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Strong Supramolecular-Based Magnetic Exchange in π-Stacked Radicals. Structure and Magnetism of a Hydrogen-Bonded Verdazyl Radical:Hydroquinone Molecular Solid

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Abstract: The X-ray crystal structure and magnetic properties of a molecular crystal consisting of 1,5-dimethyl-3-(2-pyridyl)-6-oxoverdazyl radical and hydroquinone (**pyvd:hq**) are presented. The structure contains a two-dimensional network of hydrogen bonds involving the hydroquinones and the pyridine ring of the **pyvd** radical. The radicals adopt an unusual head-over-tail (antiparallel) π-stacked array perpendicular to the hydrogen-bonded planes. The variable-temperature magnetic susceptibility data can be modeled using a one-dimensional antiferromagnetic chain model, with $J = -58$ cm^{-1}. The strength of the magnetic coupling is very unusual because there are no close intermolecular radical−radical contacts to provide conventional pathways for magnetic interactions. A pathway for coupling is proposed involving the mediation of magnetic exchange interactions between radical centers by the pyridine rings. Density functional calculations on the **pyvd** radical, as well as aggregates thereof based on the X-ray structure, have been employed in attempts to understand the possible mechanisms by which the strong magnetic interactions are achieved.

Introduction

The magnetic properties of organic materials have been intensely studied in recent years. One of the main motivations behind this multidisciplinary stream of research, which brings together synthetic chemistry, theory, and solid-state physics, is the prospect of creating new magnetic materials from nonmetallic components.[1] One of the substantial challenges in this field is to develop structure/magnetism correlations as an aid in the design of new magnetic materials. This challenge is embodied in attempts to relate intermolecular magnetic exchange interactions (as evidenced from magnetic susceptibility) and specific solid-state packing patterns. In this sense, the idea that molecular magnetism is very much a "*supramolecular* function" is now well recognized.[2] Consequently, there have been significant efforts to introduce the concepts and strategies of crystal engineering to radical-based structure design. This has been achieved through the synthesis of radical derivatives bearing a variety of supramolecular synthons[3] (usually hydrogen bond donors and/or acceptors) which may influence the solid-state structure and may also provide new pathways for intermolecular magnetic communication between radicals.[4−14] Although some progress has been made in controlling molecular packing, the magnetic interactions through noncovalent interactions are generally very weak. These weak interactions effectively limit the possibility of bulk magnetic order in organic materials to extremely low temperatures.

The organic radicals that have been subjected to solid-state magnetic investigations are limited in scope. The main limitation is likely the scarcity of open-shell organic molecules with sufficient stability to exist as radicals in the condensed phase. Nitroxides (**1**) and nitronyl nitroxides (**2**) have traditionally dominated this field of research because of their exceptional stability. However, as supramolecular building blocks they are less than ideal. The chemical requirements for stability (generally the carbon atoms α to the NO functionality must not contain hydrogen atoms) render the molecular structures of these radicals highly nonplanar. Heterocyclic thiazyl radicals (e.g., **3**,[15,16] **4**[17,18]) and verdazyl radicals (**5**) are appealing building blocks for radical-based solids because of their planar rings, relative lack of bulky substituents, and preponderance of potential hydrogen-bonding acceptor sites. The magnetic properties of several verdazyl derivatives have been reported,[19−24] although supramo-

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(1) *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999.

(2) *Magnetism: A Supramolecular Function*; Kahn, O., Ed.; Kluwer: Dordrecht, 1996.

(3) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311.

(4) Hernàndez, E.; Mas, M.; Molins, E.; Rovira, C.; Veciana, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 882.

(5) Cirujeda, J.; Hernandez-Gasió, E.; Rovira, C.; Stanger, J. L.; Turek, P.; Veciana, J. *J. Mater. Chem.* **1995**, *5*, 243.

(6) Akita, T.; Mazaki, Y.; Kobayashi, K. *J. Chem. Soc., Chem. Commun.* **1995**, 1861.

(7) Izuoka, A.; Kumai, R.; Sugawara, T. *Adv. Mater.* **1995**, *7*, 672.

(8) Akida, T.; Kobayashi, K. *Adv. Mater.* **1997**, *9*, 346.

(9) Matsushita, M. M.; Izuoka, A.; Sugawara, T.; Kobayashi, T.; Wada, N.; Takeda, N.; Ishikawa, M. *J. Am. Chem. Soc.* **1997**, *119*, 4369.

(10) Jürgens, O.; Cirujeda, J.; Mas, M.; Cabrero, A.; Vidal-Gancedo, J.; Rivera, C.; Molins, E.; Veciana, J. *J. Mater. Chem.* **1997**, *7*, 1723.

(11) Stroh, C.; Romero, F. M.; Kyritsakas, N.; Catala; Turek; Ziessel *J. Mater. Chem.* **1999**, *9*, 875.

(12) Papoutsakis, D.; Kirby, J. P.; Jackson, J. E.; Nocera, D. G. *Chem. Eur. J.* **1999**, *5*, 1474.

(13) Endtner, R.; Rentschler, E.; Bläser, D.; Boese, R.; Sustmann, R. *Eur. J. Org. Chem.* **2000**, 3347.

(14) Romero, F. M.; Ziessel, R.; Bonnet, M.; Pontillon, Y.; Ressouche, E.; Schweizer, J.; Delley, B.; Grand, A.; Paulsen, C. *J. Am. Chem. Soc.* **2000**, *122*, 1298.

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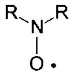
lecular strategies with respect to this radical framework remain essentially unexplored.[25] Herein we present the structure, magnetism, and computational studies of a verdazyl radical whose solid-state structure simultaneously possesses two of the common hallmarks of supramolecular chemistry, i.e., hydrogen bonding and π stacking. As we demonstrate below, the magnetic properties of this material are highly unusual in that strong magnetic exchange interactions are prevalent *despite the absence of close intermolecular contacts exclusively involving atoms bearing substantial spin density*, a finding with broad implications for understanding the magnetic properties of organic solids.



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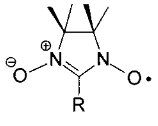

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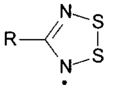

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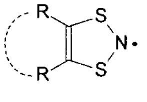

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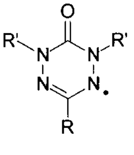

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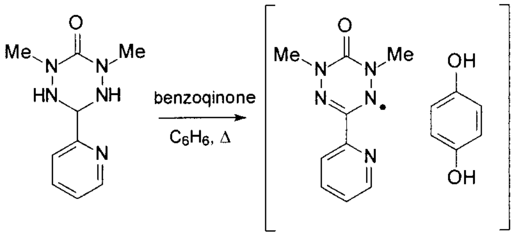
Experimental Section

Crystal Structure Determination The **pyvd:hq** complex was synthesized as previously described.[26] Dark orange/maroon blocks needles were prepared by recrystallization from benzene/ethyl acetate, mounted on a glass fiber, and transferred to an Enraf Nonius CAD4 diffractometer for cell determination and data collection. Data collection was performed using Mo Kα radiation (0.7093 Å). The raw data were processed, solved, and refined by full-matrix least-squares refinement with the NRCVAX suite of programs. Direct methods were used to solve the structure. Hydrogen atoms were constrained to idealized positions. Crystal data for **pyvd:hq**: $C_{15}H_{16}N_5O_3$, $M = 314.33$, triclinic, space group = $P\bar{1}$ (No. 2), $a = 6.8197(10)$ Å, $b = 10.4498(10)$ Å, $c = 10.7385(10)$ Å, $\alpha = 85.930(10)°$, $\beta = 80.161(10)°$, $\gamma = 87.029(10)°$, $U = 751.50(15)$ Å^3, $T = 293$ K, $Z = 2$, 2793 reflections collected, 2637 unique ($R_{\mathrm{int}} = 0.008$), $R(F) = 0.050$, $R_w(F) = 0.081$, GOF = 1.04.

Magnetic Susceptibility. Variable-temperature magnetic data (2−300 K) were obtained with a Quantum Design MPMS5S Squid magnetometer operating at 0.1−0.5 T. Calibrations were carried out with a palladium standard cylinder, and temperature errors were determined with $[H_2TMEN][CuCl_4]$.[27]

Scheme 1



pyvdH$_3$ **pyvd : hq**

Computational Studies. Calculations were made using DGauss[28] employing the exchange and correlation functionals of Becke[29] and Perdew,[30,31] respectively (BP86), together with an extra-fine integration grid. A DFT-optimized DZVP basis set with contractions H [2s], C, N, O [3s, 2p 1d] was used.[32] Calculation of the magnetic couplings using a broken symmetry "wave function" was performed on a stacked three-radical model using the X-ray geometry.

Results

Description of the Structure. As previously described,[26] oxidation of the tetrazane **pyvdH$_3$** with 1,4-benzoquinone affords the 1,5-dimethyl-3-(2-pyridyl)-6-oxoverdazyl radical **pyvd**, which crystallizes in a 1:1 stoichiometry with hydroquinone, the reaction byproduct (Scheme 1).This material (**pyvd:hq**) can be recrystallized without decomposition of the radical and is indefinitely stable in the solid state. The two components can be easily separated by chromatography, but the as-purified radical decomposes within a day. Similar stability problems are encountered in the synthesis of **pyvd** when **pyvdH$_3$** is oxidized with other reagents. The long-term stability of this radical therefore relies on lattice stabilization as its hydroquinone complex.

The crystal structure of **pyvd:hq** confirms its composition as a 1:1 verdazyl:hydroquinone complex. The molecular structural parameters of the hydroquinone molecules are unremarkable. An ORTEP drawing of the **pyvd** radical is presented in Figure 1. The verdazyl ring of **pyvd** is essentially planar and is nearly coplanar with the 2-pyridyl substituent (torsion angle = 2.4°). The internal structural features of the verdazyl ring are consistent with other crystallographically characterized 6-oxoverdazyls.[24,33] Two views of the packing in the **pyvd:hq** complex are shown in Figures 2 and 3. The **pyvd** molecules assemble into head-over-tail stacks parallel to the x axis. The molecules are aligned such that the verdazyl moiety of each **pyvd** is nearly superimposed over the pyridine ring of the nearest neighbor within the stacks (Figure 2). The mean interplanar separations within the stacks alternate slightly (3.37 and 3.44 Å). The hydroquinones reside in layers between the **pyvd** stacks in the xz plane (Figure 3). There are two crystallographically independent hydroquinone sites centered at special positions ($^1/_2$,0,0) and ($^1/_2$,0,$^1/_2$) (hereafter referred to as HQA and HQB, respectively). Both of the OH groups of HQA are hydrogen-bonded to the oxygen atoms of the HQB molecules, creating hydrogen-bonded chains running along the z axis. Both OH groups of HQB are hydrogen-bonded to the pyridine nitrogen atoms of

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[15] Banister, A. J.; Bricklebank, N.; Lavender, I.; Rawson, J. M.; Gregory, C. I.; Tanner, B. K.; Clegg, W.; Elsegood, M. R. J.; Palacio, F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2533.

[16] Antorrena, G.; Davies, J. E.; Hartley, M.; Palacio, F.; Rawson, J. M.; Smith, J. N. B.; Steiner, A. *Chem. Commun.* **1999**, 1393.

[17] McManus, G. D.; Rawson, J. M.; Feeder, N.; Palacio, F.; Oliete, P. *J. Mater. Chem.* **2000**, *10*, 2001.

[18] Fujita, W.; Awaga, K. *Science* **1999**, *286*, 261.

[19] Takeda, K.; Konishi, K.; Nedachi, K.; Mukai, K. *Phys. Rev. Lett.* **1995**, *74*, 1673.

[20] Kremer, R. K.; Kanellakopulos, B.; Bele, P.; Brunner, H.; Neugebauer, F. A. *Chem. Phys. Lett.* **1994**, *230*, 255.

[21] Mukai, K.; Kawasaki, S.; Jamali, J. B.; Achiwa, N. *Chem. Phys. Lett.* **1995**, *241*, 618.

[22] Mukai, K.; Wada, N.; Jamali, J. B.; Achiwa, N.; Narumi, Y.; Kindo, K.; Kobayashi, T.; Amaya, K. *Chem. Phys. Lett.* **1996**, *257*, 538.

[23] Mukai, K.; Nuwa, M.; Suzuki, K.; Nagaoka, S.; Achiwa, N.; Jamali, J. B. *J. Phys. Chem. B* **1998**, *102*, 782.

[24] Brook, D. J. R.; Fox, H. H.; Lynch, V.; Fox, M. A. *J. Phys. Chem.* **1996**, *100*, 2066.

[25] Allemand, P. M.; Srdanov, G.; Wudl, F. *J. Am. Chem. Soc.* **1990**, *112*, 9391.

[26] Barr, C. L.; Chase, P. A.; Hicks, R. G.; Lemaire, M. T.; Stevens, C. L. *J. Org. Chem.* **1999**, *64*, 8893.

[27] Brown, D. S.; Crawford, V. H.; Hall, J. W.; Hatfield, W. E. *J. Phys. Chem.* **1977**, *81*, 1303.

[28] DGauss 5.0 Oxford Molecular Group, Inc., 1999: Andzelm, J.; Wimmer, E. *J. Chem. Phys.* **1992**, *96*, 1280.

[29] Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

[30] Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

[31] Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406.

[32] Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560.

[33] Neugebauer, F. A.; Fischer, H.; Krieger, C. *J. Chem. Soc., Perkin Trans. 2* **1993**, 535.

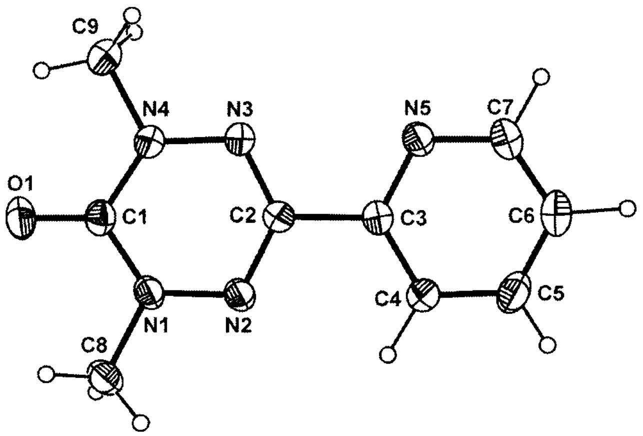


Figure 1. ORTEP drawing of **pyvd**. Ellipsoids are drawn at 30% probability. Selected bond lengths [Å]: C1−O1 1.217(3), C1−N1 1.367(4), C1−N4 1.379(4), N1−N2 1.365(3), N3−N4 1.358(3), N2−C2 1.323(4), N3−C2 1.321(4), C2−C3 1.489(4), N1−C8 1.454(4), N4−C9 1.460(4). Selected bond angles [°]: O1−C1−N1 123.0(3), O1−C1−N4 123.0(3), N1−C1−N4 114.0(2), N1−N2−C2 114.8(2), N2−C2−N3 127.5(2), C2−N3−N4 114.9(2), N3−N4−C1 124.4(3), N4−N4−C9 116.2(3), N2−N1−C8 115.6(3), N2−C2−C3 115.65.

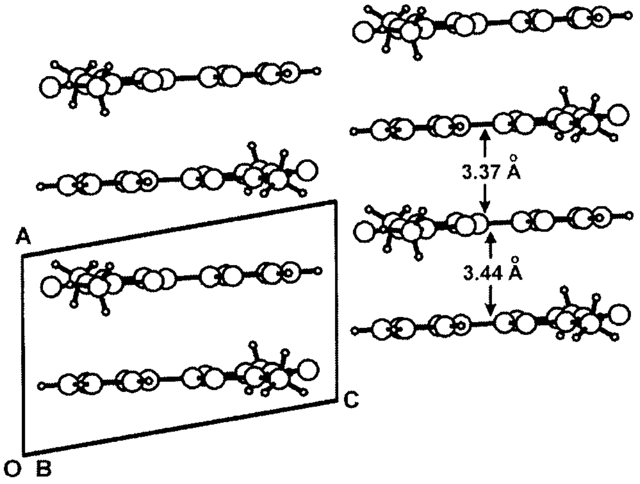


Figure 2. Antiparallel π-stacking of **pyvd** radicals in **pyvd:hq**. The hydroquinone molecules are omitted for clarity.

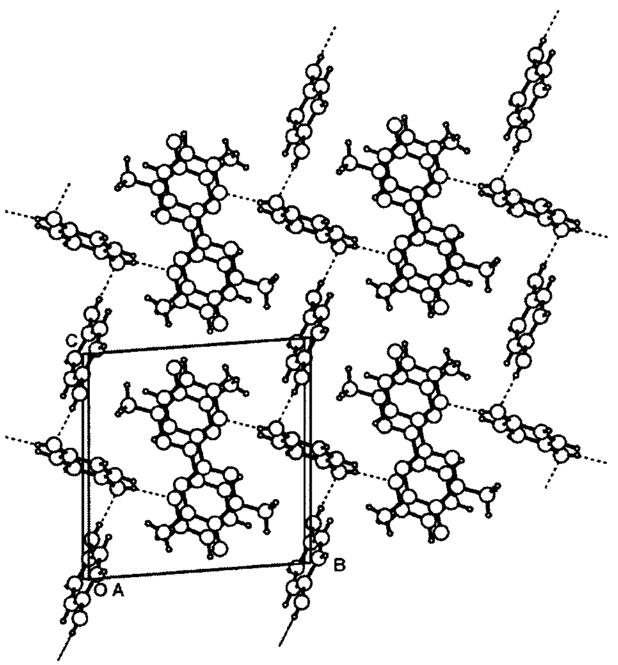


Figure 3. Molecular packing of **pyvd:hq** parallel to the *yz* plane. Hydrogen bonds are indicated by dashed lines.

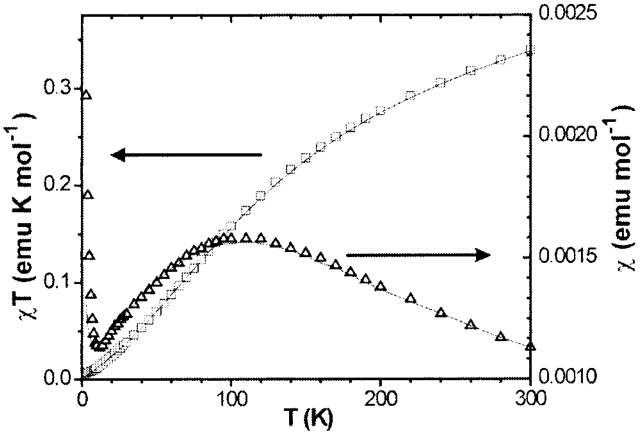
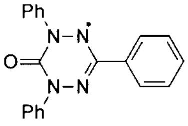


Figure 4. Temperature dependence of χ (△) and χT (○) for **pyvd:hq**.

neighboring verdazyl radicals. The orientation of the HQB molecules is nearly perpendicular to the **pyvd** molecules, such that the pairs of hydrogen bonds involving individual HQB are with two pyridine rings that are out of registry with one another by half a unit cell. Thus, as Figure 3 illustrates, the **pyvd:hq** structure consists of a two-dimensional net of hydrogen bonds in the *yz* plane and π-stacked radicals running perpendicular to this plane parallel to *x*.

Magnetic Behavior of the Complex. Variable-temperature magnetic susceptibility measurements were carried out on a microcrystalline sample of **pyvd:hq**. The temperature dependence of the susceptibility (presented as χT vs T and χ vs T) is shown in Figure 4. At 300 K, the value of χT (0.34 emu K mol^{-1}) is slightly less than the expected value of 0.375 for isolated $S = {}^{1}/_{2}$ spins. As the temperature is lowered, χT also decreases rapidly, indicative of strong antiferromagnetic coupling. The broad maximum at 110 K in the χ vs T plot suggests low-dimensional antiferromagnetic interactions, and indeed the magnetic data could be fit to a 1D regular chain model[34] with the following parameters: $J = -58(2)$ cm^{-1}, $\theta = -3$ K, $g = 2.0025(2)$, ρ (fraction of uncoupled spins) = 0.006 ($R = 0.037$, where $R = [\sum(\chi_{obs} - \chi_{calc})^2/\sum(\chi_{obs})^2]^{1/2}$). The exchange coupling of −58 cm^{-1} stands out as one of the larger intermolecular magnetic interactions observed in organic molecular solids. The head-over-tail stacking motif that we believe is responsible for the magnetic properties (see below) is an extremely rare one in radical-based crystal structures. The 1,3,5-triphenyl-6-oxoverdazyl **6** adopts an analogous head-over-tail one-dimensional stacked structure in which verdazyl rings are aligned over phenyl groups.[20] The variable-temperature magnetic data for **6** were also fit to a 1D regular chain model with $J = -6$ cm^{-1}. The considerably weaker intermolecular coupling in **6** compared to that in **pyvd:hq** is consistent with the significantly larger intrastack interplanar separation (3.65 Å) in the former.



6

Computational Studies on pyvd and Aggregates Thereof. In attempts to understand the magnetic properties of the **pyvd:**

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[34] Kahn, O. *Molecular Magnetism*; VCH: New York, 1993. The spin Hamiltonian is of the form $\mathbf{H} = J\sum_i \mathbf{S}_i \cdot \mathbf{S}_{i'}$.

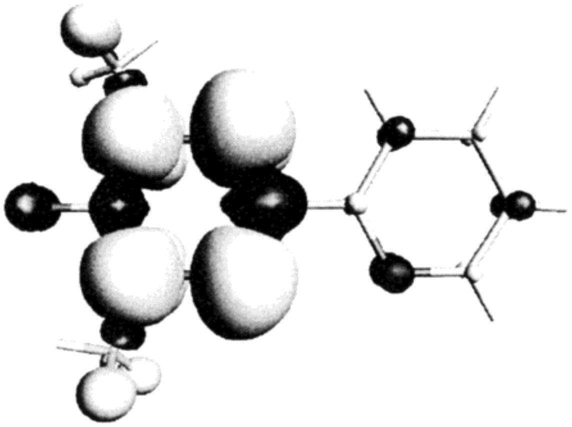
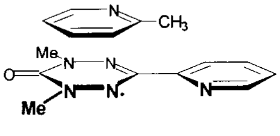


Figure 5. Calculated spin density of the **pyvd** radical. Light shading indicates positive spin density, and dark shading indicates negative spin density.

hq structure, we have employed density functional (DFT) calculations on the **pyvd** radical and related aggregates based on the X-ray crystal structure. Three single-point calculations were performed, on (1) the **pyvd** radical, to determine its spin distribution, (2) the radical with a 2-methylpyridine group stacked on top of the verdazyl ring (i.e., **7**) based on the crystal structure, to determine the extent of direct intermolecular spin transfer from verdazyl to pyrdine, and (3) a stack containing three **pyvd** radicals (i.e., **8**) to calculate the quartet−doublet energy gap, which can be viewed as a discrete model for the one-dimensional coupling in the crystal structure.



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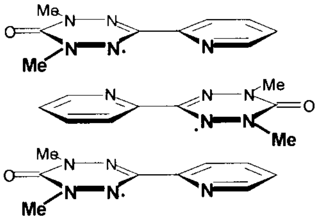

8

6-Oxoverdazyls are known from EPR and computational studies to be π radicals with the spin density mainly located on the four verdazyl ring nitrogen atoms; there is minimal spin leakage onto the C3 substituent.[33,35−37] Accordingly, the DFT calculation on a single **pyvd** radical indicates that the pyridine ring contains only a very small amount of negative spin density (Figure 5 and Table 1). This is consistent with the previously reported solution EPR spectrum of **pyvd**, for which the hyperfine couplings to the pyridine nitrogen and aromatic protons are substantially smaller than the spectral resolution (<1 G).[26] The calculation on substructure **7** was performed to examine the extent of spin transfer from the verdazyl ring to the pyridine stacked over it. As is evident from the results in Table 1, the spin density distribution in the **pyvd** portion of **7** remains unchanged, and there is effectively no intermolecular spin transfer to the 2-methylpyridine ring.

The three-radical stack **8** represents the smallest substructure of the **pyvd:hq** lattice for which intermolecular intracolumnar coupling can be expected. For this system, a broken symmetry[38] ($\alpha\beta\alpha$ doublet) solution could be calculated and compared to the high-spin quartet ($\alpha\alpha\alpha$) as an approximation for the one-dimensional stacks in the structure of **pyvd:hq**. The $\alpha\beta\alpha$ doublet is not a true spin state, but it is known that the difference between such a mixed state and the high-spin state should give the correct sign and magnitude of the magnetic coupling.[39] The calculated energy difference between the $\alpha\beta\alpha$ and the $\alpha\alpha\alpha$ states ($=2J$) is -241 cm^{-1}, a value that is within the same order of magnitude as the experimental $2J$ value of -116 cm^{-1} (i.e., $J = -58$ cm^{-1}).

Table 1. DFT-Calculated Spin Populations for **pyvd** and the Pyridine-over-**pyvd** Structure **7**

		structure **7**	
atom	pyvd	**pyvd** fragment	2-methylpyridine fragment
O1	−0.011	−0.011	
N1	0.198	0.199	
N2	0.343	0.342	
N3	0.342	0.341	
N4	0.204	0.203	
N5	−0.011	−0.011	0.000
C1	−0.016	−0.016	
C2	−0.067	−0.067	
C3	0.008	0.008	−0.001
C4	−0.010	−0.010	0.002
C5	0.008	0.008	0.001
C6	−0.011	−0.011	0.000
C7	0.007	0.007	0.000
C8	−0.006	−0.006	
C9	−0.008	−0.008	

Discussion

Based on the magnetic properties of **pyvd:hq** in light of its crystal structure, the most likely pathway for one-dimensional magnetic exchange would seem to be through the radical/pyridine π stacks. Because the radicals are stacked in a head-to-tail fashion, however, there are *no* intermolecular contacts involving exclusively the four verdazyl nitrogen atoms which, as discussed above, carry nearly all of the spin density. Thus, the magnetic properties exhibited by this system are unique insofar as *they cannot be rationalized on the basis of "close" intermolecular contacts between spin-bearing atoms*. The absence of such contacts requires that the strong exchange involves the pyridine rings in the exchange mechanism. In this context, the use of a *regular* chain model to fit the magnetic data may at first glance seem surprising, given that the interplanar separations within the stacks alternate slightly (3.37 and 3.44 Å). However, if the pyridine ring is treated in this model as a magnetic *coupling* unit that does not itself carry significant spin density, then there is only one nearest-neighbor radical−radical interaction, which occurs through the pyridine rings (Figure 6). An alternating 1-D chain model with two different exchange coupling values J_1 and J_2 would be inappropriate, because this model requires alternating distances between spin centers.

Intermolecular magnetic interactions are usually interpreted using a spin density approach[40] ("McConnell I") or a charge-transfer approach[41] ("McConnell II"). In the former approach, the total spin density on each molecular unit must be known, and close intermolecular contacts between atoms carrying significant spin density are identified. In the present compound,

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(35) Neugebauer, F. A.; Brunner, H.; Hausser, K. H. *Tetrahedron* **1971**, *27*, 3623.

(36) Neugebauer, F. A.; Fischer, H.; Siegel, R. *Chem. Ber.* **1988**, *121*, 815.

(37) Öhrström, L.; Grand, A.; Pilawa, B. *Acta Chem. Scand.* **1996**, *50*, 458.

(38) (a) Noodlemann, L.; Davidson, E. R. *Chem. Phys.* **1979**, *70*, 4903. (b) Noodlemann, L. *J. Chem. Phys.* **1981**, *74*, 5737.

(39) (a) Barone, V.; di Matteo, A.; Mele, F.; Moreira, I. D.; Illas, F. *Chem. Phys. Lett.* **1999**, *302*, 240. (b) Bencini, A.; Totti, F.; Daul, C. A.; Doclo, K.; Fantucci, P.; Barone, V. *Inorg. Chem.* **1997**, *36*, 5022.

(40) Yoshizawa, K.; Hoffmann, R. *J. Am. Chem. Soc.* **1995**, *117*, 6921.

(41) Miller, J. S.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 2850.

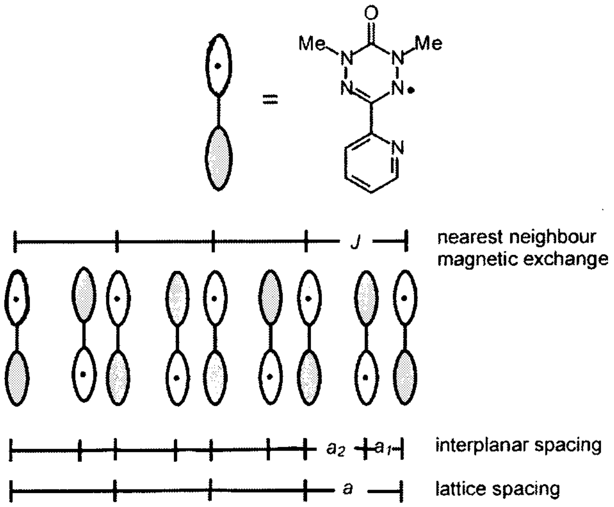
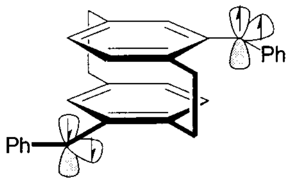


Figure 6. Schematic depiction of the head-over-tail stacks of **pyvd** contained in the structure of **pyvd:hq**, with nearest-neighbor exchange interactions *J* indicated.

the shortest intermolecular contacts involving only the four verdazyl nitrogens are 4.5 Å—at this distance any magnetic coupling would be extremely weak. It could be argued that there is sufficient spin polarization of the pyridine ring to account for magnetic exchange by the spin polarization mechanism. However, the spin density on the pyridine ring is negative, while the spin on the verdazyl ring is (predominantly) positive. This would normally fit the requirements for intermolecular *ferromagnetic* coupling, which is clearly not observed here. Finally, it is instructive to compare the magnetic coupling in the **pyvd:hq** structure to that of another "π-stacked" arrangement of antiferromagnetically coupled spins. The *meta*-cyclophanedicarbene **9** is one of a triad of cyclophanedicarbenes that were prepared to confirm the validity of the McConnell I (spin polarization) mechanism for magnetic exchange in π-stacked radicals.[42] Exchange interactions between the two $S = 1$ carbene centers arise from the pronounced spin density on the central (cyclophane) benzene rings, and, because the two rings have atoms with substantial positive spin density superimposed on top of one another, antiferromagnetic coupling between the two carbenes was predicted and observed. The strength of the antiferromagnetic coupling in **9** (-49 cm^{-1}) is roughly the same as we have found in the **pyvd:hq** structure. Yet the central benzene rings carry *one order* of magnitude more spin density than the pyridine ring of **pyvd**, and in addition the two cyclophane rings are forced to be only about 3.0 Å apart, nearly *half an angstrom* closer together than the average pyridine–verdazyl intrastack separation. The disparity in both spin distribution and stacking distance between **9** and **pyvd:hq** would seem to argue against a common mechanism for antiferromagnetic coupling in these systems. For these reasons we believe the magnetic properties of **pyvd:hq** cannot be explained adequately by a spin polarization mechanism.



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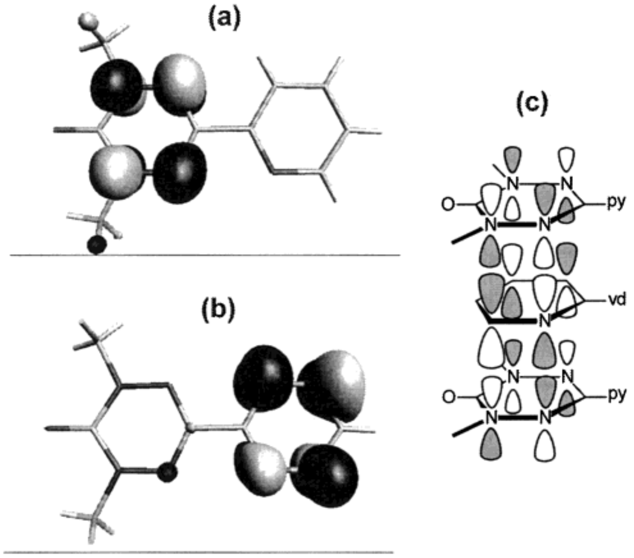

Figure 7. (a) SOMO of **pyvd**. (b) Second LUMO of **pyvd**. (c) Schematic illustration of proposed antiferromagnetic coupling of two pyvd radicals mediated by the second LUMO.

The charge-transfer mechanism for magnetic coupling, which involves configurational mixing of charge-transfer states with the ground electronic state of the molecule, is more difficult to quantify or prove. This model has been used to explain the intrastack ferromagnetic coupling in $M^{III}(Cp^*)_2{}^{+\bullet}TCNE^{-\bullet}$ and $TCNQ^{-\bullet}$ salts,[43] although a spin density mechanism has been proposed as an alternative spin coupling mechanism.[44] In such systems, excitations from a donor α-SOMO or HOMO to the acceptors α-SOMO or LUMOs have been invoked. In **pyvd**, the singly occupied molecular orbital (SOMO) is a delocalized π orbital located almost exclusively on the four verdazyl ring nitrogen atoms (Figure 7a). Although the configuration mixing of SOMOs on two adjacent radicals is unlikely because of the donor character of both orbitals, excitations from the SOMO on one radical to one of the acceptor-centered LUMOs on a neighboring molecule seem more likely. We note that the second LUMO is based on the pyridine ring and has the same symmetry as that of the SOMO (Figure 7b). Although the energy difference between these two orbitals is substantial ($E_{\mathrm{SOMO}} = -4.52$ eV; $E_{\mathrm{2LUMO}} = -0.17$ eV), direct orbital interactions between these two orbitals may be strong enough to produce the observed magnetic coupling (-58 cm^{-1}). It is interesting to speculate on an antiferromagnetic spin coupling mechanism that could arise from communication of two **pyvd** SOMOs as mediated by the pyridine-based empty orbital. This is depicted schematically for a three-molecule stack in Figure 7c. An alternative way of thinking about the charge-transfer mechanism involves excitation from the SOMO of one molecule to the second LUMO of an adjacent molecule, which produces a **pyvd** diradical (anion). The electronic structure of this excited state has one electron in each of the SOMO and second LUMO, and as such this closely resembles the 1,1′,5,5′-tetramethyl-6,6′-dioxo-3,3′-biverdazyl biradical **10**, for which the (intramolecular) coupling has been

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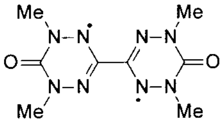
[42] Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 2631.

[43] Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 385.

[44] Kollmar, C.; Couty, M.; Kahn, O. *J. Am. Chem. Soc.* **1991**, *113*, 799.

determined to be −887 cm^{-1}.[24]



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Summary

Magnetostructural correlations in organic materials involve detailed analysis of magnetic data in relation to crystallographic information. The current paradigm for these correlations involves identification of short intermolecular contacts between atoms bearing significant amounts of spin density (for example, O- -O and O- -N contacts in nitroxide radicals) to rationalize the nature (ferro- vs antiferromagnetic) and magnitude of intermolecular magnetic exchange. This is particularly prevalent in cases when intermolecular exchange coupling is found to be relatively strong.[15,17,45−47] Although recent statistical analyses of structure−magnetism relationships in a wide range of nitroxide radicals highlight some of the limitations of such approaches,[48,49] this remains the predominant means of analysis of magnetic properties of radical-based molecular crystals.

The magnetic behavior of **pyvd:hq** demonstrates that the above approach to understanding the magnetic properties of organic solids is not without its limitations. The strong magnetic coupling in conjunction with the lack of close radical−radical contacts are completely at odds with virtually all other magnetically and structurally characterized radicals. We have suggested that a *supramolecular* spin coupling mechanism directly involving the pyridine rings is the most likely explanation. In this model, therefore, each **pyvd** molecular stack contains *two* one-dimensional AF chains. There may be some interaction between the two magnetic chains, which would produce a molecular spin-ladder structure;[50] however, the long contact distances between spin-bearing atoms and their poor orientational overlap renders the cross-chain interactions extremely weak. In any event, the mechanism by which the strong antiferromagnetic coupling occurs is at this point unclear; however, both the observation of strong magnetic coupling and the lack of close intermolecular contacts are indisputable. Together these facts cast doubts on the efficacy of the generally accepted idea that close contacts are required for strong magnetic coupling. Attempts to rationalize magnetic properties on the basis of short radical−radical contacts are still certainly valid, but this may be an incomplete or oversimplified approach, and in fact strong magnetic coupling can arise *without such contacts at all.* This raises the interesting possibility of exploiting strong noncovalent, or supramolecular, interactions as a means of realizing new organic magnetic materials.

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Supporting Information Available: Details of the crystal structure of **pyvd:hq** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(45) Yoshioka, N.; Irisawa, M.; Mochizuki, Y.; Kato, T.; Inoue, H.; Ohba, S. *Chem. Lett.* **1997**, 257.

(46) Reznikov, V. A.; Ovcharenko, I. V.; Pervukhina, N. V.; Ikorskii, V. N.; Grand, A.; Ovcharenko, V. I. *Chem. Commun.* **1999**, 539.

(47) Panthou, F. L.; Luneau, D.; Laugier, J.; Rey, P. *J. Am. Chem. Soc.* **1993**, *115*, 9095.

(48) Deumal, M.; Cirujeda, J.; Veciana, J.; Novoa, J. J. *Adv. Mater.* **1998**, *10*, 1461.

(49) Deumal, M.; Cirujeda, J.; Veciana, J.; Novoa, J. J. *Chem. Eur. J.* **1999**, *5*, 1631.

(50) Rovira, C. *Chem. Eur. J.* **2000**, *6*, 1723.