C28 / Å	3.745(3)	3.896(5)	4.077(7)	4.131(7)

[a] Ref. [S1].

a)

b)

c)

Fig. S6. One-dimensional structures along the *a*-axis, formed by the combination of the dimers (i) and (ii), as shown in Figs. S4 and S5, respectively, along the *c*-axis at (a) 220, (b) 250 and (c) 280 K. Red, blue and green molecules represent *x*,*y*,*z*, 2-*x*, 1-*y*, 1-*z* and 1-*x*, 1-*y*, 1-*z*, respectively.

Table S5. Intermolecular structural parameters.

T / K	93 [a]	220	250	280
C14···C14 / Å	3.475(2)	3.432(4)	3.270(7)	3.25(1)
C14A···C19 / Å	---	---	3.82(2)	3.78(2)
C14A···C36 / Å	---	---	3.74(2)	3.75(2)
C15A···C18 / Å	---	---	3.43(2)	3.50(2)
C16A···C38 / Å	---	---	3.76(2)	3.80(2)
C16A···C39A / Å	---	---	3.85(5)	3.89(6)
C20···C39 / Å	3.828(3)	3.885(6)	3.85(2)	3.87(2)
C38···C39A / Å	---	---	3.82(2)	3.76(4)
C39···C40 / Å	3.709(3)	3.745(7)	3.85(2)	3.86(2)
C39A···C40 / Å	---	---	3.83(4)	3.85(5)

[a] Ref. [S1].

Table S6. The energy levels and $\langle S^2 \rangle$ in the triplet and singlet spin states for **1-Ge** at 280 K.

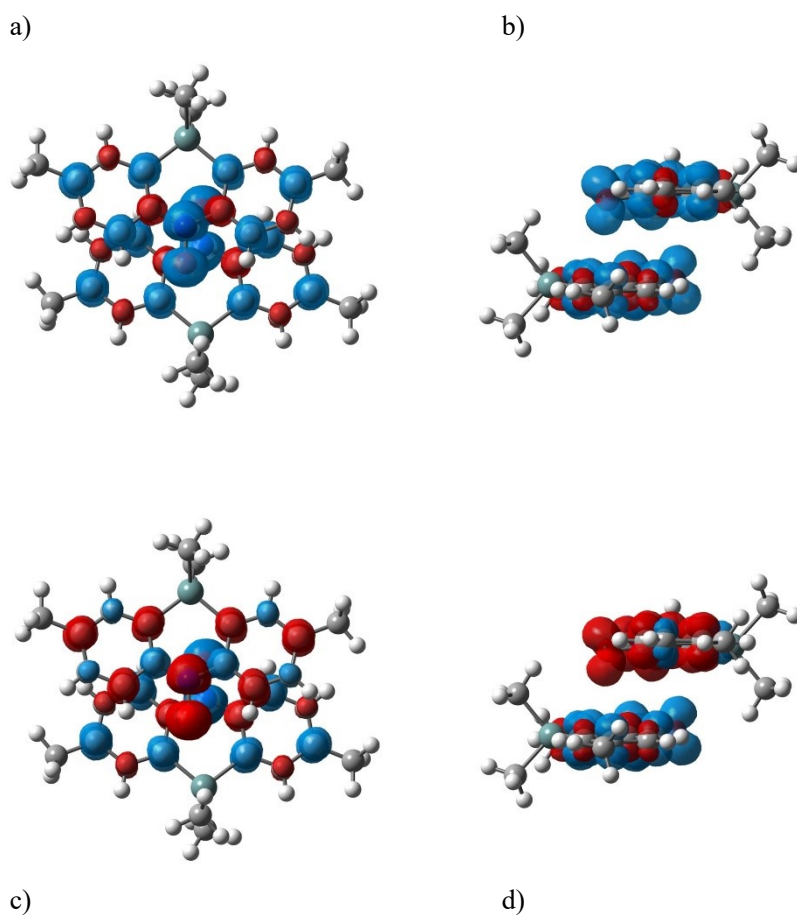| Spin states	E / au	$\langle S^2 \rangle$
$S = 1$ (triplet)	−3889.83608456	2.0004
$S = 0$ (singlet)	−3889.83604686	0.2017

Fig. S7. Spin density maps drawn from the DFT MO calculations accompanied with the dimer (i) in **1-Ge** in the (a, b) triplet and (c, d) singlet states. The geometrical parameters are from the crystallographic results. Blue and red lobes stand for positive and negative spin densities, respectively, with the isocontour of 0.002 e $Å^{-3}$.

Table S7. The energy levels and $\langle S^2 \rangle$ in the triplet and singlet spin states for **1-Ge** (dimer) at 280 K.

Spin states	E / au	$\langle S^2 \rangle$
$S = 1$ (triplet)	-5655.17586761	2.0006
$S = 0$ (singlet)	-5655.17572579	0.2379

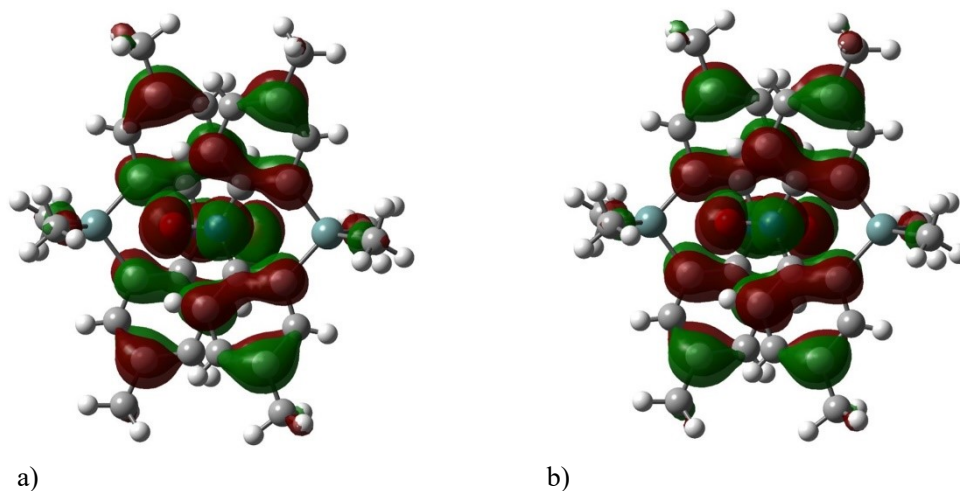a)   b)

Fig. S8. The α spin in two SOMOs, which are (a) #161 (−4.90 eV) and (b) #162 (−5.06 eV), for **1-Ge** with the isocontour of 0.02.

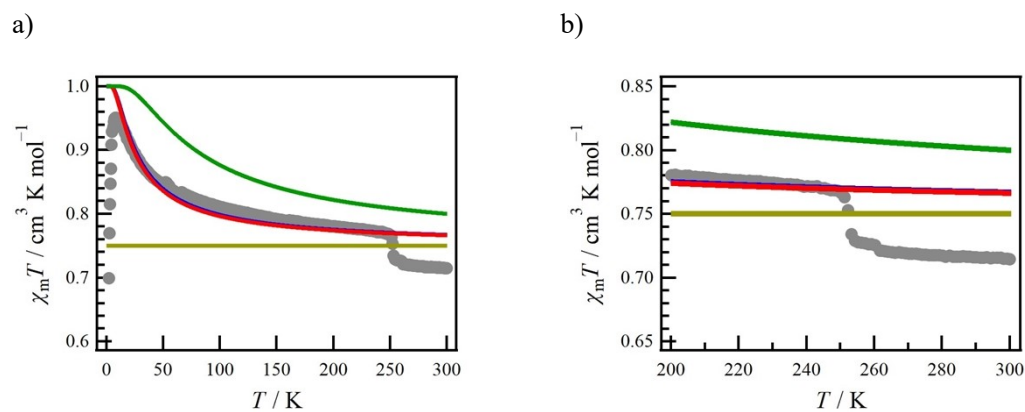a)   b)

Fig. S9. (a) The experimental and simulated $\chi_m T$ vs. T curves for **1-Ge**. The red, blue, green and yellow solid lines are derived from $2J/k_B$ of +13.81, +13.21, +43 and 0 K with g-value fixed at 2.0. (b) Extended view around the transition temperature.

Table S8. The energy levels and $\langle S^2 \rangle$ in the triplet and singlet spin states for **1-Ge** (dimer) at 280 K.

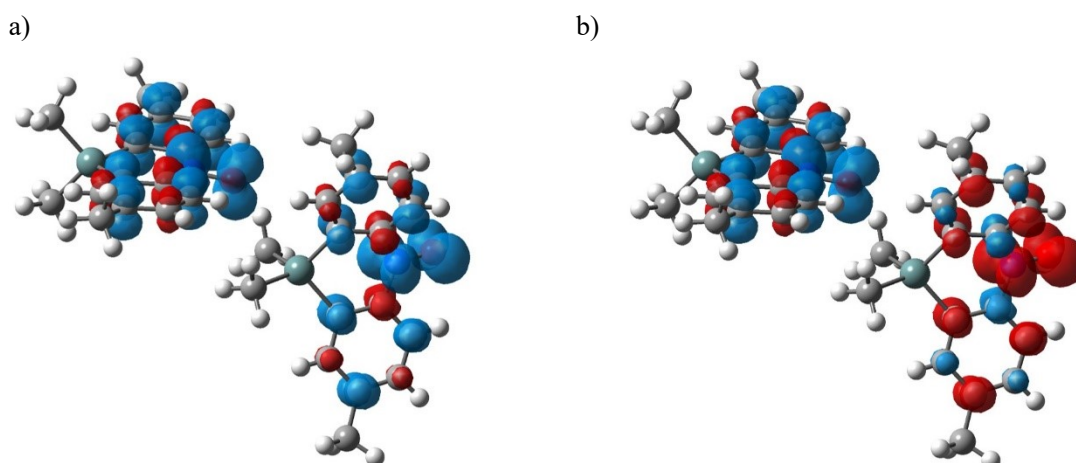|	Spin states	E / au	$\langle S^2 \rangle$	$2J\, k_\mathrm{B}^{-1}$ / K
UB3LYP	$S = 1$ (triplet)	−5655.17729113	2.0005	
/6-311+g(2d,p)	$S = 0$ (singlet)	−5655.17729358	0.2121	−0.865
UM06-X	Triplet	−5654.47169989	2.0005	
/6-311+g(2d,p)	Singlet	−5654.47170126	0.2220	−0.486

a)   b)

Fig. S10. Spin density maps drawn from the DFT MO calculations (UB3LYP/6-311+g(2d,p)) accompanied with the dimer through the CH···O contacts in **1-Ge** in the (a) triplet and (b) singlet states. The geometrical parameters are from the crystallographic results. Blue and red lobes stand for positive and negative spin densities, respectively, with the isocontour of 0.002 e Å^{-3}.

Table S9. The energy levels and $<S^2>$ in the triplet and singlet spin states for **1-Ge** (dimer) at 280 K dependent on parallel shift between the NO dimers (UB3LYP/6-31+g(d,p)).

d / Å	Spin states	E / au	$<S^2>$	$2J'\,k_{\mathrm{B}}^{-1}$ / K
0.000 (STD)	$S = 1$ (triplet)	−5650.90482227	2.0006	
	$S = 0$ (singlet)	−5650.90468881	0.2335	+47.67
−0.075	Triplet	−5650.90497624	2.0006	
	Singlet	−5650.90488737	0.2334	+31.742
−0.175	Triplet	−5650.90521614	2.0006	
	Singlet	−5650.90521755	0.2327	−0.503
−0.275	Triplet	−5650.90546235	2.0006	
	Singlet	−5650.90558372	0.2316	−43.306
−0.375	Triplet	−5650.90551745	2.0006	
	Singlet	−5650.90577935	0.2300	−93.365
−0.475	Triplet	−5650.90556918	2.0006	
	Singlet	−5650.90597959	0.2281	−146.150
−0.575	Triplet	−5650.90541943	2.0006	
	Singlet	−5650.90597203	0.2262	−196.574
+0.125	Triplet	−5650.90461648	2.0006	
	Singlet	−5650.90445373	0.2330	+58.117
+0.225	Triplet	−5650.90449057	2.0006	
	Singlet	−5650.90434251	0.2321	+52.844
+0.325	Triplet	−5650.90438063	2.0006	
	Singlet	−5650.90427408	0.2308	+38.001
+0.425	Triplet	−5650.90427480	2.0006	
	Singlet	−5650.90422757	0.2293	+16.830
+0.525	Triplet	−5650.90417635	2.0006	
	Singlet	−5650.90419600	0.2279	−6.997
+0.625	Triplet	−5650.90418227	2.0005	
	Singlet	−5650.90426607	0.2267	−29.820

Table S10. The energy levels and $<S^2>$ in the triplet and singlet spin states for **1-Ge** (dimer) at 280 K dependent on vertical shift between the NO dimers (UB3LYP/6-31+g(d,p)).

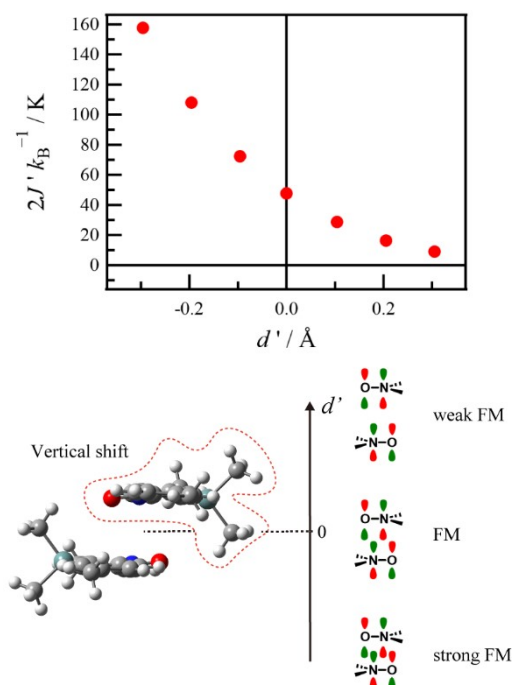| d / Å	Spin states	E / au	$<S^2>$	$2J'\,k_B^{-1}$ / K
0.000 (STD)	$S = 1$ (triplet)	−5650.90482227	2.0006	
	$S = 0$ (singlet)	−5650.90468881	0.2335	+47.67
−0.0956	Triplet	−5650.90346575	2.0006	
	Singlet	−5650.90326317	0.2337	+72.369
−0.1956	Triplet	−5650.90160106	2.0006	
	Singlet	−5650.90129831	0.2338	+108.159
−0.2956	Triplet	−5650.89878713	2.0006	
	Singlet	−5650.89834612	0.2337	+157.545
+0.1044	Triplet	−5650.90582661	2.0006	
	Singlet	−5650.90574654	0.2331	+28.594
+0.2044	Triplet	−5650.90650903	2.0006	
	Singlet	−5650.90646313	0.2328	+16.389
+0.3044	Triplet	−5650.90690688	2.0006	
	Singlet	−5650.90688206	0.2324	+8.860

Fig. S11. Intermolecular interaction constants $2J'/k_B$ dependent on vertical shift between the NO dimers in the HTP state.

References

S1. S. Ogawa, T. Kanetomo, M. Enomoto, Spiro-centre substitution effects in intramolecular spin-spin interactions of spirobiacridine diradicals, *Org. Chem. Front.*, 2024, **11**, 3004–3011.