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Paramagnetic Susceptibilities of Some DPPH Derivatives

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The static magnetic susceptibilities of polycrystalline samples of 1,1-bis(*p*-chlorophenyl)-2-picrylhydrazyl (Cl-DPPH), 1,1-bis(*p*-bromophenyl)-2-picrylhydrazyl (Br-DPPH), and 1,1-bis(*p*-methoxyphenyl)-2-picrylhydrazyl (CH_3O-DPPH) were measured in the temperature range from 10°K to 300°K. These three substances showed strong paramagnetism comparable to that of DPPH, having relatively weak interaction energies between their unpaired electrons. Of these, the paramagnetic susceptibility of CH_3O-DPPH was analysed on the basis of the singlet-triplet model with the energy separation of $2J/\boldsymbol{k}=33.8$°K.

The typical neutral organic free radical, 1,1-diphenyl-2-picrylhydrazyl (DPPH), is known to have a sharp, exchange-narrowed ESR absorption line. A number of investigations have been carried out to find a transition to the magnetic ordered state on DPPH at a low temperature.[1-4] All of these measurements (except for the work of Gerritsen *et al.*[2]) agree with each other concerning the following points that the paramagnetic susceptibility of this compound obeys the Curie-Weiss law, having a Weiss constant of about -25°K between 60°K and room temperature, that it deviates at lower temperatures, and that no antiferromagnetic transition has been found, at least above liquid helium temperature.

The magnetic susceptibility of another neutral free radical, *N*-picrylaminocarbazyl (PAC), the molecular structure of which is very similar to that

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[1] L. S. Singer and E. G. Spencer, *J. Chem. Phys.*, **21**, 939 (1953).

[2] H. J. Gerritsen, R. Okkes, H. M. Gijsman and J. Van Den Handel, *Physica*, **20**, 13 (1954).

[3] W. Duffy, Jr., *J. Chem. Phys.*, **36**, 490 (1962).

[4] A. Van-Itterbeek and M. Labro, *Physica*, **30**, 157 (1964).

of DPPH, behaves quite differently.[5] The magnetic susceptibility *versus* the temperature curve has a broad maximum at about 70°K. The difference in behaviour between these two compounds can mainly be attributed to the different crystal structures. However, there is another remarkable difference between them, *i. e.*, the difference in the distribution of the unpaired electron over the molecule. The electron spin resonance spectra of these compounds differ considerably from each other.[6] The spectra of DPPH and PAC apparently consist of five lines and four lines respectively; these ESR spectra can be explained in terms of almost equal hyperfine coupling constants of the two central nitrogens in the former, whereas in the latter one nitrogen should have twice as large a coupling constant as the other. This remarkable difference in the distribution of the unpaired electron is probably one of the factors distinguishing the magnetic behaviour of these compounds. The ratio of the hyperfine coupling constants of the two hydrazyl nitrogens in DPPH changes when the substituents are introduced into the para-positions of the two phenyl groups.[7] We intended to investigate the change in the magnetic properties when the distribution of the unpaired electron varied in the molecule.

In this paper we will present the results of our measurements of the temperature dependence of the static magnetic susceptibilities of several DPPH derivatives, *i. e.*, 1,1-bis(*p*-chlorophenyl)-2-picrylhydrazyl (abbreviated as Cl-DPPH), 1,1-bis(*p*-bromophenyl)-2-picrylhydrazyl (Br-DPPH), and 1,1-bis(*p*-methoxyphenyl)-2-picrylhydrazyl (CH_3O-DPPH) (Fig. 1). Among these, the paramagnetic susceptibility of CH_3O-DPPH is analysed on the basis of the singlet-triplet model, whereas the other two obey Curie law in the high-temperature range in spite of the appearance of the maximum in the susceptibility-*vs.*-temperature curve in Br-DPPH at 15°K.

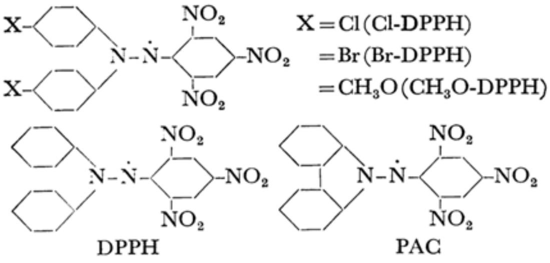

Fig. 1. Molecular structures of DPPH, derivatives of DPPH, and PAC.

Experimental

The susceptibility measurements were made by the Faraday method. Figure 2 shows the apparatus schematically. A quartz bucket containing a powder sample of a few mg or more was suspended by a quartz string from the arm of a vacuum balance, a Sartorius Electrono microbalance. Helium gas (30 mmHg) which had been purified by passing it through an active charcoal at 77°K was admitted around the sample to facilitate the heat exchange. Each measurement was carried out continuously from 10°K to 300°K, the output of the microbalance being recorded on a X-Y recorder as a function of the e.m.f. of an Au : CO-Cu thermocouple. As the thermocouple was placed below the sample bucket (Fig. 2), the temperature in the sample was calibrated by measuring several times the susceptibilities of the paramagnetic salts whose susceptibilities are known, *i.e.*, Mohr's salt $(Fe(NH_4)_2(SO_4)_2\cdot 6H_2O)$ and Tutton's salt $(Mn(NH_4)_2(SO_4)_2\cdot 6H_2O)$, under the same conditions as for the usual measurements. The rate of raise of the temperature was set similarly for each run by controlling the pressure in the wall of the inner Dewar vessel. The Dewar vessel was placed between

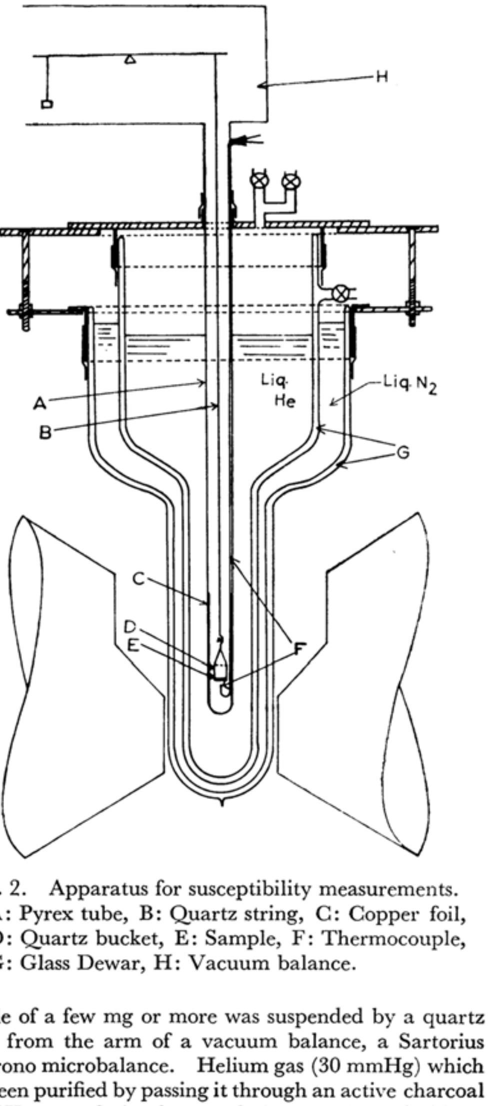

Fig. 2. Apparatus for susceptibility measurements. A: Pyrex tube, B: Quartz string, C: Copper foil, D: Quartz bucket, E: Sample, F: Thermocouple, G: Glass Dewar, H: Vacuum balance.

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[5] R. S. Rhodes, J. H. Burgess and A. S. Edelstein, *Phys. Rev. Letters*, **6**, 462 (1961).

[6] C. Kikuchi and V. W. Cohen, *Phys. Rev.*, **93**, 394 (1954).

[7] M. M. Chen, K. V. Sane, R. I. Walter and J. A. Weil, *J. Phys. Chem.*, **65**, 713 (1961).

the Sucksmith-type pole pieces with a pole gap of 5 cm, as is illustrated in Fig. 2. The sample bucket was adjusted so as to locate it at the plateau of $H\cdot\partial H/\partial x$ (usually 6.31×10^6 gauss²/cm). At 10°K and also at room temperature while the susceptibility measurements were made the field strength was changed in order to check the field dependence. The field strength was calibrated by measuring the susceptibility of sucrose, the mass susceptibility of which was taken to be -0.566×10^{-6} emu/g.

The solvents for the recrystallization of the measured samples, Cl-DPPH, Br-DPPH, and CH_3O-DPPH, were benzene, benzene, and carbon tetrachloride respectively. All these samples were provided by R. I. Walter. Their molecular structures are illustrated in Fig. 1, along with those of DPPH and PAC.

Results and Discussion

The paramagnetic susceptibilities of all these compounds were comparable to that of DPPH; they all increased with a decrease in the temperature, as was mentioned in the previous communication.[8] In Br-DPPH and CH_3O-DPPH, however, the susceptibility reached its maximum value at 15°K and 21°K respectively, and then it decreased with the decrease in the temperature.

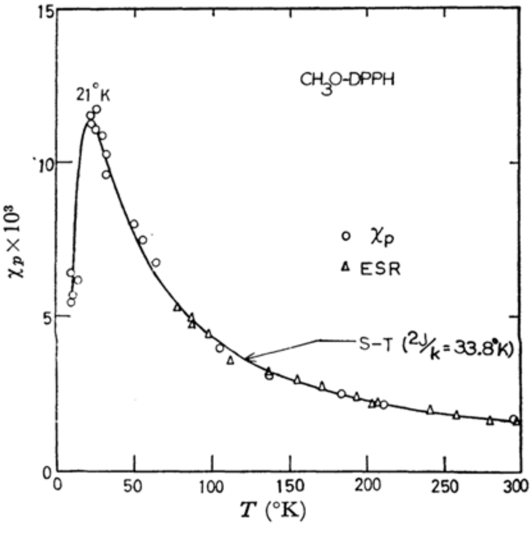

Fig. 3. Paramagnetic molar susceptibility of CH_3O-DPPH. Data are corrected for diamagnetism and an assumed impurity. The solid line is the theoretical fit based on singlet-triplet model with $2J/k=33.8°$ K. The ESR data (arbitrarily normalized at 300° K) are also plotted.

The data were analysed by the formula;

$$\chi(T)=f(T)+\frac{C}{T}+D \tag{1}$$

where $\chi(T)$ is the observed susceptibility at temperature, T; where the term C/T denotes the contribution from the assumed isolated paramagnetic "impurities"; where D is a diamagnetic term, and where $f(T)$ is a function of the temperature, which is assumed to have one of the following four forms:

1) $f(T)=\boldsymbol{N}g^2\beta^2/4\boldsymbol{k}T$ (Curie law), (1-a)

2) $f(T)=\boldsymbol{N}g^2\beta^2/4\boldsymbol{k}(T-\theta)$ (Curie-Weiss law), (1-b)

3) $f(T)=\boldsymbol{N}g^2\beta^2/\boldsymbol{k}T\cdot(3+\exp(2J/\boldsymbol{k}T))^{-1}$ (singlet-triplet model), (1-c)

4) $f(T)=\boldsymbol{N}g^2\beta^2/4\boldsymbol{k}T\cdot\exp(-J/\boldsymbol{k}T)$ (linear Ising model). (1-d)

In Eqs. (1-c), (1-d), we assumed the following spin exchange Hamiltonian:

$$\mathscr{H}=\sum_{i}^{N/2}(2J\boldsymbol{S}_{2i-1}\boldsymbol{S}_{2i}+2J'\boldsymbol{S}_{2i}\boldsymbol{S}_{2i+1}), \tag{2}$$

and took $J\neq J'=0$ and $J=J'\neq0$, $\boldsymbol{S}_i\boldsymbol{S}_j=S_i^zS_j^z$, respectively.

In Eq. (1), the first term and the parameters C and D were chosen to give the best fits to the observed values. The results are shown in Figs. 3—5. Equation (1) reproduces fairly well the paramagnetic susceptibility data of CH_3O-DPPH if we take $f(T)$ as Eq. (1-c) with $2J/\boldsymbol{k}=33.8$°K (the singlet-triplet energy separation) and if we assume the concentration of the impurity of spin 1/2 to be 8.7%, as is shown in Fig. 3. The maximum of χ_p was found at 21°K. The ESR measurement was

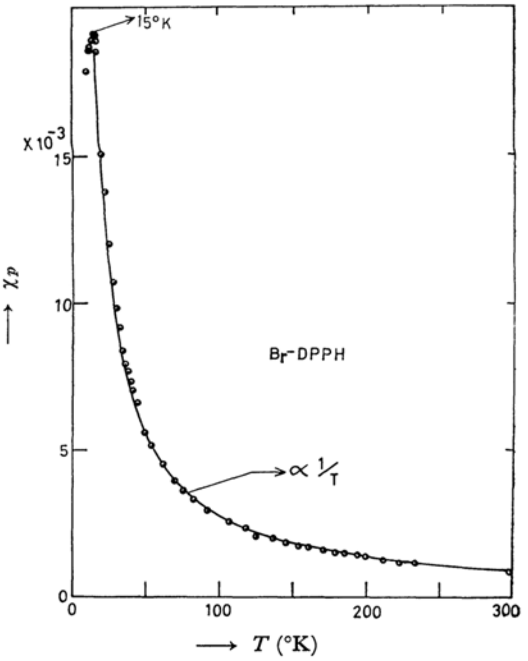

Fig. 4. Paramagnetic susceptibility of Br-DPPH.

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[8] N. Ohigashi and H. Inokuchi, This Bulletin, **41**, 269 (1968).

made on this powder sample between 77°K and room temperature. The absorption spectrum was very sharp, ΔH_{msl} being smaller than 1 gauss. As the absorption shape did not change with the temperature, the peak heights of the first derivative curves were thought to be proportional to the absorption intensity. These values are in good agreement with the static susceptibility data (Fig. 3), confirming that the observed strongly exchange-narrowed ESR absorption line at $g=2$ has the same origin as that giving rise to the static paramagnetic susceptibility.

The susceptibility, χ_p, of Br-DPPH had its maximum at 15°K and at higher temperatures followed a Curie law (Fig. 4), whereas that of Cl-DPPH obeyed a Curie law over the entire temperature range (Fig. 5). There is some evidence that the χ_p of Cl-DPPH has its maximum near 10°K, but our present apparatus can not give detailed information in this temperature region. The line widths at room temperature of the ESR absorption lines of these two compounds were about four times broader than that of CH_3O-DPPH. Further, in contrast to CH_3O-DPPH, they became narrow (about 2/3) when the temperature was lowered to 77°K. This fact probably suggests that in these two compounds, the crystal lattice spacings change with the temperature more rapidly than that of CH_3O-DPPH, and that the sudden decreases in the magnetic susceptibilities at 15°K and 10°K may be explained by the phase transitions. On the other hand, the χ_p of CH_3O-DPPH is represented by a single equation based on the singlet-triplet model from 10°K to 300°K, indicating that no phase transition occurs in this temperature range; this is consistent with the fact that no change in the line shape or width of the ESR absorption line is found from 77°K to room temperature.

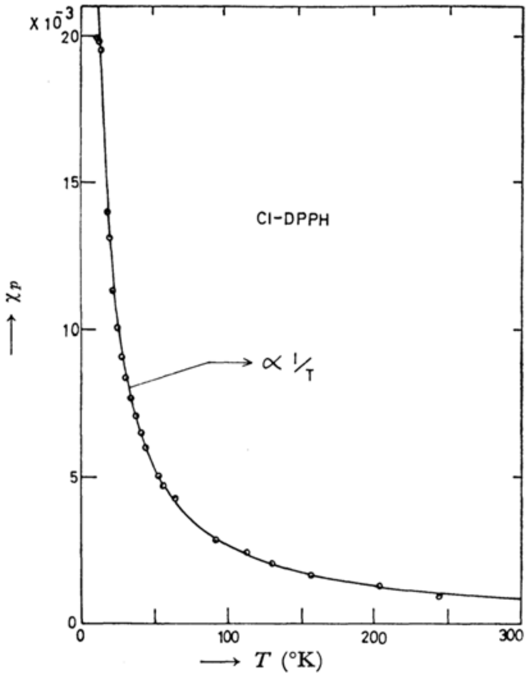

Fig. 5. Paramagnetic susceptibility of Cl-DPPH.

As has been seen above, Cl- and Br-DPPH behave differently from CH_3O-DPPH. The crystal structures of these compounds have not yet been analysed. However, several crystal modifications of DPPH are known according to the solvents from which the crystals are grown. Our samples were crystallized from different solvents, benzene and carbon tetrachloride, but it has been inferred that their magnetic susceptibilities depend little on the solvents used for recrystallization. This is because the susceptibilities of the DPPH crystal measured by several authors seem to show small influences of solvents, whether or not the crystal contains molecules of solvation.[1–3] This suggests that the relative arrangement of the nearest neighbouring molecules is but little altered when the crystal structure changes. Similarly, in the DPPH derivatives used in this work, the arrangement of the neighbouring molecules may be determined mainly from the interaction between DPPH derivative molecules, but not from the interaction between the free radical molecule and a solvent molecule. Considering the size of the substituent, CH_3O-DPPH may fairly differ in the arrangement of molecules in the crystal from the other two radicals, Br- and Cl-DPPH.

The crystal structure of DPPH crystallized from benzene was recently determined by Williams.[9] His results show that the hydrazyl nitrogens of DPPH are surrounded sterically by the other atoms of the same molecule, indicating that the unpaired electron of DPPH is stabilized not only by conjugation with phenyl rings but also by the steric hindrance. In such circumstances, interaction among unpaired electrons in the crystal is generally small, but it may increase if the delocalization of an unpaired electron over a molecule advances upon the introduction of substituents. Of the three compounds studied, CH_3O-DPPH has the smallest hyperfine coupling constants for nitrogen nuclei,[7] suggesting that the unpaired electron in this compound delocalizes over the phenyl rings most extensively. The larger intermolecular interaction observed in CH_3O-DPPH may be attributed partly to this delocalization of the unpaired electron.

The magnetic interactions observed in DPPH-derivative crystals are smaller than those of many ion radical salts such as TCNQ anion radical salts, which crystallize with their molecular planes parallel

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[9] D. E. Williams, *J. Am. Chem. Soc.*, **89**, 4280 (1967).

to each other.[10] The stabilization of unpaired electrons by the steric hindrance may explain this fact.

We wish to thank Professor R. I. Walter, Haverford College, for kindly providing samples.

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[10] D. B. Chesnut and W. D. Phillips, *J. Chem. Phys.*, **35**, 1002 (1961); R. G. Kepler, *ibid.*, **39**, 3528 (1963).