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The Crystal Structure of the 1,3-Di-*p*-tolyl-5-phenylverdazyl Radical[1]

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Synopsis. The crystals of 1,3-di-*p*-tolyl-5-phenylverdazyl are monoclinic, with the space group $P2_1/c$ and with $a=10.66(1)$, $b=21.76(1)$, $c=8.171(6)$ Å, $\beta=98.8(1)°$, and $Z=4$. The crystal structure has been determined by means of X-ray diffraction. The molecular structure is similar to those of other verdazyls. The molecules are packed in a column along the c axis.

Following the conventional procedure, the paramagnetic susceptibility of 1,3-di-*p*-tolyl-5-phenylverdazyl (DTPV) has been discussed in this series.[2] A linear chain of Ising spins has been proposed for DTPV crystals, with the suggestion of another possibility of an alternating linear chain of Heisenberg spins. The latter possibility correlates with the alternation in the molecular packing. In order to examine whether there is such an alternation in the DTPV crystal, crystal-structure analysis has been carried out by means of X-ray diffraction. No alternation appears in the revealed crystal structure.

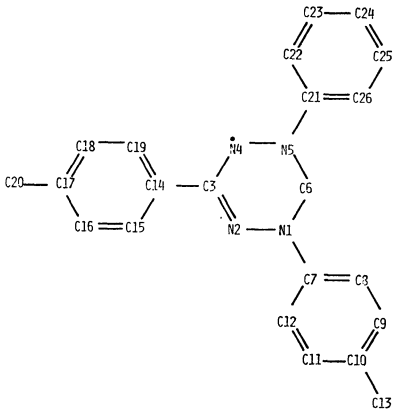

Fig. 1. The chemical structure and numbering system of 1,3-di-*p*-tolyl-5-phenylverdazyl (DTPV).

Experimental

Material and Procedure. The DTPV was prepared from *p*-tolualdehyde, *p*-toluidine, aniline, and formaldehyde, following the procedure of Kuhn and Trischmann.[3] The crystals were purified several times through recrystallization from a methanol solution; mp=116.0—116.5 °C.

The unit-cell parameters were refined on a manually-operated four-circle diffractometer. The intensity data were collected on the same diffractometer with Zr-filtered Mo $K\alpha$-radiation up to $2\theta=45°$ through a single scan per peak for all the reflections. The background intensities around an arbitrary axis were measured as a function of the Bragg angle, and this function was assumed for all the reflections. The reflection intensities were corrected for Lorentz and polarization effects.

Crystal Data. $C_{22}H_{21}N_4$, $M=341.43$, monoclinic, space group $P2_1/c$, $a=10.66(1)$, $b=21.76(1)$, $c=8.171(6)$ Å, $\beta=98.8(1)°$, $V=1873$ Å^3, $D_m=1.2$ (by floatation), $D_x=1.210$ g/cm^3, and $Z=4$.

Structure Determination and Refinement

The structure was solved by the direct method using the *SORTE* program,[4] with the positions of all the 26 non-hydrogen atoms located on an *E*-map. Those positions were refined by the blockdiagonal least-squares procedure. The positions of the 15 ring hydrogen atoms were deduced from a difference Fourier map. Those of the methyl hydrogen atoms were not, however, located from the difference Fourier maps and were ignored in the present refinement in view of the accuracy of the intensity data. The discrepancy index, R, for 1487 non-zero reflections was finally reduced to 0.11 by fullmatrix least-squares refinement with anisotropic thermal parameters for the non-hydrogen atoms and isotropic ones for the ring hydrogen atoms. The hydrogen isotropic thermal parameters ranged between 3.5 and 5.2 Å^2; these values were fixed in the final stage of the refinement. The atomic scattering factors were adopted from the International Tables for X-Ray Crystallography.[5] The final positional parameters of the non-hydrogen atoms are shown in Table 1*; the numbering system refers to Fig. 1.

Discussion

Table 2 shows the bond distances and bond angles. There is no significant difference between the molecular dimensions of DTPV and those of the other verdazyls.[6] The sums of the three bond angles around the three-coordinated nitrogen atoms, N1 and N5, are 360 and 359°. The atomic deviations of N1 and N5 from the planes defined by the N2, C6, and C7 atoms and by the N4, C6, and C21 atoms are 0.04 and 0.08 Å respectively. These two results show the sp^2 hybridization for the three-coordinated nitrogen atoms, which, accordingly, contribute two π-electrons per atom to the π-system. The conformation of the 1,2,4,5-tetrazinyl ring is an unsymmetrical boat form, with four coplanar nitrogen atoms (N-plane) and these atomic deviations from this plane: C3, −0.14; C6, −0.64; C7, 0.45; C8, 0.19; C12, 1.23; C14, −0.27; C21, 0.40; C22, 1.07; and C26, 0.14 Å. The dihedral angle between the N- and the C3-tolyl planes is 7°. Those between the N2-C6-C7 plane and the N1-tolyl plane and between the N4-C6-C21 plane and the N5-phenyl plane are 14 and 10° respectively.

* Lists of the observed and calculated structure factors (List A), of the thermal parameters (B), and of the positions of the ring hydrogen atoms (C) are kept by the office of the Chemical Society of Japan, (Document No. 8027).

Table 1. The positional parameters, with their estimated standard deviations in parentheses
The values have been multiplied by 10^4.

Atom	x	y	z
N1	5773(12)	2661(6)	4193(13)
N2	6427(9)	3182(6)	3927(12)
C3	5798(14)	3711(6)	3730(15)
N4	4523(11)	3736(5)	3441(12)
N5	3862(10)	3214(6)	3705(13)
C6	4588(16)	2788(7)	4825(18)
C7	6273(13)	2075(7)	4020(16)
C8	5775(15)	1540(7)	4637(16)
C9	6355(22)	981(7)	4394(25)
C10	7370(15)	886(7)	3546(18)
C11	7772(13)	1425(9)	2901(19)
C12	7272(14)	2021(6)	3145(18)
C13	7929(13)	249(6)	3291(16)
C14	6501(13)	4274(6)	3607(15)
C15	7796(16)	4260(6)	3657(20)
C16	8463(12)	4819(8)	3510(18)
C17	7958(14)	5404(6)	3308(16)
C18	6617(17)	5367(7)	3311(22)
C19	5910(13)	4839(8)	3435(18)
C20	8662(12)	5978(5)	3212(16)
C21	2559(12)	3204(6)	3105(16)
C22	2062(15)	3598(7)	1984(20)
C23	734(16)	3596(7)	1365(18)
C24	7(12)	3152(8)	1905(18)
C25	512(16)	2736(8)	3037(21)
C26	1798(14)	2740(6)	3651(16)

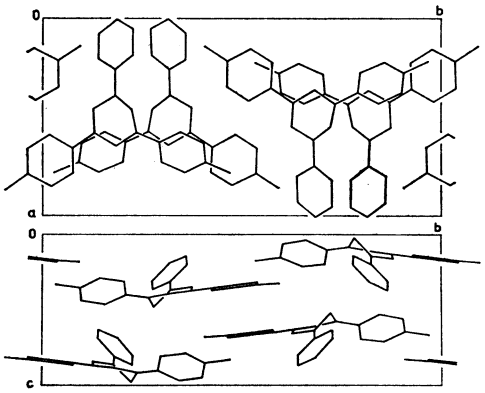

Fig. 2. The molecular packing of DTPV.

These dihedral angles can be regarded as the twist angles about the corresponding inter-ring bonds. These small twist angles and the unsymmetrical boat form of the 1,2,4,5-tetrazinyl ring have also been observed in other verdazyls.[6] Such a molecular structure of the verdazyls, containing a four-coordinated carbon atom or C6, makes the unpaired electron delocalize over the whole framework.[7]

The molecules in the crystal are packed in a column along the c axis, as is shown in Fig. 2. The shortest N...N, N...C, and C...C intermolecular atomic contacts appear in this column and are as follows: N1...N1, 4.15; N1...C12, 3.45; and C8...C3, 3.39 Å. The intermolecular contacts all seem not to be shorter than the normal van der Waals distances. There is no alternation in the molecular packing, as can be seen from Fig. 2. Therefore, the crystal structure does not support the possibility of the alternating linear chain of the spins in the DTPV crystal. For another reason, the linear chain of Ising spins is also doubtful. Based on the crvstal structure and the data from the magnetic-resonance spectroscopies, the magnetic susceptibility of the DTPV crystal will be re-

Table 2. Bond distances [l/Å] and bond angles [ϕ/°]
The estimated standard deviations are 0.02 Å and 1° respectively.

Atoms	Distance	Atoms	Distance
N1-N2	1.37	N2-C3	1.33
C3-N4	1.35	N4-N5	1.37
N5-C6	1.44	C6-N1	1.46
N1-C7	1.40	C7-C8	1.41
C8-C9	1.39	C9-C10	1.39
C10-C11	1.38	C11-C12	1.43
C12-C7	1.38	C10-C13	1.54
C3-C14	1.45	C14-C15	1.38
C15-C16	1.42	C16-C17	1.38
C17-C18	1.43	C18-C19	1.39
C19-C14	1.38	C17-C20	1.47
N5-C21	1.40	C21-C22	1.31
C22-C23	1.43	C23-C24	1.35
C24-C25	1.35	C25-C26	1.39
C26-C21	1.41		
Atoms	Angle	Atoms	Angle
N1-N2-C3	119	N2-C3-N4	122
C3-N4-N5	118	N4-N5-C6	113
N5-C6-N1	108	C6-N1-N2	113
C6-N1-C7	125	N2-N1-C7	122
N2-C3-C14	119	N4-C3-C14	118
N4-N5-C21	118	C6-N1-C21	128
N1-C7-C8	123	C7-C8-C9	118
C8-C9-C10	127	C9-C10-C11	112
C10-C11-C12	125	C11-C12-C7	119
C12-C7-C8	119	C12-C7-N1	118
C9-C10-C13	123	C11-C10-C13	124
C3-C14-C15	121	C3-C14-C19	122
C14-C15-C16	119	C15-C16-C17	127
C16-C17-C18	109	C17-C18-C19	127
C18-C19-C14	120	C19-C14-C15	118
C16-C17-C20	127	C18-C17-C20	125
N5-C21-C22	121	N5-C21-C26	119
C21-C22-C23	121	C22-C23-C24	118
C23-C24-C25	121	C24-C25-C26	121
C25-C26-C21	118	C26-C21-C22	120

examined in a separate paper.[8]

The calculations were performed at the Computer Centers of Kyoto and Ehime Universities, using the UNICS program system.[9]

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