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MAGNETIC PROPERTIES OF ORGANIC STABLE RADICALS. IV.
DPPH AND ITS SOLVENT COMPLEXES

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Magnetic susceptibility of organic stable radicals, DPPH and its solvent complexes has been measured. Susceptibility of solvent free DPPH shows a maximum at 11°K and is well fitted to the pair model (δ/k = 17.64°K). DPPH·B_z has a χ_{max} at 0.65°K but remains constant down to 0.1°K. DPPH·¼CCl_4 has two Weiss-constants: θ_{High} =-26.0°K and θ_{Low} = -0.3°K. Spin concentration of the last complex in low temperature range (below 4.2°K) is a half of that of high temperature range (above 30°K).

Magnetic properties of organic stable radical, α,α'-Diphenyl-β-picryl hydrazyl (DPPH), have been studied by many authors. However some questions are remained to be solved.

1) DPPH complexes with some kinds of solvent molecules(1) exhibit various magnetic properties.

2) Temperature dependence of their magnetic susceptibilities results in two Weiss constants, θ_{High} and θ_{Low}, and low temperature spin concentration (C_{Low}) is a half of the higher one.

3) Anisotropy of ESR g-value becomes larger with lowering temperature(2).

Duffy Jr. explained the magnetic susceptibilities of DPPH complexes with "Two sublattice model"(3); on the other hand, Kommandeur proposes "Narrow band model"(4). In order to clarify these questions we have remeasured magnetic susceptibility of these complexes and obtained somewhat different results described in the following.

Samples were recrystallized several times from pure ether, benzene, chloroform, carbontetrachloride and acetone solution, respectively. They are classified into the following three categories from chemical analysis and crystallographic data obtained by D.E. Williams1a). These are shown in Table I. The susceptibility measurements were undertaken using a magnetic torsion balance from 77°K to 1.7°K and using a ballistic galvano-meter at the temperatures below 1.7°K obtained by adiabatic demagnetization of chromium potassium alum. The data below 1.7°K is normalized to the magnetic torsion balance data of liquid helium temperature range. The results are shown in Fig. 1.

Table I Crystal Structures of DPPH

a) Solvent free DPPH (from ether): orthorhombic $Z = 8$ Pnam
$a = 16.75$ $b = 7.838$ $c = 26.85$ Å
b) DPPH·Benzene (1:1): monoclinic $Z = 2$ Pc
$a = 7.764$ $b = 10.648$ $c = 14.780$ Å $\beta = 109.05°$
c) DPPH·¼CCl_4 (4:1) also $CHCl_3$, $(CH_3)_2CO$
triclinic $Z = 4$ $P\bar{1}$
$a = 13.58$ $b = 18.91$ $c = 7.555$ Å $\alpha = 92.2$ $\beta = 101.6$ $\gamma = 95°$

Result and Discussion

a) Solvent free DPPH

The magnetic susceptibility of the solvent free DPPH which was recrystallized from the ether solution reaches a maximum at 11°K with decrease of temperature, then rapidly decreases. But below 2.5°K it increases again. Experimental results are best fitted to the pair model with $\delta/k = 17.64°K$, where δ is the energy separation between the singlet and the triplet levels. Similar results are reported in other para-substituted DPPHs such as DPPH·$(CH_3O)_2$(5) and DPPH·$(NO_2)_2$(3). Deviation from the pair model at low temperature side is probably due to the paramagnetic impurity which was checked by broad line NMR measurements(8).

b) DPPH·Benzene (1:1)

The susceptibility χ_M of benzene complex of DPPH obeys the Curie-Weiss law with $\theta = -0.5°K$. Below 3°K it deviates from this law and reaches χ_{max} at 0.65°K. The data are well fitted to the pair model with $\delta/k = 1.04°K$ above 0.4°K. However, χ_M remains constant value of $2/3\ \chi_{max}$ below 0.3°K. These results are consistent with Edelstein's ESR measurement(6) but not with Prokhorov's(7) below 0.4°K.

c) DPPH·¼CCl_4 (also ¼$CHCl_3$, ¼$(CH_3)_2CO$)

As many authors have reported(3),(4), in higher temperature range susceptibility obeys the Curie-Weiss law with $\theta_{High} = -26.0°K$ and the spin concentration is 100% at 77°K. Below 30°K, the gradient of χ-T curve increases gradually and susceptibility obeys the Curie-Weiss law with $\theta_{Low} = -0.3°K$. The spin concentration is about 50% at 4.20°K.

The large magnetic interaction of solvent free DPPH will be expected from the fact that DPPH molecules are packed most densely in solvent free DPPH crystals[1a]. In the case of DPPH·Bz(1b), benzene molecules separate DPPH molecules one another and J is smaller than that of solvent free DPPH. The third case is the DPPH·¼CCl_4 crystals. Carbontetrachloride molecules separate DPPH molecules but not equally. So there may be two magnetically different sites in a unit cell as Duffy Jr. proposed. Then the susceptibility curve will be a superposition of two pair model curves with different δs. However, we cannot yet conclude whether "Two sublattice model" is appropriate to explain these phenomena or not. We are now undertaking NMR(8) and ESR measurements of these DPPH solvent complexes and X-ray analysis of DPPH·¼CCl_4 to make clear the magnetic structure.

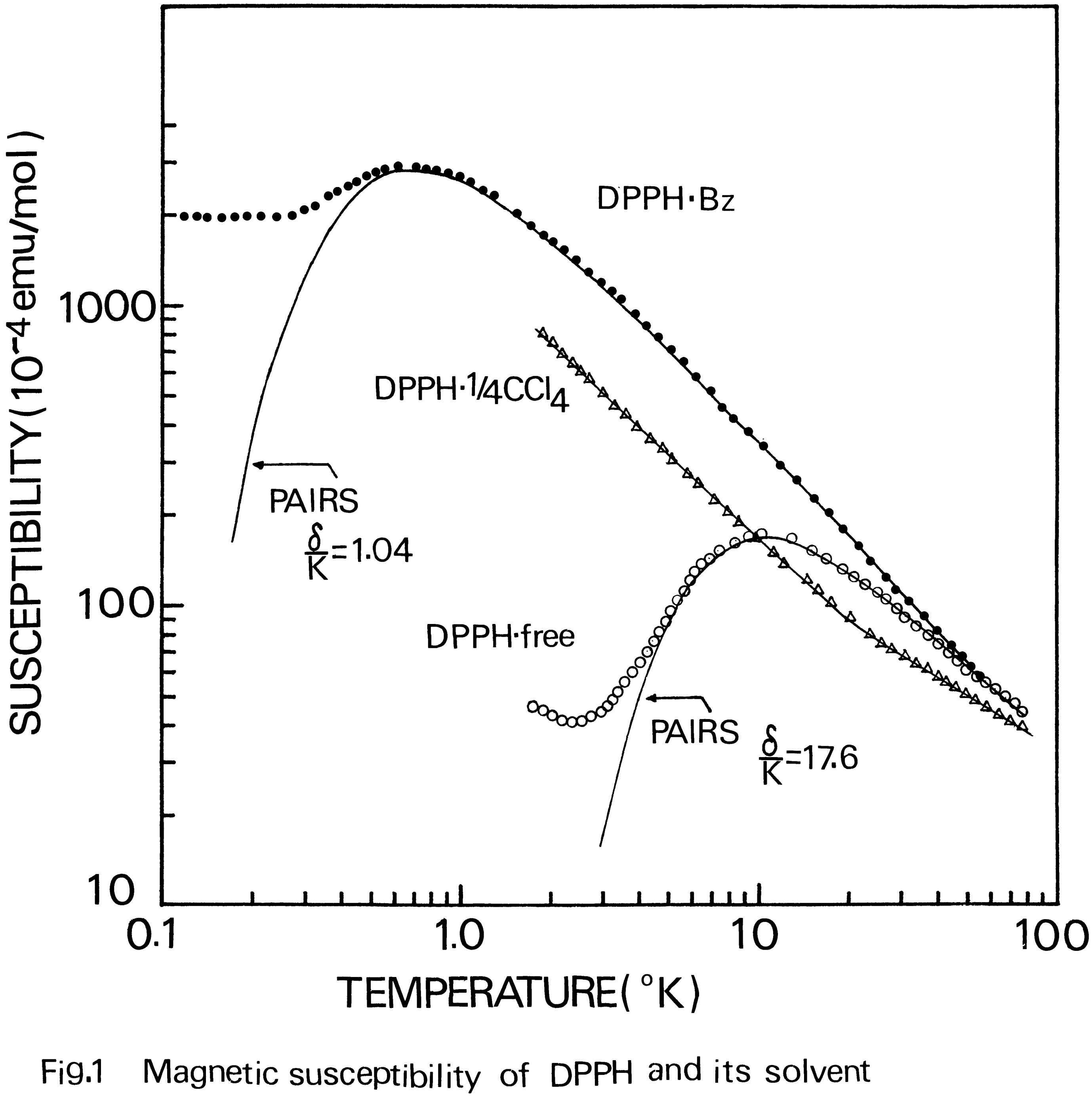

Fig.1 Magnetic susceptibility of DPPH and its solvent complexes

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