

terminal Ag-S bonds. Such an elongation is not observed. Even more important is the fact that the thiourea group involved in the sharp bridge bond does not have an elongated S-C distance. In fact, all the S-C distances are within less than a standard deviation ( $\pm 0.016$  Å) of the S-C distance found in free thiourea.

The additional use of empty sulfur 3d orbitals without the use of filled Ag 4d orbitals does not alleviate this problem. A possible explanation for the invariance of the thiourea S-C bond length on complex formation can be seen by referring to Figure 2. In addition to the electron-deficient three-center bond previously described, a three-center bonding MO can be constructed from the sulfur 3d<sub>xy</sub> and appropriately oriented Ag 4d ( $\beta$ ) orbitals. These would lead to a bonding  $\pi$  three-center MO,  $\psi_{\pi} = \beta_1 + \beta_2 + d_{xy}$ , and a nonbonding MO,  $\psi_{nb} = \beta_1 - \beta_2$ . The four electrons, two from each Ag 4d orbital, would then be accommodated in these orbitals.  $\psi_{\pi}$  would be able to return much of the charge withdrawn from the S-C p $\pi$  MO by the three-center  $\sigma$ -p $\pi$ - $\sigma$  electron-deficient MO. It is to be noted that  $\psi_{nb}$  is antibonding with respect to metal-metal bonding, and there is little to be gained by forming metal-metal bonds from any of the other filled metal orbitals. The other sulfur 3d orbitals would not interact with the silver 4d orbitals in such a way as to return charge to the S-C p $\pi$  MO. For comparison, a Ag-Ag distance of 3.03 Å has been observed in AgP(CH<sub>3</sub>)<sub>3</sub>·C<sub>2</sub>H<sub>4</sub>;<sup>11</sup> and the Ag-Ag distance in metallic silver is 2.889 Å.<sup>5</sup>

On the other hand, for the Ag<sub>2</sub>-S<sub>2</sub>-Ag<sub>1</sub> wide angle bridge (133°) the angle between the Ag<sub>1</sub>-Ag<sub>2</sub> midpoint and the S<sub>2</sub>-C bond is 154°; but the lines defined by Ag<sub>2</sub>-Ag<sub>1</sub> and the nitrogen atoms of this thiourea group are also parallel. This bridging is most easily understood in terms of two filled sp<sup>2</sup> sulfur orbitals forming two electron-pair donor-acceptor bonds. These orbitals are nonbonding in thiourea itself and use of these orbitals would not elongate the S-C bond distance. Hence, the use of S 3d or Ag 4d orbitals is not demanded in this bridge.

The geometry of the nonbridged Ag<sub>2</sub>-S<sub>4</sub> and Ag<sub>1</sub>-S<sub>3</sub> bonds is easily understood in terms of a sp<sup>2</sup> sulfur donor orbital.

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(12) All correspondence should be addressed to this author.

E. A. Vizzini and E. L. Amma<sup>12</sup>

Department of Chemistry, University of South Carolina  
Columbia, South Carolina 29208

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## On the Interpretation of Nuclear Magnetic Resonance Spectra of Stereoregular Polymers

Sir:

In a paper published recently,<sup>1</sup> one of the present authors and his collaborators concluded that typical isotactic polymer chains are stereoirregular to an

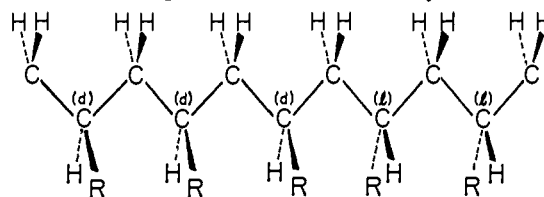
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appreciable degree. This conclusion was reached on the grounds that the chain dimensions (*i.e.*, the unperturbed mean square end-to-end length  $\langle r^2 \rangle_0$ ) and their temperature coefficients, as found by experiment for those isotactic polymers which have been investigated,<sup>2-5</sup> are irreconcilable with a perfect stereoregular structure. Syndiotactic units were cited<sup>1</sup> as seemingly the most likely source of stereoirregularity. The presence of 5-10% of such units would bring theoretical calculations<sup>1</sup> into agreement with experiments<sup>2</sup> on isotactic poly(*n*-butene-1) and poly(*n*-pentene-1). Results for other isotactic chains, including especially polypropylene<sup>3</sup> and poly(isopropyl acrylate),<sup>5</sup> though perhaps less complete, point to a similar degree of departure from perfect stereoregularity.

The postulation of so large a proportion of syndiotactic units (*i.e.*, dyads) would appear to be at variance with the nmr spectra of typical isotactic polymers, notably polypropylene<sup>6,7</sup> and poly(isopropyl acrylate).<sup>8</sup> Their  $\beta$ -proton (CH<sub>2</sub>) spectra give no evidence whatever of a discernible peak at the location of the singlet which characterizes the predominantly syndiotactic polymer. From 100-Mc nmr spectra of carefully extracted isotactic polypropylene published recently by Natta and co-workers,<sup>7</sup> the absence of a syndiotactic peak would seem to imply a level not exceeding 2% for such dyads.<sup>9</sup>

It is the burden of this communication to point out that *the nmr peak for an isolated syndiotactic unit in a preponderantly isotactic chain should occur at a location differing, perhaps markedly, from that for such a unit in an all-syndiotactic chain.* The peak for the isolated syndiotactic dyad may well be obscured by one of the quartet of peaks for methylene groups of the isotactic units. Certainly, these protons should not appear at the same location as found for the syndiotactic chain, and their shift could conceivably be as large as the 0.39-ppm shift<sup>7</sup> between the nonequivalent protons in the isotactic chain.

This result follows directly from analysis of the conformation of the predominantly isotactic chain in the neighborhood of a syndiotactic dyad. Consider for example the portion of a vinyl polymer chain which is represented in its planar conformation by



The letters *d* and *l* serve to differentiate the two sets of asymmetric centers.<sup>1</sup> Let the rotational states for a given bond be designated *t*, *g*<sup>+</sup>, and *g*<sup>-</sup> for *trans*, *gauche*<sup>+</sup>, and *gauche*<sup>-</sup>, respectively. Then the ster-

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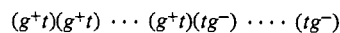
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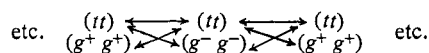
ically allowed conformations for a stereoregular sequence of  $d$  units are typified by



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  $(g^-l)_{x_l-y}(tg^+)_y$ . 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



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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P. J. Flory, J. D. Baldeschwieler

Department of Chemistry, Stanford University  
Stanford, California 94305

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## Six-Coordinate Trigonal-Prismatic Complexes of First-Row Transition Metals<sup>1</sup>

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  $Re(S_2C_2Ph_2)_3$ <sup>2</sup> and  $Mo(S_2C_2H_2)_3$ .<sup>3</sup> 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  $Mo$ .<sup>4</sup> 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  $V(S_2C_2Ph_2)_3$ ,<sup>5,6</sup> 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  $Cr(S_2C_2Ph_2)_3$ ,<sup>5,6</sup> and  $(NEt_3)[V(S_2C_2Ph_2)_3]$ <sup>7</sup> 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  $a = 19.25$ ,  $b = 11.31$ ,  $c = 18.01$  Å,  $\beta = 106^\circ 20'$ . The observed extinctions and a negative piezoelectric test<sup>8a</sup> indicate the centrosym-

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(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.

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