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The Magnetic Properties of Verdazyl Free Radicals. VIII. The Crystal Structure of 1,3,5-Tri-*p*-tolylverdazyl Radical

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The crystal structure of 1,3,5-tri-*p*-tolylverdazyl has been determined by X-ray diffraction. The crystals are monoclinic, with the space group of $P2_1/m$ and with $a=8.173(3)$, $b=20.23(1)$, $c=6.075(2)$ Å, $\beta=105.4(1)°$, and $Z=2$. The structure was deduced from the sharpened Patterson synthesis and refined by the block-diagonal least-squares method to the final R value of 0.048 for the 1212 non-zero reflections collected by the counter-method. The *sym*-tetrazinyl ring has an asymmetrical boat form. The molecules are arranged approximately parallel to the $(20\bar{1})$ plane. The maximum intermolecular overlap is observed between the *sym*-tetrazinyl and *C*-tolyl groups, suggesting a weak exchange interaction between unpaired electrons.

For studying the magnetic properties of radical solids with an unpaired electron delocalized over the whole molecular frame-work, precise knowledge about both the spin-density distribution and the crystal structure is of great importance. Based on such knowledge, the magnetic properties of 1,3,5-triphenylverdazyl and galvinoxyl radicals were discussed in a previous paper.[1] However, there has thus far been little systematic study in this area. Thereupon, crystal structure analyses were carried out on verdazyls, which exhibit magnetic properties different from one to another in spite of their similar spin-density distributions. Figure 1 shows a generalized canonical formula of the verdazyls of our interest. Their spin distributions have been published elsewhere.[2]

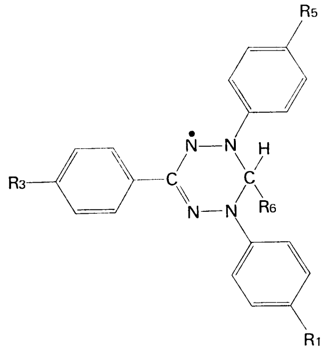

Fig. 1. Constitutional formula of verdazyl radicals. R_1, R_3, and R_5 stand for H, CH_3, and so on. R_6 is H or CH_3.

This and the following papers describe the crystal structures of 1,3,5-tri-*p*-tolylverdazyl (TTV), and 1,3,5-triphenyl-6-methylverdazyl (MeTPV)[3] respectively, whose magnetic susceptibilities indicate, respectively, a weak exchange interaction and a fairly strong isotropic exchange interaction between the unpaired electrons. The details of the magnetic properties of them and of other radicals will be presented in a separate paper.

Experimental

The TTV was prepared from *p*-tolualdehyde, *p*-toluidine, and formaldehyde by a method analogous to that described by Kuhn and Trischmann[4] (Found: C, 78.07; H, 6.65; N, 15.54%; Calcd for $C_{23}H_{23}N_4$: C, 77.72; H, 6.52; N, 15.76%). The crystals used for the structure analysis were obtained by standing a solution of TTV in a mixture of acetone and methanol at room temperature.

Table 1. Crystal data

Molecular formula	$C_{23}H_{23}N_4$
Molecular weight	355.5
Melting point	137—138 °C
Specimen used for the data collection	*ca.* $(0.25\ \text{mm})^3$
Crystal system	Monoclinic
Cell dimensions;	
a	8.173 ± 0.003Å
b	20.23 ± 0.01
c	6.075 ± 0.002
β	$105.4\pm0.1°$
V	968.2Å^3
Z	2
Density (calculated)	$1.222\ \text{g/cm}^3$
Density (observed by flotation)	1.214
$F(000)$	378
Linear absorption coefficient	$0.9\ \text{cm}^{-1}$ (Mo$K\alpha$)
Systematic absence	$0k0$: $k=2n+1$
Space group	$P2_1/m$ or $P2_1$

The unit-cell dimensions obtained from Weissenberg photographs were refined by the least-squares method by employing higher-order reflections measured on an automated four-circle diffractometer with Mo$K\alpha$ radiation ($\lambda=0.7107$ Å) monochromated by a graphite crystal. The crystal data are given in Table 1. The intensities of 2321 independent reflections up to $2\theta=55°$ were measured on the same diffractometer using Mo$K\alpha$ radiation. An ω–2θ scan technique was employed. The reflections with $|F_o|$ values of less than $(10/3)\sigma(F_o)$ were measured up to four times. The intensities were corrected for Lorentz and polarization effects. Neither absorption nor extinction corrections were made. A total of 1212 reflections with $|F_o|$ values not less than $2.5\sigma(F_o)$ were regarded as non-zero reflections and were used for the structure analysis.

Structure Determination and Refinement

Wilson's statistics indicated the presence of a center of symmetry. A three-dimensional Patterson map showed 98 resolved peaks in an asymmetric unit. Of

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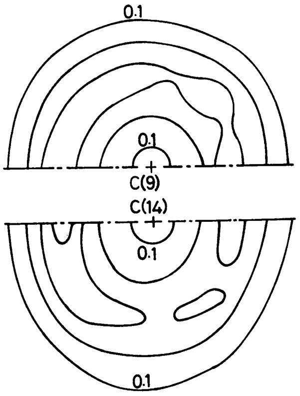

Fig. 2. Difference Fourier maps of the methyl hydrogen atoms. The sections correspond to the planes defined by the methyl hydrogen atoms. The contours are at intervals of 0.1 e/Å^3. The numbering system is referred to Fig. 3.

these, seven prominent peaks were arranged on a line (*0*, *v*, *0*); this suggested the presence of a plane of symmetry. Accordingly, the space group of P2$_1$/m was adopted. The starting model was deduced from the Patterson map with the aid of the molecular geometry of 1,3,5-triphenylverdazyl (TPV).[5] This model gave an *R* value of 0.27.

The block-diagonal least-squares refinement was then undertaken; the *R* value decreased to 0.12 after four cycles of refinement with individual isotropic thermal parameters. Three further cycles of refinement with anisotropic thermal parameters reduced the *R* value to 0.095. At this stage, a difference Fourier map was synthesized, from which the positions of the eight ring-hydrogen atoms were located. With anisotropic thermal parameters for the non-hydrogen atoms and isotropic ones for the hydrogen atoms, four cycles of refinement reduced the *R* value to 0.071. A new difference Fourier map was then computed. As is shown in Fig. 2, there were annular distributions of the residual electron densities near the methyl carbon atoms. The following approximation was then introduced tentatively in order to execute further refinement. The methyl groups ($-CH_3$) were replaced by $-CH_6$, in which the atomic weights for the hydrogen atoms were one half of those for the corresponding ordinary methyl hydrogen atoms. Of course, the $-CH_6$ groups satisfied the symmetry required. The C–H bond length was obtained by inspecting the residual electron-density map. The refinement was continued until all the positional shifts for the non-hydrogen atoms became less than 0.25 σ. The final *R* value was 0.048 for the 1212 reflections.

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

Atom	x[a]	y[a]	z[a]
C (1)	−606 (6)	2500	−107 (7)
C (2)	−2183 (5)	2500	−4450 (7)
C (3)	433 (4)	3635 (1)	−685 (5)
C (4)	1169 (4)	3725 (2)	1640 (5)
C (5)	2157 (4)	4275 (2)	2389 (5)
C (6)	2431 (4)	4756 (2)	920 (6)
C (7)	1643 (4)	4668 (2)	−1381 (6)
C (8)	680 (4)	4116 (2)	−2178 (5)
C (9)	3485 (5)	5355 (2)	1775 (7)
C (10)	−3460 (5)	2500	−6679 (7)
C (11)	−4060 (4)	3086 (2)	−7763 (5)
C (12)	−5183 (4)	3082 (2)	−9913 (6)
C (13)	−5727 (5)	2500	−11042 (7)
C (14)	−6888 (6)	2500	−13418 (8)
N (1)	−515 (3)	3071 (1)	−1506 (4)
N (2)	−1598 (3)	3090 (1)	−3616 (4)

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)	280(11)	23(1)	277(14)		98(10)	
C(2)	149(7)	23(1)	266(12)		68(8)	
C(3)	155(5)	23(1)	287(9)	3(2)	48(5)	−7(2)
C(4)	238(7)	29(1)	285(9)	−3(2)	51(7)	−4(3)
C(5)	213(7)	35(1)	326(11)	−5(2)	24(7)	−26(3)
C(6)	161(6)	28(1)	445(12)	−2(2)	76(7)	−25(3)
C(7)	189(6)	27(1)	410(12)	−3(2)	87(7)	2(3)
C(8)	182(6)	26(1)	300(10)	0(2)	52(6)	2(3)
C(9)	211(7)	35(1)	623(17)	−22(3)	88(9)	−46(4)
C(10)	135(7)	23(1)	278(13)		69(8)	
C(11)	187(6)	23(1)	353(11)	3(2)	20(6)	−7(2)
C(12)	187(6)	26(1)	361(10)	8(2)	21(6)	14(3)
C(13)	136(7)	31(1)	297(14)		48(8)	
C(14)	174(9)	41(2)	324(15)		20(9)	
N(1)	211(5)	23(1)	243(7)	−5(2)	43(5)	−0(2)
N(2)	173(5)	24(1)	267(7)	−2(1)	33(5)	−1(2)

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

Atom	x[a]	y[a]	z[a]	B_{iso}
H(C1-1)	−181(6)	250	20(8)	5.5(13)
H(C1-2)	48(5)	250	125(6)	2.9(8)
H(C4)	106(4)	337(2)	277(5)	4.7(8)
H(C5)	284(3)	430(1)	400(4)	2.7(6)
H(C7)	179(4)	505(2)	−245(5)	4.4(8)
H(C8)	−1(4)	409(1)	−379(5)	3.3(6)
H(C11)	−364(4)	351(1)	−698(5)	3.6(7)
H(C12)	−561(4)	352(2)	−1067(5)	4.2(7)

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

Unit weight was given to all the reflections. The atomic scattering factors used were taken from "International Tables for X-Ray Crystallography."[6] The final atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms are listed in Tables 2 and 3 respectively. The final parameters for the hydrogen atoms are shown in Table 4. The observed and calculated structure factors are compared in Table 5.

Table 5. The observed and calculated structure factors (×10)

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
H,L = -1,-7			4	33	29	5	32	26	7	32	23	H,L = 0,-7			5	23	20	H,L = 1,-7			2	27	32
4	30	27	H,L = 2,-7			0	28	32	1	29	28	2	34	34	4	19	25	7	21	20	11	28	22
H,L = 3,-7			7	25	27	8	39	38	11	20	19	H,L = 4,-7			1	32	32	7	37	36	8	44	48
9	43	47	10	30	36	H,L = 5,-7			1	49	47	2	29	30	6	39	40	H,L = 6,-7			1	51	52
H,L = 7,-7			2	45	51	H,L = -3,-6			1	18	16	5	29	25	6	27	24	7	41	34	8	21	19
9	53	46	H,L = -2,-6			1	14	15	9	32	26	12	26	23	H,L = -1,-6			0	12	11	1	55	56
2	35	39	6	18	5	9	32	32	13	22	24	14	22	19	H,L = 0,-6			0	37	40	2	62	69
3	33	35	4	33	28	5	20	25	6	21	19	7	26	27	12	28	25	14	44	44	15	30	30
16	35	29	H,L = 1,-6			1	22	22	4	29	25	5	34	39	6	29	28	7	39	37	8	31	33
10	21	15	16	20	22	H,L = 2,-6			0	36	35	1	37	33	3	51	55	4	43	46	5	32	31
6	36	39	7	75	74	8	71	73	9	95	97	10	34	38	11	37	39	16	26	26	H,L = 3,-6		
0	37	36	1	36	36	2	30	28	3	70	76	4	101	105	5	26	22	6	62	65	8	55	56
9	32	38	10	62	67	12	52	50	14	37	39	15	31	32	H,L = 4,-6			0	125	127	1	57	61
2	30	32	3	27	25	4	22	22	15	21	25	H,L = 5,-6			0	133	137	1	56	56	2	26	28
3	27	28	5	26	24	9	28	30	H,L = 6,-6			1	36	30	3	56	58	4	39	35	9	30	25
H,L = 7,-6			1	27	26	2	33	32	H,L = 8,-6			5	33	30	H,L = -5,-5			3	47	43	7	32	29
9	69	68	H,L = -4,-5			0	31	30	6	25	23	7	35	29	13	22	19	H,L = -3,-5			0	82	87
1	33	37	7	19	23	11	24	22	15	21	16	H,L = -2,-5			0	96	109	2	60	66	3	33	43
9	37	41	10	57	58	11	26	17	15	28	24	H,L = -1,-5			1	29	33	2	21	30	3	14	16
4	58	60	7	24	23	9	87	87	10	34	36	H,L = 0,-5			0	76	73	1	55	55	2	32	36
3	31	35	4	29	32	5	40	46	7	172	172	8	84	90	9	133	132	10	68	68	11	58	60
15	25	23	16	29	30	17	22	19	18	24	16	H,L = 1,-5			2	24	24	3	82	83	4	95	102
5	54	54	6	188	189	7	120	124	8	105	107	9	29	26	10	101	105	11	53	57	12	124	126
13	48	52	14	20	21	H,L = 2,-5			0	29	33	2	89	91	3	124	131	4	82	84	7	30	26
8	37	42	14	38	37	15	50	48	16	57	59	H,L = 3,-5			0	204	208	2	95	93	3	84	87
4	60	62	7	39	43	8	25	26	9	28	22	10	36	36	11	29	34	12	22	21	14	17	23
15	49	49	16	78	78	18	53	54	H,L = 4,-5			0	113	109	1	25	25	2	82	86	4	51	48
5	27	29	6	33	30	7	37	38	12	43	46	13	29	36	16	27	25	18	32	34	19	28	32
H,L = 5,-5			0	63	63	1	44	44	3	17	17	8	28	30	9	43	46	17	26	30	18	33	33
H,L = 6,-5			1	42	43	4	34	34	7	23	27	9	31	32	11	31	33	H,L = 7,-5			0	34	39
1	40	36	7	47	45	9	42	42	13	13	8	15	19	17	H,L = 8,-5			0	53	52	1	25	24
2	33	32	H,L = 9,-5			1	38	39	3	55	57	H,L = -7,-4			5	31	29	H,L = -6,-4			10	20	19
H,L = -5,-4			2	28	27	3	29	29	4	38	32	7	20	21	14	38	36	H,L = -4,-4			0	113	118
1	31	32	2	51	51	5	17	4	6	46	46	7	28	27	8	23	23	11	44	48	12	51	45
13	28	27	16	55	47	H,L = -3,-4			0	24	23	2	38	40	3	13	12	4	28	29	6	90	95
7	61	61	8	66	66	9	58	58	11	55	55	12	72	70	H,L = -2,-4			0	60	60	1	67	65
2	42	46	3	41	38	4	37	37	5	27	23	6	87	92	7	67	63	8	25	15	9	254	258
10	35	37	12	66	66	13	16	14	14	14	12	16	34	32	18	23	20	H,L = -1,-4			0	50	46
1	13	19	3	19	17	4	38	37	5	27	26	6	225	232	7	46	46	8	199	201	9	250	254
10	195	203	11	27	29	12	109	110	13	29	27	21	17	12	H,L = 0,-4			0	110	106	1	32	28
2	27	29	3	13	19	4	69	71	5	137	138	6	78	85	7	50	53	8	41	44	9	26	24
10	35	39	11	21	21	12	96	94	13	111	112	14	68	65	15	18	22	17	26	27	H,L = 1,-4		
0	206	199	1	24	22	2	149	156	3	61	65	4	23	28	5	108	110	6	101	107	8	49	52
9	41	41	10	31	25	11	32	35	12	109	110	13	81	86	14	27	21	16	92	96	17	29	26
18	37	47	H,L = 2,-4			0	93	92	1	129	131	2	30	25	3	61	60	4	170	171	5	28	25
6	25	31	7	26	23	10	22	18	12	43	44	14	107	107	16	68	67	17	65	63	18	38	37
19	27	30	H,L = 3,-4			0	40	43	1	32	36	4	34	36	5	24	20	6	48	48	7	47	49
8	52	53	11	25	32	12	36	42	13	15	20	14	45	48	15	40	37	16	35	30	H,L = 4,-4		
1	30	29	3	39	44	5	55	53	6	116	114	7	21	19	9	30	30	12	65	65	15	26	25
17	51	48	18	21	19	13	36	34	H,L = 5,-4			1	18	13	2	65	71	3	85	87	5	39	40
6	55	52	7	65	66	8	29	31	9	120	122	11	21	29	12	29	29	15	37	36	18	21	15
H,L = 6,-4			0	106	110	1	14	4	2	37	32	3	53	57	7	18	20	8	30	30	9	46	45
15	39	37	18	45	40	H,L = 7,-4			0	109	119	1	118	122	2	16	11	3	40	42	5	20	17
6	24	18	7	29	25	9	42	41	11	26	27	12	29	22	13	39	38	15	36	32	17	56	51
H,L = 8,-4			2	45	49	4	51	55	5	43	45	9	45	50	14	38	40	H,L = 9,-4			4	18	23
8	31	26	9	36	31	10	22	6	H,L = 10,-4			1	14	13	5	35	32	H,L = -8,-3			7	21	9
H,L = -7,-3			0	43	42	2	24	24	7	26	18	H,L = -6,-3			0	77	82	1	35	32	2	58	56
3	32	29	4	43	40	5	45	46	8	22	28	10	29	24	13	28	25	14	23	18	15	32	28
16	57	51	H,L = -5,-3			0	49	50	3	57	58	4	122	119	5	72	73	7	57	54	8	32	30
10	14	17	11	64	60	14	68	61	17	16	12	H,L = -4,-3			0	53	47	1	53	53	2	17	22
3	36	37	4	51	50	6	126	126	7	171	173	8	34	33	11	96	89	12	91	90	15	34	34
16	24	23	18	25	19	H,L = -3,-3			0	52	54	1	11	2	2	71	67	4	78	78	5	36	32
6	72	70	7	170	170	8	329	333	9	119	117	10	244	240	11	49	51	22	36	30	H,L = -2,-3		
0	32	33	1	138	128	2	133	131	3	71	64	4	47	41	5	48	47	6	64	63	7	116	114
9	115	115	10	94	92	11	141	141	12	79	82	14	28	27	15	23	18	17	36	34	21	33	31
H,L = -1,-3			0	254	244	1	93	86	2	105	100	3	103	96	4	20	16	5	75	74	6	86	85
7	54	56	8	57	62	9	75	82	10	146	143	11	37	40	12	31	33	13	60	54	14	60	58
16	39	44	17	43	44	18	52	56	H,L = 0,-3			0	129	122	1	343	328	2	284	276	3	123	119
4	79	70	5	31	22	6	25	32	8	38	34	11	68	64	12	111	114	13	66	66	15	80	91
16	57	57	17	88	93	19	49	54	20	45	44	H,L = 1,-3			0	98	94	1	54	56	2	25	22
3	42	44	4	142	138	5	88	83	6	71	66	7	81	74	8	49	39	9	45	43	12	35	38
13	52	52	14	53	55	15	19	11	24	13	14	H,L = 2,-3			1	132	134	2	52	46	3	161	159
4	96	95	5	139	142	6	63	62	7	15	19	8	76	77	9	108	105	10	55	56	12	40	35
13	27	27	14	41	49	15	38	38	16	29	28	21	39	38	23	26	23	H,L = 3,-3			0	26	23
1	45	45	2	48	51	3	31	36	4	68	65	5	195	188	6	224	219	7	197	192	8	44	53
9	83	90	10	61	57	11	99	94	12	72	73	13	84	87	14	22	22	18	22	19	23	50	43
H,L = 4,-3			0	107	101	1	37	33	2	159	155	3	47	48	4	44	46	5	14	9	6	92	89
7	37	40	8	21	21	13	66	69	16	48	48	20	26	29	H,L = 5,-3			0	17	11	1	262	263
2	137	141	3	53	52	4	19	14	5	24	29	7	75	74	9	94	91	10	59	57	11	31	38
15	66	62	16	65	66	17	103	102	19	58	54	H,L = 6,-3			0	103	106	2	166	174	3	96	95
4	60	60	5	32	31	6	26	29	7	74	75	8	27	28	10	73	72	11	89	95	12	62	67
14	64	64	15	29	29	16	62	59	18	39	41	20	35	43	H,L = 7,-3			0	47	53	1	41	38
4	19	16	7	22	16	8	78	80	10	57	56	11	52	46	19	21	17	H,L = 8,-3			1	31	33
5	38	34	7	71	68	8	111	106	9	45	48	10	66	68	11	33	38	15	22	12	H,L = 9,-3		
2	24	17	3	20	11	4	44	42	7	30	28	H,L = 10,-3			2	27	27	5	39	34	6	18	14
H,L = -9,-2			0	24	24	3	24	33	H,L = -8,-2			0	88	82	1	56	51	3	27	32	H,L = -7,-2		
0	41	40	1	57	57	2	98	96	4	40	42	5	51	51	9	29	27	13	32	28	14	26	27
16	43	41	H,L = -6,-2			0	25	27	1	30	34	3	61	60	4	116	115	5	95	101	10	32	35
13	17	23	14	32	35	H,L = -5,-2			0	73	72	3	24	21	4	63	64	5	71	75	6	149	153
7	95	95	8	236	238	9	57	56	10	158	155	11	52	51	12	57	52	13	33	36	18	29	25

Table 5. (Continued)

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
H,L = -4,-2			0	42	36	1	92	89	2	79	78	3	61	61	4	133	133	5	174	171	6	72	73
7	28	31	8	56	56	9	17	17	10	20	23	11	44	48	12	29	27	13	27	31	14	54	58
15	28	31	16	25	22	17	36	34	H,L = -3,-2			1	79	77	2	172	168	3	61	61	4	55	56
5	68	68	6	30	30	7	37	37	8	76	75	10	67	73	11	32	33	12	24	19	14	73	77
16	40	43	20	34	34	H,L = -2,-2			0	317	301	1	514	488	2	19	21	3	53	49	4	113	106
5	119	118	6	20	15	8	62	62	10	118	115	13	83	84	14	26	31	15	22	32	17	122	132
18	53	58	19	69	72	H,L = -1,-2			0	152	144	1	52	60	2	139	134	3	143	136	4	71	65
5	25	23	6	68	67	7	82	83	8	27	28	9	132	120	10	89	77	11	86	84	13	23	23
14	19	22	15	39	40	16	23	21	20	28	27	H,L = 0,-2			0	329	313	2	244	234	3	129	128
4	120	120	5	118	111	6	76	72	7	44	37	8	220	209	9	88	84	10	131	124	11	59	50
12	15	12	15	25	26	17	44	40	19	66	66	20	22	26	H,L = 1,-2			0	25	28	2	44	44
3	93	92	4	203	200	5	211	209	6	24	24	7	381	366	8	330	315	9	96	92	10	234	229
11	224	215	12	31	33	13	30	18	19	49	43	22	34	36	23	48	45	25	36	36	H,L = 2,-2		
0	72	69	1	22	27	2	164	159	3	199	196	4	211	205	5	160	154	6	13	9	7	56	50
9	23	20	11	54	51	12	20	19	13	41	41	14	104	99	16	107	107	17	46	50	18	31	29
21	21	20	H,L = 3,-2			0	173	172	1	466	462	2	31	22	3	167	153	4	198	183	5	146	140
7	177	175	9	139	139	11	46	35	12	51	48	13	87	93	14	79	76	15	118	116	16	39	41
17	155	150	18	50	52	19	53	60	21	15	17	H,L = 4,-2			0	603	593	2	290	289	3	45	45
4	272	269	5	241	231	6	114	118	8	48	47	9	57	53	10	25	15	12	45	51	13	171	170
14	193	192	16	106	100	18	134	130	19	31	32	20	48	51	23	19	20	H,L = 5,-2			2	54	52
4	68	72	5	138	140	6	93	91	7	37	32	8	43	42	9	99	105	10	70	66	11	75	80
12	42	35	13	79	81	14	44	44	16	43	46	17	21	15	H,L = 6,-2			0	26	27	1	61	56
2	30	35	3	85	81	6	42	40	7	84	90	8	177	179	9	187	189	10	131	123	11	92	91
13	19	19	17	32	26	18	16	12	H,L = 7,-2			0	55	53	6	102	103	7	31	24	8	50	48
9	59	53	12	72	69	H,L = 8,-2			0	71	78	5	16	19	6	30	27	7	39	34	8	44	39
9	40	40	10	52	54	11	42	43	12	38	39	14	25	18	H,L = 9,-2			0	27	26	4	42	43
5	20	18	14	29	22	H,L = 10,-2			1	30	32	H,L = -9,-1			0	63	59	1	53	50	2	23	19
H,L = -8,-1			0	42	40	1	46	46	2	55	55	3	33	36	12	27	22	H,L = -7,-1			2	41	43
5	69	72	6	77	71	8	133	136	9	42	40	10	92	93	11	39	38	12	28	27	16	28	26
H,L = -6,-1			0	63	67	1	55	56	2	27	29	4	98	100	5	16	5	6	37	37	7	168	177
9	60	57	11	113	115	12	41	47	14	21	21	15	37	38	16	15	18	H,L = -5,-1			0	27	26
1	33	30	2	50	43	3	73	75	4	72	74	5	51	55	8	21	29	11	28	33	12	19	18
14	25	29	15	47	48	16	36	37	17	18	17	22	29	25	H,L = -4,-1			0	125	128	1	233	234
2	54	52	3	232	235	4	61	63	6	51	48	7	26	25	9	15	20	10	57	57	12	92	96
13	33	28	14	52	59	15	102	117	17	60	61	18	36	40	19	45	46	21	41	41	H,L = -3,-1		
0	197	138	1	20	16	2	36	32	3	111	108	4	68	68	5	158	148	6	126	118	7	49	48
8	75	77	11	26	19	12	93	89	13	38	35	14	36	39	15	19	27	18	52	57	H,L = -2,-1		
0	113	107	2	62	62	5	82	78	6	107	98	7	173	167	8	55	55	9	139	132	10	65	64
11	137	126	13	55	51	15	61	67	16	46	52	17	36	40	18	34	38	21	42	41	22	36	33
24	27	22	25	15	9	H,L = -1,-1			0	129	119	1	158	158	2	201	192	3	151	141	5	134	132
6	151	150	7	83	88	8	436	412	9	501	468	20	166	164	11	22	12	12	55	48	16	34	32
19	67	69	20	28	30	23	49	42	24	33	32	H,L = 0,-1			0	924	915	1	279	268	2	203	198
3	74	70	4	17	9	5	261	242	6	252	246	7	159	151	8	27	35	9	27	25	10	30	25
11	113	105	12	168	158	13	102	97	14	35	32	18	95	110	19	110	112	21	22	22	H,L = 1,-1		
0	458	454	1	664	659	2	339	317	3	31	27	4	265	260	5	62	60	7	263	255	8	58	52
9	192	189	10	91	86	11	187	178	12	112	109	13	102	104	14	84	81	15	24	27	16	25	32
17	139	140	19	107	113	H,L = 2,-1			0	891	898	1	248	234	2	1430	1421	3	576	568	4	80	75
5	26	29	6	12	19	7	69	65	8	76	74	9	30	31	10	78	88	11	75	67	12	62	62
13	44	39	14	37	40	15	70	87	16	370	366	18	146	145	20	105	107	21	44	51	H,L = 3,-1		
0	261	255	1	81	84	2	183	184	3	337	333	4	76	73	5	174	169	6	215	209	7	197	193
8	41	36	11	50	51	12	118	116	13	151	150	14	16	13	15	54	51	16	47	44	18	34	38
19	23	18	21	45	46	23	17	15	25	25	23	H,L = 4,-1			0	100	115	1	126	124	2	71	65
3	50	44	4	132	132	5	372	372	6	316	310	7	242	246	8	135	136	10	92	88	11	45	44
12	130	131	13	129	129	14	47	51	16	21	24	18	36	32	19	44	41	23	35	34	H,L = 5,-1		
0	61	61	1	55	32	2	69	66	3	34	39	4	165	161	5	48	51	7	61	57	8	39	39
9	212	212	10	77	75	11	21	19	12	26	25	15	29	28	16	29	29	22	46	43	H,L = 6,-1		
0	75	72	1	20	22	2	70	68	3	64	72	4	61	66	7	91	92	8	84	83	9	98	91
10	22	17	11	36	35	13	21	16	16	31	31	18	23	20	H,L = 7,-1			0	70	63	2	61	65
3	29	33	4	25	27	6	18	18	8	40	39	11	34	37	13	19	20	16	19	19	H,L = 8,-1		
0	60	57	1	73	75	2	24	27	3	23	22	5	30	31	10	42	44	13	38	34	H,L = 9,-1		
3	25	24	H,L = 10,-1			1	17	16	3	23	22	7	57	60	8	19	18	H,L = -10,0			0	41	39
H,L = -9,0			5	36	35	6	45	47	8	51	45	10	43	42	H,L = -8,0			0	46	41	2	38	42
5	46	46	6	48	51	7	54	53	9	120	121	11	42	38	H,L = -7,0			0	82	87	2	25	24
6	52	48	11	22	18	12	33	36	18	27	26	H,L = -6,0			1	85	105	3	142	147	4	45	47
5	30	34	6	47	48	8	42	42	9	26	30	12	46	51	13	46	46	15	80	80	17	26	32
H,L = -5,0			0	62	64	1	118	123	3	104	102	4	87	83	5	31	36	6	12	15	7	16	22
8	40	41	13	19	24	15	37	39	19	24	25	22	21	12	H,L = -4,0			0	51	53	1	29	33
2	53	53	3	29	25	5	215	213	6	33	36	7	130	126	8	21	20	9	63	66	12	56	61
14	56	63	15	24	34	23	44	39	H,L = -3,0			0	85	90	1	38	41	2	46	42	3	120	125
5	199	200	6	159	167	7	371	369	8	153	157	9	140	142	10	123	128	11	104	106	12	53	48
13	50	54	15	29	24	16	31	33	17	39	44	20	35	31	21	34	32	25	57	55	H,L = -2,0		
0	47	57	1	55	53	2	479	508	5	702	757	4	376	399	5	63	60	6	151	159	7	63	57
8	59	65	9	226	228	10	185	186	11	73	73	12	44	43	13	46	45	14	33	40	15	80	79
16	68	73	17	27	31	18	45	45	20	54	55	21	80	80	22	61	57	H,L = -1,0			0	425	476
1	96	103	2	108	108	3	619	667	4	442	463	5	137	137	6	69	70	7	139	143	8	108	96
9	205	208	10	56	56	12	34	34	13	29	29	14	64	71	15	155	161	18	59	61	19	70	72
21	46	51	H,L = 0,0			2	428	439	4	462	469	8	148	153	12	44	38	14	226	227	16	203	211

Results and Discussion

Molecular Structure. In the $P2_1/m$ space group the general positions are fourfold. There are only two component molecules in a unit cell; therefore, the TTV molecule has a plane of symmetry. The molecular structure of TTV is illustrated in Figs. 3 and 4, while its molecular dimensions are shown in Tables 6 and 7. The conformation of the *sym*-tetrazinyl ring is an asymmetrical boat form, C(1) and C(2) being below the N(1)N(2)N(2′)N(1′) plane (called the N-plane for short) by 0.605 and 0.119 Å respectively. The corresponding dihedral angles at both ends of the N-plane are 43.9° and 11.3° respectively. These values are in agreement with those in TPV and MeTPV. N(1) is displaced by 0.068 Å above the C(1)N(2)C(3) plane. The three bond angles around N(1) are 123.6, 118.6, and 117.2 degrees, giving 359.4° in total. These angles also correspond closely to those in TPV and MeTPV, as can be seen from Table 8, where the *sym*-tetrazinyl rings of some compounds are compared. Thus, the bonds of the three-coordinated nitrogen atom of symmetrical verdazyl are almost on one plane. The *N*-tolyl group is warped out of the N-plane, the upward deviation of C(3) from the N-plane being 0.394 Å (16.4° for the angle between the N(1)–C(3) bond and the N-plane), while the plane of the *C*-tolyl group is practically parallel to the N-plane.

The dihedral angle between the plane of the *N*-tolyl group and the C(1)N(2)C(3) plane is 14.7 degrees. This angle can be considered as a twist angle about the N(1)–C(3) bond, because the N(1) atom does not deviate much from the C(1)N(2)C(3) plane. This twist angle is smaller than the mean values of 28° in 1,3,5-triphenylbenzene[7] and 18° in TPV. Since the TTV molecule has a plane of symmetry, the twist angle about the N(1′)–C(3′) bond is −14.7°. Thus,

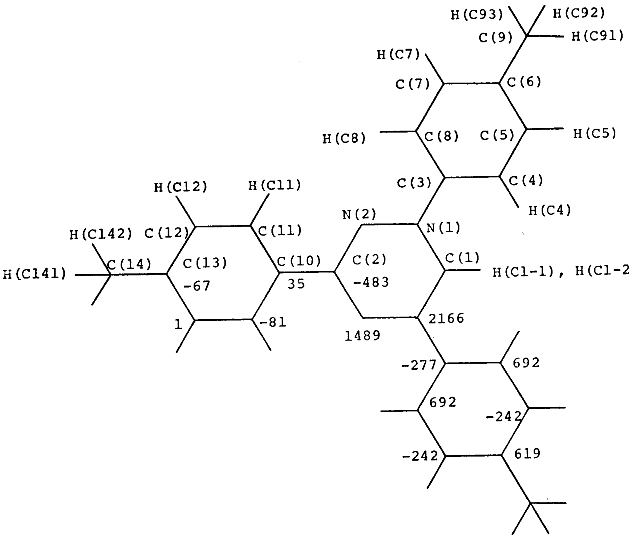

Fig. 3. Numbering system and spin densities (×10⁴). The reflected atom will be represented in terms of its counterpart's symbol followed by a prime, *e.g.* N(1′). *N*-Tolyl and *C*-tolyl are at the upper right and at the far left, respectively.

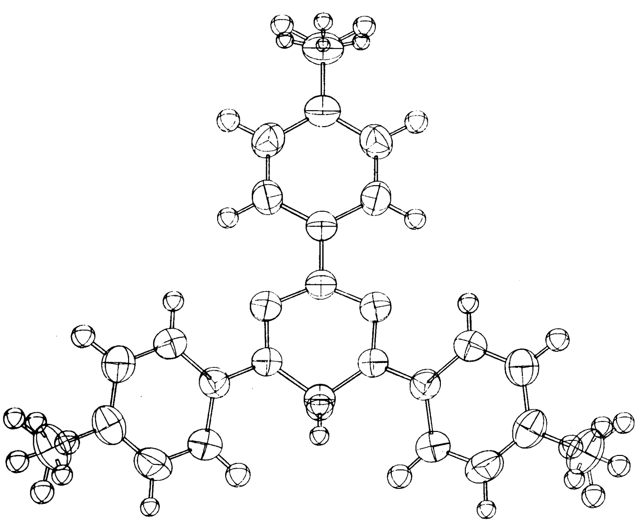

Fig. 4. Molecular structure and thermal ellipsoids.[14) An approximation made on the methyl groups is referred to the text. The thermal ellipsoids enclosing a probability of 50%, except for hydrogen atoms, were viewed approximately along the normal of the nitrogen plane.

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

Bond	Length	Bond	Length
C(1)-N(1)	1.447(4)	C(7)-C(8)	1.378(4)
N(1)-N(2)	1.352(3)	C(8)-C(3)	1.381(4)
N(2)-C(2)	1.334(3)	C(6)-C(9)	1.496(5)
N(1)-C(3)	1.394(4)	C(2)-C(10)	1.474(5)
C(3)-C(4)	1.393(4)	C(10)-C(11)	1.381(3)
C(4)-C(5)	1.379(5)	C(11)-C(12)	1.382(4)
C(5)-C(6)	1.379(5)	C(12)-C(13)	1.376(4)
C(6)-C(7)	1.387(4)	C(13)-C(14)	1.502(6)
C(1)-H(Cl-1)	1.05(5)	C(7)-H(C7)	1.04(3)
C(1)-H(Cl-2)	1.04(3)	C(8)-H(C8)	1.00(3)
C(4)-H(C4)	1.02(3)	C(11)-H(C11)	1.00(3)
C(5)-H(C5)	0.99(2)	C(12)-H(C12)	1.01(3)
Atoms	**Distance**	**Atoms**	**Distance**
C(1)---C(4)	2.924(4)	C(4)---H(Cl-1)	3.42(3)
C(1)---C(10)	4.054(5)	C(4)---H(Cl-2)	2.54(1)
N(2)---C(8)	2.770(4)	C(10)---H(Cl-1)	4.03(5)
N(2)---C(11)	2.776(3)	H(C4)---H(Cl-1)	3.01(5)
C(1)---H(C4)	2.59(3)	H(C4)---H(Cl-2)	1.98(4)
N(2)---H(C8)	2.42(3)	H(C4)---H(C4′)	3.50(7)
N(2)---H(C11)	2.43(3)	H(C8)---H(C11)	3.29(4)

the configuration of the two *N*-tolyl groups is anti-propellor. However, H(C4) and H(C4′) are still staggered betwen H(Cl-1) and H(Cl-2). In comparison with the no-twist case, the configuration mentioned above enlarges the distance between H(C4) and H(C4′) and simultaneously decreases the repulsion between the *N*-tolyl groups and the methylene group. A parallel description holds in the cases of TPV and MeTPV as well.

The equation of the least-squares plane through five atoms, C(1), C(2), C(3), N(1), and N(2), is given by:

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

N(1′)-C(1)-N(1)	105.9(3)	C(1)-N(1)-N(2)	117.2(2)
N(1)-N(2)-C(2)	114.4(1)	N(2)-C(2)-N(2′)	126.8(3)
C(1)-N(1)-C(3)	123.6(2)	N(2)-N(1)-C(3)	118.6(1)
N(1)-C(3)-C(4)	121.3(2)	C(3)-C(4)-C(5)	119.9(2)
C(4)-C(5)-C(6)	122.5(3)	C(5)-C(6)-C(7)	116.7(2)
C(6)-C(7)-C(8)	121.9(2)	C(7)-C(8)-C(3)	120.6(2)
C(8)-C(3)-C(4)	118.4(2)	C(8)-C(3)-N(1)	120.4(2)
C(5)-C(6)-C(9)	121.6(3)	C(7)-C(6)-C(9)	121.6(2)
N(2)-C(2)-C(10)	116.3(2)		
C(2)-C(10)-C(11)	120.9(2)		
C(10)-C(11)-C(12)	120.6(2)		
C(11)-C(12)-C(13)	121.4(2)		
C(12)-C(13)-C(12′)	117.7(3)		
C(11)-C(10)-C(11′)	118.2(3)		
C(12)-C(13)-C(14)	121.1(2)		

Table 8. Comparison of mean bond lengths (Å) and of mean bond angles (degree)

Compound[a)	TTV	TPV	MeTPV	TEAZN	DPAZN
Reference	this work	5	3	8	9
Length;					
N(1)-N(2)	1.352	1.351	1.358	1.321	1.314
N(2)-C(2)	1.334	1.338	1.335	1.334	1.346
C(2)-C(10)	1.474	1.485	1.487		1.454
N(1)-C(3)	1.394	1.414	1.404		
N(1)-C(1)	1.447	1.443	1.457		
C–C single bond			1.517		
Angle;					
N(1)-N(2)-C(2)	114.4	114.4	114.4	116.0	119.1
N(2)-C(2)-N(2′)	126.8	126.8	126.8	127.4	121.8
N(2)-C(2)-C(10)	116.3	116.6	116.5		119.1
N(1)-C(1)-N(1′)	105.9	106.1	104.3		
C(1)-N(1)-C(3)	123.6	122.8	123.8		
N(2)-N(1)-C(3)	118.6	117.4	118.1		
N(2)-N(1)-C(1)	117.2	117.8	117.7		

a) TTV; 1,3,5-tri-*p*-tolylverdazyl, TPV; 1,3,5-triphenyl-verdazyl, MeTPV; 1,3,5-triphenyl-6-methyl-verdazyl, TEAZN; *sym*-tetrazine, DPAZN; 3,6-diphenyl-*sym*-tetrazine.

$$0.8868X - 0.3856Y - 0.2521Z + 2.3566 = 0 \text{ (Å)}, \quad (1)$$

where the Cartesian reference axes are taken as follows: $X = ax + cz\cos\beta$, $Y = by$, and $Z = cz\sin\beta$. The atomic deviations from this plane are C(1) = −0.001, C(2) = 0.117, C(3) = 0.035, N(1) = 0.026, and N(2) = −0.161 Å. The dihedral angle between this and the *N*-tolyl planes is close to that of the twist about the N(1)–C(3) bond. Accordingly, it seems reasonable to divide the TTV molecule into three planes. Two of them are the plane defined by Eq. (1) and its mirror image. The last one covers the *C*-tolyl group and the C(2) atom, at which the three planes intersect. On the other hand, N(2)–C(2)–N(2′) angle is close to that of the ideal trigonal bond. Therefore, the molecular structure of TTV seems to be favorable for the delocalization of an unpaired π-electron. The above consideration holds in both TPV and MeTPV. Actually, the dimensions of the *sym*-tetrazinyl ring of verdazyls are similar to those of TEAZN and DPAZN, both of which are planar molecules with conjugated double bonds.[8,9]

To summarize, the mutually distinguishable magnetic properties of TTV, MeTPV, and TPV can probably be attributed to the variety of the molecular packing patterns of the respective radicals, taking account of the similarity in molecular structure as well as in this spin-density distribution.[2]

Residual Electron Densities. None of the methyl hydrogen atoms could be located unequivocally, as is shown in Fig. 2. Such annular distributions of the electron densities suggest the rotation of the methyl groups about the C–C bond.

The final difference Fourier map was then calculated. The residual electron densities on this map varied from -0.16 to $0.16\ e/\text{Å}^3$. A composite electron-density map is shown in Fig. 5. The standard deviation of the electron density, $\sigma(\rho)$, was estimated to be $0.02\ e/\text{Å}^3$ following the method of Cruickshank.[10] The residual electron densities at the middle point of every bond exceed $2\sigma(\rho)$; this is probably to be attributed to the aspherical distribution of electrons as a result of the bond formation.

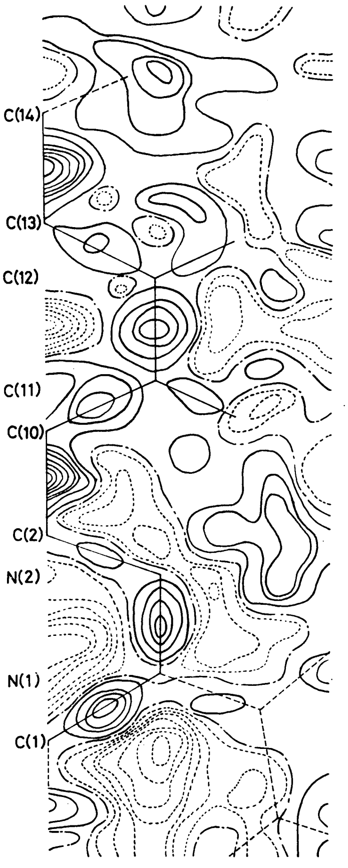

Fig. 5. The final composite residual electron-density sections through the pair of bonds between non-hydrogen atoms and between their counterparts on the opposite side beyond the mirror plane. The contours are at intervals of $0.02\ e/\text{Å}^3$. The solid, dashed, and broken contours indicate positive, zero, and negative values, respectively. The solid and broken straight lines represent the bonds on and out of the section, respectively.

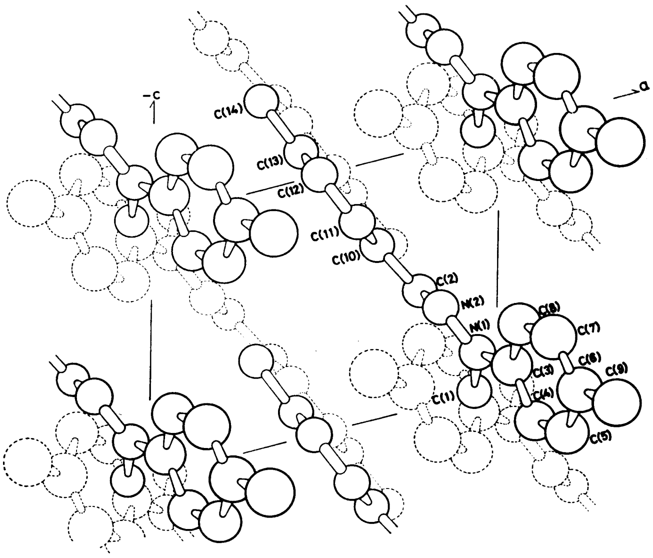

Fig. 6. Mutual arrangement of the molecules viewed along the b-axis. The hydrogen atoms were not drawn.

Table 9. 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
N(1)	C(14)	3.647(6)	$1+x,\ y,\ 1+z$
C(1)	C(10)	3.516(7)	$x,\ y,\ 1+z$
C(10)	C(14)	3.836(7)	$x,\ y,\ 1+z$
H(Cl–1)	C(12)	2.99(5)	$x,\ y,\ 1+z$
H(Cl–2)	C(10)	2.61(6)	$x,\ y,\ 1+z$
H(Cl–2)	C(11)	2.75(5)	$x,\ y,\ 1+z$
C(4)	C(14)	3.891(4)	$1+x,\ y,\ 2+z$
C(3)	C(9′)	3.707(5)	$-x,\ 1/2+y,\ -z$
C(8)	C(9′)	3.638(5)	$-x,\ 1/2+y,\ -z$
C(12)	C(9′)	3.746(5)	$-x,\ 1/2+y,\ -1-z$
C(9)	C(7)	4.053(5)	$1-x,\ 1/2+y,\ -z$
C(9)	C(5′)	4.943(6)	$1-x,\ 1/2+y,\ -z$
C(9)	C(9′)	3.960(9)	$1-x,\ 1/2+y,\ -z$

Molecular Packing. The mutual arrangement of the TTV molecules is shown in Fig. 6. The pertinent intermolecular contacts and their estimated standard deviations are listed in Table 9.

The shortest C···C, C···N, C···H, and N···H intermolecular distances are 3.516 Å along [001], 3.647 Å along [101], 2.16 Å along [001], and 2.89 Å along [101] respectively. The fairly planar molecules are arranged in sheets approximately parallel to the $(20\bar{1})$ plane. A complete overlap of the molecular plane is observed between the *sym*-tetrazinyl and *C*-tolyl groups, while the other interplanar overlaps are incomplete. The interplanar distance of the complete overlap is roughly 4.2 Å. This maximum overlap leads to a column along the c-axis.

It is worth noting that the TTV crystal contains only two molecules in the unit cell with the center of symmetry. Fortunately, for the purpose of magnetic resonance studies, this means that the so-called similar-dissimilar relation can be disregarded. In general, the resonance spectra consist of contributions from both the single molecules and the whole crystal. However, it is quite difficult to resolve the spectrum into the component contributions, particularly when dissimilar paramagnetic molecules or different magnetic sites are present. Therefore, we presume that the TTV crystal will give more knowledge peculiar to the verdazyl single molecule in the solid phase than any other verdazyl crystal will give.

Spin Densities and Exchange Interaction. Following the method of Fischer, who has treated the lone pairs on N(1) and N(1′) as π-electrons,[11] the McLachlan spin densities of TTV were calculated. The results are shown in Fig. 3. Those values can explain the qualitative ENDOR (electron nuclear double resonance) spectra of TTV. A considerable amount of spin density can be observed on every atom in the π-electron framework.[2]

On the other hand, the magnitude of the exchange interaction between the π-electron spins may be conjectured on the basis of the spin densities and the molecular packing. For the sake of simplicity, we focus our attention on the column along the c-axis. The exchange interaction of conjugated π-spin radicals being considered, the following two-spin Hamiltonian proposed by McConnell[12] is certainly useful:[1]

$$H^{AB} = -\boldsymbol{S}^A \cdot \boldsymbol{S}^B \sum_{ij} J_{ij}^{AB} \rho_i^A \rho_j^B, \tag{2}$$

where $\boldsymbol{S}^A$ and $\boldsymbol{S}^B$ are the total spins on the A and B molecules and where ρ_i^A and ρ_j^B are the π-spin densities on the i and j atoms of A and B molecules. The exchange integral, J_{ij}^{AB}, depends on the overlap integral between the $2p_z\pi$-orbitals of the i and j atoms, and is certainly negative for all the interatomic contacts in the present case,[1] though we cannot estimate its precise magnitude at present. Using the spin densities in Fig. 3, we consider that the contribution due to the overlap integrals between the *sym*-tetrazinyl and the *C*-tolyl groups is ferromagnetic: that is, the sum in Eq. (2) is positive, while the other contributions are antiferromagnetic. This implies that the effective exchange integral, $|J|$, is small when the summation is carried out over all the atoms in the adjacent molecules. In fact, the magnetic susceptibility of TTV follows the Curie-Weiss law with a negative Weiss constant of *ca.* −1 K down to the lowest temperature reached, 1.8 K. Therefore, we presume that the weak exchange interaction inferred from the susceptibility can be attributed mainly to such competitive contributions.

Computer Programs. All 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 the Universal Crystallographic Computation Program System, UNICS.[13] The thermal ellipsoids were drawn on a HITAC 5020E computer at the Computer Center, the University of Tokyo.[14]

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