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CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF 1,5-DIPHENYL-3-(*p*-METHACRYLOYLOXYMETHYLPHENYL) VERDAZYL RADICAL.

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Abstract The crystal structure of 1,5-diphenyl-3-(*p*-methacryloyloxymethyl phenyl)verdazyl radical has been determined. It shows a non-symmetrical antipropeller conformation of its three aryl rings. The molecules are packed in a tilted face-to-face and head-to-tail array giving rise to close overlaps between π-orbitals of *sym*-tetrazinyl and C-aryl rings of neighbour molecules. The a.c. magnetic susceptibility data indicate that this compound behaves as a quasi-ideal S = 1/2 paramagnet. This quasi-ideal magnetic insulation of the molecules is interpreted in terms of the McConnell's formalism.

INTRODUCTION

The search for organic molecular solids showing magnetic ordering (ferro-, ferri-, antiferro-, metamagnetic-, etc.) is an area of increasing interest[1]. 1,5-diphenyl-3-(*p*-methacryloyloxymethylphenyl)verdazyl radical (DMVz) has been reported to exhibit interesting magnetic behaviour[2]. Above 100K the temperature dependence of the paramagnetic susceptibility follows the Curie-Weiss law with a large negative Weiss constant (-21.9K), suggesting the existence of rather strong antiferromagnetic intermolecular interactions in the material. In addition, a deviation from the typical behaviour of an antiferromagnet occurs below 100K. Thus, from 100 to 4K the paramagnetic susceptibility increases continously as the temperature lowers, the observed susceptibility being always higher than the

extrapolated from Curie-Weiss law. This behaviour contrasts with that previously reported for other verdazyl radicals and most organic free radicals[3]. The magnetic behaviour of 1,3,5-triphenylverdazyl (TPVz)[4], 1,3-di-*p*-tolyl-5-phenyl verdazyl (DTPVz)[5], 1,3,5-triphenyl-6-metylverdazyl (MeTPVz)[6], 1,5-diphenyl-3-(4-chlorophenyl)verdazyl (ClP-DPVz)[7], and 1-(4-methoxyphenyl)-3,5-diphenylverdazyl (MeOP-DPVz)[8] radicals follow well a model of isolated magnetic linear chains with antiferromagnetic intrachain interactions. Consequently, their magnetic properties have been explained in the context of one-dimensional Heisenberg or Ising models in a broad temperature range. Deviations from these models appear to be significant only below 100K. On the other hand, the magnetic susceptibility of 1,3,5-tri-p-tolylverdazyl radicals (TTVz) follows, down to 1.8K, the Curie-Weiss law with a negative Weiss constant, Θ = -1K[9].

Since Kamachi et al.[2], have only reported a qualitative description of the magnetic anomalies of DMVz without further analysis we have undertaken a reinvestigation of this interesting compound. In this communication we present the crystal structure of DMVz radical and the a.c. magnetic susceptibility measurements in a broad temperature range. The observed magnetic behaviour is tied to the molecular and crystal structure in the material within McConnell's formalism[10]. In order to elucidate magneto-structural relationships, a comparison between DMVz and other verdazyl radicals is also given.

RESULTS AND DISCUSSION

Molecular geometry and conformation

Figure 1 shows the structure of DMVz radicals together with some selected bond distances. The Bond distances and angles of DMVz radicals are very close to those reported for other verdazyl radicals[6,7,9,11,12]. The N(1), N(2), N(4) and N(5) atoms lie in a plane (refered to as the N-plane) and C(3) and C(6) are 0.144 and 0.629 Å away from this plane. The corresponding dihedral angles at both ends of the *sym*-tetrazinyl ring are 14.0 and 46.2° respectively. Therefore, the *sym*-tetrazinyl ring has an asymmetrical boat conformation which is similar to those

reported for other verdazyl radicals (dihedral angles, ca 11° and 44°). The sums of the three bond angles around the three-coordinated N(1), N(5), and C(3) atoms are 360°, 359° and 360° respectively, indicating sp^2 hybridization in those atoms. Accordingly, the unpaired electron of DMVz radicals must be delocalized over five of the atoms of the *sym*-tetrazinyl ring; i.e., N(1), N(2), C(3), N(4) and N(5). In order to give the molecular conformation and to analyze the unpaired electron delocalization in the rest of the molecule, the mutual arrangement of the three aromatic rings is best described by the so called π-twist angles. Such angles are defined as those between the normal to the least-square mean plane for each aromatic ring and the p-orbital axis of the N(1), N(5) and C(3) atoms. The π-twist angles of the N(1)-phenyl, N(5)-phenyl and C(3)-aryl rings are 19.4, -11.7 and 27.5°, respectively.

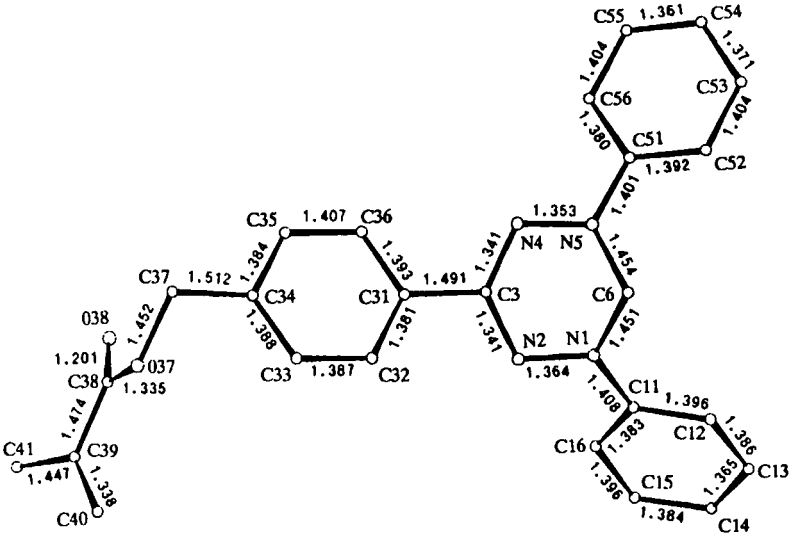

FIGURE 1 Perspective view of DMVz radical showing atom numbering scheme and bond distances

The two N-phenyl rings are twisted in opposite directions with angles which are close to those observed in other verdazyl radicals (from 10° to 21°), while the C-aryl ring is more twisted than in most cases (from 0° to 7°)[6,9,11,12]. A strong deviation from coplanarity between the C-aryl ring and N-plane has been

described only for the ClP-DPVz radical, π-twist angle of 25.2°, where strong intermolecular (Cl ... Cl) forces exist[7]. The non-symmetrical antipropeller conformation of DMVz radical seems to be favourable for a large delocalization of the unpaired electron on both the *sym*-tetrazinyl ring and the three aromatic rings, especially on the two N-phenyl rings.

Molecular packing

The mutual arrangement of the DMVz molecules is shown in Figure 2. The molecules are packed in thick sheets, c/2 wide, parallel to the ab plane. The unit cell, with Z=8, consists of two such molecular sheets which are mutually related by an inversion center. The number of intermolecular distances shorter than 4.0 Å from a reference molecule to its 16 neighbouring molecules[13] is 393, 70 of which possess an intersheet character. Inside the sheets, the molecules pack in a tilted face-to-face and head-to-tail array along the b-axis, so that incomplete and very close overlaps between the *sym*-tetrazinyl and C-aryl rings are observed. At first glance, each molecular sheet might be described as an array of molecular chains parallel to the b-axis. However, this is a too simple packing description, since there are 192 intermolecular approaches shorter than 4.0 Å from each molecule to its neighbours (2) at the same chain and 131 approaches to its neighbours (6) in the two adjacent chains. These figures clearly show the complexity of intermolecular interactions in this sheet-like crystal structure,which is unprecedented in other verdazyl radicals.

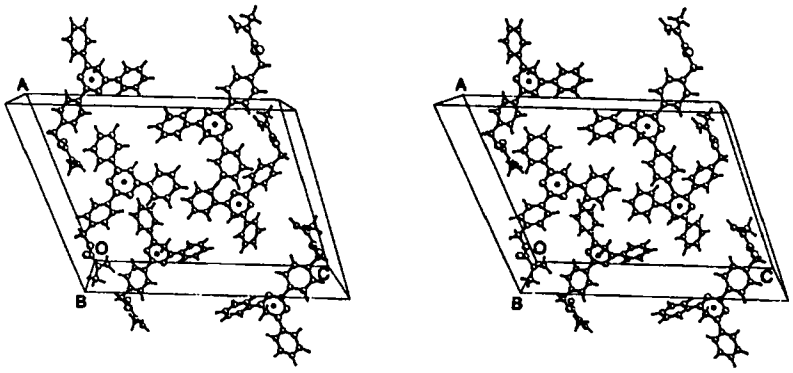

FIGURE 2 Stereoscopic view of the crystal structure of DMVz radical

Magnetic Susceptibility

The experimental data have been corrected for the diamagnetic contribution of the molecule using Pascal's constants (χ_{dia} = -0.354 . 10^{-3} emu/mol)[14]. The temperature dependence of the inverse of paramagnetic susceptibility is shown in Figure 3. The data follow a Curie Weiss law with C = 0.397 emu K/mole and Θ = -1.24K. Therefore, DMVz radicals exhibit a constant effective magnetic moment, μ_{eff}, of 1.78 μ_B. A significiant feature of these magnetic measurements is that they disagree with previously reported ones[2]. Our results correspond to a quasi-ideal S = 1/2 paramagnet possessing very weak deviation from Curie law, while those reported by Kamachi et al. seem to indicate a rather strong deviation

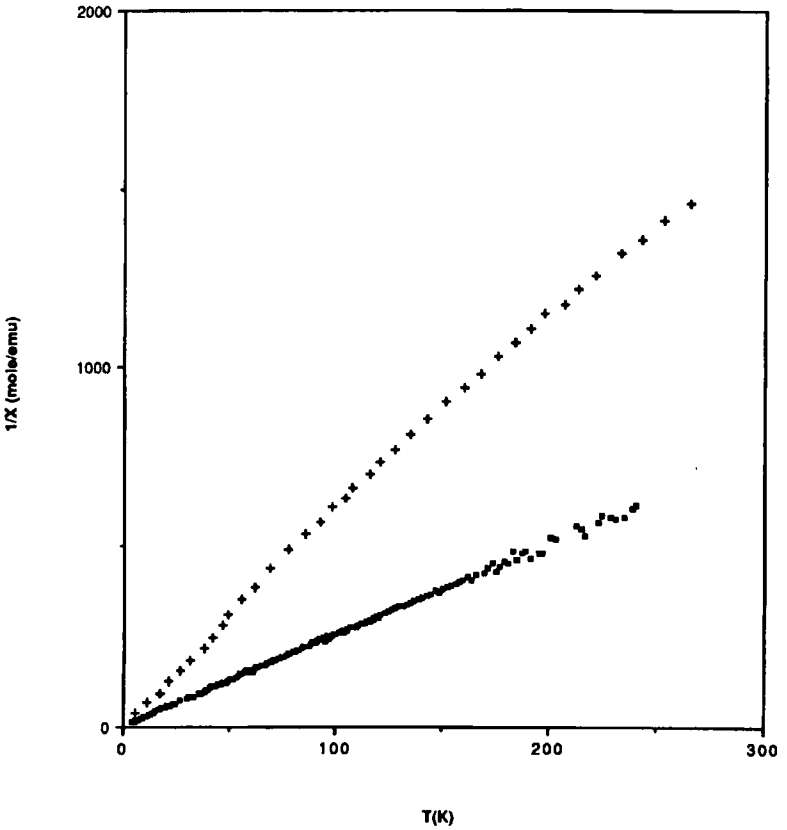

FIGURE 3 Temperature (K) dependence of χ^{-1} (emu/mole)$^{-1}$ for DMVz radicals. The squares correspond to the experimental data obtained in this work and the crosses to Kamachi et al. data

from this behaviour. Although these authors do not provide further analysis of their measurements, it is possible to determine from their figure an effective moment of the sample at low temperatures (4.2 to 60K) ,μ_{eff}=0.91 μ_B. Both, the low value of μ_{eff} and the lack of linearity of the χ^{-1} vs. T plot reported by these authors, might be adscribed to low radical purity of the studied sample. In Figure 3 we compare the temperature dependence of χ^{-1} for both sets of measurements.

Intermolecular magnetic interactions

It is also interesting to compare the magnetic behaviour of DMVz with other verdazyl radicals. We have already mentioned that such derivatives as TPVz, DTPVz, MeTPVz, ClP-DPVz, and MeOP-DPVz present a low dimensional magnetic behaviour. On the contrary, DMVz and TTVz do not exhibit deviation from the Curie Weiss law down to 4.2 and 1.8K, respectively. Since magnetic interactions in these compounds are intermolecular and no charge transfer processes between neighbour molecules are present, it is convenient to base the comparative analysis in the frame of the expanded form of the Heisenberg Hamiltonian proposed by McConnell[10],

$$\mathcal{H} = - \sum_{AB} \hat{s^A} s^B \sum_{ij} J_{ij}^{AB} \hat{\rho_i^A} \rho_j^B \qquad (1)$$

where S^A and S^B are the total spin moments of molecules A and B, ρ^A and ρ^B the π-spin densities on atoms i and j of molecules A and B, respectively, and J_{ij}^{AB} is the magnetic exchange integral between interacting atoms. The second sum extends over all the pairs of interacting atoms which can be formed in molecules A and B. The first sum extends over all the interacting molecules in the solid although in practice intermolecular interaction other than between nearest neighbours may be negligible. McConnell's formulation emphasizes that magnetic behaviour in a molecular solid is governed by both the magnetic exchange integrals and the product of spin densities of different atoms from distinct molecules. A major drawback to quantitative estimations following this procedure even in simple cases, is the difficulty of calculating accurately J_{ij}^{AB}, since it is very sensitive to both interatomic distances and the relative orientation of the interacting $2p_z$-orbitals. However, it is still possible to obtain

qualitative information roughly correlating J_{ij}^{AB} with the mutual dispositions of interacting atoms, in particular those with large spin densities. Thus, Eq. 1 has permitted interpretation, at the molecular level, the macroscopic magnetic behaviour of several radicals and carbenes[15,16].

Differences in the magnetic behaviour of solid triarylverdazyl radicals have been ascribed to their distinct molecular packing (different set of J_{ij}^{AB} values) rather than to differences in their spin density distribution (similar set of A and B values).[16] The analysis of ESR and ENDOR spectra indicate that these radicals have similar spin distributions; furthermore, most of their spin density is located on the *sym*-tetrazinyl and N-aryl rings, only a small amount of it (< 5%) being left on the C-aryl ring[17]. Deviation from coplanarity in the C(3)-aryl ring of DMVz radical is not expected to produce a significant redistribution of the spin density, since the semi-occupied molecular orbital has a node at C(3) atom and the operative mechanism in the transmission of spin onto this ring is the spin polarization one. Therefore, it is acceptable to assume that the spin density distribution of DMVz is similar to that of other verdazyl radicals, as is indeed confirmed by the identical ESR hyperfine coupling constants observed for the four equivalent N atoms.

The most relevant intermolecular contacts among atoms with large spin densities in DMVz and TTVz radicals are those between N atoms of the *sym*-tetrazinyl ring (the atoms with the largest spin densities)[17] and C atoms of the C(3)-aryl ring. Both the interatomic separations and the relative orientation of the overlaping $2p_z$-orbitals are adequate to produce significant J_{ij}^{AB} values. Despite this favourable situation, the extremely low spin densities located on the atoms of C(3)-aryl ring suggest a null (or very low) intermolecular magnetic interaction, as is indeed observed from the magnetic susceptibility measurements.

Intermolecular contacts between *sym*-tetrazinyl and C-aryl rings are not present in TPVz, DTPVz, MeTPVz, and ClP-DPVz radicals. Instead of such contacts the N-atoms are close to atoms with higher spin densities (N and/or C atoms of N-aryl rings of neighbour molecules) explaining thus the low dimensional magnetic behaviour observed in such racicals.

In conclusion, the macroscopic magnetic behaviour of DMVz radicals has

been rationalized at the molecular level in terms of a quasi-ideal magnetic insulation of the radical molecules.

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