References

ABBONA, F. & FERRARIS, G. (1970). *Period. Miner.* **39**, 183–210.

BAUR, W. H. (1970). *Trans. ACA*, **6**, 125–155.

BRASSE, R., GUÉRIN, H. & MATTRAT, P. (1970). *Bull. Soc. Chim. Fr.* pp. 2069–2072.

BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. ORNL-TM-305, Oak Ridge National Laboratory. Oak Ridge, Tennessee.

CALLERI, M. & FERRARIS, G. (1967). *Period. Miner.* **36**, 1–23.

CHIDAMBARAM, R., SEQUIRA, A. & SIKKA, S. K. (1964). *J. Chem. Phys.* **41**, 3616–3622.

CURRY, N. A. & JONES, D. W. (1971). *J. Chem. Soc.* (*A*), pp. 3725–3729.

DENNE, W. A. & JONES, D. W. (1971). *J. Cryst. Mol. Struc.* **1**, 347.–354.

DURIF, A. (1971). *Bull. Soc. Fr. Minér. Crist.* **94**, 556–557.

FERRARIS, G. (1969). *Acta Cryst.* B**25**, 1544–1550.

FERRARIS, G. & CHIARI, G. (1970). *Acta Cryst.* B**26**, 403–410.

FERRARIS, G. & FRANCHINI-ANGELA, M. (1972). *Acta Cryst.* B**28**, 3572–3583.

FERRARIS, G., JONES, D. W. & YERKESS, J. (1971). *Acta Cryst.* B**27**, 349–354.

FERRARIS, G., JONES, D. W. & YERKESS, J. (1972). *Acta Cryst.* B**28**, 209–214.

GUÉRIN, H. (1941). *Ann. Chim.* **16**, 101–102.

HAMILTON, W. C. (1966). *World List of Crystallographic Computer Programs*, program No. 225.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

PIERROT, R. (1964). *Bull. Soc. Fr. Minér. Crist.* **87**, 169–211.

SUTOR, D. J. (1967). *Acta Cryst.* **23**, 418–422.

Acta Cryst. (1973). B**29**, 96

Crystal Structure of 2,4,6-Triphenylverdazyl

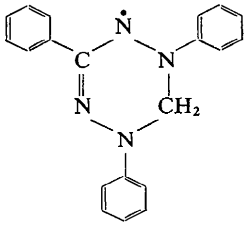
BY DONALD E. WILLIAMS

Department of Chemistry, University of Louisville, Louisville, Kentucky 40208, *U.S.A.*

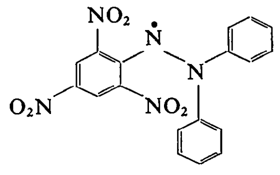
(*Received* 22 *May* 1972; *accepted* 17 *August* 1972)

The stable free radical 2,4,6-triphenylverdazyl ($C_{20}N_4H_{17}$) crystallizes in space group $P2_12_12_1$ with four molecules per cell. The lattice constants are $a = 18.467(2)$, $b = 9.854(1)$, and $c = 8{\cdot}965(1)$ Å. X-ray intensity data were collected on a quarter-circle diffractometer with scintillation-counter detection. The crystal structure was solved by molecular packing analysis, and was refined by structure-factor least-squares calculations using individual anisotropic temperature factors and calculated hydrogen positions. The final discrepancy index was 0·076 for 1309 reflections which were more than one standard deviation above background. The verdazyl ring is nonplanar, with the methylene carbon atom displaced 0·59 Å from the plane of the four nitrogen atoms. The phenyl groups attached to N(2) and N(4) are also warped out of the plane of the nitrogen atoms; in addition, these phenyl groups are twisted by 23 and 13° respectively, about the phenyl–nitrogen bonds.

The class of stable free radicals called the verdazyls Kuhn & Trischmann, 1963) is based on the 3,4-dihydro-*s*-tetrazin-1(2*H*)-yl ring system. A very stable and crystalline member of this series is the 2,4,6-triphenyl substituted compound (Kuhn & Trischmann, 1964), TPV:



TPV is geometrically similar to 1,3,5-triphenylbenzene, except that a preliminary X-ray diffraction study (Williams, 1969*b*) showed that the methylene carbon atom is significantly out of the plane of the central ring. The e.s.r. spectrum (Kuhn & Trischmann, 1964) indicates approximately equal sharing of the unpaired electron among the four nitrogen atoms. The radical is even more stable than 2,2-diphenyl-1-picrylhydrazyl (DPPH), where the unpaired electron is shared primarily by only two nitrogen atoms, and is further shielded and stabilized by *o*-nitro groups (Williams, 1967):



Experimental

Crystals of TPV suitable for X-ray diffraction measurements were kindly supplied by Dr F. A. Neugebauer. Weissenberg photographs were used to obtain the space group and preliminary unit-cell dimensions. Accurate lattice constants were obtained by a least-squares fit (Williams, 1964) to eight reflections above $2\theta = 154°$ (Cr $K\alpha$), using the Nelson–Riley (1945) extrapolation function. Crystal data are given in Table 1.

Table 1. *Crystal data for* 2,4,6-*triphenylverdazyl*

$a = 18{\cdot}467$ (2) Å
$b = 9{\cdot}854$ (1)
$c = 8{\cdot}965$ (1)
$V = 1631{\cdot}4$ Å^3
λ(Cr $K\alpha_1$) = 2·28962 Å
$C_{20}N_4H_{17}$
M.W. 313·385
Space group: $P2_12_12_1$
$Z = 4$
$D_x = 1{\cdot}276$ g cm^{-3}

Intensity data were taken (up to $2\theta = 50°$) using Zr-filtered Mo $K\alpha$ radiation. A manually operated quarter-circle single-crystal orienter was used with a 3·33° (100 sec) scan in 2θ, using $\omega = 2\theta$ coupling. A scintillation-counter detector was used with pulse-height selection; background counts were estimated from ratemeter charts. Of 1685 reflections scanned, 1309 were at least one standard deviation above the background under the experimental conditions.

The standard deviation of the intensity was estimated by the formula

$$\sigma^2(I) = C_t + (K_tC_t)^2 + (K_bC_b)^2 ,$$

where $\sigma(I)$ is the standard deviation of the intensity, C_t and C_b are the total and background counts, and $K_t = K_b = 0{\cdot}05$; $\sigma(F)$ was obtained by the finite difference method (Williams & Rundle, 1964). The variation of selected standard reflections during the data-collection period was less than 3%, indicating no significant crystal decomposition due to X-ray exposure. The Lorentz and polarization corrections were made in the usual manner; no absorption or extinction correction was made. Structure-factor least-squares refinement (*SFLS*) was based on the minimization of $\sum[(F_o - |F_c|)]^2/\sigma^2(F_o)]$. The final refinement utilized the full matrix of the normal equations (217 variables); the resulting variance–covariance matrix was used to estimate standard deviations of the derived distances and angles (Busing, Martin & Levy 1964). Anisotropic temperature factors were of the form

$$\exp\,(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)\,.$$

The scattering factors used for carbon and nitrogen are those of Hanson, Hermann, Lea & Skillman (1964); for hydrogen, Stewart, Davidson & Simpson (1965).

Molecular packing analysis

The atomic connectivities were already known; the expected molecular degrees of freedom were the three phenyl twist angles and possible deviations of the verdazyl ring from planarity. We expected that the phenyl twist angles would not exceed about 30°, since this angle of twist is sufficient to relieve the *o*-hydrogen steric strain, without losing too much conjugation energy. A prototype exemplary structure was 1,3,5-triphenylbenzene (Farag, 1954), where the twist angles are 34, −27, and 24°; in TPV the arrangement and number of hydrogen atoms on the central ring is different.

For our trial molecular model we used a planar structure with 120° bond angles and the following interatomic distances: in verdazyl rings, 1·35 Å; in benzene rings, 1·40; in ring–ring bonds, 1·45; C–H, 1·03; HCH angle in verdazyl rings, 109·5°. The trial angular orientation of the planar molecule was taken in the (121) crystallographic plane, which had the largest observed structure factor. This initial orientation of the molecular plane was only 14° in error, based on the final refined model. The trial coordinates and orientation matrix are given in Table 2. The second column of the matrix gives the direction cosines of the trial molecular plane. The angular orientation about this vector was arbitrary; the total angular error of the trial orientation was 26·7°.

Table 2. *Coordinates of idealized planar model* (Å) *and orientation matrix A*

Atom	X	Z	Atom	X	Z
N(1)	−0·67	−1·17	H(3*a*)*	1·94	0·00
N(2)	0·67	−1·17	H(3*b*)†	1·94	0·00
C(3)	1·35	0·00	H(8)	−0·33	−3·64
N(4)	0·67	1·17	H(9)	0·89	−5·74
N(5)	−0·67	1·17	H(10)	3·31	−5·74
C(6)	−1·35	0·00	H(11)	4·53	−3·64
C(7)	1·40	−2·42	H(12)	3·31	−1·53
C(8)	0·70	−3·64	H(14)	3·31	1·53
C(9)	1·40	−4·85	H(15)	4·53	3·64
C(10)	2·80	−4·85	H(16)	3·31	5·74
C(11)	3·50	−3·64	H(17)	0·89	5·74
C(12)	2·80	−2·42	H(18)	−0·33	3·64
C(13)	1·40	2·42	H(20)	−2·99	2·10
C(14)	2·80	2·42	H(21)	−5·41	2·10
C(15)	3·50	3·64	H(22)	−6·63	0·00
C(16)	2·80	4·85	H(23)	−5·41	−2·10
C(17)	1·40	4·85	H(24)	−2·99	−2·10
C(18)	0·70	3·64			
C(19)	−2·80	0·00			
C(20)	−3·50	1·21			
C(21)	−4·90	1·21			
C(22)	−5·60	0·00			
C(23)	−4·90	−1·21			
C(24)	−3·50	−1·21			

* $Y = 0{\cdot}84$
† $Y = -0{\cdot}84$

$$A = \begin{bmatrix} 0{\cdot}97374 & 0{\cdot}22759 & 0{\cdot}00000 \\ -0{\cdot}19950 & 0{\cdot}85356 & -0{\cdot}48127 \\ -0{\cdot}10953 & 0{\cdot}46864 & 0{\cdot}87656 \end{bmatrix}$$

Using this trial molecular orientation, the repulsion energy between molecules in the crystal was minimized by least-squares calculations, using the computer program *PCK*5 (Williams, 1969*a*). In this program the quantity

$$\mathrm{RP} = \tfrac{1}{2} \sum w(d_o - d_c)^2, \quad d_c < d_o ,$$

is minimized, where the sum is over all nonbonded interatomic contacts of the reference molecule with surrounding molecules. This procedure is referred to in this paper as molecular packing analysis (MPA). The variables were three translations and three rotations of the rigid planar molecule. The observed space group and unit-cell dimensions were used. The values of the nonbonded potential parameters w and d_o are given in Table 3; d_c is a calculated distance for the trial model.

Table 3. *Nonbonded potential parameters*

Type	d_o	w
C···C	3·65	1·87
C···H	3·03	1·56
H···H	2·88	1·00
N···N	3·65	1·87
N···C	3·65	1·87
N···H	3·03	1·56

The steps in the solution of the molecular packing problem are included in Table 4. The Cheshire space group (Hirshfeld, 1968) is *Pmmm*, and the molecular center of the reference molecule may be placed in the range $0 \leq X_o \leq a/4$, $0 \leq Y_0 \leq b/4$, and $0 \leq Z_0 \leq c/4$. Using the (121) orientation matrix, we explored this volume on a 2 Å grid (twelve grid points) for the position of the molecular center. Two of the twelve trial models (models I and II, Table 4) converged to a structure (model III) with the lowest packing index, RP = 9·2. The other trial models converged to false minima with higher values of RP.

The two trial models which converged to model III had atoms which deviated from their correct positions by the amounts indicated in Table 4. Note that the mean deviations of the carbon and nitrogen atoms of 1·86 and 2·65 Å, and maximum deviations of 3·53 and 4·33 Å, did not prevent convergence. The resulting packing model for the planar molecule had a mean deviation of 0·78 Å and a maximum deviation of 1·61 Å. The angular deviation of the molecule was reduced to 9·3°. The structure factor discrepancy index, RSF = 0·434, for the 23 lowest angle reflections showed a glimmer of hope for the model.

The phenyl twist angles were now systematically varied, first by ±10, then ±5, and finally by ±2°. The packing index, RP, was thus reduced to 5·3, and RSF(23) was reduced to 0·336. The mean atomic deviation for this structure (model IV) was reduced to 0·54 Å; the maximum deviation was 1·14 Å. The angular deviation was reduced to a remarkably low 1·7° for this model with four rings, each planar. The best possible fit of this model to the final observed structure still has a mean atomic deviation of 0·24 Å, because of the nonplanarity of the verdazyl ring. Model IV actually had the CH_2 group misplaced by a 120° rotation of the verdazyl ring; although this affects the molecular packing-analysis result, we have renumbered

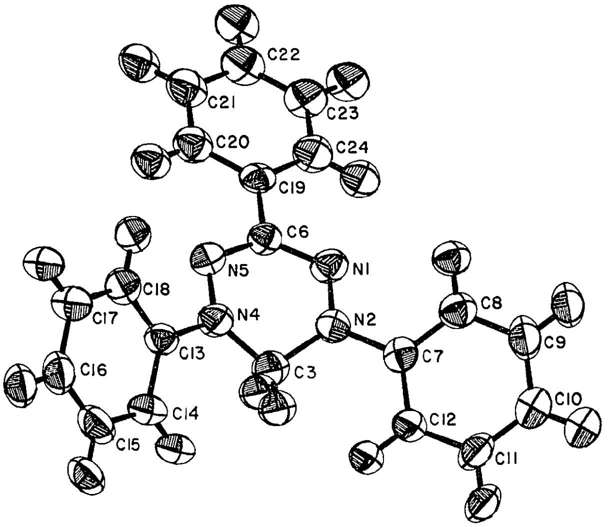


Fig. 1. The molecular structure and atomic numbering system. The thermal ellipsoids are drawn at the 50% probability level (Johnson, 1965).

Table 4. *Structural models for* 2,4,6-*triphenylverdazyl*

Model	Mean atomic deviation	Maximum atomic deviation	Packing index RP	Structure factor indices[i]			
				RSF(23)	RSF(138)	RSF(861)	RSF(1309)
I[a]	1·86 Å	3·53 Å	207·0				
II[b]	2·65	4·33	186·6				
III[c]	0·78	1·61	9·2	0·434			
IV[d]	0·54	1·14	5·3	0·336	0·464		
V[e]	0·34	0·75		0·224	0·292		
VI[f]	0·12	0·59			0·171	0·213	
VII[g]	0·011	0·020				0·067	0·116
VIII[h]	0·000	0·000	1·8	0·058	0·044	0·053	0·076

(*a*) Idealized planar molecule centered at (4,2,0), orientation matrix *A*.
(*b*) Idealized planar molecule centered at (4,2,2), orientation matrix *A*.
(*c*) Result of MPA treatment of I or II.
(*d*) Result of MPA treatment of III, with ring twists of 22, −26, and 4°.
(*e*) Result of *RBSFLS* treatment of IV, treating each ring as a planar rigid body.
(*f*) Same as V, but with tetrazinyl ring rotated 120°.
(*g*) Result of *SFLS* treatment of VI, with individual isotropic temperature factors and calculated hydrogen positions.
(*h*) Result of *SFLS* treatment of VII, with individual anisotropic temperature factors and calculated hydrogen positions.
(*i*) $\mathrm{RSF}(n) = \sum ||F_o| - |F_c|| / \sum |F_o|$ for n reflections.

the atoms of the verdazyl ring in obtaining the above atomic deviations.

Refinement of the structure

Model IV was now subjected to rigid-body structure-factor least-squares refinement (*RBSFLS*), using a modified version of the program of Busing, Martin, & Levy (1962). In this treatment all atoms, including hydrogens, were included and each planar ring was treated as an independent unit with six degrees of freedom. A limited set of data was used (138 reflections) and the structure factor discrepancy index was reduced from 0·464 to 0·292, where refinement stopped (model V).

Now three molecular packing models were tried, with the verdazyl ring rotated by 120° each time. The packing index, RP, indicated that the CH_2 group was better placed 120° from its position in model V. When this was done, the *RBSFLS* refinement was resumed, until RSF(138) dropped to 0·171. The mean atomic deviation was now reduced to 0·12 Å, with a maximum of 0·59 Å (model VI). Since this model still was constrained to a planar verdazyl ring the maximum deviation was for C(3), which is 0·59 Å (coincidentally) out of the verdazyl ring plane in the final structure.

The phase problem was now definitely solved, and routine *SFLS* with isotropic temperature factors for the individual heavy atoms, with calculated hydrogen positions, yielded RSF (861 reflections) = 0·067 (model VII). Further anisotropic refinement using all data, and again using calculated hydrogen positions, yielded RSF(1309 reflections) = 0·076 (model VIII). The hydrogen atoms were assigned the same anisotropic temperature factors as the attached carbon atoms. The phenyl C–H distance was assumed to be 1·027 Å; and the methylene C–H distance was assumed to be 1·040 Å. Local C_{2v} symmetry was assumed at the methylene group, with a tetrahedral H–C–H angle. The packing index, RP, of the final observed structure was found to be 1·8. The final values of the parameters are given in Table 5. A listing of the observed and calculated structure factors is given in Table 6.

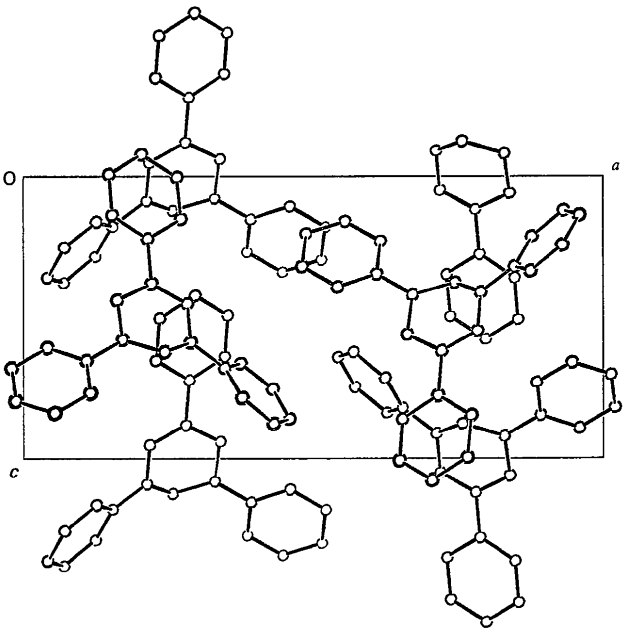


Fig. 2. The packing structure. The reference asymmetric unit is at the upper left.

Table 5. *Final values of the parameters* (× 10^4)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	2175	2576	−480	27	84	127	1	0	9
N(2)	2117	2013	886	28	106	100	6	12	19
C(3)	2568	854	1226	32	100	157	6	12	25
N(4)	3292	1224	790	26	117	113	1	6	26
N(5)	3385	1719	−605	32	108	95	5	5	15
C(6)	2793	2294	−1190	26	89	77	−2	0	2
C(7)	1532	2428	1788	24	93	84	−5	1	10
C(8)	1258	3718	1632	28	129	89	−5	−2	7
C(9)	705	4160	2542	37	102	137	−6	7	18
C(10)	416	3329	3603	23	162	155	7	5	11
C(11)	686	2075	3772	27	175	135	−15	14	28
C(12)	1233	1575	2852	33	84	110	−14	2	11
C(13)	3912	707	1527	26	75	103	5	4	−15
C(14)	3845	−207	2690	26	96	160	3	14	27
C(15)	4459	−691	3395	34	121	148	24	2	37
C(16)	5131	−250	2965	31	138	174	7	−10	28
C(17)	5200	639	1795	22	160	176	2	0	5
C(18)	4586	1125	1072	32	100	114	−3	−4	7
C(19)	2857	2726	−2771	28	58	119	−11	−6	−1
C(20)	3471	2476	−3613	35	132	118	2	9	12
C(21)	3522	2856	−5068	40	139	85	5	17	−1
C(22)	2960	3493	−5763	40	166	88	−19	−9	6
C(23)	2349	3768	−4962	34	164	123	−26	−17	23
C(24)	2284	3384	−3475	33	119	117	−10	−2	6
H(3*a*)	2548	643	2361						
H(3*b*)	2394	11	628						
H(8)	1474	4337	825						
H(9)	508	5129	2427						
H(10)	2	3662	4275						
H(11)	471	1455	4580						
H(12)	1431	607	2968						
H(14)	3341	−523	3023						
H(15)	4412	−1368	4260						
H(16)	5584	−606	3500						
H(17)	5705	954	1462						
H(18)	4633	1802	206						
H(20)	3895	1987	−3103						
H(21)	3985	2658	−5664						
H(22)	2998	3774	−6863						
H(23)	1925	4257	−5472						
H(24)	1821	3582	−2879						

Discussion

Table 7 shows the observed bond distances and bond angles. The estimated standard deviations are 0·007 Å and 0·7° respectively. Fig. 1 shows the atomic numbering system. The verdazyl ring contains four distinct types of atoms: four- and three-coordinated carbon, and three- and two-coordinated nitrogen. This situation leads to very different C–N distances at each end of the ring. At the saturated end the mean C–N distance is 1·443 Å, while at the aromatic end the C–N distance is decreased to a mean value of 1·338 Å.

Using the observed mean N–N distance of 1·351 Å, a planar model with 120° N–N–C angles would have a N–C(6)–N angle of 123·6°. In addition, the steric requirements of the lone pairs on the digonal nitrogens may be expected to decrease the N–N–C(6) angles below 120°. This effect is observed in DPPH, where the N–N–C angle is 118·5°, and in *s*-tetrazine, where this angle is 116·0° (Bertinotti, Giacomello & Liquori, 1956). This effect is also predicted by valence-shell electron-pair repulsion (VSEPR) theory (Gillespie, 1967). The decrease in the N–N–C(6) angles below 120° would be expected to further increase the N–C(6)–N angle. Thus, the observed N–C(6)–N angle of 126·8° and mean N–N–C(6) angle of 114·4° are shifted in the expected directions.

At the other end of the ring, these considerations leave the predicted N–C(3)–N angle as 116° for a planar model. For this angle to approach the expected tetrahedral value, while retaining approximately 120° N–N–C(3) angles, it is necessary for C(3) to become nonplanar with the rest of the ring. The observed structure shows that the N–C(3)–N angle is 106·1°; it appears therefore that either the N–C(6)–N angle or the N–N–C(6) angles (or both) are strained toward larger than equilibrium values. This strain pushes N(2) and N(4) closer together, resulting in a N–C(3)–N angle smaller than tetrahedral.

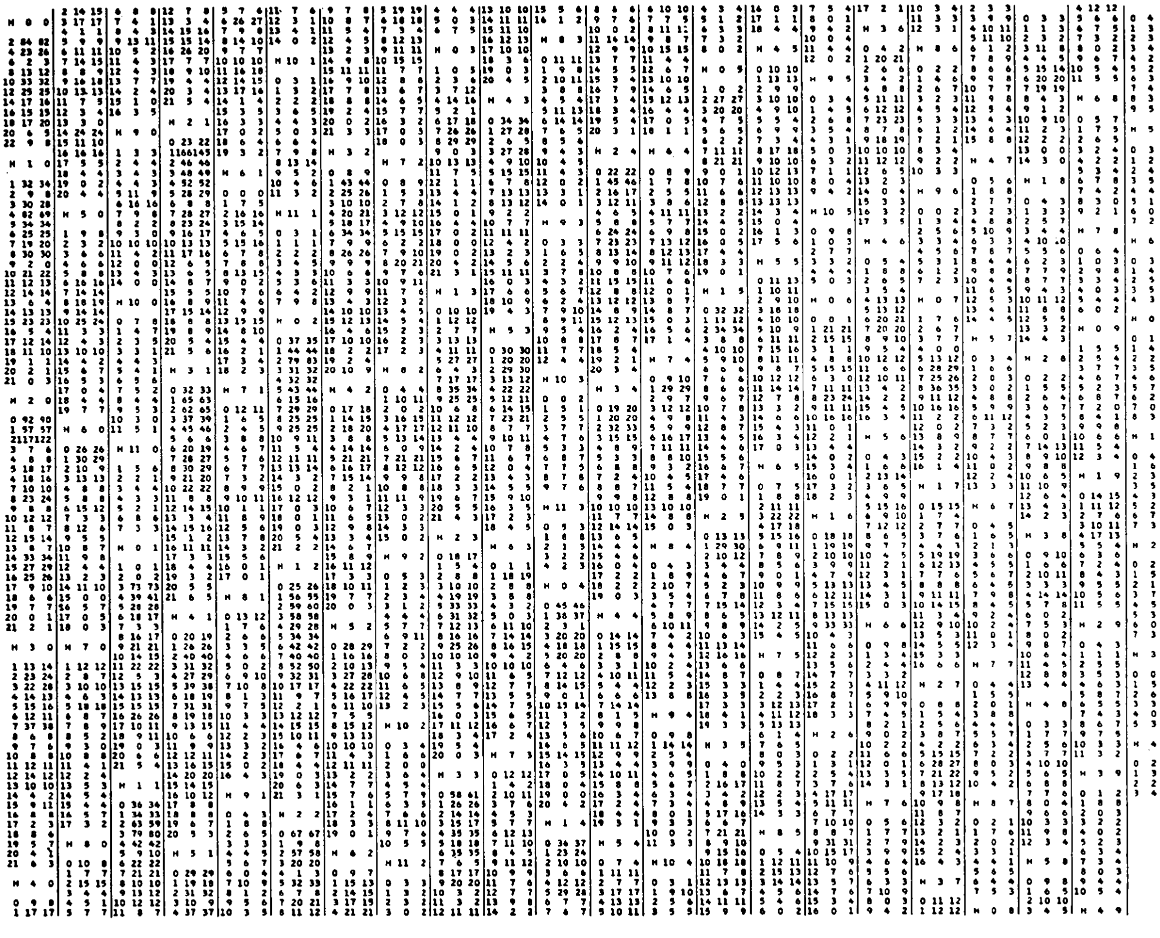
Using the observed bond distances in the verdazyl, ring, the formulae of Jenkins (1955) may be used to calculate the bond orders, $P_{\alpha\beta}$, of the various bonds:

$$P_{\mathrm{CC}}=(d_{\mathrm{CC}}^{-2}-0{\cdot}2868)/0{\cdot}1334$$
$$P_{\mathrm{CN}}=(d_{\mathrm{CN}}^{-2}-0{\cdot}316)/0{\cdot}144$$
$$P_{\mathrm{NN}}=(d_{\mathrm{NN}}^{-2}-0{\cdot}263)/0{\cdot}193\,.$$

We obtain observed bond orders of 1·68 for N(1)–C(6), 1·48 for N(1)–N(2), and 1·15 for N(2)–C(3). The effect of conjugation of the phenyl groups with the verdazyl ring is shown in the observed bond orders of 1·25 for C(6)–C(19), and 1·28 for N(2)–C(7).

The observed bond orders are in reasonable agreement with values calculated by a LCAO–MO method (Fischer, 1967). The largest discrepancy is the calculated value of 1·52 for the bond order of N(2)–C(7); this bond was predicted by Fischer to be 1·368 Å, compared

Table 6. *Comparison of the magnitudes of the observed and calculated structure factors.* The three entries for each reflection are *h*, *F*$_o$, and |*F*$_c$|.



with the observed distance of 1·414 Å. The other predicted distances calculated by Fischer agree with the observed distances within 0·03 Å; no prediction was made for N(2)–C(3). The observed N–N distance of 1·351 Å in TPV may be compared to the observed N–N distance of 1·334 Å in DPPH.

The observed foreshortening of the N(2)–C(3) bond is probably caused by the net positive charge on N(2); Fischer calculated this charge as +0·48 electron units.

The four nitrogen atoms of the verdazyl ring are planar within experimental error; the equation of this (plane I) is given in Table 8. The distances from the least-squares plane are: N(1), 0·011; N(2), −0·012; N(4), 0·012; N(5), −0·011 Å. The ring has an unsymmetrical boat configuration, with both C(3) and C(6) out of the nitrogen plane on the same side. C(6) is displaced by only −0·099 Å, while C(3) is displaced by −0·590 Å. The dihedral angle between plane I and the N(2)–C(3)–N(4) plane is 42·9°; and the dihedral angle between plane I and the N(1)–C(6)–N(5) plane is 9·5°. The n.m.r. spectrum of 3,3-dideutero-TPV shows line broadening which has been interpreted to indicate a C(6) ring inversion occurring in di-t-butyl nitroxide solution (Brunner, Hausser & Neugebauer, 1971).

The downward displacement (Fig. 1) of C(3) from plane I necessarily leads to upward displacements of C(7) and C(13) if planarity is retained about N(2) and N(4). The observed displacements are +0·300 Å for C(7) and +0·220 Å for C(13); C(19) is displaced downward also by −0·259 Å in order to retain planarity about C(6). Plane V, through N(1), C(3), and C(7), shows that N(2) is displaced by +0·084 Å and C(10) is displaced by −0·056 Å. Plane VI, through C(3), N(5), and C(13), shows that N(4) is displaced by +0·145 Å and C(16) is displaced by −0·238 Å. Plane VII, through N(1), N(5), and C(19), shows that C(6) is displaced by −0·025 Å and that C(22) is displaced by −0·010 Å. We presume that these small deviations are caused by bending of the phenyls by intermolecular packing forces.

The equations of the planes of the phenyl groups are also shown in Table 8. Each phenyl ring is planar within experimental error; the small deviations of N(2), N(4), and C(6) from their respective phenyl planes are presumably also caused by intermolecular packing forces.

The twist angles of the phenyl groups can be defined in several ways. For TPV we have chosen the following definition: the twist angle is the angle between the phenyl least-squares plane and the plane defined by the two β-atoms and the attached phenyl carbon. The α-atom is not included in the latter plane, but does not deviate much in TPV. Thus, the twist angle of ring C(7)–C(12) is the angle between plane I and plane V of Table 8; this angle is 23·0°.

Table 7. *Bond distances* (Å) *and angles* (°)

N(1)–N(2)	1·348	C(7)—C(8)	1·374	C(15)–C(16)	1·370
N(1)–C(6)	1·337	C(7)—C(12)	1·386	C(16)–C(17)	1·372
N(2)–C(3)	1·445	C(8)—C(9)	1·378	C(17)–C(18)	1·391
N(2)–C(7)	1·411	C(9)—C(10)	1·364	C(19)–C(20)	1·384
C(3)–N(4)	1·440	C(10)–C(11)	1·342	C(19)–C(24)	1·392
N(4)–N(5)	1·353	C(11)–C(12)	1·394	C(20)–C(21)	1·361
N(4)–C(13)	1·417	C(13)–C(14)	1·383	C(21)–C(22)	1·363
N(5)–C(6)	1·338	C(13)–C(18)	1·374	C(22)–C(23)	1·365
C(6)–C(19)	1·485	C(14)–C(15)	1·382	C(23)–C(24)	1·391
N(2)–N(1)–C(6)	114·5	N(2)—C(7)—C(8)	119·5	C(14)–C(15)–C(16)	120·3
N(1)–N(2)–C(3)	118·2	N(2)—C(7)—C(12)	121·6	C(15)–C(16)–C(17)	120·1
N(1)–N(2)–C(7)	117·5	C(8)—C(7)—C(12)	118·9	C(16)–C(17)–C(18)	120·0
C(3)–N(2)–C(7)	123·3	C(7)—C(8)—C(9)	120·3	C(13)–C(18)–C(17)	119·8
N(2)–C(3)–N(4)	106·1	C(8)—C(9)—C(10)	120·9	C(6)—C(19)–C(20)	122·3
C(3)–N(4)–N(5)	117·4	C(9)—C(10)–C(11)	119·1	C(6)—C(19)–C(24)	120·4
C(3)–N(4)–C(13)	122·2	C(10)–C(11)–C(12)	121·9	C(20)–C(19)–C(24)	117·3
N(5)–N(4)–C(13)	117·3	C(7)—C(12)–C(11)	118·8	C(19)–C(20)–C(21)	122·0
N(4)–N(5)–C(6)	114·2	N(4)—C(13)–C(14)	121·0	C(20)–C(21)–C(22)	120·8
N(1)–C(6)–N(5)	126·8	N(4)—C(13)–C(18)	119·1	C(21)–C(22)–C(23)	118·7
N(1)–C(6)–C(19)	117·6	C(14)–C(13)–C(18)	120·0	C(22)–C(23)–C(24)	121·4
N(5)–C(6)–C(19)	115·5	C(13)–C(14)–C(15)	119·8	C(19)–C(24)–C(23)	119·7

Table 8. *Equations of planes and distances of atoms from planes* (Å)

Plane	Atoms	Equation of plane	Atomic deviations
I	N(1), N(2), N(4), N(5)	$0\cdot3329X+0\cdot8551Y+0\cdot3974Z=3\cdot3249$	C(3), −0·590; C(6), −0·099; C(7), +0·300; C(13), +0·220; C(19), −0·259
II	C(7)–C(12)	$0\cdot6724X+0\cdot3348Y+0\cdot6602Z=3\cdot7538$	C(7)–C(12), ≤0·015; N(2), +0·064
III	C(13)–C(18)	$-0\cdot0486X+0\cdot7614Y+0\cdot6465Z=1\cdot0581$	C(13)–C(18), ≤0·012; N(4), +0·023
IV	C(19)–C(24)	$0\cdot3776X+0\cdot8833Y+0\cdot2780Z=3\cdot6745$	C(19)–C(24), ≤0·007; C(6), −0·027
V	N(1), C(3), C(7)	$0\cdot6361X+0\cdot6487Y+0\cdot4177Z=4\cdot0214$	N(2), +0·084; C(10), −0·056
VI	C(3), N(5), C(13)	$0\cdot0015X+0\cdot8869Y+0\cdot4619Z=1\cdot2610$	N(4), +0·145; C(16), −0·238
VII	N(1), N(5), C(19)	$0\cdot3514X+0\cdot8933Y+0\cdot2801Z=3\cdot5580$	C(6), −0·025; C(22), −0·010

Table 8 (*cont.*)

Dihedral angles

First plane	Second plane	Angle
I	N(2), C(3), N(4)	42·9°
I	N(1), C(6), N(5)	9·5
V	II	23·0
VI	III	13·1
VII	IV	1·6

Similarly, for phenyl C(13)–C(18), the angle between plane III and plane V is 13·1°. For phenyl C(19)–C(24), the angle between plane IV and plane VII is 1·6°. Thus, phenyl group C(19)–C(24) is essentially coplanar with the attached β-atoms, and is positioned to obtain maximum conjugation through overlap of the *p* orbitals on C(6) and C(19).

The geometries of phenyl C(7)–C(12) and phenyl C(13)–C(18) are more complex. As shown above, C(3) is below the plane of the verdazyl nitrogens. H(12) and H(14) are staggered between H(3*a*) and H(3*b*). Thus, as the methylene group moves down, these phenyls will twist accordingly; and atoms C(7) and C(13) will rise above plane I. This configuration is antipropellor; the two twists are in opposite directions.

As evidence for the above analysis we cite the distances between calculated hydrogen positions: H(3*a*)–H(12), 2·13; H(3*a*)–H(14), 1·95; H(3*b*)–H(12), 2·81; H(3*b*)–H(14), 2·82 Å. Therefore it appears that the phenyls are pushing the CH_2 group toward plane I, or conversely the CH_2 group is causing the phenyls to twist. The nonplanarity of the CH_2 group carbon is opposed by conjugation of the two neighboring phenyls with the verdazyl ring. If this analysis is correct, 6-phenylverdazyl should have C(3) even more out of plane than it is in TPV. We presume that the differences in geometry between phenyl C(7)–C(12) and phenyl C(13)–C(18) are caused by intermolecular packing forces.

Fig. 2 shows how the TPV molecules pack in the unit cell. The reference molecule is at the upper left in the figure. The intermolecular contacts all seem to be at normal van der Waals distances. The shortest distances are as follows: H(20) to H(10) of the molecule related by a screw axis at $(x,\frac{1}{4},0)$, 2·39; H(14) to N(1) of the molecule related by a screw axis at $(\frac{1}{4},0,z)$, 2·61; H(12) to N(5) of the molecule related by the same symmetry operation, 2·65; C(22) to H(8) of the molecule related by the inverse of this same operation, 2·77; C(14) to N(1) of the molecule related by the same symmetry operation, 3·42; and C(23) to C(7) of the molecule related by a *c* cell translation, 3·54 Å.

The packing index, RP, for the final observed structure was 1·8. A packing refinement starting from the observed structure, using the observed molecular shape, led to a decrease in RP to 1·5. This refined packing structure had mean and maximum deviations of the heavy atoms from the observed structure of 0·11 and 0·16 Å respectively. This result indicated that the approximate nonbonded potentials used were quite adequate to define the molecular position. Apparently errors in the molecular shape were the cause of larger deviations during the early stages of the solution of the phase problem by packing analysis, as shown in Table 4.

References

Bertinotti, F., Giacomello, G. & Liquori, A. M. (1956). *Acta Cryst.* **9**, 510–514.

Brunner, H., Hausser, K. H. & Neugebauer, F. A. (1971). *Tetrahedron*, **27**, 3611–3621.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Farag, M. S. (1954). *Acta Cryst.* **7**, 117–121.

Fischer, P. H. H. (1967). *Tetrahedron*, **23**, 1939–1952.

Gillespie, R. J. (1967). *Angew. Chem. Int. Ed.* **6**, 819–830.

Hanson, H. P., Herman, F., Lea, J. D. & Skillman, S. (1964). *Acta Cryst.* **17**, 1040–1044.

Hirshfeld, F. L. (1968). *Acta Cryst.* A**24**, 301–311.

Jenkins, H. O. (1955). *J. Amer. Chem. Soc.* **77**, 3168–3169.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Kuhn, R. & Trischmann, H. (1963). *Angew. Chem. Int. Ed.* **3**, 155.

Kuhn, R. & Trischmann, H. (1964). *Mh. Chem.* **95**, 457–479.

Nelson, J. B. & Riley, D. P. (1945). *Proc. Phys. Soc. (Lond.)* **57**, 160–177.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3177.

Williams, D. E. (1964). U. S. Atomic Energy Commission Report IS-1052, pp. 1–17.

Williams, D. E. (1967). *J. Amer. Chem. Soc.* **89**, 4280–4287.

Williams, D. E. (1969*a*). *Acta Cryst.* A**25**, 464–470.

Williams, D. E. (1969*b*). *J. Amer. Chem. Soc.* **91**, 1243–1245.

Williams, D. E. & Rundle, R. E. (1964). *J. Amer. Chem. Soc.* **86**, 1660–1666.