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STATIC MAGNETIC SUSCEPTIBILITY OF 1.1 DIPHENYL-2-PICRYL HYDRAZYL RECRYSTALLIZED POWDERS

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Résumé. — On a mesuré à température ordinaire les susceptibilités du radical libre stable 1,1-diphényl-2-picryl hydrazyl sous forme pulvérulente et sur des échantillons recristallisés à partir de divers solvants. On a aussi évalué la susceptibilité statique à l'aide de résultats obtenus par analyse microchimique et par ESR. On interprète les différences entre valeurs correspondant à divers solvants sur la base d'une décroissance de l'énergie d'échange, et des propriétés des paires d'électrons des solvants.

Abstract. — The powder susceptibilities of crystalline stable free radical 1.1-diphenyl-2-picryl hydrazyl and its samples recrystallized from various solvents have been measured at room temperature. The value of static susceptibility has also been evaluated with the help of the data obtained from microchemical analysis of the sample as well as from ESR measurements. The discrepancies in the two values of the recrystallized samples have been interpreted on the basis of decrease in exchange interaction and the lone pair properties of the solvents used.

1. Introduction. — 1.1-diphenyl-2-picryl hydrazyl (DPPH) like other solid free radicals show a single narrow resonance line compared to width expected from dipolar broadening. The narrowness of the line has been interpreted in terms of the exchange interaction [1] between the unpaired electrons in the radical according to the theories on ESR linewidth [2]-[4]. The sample of DPPH recrystallized from different solvents show broader line and the broadening has been attributed to a decrease in exchange interaction [5] between the unpaired spins. In order to give full justification to the interpretation of ESR data, the static susceptibility of the powder sample of DPPH as well as of the samples of DPPH recrystallized from a number of solvents has been measured. The value of static susceptibility has also been computed with the help of microchemical analysis data and the data on ESR. The discrepancies in the two values have been interpreted on the basis of exchange interaction and lone pair properties of the various solvents. These properties of the solvents will further help in interpreting the different amounts of narrowing caused by different solvents for the same magnetic dilution of the free radical.

2. Apparatus and method of measurements. — The Faraday method has been used for measuring the static susceptibility of the samples. The expression for susceptibility using this method is given as

$$\chi_m = F/mH \frac{dH}{dZ} \quad (1)$$

where χ_m is the specific or mass susceptibility and m is the mass of the specimen. F is the force experienced by the sample when placed in non-uniform magnetic field. In this case the specimen is so small that $H dH/dZ$ may be regarded as constant through this volume or at least its mean value may be employed without an appreciable error. The apparatus consists of the following parts.

2.1. — The electromagnet, which consists of two tapered pole pieces of soft iron. It gives a field of about 22 kOe in 1 cm pole gap with pole pieces of 2.5 cm face, when the coil draws a maximum allowable current of 5 A.

2.2. — A single pan Mettler analytical balance model H 16 GD, which is provided with an arrangement for weighing below the weighing compartment. It has a capacity of 80 gms and the range of optical scale is 200 mg. The least count of the balance is 10^{-5} gm. The accuracy in optical range for differential weighing is $\pm 2 \times 10^{-5}$ gm.

2.3. — The sample holder, which consists of a suspension system made of pyrex glass rod and a pyrex glass tube of about 3 mm internal diameter, contains the powdered sample, which is suspended below the pan of the balance.

The complete detail of the set up including the arrangement for static magnetic field as well as the sample holder is described elsewhere [6], [7]. In practice, the eq. (1) has not been used directly, but the balance is standardized with the help of a standard

substance of known susceptibility like $\text{HgCo}(\text{CNS})_4$ and Mohr's salt etc. We used $\text{HgCo}(\text{CNS})_4$ for calibration. The value of susceptibility per unit rate of $\Delta m/m$ has been determined which has served as calibration constant. The value of χ_m obtained has also been corrected for diamagnetism using Pascal's constants [7],

$$(\chi_m)_{\text{correct}} = \chi_m + D \quad (2)$$

where D is diamagnetic correction.

The preparation of the sample as well as its ESR data has been described in separate communication [8]-[10]. The microchemical analysis of each sample has been performed and the data are presented in table I. In order to get the susceptibility theoretically following expression has been used.

$$(\chi_m)_{\text{theor}} = \frac{N' g^2 \beta^2 S(S+1)}{3KT} \quad (3)$$

where N' is the number of magnetic ions per gram and rest of the symbols have their usual meaning. The values of g , the spectroscopic splitting factor, have been taken from the ESR measurements [8]-[10] and N' have been obtained from the data of microchemical analysis using the following relation

$$N' = \frac{Nm}{M} \quad (4)$$

where N is the Avogadro's number, M ($= 394.33$) is the molecular weight of the DPPH and m is the weight of the free radical in one gram complex.

3. Results and discussion. — The mass susceptibility χ_m per gram of DPPH powder and its all recrystallized samples have been measured at room temperature. The value of $(\chi_m)_{\text{theor}}$ and the diamagnetic corrections of all samples have been evaluated by using the data of microchemical analysis and ESR [8]-[10]. All results are given in table I and nearly in all the samples the magnetic susceptibility has been found to increase. The percentage concentration of the free radical DPPH is calculated and its value is 65.6 %. The magnetic susceptibility of DPPH free radical powder has been measured by different workers [11]-[16]. The temperature variation of the susceptibility has shown that at ordinary temperature the substance shows an antiferromagnetic coupling and a transition from antiferromagnetic to ferromagnetic coupling takes place at lower temperature.

When the free radical are recrystallized from different solvents, molecular addition complexes are formed [11], [17], [18] with the result that the free radicals are diluted as well as slight changes in lattice are also produced [19], [20]. Such recrystallized samples on ESR study have shown pronounced broadening in linewidth [11], [17], [18]. Both the linewidth parameters like dipole-dipole interaction and exchange interaction decrease [5] but decrease in the latter is more than the former because it being of exponential form [21]. Hence the exchange interaction seems to play the main role in producing the broadening in the linewidth. The broadening of the resonance or the decrease in the exchange may be attributed to an increase in the correlation time of the exchange motion and this finally may results in producing the magnetic ordering in the system. The increase in magnetic

TABLE I

S. No.	Sample	Ratio of DPPH to solvents by weight	$N' \times 10^{-20}$	g values	$(\chi_m)_{\text{theor}} \times 10^6/\text{gm}$ (Cgs)	$(\chi_m)_{\text{exp}} \times 10^6/\text{gm}$ (Cgs)	Amount of diamagnetic correction $\times 10^6/\text{cm}$ (Cgs)	$(\chi_m)_{\text{Correct}} \times 10^6/\text{gm}$ (Cgs)
1	DPPH powder	...	15.27	2.003 6	3.18	1.58	0.50	2.08
	Samples of DPPH recrystallized from							
2	Pyridine	1 : 3.7	3.25	2.003 2	0.68	15.50	0.60	16.10
3	2,4-dinitrofluorobenzene	1 : 4.5	2.78	2.003 4	0.58	10.82	0.45	11.27
4	Diallylamine	...	...	2.003 7	...	9.32	...	...
5	Tetrahydrofuran	1 : 1.5	6.11	2.003 7	1.29	3.19	0.63	3.82
6	Methylene-chloride	1 : 1.0	7.64	2.003 5	1.59	2.10	0.56	2.66
7	Chlorobenzene	1 : 1.2	6.95	2.003 3	1.45	2.40	0.58	2.98
8	Dimethyl Formamide	1 : 3.2	3.64	2.003 3	0.76	2.64	0.63	3.27
9	Di- <i>n</i> -Amylamine	...	...	2.000 7	...	2.13	...	...
10	Benzene	1 : 0.7	8.98	2.003 6	1.87	2.55	0.59	3.14
11	Carbon Tetrachloride	1 : 1.2	6.95	2.003 5	1.48	2.00	0.53	2.53
12	Benzyl Chloride	1 : 5.5	2.35	2.003 6	0.49	1.24	0.64	1.88
13	Chloroform	1 : 1.0	7.64	2.003 6	1.59	1.18	0.54	1.72
14	Isobutylamine	1 : 6.0	2.18	2.002 8	0.46	0.60	0.80	1.40
15	Dibenzylamine	1 : 10.0	1.39	2.003 4	2.29	0.18	0.67	0.85
16	Benzylamine	1 : 19.8	0.73	2.003 6	0.15	0.15	0.69	0.84
17	Benzaldehyde	1 : 5.9	2.21	2.003 1	0.46	0.14	0.60	0.74
18	N-Propyl Cyanide	1 : 0.25	12.22	2.003 5	2.55	1.54	0.55	2.09

ordering in the recrystallized samples will ultimately be effective in increasing the magnetic susceptibility of the compound. The amount of increase in magnetic ordering or decrease in exchange depends upon the nature of the solvent and also on its affinity of complex formation with the free radical molecule. With the result the samples of DPPH recrystallized from different solvents have shown different value of susceptibility.

In some of the recrystallized samples given in table I, the magnetic susceptibility has been found to increase more rapidly than others. For example the samples of DPPH recrystallized from solvents, pyridine, 2,4-dinitrofluorobenzene and diallylamine have shown large abnormalities whereas the samples of diamylamine, tetrahydrofuran, methylene-chloride, chlorobenzene and dimethylformamide have shown lesser abnormality as far as susceptibility data are concerned. The abnormal behaviour of these solvents apart from their other properties may be correlated to some extent to their structural formula. As such nearly all the solvents are diamagnetic but in association with the free radical they behave quite differently as regards the magnetic property. A general survey of the chemical structures of these solvents show that each of them has got an atom having a lone pair of electrons on them namely either on oxygen atom (tetrahydrofuran), or nitrogen (pyridine, 2,4-dinitrofluorobenzene, diamylamine, diallylamine and dimethyl-formamide) or chlorine (dichloromethane and chlorobenzene). Thus it is quite probable that when the free radical and any one of such solvents containing a lone pair form a compound (either a complex or associated) the increased magnetic susceptibility on account of increased magnetic ordering

due to decrease of exchange among the lone electron of the free radical may further increase due to the presence of effective lone pair of the electrons of the solvent molecule. The lone pair of electrons present on nitrogen atoms with benzene ring has been found more effective in this process. One lone electron of the free radical may have some exchange activity with the lone pair of electrons of solvents and thus may produce broadening in their ESR lines. The conclusion derived from these theoretical as well as experimental parameters will further help in interpreting the data on ESR.

Further samples of DPPH recrystallized from benzylchloride, Chloroform, isobutylamine, dibenzylamine, benzylamine and benzaldehyde have not shown any abnormal behaviour in comparison to those cited above. The value of magnetic susceptibility of these complexes has decreased than that of parent free radical. It appears from the data of microchemical analysis that most of them have sufficiently been diluted and is just possible that the effect of increase in magnetic ordering due to decrease in exchange and also the effects of lone pair electrons of the solvents could not be able to compensate the decrease in susceptibility due to magnetic dilution of the parent free radical in the complexes. Moreover it is possible that the molecular addition complexes might have been formed in such a way that the lone pairs of the solvents, any how, could not be able to contribute their share to the value of susceptibility of their complexes.

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