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Structures of Two Modifications of Bis(dicyclohexylthiophosphoryl) Disulfide. Evidence for $p\pi-d\pi$ Contribution to P—S Single Bonds

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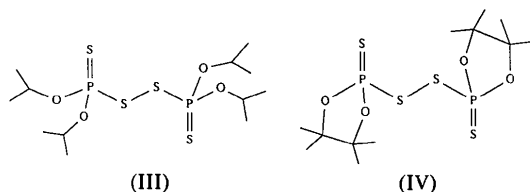
Abstract. The crystal modification of the title compound is solvent dependent. Crystallization from 2-propanol/CH₂Cl₂ produces a monoclinic CH₂Cl₂ solvate, (I). Crystallization from a number of other solvent systems produces a triclinic form, (II). (I): C₂₄H₄₄P₂S₄·CH₂Cl₂, $M_r = 607.76$, monoclinic, $C2/c$, $a = 16.887$ (3), $b = 14.860$ (3), $c = 12.574$ (3) Å, $\beta = 100.22$ (2)°, $V = 3105.2$ Å³, $Z = 4$, $D_x = 1.30$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 5.8$ cm⁻¹, $F(000) = 1296$, $T = 294$ (1) K, $R = 0.046$ for 1320 unique observed reflections with $F_o^2 > 3.0\sigma(F_o^2)$. (II): C₂₄H₄₄P₂S₄, $M_r = 522.82$, triclinic, $P\bar{1}$, $a = 20.392$ (3), $b = 12.302$ (3), $c = 12.749$ (2) Å, $\alpha = 68.66$ (2), $\beta = 103.25$ (1), $\gamma = 107.26$ (2)°, $V = 2818.2$ Å³, $Z = 4$, $D_x = 1.23$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 4.5$ cm⁻¹, $F(000) = 1128$, $T = 294$ (1) K, $R = 0.034$ for 6551 unique observed reflections with $F_o^2 > 3.0\sigma(F_o^2)$. In (I) the molecule has twofold molecular and crystallographic symmetry. The two independent molecules in (II) have essentially the same geometry but different from that of (I). The P—S—S—P skeleton is skewed with a torsion angle of 106.35 (7)° in (I) and 129.8 (3)° (ave) in (II). In (I) the configurations of the two ends are identical with S—P—S—S = 24.7 (1)°, but in (II) the two ends are different with S—P—S—S = 173.2 (2) and 21.4 (6)° (ave). The approach to planarity of the S—P—S—S unit (*cis* or

trans) is interpreted as evidence of a $p\pi-d\pi$ interaction in the P—S 'single' bond.

Introduction. The disulfide bond in chemical systems has been widely studied both experimentally and theoretically. Apart from the intrinsic chemical value of these studies they also help to shed light on the behavior of many biologically important molecules that contain disulfide links. Recently there have been a number of in depth theoretical studies on the prototype molecules H₂S₂ (Marsden & Smith, 1988; Rauk, 1984), MeSSMe (Rauk, 1984) and EtSSMe (Ohsaku & Allinger, 1988). These studies confirm that the preferred S—S torsion angle, θ , is close to 90°. Previous studies suggest that this may increase with large substituents (Jørgensen & Snyder, 1980). It is well known that there is observable restriction to rotation about the disulfide bond [experimental results to compare with theoretical calculations are referenced by Marsden & Smith (1988), Rauk (1984) and Ohsaku & Allinger (1988)]. The calculations all indicate that the *trans* barrier is lower than the *cis* barrier by a factor of 2–3. There is, however, a significant energy maximum at $\theta = 180^\circ$.

We have been interested in disulfides where the substituents are not alkyl, but dialkylthiophosphoryl groups. Recently we realized that our assumptions

that these molecules behave as simple disulfides may not be correct. There are only two structurally characterized molecules of this type, [$(i\text{PrO})_2\text{P}(\text{S})\text{S}_2$] $_2$, (III) (Lawton, 1970; Tkachev, Atovmyan & Shchepinov, 1976), and [$\text{C}_6\text{H}_{12}\text{O}_2\text{P}(\text{S})\text{S}_2$] $_2$, (IV) (Yadav, Bohra, Mehrotra, Rai & Srivastava, 1989).



In (IV) the value for the torsion angle is quite normal for a disulfide, $\theta = 94^\circ$. In contrast, for (III) $\theta = 180^\circ$, *i.e.* the determined conformation is that predicted to be at a maximum on the rotational-energy coordinate of dialkyl disulfides. There is no obvious steric reason for this difference in conformation, hence we have begun a structural study of this type of molecule and report the structures of two different crystal modifications of bis(dicyclohexylthiophosphoryl) disulfide.

Experimental. [$(\text{C}_6\text{H}_{11})_2\text{PS}_2$] NH_4 was prepared by the reported method (Rauhut, Currier & Wystrach, 1961). Reagent grade solvents were used without further purification. Preparation of [$(\text{C}_6\text{H}_{11})_2\text{PS}_2$] $_2$: (a) from [$(\text{C}_6\text{H}_{11})_2\text{PS}_2$] NH_4 by I_2 oxidation (Maier, 1965); (b) from [$(\text{C}_6\text{H}_{11})_2\text{PS}_2$] NH_4 by Ce^{IV} oxidation – a mixture of [$(\text{C}_6\text{H}_{11})_2\text{PS}_2$] NH_4 (4 mol) and $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (1 mol) in ethanol was heated to reflux for 15 min. Removal of solvent and extraction with CH_2Cl_2 gave a yellow product which rapidly turned purple. Attempted crystallization from 2-propanol/ CH_2Cl_2 gave pale-yellow crystals of the title compound [form (I)] and a red solution of undetermined composition.

Crystals were obtained from the authentic sample [preparation (a)] of [$(\text{C}_6\text{H}_{11})_2\text{PS}_2$] $_2$ by slow evaporation of solutions in acetone/methanol, ethanol/ CH_2Cl_2 , acetone/2-propanol and 2-propanol/ CH_2Cl_2 . The unit cells determined below indicate that form (II) crystallizes from the first three solvent systems and form (I) only from 2-propanol/ CH_2Cl_2 .

Crystals [(I) $0.24 \times 0.20 \times 0.12$, (II) $0.32 \times 0.20 \times 0.15$ mm] were mounted on glass fibers. Preliminary examination and data collection were performed with $\text{Mo } K\alpha$ radiation on an Enraf-Nonius CAD-4 diffractometer. Unit-cell parameters were obtained from the setting angles of 25 reflections ($10 < \theta < 14^\circ$). Intensities were measured using ω - 2θ scans [(I): $2\theta_{\text{max}} = 52.0^\circ$; $0 < h < 20$, $0 < k < 18$, $-14 < l < 14$; 2000 total, 1623 unique, $R_{\text{int}} = 0.040$; (II): $2\theta_{\text{max}} = 48.0^\circ$; $0 < h < 23$, $-13 < k < 13$, $-13 < l < 13$; 9120 total, 8834 unique; $R_{\text{int}} = 0.015$]. An empirical

absorption correction [transmission factors 0.84–1.00 (I), 0.97–1.00 (II)] and decay correction (three intensity check reflections measured after every 1 h exposure) were applied. Decay was particularly important for (I) (31.2%) due to some desolvation during data collection. Both structures were solved by direct methods and refined on F [$w = 4F_o^2/\sigma^2(F_o^2)$] by full-matrix least squares with H atoms in ideal positions ($\text{C}-\text{H} = 0.95 \text{ \AA}$) and restrained to ride on the atom to which they are bonded [(I): $\Delta/\sigma_{\text{max}} = 0.01$, $R = 0.046$, $wR = 0.050$, $S = 1.39$ for 150 variables and 1320 reflections with $F_o^2 > 3.0\sigma(F_o^2)$; $\Delta\rho_{\text{max}} = 0.27$ (7), $\Delta\rho_{\text{min}} = -0.36$ (7) e \AA^{-3} ; (II): $\Delta/\sigma_{\text{max}} = 0.02$, $R = 0.034$, $wR = 0.047$, $S = 1.50$ for 541 variables and 6551 reflections with $F_o^2 > 3.0\sigma(F_o^2)$; $\Delta\rho_{\text{max}} = 0.24$ (5), $\Delta\rho_{\text{min}} = -0.22$ (5) e \AA^{-3}]. Scattering factors were taken from Cromer & Waber (1974) and anomalous-dispersion coefficients were those of Cromer (1974). All calculations were carried out on a VAX 11/750 using *SDP* (Frenz, 1978).

Final atomic parameters are reported in Tables 1* and 2, and selected derived bond lengths and angles in Tables 3 and 4. Normal *ORTEPII* (Johnson, 1971) plots of the molecules are given in Figs. 1 and 2.

Discussion. The reaction of $(\text{C}_6\text{H}_{11})_2\text{PS}_2^-$ ions with cerium(IV) species in ethanol solution gave rise to a number of transient colored species. The only pure compound isolated from the reaction was, however, the oxidation product $(\text{C}_6\text{H}_{11})_2\text{P}(\text{S})\text{S}-\text{SP}(\text{S})(\text{C}_6\text{H}_{11})_2$. This is not the first time that we have obtained such a dimer from the reaction of an *f* element with a dithiophosphinate salt. In the reaction of such ligands with uranium(IV) solutions in the presence of air a double redox reaction takes place where the ligand is oxidized to the dimer and also the uranium(IV) is oxidized to UO_2^{2+} (Storey, Zonnevillle & Pinkerton, 1983). In this case, however, the oxidizing agent was molecular oxygen. In the present case, from the colors observed during the reaction, it is not unreasonable to postulate that the reaction passes through formation of a cerium(IV) complex which then undergoes photochemical reaction. There is a precedent for this interpretation in the dithiophosphinate chemistry of cobalt(III) where the complexes may be isolated but undergo a photochemical redox reaction upon irradiation to give the disulfide and the corresponding cobalt(II) complex (Costanzo, Fraga, Giuffrida & Condorelli, 1978).

* Lists of calculated and observed structure factors, anisotropic thermal parameters, calculated H-atom positions, and complete tables of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53639 (52 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors for (I)

$B_{eq} = (8\pi^2/3) \text{ trace } U.$				
	x	y	z	$B_{eq}(\text{\AA}^2)$
S1	0.49280 (7)	0.03082 (8)	0.1685 (1)	3.53 (3)
S2	0.36844 (7)	0.20228 (8)	0.2238 (1)	3.73 (3)
Cl	0.5428 (1)	0.4682 (1)	0.3583 (2)	10.27 (6)
P	0.38899 (7)	0.11518 (8)	0.1176 (1)	2.68 (3)
C1	0.3061 (3)	0.0348 (3)	0.0784 (3)	3.0 (1)
C2	0.3220 (3)	-0.0351 (3)	-0.0033 (4)	3.8 (1)
C3	0.2495 (3)	-0.0968 (3)	-0.0366 (4)	5.1 (1)
C4	0.2269 (3)	-0.1414 (3)	0.0623 (4)	5.3 (1)
C5	0.2112 (3)	-0.0732 (3)	0.1460 (4)	5.1 (1)
C6	0.2828 (3)	-0.0101 (3)	0.1784 (4)	4.1 (1)
C7	0.4135 (2)	0.1617 (3)	-0.0070 (3)	3.0 (1)
C8	0.4819 (3)	0.2300 (3)	0.0161 (4)	4.3 (1)
C9	0.4989 (3)	0.2729 (3)	-0.0878 (4)	5.0 (1)
C10	0.4246 (3)	0.3162 (3)	-0.1514 (4)	4.7 (1)
C11	0.3590 (3)	0.2471 (3)	-0.1773 (4)	4.2 (1)
C12	0.3390 (3)	0.2037 (3)	-0.0766 (4)	4.0 (1)
C13	0.500	0.4077 (5)	0.250	7.1 (3)

Table 2. Fractional atomic coordinates and equivalent isotropic temperature factors for (II)

$B_{eq} = (8\pi^2/3) \text{ trace } U.$				
	x	y	z	$B_{eq}(\text{\AA}^2)$
S1	0.36352 (4)	0.39351 (7)	0.18822 (7)	4.87 (2)
S2	0.28339 (3)	0.25676 (6)	0.40850 (6)	3.71 (2)
S3	0.25976 (3)	0.08883 (6)	0.52724 (6)	3.76 (2)
S4	0.10435 (4)	0.13534 (7)	0.36251 (6)	4.36 (2)
S5	0.31673 (4)	0.75275 (7)	0.57199 (6)	4.23 (2)
S6	0.21662 (3)	0.56269 (6)	0.75289 (5)	3.50 (2)
S7	0.22127 (3)	0.46519 (6)	0.92348 (6)	3.70 (2)
S8	0.12055 (4)	0.66232 (6)	0.88844 (6)	4.34 (2)
P1	0.35357 (3)	0.24586 (6)	0.31607 (5)	2.99 (2)
P2	0.14812 (3)	0.04597 (6)	0.50640 (5)	2.92 (2)
P3	0.32063 (3)	0.65111 (6)	0.73013 (5)	2.79 (2)
P4	0.14500 (3)	0.51169 (5)	0.98056 (5)	2.87 (2)
C1	0.4350 (1)	0.2338 (2)	0.4116 (2)	3.06 (6)
C2	0.4315 (1)	0.1172 (2)	0.5126 (2)	3.64 (7)
C3	0.5028 (1)	0.1156 (3)	0.5832 (3)	4.51 (8)
C4	0.5305 (2)	0.2233 (3)	0.6249 (3)	5.28 (9)
C5	0.5341 (2)	0.3381 (3)	0.5263 (3)	4.95 (9)
C6	0.4645 (1)	0.3441 (2)	0.4524 (2)	4.07 (7)
C7	0.3180 (1)	0.1086 (2)	0.2778 (2)	3.28 (6)
C8	0.2490 (1)	0.1130 (3)	0.1994 (2)	4.26 (7)
C9	0.2207 (2)	0.0008 (3)	0.1630 (2)	5.01 (8)
C10	0.2732 (2)	-0.0199 (3)	0.1088 (2)	5.08 (8)
C11	0.3407 (2)	-0.0264 (3)	0.1891 (3)	5.05 (8)
C12	0.3702 (1)	0.0874 (2)	0.2219 (2)	4.22 (7)
C13	0.1290 (1)	-0.1161 (2)	0.5339 (2)	3.21 (6)
C14	0.0533 (1)	-0.1738 (3)	0.5562 (3)	4.58 (8)
C15	0.0354 (2)	-0.3085 (3)	0.5712 (3)	6.4 (1)
C16	0.0489 (2)	-0.3306 (3)	0.4688 (3)	6.9 (1)
C17	0.1233 (2)	-0.2751 (3)	0.4482 (3)	5.58 (9)
C18	0.1429 (2)	-0.1416 (2)	0.4328 (2)	4.36 (7)
C19	0.1305 (1)	0.0725 (2)	0.6280 (2)	3.14 (6)
C20	0.1503 (2)	0.2064 (2)	0.6143 (2)	4.38 (8)
C21	0.1338 (2)	0.2289 (3)	0.7146 (3)	5.77 (9)
C22	0.1688 (2)	0.1579 (3)	0.8268 (3)	5.42 (9)
C23	0.1472 (2)	0.0253 (3)	0.8402 (2)	5.03 (9)
C24	0.1650 (2)	0.0007 (2)	0.7423 (2)	3.93 (7)
C25	0.3547 (1)	0.7322 (2)	0.8328 (2)	2.91 (6)
C26	0.3130 (1)	0.8239 (2)	0.8150 (2)	4.10 (7)
C27	0.3436 (2)	0.8953 (2)	0.8982 (2)	4.61 (8)
C28	0.4192 (2)	0.9562 (3)	0.8882 (3)	5.36 (9)
C29	0.4604 (2)	0.8644 (3)	0.9078 (3)	5.54 (9)
C30	0.4315 (1)	0.7930 (2)	0.8252 (2)	4.25 (7)
C31	0.3698 (1)	0.5369 (2)	0.7620 (2)	3.30 (6)
C32	0.3358 (2)	0.4500 (2)	0.6936 (2)	4.47 (8)
C33	0.3819 (2)	0.3652 (3)	0.7111 (3)	5.83 (9)
C34	0.4003 (2)	0.2990 (3)	0.8352 (3)	6.0 (1)
C35	0.4338 (2)	0.3855 (3)	0.9024 (3)	5.08 (8)
C36	0.3867 (1)	0.4689 (2)	0.8873 (2)	4.15 (7)
C37	0.0722 (1)	0.3810 (2)	0.9889 (2)	2.93 (6)
C38	0.0929 (1)	0.2630 (2)	1.0612 (2)	3.31 (6)
C39	0.0292 (2)	0.1578 (2)	1.0710 (2)	4.05 (7)
C40	-0.0065 (2)	0.1509 (2)	0.9548 (2)	4.13 (7)
C41	-0.0269 (2)	0.2685 (3)	0.8814 (3)	4.61 (8)
C42	0.0361 (1)	0.3753 (2)	0.8708 (2)	3.95 (7)
C43	0.1866 (1)	0.5041 (2)	1.1255 (2)	3.10 (6)
C44	0.1339 (1)	0.4969 (2)	1.1984 (2)	4.02 (7)
C45	0.1687 (2)	0.5011 (3)	1.3170 (2)	5.09 (8)
C46	0.2281 (2)	0.6110 (3)	1.3110 (3)	6.10 (9)
C47	0.2808 (2)	0.6139 (3)	1.2427 (3)	5.51 (9)
C48	0.2479 (2)	0.6128 (2)	1.1230 (2)	4.46 (8)

The usual route to these disulfides employs iodine as the oxidizing agent (Maier, 1965). This reaction is rapid and quantitative, indeed the reaction may be carried out as a titration to a colorimetric end point to control the stoichiometry. In contrast, the reaction with cerium(IV) appears to be slower and may not go to completion as the final solution remains colored. Because of the difference in the reaction behavior and because of the steric bulk of the cyclohexyl groups, it seemed reasonable to suppose that there might be formation of different conformers in the two different reactions, perhaps due to a cerium-mediated template synthesis. Our initial observation of two crystal modifications seemed to support this hypothesis. However, subsequent crystallization studies in different solvents indicate that the form obtained depends only on the solvent used and not on the choice of oxidant.

In (I) the disulfide molecule sits on a crystallographic twofold axis, *i.e.* it has rigorous twofold symmetry, whereas in (II) there are two independent essentially identical molecules in the unit cell, neither of which has any crystallographically imposed symmetry. However, (I) does not have the same geometry as (II). In both cases the two ends of the molecule may, in a first analysis, be considered as normal examples of tetrahedral phosphorus with one atom single bonded [P—S = 2.137 (9) Å ave] and the other double bonded [P=S = 1.939 (3) Å ave] to the P atom (but see below).

The most interesting part of the structure lies in the analysis of the S—P—S—P—S skeleton and in its comparison with that observed for the analogs (III) (Lawton, 1970; Tkachev, Atovmyan & Shchepinov, 1976) and (IV) (Yadav, Bohra, Mehrotra, Rai & Srivastava, 1989), and for the prototype molecules H₂S₂, MeSSMe and MeSSEt (Marsden & Smith,

1988; Rauk, 1984; Ohsaku & Allinger, 1988). The S—S bond length is similar in all cases: (I) 2.021 (2); (II) 2.0637 (8), 2.0621 (9); (III) 2.109 (4); (IV) 2.058 (7); H₂S₂ 2.061; MeSSMe 2.038; MeSSEt 2.031 Å. Any lengthening of the S—S bond is accompanied by shortening of the neighboring P—S

Table 3. Selected bond distances (Å) and angles (°) for (I) with e.s.d.'s in parentheses

S1—S1'	2.021 (2)	S1—P	2.158 (2)
S2—P	1.935 (2)	P—C1	1.839 (4)
P—C7	1.826 (4)		
S1'—S1—P	104.25 (7)	S1—P—S2	114.82 (7)
S1—P—C1	104.0 (1)	S1—P—C7	100.3 (1)
S2—P—C1	113.4 (1)	S2—P—C7	115.8 (1)
C1—P—C7	107.1 (2)		

Table 4. Selected bond distances (Å) and angles (°) for (II) with e.s.d.'s in parentheses

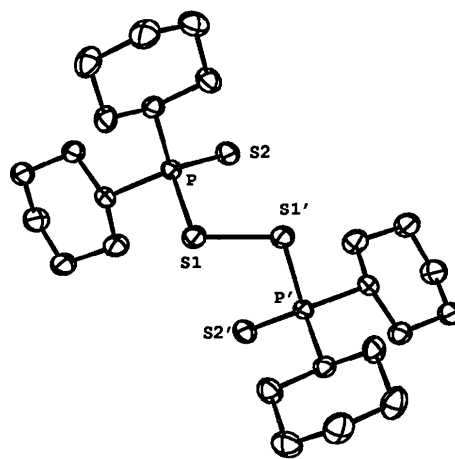
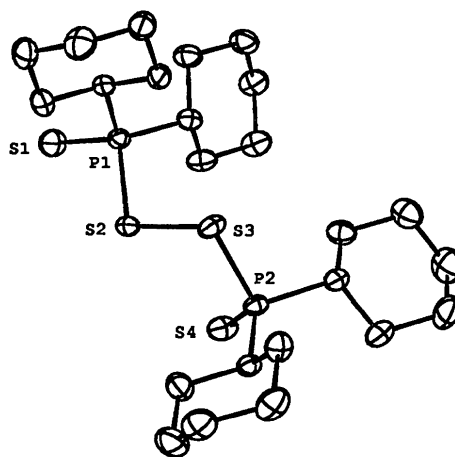
Molecule A		Molecule B	
S1—P1	1.9430 (9)	S5—P3	1.9456 (8)
S2—S3	2.0637 (8)	S6—S7	2.0621 (9)
S2—P1	2.111 (1)	S6—P3	2.1094 (9)
S3—P2	2.1550 (9)	S7—P4	2.151 (1)
S4—P2	1.9325 (9)	S8—P4	1.9384 (9)
P1—C1	1.831 (2)	P3—C25	1.820 (3)
P1—C7	1.824 (3)	P3—C31	1.838 (3)
P2—C13	1.828 (3)	P4—C37	1.825 (2)
P2—C19	1.825 (3)	P4—C43	1.828 (2)
S3—S2—P1	105.35 (5)	S7—S6—P3	104.29 (4)
S2—S3—P2	102.77 (4)	S6—S7—P4	104.01 (4)
S1—P1—S2	105.48 (5)	S5—P3—S6	104.96 (4)
S1—P1—C1	112.25 (7)	S5—P3—C25	114.56 (7)
S1—P1—C7	114.98 (8)	S5—P3—C31	112.61 (9)
S2—P1—C1	107.2 (1)	S6—P3—C25	107.41 (9)
S2—P1—C7	107.60 (9)	S6—P3—C31	108.34 (8)
C1—P1—C7	108.9 (1)	C25—P3—C31	108.6 (1)
S3—P2—S4	115.25 (4)	S7—P4—S8	116.05 (4)
S3—P2—C13	100.56 (9)	S7—P4—C37	102.7 (1)
S3—P2—C19	102.56 (8)	S7—P4—C43	99.7 (1)
S4—P2—C13	115.30 (8)	S8—P4—C37	113.52(8)
S4—P2—C19	113.27 (9)	S8—P4—C43	115.4 (1)
C13—P2—C19	108.5 (1)	C37—P4—C43	107.9 (1)

bond: (I) 2.158 (2); (II) 2.111 (1), 2.1550 (9), 2.1094 (9), 2.151 (1); (III) 2.072 (2); (IV) 2.082 (6) Å. A more intriguing observation concerns the torsion angle about the S—S bond. Whereas this angle is quite similar for H₂S₂, MeSSMe, MeSSEt and (IV) (90.8, 84.7, 84.4 and 93.6°, respectively), compound (III) lies on a crystallographic center of symmetry, thus the P—S—S—P torsion angle is constrained to be 180°. The corresponding angle for (I) is -106.35 (7)° whereas in (II) its magnitude is much larger [-130.23 (4) and 129.34 (4)°]. This range of angles for the phosphorus-containing molecules implies that the rotational-energy minimum for dithiophosphoryl disulfides is flat, that the *trans* barrier to rotation is low and that it appears to have completely disappeared in (III). This is in contrast to the case for dialkyl disulfides described above. However, it has previously been postulated for very bulky dialkyl disulfides (Jørgensen & Snyder, 1980). A flat minimum is also supported by preliminary calculations (MNDO) on model dithiophosphoryl disulfide molecules (Gallacher, Karaman & Pinkerton, 1990).

A most intriguing aspect of these structures is that there is clearly some driving force to make the PS₃

unit planar. Examination of the appropriate S—P—S—S torsion angles [(I) 24.7 (1); (II) 170.43 (4)/20.62 (6), -176.01 (4)/-22.20 (6); (III) 180.0; (IV) 170.5°] shows that the *trans* structures have close to the ideal staggered conformation whereas the *cis* structures have been twisted by greater than 35° away from the ideal towards a planar configuration. We interpret this to mean that there is a significant π interaction in the P—S 'single' bond.

Further indication of the strength of the P—S π bond is found in the comparison of the S—P—S valence angles [(I) 114.82 (7); (II) 105.48 (5), 115.25 (4), 104.96 (4), 116.05 (4); (III) 104.8 (1); (IV) 103.3°]. This angle is less than the ideal tetrahedral angle for the *trans* S—P—S—S fragments due to the steric requirement of the bulky cyclohexyl groups.

Fig. 1. Perspective view of the (C₆H₁₁)₂P(S)S—SP(S)(C₆H₁₁)₂ molecule, (I).Fig. 2. Perspective view of the (C₆H₁₁)₂P(S)S—SP(S)(C₆H₁₁)₂ molecule, (II).

However, it opens up by 10° to become greater than the ideal tetrahedral angle in the *cis* $S^1-P-S^2-S^3$ unit despite the steric requirement of the cyclohexyl groups. This is due to the $S^1 \cdots S^3$ steric interaction becoming important as the molecule approaches an eclipsed configuration. The large valence angle and the low $S-P-S$ torsion angle give some measure of the driving force to obtain a completely planar *cis* configuration and hence the strength of the $p\pi-d\pi$ interaction.

Under the ideal point symmetry at phosphorus of C_s , the filled non-bonding p orbital (or hybrid of π character) on the bridging S atom and the d_{xz} and d_{yz} orbitals on phosphorus transform as A'' ; thus maximum overlap would take place when the $S-P-S$ fragment is planar (torsion angle 0 or 180°). This suggests a mechanism for lowering the *trans* barrier to rotation discussed above. We can think of the barrier as largely due to repulsion of the filled p orbitals on adjacent S atoms (Pauling, 1949). If this electron density is polarized towards phosphorus and away from the $S-S$ bond, the barrier will thus be lowered.

We note that there is nothing unusual about the $P-S$ bond lengths. This suggests that if the π interaction we propose to explain the current structural parameters exists, then it should contribute to all $P-S$ single bonds at tetrahedral phosphorus.

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Structure of 2'-Deoxy-5-azacytidine (Decitabine) Monohydrate

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Abstract. $C_8H_{12}N_4O_4 \cdot H_2O$, $M_r = 246.2$, monoclinic, $P2_1$, $a = 13.487$ (17), $b = 7.611$ (10), $c = 5.340$ (1) Å, $\beta = 100.56$ (1)°, $V = 538.9$ (1.4) Å³, $Z = 2$, $D_x = 1.52$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.74$ cm⁻¹, $F(000) = 240$, $T = 293$ K, final $R(F) = 0.060$, $wR = 0.069$ for 578 unique observed [$I > 3\sigma(I)$] reflections. The structure establishes that decitabine is the β -D-anomer of 2'-deoxy-5-azacytidine, and that the crystals contain a hydrogen-bonded water molecule.

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Introduction. Decitabine (1) is believed to be the β -D-anomer of 2'-deoxy-5-azacytidine. It has strong antileukemic properties *in vitro* as well as *in vivo* (Momparler, 1985; Momparler, Rivard & Gyger, 1985). ¹H NMR spectroscopy showed only small differences between α - and β -anomers, while various other assignments have also been made (Ben-Hatter & Jiricny, 1986; Piskala & Sorm, 1978; Srivastava, Robbins, Takusagawa & Berman, 1981). It is there-

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