

## Structure of Sodium Diethyldithiophosphate Dihydrate

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**Abstract.**  $(C_2H_5)_2PS_2Na \cdot 2H_2O$ ,  $M_r = 212.25$ , triclinic,  $P\bar{1}$ ,  $a = 6.1205$  (7),  $b = 6.592$  (1),  $c = 14.444$  (2) Å,  $\alpha = 98.48$  (1),  $\beta = 95.07$  (1),  $\gamma = 115.55$  (1)°,  $V = 512.38$  (9) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.40$ ,  $D_x = 1.376$  (1) g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 9.10$  cm<sup>-1</sup>,  $F(000) = 224$ ,  $T = 295$  K,  $R = 0.026$  for 1294 unique observed reflections [ $I > 3\sigma(I)$ ]. Each Na is surrounded by four water O and two S atoms in a distorted octahedral environment. The octahedra are connected by edge-sharing into layers parallel to the  $ab$  plane with every third octahedron missing. The diethyldithiophosphate ion is monodentate and each S is involved in two hydrogen bonds. In order to describe a weakly resolved disorder of the  $PS_2$  unit cumulant expansion (Gram–Charlier) terms up to fourth-order were included in the temperature factors of the S and P atoms.

**Introduction.** Substituted dithiophosphate and dithiophosphate ligands,  $R_2PS_2^-$ , form complexes with a variety of metals, where they exhibit a great diversity of coordination pattern (Mehrotra, Srivastava & Chauhan, 1984). While these ligands can be basically divided into monodentate, bidentate and bridging, structural details show more complex differentiation (Haiduc, 1981). For most transition metals the coordination is symmetrical while unsymmetrical coordination is often observed for non-transition metals. Most of the structural work carried out so far has been with the dithiophosphate ligand while structure reports of dithiophosphate complexes are comparatively rare. We have therefore started a project aiming to document structural changes brought about by  $R$ -group variation. Since we are working mainly with the diethyldithiophosphate ligand it was of interest to determine the X-ray crystal structure of its sodium salt.

**Experimental.** The title compound was prepared as described by Kuchen, Strolenberg & Metten (1963). Crystals in the form of thin colourless plates were obtained from an aqueous solution by slow evaporation; approximate dimensions of selected crystal  $0.20 \times 0.30 \times 0.05$  mm.  $D_m$  was measured pycnometrically in cyclohexane. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å),  $\omega/2\theta$  scan,  $\Delta\omega = 0.7^\circ$  +

$0.5^\circ \tan\theta$ . Cell constants were determined by least squares from setting angles of 36 reflections in the range  $10 < \theta < 22^\circ$ . Data were corrected for Lorentz and polarization effects. Absorption correction (numerical integration) for crystal defined by 6 faces: {100}, {010}, {001}, grid  $10 \times 10 \times 5$ , transmission factor 0.85–0.96. Two standard reflections measured every hour showed no significant variation, 1935 reflections measured, 1767 unique,  $R_{\text{int}} = 0.024$ , 1294 with  $I > 3\sigma_c(I)$  used in refinement ( $\sigma_c$  from counting statistics). Index range  $h -7 \rightarrow 7$ ,  $k 0 \rightarrow 7$ ,  $l -17 \rightarrow 17$ ;  $(\sin\theta)/\lambda < 0.60$  Å<sup>-1</sup>. The structure was solved by direct methods (MULTAN80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All H atoms were located from electron density maps. Least-squares refinement minimizing  $\sum w(|F_o| - |F_c|)^2$ ; all non-H atoms were treated anisotropically and all H atoms isotropically,  $w = [\sigma_c^2(F_o) + (0.020F_o)^2]^{-1}$ ,  $R = 0.033$ ,  $wR = 0.041$ ,  $S = 1.02$ ,  $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}} = 0.80/-0.22$  e Å<sup>-3</sup>, 147 parameters. No extinction effects were detected.

The refinement with harmonic  $\beta$  tensors to describe the thermal motion resulted in residual electron density in the plane of the  $PS_2$  unit (Fig. 1a). A split-atom model was tried but rejected since most of the residual density remained unexplained. The density distribution suggested that anharmonic tensors might describe the thermal motion more closely. Therefore third- and fourth-order ( $\gamma$  and  $\delta$ ) tensor components in the Gram–Charlier expansion were included in the refinement for the P and S atoms. Inclusion of third-order coefficients only did not improve the  $R$  values significantly. Components of anharmonic tensors less than one standard deviation from zero were then fixed to zero. A total of 13  $\gamma$  and 24  $\delta$  components were refined in the final cycles of least squares (184 parameters in all). The refinement resulted in:  $R = 0.026$ ,  $wR = 0.034$ ,  $S = 0.99$ ,  $(\Delta/\sigma)_{\text{av}} = 0.08$  (8),  $(\Delta/\sigma)_{\text{max}} = 0.77$  [ $U_{\text{iso}}(\text{HC21})$ ],  $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}} = 0.28/-0.18$  e Å<sup>-3</sup>. The  $R$ -factor test (Hamilton, 1965) was applied to this new model,  $wR(2)/wR(1) = 1.206$ ,  $\mathcal{R}_{37,1110,0.005} \approx 1.03$ . The hypothesis that the thermal motion should be described by a harmonic rather than an anharmonic model may be rejected at the 99.5% confidence level, assuming no systematic errors in the data. The anharmonic components have numerical values as large

as  $7.5\sigma$ ,  $6.8\sigma$  and  $6.2\sigma$  for  $\delta_{2222}$  for P, S2 and S1 respectively. A difference electron density map in the  $PS_2$  plane after anharmonic tensor refinement is shown in Fig. 1(b). The probability density function for the  $PS_2$  plane is shown in Fig. 1(c), after inclusion of third- and fourth-order tensors. The maximum change in atomic coordinates following this refinement is  $0.004$  (1) Å for P(z). The total shifts in position for P, S1 and S2 are  $0.0065$  (15),  $0.0031$  (13) and  $0.0039$  (15) Å, respectively. The  $\beta_{ij}$  values increased generally, with maximum changes for  $\beta_{22}$  of  $9.8\sigma$ ,  $8.9\sigma$  and  $8.2\sigma$  for P, S1 and S2, respectively. The shifts in bond lengths and angles were all less than  $2\sigma$ .

The data and the final model were compared by probability-plotting (Abrahams & Keve, 1971) of ordered values of  $\delta R_1 = \Delta F_i / \sigma(|F_o|_i)$  vs those expected for ordered normal deviates [ $\sigma(|F_o|_i) = w^{-1/2}$ ]. The result was a slope of  $0.923$  (2), an intercept of  $0.03$  (2) and a correlation coefficient of  $0.9976$ . It is concluded from the slope and intercept and the related  $S$  value that the systematic errors are small and  $\sigma(|F_o|)$  is on average rather well estimated.

Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). The system of computer programs used in this study is described by Lundgren (1982).

**Discussion.** The final atomic parameters are given in Table 1,\* a view of the ligand with the atom-numbering scheme is shown in Fig. 2 and a stereoview of the crystal packing is in Fig. 3. Selected bond distances and angles are listed in Table 2.

\* Lists of structure factors, hydrogen-atom distances, anisotropic displacement parameters and third- and fourth-order cumulants in the Gram-Charlier expansion have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51464 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

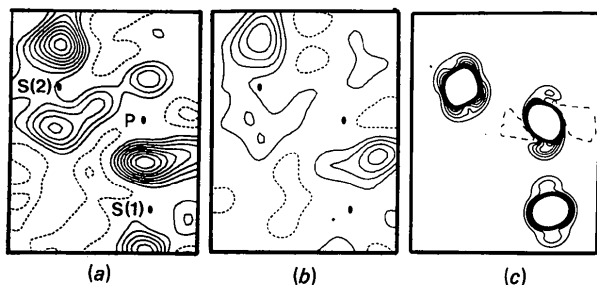


Fig. 1. Residual electron density in the  $PS_2$  plane following refinement of (a) the harmonic model, (b) the anharmonic model. (c) The probability density function map in the  $PS_2$  plane following refinement of the anharmonic model. Contour intervals at  $0.05 \text{ e } \text{Å}^{-3}$  in (a) and (b); in (c) the intervals are drawn on an arbitrary scale with the central parts omitted for clarity.

Table 1. Fractional atomic coordinates with equivalent isotropic displacement parameters ( $\text{Å}^2$ ) for the non-H atoms and isotropic displacement parameters for H atoms

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
Na	0.1634 (2)	0.8310 (2)	0.48317 (7)	0.0393 (4)
P	0.3111 (1)	0.6796 (2)	0.74836 (7)	0.0360 (5)
S1	0.2926 (2)	0.9757 (2)	0.78120 (6)	0.0472 (5)
S2	0.3147 (1)	0.5738 (1)	0.60914 (9)	0.0402 (7)
C1	0.0475 (5)	0.4437 (5)	0.7774 (2)	0.047 (1)
C2	0.0181 (7)	0.4661 (7)	0.8809 (2)	0.064 (2)
C3	0.5849 (5)	0.6939 (6)	0.8165 (2)	0.049 (1)
C4	0.6461 (7)	0.8099 (8)	0.9217 (2)	0.066 (2)
O1	0.0993 (4)	0.1071 (3)	0.4076 (1)	0.0427 (8)
O2	0.4948 (3)	0.8307 (3)	0.4063 (1)	0.0408 (8)
H11	-0.099 (5)	0.452 (5)	0.735 (2)	0.022 (7)
H12	0.066 (6)	0.317 (6)	0.764 (3)	0.041 (10)
H21	0.152 (7)	0.439 (7)	0.912 (3)	0.055 (11)
H22	0.023 (6)	0.617 (6)	0.906 (3)	0.039 (10)
H23	-0.153 (8)	0.344 (8)	0.894 (3)	0.070 (13)
H31	0.706 (6)	0.784 (5)	0.787 (2)	0.028 (9)
H32	0.554 (5)	0.531 (6)	0.813 (2)	0.023 (8)
H41	0.806 (7)	0.845 (6)	0.945 (3)	0.050 (11)
H42	0.643 (7)	0.963 (8)	0.934 (3)	0.060 (12)
H43	0.545 (10)	0.732 (10)	0.959 (4)	0.087 (20)
HO11	0.002 (7)	0.093 (6)	0.348 (3)	0.052 (11)
HO12	0.238 (8)	0.177 (8)	0.406 (3)	0.059 (14)
HO21	0.523 (7)	0.874 (7)	0.355 (3)	0.053 (12)
HO22	0.534 (7)	0.727 (7)	0.396 (3)	0.040 (12)

Table 2. Bond distances (Å) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

Symmetry code: (i)  $x, y+1, z$ ; (ii)  $-x, 1-y, 1-z$ ; (iii)  $1-x, 2-y, 1-z$ ; (iv)  $1-x, 1-y, 1-z$ .

Na—O1 <sup>i</sup>	2.405 (2)	S1—P—S2	115.77 (7)
Na—O1 <sup>ii</sup>	2.463 (2)	C1—P—C3	106.54 (17)
Na—O2	2.397 (2)	P—C1—C2	116.18 (23)
Na—O2 <sup>iii</sup>	2.496 (2)	P—C3—C4	116.30 (23)
Na—S2	3.001 (1)	S1—P—C1	111.09 (12)
Na—S2 <sup>iv</sup>	2.998 (1)	S1—P—C3	110.85 (12)
P—S1	1.993 (2)	S2—P—C1	105.12 (11)
P—S2	2.034 (2)	S2—P—C3	106.95 (11)
P—C1	1.829 (3)		
P—C3	1.825 (3)		
C1—C2	1.516 (4)		
C3—C4	1.530 (4)		
S1—S2	3.411 (2)		

#### Hydrogen bonds

	O...S	H...S	O—H...S
O1—HO11...S1 <sup>ii</sup>	3.281 (2)	2.32 (4)	169 (3)
O1—HO12...S2 <sup>iv</sup>	3.338 (2)	2.57 (5)	175 (4)
O2—HO21...S1 <sup>iii</sup>	3.297 (2)	2.47 (4)	167 (4)
O2—HO22...S2 <sup>iv</sup>	3.327 (2)	2.52 (5)	171 (4)

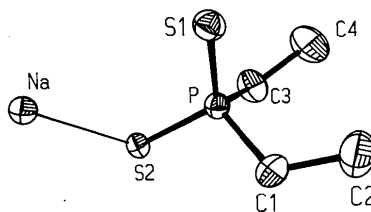


Fig. 2. View of the ligand with the atom-numbering scheme. The harmonic parts of the displacement ellipsoids are drawn at the 50% probability level.

Each Na is coordinated by four water O and two S atoms forming a distorted octahedron. The ranges of Na—O and Na—S distances are 2.397–2.497 (2) and 2.997–3.001 (1) Å, respectively. A similar octahedron was found in sodium 1-pyrrolidinecarbodithioate dihydrate (Albertsson, Oskarsson, Ståhl, Svensson & Ymén, 1980). The octahedra are linked together by edge-sharing to form layers in the *ab* plane with every third octahedron missing. The two-dimensional net of Na polyhedra is further stabilized by a network of hydrogen bonds involving S2 and the two water molecules, Fig. 4. The S1 atom is not involved in the coordination to Na, and it is located above the triangular face normal to the *ab* plane. In this position it accepts two OH...S hydrogen bonds from the two water molecules at the corners of the triangular face. The distance from S1 to the triangular face is 2.577 (1) Å.

The two P—S bond distances are not equal as is usually found in coordination compounds. In  $(C_6H_5)_2P(S)SH$  (Krebs & Henkel, 1981) the bond distances are 1.954 (1) and 2.077 (1) Å for the double and single bond, respectively, compared with 1.993 (2) and 2.034 (2) Å in this compound. Since both bond lengths are intermediate between a single and a double bond the negative charge is partially delocalized over the P—S

bonds. The P atom is bonded to two C and two S atoms in a distorted tetrahedron. The S—P—S angle of 115.77 (7)° is considerably larger and the C—P—C angle of 106.5 (2)° smaller than the tetrahedral angle. This distortion has also been observed in potassium dimethyl- and dibenzylidithiophosphate (Coppens, MacGillavry, Hovenkamp & Douwes, 1962; Hazel & Collin, 1972) with S—P—S angles of 118.2 (8) and 120.0 (1)° and O—P—O angles of 86 (3) and 96.6 (2)°, respectively.

The orientation of the ethyl groups is almost parallel to the *c* axis; the angles are 10.5 and 26.2° for C1—C2 and C3—C4, respectively. The conformation of the ethyl groups can be described by the torsion angles C1—P—C3—C4 and C2—C1—P—C3; these are 60.1 (3) and -78.4 (3)°, corresponding to a synclinal, antisynclinal (*sc*, -*sc*) conformation (Klyne & Prelog, 1969).

In the *c* direction the structure is stabilized by van der Waals forces between the ethyl groups. The shortest C—C contact along *c* is 3.442 (8) Å (C2—C2, -*x*, 1-*y*, 1-*z*). Fig. 2 shows the crystal packing with hydrogen bonds indicated.

The inclusion of anharmonic tensors improved the model significantly as shown in *Experimental* and in Figs. 1(a) and 1(b). The higher-order terms describe anharmonic motions and/or disorder. Since the fourth-order terms ( $\delta$ ) are more important than the third-order terms ( $\gamma$ ) our conclusion is that the anharmonic coefficients describe a weakly resolved disorder in the  $PS_2$  moiety (Kuks, 1983).

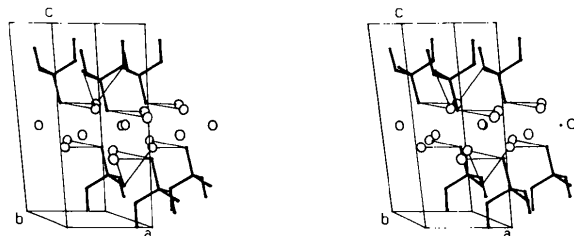


Fig. 3. Stereoview of the crystal packing. The harmonic parts of the displacement ellipsoids are drawn at the 50% probability level for Na and O. Part of the hydrogen-bond system is indicated with thin lines.

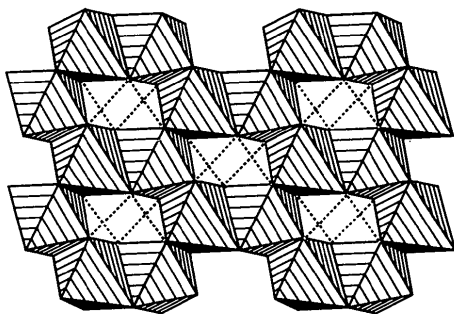


Fig. 4. Packing of the distorted octahedra in the *ab* plane. Hydrogen bonds are indicated with dashed lines.

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