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CRYSTAL STRUCTURE OF AZAGALVINOXYL - OBSERVATION OF THE RADICAL DIMER IN THE SOLID STATE

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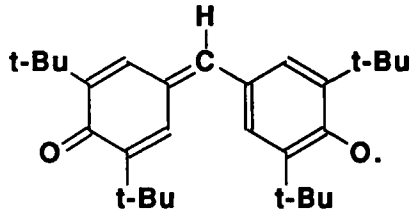
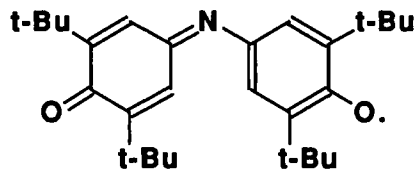
Abstract The molecular structure and crystal packing of azagalvinoxyl radical have been determined by X-ray diffraction. The molecule is far deviated from planar and two aroxy rings are twisted by 47.03°. Relatively strong interaction between two molecules in the unit cell is indicative of the existence of radical dimer which explains the singlet-triplet magnetic behavior of azagalvinoxyl.

INTRODUCTION

Stable organic free radicals prepared from sterically hindered phenols have been known for many years.[1] Among them, the 2,6-di-*t*-butyl-4-(3,5-di-*t*-butyl-4-oxycyalohexa-2,5-dienylidene methyl)phenoxy radical, galvinoxyl, **I**, has received a great deal of attention because of it exhibits ferromagnetic coupling in the solid state.[2] Below 85 K, **I**, however, undergoes a first order phase transition to a very weakly magnetic state.[2a,b] This structural transformation is unknown. The nitrogen analogue, the 2,6-di-*t*-butyl-4-(3,5-di-*t*-butyl-4-oxycyclohexa-2,5-dienylidene amino)phenoxy radical, azagalvinoxyl, **II**, although it has been characterized to be a ground state singlet with a thermally accessible excited triplet state by magnetic susceptibility has been poorly characterized.[2b] Herein we report the magnetic susceptibility and the molecular structure of **II** and is compared to **I**.



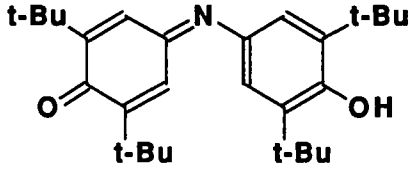
I



II

PREPARATION OF AZAGALVINOXYL

Azagalvinoxyl, **II**, was generated by oxidation of the corresponding phenol, **III**, which synthesized following Coppinger's method[1d,3] with lead peroxide in octane under nitrogen atmosphere. Recrystallization of **II** from *n*-octane under nitrogen in freezer provided greenish-black microcrystalline solid with metallic luster.



III

STRUCTURE

Black plate-like single crystals of **II** were obtained from methylene chloride solution layered with acetonitrile under nitrogen in freezer. The single crystal structure with the triclinic symmetry, space group [$P\bar{1}$ (No. 2), a = 10.672 (5) Å, b = 12.298 (6) Å, c = 10.288 (5) Å, α = 102.81 (4)°, β = 93.13 (4)°, γ = 97.43 (4)°, V = 1300.7 Å^3, Z = 2, $\mu(Mo_{K\alpha})$ = 0.62 cm^{-1}, T = = -100°C, ρ_{calcd} = 1.079 g cm^{-3}, R = 0.046, R_w = 0.043 for 1822 unique reflections ($I \geq 3.0\ \sigma(I)$), $2\theta_{max}$ = 47° for $Mo_{K\alpha}$ radiation (λ = 0.71069 Å) on a Syntex R3 diffractometer]. A labeling diagram and stereoview are presented in Figures 1 and 2. Tables 1 - 5 contain atomic coordinates, anisotropic thermal parameters, bond angle, and inter- and intramolecular interactions.

TABLE 1 Fractional Coordinates, x10^4 Å, and Isotropic Thermal Parameters for II

Atom	x	y	z	B_{ISO}, Å^2
O(1)	4294(3)	-2172(2)	1127(3)	3.3(1)'
O(1')	1510(3)	4643(2)	5890(3)	4.2(1)'
N(1)	4868(3)	1757(3)	4925(3)	2.6(1)'
C(1)	4415(4)	-1285(3)	2010(4)	2.4(1)'
C(1')	2345(4)	4065(3)	5571(4)	2.6(1)'
C(2)	3325(3)	-968(3)	2772(3)	2.1(1)'
C(2')	2166(3)	3183(3)	4282(3)	2.1(1)'
C(3)	3495(4)	20(3)	3709(4)	2.4(1)'
C(3')	3010(4)	2452(3)	4093(3)	2.3(1)'
C(4)	4675(4)	746(3)	4001(3)	2.1(1)'
C(4')	4065(4)	2486(3)	5050(4)	2.3(1)'
C(5)	5736(4)	426(3)	3315(4)	2.3(1)'
C(5')	4323(4)	3451(3)	6180(4)	2.5(1)'
C(6)	5643(4)	-527(3)	2323(3)	2.1(1)'
C(6')	3550(4)	4242(3)	6449(4)	2.3(1)'
C(7)	2051(4)	-1719(3)	2460(4)	2.5(1)'
C(7')	1045(4)	3150(3)	3284(4)	2.4(1)'
C(8)	1055(4)	-1242(4)	3342(4)	3.8(1)'
C(8')	1091(4)	2264(4)	1998(4)	4.1(2)'
C(9)	1543(4)	-1844(4)	1000(4)	3.6(1)'
C(9')	-197(4)	2850(3)	3877(4)	3.3(1)'
C(10)	2168(4)	-2892(3)	2711(4)	3.5(1)'
C(10')	1075(4)	4293(4)	2915(4)	3.6(1)'
C(11)	6750(4)	-809(3)	1496(4)	2.3(1)'
C(11')	3819(4)	5265(3)	7624(4)	2.7(1)'
C(12)	6386(4)	-827(3)	23(4)	3.4(1)'
C(12')	2857(4)	5193(3)	8657(4)	3.6(1)'
C(13)	7123(4)	-1952(3)	1611(4)	3.2(1)'
C(13')	3756(4)	6345(4)	7113(4)	4.1(1)'
C(14)	7930(4)	77(4)	1954(4)	3.6(1)'
C(14')	5141(4)	5357(4)	8296(4)	4.0(1)'
H(3)	2808	242	4206	a
H(3')	2925	1889	3283	a
H(5)	6527	898	3561	a

H(5')	5065	3503	6750	a
H(8)	272	-1724	3119	a
H(8')	952	-513	3207	a
H(8')	396	2255	1391	a
H(8")	1329	-1173	4256	a
H(8"')	1076	1546	2203	a
H(8'")	1865	2444	1613	a
H(9)	742	-2317	819	a
H(9')	2122	-2181	414	a
H(9')	-889	2830	3250	a
H(9")	1447	-1128	837	a
H(9"')	-252	3401	4671	a
H(9'")	-212	2131	4079	a
H(10)	1371	-3355	2510	a
H(10')	2458	-2817	3618	a
H(10')	1851	4465	2528	a
H(10')	383	4274	2294	a
H(10")	1039	4865	3701	a
H(10"')	2765	-3224	2147	a
H(12)	7067	-999	-496	a
H(12')	6182	-107	-37	a
H(12')	2901	4533	8979	a
H(12')	3037	5838	9374	a
H(12")	2026	5162	8245	a
H(12"')	5662	-1382	-298	a
H(13)	7812	-2107	1091	a
H(13')	6416	-2521	1291	a
H(13')	2935	6313	6687	a
H(13')	3920	6981	7845	a
H(13")	4374	6399	6492	a
H(13"')	7359	-1924	2520	a
H(14)	8610	-118	1430	a
H(14')	8189	115	2873	a
H(14')	5752	5440	7669	a
H(14')	5293	6005	9026	a
H(14")	5224	4705	8619	a

H(14")	7747	796	1874	[a]

[a] Hydrogen fixed atom coordinates (B_{ISO} = 3.0 Å^2)

TABLE 2 Anisotropic Thermal Parameters, 10^3 Å, for II

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	43(2)	33(2)	42(2)	4(1)	5(1)	-8(2)
O(1')	41(2)	57(2)	53(2)	29(2)	-7(2)	-16(2)
N(1)	30(2)	36(2)	33(2)	15(2)	1(2)	0(2)
C(1)	34(3)	31(3)	26(2)	9(2)	-1(2)	7(2)
C(1')	33(3)	29(3)	38(3)	11(2)	5(2)	3(2)
C(2)	28(3)	29(3)	23(2)	9(2)	-3(2)	9(2)
C(2')	26(2)	28(2)	28(2)	9(2)	5(2)	8(2)
C(3)	25(3)	40(3)	30(2)	14(2)	-1(2)	12(2)
C(3')	32(3)	27(2)	27(2)	8(2)	2(2)	5(2)
C(4)	33(3)	30(3)	20(2)	16(2)	-1(2)	7(2)
C(4')	25(2)	33(3)	29(2)	12(2)	5(2)	3(2)
C(5)	29(3)	32(3)	28(2)	8(2)	-4(2)	6(2)
C(5')	29(3)	36(3)	27(2)	6(2)	-4(2)	4(2)
C(6)	31(3)	27(2)	22(2)	10(2)	0(2)	7(2)
C(6')	33(3)	29(3)	27(2)	8(2)	-1(2)	6(2)
C(7)	25(2)	34(3)	37(2)	3(2)	-2(2)	12(2)
C(7')	27(2)	35(3)	30(2)	14(2)	0(2)	4(2)
C(8)	33(3)	56(3)	53(3)	-2(2)	2(2)	14(2)
C(8')	50(3)	74(4)	33(3)	32(3)	-12(2)	5(2)
C(9)	33(3)	55(3)	46(3)	-1(2)	-11(2)	16(2)
C(9')	36(3)	43(3)	46(3)	8(2)	-8(2)	8(2)
C(10)	40(3)	41(3)	53(3)	0(2)	-3(2)	17(2)
C(10')	37(3)	54(3)	55(3)	21(2)	0(2)	24(2)
C(11)	30(3)	30(2)	27(2)	7(2)	5(2)	5(2)
C(11')	34(3)	28(3)	36(2)	9(2)	-1(2)	-2(2)
C(12)	43(3)	51(3)	38(3)	18(2)	15(2)	8(2)
C(12')	56(3)	38(3)	39(3)	16(2)	9(2)	-4(2)
C(13)	39(3)	40(3)	48(3)	19(2)	11(2)	9(2)
C(13')	60(3)	36(3)	54(3)	9(2)	-3(2)	-2(2)
C(14)	38(3)	47(3)	53(3)	14(2)	18(2)	7(2)
C(14')	47(3)	46(3)	50(3)	12(2)	-6(2)	-11(2)

Unlike nearly flat molecules packing in the crystal of I,[4] significantly large twist angle (47.03°) of two aroxy rings in azagalvinoxyl radical molecule has been observed, Fig. 2. This probably results from the strong repulsion due to the lone paired electrons on nitrogen atom and the smaller C4-N1-C4' bond angle (123.6°) in comparison with the corresponding angle at the central carbon (134°) in galvinoxyl. Also, two aroxy rings in II are found to be unequally twisted, that is, the dihedral angles between ring A, ring B and the C4-N1-C4' plane are 43.8 and 10.9°, respectively. These unequal twist angles and the bond lengths of N1-C4' and C1'-O1' suggest that free radical is mostly localized on ring A and ring B is preferably described as a quinoid ring. There are two molecules in each unit cell with the stacking face-to-face between the planes containing ring A and nitrogen. The distance between two planes is shorter than the normal van der Waals distances, for example, the distance between C4 atoms in two molecules is 3.150 (7) Å. Thus, this strong interaction can be considered as the dimerization of two molecules which is in consistent with the early prediction.[2b] This dimerization mechanism might be relevant to the first-order phase transition found in galvinoxyl at low temperature which cause a dramatic change in its magnetic property.[2a,b]

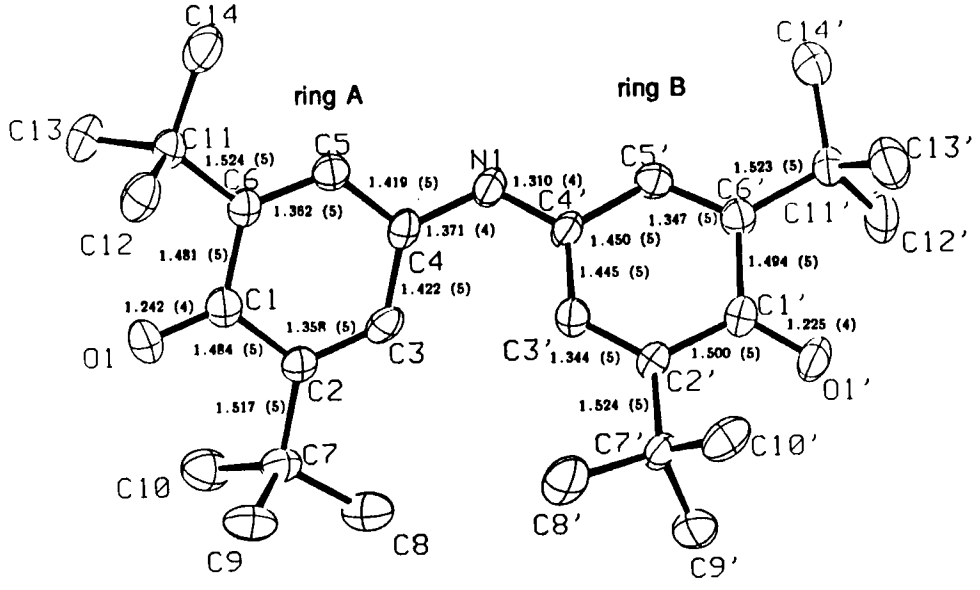


FIGURE 1. Atom labeling diagram of **II**.

TABLE 3 Intramolecular Bond Distance, Å, for **II**

Bond	Distance	Bond	Distance
O(1)-C(1)	1.242 (4)	O(1')-C(1')	1.225 (4)
N(1)-C(4)	1.371 (4)	N(1)-C(4')	1.310 (4)
C(1)-C(2)	1.484 (5)	C(1)-C(6)	1.481 (5)
C(1')-C(2')	1.500 (5)	C(1')-C(6')	1.494 (5)
C(2)-C(3)	1.358 (5)	C(2)-C(7)	1.517 (5)
C(2')-C(3')	1.344 (5)	C(2')-C(7')	1.524 (5)
C(3)-C(4)	1.422 (5)	C(3')-C(4')	1.445 (5)
C(4)-C(5)	1.419 (5)	C(4')-C(5')	1.450 (5)
C(5)-C(6)	1.362 (5)	C(5')-C(6')	1.347 (5)
C(6)-C(11)	1.524 (5)	C(6')-C(11')	1.523 (5)
C(7)-C(8)	1.526 (5)	C(7)-C(9)	1.537 (5)
C(7)-C(10)	1.540 (5)	C(7')-C(8')	1.524 (5)
C(7')-C(9')	1.525 (5)	C(7')-C(10')	1.532 (5)
C(11)-C(12)	1.537 (5)	C(11)-C(13)	1.537 (5)
C(11)-C(14)	1.532 (5)	C(11')-C(12')	1.526 (5)
C(11')-C(13')	1.541 (5)	C(11')-C(14')	1.516 (5)

TABLE 4 Bond Angles, deg, for **II**

Atoms	Angle	Atoms	Angle
C(4)-N(1)-C(4')	123.6 (3)	C(2')-C(3')-C(4')	123.5 (3)
O(1)-C(1)-C(2)	120.2 (4)	C(3)-C(4)-C(5)	119.4 (3)
O(1)-C(1)-C(6)	120.9 (4)	C(3')-C(4')-C(5')	117.7 (3)
O(1')-C(1')-C(2')	119.9 (4)	C(4)-C(5)-C(6)	122.0 (4)
O(1')-C(1')-C(6')	120.4 (4)	C(4')-C(5')-C(6')	123.1 (4)
N(1)-C(4)-C(3)	124.0 (4)	C(1)-C(6)-C(5)	118.7 (4)
N(1)-C(4)-C(5)	116.6 (4)	C(1)-C(6)-C(11)	119.4 (3)
N(1)-C(4')-C(3')	125.0 (3)	C(5)-C(6)-C(11)	121.8 (4)
N(1)-C(4')-C(5')	117.1 (4)	C(1')-C(6')-C(5')	117.3 (3)
C(2)-C(1)-C(6)	118.9 (3)	C(1')-C(6')-C(11')	119.2 (3)
C(2')-C(1')-C(6')	119.7 (3)	C(5')-C(6')-C(11')	123.5 (4)
C(1)-C(2)-C(3)	118.1 (4)	C(2)-C(7)-C(8)	111.9 (3)
C(1)-C(2)-C(7)	120.1 (3)	C(2)-C(7)-C(9)	110.8 (3)
C(3)-C(2)-C(7)	121.8 (4)	C(2)-C(7)-C(10)	110.4 (3)
C(1')-C(2')-C(3')	117.1 (3)	C(8)-C(7)-C(9)	107.1 (3)

C(1')-C(2')-C(7')	119.0 (3)	C(8)-C(7)-C(10)	107.0 (3)
C(3')-C(2')-C(7')	123.9 (3)	C(9)-C(7)-C(10)	109.4 (3)
C(2)-C(3)-C(4)	122.8 (4)	C(2')-C(7')-C(8')	111.0 (3)
C(2')-C(7')-C(9')	110.0 (3)	C(12)-C(11)-C(14)	107.0 (3)
C(2')-C(7')-C(10')	110.1 (3)	C(13)-C(11)-C(14)	107.3 (3)
C(8')-C(7')-C(9')	107.9 (3)	C(6')-C(11')-C(12')	110.9 (3)
C(8')-C(7')-C(10')	107.6 (3)	C(6')-C(11')-C(13')	109.4 (3)
C(9')-C(7')-C(10')	110.1 (3)	C(6')-C(11')-C(14')	110.9 (3)
C(6)-C(11)-C(12)	109.5 (3)	C(12')-C(11')-C(13')	109.4 (3)
C(6)-C(11)-C(13)	111.1 (3)	C(12')-C(11')-C(14')	108.9 (3)
C(6)-C(11)-C(14)	111.8 (3)	C(13')-C(11')-C(14')	107.3 (4)
C(12)-C(11)-C(13)	110.0 (3)		

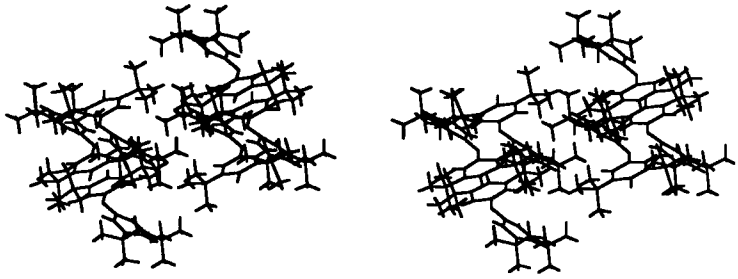


FIGURE 2. Stereoview of the unit cell of **II**.

TABLE 5 Nonbonding Bond Distance, Å, for **II**

Atoms	Distance	Atoms	Distance
O(1)···C(9)	3.014 (5)	O(1')···C(10')[a]	3.380 (5)
O(1)···C(10)	3.018 (5)	N(1)···C(1)[b]	3.395 (5)
O(1)···C(12)	3.027 (5)	N(1)···C(2)[b]	3.359 (5)
O(1)···C(13)	3.000 (5)	C(3)···C(4)[b]	3.348 (5)
O(1')···C(9')	2.999 (5)	C(3)···C(4)[b]	3.348 (5)
O(1')···C(10')	2.996 (5)	C(3)···C(5)[b]	3.307 (5)
O(1')···C(12')	3.013 (5)	C(4)···C(4)[b]	3.150 (7)
O(1')···C(13')	2.986 (5)	C(3)···C(3')	3.045 (5)

[a] -x, 1-y, 1-z [b] 1-x, -y, 1-z

MAGNETIC SUSCEPTIBILITY

The measured paramagnetic susceptibility, χ_p, obey the Curie-Weiss expression above 120 K with an effective moment, μ_{eff} = 2.58 μ_B and θ = -43 K, Fig. 3.[2] Below 120 K the susceptibility can be fit by the Bleaney-Bowers equation[6] (eq. 1 where N = Avogadro's number, g the Lande g factor, k_B the Boltzmann constant, and μ_B the Bohr magneton) with an ΔE_{S-T} (the energy separation between the singlet ground state and the triplet excited state) of 66 cm^{-1} (95 K, 8 meV, 0.2 kcal/mol), Fig. 3. Our result are in a good agreement with the previous report by Mukai who report a ΔE_{S-T} of 60.5 cm^{-1} [2b] and a lower susceptibility due to the "impurity." Our data indicates a higher impurity

$$\chi = [g^2 N\mu_B^2/k_BT] / [3+ \exp(-\Delta E_{S-T}/k_BT)] \quad [1]$$

of S = 1/2 **II** in our sample (5.9%). This experimental curve apparently suggests that **II** consists of the dimers with a singlet ground state and a triplet excited state in the solid state. The structure confirms Mukai's prediction that azagalvinoxyl dimerizes is the solid.[2b]

COMPARISON WITH GALVINOXYL

Although **I** and **II** are isoelectronic, they possess quite different magnetic properties. Magnetic susceptibility of azagalvinoxyl indicates that it consists of a singlet ground state and a triplet excited state whereas **I** exhibits ferromagnetic coupling. The observed radical dimer of **II** by x-ray structure determination is consistent with the data. The phase transition observed for galvinoxyl is not understood. This phase transition might be due to a similar dimerization we observed in azagalvinoxyl, but is unlikely to be similar as this leads to single-triplet, not diamagnetic behavior. Further studies of sterically hindered phenoxy radicals, including the low-temperature structure determination of galvinoxyl are in progress.

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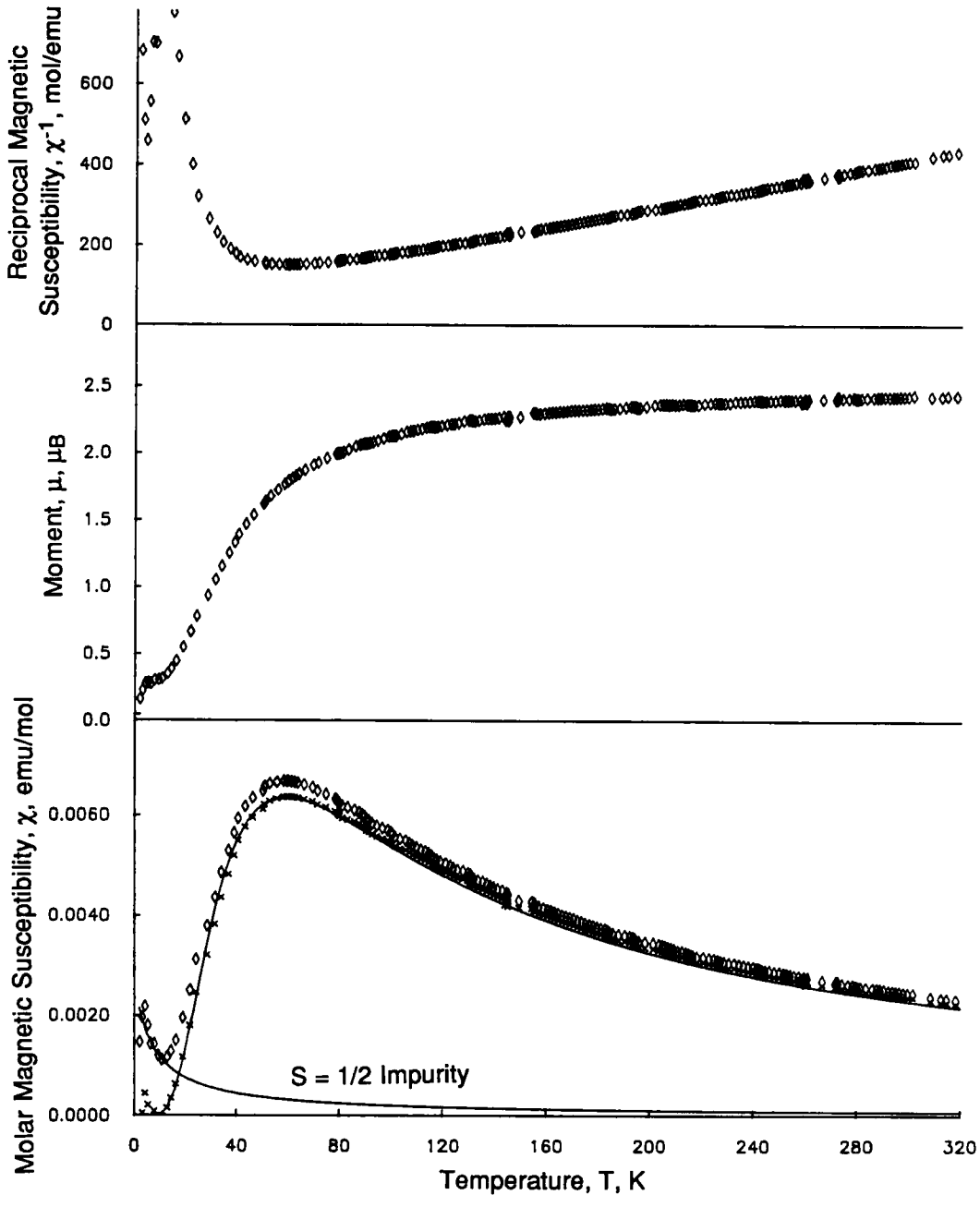

FIGURE 3 Corrected reciprocal molar magnetic susceptibility (top), moment (middle), and corrected molar magnetic susceptibility ( ) and fit to eq. 1 (x) with ΔE_{S-T} of -66 cm^{-1} (bottom) of II vs temperature.

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