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Anomalous Magnetic Properties of Stable Crystalline Phenoxyl Radicals

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The results of static magnetic susceptibility measurements in the 1.8—300°K temperature range are reported on powder samples of the stable aromatic free radicals: 2,6-di-*t*-butyl-4(3,5-di-*t*-butyl-4-oxocyclohexa-2,5-dienylidene methyl) phenoxyl (Galvinoxyl) and 2,6-di-*t*-butyl-4(3,5-di-*t*-butyl-4-oxocyclohexa-2,5-dienylidene amino) phenoxyl (BIP) radicals. The susceptibility of Galvinoxyl follows the Curie-Weiss law above $T_c=81\pm1$°K, depending on the sample, with a Weiss constant of 11 ± 3°K. However, at $T_c=81$°K, χ_p rapidly decreases, and below 66°K the susceptibility again increases, with different spin concentrations for independently-prepared samples as the temperature is lowered. A maximum at 81°K was also found by the EPR measurements; the anomaly of the susceptibility at this temperature is probably due to a first-order phase transition induced magnetically, accompanying the pairing of magnetic spins, judging from the results of differential thermal analysis and the magnetic susceptibility measurements. On the other hand, the magnetic susceptibility of the BIP radical exhibits a broad maximum at 54 ± 2°K. This susceptibility can be explained approximately using a model which consists of a singlet ground state and a triplet state lying slightly above the ground state.

2,6-Di-*t*-butyl-4-R-substituted-phenols produce the corresponding phenoxyl radicals upon oxidation with lead peroxide or, preferably, with an alkaline solution of potassium ferricyanide in various organic solvents. The magnetic properties of these phenoxyls in solution have been studied by a number of investigators with the aid of the electron paramagnetic resonance (EPR) spectra.[1-3]

Solvent-free solids of the phenoxyls produced with such oxidations were studied by Müller *et al.*

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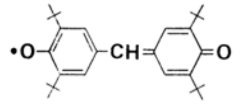
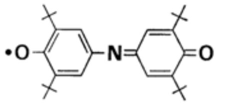
at room temperature[4,5] and, in some cases, at the temperature of liquid nitrogen[6]; they ascertained the absolute paramagnetic contribution to the susceptibility by using Pascal's constants to estimate the diamagnetic correction, χ_d, thus estimating the concentration of the radicals. However, it has not been clear whether or not the observed susceptibility generally follows the Curie-Weiss law.

In a previous paper[7] we have reported an anomaly in the magnetic susceptibility of the Galvinoxyl radical at 82.5°K from the results of the susceptibility measurements between 63°K and 289°K, and have suggested that this radical may have similarities with the well-known anomaly in the magnetic susceptibility of Wurster's blue perchlorate (WB) at 186°K,[8-11] which is explained by the orthorhombic-monoclinic phase transition in which Wurster's blue cations pair up to form dimers with ground singlet states and excited triplet states.[12] Recently, another explanation has been proposed by G. T. Pott *et al.* for the mechanism of the above transition.[13]

In the present paper, first, in order to obtain further information about the transition of Galvinoxyl and the general nature of these neutral radical solids, we have measured the temperature dependence of the magnetic susceptibilities of the solid radicals of a similar molecular structure, including 2,6-di-*t*-butyl-4(3,5-di-*t*-butyl-4-oxocyclohexa-2,5-dienylidene methyl) phenoxyl (Galvinoxyl) and 2,6-di-*t*-butyl-4(3,5-di-*t*-butyl-4-oxocyclohexa-2,5-dienylidene amino) phenoxyl (Bisindophenoxyl; BIP) radical, between 1.8°K and 300°K; these radicals are known to be thermally stable and to be inert to oxygen. Secondly, the measurements of the electron paramagnetic resonance of Galvinoxyl and the differential thermal analyses of the phenoxyl radical and the corresponding phenol were undertaken in order to investigate the properties of the transition.


Galvinoxyl


BIP

+ : tBu

Extensive work, has been performed on other free radical solids,[14-17] especially tetracyanoquinodimethane (TCNQ) salts, in which the electrons interact to form singlet-triplet pairs. The present evidence indicates that such pairing is also present in the BIP radical hindered by tertiary butyl groups, but in the case of Galvinoxyl the susceptibility below the transition point can not be explained by the hypothesis of a simple pairing such as was observed in Wurster's blue perchlorate.

Experimental

Preparation of Specimens. Galvinoxyl, mp 151.5—153.0°C, was prepared from 2,6-di-*t*-butylphenol according to the method of Kharasch and Joshi[18] or Coppinger.[19] After condensation with formaldehyde, the product was oxidized with lead peroxide in ether. A very dark blue crystalline compound was isolated from the ethereal solution.

The BIP radical, mp 155°C, was synthesized following the method of Coppinger[20] and then recrystallized from isooctane under nitrogen gas in a freezer. This melting point is higher than that (132—133°C) of the corresponding phenol. The samples were stored in the dark at a cool ambient temperature under a vacuum.

Measurements. The susceptibility measurements were carried out in the continuous temperature range between 1.8°K and 300°K using a magnetic torsion balance on powder samples of about 100 mg in a heterogeneous magnetic field up to about 10 koe. The details of the apparatus were described previously.[21] After loading the samples in an open quartz bucket into the apparatus, the sample chamber was evacuated to about 10^{-5} mmHg and a small amount of helium was admitted to the apparatus to act as a heat-transfer gas. The temperature of the sample was determined by a AuCo-Chromel thermocouple for the higher temperatures and by a carbon resistance thermometer for the low temperatures, with a supplement of Mn-tutton salt.

The data have been corrected for diamagnetism using the Pascal's constants.[22] The diamagnetic contribution to Galvinoxyl was calculated to be $-276\times$

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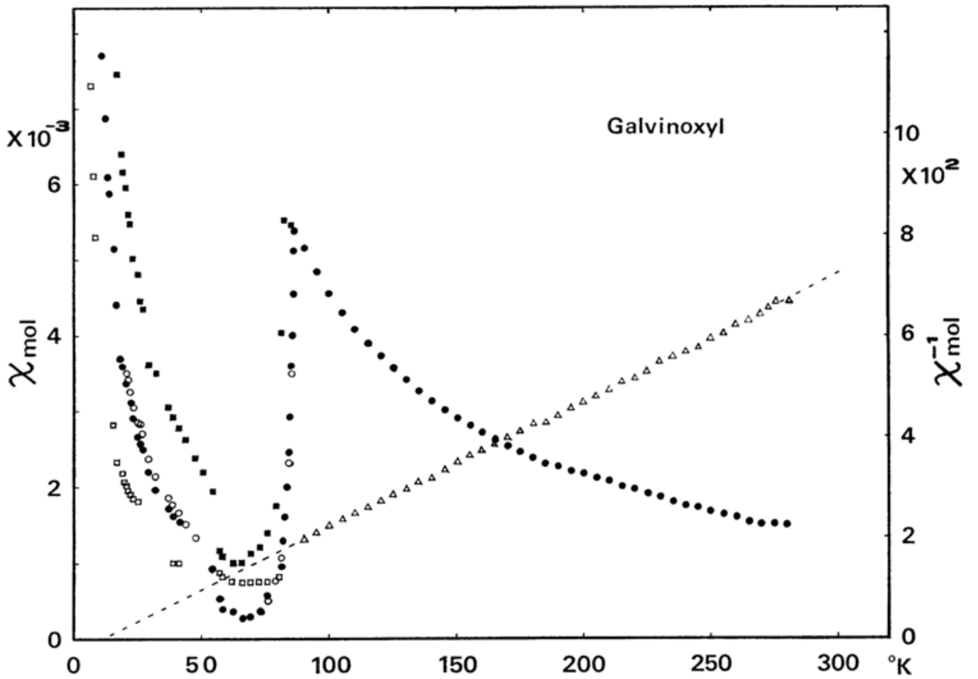

Fig. 1. (a) Molar susceptibilities of the Galvinoxyl radicals *versus* temperature (1.8—300°K). Sample numbers 1, 2, 3 and 3′ are denoted in the figure as ■, □, ● and ○, respectively. (b) Inverse molar susceptibility of the Galvinoxyl in the high-temperature region (82—300°K) (open triangle, △).

10^{-6} emu/mol, a value which agrees well with the measured value of -265×10^{-6} emu/mol for the corresponding phenol. The diamagnetic correction for BIP was also obtained from the Pascal's constants and/or from the measured values for the corresponding phenol. The absolute susceptibilities were determined using Mn-tutton salt or Mohr's salt as standards. The relative data were estimated to be reliable to within about $\pm3\%$ over the entire temperature range, while the absolute susceptibilities were estimated to be correct to within $\pm5\%$.

All the EPR measurements were taken with a JEOL 3BX spectrometer, with a 100-kc-field modulation and equipped with a field dial and a variable temperature-control unit. Highly-diluted crystals such as Mn^{2+} in CdS were used as standards. The first derivative of the absorption was observed, and the relative magnetic susceptibility was taken as proportional to the product of the height times the square of the peak-to-peak linewidth of the first derivative.

Results and Discussion

Galvinoxyl. The magnetic susceptibilities obtained for three independently-prepared Galvinoxyl radicals (denoted as Sample Nos. 1, 2 and 3) are shown in Fig. 1 as a function of the temperature. These have been corrected for the diamagnetic contribution of $\chi_{dia}=-276\times10^{-6}$ emu/mol calculated by the Pascal's method. This value agrees well with the measured value of $\chi_{dia}=-265\times10^{-6}$ emu/mol for the corresponding phenol. When the temperature of the radical sample is lowered from room temperature, χ_p increases following the Curie-Weiss law, $\chi_p=C/(T-\theta)$, with the same C_H and θ_H values within the range of experimental errors, reaching a maximum at about $T_c=81$°K, depending on the sample. After passing through the maximum, within about three degrees χ_p decreases rapidly by about 80 percent of its maximum value, and afterward falls off gradually till 66°K. However, below 66°K the susceptibilities increase again as the temperature is lowered. The radical spins in the low-temperature region (5—50°K) obey only the Curie-Weiss law, as is apparent from the $1/\chi_p$-T curve shown in Fig. 2. On the other hand, the spin concentrations differ individually for each sample. The different values of C_L and θ_L obtained for three samples are listed in Table 1, where the subscripts, L and H, refer to the low- and high-temperature regions respectively. These values of C_L are from about three to ten times smaller than that in the high-temperature section (83—300°K). At still lower temperatures (1.8—5°K) the susceptibility again deviates from the Curie-Weiss law. Further, two independent runs about the sample 3 were examined, resulting in a considerable accordance (denotd as 3′ in Fig. 2).

EPR measurements were done with a polycrystalline Galvinoxyl radical in the temperature range between room temperature and the temperature of liquid nitrogen, using a microwave

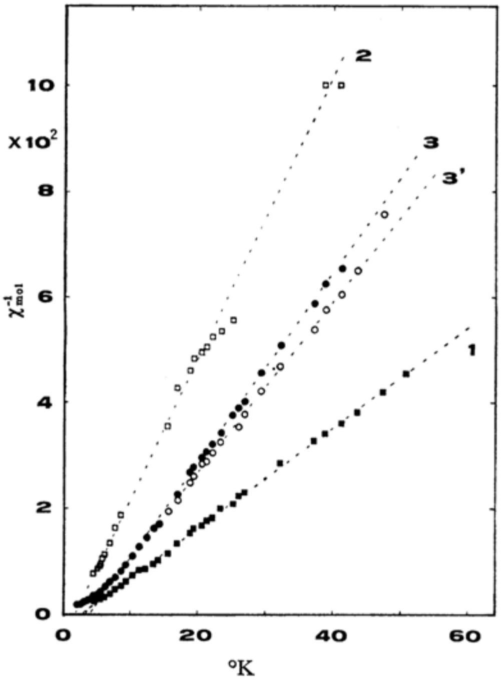

Fig. 2. Inverse molar susceptibilities of the Galvinoxyl radicals *versus* temperature (1.8—50°K). Sample numbers 1, 2, 3 and 3′ are denoted in the figure as ■, □, ● and ○, respectively.

frequency of about 9300 Mc/sec, in order to ascertain the anomaly in the magnetic susceptibility. The paramagnetic absorption spectrum of the Galvinoxyl exhibits one asymmetric line, with a line width of about 5 gauss; this can usually be attributed to the presence of an anisotropic *g*-value. The line-width is temperature-independent within the range of experimental error from 77°K to room temperature. Since a transition has been found by measuring the static magnetic susceptibility, the absorption was carefully examined above and below $T_c=81$°K. However, no appreciable change in the position and shape of the absorption line could be found in this temperature range. Since the line-width of the magnetic-resonance absorption curve of this radical is approximately constant, the height of the derivative is proportional to the susceptibility. This relative magnetic susceptibility. I_{EPR}, of Galvinoxyl as a function of the temperature is shown in Fig. 3; the maximum of the static susceptibility at 81°K was also found by measuring the electron paramagnetic resonance. The value of the Curie-Weiss constant obtained from the $1/I_{EPR}$-T curve, shown in Fig. 3, $\theta=1\pm5$°K, shows a qualitative agreement with the value, $\theta=11\pm3$°K, obtained from the static magnetic measurements.

If the sudden decrease in magnetic susceptibility is due to the first-order phase transition, the maximum should be found by differential thermal analysis (DTA). In fact, the DTA curve of powdered Galvinoxyl shows a peak around 82°K. On the other hand, the DTA for the corresponding phenol does not show any anomaly at the transition

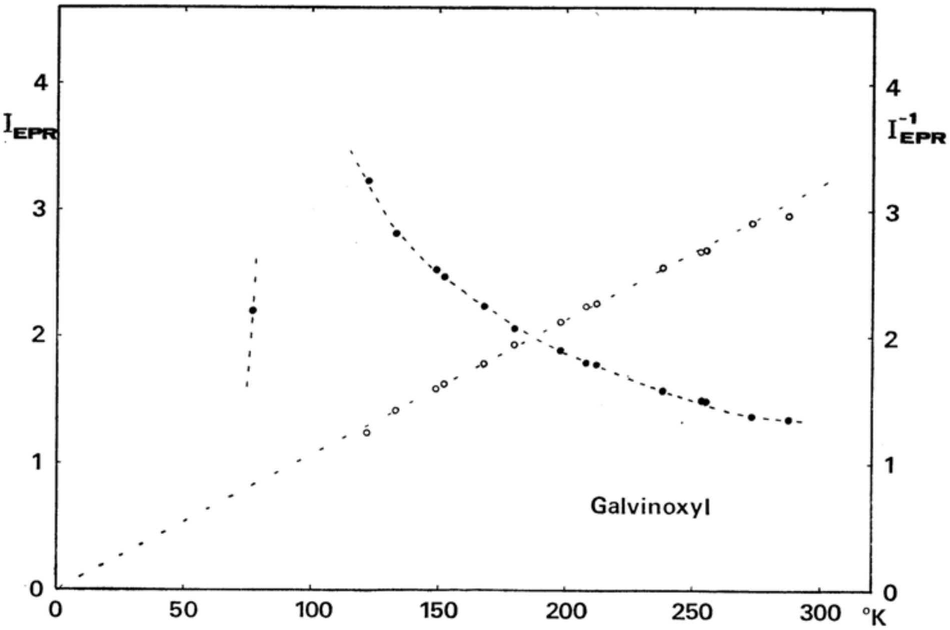

Fig. 3. (a) Relative intensity (full circle, ●) and (b) relative inverse intensity(open circle, ○) of the EPR absorption of the Galvinoxyl radical.

TABLE 1. VALUES OF T_C, C_H, θ_H, C_H/C_T, C_L, θ_L, C_L/C_T, AND C_L/C_H

Sample	T_C (°K)	C_H (emu °K/mol)	θ_H (°K)	C_H/C_T (%)	C_L (emu °K/mol)	θ_L (°K)	C_L/C_T (%)	C_L/C_H (%)
1	81	0.400	11	106	0.105	2.8	27.7	26.2
2	84.5	0.419	8	111	0.037	1.8	10.0	9.0
3	86	0.401	11	106	0.056	3.9	14.7	13.9
3′	86	0.401	11	106	0.058	3.2	15.3	14.4

temperature.[23] The high-temperature structure of the Galvinoxyl radical can be understood simply as a molecular crystal composed of unpaired neutral radicals, showing a spin concentration of about 106% as $S=1/2$, following the Curie-Weiss law. Therefore, it is highly probable that the transition found by measuring magnetic susceptibility and the electron paramagnetic resonance absorption for Galvinoxyl is due to the first-order phase transition induced magnetically, accompanied by a pairing of the magnetic spins. This magnetically-induced phase transition of Galvinoxyl differs from that of WB, which can be explained remarkably well in terms of an elementary theory of non-interacting triplet excitons, judging from the results of the pressure dependence of the exchange-narrowed magnetic resonance.[24]

The anomalies in magnetic susceptibility and DTA observed for the Galvinoxyl radical may be characteristic of the hindered phenoxyl radical solids. For example, the rotation of the tertiary butyl group or the intermolecular bonding between oxygen atoms may be responsible for the anomaly. Thus, we have measured the magnetic susceptibility of the BIP radical between 1.8°K and 300°K, for this radical has a molecular structure similar to that of the Galvinoxyl radical. The magnetic susceptibility of the BIP radical, the –CH= group situated at the center of the Galvinoxyl replaced with the –N= group, shows a broad maximum around 54°K, as will be described below. This experimental fact shows that the transition in Galvinoxyl is presumably related to the –CH= group.

Since the anomaly in Galvinoxyl is thought to be the transition accompanied by a pairing of the magnetic spins at the position of the –CH= group, and since the magnetic susceptibilities in the low-temperature region (5—50°K) obey the Curie-Weiss law, with different spin concentrations for the three samples, the low-temperature susceptibilities are probably due to the residual unpaired Galvinoxyl radicals with a spin of $1/2$, radicals which will be randomly located in the lattice. Their concentrations, which can be calculated from the C_L values in Table 1, have been found to vary from about 10 to 30 mol%. This explanation can be supported by assuming that the magnetic spins are mostly clustered in groups of two in the crystals and that the exchange interactions between radical spins are large.

Another possible explanation is that the increase in susceptibility at low temperatures may be caused by the linear Ising rings, consisting of odd numbers of the radical molecules. When the phase transition induced by a coupling of magnetic spins leaves an odd number of coupled electrons in a segment, one electron spin will remain unpaired as the spins couple antiferromagnetically at a low temperature.

On the other hand, the values of θ in Table 1 are positive in both the high- and low-temperature regions of Galvinoxyl. This is unlike the negative values of θ obtained from most other organic radical solids, including several phenoxyl radicals.[25] This fact shows a possibility of weak ferromagnetism. The question about the observed ferromagnetic Weiss constants will be discussed elsewhere.

Bisindophenoxyl. The results of the susceptibility measurements on BIP are presented in Fig. 4, where the data have been corrected for a calculated diamagnetism of -268×10^{-6} emu/mol. This diamagnetism value also accords well with the measured value of $\chi_{\text{dia}}=-258\times10^{-6}$ emu/mol for the corresponding phenol.

The data were corrected for the presence of paramagnetic impurities by using the low-temperature measurements to determine their concentrations. In the region from 1.8—10.1°K, the Curie-Weiss law was observed corresponding to a spin concentration of 3.6% and a Weiss constant of -1.6 ± 0.1°K. When this low-temperature impurity curve is extrapolated to higher temperatures and subtracted from the experimental curve observed there, the corrected curve shown in Fig. 5 is obtained. The experimental curve has a general appearance very similar to that observed for such crystalline organic radicals as TCNQ salts,[15] picryl amino carbazyl (PAC),[16] and biphenyl-potassium salts.[17] In the case of the BIP radical. the unpaired electrons on the

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[23] Motivated with these findings, we now proceed to measure the low temperature heat capacities of Galvinoxyl and the phenol from 13 to 300°K. There is a sharp rise in the heat capacity of Galvinoxyl at 81.5°K. Details will be published in this Bulletin by S. Seki, H. Suga, A. Kosaki, Y. Deguchi and the author.

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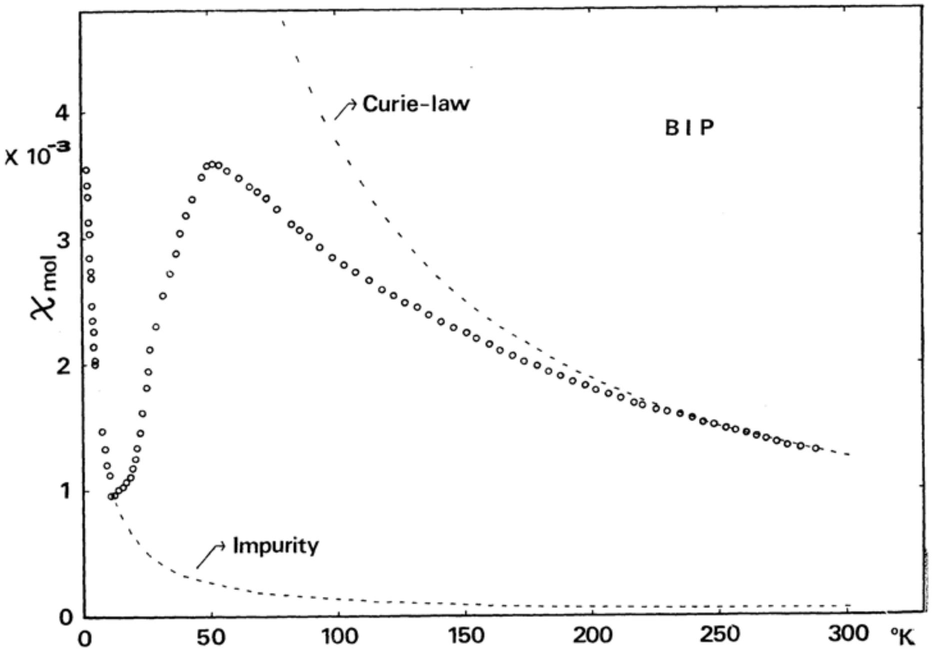

Fig. 4. Molar susceptibility of the BIP radical *versus* temperature (1.8—300°K). The "impurity curve" is an extrapolation of the low-temperature Curie-Weiss data.

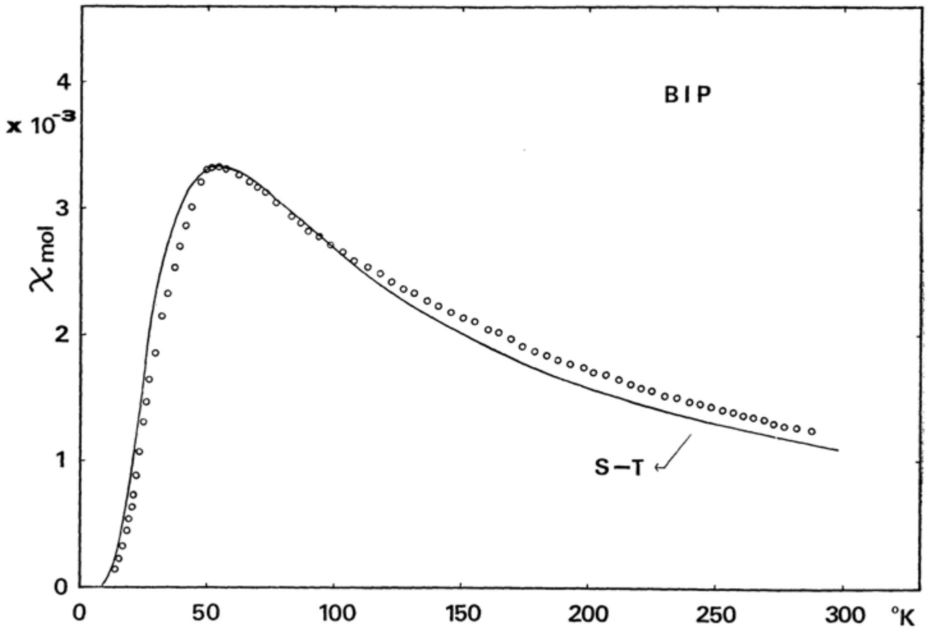

Fig. 5. Subtracted molar susceptibility of the BIP radical *versus* temperature (1.8—300°K). The solid curve is theoretical fits as explained in the text.

BIP molecules also appear to be paired up by an exchange interaction in quasimolecular states. The paramagnetic contribution to the susceptibility of BIP can be fitted approximately to the expression:

$$\chi_p = \frac{2Ng^2\beta^2}{kT} \cdot \frac{1}{3+e^{\delta/kT}} \qquad (1)$$

which corresponds to an assembly of N quasimolecules with a singlet ground state and a triplet state lying by an energy, δ, above the ground state. If the temperature at which the susceptibility shows a maximum is defined as T_{max}, one can determine the singlet-triplet separation (δ) by using the relation $\delta = 1.61kT_{max}$. The theoretical curves require multiplication by a constant p to match the experimental data. Thus, with $\delta/k=87$ and $p=0.964$, the theoretical curves can be fitted to the experimental data, assuming that N is equal to one half of the number of BIP radicals and that $g=2.00$. The agreement between theory and experiment in the case of BIP is enough to conclude that the BIP radical forms radical dimers. The singlet-triplet separation can be estimated to be $\delta=60.5\ \mathrm{cm}^{-1}$, using the value for $T_{\max}(54\pm2^{\circ}\mathrm{K})$ determined from the experiment.

In order to obtain further information about the magnetic property of the above radical, EPR measurements were made. The EPR spectrum of BIP shows one sharp, asymmetric line, with a line width of 3 gauss, which is temperature-independent between 77°K and room temperature. The expected zero-field splittings for the BIP entities in the triplet states are not observed over the accessible temperature range, although the magnetic susceptibility of BIP follows Eq. (1). This is probably because the zero-field splittings for BIP are collapsed into a single sharp line by the exchange-narrowing effect arising from the high concentration of triplet-state entities in this temperature range.

The crystalline organic free radicals, such as Wurster's blue perchlorate (WB),[12] TCNQ salts,[14,15] and PAC,[16] in which the electrons interact to form singlet-triplet pairs, are thought to be plate-like molecules and to be stacked face-to-face to form alternating chains. In the case of BIP, each phenyl ring (π-ring) being masked by the tertiary butyl groups, the oxygen atoms in BIP may play an important role in the above pairing. However, we could not observe any broad maxima for the other hindered phenoxyl radical solids.[25] Thus, the present evidence indicates that no such pairing is present in hinderd phenoxyl radicals.

EPR measurements of the photodissociation-products of tetraphenyl-hydrazine in a rigid solution at 77°K have indicated that the principal product of this dissociation is the dimer of the diphenyl amino (DPA) radical; this has been established by observing the half-field signal and the computer simulation of the EPR spectra.[26] It was proposed that, in the DPA radical dimer, a configuration of minimal repulsion, that is, with the planes each containing two nitrogens and the axes of the phenyl rings at right angles to each other, might be favored, particularly at low temperatures. The BIP radical dimer may have a configuration similar to that of the diphenyl amino radical dimer. However, until the crystal structure analyses are worked out in sufficient detail to give the exact relative positions of the magnetic molecules, they are of dubious value for our understanding of the exchange interactions in these compounds.

On the other hand, the theoretical value of the susceptibility at $T_{\max}$ exhibits a good agreement with the experimental value, as is shown in Fig. 5. However, the experimental susceptibility for BIP was observed to fall a little more rapidly than the theoretical susceptibility at temperatures below $T_{\max}$, while above $T_{\max}$ the reverse is preferably true. It is well known that the exchange interaction, J, is strongly dependent on the intermolecular distance, and that the physical systems of interest are those in which the molecular entities are really supermolecules, that is, aggregates of weakly-bound molecules. Therefore, the exchange interaction between the BIP radicals, $|J|$ $(=\delta/2)$, may show temperature-dependence. In fact, the values for $|J|$ calculated from the magnitude of the susceptibility at 20, 30, 40, 54, 72.6, 98.5, 127, 160, 202, 240, and 288°K were 33.2, 32.2, 31.9, 30.2, 30.4, 30.0, 25.4, 18.0, 11.1, 4.1, and $1.0\ \mathrm{cm}^{-1}$ respectively.

Such deviations from normal behavior have also been found by, for example, magnetic susceptibility measurements[15] or the anomalous exchange-narrowing results in the EPR spectra[27] of some TCNQ salts. Chesnut[28] has suggested that the presence of an attractive interaction between the excitons may be responsible for the experimentally-observed decreases in J with the temperature. However, a self consistent-field treatment by Soos[29] of a linear antiferromagnetic lattice of any degree of alternation also predicts a decrease in the energy gap, δ, with an increase in the temperature. In addition, other explanations,[30,31] opposite to the model of interacting triplet excitons, have been proposed. Consequently, better theoretical and experimental studies will be required before the temperature dependence of the exchange interaction on the BIP radical can be fully interpreted.

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