ically allowed conformations for a stereoregular sequence of d units are typified by

$$(g^+t)(g^+t)\cdots(g^+t)(tg^-)\cdots\cdot(tg^-)$$

where the letters denoting the states for a pair of bonds between consecutive substituted skeletal carbons are enclosed in parentheses. Only one inversion from the right-handed (*i.e.*, g^+t) to left-handed (*i.e.*, tg^-) helical conformation is permitted if strong steric overlaps are to be avoided. More generally, a d sequence comprising x_d units can assume the conformations $(g^+t)_{x_d-y}(tg^-)_y$ where $0 \leq y \leq x_d$. Similarly, for an l sequence the allowed conformations are $(g^-t)_{x_l-y}(tg^+)_y$. It will be apparent that for two isotactic sequences adjoining a dl (*i.e.*, syndiotactic) dyad, one or the other or both of the immediate neighbor bonds will be *gauche* with high probability; rarely will the adjoining pairs be simultaneously (g^+t) and (tg^+), respectively, if the isotactic sequences are long.

The sterically allowed conformations for a dl dyad are (tt) and (g^+g^+); those for an ld dyad are (tt) and (g^-g^-). Occurrence of the isolated dl dyad of the chain depicted above in the (g^+g^+) conformation would require the improbable occurrence of (g^+t) *and* (tg^+) conformations for the respective neighboring isotactic dyads. Thus, a lone syndiotactic dyad situated in a predominantly isotactic chain will occur overwhelmingly in the (tt) conformation.

The allowed conformations for an all-syndiotactic chain are represented by

$$\begin{tikzcd}
\text{etc.} & (tt) \arrow[r, leftrightarrow] \arrow[dr, leftrightarrow] & (tt) \arrow[r, leftrightarrow] \arrow[dr, leftrightarrow] & (tt) & \text{etc.} \\
& (g^+g^+) \arrow[ur, leftrightarrow] & (g^-g^-) \arrow[ur, leftrightarrow] & (g^+g^+) &
\end{tikzcd}$$

X-Ray diffraction of crystalline syndiotactic polymers suggests a preference for the helical conformation $(g^+g^+)(tt)(g^+g^+)(tt)(g^+g^+)$, etc., or for its left-handed analog $(tt)(g^-g^-)(tt)(g^-g^-)(tt)$, etc., over the all-*trans* form, $(tt)(tt)(tt)$, etc. Thus, a dl dyad in a syndiotactic chain may, in the course of time, assume both (g^+g^+) and (tt) conformations, the latter being somewhat more prevalent than the former, depending on the extent to which repetition of the (tt) conformation is competitive with alternation with (gg). Preferences in this regard depend on the character of the R group and involve more detailed considerations than we wish to enter upon here.

It is thus apparent that the time-average conformation for an isolated dl (or ld) dyad will differ markedly from that for such a dyad within a predominantly syndiotactic chain. Their nmr spectra must be expected in general to differ accordingly. Similar considerations apply to the triad spectra, manifested, for example, in the spectrum of the methyl group of polypropylene ($R = CH_3$). Thus, the spectrum of the heterotactic triad dd^*l, where the asterisk marks the center with which the resonant protons are affiliated, should differ, depending upon whether it occurs in a chain which is predominantly syndiotactic or in one which is otherwise isotactic.

For the opposite case of an isotactic dyad isolated in an otherwise syndiotactic chain, it can be shown that the average conformation should approximate that for the same dyad in an all-isotactic chain. Thus, a dd dyad isolated in a syndiotactic chain may occur as (g^+t) and (tg^-) with equal probability, similar to the situation in an otherwise isotactic chain. (The spectra of these two conformers, being mirror images, will, incidentally, be identical). The nmr spectrum for the dd (or ll) dyad situated within a predominantly syndiotactic chain should resemble closely the spectrum for the same dyad in an all-isotactic chain.

Considerations of this nature should be carefully weighed in the interpretation of nmr spectra of polymer molecules having asymmetric centers.

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Six-Coordinate Trigonal-Prismatic Complexes of First-Row Transition Metals[1]

Sir:

The recent discovery of trigonal-prismatic coordination for molecular six-coordinate metal complexes has added a new dimension to structural inorganic chemistry. Single crystal X-ray studies have established the trigonal-prismatic geometry for the six-coordinate complexes $Re(S_2C_2Ph_2)_3$[2] and $Mo(S_2C_2H_2)_3$.[3] In addition, spectroscopic and powder X-ray measurements strongly indicate this coordination structure for the $M(S_2C_2Ph_2)_3$, $M(tdt)_3$, and $M(bdt)_3$ systems with M = Re, W, and Mo.[4] It is noteworthy that all the well-established examples of trigonal-prismatic six-coordination involve second- and third-row transition metals.

Here we report the structure of $V(S_2C_2Ph_2)_3$,[5,6] which becomes the first example of trigonal-prismatic coordination in a molecular six-coordinate complex containing a first-row transition metal. The electronic structural implications of the strikingly similar molecular structural features of $Re(S_2C_2Ph_2)_3$, $Mo(S_2C_2H_2)_3$, and $V(S_2C_2Ph_2)_3$ are explored, and a suggestion of one factor important in stabilizing trigonal-prismatic coordination is put forward. We also report evidence that strongly suggests trigonal-prismatic coordination for the $Cr(S_2C_2Ph_2)_3$[5,6] and $(NEt_4)[V(S_2C_2Ph_2)_3]$[7] complexes.

Purple-black crystals of $V(S_2C_2Ph_2)_3$ were examined by Weissenberg and precession photography and found to be monoclinic. The compound crystallizes in a cell with dimensions $a = 19.25$, $b = 11.31$, $c = 18.01$ A, $\beta = 106° 20'$. The observed extinctions and a negative piezoelectric test[8a] indicate the centrosym-

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(1) Acknowledgment is made to the National Science Foundation for support of this research. We thank Dr. Sam LaPlaca for several very helpful discussions.

(2) R. Eisenberg and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 3776 (1965); *Inorg. Chem.*, **5**, 411 (1966).

(3) A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *J. Am. Chem. Soc.*, **87**, 5798 (1965).

(4) (a) E. I. Stiefel and H. B. Gray, *ibid.*, **87**, 4012 (1965); (b) E. I. Stiefel, R. Eisenberg, R. C. Rosenberg, and H. B. Gray, *ibid.*, in press; tdt = toluene-3,4-dithiolate; bdt = benzene-1,2-dithiolate.

(5) Possible names for these complexes include tris(*cis*-1,2-diphenylethene-1,2-dithiolato)metal, tris(*cis*-stilbenedithiolato)metal, and tris(dithiobenzil)metal. We suggest that no formal oxidation state be assigned to the metal in naming these unusual compounds.

(6) (a) G. N. Schrauzer, H. W. Finck, and V. Mayweg, *Angew. Chem.*, **76**, 715 (1964); (b) J. H. Waters, R. Williams, H. B. Gray, G. N. Schrauzer, and H. W. Finck, *J. Am. Chem. Soc.*, **86**, 4199 (1964).

(7) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **4**, 55 (1965).

metric space group C2/c. The experimental density of 1.36 ± 0.05 g/cm^3 is in good agreement with the calculated value of 1.371 g/cm^3 for four molecules in the unit cell. Therefore, vanadium is required to occupy one of the fourfold special positions of the space group.

Intensity data were collected at room temperature by the equiinclination Weissenberg technique. Zirconium-filtered Mo Kα radiation was employed. The intensities were estimated visually and reduced to values of F_o by standard procedures. The structure was solved by the usual combination of Patterson, Fourier, and least-squares calculations.[8b] The refinement of the structure was carried out by a full-matrix least-squares procedure in which the function minimized was $\Sigma w(F_o - F_c)^2$, w being the weight of the individual reflection. In the final cycles, vanadium and sulfur atoms were assigned anisotropic temperature factors. This final refinement for 116 positional and thermal parameters converged to a conventional R factor ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.077 for 1516 nonzero reflections.

Vanadium occupies the 4(e) special positions of the space group with the twofold axis bisecting one of the five-membered metal-chelate rings. The six sulfur atoms are arranged about vanadium in trigonal-prismatic coordination. The average V-S bond length is 2.338 ± 0.004 A; the average S-V-S bond angle is 81.7 ± 0.1°. The prism is slightly distorted about the threefold axis with independent interligand S-S distances of 2.927, 3.088, and 3.178 A. The estimated standard deviations for each of these values is 0.006 A. The intraligand S-S distances average 3.058 A. The five-membered metal-chelate rings are approximately planar and coincide with the dihedral mirror planes about a threefold symmetry axis. The average S—C and C=C distances are 1.69 and 1.40 A, with estimated standard deviations of 0.01 and 0.02 A, respectively. The phenyl rings are twisted out of the planes of the metal-chelate rings and thus apparently are not conjugated with them. The calculated dihedral angles between the metal-chelate and phenyl rings range from 46 to 57°. All intermolecular contacts appear normal. The vanadiums are well separated with nearest neighbors over 10 A apart.

The average dimensions of the prism are strikingly similar to those found for $Re(S_2C_2Ph_2)_3$[2] and $Mo(S_2C_2H_2)_3$.[3] Thus one significant feature that emerges on examining the three structures is the near constancy of the average interligand S-S distances [3.064 A in $V(S_2C_2Ph_2)_3$, 3.050 A in $Re(S_2C_2Ph_2)_3$, and 3.11 A in $Mo(S_2C_2H_2)_3$]. This same average S-S value (3.05–3.11 A range) has also been observed in structural determinations of several bis-planar complexes[9-14] involving similar complexes. We suggest that the observed S-S distance is relatively short for nominally "nonbonded" ligand atoms and indicates that there are interdonor-atom bonding forces present in these complexes which are considerably stronger than in classical octahedral systems. According to this hypothesis, S-S bonding is a significant factor in the stabilization of trigonal-prismatic coordination. Thus the rather remarkable fact that the Re-S and Mo-S distances of 2.325 and 2.33 A, respectively, are not significantly longer than the V-S bond length is interpreted as a consequence of the role played by S-S bonding in the molecular trigonal prism.

Table I. Electronic Spectra of ML_3 Complexes

Complex	Solvent	Maxima, cm^{-1} (ϵ)
$V(S_2C_2Ph_2)_3$	$CHCl_3$	9850 (1500), 13,310 (27,400), 17,940 (14,600), 23,500 (sh), 39,200 (65,300)
	Solid[a]	9300, 12,200, 17,500, 23,000
$Cr(S_2C_2Ph_2)_3$	$CHCl_3$	14,560 (3000), 17,200 (21,000), 35,810 (58,000), 40,320 (63,000)
	Solid[a]	13,900, 16,800
$(NEt_4)[V(S_2C_2Ph_2)_3]$	CH_3CN	14,200 (10,000), 16,600 (12,000), 37,600 (71,000), 42,000 (61,000)

[a] Measured below 30,000 cm^{-1}.

The $Cr(S_2C_2Ph_2)_3$ complex, which was found to be isomorphous with its V analog by X-ray powder pattern measurements,[2] is assumed to be trigonal prismatic in the solid. Electronic spectra of $Cr(S_2C_2Ph_2)_3$, $V(S_2C_2Ph_2)_3$, and $(NEt_4)[V(S_2C_2Ph_2)_3]$ are presented in Table I. The fact that the $CHCl_3$ solution electronic spectra of $V(S_2C_2Ph_2)_3$ and $Cr(S_2C_2Ph_2)_3$ are essentially identical with their respective spectra in solid samples shows that in both cases the trigonal-prismatic structure is maintained in liquid solution. Furthermore, trigonal-prismatic coordination is suggested for $V(S_2C_2Ph_2)_3^-$ from a comparison of its electronic spectrum with that of the isoelectronic $Cr(S_2C_2Ph_2)_3$ complex.

It is important at this stage to examine the VL_3^n complexes similar to $V(S_2C_2Ph_2)_3$ for evidence relating to structure. A possibly meaningful structural clue may be extracted by examining the polarographic behavior[7] of the VL_3^n and related complexes. The $V(S_2C_2Ph_2)_3$ complex exhibits two reversible reduction waves in CH_3CN *vs.* sce at +0.30 ($0 \rightarrow -1$) and −0.71 v ($-1 \rightarrow -2$). However, the $V(tdt)_3^{2-}$ complex shows no reversible $-2 \rightarrow -1$ oxidation wave, and instead an ill-defined discontinuous oxidation wave in the +0.4 to +0.6 v range is observed.[7] All our experience with analogous tdt and $S_2C_2Ph_2$ complexes would lead us to expect a reversible oxidation wave with $E_{1/2} = -0.5$ v for a trigonal-prismatic $V(tdt)_3^{2-}$ complex.[15] An interesting possibility is that the structure of the red-purple $V(tdt)_3^{2-}$ complex (and other $VL_3^{2-,3-}$ systems) is closer to the idealized octahedral situation. Structural work currently in progress should provide the needed information on this point.

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(8) (a) We thank Dr. James A. Ibers for this experimental investigation. (b) Programs for the IBM 7094 used in this work were local modifications of Zalkin's FORDAP Fourier program, the Busing–Levy ORFLS least-squares program, and various crystallographic programs written at Brookhaven National Laboratory.

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(12) C. J. Fritchie, Jr., *Acta Cryst.*, **20**, 107 (1966).

(13) M. R. Truter, quoted in G. N. Schrauzer and V. P. Mayweg *J. Am. Chem. Soc.*, **87**, 1483 (1965).

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(15) Although several examples are available, a particularly pertinent comparison comes from the $Re(S_2C_2Ph_2)_3^n$ and $Re(tdt)_3^n$ complexes (ref 4). It is well established that the $n = 0$ complexes are trigonal prismatic and exhibit three reversible reduction waves as well as one reversible oxidation wave. For any given wave the tdt complex has a slightly less negative potential than the $S_2C_2Ph_2$ complex.

Detailed electronic structural calculations and single-crystal esr experiments on $V(S_2C_2Ph_2)_3$ are in progress and will be reported in full in a forthcoming paper.

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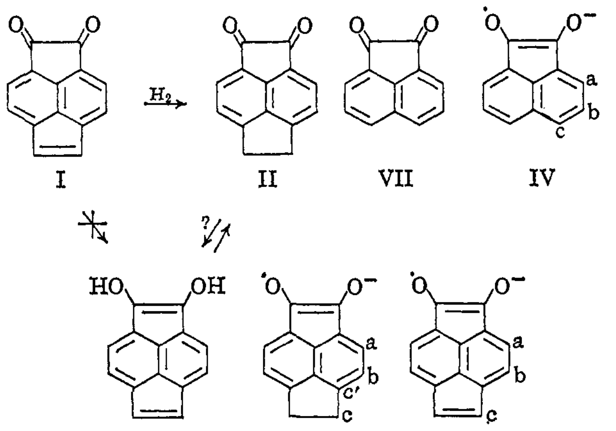
Pyracylenes. Radical Anions Related to Pyracyloquinone

Sir:

Recently,[1] one of us reported the preparation of a pyracylene derivative, pyracyloquinone (I). Theoretically, reduction of this compound could lead to the much sought after pyracylene system; however, catalytic reduction produced[1] only 1,2-diketopyracene (II). Other reducing agents such as trimethyl phosphite, zinc, and sodium have led only to undefined products. Since it appeared the derivatives of III were highly unstable, more suitable techniques for studying such systems were necessary.



The initial products of reduction of quinones and oxidation of hydroquinones in alkaline media involve semiquinone anions as intermediates.[2] These species can be detected and their structures deduced from esr measurements. The conversion of the quinone (I) and the keto form of the hydroquinone (II), both of which were in hand,[1] to pyracylosemiquinone would demonstrate the existence and relative stability of the pyracylene aromatic system.

The anion radicals IV, V, and VI were generated from the corresponding quinones VII, II, and I by the method of Russell[2a] (solution in 0.1 *M* potassium *t*-butoxide in freshly distilled DMSO). The esr spectral data[3] are summarized in Table I. Whereas IV and V were stable for many hours at room temperature, VI slowly decomposed to produce a very complicated spectrum over a period of a few hours. The coupling constants observed for acenaphthasemiquinone (IV) agree well with the reported values[4] for the same radical species generated electrolytically. The values of a_a and a_b found for V are quite close to the corresponding ones for IV, as might be anticipated. Unfortunately, no satisfactory model for comparison with the splitting by the methylene hydrogens, a_c, of V exists. As expected, calculations[5] employing the experimental[6] charge density (ρ_c of IV) indicate a value of 2.03 gauss[7] for a_c of V, somewhat higher than that observed. The inductive effect of the methylene bridge should reduce the odd-electron density at the aromatic carbon C′ of V corresponding to position C of IV, thus reducing the splitting by the methylene hydrogens.

Table I. Esr Spectral Data[a]

Semiquinone	a_a	a_b	a_c	g
IV[b]	1.18	0.27	1.28	2.0044
V[b]	1.15	0.21	1.38	2.0043
VI[c]	1.41	2.45	2.12	2.0030

[a] Coupling constants are reported in gauss. [b] a value ± 0.02 gauss, g value ± 0.0001. [c] a value $\pm$ 0.02 gauss, g value ± 0.0002.

The higher coupling constants for pyracylosemiquinone (VI) indicate the presence of substantially greater spin density in the carbon framework of VI than for IV or V. These coupling constants, converted to spin densities by the McConnell relationship, are compared to values calculated by Hückel molecular orbital theory in Table II. The excellent agreement of the experimental and calculated spin densities provides the assignment of the coupling constants as presented in Tables I and II. Of particular interest is the prediction that the largest spin density resides at position b. This result is not predicted by naïve valence bond methods, for resonance structures which put an odd electron at b do not have the benefit of benzene resonance stability as do those structures with an odd electron at a or c.

Table II. Comparison of Experimental and Calculated[a] Quantities for Pyracylosemiquinone (VI)

	Spin density at position				
	a	b	c	λ[b]	g
Calculated	0.048	0.106	0.086	0.1192	2.0028
Experimental	0.059[c]	0.102[c]	0.088[c]		2.0030

[a] This calculation employed $h_O = 0.8$ and $k_{CO} = 1.0$. The results are relatively insensitive to variation in these parameters. See A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 117. [b] Refers to $E = \alpha + \lambda\beta$ for the highest occupied molecular orbit of VI. [c] Obtained from $a_r = Q\rho_r$ with $Q = 24$.

The significance of the g value for organic molecules has virtually been ignored until very recently.[8] Pub-

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[1] B. M. Trost, *J. Am. Chem. Soc.*, **88**, 853 (1966).

[2] For leading references see (a) E. R. Talaty and G. A. Russell, *ibid.*, **87**, 4867 (1965); (b) B. G. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, **43**, 4191 (1965).

[3] A dual cavity-equipped Varian V-4502 spectrometer with 9-in. magnet was employed. As a reference standard, peroxylamine disulfonate (a = 13.0 gauss, g = 2.0055) was used.

[4] Dehl and Fraenkel report a_a = 1.17 gauss, a_b = 0.27 gauss, and a_c = 1.27 gauss. See R. Dehl and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 1793 (1963).

[5] Using Q (aliphatic) $= A + B\cos^2\theta$ where $A = -1.1$ (J. P. Colpa and E. de Boer, *Mol. Phys.*, **7**, 333 (1963)), $B = 50$ (R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963)), and θ is the angle between the axis of the p orbital at the aromatic carbon C′ and the C′–C–H plane (in this case $\theta \cong 30°$).

[6] Using the McConnell relationship $a_c = Q\rho_c$ where ρ_c is the spin density at position c of IV and Q (aromatic) = 24.

[7] If the best HMO value calculated by Dehl and Fraenkel[4] is employed, the predicted a_c value is 1.46 gauss for V—a fortuitous agreement with the experimental value.

[8] For an excellent discussion of the importance of the g value in interpretation, see ref 2b.