their hospitality during his sabbatical leave when this manuscript was prepared.

**Registry No.** 1, 90605-30-4; $PhCO_2Et$, 93-89-0; $CH_3(CH_2)_{10}CO_2Et$, 106-33-2; $p$-$MeOC_6H_4CO_2Et$, 94-30-4; *cis*-$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2Me$, 112-62-9; $PhCO_2$-*i*-Pr, 939-48-0; $PhCO_2$-*t*-Bu, 774-65-2; PhCN, 100-47-0; $PhCH_2CN$, 140-29-4; $PhCONH_2$, 55-21-0; $PhCO_2H$, 65-85-0; $PhCH_2OH$, 100-51-6; $CH_3(CH_2)_{11}OH$, 112-53-8; $p$-$MeOC_6H_4CH_2OH$, 105-13-5; *cis*-$CH_3(CH_2)_7CH{=}CH(CH_2)_8OH$, 143-28-2; $PhCH_2NH_2$, 100-46-9.

# Conformational Analysis of S-C-P Anomeric Interactions. 2.[1] X-ray Crystallographic Evidence against the Importance of $n_S \rightarrow \sigma^*_{C-P}$ Conjugation in Axial 2-[1,3]Dithianyldiphenylphosphine Oxide

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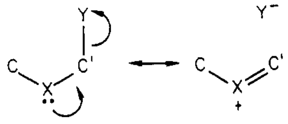
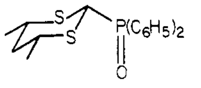
The discovery of a predominant axial conformation in 2-[1,3]dithianyldiphenylphosphine oxide (1) was reported recently.[1] This finding was remarkable from several points of view: (1) it constituted the first account of the existence of an anomeric interaction between second-row elements sulfur and phosphorus,[2] (2) unlike other reported examples of the anomeric effect,[3] it involved a fully bonded substituent (i.e., there are no lone pairs of electrons on the axially oriented phosphorus atom),[4] and (3) the overall steric demands of an axial diphenylphosphinoyl group may be quite substantial (Scheme I).[5]

Although dipole–dipole interactions were initially invoked to account for the anomeric effect,[6] X-ray crystallographic data led Romers, Altona, et al.[7] to suggest that delocalization of nonbonding electrons into the antiperiplanar adjacent polar bond contributes to the stability of the axial conformer. According to this proposal, in gauche (axial) C–X–C′–Y systems the C′–X distances are significantly shorter than normal while the C′–Y bond lengths are longer than normal. This description of the anomeric effect has received support from the results of a considerable number of experimental[8] and theoretical[9] investigations.



We here report the results of an X-ray analysis of *r*-2-(diphenylphosphinoyl)-*c*-4,*c*-6-dimethyl-1,3-dithiane (2).



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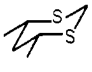

3

Comparisons with structural data for 1-axial[1] as well as *cis*-4,6-dimethyl-1,3-dithiane (3)[10] were made in order to examine the possible importance of $n_S \rightarrow \sigma^*_{C-P}$ interactions which, if significant, would be manifested in shortened C–S and elongated C–P distances in the axial vs. equatorial form.

Scheme I

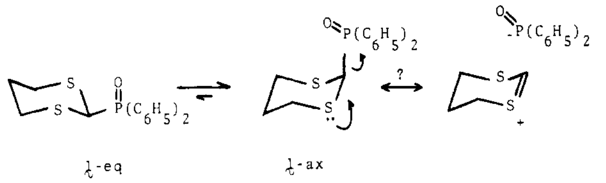

Table I. Selected Interatomic Distances and Angles in 1-Axial, 2, and 3, with Standard Deviations in Parentheses

| | 1-axial[a] | 2[b,c] | 3[d] |
|---|---|---|---|
| | Bond Lengths (Å) | | |
| S(1)–C(2) | 1.809 (3)[e] | 1.810 (4), 1.808 (4) | 1.792 (5)[e] |
| S(1)–C(6) | 1.810 (3)[e] | 1.818 (5), 1.835 (5) | 1.823 (4)[e] |
| C(2)–P | 1.825 (3) | 1.840 (4) | |
| C(5)–C(6) | 1.517 (5)[e] | 1.520 (7), 1.506 (7) | 1.518 (5)[e] |
| P–O | 1.486 (2) | 1.481 (3) | |
| | Bond Angles (deg) | | |
| C(2)–S(1)–C(6) | 101.3 (1)[e] | 97.9 (2), 97.3 (2) | 99.2 (2)[e] |
| S(1)–C(2)–S(3) | 114.5 (1) | 113.1 (2) | 114.5 (3) |
| S(1)–C(2)–P | 110.4 (1)[e] | 106.4 (2), 112.5 (2) | |
| S(1)–C(6)–C(5) | 113.9 (2)[e] | 112.7 (4), 113.3 (4) | 112.8 (3)[e] |
| C(4)–C(5)–C(6) | 113.3 (3) | 115.6 (4) | 116.7 (3) |

[a] Reference 1. [b] Present work. [c] Since this molecule deviates significantly from $C_s$ symmetry the bond lengths and angles of each half are listed separately. [d] Reference 10. [e] Mean values, averaged assuming $C_s$ ring symmetry.

## Results and Discussion

The crystal structure of 2 was solved by direct methods.[11] Refinement of atomic parameters[12] converged to

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(4) It is then clear that the anomeric effect does not require a lone pair of electrons on the acceptor atom.

(5) In spite of the long C–P and C–S bonds, the steric repulsion present in axial-1 may be worth ca. 1.25 kcal/mol (see footnote 16 in ref 1). The experimental measurement of the steric demand of an axial diphenylphosphinoyl group on model compounds has been initiated (Juaristi, E.; López-Núñez, N. A.; Hutchins, R. O., work in progress).

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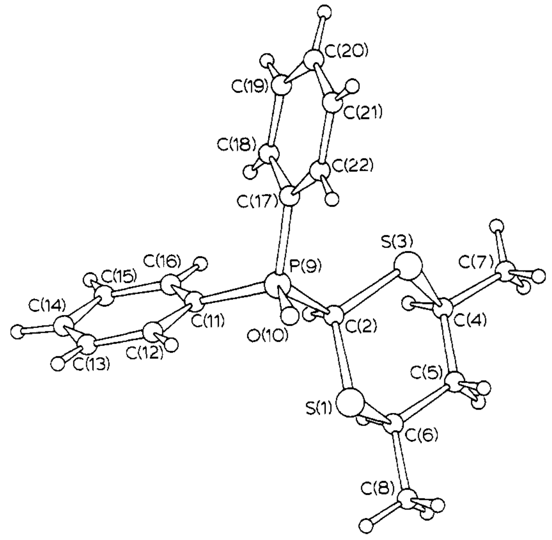

**Figure 1.** Structure and solid-state conformation of **2**; small circles denote hydrogen atoms.

$R = 0.048$[13] over 2128 reflections. A view of the solid-state conformation is in Figure 1. The 1,3-dithiane ring has a chair conformation[14] with an equatorially oriented substituent at C(2), and the diphenylphosphinoyl oxygen atom is gauche to both sulfur atoms but is asymmetrically disposed[15] with respect to them in order to accomodate nonbonded interactions between the bulky substituent and the ring atoms. The heterocyclic ring in **2** is slightly more puckered around C(2) than in **3**[10] and significantly more puckered than in **1**-axial where relief must be gained from severe 1,3-diaxial nonbonded interactions between the phosphinoyl substituent and the ring hydrogen atoms at C(4) and C(6).

Selected bond lengths and angles for **2** together with corresponding values for **1**-axial and **3** are in Table I. Comparison of these values reveals that although the mean S(1)–C(6) distance in **2** is slightly longer than that in **1**-axial, it is very close to that in **3**, and accordingly, the elongation may be ascribed to the introduction of the methyl substituents into the 1,3-dithiane ring.[10] The C–P distance in **2** is quite similar to, but possible significantly longer than, that in **1**-axial. This latter observation, as well as the lack of any significant difference in the mean S(1)–C(2) lengths, is contrary to expectations if an $n_S \rightarrow \sigma^*_{C-P}$ interaction makes an important contribution to the preferred axial conformation in **1**. Alternative rationalizations of the effect(s) responsible for the conformational behavior of **1** will be discussed in a forthcoming paper.[16]

## Experimental Section

***r*-2-(Diphenylphosphinoyl)-*c*-4,*c*-6-dimethyl-1,3-dithiane (2).** *cis*-4,6-Dimethyl-1,3-dithiane (**3**)[17] (297 mg, 2 mmol) was placed in a dry round-bottomed flask provided with a magnetic stirring bar and capped with a rubber septum. The flask was flushed with nitrogen prior to the addition of 7 mL of dry THF via a cannula, after which the solution was cooled to −22 °C and *n*-butyllithium (1.53 mL of a 1.37 M hexane solution, 2.1 mmol, 5% excess) was syringed into it dropwise. The resulting solution was stirred for 90 min at −20 °C following which it was added to a THF solution (ca. 10 mL) of chlorodiphenylphosphine (530 mg, 2.4 mmol, 20% excess) and tetramethylethylenediamine (232 mg, 2 mmol) also at −20 °C. The reaction mixture was stirred at this temperature for 90 min and subsequently at room temperature for a further 3 h before being quenched with saturated aqueous ammonium chloride. Extraction with $CHCl_3$ followed by the usual workup procedure afforded 146 mg (21% yield) of **2** as a white solid: mp 233–235 °C; $^1H$ NMR (90 MHz, $CDCl_3$; $Me_4Si$) $\delta$ 1.23 (d, $^3J_{CH_3-C-H} = 6.6$ Hz, 6 H), 1.3 (d of t, $J_{gem} = 14.1$ Hz, $J_{anti} = 12$ Hz, 1 H), 2.06 (d of t, $J_{gem} = 14.1$ Hz, $J_{gauche} = 2.5$ Hz, 1 H), 2.9 (m, 2 H), 4.98 (d, $^2J_{P-C-H} = 15$ Hz, 1 H), 7.3–8.15 (m, 10 H); IR 3090 (w), 2882 (s), 1439 (s), 1194 (vs) $cm^{-1}$; MS, *m/e* 348 ($M^+$), 315 ($M^+ - 33$), 201 ($M^+ - 147$), 147 ($M^+ - 201$), 77 ($M^+ - 271$).

**Crystal Data:** $C_{18}H_{21}OPS_2$ (**2**) $M_r$ 348.47; monoclinic; $a = 38.886$ (16) Å, $b = 5.773$ (2) Å, $c = 16.651$ (7) Å, $\beta = 104.60$ (1)°, $U = 3617.3$ Å$^3$, $Z = 8$, $d_{calcd} = 1.280$ g cm$^{-3}$; absorption coefficient for Cu K$\alpha$ radiation ($\lambda = 1.5418$ Å), $\mu = 33.8$ cm$^{-1}$. Space group $Cc(C_s^4)$ or $C2/c(C_{2h}^6)$ from systematic absences: $hkl$ when $h + k \neq 2n$, $h0l$ when $l \neq 2n$; shown to be the latter by structure solution and refinement.

Intensity data ($hk\pm l$), recorded on an Enraf-Nonius CAD-3 automated diffractometer from a crystal of dimensions ca. 0.16 × 0.18 × 0.80 mm as described previously[10] (Ni-filtered Cu K$\alpha$ radiation; $\theta$–$2\theta$ scans, $\theta_{max} = 67°$), yielded 3239 independent values from which those 2128 with $I > 2.0\sigma(I)$ were retained for the structure analysis.

**Structure Analysis and Refinement.** The crystal structure of **2** was solved by direct methods.[11] Full-matrix least-squares adjustment of atomic positional and thermal parameters converged to $R = 0.048$.[13] For structure–factor calculations, scattering factors for carbon, oxygen, phosphorus, and sulfur were from ref 18, and for hydrogen from ref 19; the values for phosphorus and sulfur were corrected for anomalous dispersion effects.[20] In the least-squares iterations, the weighting scheme used: $w^{1/2} = 1$ for $|F_o| \leq 60.0$, and $w^{1/2} = 60.0/|F_o|$ for $|F_o| > 60.0$, showed no systematic dependence of $\langle w\Delta^2 \rangle$ when analyzed in ranges of $|F_o|$ and $\sin\theta$. Final atomic positional and thermal parameters are in Tables II–IV in supplementary material.[12]

**Registry No.** 1, 83476-36-2; 2, 83463-92-7; 3, 22452-23-9.

**Supplementary Material Available:** Fractional atomic coordinates (Tables II and IV), anisotropic thermal parameters (Table III), bond lengths and angles (Table V), torsion angles (Table VI), displacements of atoms from selected least-squares planes (Table VII), and a list of observed and calculated structure amplitudes (Table VIII) (22 pages). Ordering information is given on any current masthead page.

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(12) Supplementary material; see paragraph at end of paper.

(13) $R = \sum||F_o| - |F_c||/\sum|F_o|$.

(14) Endocyclic torsion angles, $\omega_{ij}$ (°), around the bonds between atoms $i$ and $j$ in **2** follow: $\omega_{1,2} = -64.9°$, $\omega_{2,3} = 64.1°$, $\omega_{3,4} = -59.2°$, $\omega_{4,5} = 65.2°$, $\omega_{5,6} = -65.4°$, $\omega_{6,1} = 59.5°$; corresponding values are −61.8°, 61.8°, −56.8°, 63.8°, −64.2°, 57.3° in **3**, and −55.4°, 54.3°, −55.8°, 66.4°, −67.3°, 58.6° in **1**-axial.

(15) S–C–P–O torsion angles are 32.9° and −91.5° in **2**.

(16) Juaristi, E.; Valle, L.; Valenzuela, B. A., unpublished results.

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# Reaction of Alcohols with Zinc Halide, Diethyl Azodicarboxylate, and Triphenylphosphine. An Effective Method for the Preparation of Halides

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Alkyl halides are important intermediates in organic synthesis. The conversion of alcohols into their corresponding halides is frequently a useful and necessary synthetic operation. During recent research in the syn-

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