The Magnetic Properties of Verdazyl Free Radicals. IX. The Crystal Structure of 1,3,5-Triphenyl-6-methylverdazyl Radical

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The crystal structure of 1,3,5-triphenyl-6-methylverdazyl has been determined by X-ray diffraction. The crystals are orthorhombic, with the space group of Pnma and with $a=18.25(1)$, $b=16.65(1)$, $c=5.776(2)$ Å, and $Z=4$. The structure was deduced from the sharpened Patterson synthesis and was refined by the block-diagonal least-squares method to the final R value of 0.055 for 960 non-zero reflections collected on an automated four-circle diffractometer. The *sym*-tetrazinyl ring has an asymmetrical boat form, as has been observed in both 1,3,5-triphenylverdazyl and 1,3,5-tri-*p*-tolylverdazyl. The complete intermolecular overlap was observed in a tilted face-to-face array along the c-axis; this accounts for a fairly strong antiferromagnetic exchange interaction between the unpaired electrons.

In the last paper,[1] the present authors have reported the crystal structure of 1,3,5-tri-*p*-tolylverdazyl (TTV), whose electron-spin exchange interaction energy, $|J/k|$, is 1 K at most.[2] The qualitative explanation for the weak exchange interaction has been made on the basis of the crystal structure and π-electron spin densities.[1] On the other hand, the magnetic susceptibility *vs.* temperature curve of 1,3,5-triphenyl-6-methylverdazyl (MeTPV) has a broad maximum in the vicinity of 12 K. This susceptibility can be well described by the linear antiferromagnetic Heisenberg model,[3] and the estimated exchange integral, $|J/k|$, is about 10 K.[2] However, ESR and ENDOR measurements have indicated that the spin-density distribution of MeTPV is almost the same as that of TTV.[4] These facts have made us select MeTPV for the crystal-structure analysis.

Experimental

The crystals of MeTPV prepared by the method of Kuhn and Trischmann[5] were obtained by the recrystallization from an acetone–methanol solution. The results of the elementary analysis showed reasonable values; Found: C, 77.10; H, 5.97; N, 17.03%. The ESR spectrum measured in degassed 2-methyltetrahydrofuran exhibited nine lines, with the nitrogen hyperfine coupling constant of 5.6 gauss. This value was in agreement with the constant of 5.8 gauss (observed in benzene) presented in the literature.[5] However, the melting point of the present sample was higher by ten degrees than the value in the literature;[5] Obs., 193.5—194.5 °C; Lit., 183—184 °C.

The crystal data are shown in Table 1. The lattice constants and intensity data were obtained by using an automatic four-circle diffractometer with Mo$K\alpha$ radiation ($\lambda=0.7101$ Å) monochromated by a graphite crystal. A total 2089 independent reflections were measured up to $2\theta=55°$ by employing the ω-scan technique. Out of these, 960 reflections with $|F_o|$ values not less than $2.5\sigma(F_o)$ were regarded as non-zero reflections and were adopted for the structure determination. The Lorentz and polarization corrections were made as usual, but the correction for absorption was not made in view of the small size of the specimen and the low absorption coefficient.

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TABLE 1. CRYSTAL DATA

Molecular formula	$C_{21}H_{19}N_4$
Molecular weight	327.4
Melting point	193.5—194.5 °C
Specimen used for the data collection	*ca.* (0.25 mm)^3
Crystal system	Orthorhombic
Cell dimensions;	
a	18.25±0.01Å
b	16.65±0.01
c	5.776±0.002
V	1755Å^3
Z	4
Density (calculated)	1.233 g/cm^3
Density (observed by flotation)	1.227
$F(000)$	692
Linear absorption coefficient	0.9 cm^{-1} (Mo$K\alpha$)
Systematic absence;	
$0kl$	$k+l=2n+1$
$hk0$	$h=2n+1$
Space group	Pnma or $Pn2_1a$

Structure Determination and Refinement

Wilson's statistics indicated the presence of the center of symmetry; therefore, the Pnma space group was adopted. The crystal structure was solved by the Patterson method. The starting model gave an R value of 0.23. Thereupon, the block-diagonal least-squares refinement was undertaken. Several cycles of the refinement with anisotropic thermal parameters reduced the R value to 0.096. At this stage of the refinement, all the positions of hydrogen atoms were located from a difference Fourier map. With anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for hydrogen atoms, the final R value was 0.055 for 960 non-zero reflections.

Unit weight was adopted for all 960 reflections. The atomic scattering factors used were taken from the International Tables for X-Ray Crystallography.[6] The final parameters for the non-hydrogen atoms are shown in Tables 2 and 3. The positional parameters for the hydrogen atoms are listed in Table 4. The mean

TABLE 2. THE FRACTIONAL ATOMIC COORDINATES AND THEIR ESTIMATED STANDARD DEVIATIONS[a] IN PARENTHESES

Atom	x	y	z
C(1)	7166(3)	2500	−2248(10)
C(2)	8391(3)	2500	176(9)
C(3)	7542(4)	2500	−4590(11)
C(4)	6929(2)	3871(2)	−543(6)
C(5)	6346(2)	4013(2)	−2051(8)
C(6)	5906(2)	4684(3)	−1698(8)
C(7)	6044(2)	5206(2)	96(9)
C(8)	6628(2)	5064(2)	1589(8)
C(9)	7071(2)	4397(2)	1257(7)
C(10)	9175(3)	2500	878(9)
C(11)	9541(2)	3219(2)	1231(8)
C(12)	10262(2)	3215(3)	1981(8)
C(13)	10617(3)	2500	2362(13)
N(1)	7374(2)	3191(2)	−848(5)
N(2)	8069(2)	3217(2)	−16(5)

a) The coordinates have been multiplied by 10^4.

TABLE 3. THE ANISOTROPIC THERMAL PARAMETERS[a] AND THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES[b]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	27(2)	23(2)	216(18)		−11(5)	
C(2)	19(2)	22(2)	200(17)		3(5)	
C(3)	45(3)	48(3)	221(20)		12(7)	
C(4)	20(1)	18(1)	256(13)	−0(1)	7(3)	9(4)
C(5)	31(1)	29(1)	323(16)	3(1)	−23(4)	−0(4)
C(6)	31(1)	37(2)	413(19)	8(1)	−22(5)	26(5)
C(7)	30(1)	28(2)	459(19)	6(1)	1(5)	−3(5)
C(8)	27(1)	26(1)	397(17)	−1(1)	5(4)	−17(4)
C(9)	21(1)	23(1)	296(14)	−1(1)	2(4)	−0(4)
C(10)	18(2)	25(2)	215(18)		5(5)	
C(11)	23(1)	28(1)	375(16)	−2(1)	−4(4)	−11(5)
C(12)	24(1)	37(2)	440(19)	−4(1)	−4(4)	−24(5)
C(13)	20(2)	50(3)	359(24)		−5(6)	
N(1)	21(1)	22(1)	248(11)	2(1)	−11(3)	−2(3)
N(2)	19(1)	21(1)	270(11)	0(1)	−3(3)	1(3)

a) The anisotropic thermal parameters are of the form: $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)]$. b) The values have been multiplied by 10^4.

TABLE 4. THE FINAL PARAMETERS FOR HYDROGEN ATOMS AND THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES[a]

Atom	x	y	z
H(Cl)	659(3)	250	−232(10)
H(C3-1)	810(3)	250	−469(12)
H(C3-2)	736(2)	296(2)	−551(7)
H(C5)	623(2)	364(2)	−318(7)
H(C6)	550(2)	479(2)	−290(7)
H(C7)	574(2)	572(3)	21(8)
H(C8)	667(2)	544(3)	304(8)
H(C9)	749(2)	428(2)	241(7)
H(C11)	928(2)	373(2)	78(7)
H(C12)	1047(2)	372(2)	220(7)
H(C13)	1110(3)	250	290(10)

The mean thermal parameter is 3.2 Å².

a) The coordinates have been multiplied by 10^3.

TABLE 5. THE OBSERVED AND CALCULATED STRUCTURE FACTORS MULTIPLIED BY 10

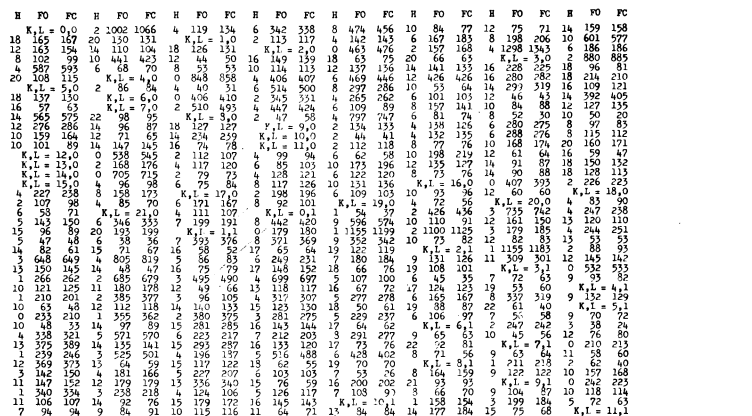
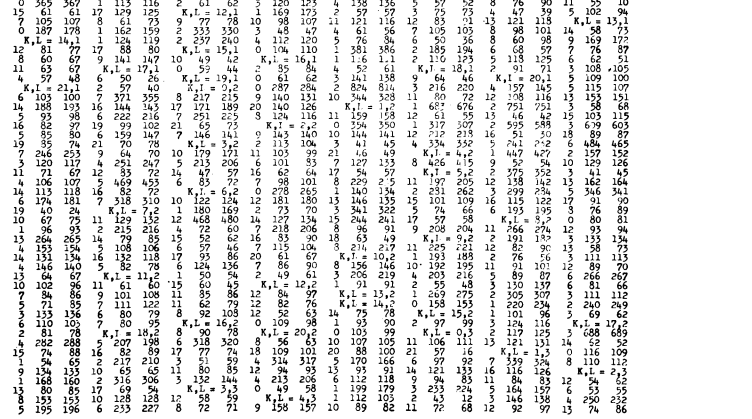


TABLE 5. (Continued)



isotropic thermal parameter for the hydrogen atoms was 3.2 Å². The observed and calculated structure factors are compared in Table 5.

Results and Discussion

The molecular structure of MeTPV and the numbering system used in this text are illustrated in Fig. 1. The bond lengths and bond angles are shown in Tables 6 and 7 respectively. The MeTPV molecule has a plane of symmetry and has the molecular structure similar to those of TTV[1] and TPV.[7]

C(1) and C(2) are below th N(1)N(2)N(2′)N(1′) plane (referred to as the N-plane) by 0.622 and 0.105 Å respectively. The corresponding dihedral angles at both ends of the N-plane are 44.1° and 10.1° respectively. Therefore, the conformation of the *sym*-tetrazinyl ring of MeTPV is an asymmetrical boat form, as has been observed in TTV and TPV. The *N*-phenyl ring is above the N-plane by 18.8°, which is the angle between the N-plane and the N(1)–C(4) bond, while the dihedral angle between the plane of the *C*-phenyl ring and the N-plane is 2.6°. The distance of N(1) from the plane through C(1), N(2), and C(4) is 0.055 Å. Accordingly, we can use the following definition for the twist angle about the N(1)–C(4) bond: the twist angle is the dihedral angle between the *N*-phenyl plane

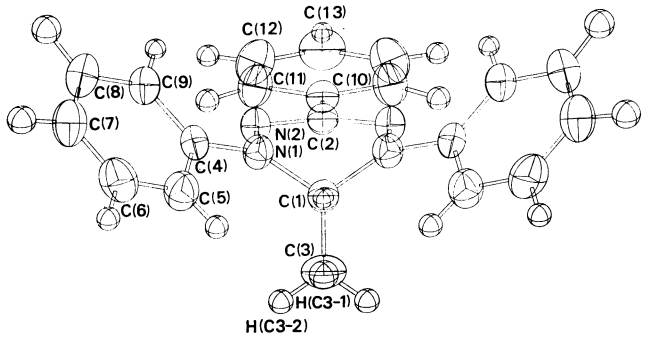


Fig. 1. The molecular structure of MeTPV viewed down the a-axis, along with the numbering system. The thermal ellipsoids enclose a probability of 50%, except for hydrogen atoms. The reflected atom will be represented in terms of its counterpart's symbol followed by a prime, *e.g.* N(1′). The ring hydrogen atom will be labelled by, for example, H(C5) where C5 stands for the ring carbon atom attached by it.

Table 6. Bond lengths, pertinent intramolecular contacts, and their estimated standard deviations in parentheses (Å)

Bond	Length	Bond	Length
C(1)–C(3)	1.517(9)	C(6)–C(7)	1.376(6)
C(1)–N(1)	1.457(4)	C(7)–C(8)	1.392(6)
N(1)–N(2)	1.358(4)	C(8)–C(9)	1.386(5)
N(2)–C(2)	1.335(4)	C(9)–C(4)	1.385(5)
N(1)–C(4)	1.404(4)	C(2)–C(10)	1.487(7)
C(4)–C(5)	1.395(5)	C(10)–C(11)	1.386(5)
C(5)–C(6)	1.392(6)	C(11)–C(12)	1.372(5)
C(1)–H(C1)	1.05(5)	C(8)–H(C8)	1.05(5)
C(3)–H(C3-1)	1.03(6)	C(9)–H(C9)	1.03(4)
C(3)–H(C3-2)	0.98(4)	C(11)–H(C11)	1.01(4)
C(5)–H(C5)	0.93(4)	C(12)–H(C12)	0.93(4)
C(6)–H(C6)	1.03(4)	C(13)–H(C13)	0.93(5)
C(7)–H(C7)	1.02(4)		
Atoms	**Distance**	**Atoms**	**Distance**
N(2)---C(11)	2.781(5)	C(2)---H(C3-1)	2.86(7)
N(1)---H(C3-1)	2.83(6)	C(2)---H(C3-2)	3.86(4)
N(1)---H(C3-2)	2.72(4)	C(10)---H(C3-1)	3.77(4)
N(2)---H(C3-1)	2.95(6)	H(C3-2)---H(C5)	2.72(5)
N(2)---H(C3-2)	3.45(4)	H(C5)---H(C5′)	3.79(8)
N(2)---H(C9)	2.49(2)	H(C9)---H(C11)	3.52(5)

Table 7. Bond angles and their estimated standard deviations (in degree)

N(1)–C(1)–N(1′)	104.3(4)	C(1)–N(1)–N(2)	117.7(2)
N(1)–N(2)–C(2)	114.4(2)	N(2)–C(2)–N(2′)	126.8(4)
N(1)–C(1)–C(3)	112.1(4)	C(1)–N(1)–C(4)	123.8(3)
N(2)–N(1)–C(4)	118.1(2)	N(1)–C(4)–C(5)	120.0(3)
N(1)–C(4)–C(9)	119.8(3)	C(4)–C(5)–C(6)	119.1(3)
C(5)–C(6)–C(7)	120.8(4)	C(6)–C(7)–C(8)	120.0(3)
C(7)–C(8)–C(9)	119.9(3)	C(8)–C(9)–C(4)	120.1(3)
C(9)–C(4)–C(5)	120.3(3)	N(2)–C(2)–C(10)	116.5(3)
C(2)–C(10)–C(11)	120.2(3)		
C(10)–C(11)–C(12)	119.9(2)		
C(11)–C(12)–C(13)	120.2(2)		
C(12)–C(13)–C(12′)	120.2(4)		
C(11)–C(10)–C(11′)	119.5(4)		
C(3)–C(1)–H(C1)	115(3)		
C(1)–C(3)–H(C3-1)	120(3)		
C(1)–C(3)–H(C3-2)	109(2)		

and the C(1)N(2)C(4) plane. This twist angle is 21.2°, which is close to the maximum value observed in TPV. The configuration of the *N*-phenyl groups is anti-propellor. The two twists of the *N*-phenyls are in opposite directions, since the MeTPV molecule has a plane of symmetry.

The methyl group attached to the tetrahedral carbon atom, C(1), occupies the *axial* position of the boat. The *ortho* hydrogen atoms, H(C5) and H(C5′), remain *staggered* between H(C1) and C(3).

A less significant molecular structural difference has been observed among three symmetrically substituted verdazyls, TPV, TTV, and MeTPV. On the other hand, the effect of the methyl groups, introduced in the TTV and MeTPV molecules, upon the spin-density distribution in a molecule has been examined by the ENDOR technique. As was expected, little effect has been revealed by the aid of a comparison of their proton hyperfine coupling constants with those of TPV.[4] Accordingly, these radical solids are optimal for our purpose to correlate the magnetic properties of a neutral radical with a delocalized unpaired electron spin with its molecular packing.

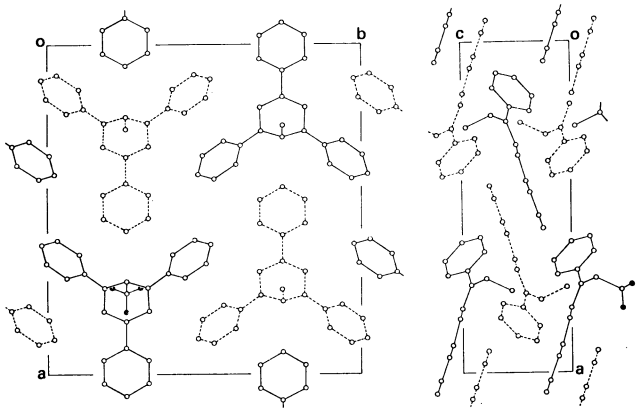


Fig. 2. The mutual arrangement of the MeTPV molecules. The left and the right were viewed along the c- and b-axis, respectively. The doubled circles in the reference molecule stand for the methyl hydrogen atoms, while the other hydrogen atoms were not drawn.

TABLE 8. PERTINENT INTERMOLECULAR CONTACTS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom (1) at (x, y, z)	Atom (2)	Distance (Å)	Symmetry operation applied to the second atom
C(12)	C(4)	3.381(6)	$1/2+x$, y, $1/2-z$
C(12)	C(5)	3.776(6)	
C(12)	C(6)	3.846(6)	
C(12)	C(7)	3.985(6)	
C(12)	C(9)	3.976(5)	
C(13)	C(1)	3.994(8)	
C(13)	N(1)	3.957(6)	
C(13)	C(4)	3.784(6)	
C(13)	C(5)	3.931(7)	
C(12)	C(5)	3.714(6)	$-1/2+x$, y, $-1/2-z$
C(13)	C(3)	3.861(9)	
N(1)	C(3)	3.806(7)	x, y, $1+z$
N(2)	C(3)	3.489(7)	
C(2)	C(3)	3.397(8)	
C(10)	C(3)	3.967(8)	
C(8)	N(1′)	3.736(5)	$3/2-x$, $1/2+y$, $1/2+z$
C(8)	N(2′)	3.514(5)	
C(8)	C(4′)	3.581(5)	
C(8)	C(9′)	3.703(6)	
C(9)	C(4′)	3.881(5)	
C(9)	C(8′)	3.991(6)	
C(9)	C(9′)	3.849(8)	
C(11)	C(6′)	3.779(6)	
C(11)	C(7′)	3.605(6)	
C(12)	C(7′)	3.979(6)	
C(6)	C(6′)	3.985(9)	$1-x$, $1/2+y$, $-z$
C(6)	C(7′)	3.681(6)	
C(7)	C(6′)	3.681(6)	
C(7)	C(7′)	3.873(8)	
N(2)	H(C3–2)	2.94(4)	x, y, $1+z$
H(C5)	C(12)	2.90(4)	$-1/2+x$, y, $1/2-z$
C(11)	H(C7′)	2.95(5)	$3/2-x$, $1/2+y$, $1/2+z$
H(C8)	N(1′)	2.94(4)	
H(C8)	N(2′)	2.55(4)	
H(C8)	C(4′)	2.92(4)	
H(C8)	C(9′)	2.96(4)	
H(C13)	H(C1)	2.71(8)	$1/2+x$, y, $1/2-z$
H(C12)	H(C5)	2.70(6)	$-1/2+x$, y, $-1/2-z$
H(C13)	H(C3–2)	2.80(6)	
H(C8)	H(C9′)	2.99(6)	$3/2-x$, $1/2+y$, $1/2+z$
H(C11)	H(C6′)	2.61(6)	
H(C11)	H(C7′)	2.77(6)	
H(C12)	H(C7′)	2.96(6)	
H(C6)	H(C7′)	2.88(6)	$1-x$, $1/2+y$, $-z$

Figure 2 shows the mutual arrangement of the MeTPV molecules. The pertinent intermolecular distances are listed in Table 8. The molecules with a plane of symmetry pack in a tilted face-to-face array along the c-axis. Within the array, the shortest intermolecular distance is 2.94 Å for the N(2)···H(C3-2) contact, and the corresponding N···C distance is 3.489 Å. The intermolecular distance between C(2) and C(3) is 3.397 Å, while the intramolecular distances of the N(1)---C(3) and N(2)---C(3) contacts are 2.468 and 3.054 Å respectively. This intermolecular distance may suggest the deformation of the methyl group from the ordinary tetrahedral conformation.

The melting point of MeTPV is higher than those of its homologues by about 50 °C. This can be mainly attributed to the complete overlap of the adjacent molecules in the array along the c-axis. Such molecular packing will certainly enhance the exchange interaction between the π-electron spins. The magnetic susceptibility of the MeTPV solid is well described by the Heisenberg linear chain model[3] down to the lowest temperature examined so far, 2 K. This fact indicates a less significant coupling of the magnetic chains. The exchange integral estimated from the susceptibility of the MeTPV solid is about -10 K, which corresponds to one of the strongest exchange interactions among those observed in verdazyl free radical solids. The present authors and their colleagues have already interpreted the magnetic properties of TPV, galvinoxyl, and TTV radical solids in terms of both the overlap of $2p_z\pi$-orbitals inferred from the molecular packing and the spin densities.[8,1] From the same point of view, the fairly strong exchange interaction in the MeTPV solid may be attributed to the complete overlap of the molecular planes in the tilted face-to-face array. The excellent magnetic linear chain is also attributable to the uniform intermolecular spacing in the array. The sufficient magnetic insulation between the magnetic chains can be explained by considering the isolation of the chemical chains or the arrays along the c-axis. Speaking in more detail, the interchain contacts occur around the hydrogen atoms or between the atoms whose $2p_z\pi$-orbitals cause a so-called π-overlap and which have small spin densities at that; this will give rise to less significant interchain exchange interactions. The magnetic properties of MeTPV will be discussed quantitatively in a separate paper, together with those of other verdazyls.

The calculations were carried out on a FACOM 270-30 computer at the Institute for Solid State Physics, the University of Tokyo, with a local version of UNICS.[9] The thermal ellipsoids were drawn on a HITAC 5020E computer at the Computer Center, the University of Tokyo.[10] This work was supported in part by a Scientific Research Grant of the Ministry of Education. Thanks are due to authors' colleagues with whom the present authors have done this series of investigations.

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