due to the Fermi-contact part of the hyperfine Hamiltonian is given by[2]

$$\Delta\omega_M/\omega = -Ah(\gamma_e/\gamma_n)S(S + 1)/3kT \quad (1)$$

where the hyperfine coupling constant is

$$A = -(4/3)\gamma_e\gamma_n\hbar|\psi(0)|^2 \quad (2)$$

Thus the shift is independent of γ_n and will have the same value in units of parts per million for protons and deuterons, being f times as small for the latter if expressed in hertz. The same conclusion is reached for the pseudo-contact shifts originating from the dipolar part of the Hamiltonian.[3] Small isotope effects on $|\psi(0)|^2$ may be ignored.

It is well known that protons in diamagnetic solutions give rise to sharp resonance lines. In this respect, it should be pointed out that the deuteron line width in pure water is about 1 Hz,[4] although in this case the main relaxation mechanism is due to interactions of the nuclear quadrupole moment with intramolecular electric field gradients.

The nuclear relaxation rate, $1/T_{2M}$, of a nucleus in a paramagnetic complex usually originates from interactions with the unpaired electrons and is composed of two main terms: dipolar and hyperfine. Assuming that $T_{1e} = T_{2e}$, e designating electron, and $\omega_e\tau_c < 1$, $\omega_e\tau_e > 1$, the correlation times being $1/\tau_e = 1/T_{1e} + 1/\tau_M$ (τ_M is the residence time of a nucleus in the complex) and $1/\tau_c = 1/\tau_e + 1/\tau_r$, the nuclear relaxation rate is given by[5]

$$T_{2M}^{-1} = (20/15)S(S + 1)\gamma_n^2g^2\beta^2r^{-6}\tau_c$$
$$+ (4/3)S(S + 1)(\pi A)^2\tau_e \quad (3)$$

(In the case that $\omega_e\tau_e < 1$ the second right-hand term should be multiplied by a factor of 2.)

Since A is proportional to γ_n (eq 2), it is seen that T_{2M}^{-1} is proportional to γ_n^2, and the line width of a deuteron in a paramagnetic complex will be smaller by a factor of f^2 than that of a proton in the same position.

Chemical exchange occurs *via* two most commonly encountered mechanisms: exchange of whole ligand molecules and reactions of hydrogen ion transfer. The latter are generally acid catalyzed. Nmr is sensitive to the faster of the two processes. A deuterium isotope effect is expected in protolytic reactions, *i.e.*, $\tau_M^D > \tau_M^H$.

The effects of chemical exchange on nuclear relaxation in solutions of paramagnetic ions have been considered in detail by Swift and Connick.[6] Under conditions of slow exchange the "excess" relaxation of the solvent nuclei is given by $1/T_{2p} = P_M/\tau_M$, P_M being the population ratio in the two environments. In this case isotope effects on the rate constant $1/\tau_M$ may become apparent. Two limiting conditions may exist for fast exchange: (a) $\tau_M^2 \ll \Delta\omega_M^{-2} \ll \tau_MT_{2M}$, $1/T_{2p} = P_M\tau_M\Delta\omega_M^2$; (b) $\tau_MT_{2M} \ll T_{2M}^2$, $\Delta\omega_M^{-2}$, $1/T_{2p} = P_M/T_{2M}$. In both cases the relaxation rate of deuterons will be f^2 times as small as that of protons. It is also seen that conditions of fast exchange for deuterons

will be attained at τ_M values f times longer than those for protons.

If $1/T_{2M} \gg |\Delta\omega_M|$, another case is obtained and $1/T_{2p} = P_M/(T_{2M} + \tau_M)$. Since T_{2M} of deuterons is f^2 times longer than that of protons, it will have a much greater influence on the observed "excess" relaxation. Thus the use of dmr offers an excellent probe for studying electron-spin relaxation (eq 3). Moreover, by comparing the relaxation times of protons and deuterons it should be possible to separate the contributions of T_{2M} and τ_M.

The use of dmr offers in general a reduction of line widths by a factor of f^2 leading to an improvement of the over-all resolution of the spectrum by a factor of f. Thus it will be easier to resolve the dmr absorption of nuclei in the vicinity of paramagnetic ions or to measure more accurately isotropic shifts under conditions of fast exchange. If there are detection difficulties due to low signal-to-noise ratio, these may be amplified by a factor of 2.35, where the relative sensitivity and line widths have been taken into account. This is the only apparent disadvantage.

We have made use of dmr for studying aqueous solutions of vanadyl(IV). For the first time it was possible to obtain the temperature dependence of the electron relaxation time from nmr measurements. The electron relaxation time is of the order of 10^{-8} sec, and its variation with temperature is in good agreement with the theoretical predictions of Kivelson, *et al.*[7] A detailed account of this work will be presented in a forthcoming publication.

(7) R. Wilson and D. Kivelson, *ibid.*, 44, 154 (1966); P. W. Atkins and D. Kivelson, *ibid.*, 44, 169 (1966).

Jacques Reuben, Daniel Fiat
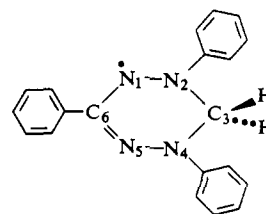*Isotope Department, The Weizmann Institute of Science
Rehovot, Israel*
Received November 30, 1968

Structure of 3,4-Dihydro-2,4,6-triphenyl-*s*-tetrazin-1(2H)-yl Free Radical by Crystal-Packing Analysis and X-Ray Diffraction

Sir:

The title compound, also referred to as 1,3,5-triphenyl-verdazyl (TPV), is a very stable free radical based on the *s*-tetrazine ring system.[1] The radical has a paramagnetic susceptibility corresponding to one unpaired electron per molecule. The electron paramagnetic resonance spectrum indicates that the unpaired electron density is about equally distributed among the four nitrogen atoms. The radical is even more stable than 2,2-diphenyl-1-picryl-hydrazyl (DPPH), where the unpaired electron is primarily distributed between two nitrogens. An investiga-

(2) N. Bloembergen, *J. Chem. Phys.*, 27, 595 (1957).
(3) H. M. McConnell and R. E. Robertson, *ibid.*, 29, 1361 (1958).
(4) P. Diehl and T. Leipert, *Helv. Chim. Acta*, 47, 545 (1964). This is a good reference for other applications of dmr.
(5) I. Solomon, *Phys. Rev.*, 99, 559 (1955); I. Solomon and N. Bloembergen, *J. Chem. Phys.*, 25, 261 (1956); N. Bloembergen, *ibid.*, 27, 572 (1957); A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961, p 311; R. E. Connick and D. Fiat, *J. Chem. Phys.*, 44, 4103 (1966).
(6) T. J. Swift and R. E. Connick, *ibid.*, 37, 307 (1962).

(1) R. Kuhn and H. Trischmann, *Monatsh. Chem.*, 95, 457 (1964).

Table I. Computer Packing of the Assumed Molecular Shape[a]

Parameter	Strong reflections starting model	Planar molecule packing result	Nonplanar molecule packing result	Obsd final structure
Translation X(Å)	4.00	5.06	4.87	5.03
Translation Y	2.00	2.03	2.15	1.76
Translation Z	0.00	0.63	0.49	0.09
Direction D_X	0.228	0.500	0.360	0.371
Direction D_Y	0.854	0.810	0.887	0.886
Direction D_Z	0.469	0.307	0.290	0.279
Angular deviation, deg[b]	13.8	8.7	0.9	0.0
Packing index, RP[c]	413.9	18.5	10.5	3.5
Diffraction data index, RSF[d]		0.434[e]	0.336[e]	0.067[f]

[a] The translations refer to the position of the molecular center relative to the origin of the unit cell; the direction cosines are those of the mean molecular plane. [b] Angle between mean plane of model molecule and the mean observed molecular plane. [c] $\mathrm{RP} = \Sigma w(d_o - d_c)^2$. [d] $\mathrm{RSF} = (\Sigma||F_o| - |F_c||)/(\Sigma F_o)$. [e] Calculated for 23 lowest angle reflections. [f] Calculated for 861 observed reflections.

tion of the structure of DPPH concluded that steric shielding of the reactive sites was very important in establishing that radical's stability.[2] In the verdazyl series the lower unpaired electron density on the nitrogens reduces the need for effective steric shielding. Thus the *o*-nitro groups which were required to provide steric shielding for stability in DPPH are unnecessary in TPV.

Conjugation with the phenyl groups also plays a part in stabilizing these radicals. It is of interest to determine the relative importance of conjugation and steric shielding in TPV for comparison with DPPH and other stable radicals.

Crystals of TPV were found to belong to the orthorhombic system, lattice constants $a = 18.467$, $b = 9.854$, and $c = 8.965$ Å, with four molecules per unit cell. Systematically absent X-ray diffraction spectra indicated the space group $P2_12_12_1$. Since no heavy atom is present, and the structure lacks a center of symmetry, the solution of the diffraction phase problem for the 24 nearly equally diffracting carbon and nitrogen atoms was not expected to be trivial.

On the other hand, considerable information was already known about the arrangement of the atoms in the molecule. Certainly the phenyl group geometries are known, and reasonable predictions could be made for the geometry of the *s*-tetrazinyl ring system. The main molecular flexibility was expected to be possible rotations of the phenyls with respect to the central ring system; these rotations would be opposed by conjugation. In the crystal structure we also need the translational and angular orientation of the molecule as a whole.

Thus the problem of locating 24 atoms (72 positional variables) can be reduced to finding only nine variables: three phenyl twist angles, three translations, and three rotations. We elected to solve the crystal structure of TPV by generating trial molecular shapes, packing the molecules into the observed crystal unit cell. The least-squares crystal-packing analysis program PCK5 was used.[3] This program minimizes the lattice repulsive energy using quadratic nonbonded interatomic repulsion functions.

Because of conjugation it was expected that the phenyl twist angles would be small, *i.e.*, less than approximately 30°. We therefore found initially the best packing position for a planar molecule. The orientation of the mean

molecular plane could be determined approximately from the distribution of strong diffraction maxima. This was possible even though the final structure indicates that half of the 24 nonhydrogen atoms deviate more than 0.25 Å from the mean molecular plane, with six atoms deviating by more than 0.7 Å.

A packing search of the asymmetric portion of the unit cell was made on a 2-Å grid using this initial angular orientation. Table I shows that the best packing result for the planar molecule was obtained starting from the grid point $X = 4$, $Y = 2$, and $Z = 0$ Å. The diffraction data for the 23 lowest angle reflections quickly confirmed this result. Even though a very approximate planar molecular shape was used, we obtained a higher packing index for all other orientations (false minima) obtained from other starting grid points.

Now using this planar molecule packing model as a starting point, we systematically varied the phenyl twist angles to obtain the lowest packing index. The fourth column of Table I shows the best fit obtained, in which case the phenyl twist angles were $+22$, -26, and $+4°$. Again, the diffraction data quickly confirmed the packing result. This packing model was then refined by structure factor least squares, treating each of the four rings as a rigid body. After the diffraction data index dropped to 0.213 (861 reflections) through use of this technique, the model was routinely refined using individual atom coordinates and individual isotropic temperature factors to a diffraction data index of 0.067.

The final molecular structure is considerably different from the best nonplanar packing model. The three phenyl rings are warped out of the N(1)N(2)N(4)N(5) plane by $+12$, $+9$, and $-6°$, respectively. The observed torsion angles about the phenyl bonds are $+30$, -22, and $-2°$. In addition, the tetrazyl ring was found to be quite nonplanar, with C(3) being displaced by -0.59 Å. The angle between planes N(1)N(2)N(4)N(5) and N(2)C(3)-N(4) is 43°. Atom C(6) is also displaced from the N(1)N(2)N(4)N(5) plane by -0.10 Å in the same direction as C(3), giving the ring a boat shape. The interplanar angle at this end of the ring is 9°. The fact that such an approximate molecular shape could be used to find the correct molecular packing position in the crystal shows the utility of packing analysis in solving the diffraction phase problem.

Figure 1 shows the bond distances and angles in and around the tetrazyl ring as refined from the X-ray data. As indicated above, the ring is nonplanar. The changes

(2) D. E. Williams, *J. Am. Chem. Soc.*, **89**, 4280 (1967).
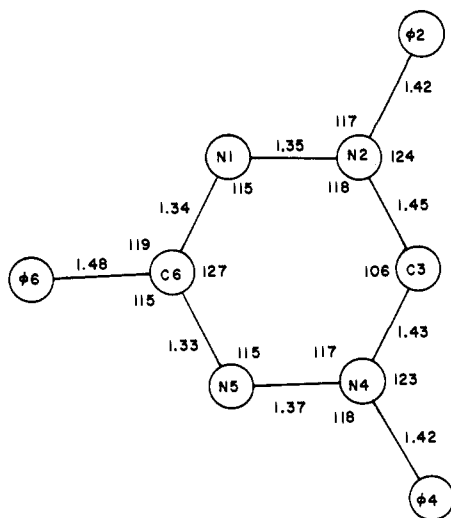(3) D. E. Williams, *Science*, **159**, 645 (1968); *Acta Cryst.*, in press.

Figure 1. Bond distances (Å) and angles (deg) in and around the verdazyl ring. The estimated standard deviations are 0.01 Å and 1 deg, respectively.

in the ring bond angles from regular trigonal geometry at N_1, N_5, and C_6 are also observed in s-tetrazine itself, where the N–C–N angle is 125° and C–N–N angle is 118°.[4] The C(6)–N(1) and C(6)–N(5) bond lengths are also very similar to the C–N bond length of 1.34 Å in s-tetrazine.

The nonplanarity of C(3) is apparently the indirect result of intramolecular strain between ϕ_2 and ϕ_4. The repulsions due to the *ortho* hydrogens on these groups are partly relieved by rotating the rings and warping them upwards. The methylene group is then forced downward in order to preserve approximate planarity around N(2) and N(4). The *ortho* hydrogens remain staggered between the two hydrogens of the methylene group.

Acknowledgment. We thank Dr. F. A. Neugebauer for supplying crystals of this compound.

(4) A. J. Merer and K. K. Innes, *Proc. Roy. Soc.* (London), **A302**, 271 (1968).

Donald E. Williams
*Chemistry Department, University of Louisville
Louisville, Kentucky 40208*

Tris(hexafluoroacetylacetonato)-π-cyclopentadienyl-zirconium. Structure and Stereochemical Nonrigidity

Sir:

We have been engaged in nmr studies of π-cyclopentadienyl derivatives of titanium, zirconium, and hafnium involving fluorinated β-diketones as ligands; examples are $(\pi\text{-}C_5H_5)Ti(hfac)_2Cl$, $(\pi\text{-}C_5H_5)Zr(tfac)_3$, and $(\pi\text{-}C_5H_5)Zr(hfac)_3$.[1,2] A very recent communication by Pinnavaia, Howe, and Butler[3] reports closely related

(1) The new compounds have been characterized by microanalysis and mass spectra. A full account of their preparation and properties will be submitted later.
(2) Abbreviations: acac = $CH_3COCHCOCH_3$; tfac = CF_3COCH-$COCH_3$; hfac = $CF_3COCHCOCF_3$.
(3) T. J. Pinnavaia, J. J. Howe, and E. D. Butler, *J. Am. Chem. Soc.*, **90**, 5288 (1968).

though complementary work, and prompts us to submit this preliminary account of our own investigation.

Nmr studies on $(\pi\text{-}C_5H_5)Zr(hfac)_3$ led us to assume a pentagonal-bipyramidal geometry for the molecule. In view of the rarity of this form of heptacoordination[4] among organometallic compounds, an X-ray single-crystal structural determination was undertaken. Crystal data are $a = 13.42 \pm 0.02$, $b = 22.94 \pm 0.02$, $c = 8.90 \pm 0.02$ Å; $\beta = 95.0 \pm 0.2°$ for space group $P2_1/n$ with four molecules per unit cell. A total of 2009 unique reflections above background were collected on a fully automated PAILRED diffractometer using crystal-monochromatized Mo Kα radiation. The data came from the nine levels, $hk0$–$hk8$, perpendicular to c. A correction for decomposition in the X-ray beam was applied, based upon the measurement of a set of standard reflections after each layer was collected. Patterson and Fourier methods established the positions of all nonhydrogen atoms. During refinement, some difficulty was experienced with the fluorine atoms, which had relatively high isotropic temperature parameters.

At the present stage of refinement, the conventional residual is 9.2%, with the zirconium and fluorine atoms allowed to vibrate anisotropically. We propose to continue refinement after the possibility of partial or complete disorder in the fluorine atom positions has been investigated.

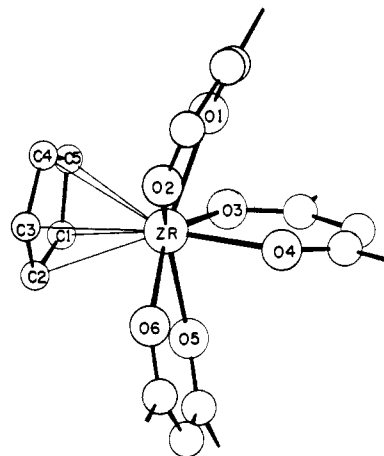The molecular structure is shown in Figure 1, from which trifluoromethyl groups have been omitted for

Figure 1. A view of the π-$C_5H_5Zr(hfac)_3$ molecule with trifluoromethyl groups omitted for clarity. Oxygen atoms labeled 1, 3, 5, 6, and 2 are in equatorial positions of the pentagonal-bipyramidal structure.

(4) We take the view that the π-cyclopentadienyl group is most conveniently regarded in this case as occupying a single coordination position. An easily visualized description of the over-all geometry is then possible. The π-cyclopentadienyl group occupies a larger share of the coordination sphere than typical ligands, as implied by the displacement of equatorial ligands in Figure 1.
The π-cyclopentadienyl ring is often regarded as tridentate, which would here imply nonacoordinate zirconium. The actual arrangement of ligands resembles neither of the regular polyhedra for nine coordination (E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), **21**, 109 (1967)), so that the molecular geometry is not aptly described in these terms. A referee has pointed out that zirconium is in fact undecacoordinate (*i.e.*, five carbons and six oxygens), and that the idealized geometry of the complex could be derived from an eicosahedron by suppressing one vertex. We do not consider that such a description is advantageous, however, since it is less familiar and less easily visualized, and deviations from eicosahedral geometry are appreciable.