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Structure of 2-Aminodinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphine-2-thione-Di-*n*-butylamine Adduct

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Abstract. $C_{29}H_{33}N_2O_2PS$, $M_r = 492.6$, triclinic, $P\bar{1}$, $a = 8.8737(6)$, $b = 12.6312(8)$, $c = 13.8424(8)$ Å, $\alpha = 111.797(6)$, $\beta = 104.103(5)$, $\gamma = 97.005(5)^\circ$, $V = 1357.9$ Å³, $Z = 2$, $D_x = 1.20$ g cm⁻³, $\lambda(Cu K\alpha) = 1.5418$ Å, $\mu = 17.9$ cm⁻¹, $F(000) = 524$, $T = 295$ K, $R = 0.065$ for 4778 observed reflections. The seven-membered phosphepine ring is in a boat conformation. The bond length, P=S, is 1.924(2) Å. The naphthalene rings are planar. The crystal structure is stabilized by an N—H \cdots N intermolecular hydrogen bond N(24) \cdots N(25) with N \cdots N distance and N—H \cdots N angle 2.72(2) Å and 166.5(2)°, respectively.

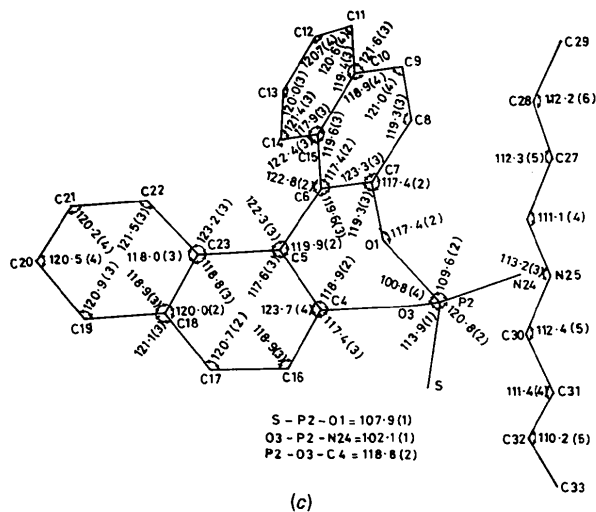
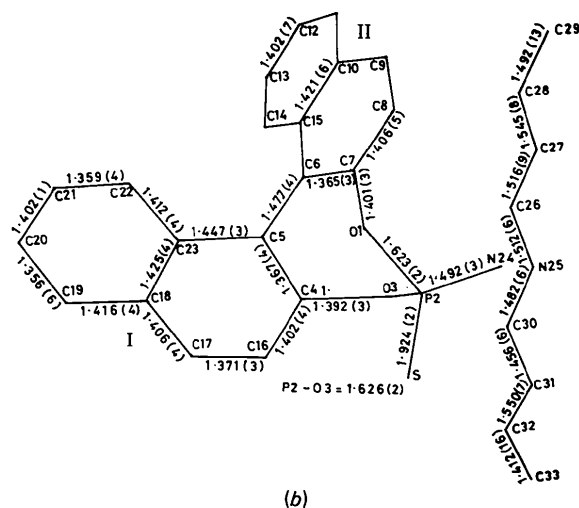
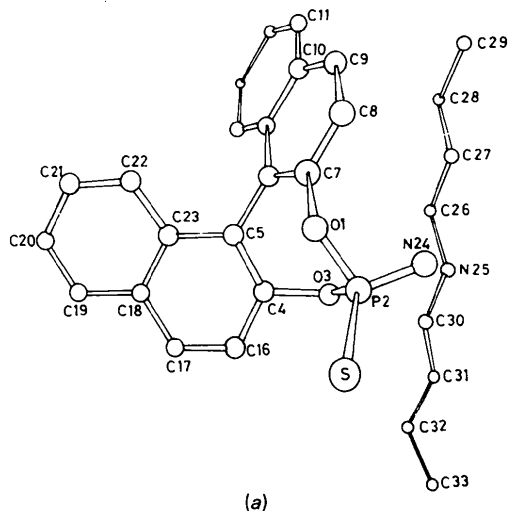
Introduction. The chemistry of organophosphorus compounds has received tremendous attention during the past two decades because of its vital role in both life-sustaining and life-destroying activities (Corbridge, 1975; Garcia-Blanco & Perales, 1972). The title compound belongs to the category of life-destroying substances *viz.* insecticides, bactericides, flame retardants, *etc.* (Ismail, 1975). The organophosphates form a wide spectrum of insecticides and pesticides effective against aphids, mites, lepidoptera, beetles, leaf-hoppers and thrips on fruits, vegetables and crops, and for this reason its X-ray structure is of great interest to our continuing investigations.

Experimental. Transparent needle-shaped crystals were obtained by slow evaporation from methanol. Crystal, 0.53 × 0.23 × 0.08 mm, used for all measurements. Accurate cell parameters obtained from least-squares refinement using 2 θ values of 25 medium-angle reflections ($35 < \theta < 45^\circ$). Intensity data collected using $\omega/2\theta$ scan technique on Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. Intensities of two standard reflections monitored periodically during data collection, no significant variation. Intensities of reflections $2 < \theta < 75^\circ$ measured (h : -10–10, k : -14–14, l : 0–14). 5385 independent reflections measured, 4778 reflections had $I > 3\sigma(I)$. The intensity data were corrected for Lorentz and polarization effects, no absorption correction was applied. The structure was solved by direct methods using the program *SHELXS86* (Sheldrick, 1986). All the H atoms except those attached to N atoms and methyl group atoms located on a difference density map. H atoms attached to N atoms and methyl groups fixed geometrically and checked in the difference map. Positional parameters of all atoms and anisotropic thermal parameters of non-H atoms refined (on F) by full-matrix least-squares methods. Final $R = 0.065$ and $wR = 0.075$ for 4778 observed reflections, $w = K/(\sigma^2|F_o| + m|F_o|^2)$ ($K = 2.3900$, $m = 0.000469$).

Table 1. Positional parameters and equivalent isotropic thermal parameters for non-H atoms with e.s.d.'s in parentheses

$$B_{eq} = (8\pi^2/3) \sum_i U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	B _{eq} (Å ²)
S	0.3417 (1)	-0.1519 (1)	0.6688 (1)	5.0
O(1)	0.5048 (2)	-0.0514 (1)	0.6608 (1)	3.9
P(2)	0.3302 (1)	-0.0053 (1)	0.6582 (1)	3.7
O(3)	0.3098 (2)	0.0946 (2)	0.7661 (1)	3.8
C(4)	0.4386 (3)	0.1449 (2)	0.8624 (2)	3.4
C(5)	0.5638 (3)	0.2260 (2)	0.8708 (2)	3.5
C(6)	0.5617 (3)	0.2578 (2)	0.7781 (2)	3.5
C(7)	0.5331 (3)	0.1716 (2)	0.6760 (2)	3.7
C(8)	0.5376 (4)	0.1944 (3)	0.5846 (2)	4.6
C(9)	0.5660 (4)	0.3067 (3)	0.5959 (3)	5.1
C(10)	0.5831 (4)	0.4010 (3)	0.6968 (3)	4.5
C(11)	0.5979 (4)	0.5178 (3)	0.7071 (3)	5.6
C(12)	0.6033 (5)	0.6055 (3)	0.8025 (3)	6.1
C(13)	0.5984 (4)	0.5827 (3)	0.8935 (3)	5.3
C(14)	0.5879 (4)	0.4713 (2)	0.8868 (2)	4.4
C(15)	0.5779 (3)	0.3766 (2)	0.7887 (2)	3.8
C(16)	0.4290 (3)	0.1117 (2)	0.9472 (2)	3.8
C(17)	0.5526 (3)	0.1608 (2)	1.0438 (2)	4.1
C(18)	0.6900 (3)	0.2395 (2)	1.0564 (2)	4.0
C(19)	0.8215 (4)	0.2861 (3)	1.1539 (3)	5.5
C(20)	0.9562 (4)	0.3583 (4)	1.1640 (3)	6.7
C(21)	0.9676 (4)	0.3888 (3)	1.0780 (3)	6.0
C(22)	0.8428 (3)	0.3468 (3)	0.9838 (3)	4.8
C(23)	0.6991 (3)	0.2728 (2)	0.9699 (2)	3.8
N(24)	0.2039 (2)	0.0000 (2)	0.5677 (2)	3.6
N(25)	-0.0108 (3)	0.1374 (3)	0.6409 (2)	5.6
C(26)	0.0415 (5)	0.2649 (4)	0.6630 (4)	8.1
C(27)	0.0959 (5)	0.2769 (4)	0.5711 (4)	7.5
C(28)	0.1393 (7)	0.4060 (6)	0.5875 (6)	10.4
C(29)	0.1826 (9)	0.4169 (6)	0.4934 (6)	12.0
C(30)	-0.0578 (5)	0.1210 (4)	0.7310 (3)	7.1
C(31)	-0.1047 (5)	-0.0023 (6)	0.7088 (4)	8.8
C(32)	-0.1346 (10)	0.0020 (7)	0.8160 (7)	13.7
C(33)	-0.1651 (14)	-0.1144 (10)	0.8065 (11)	22.3



The final (shift/e.s.d.)_{mean} = 0.10. The final difference Fourier map was featureless, with $\Delta\rho$ within $\pm 0.3 \text{ e } \text{\AA}^{-3}$. Atomic scattering factors for all the atoms provided in the *SHELX76* (Sheldrick, 1976) program. *SHELX76* used for refinement and *PARST* (Nardelli, 1983) for geometrical calculations.

Discussion. Table 1* lists the final atomic coordinates and equivalent isotropic thermal parameters of non-H atoms. The molecular diagram, atom-numbering scheme, and bond lengths and angles involving non-H atoms are shown in Fig. 1. The P=S bond length, 1.924 (2) Å, compares well with those in a related benzodioxaphosphorinane structure (Grand & Robert, 1978). The P=S bond adopts the axial orientation which is found to be a common feature in all the 1,3,2-dioxaphosphorinane compounds reported in literature (Dutasta, Grand, Robert & Taieb, 1974).

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms, least-squares-planes calculations, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53656 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 1. Atomic numbering scheme (a), with the bond lengths (Å) (b) and bond angles (°) (c) of the title compound.

X-ray studies of the conformations of similar seven-membered phosphorus rings are rarely found in the literature. Grand & Robert (1978) have studied the crystal structures of six- and seven-membered-ring phosphorus compounds. They have found that the seven-membered rings were in a chair conformation. Coulter (1975) observed a twist-chair conformation of the seven-membered ring in tetramethylene phosphoric acid. In our present study of the title compound the seven-membered ring is in a boat conformation.

The general shape of the ring may be characterized by two dihedral angles defined by the best least-squares plane through the four central atoms of the ring and the plane of the remaining C atoms. The dihedral angle between the plane O(3)—C(4)—C(5)—C(6) and O(3)—P(2)—C(7)—C(6) is 125.6 (1)° and between O(3)—P(2)—C(7)—C(6) and C(7)—O(1)—P(2) is 129.5 (1)°. The flattening of the ring at the P end is smaller in the seven-membered ring than in the six-membered ring. The torsion angles are listed in Table 2.

The average bond distances for C—O, 1.396 (3) Å, and P—O, 1.624 (2) Å, are smaller and larger, respectively, than the values found in the literature (Grand & Robert, 1978; Jones, Edwards & Kirby, 1986; Nuffel, Lenstra & Geise, 1981). The P—O—C bond angles observed in this structure are close to those found in the literature (Grand & Robert, 1978; Leopardi, Germain, Declercq, Meerssche, Robert & Jurkschat, 1982). The O—P—O bond angle, 100.8 (1)°, is lower than the average value of 104° in seven-membered rings and the S—P—O bond angle,

113.9 (1)°, is in good agreement with the reported structure (Grand & Robert, 1978).

The naphthalene rings are fused at C(4)—C(5) and C(6)—C(7) bonds. The bond lengths and angles in the naphthalene rings are normal, with an average value of 1.396 (5) Å and 120.0 (3)°, respectively. The dihedral angle between the two naphthalene rings is 120 (1)°. The least-squares plane of the seven-membered ring is inclined at angles of 136 (1) and 44.6 (1)° with rings I and II, respectively.

It is interesting to compare the change in bond angles and distances in going from a six-membered ring to seven-membered ring in which the same chemical groups are attached to the P atom. A comparison of bond lengths and angles in six-membered and seven-membered rings found in the literature and the present work is shown in Table 3. The bond lengths are equal within the e.s.d. limits, and show no significant changes in the four related compounds. But a significant variation is found in the P—N bond length of the title compound. The reason may be ascribed as follows.

In compound (A) (Fig. 2), there is minimum delocalization of the N-atom lone pair, so the P—N bond in the compound is normal. In compound (B), delocalization of the N-atom lone pair is easier because in the resonating structure (B) only hydrogen is eclipsing with P—O ring bond. Hence the P—N bond length in (B) is smaller than in (A).

The crystal structure is stabilized by an N—H...N intermolecular hydrogen bond N(24)...N(25) with N...N distance and N—H...N angle 2.72 (2) Å and 166.5 (2)° respectively (symmetry: $-x, -y, -z$). The packing of the molecule is stabilized by the hydrogen-bonding scheme and van der Waals forces.

Table 2. Torsion angles (°) with e.s.d.'s in parentheses

O(1)—P(2)—O(3)—C(4)	-44.7 (2)	C(6)—C(7)—C(8)—C(9)	-2.4 (5)
P(2)—O(3)—C(4)—C(5)	77.7 (3)	C(15)—C(6)—C(5)—C(4)	124.7 (3)
O(3)—C(4)—C(5)—C(6)	-0.7 (4)	C(15)—C(6)—C(5)—C(23)	-58.9 (4)
C(4)—C(5)—C(6)—C(7)	-51.8 (4)	C(5)—C(4)—C(16)—C(17)	-1.3 (5)
C(5)—C(6)—C(7)—O(1)	0.5 (4)	C(6)—C(5)—C(4)—C(16)	-178.4 (3)
C(6)—C(7)—O(1)—P(2)	76.1 (3)	C(5)—C(6)—C(7)—C(8)	-176.4 (3)
C(7)—O(1)—P(2)—O(3)	-48.0 (2)	C(17)—C(16)—C(4)—O(3)	-179.0 (3)
C(7)—O(1)—P(2)—S	-167.6 (2)	O(1)—C(7)—C(8)—C(9)	-179.4 (3)
C(7)—O(1)—P(2)—N(24)	59.1 (2)	O(1)—C(7)—C(6)—C(15)	-176.1 (2)
N(24)—P(2)—O(3)—C(4)	-157.6 (2)	O(3)—C(4)—C(5)—C(23)	-177.3 (3)
C(4)—O(3)—P(2)—S	70.5 (2)	N(25)—C(26)—C(27)—C(28)	176.1 (4)
C(7)—C(6)—C(15)—C(14)	171.1 (1)	C(26)—C(27)—C(28)—C(29)	-176.3 (5)

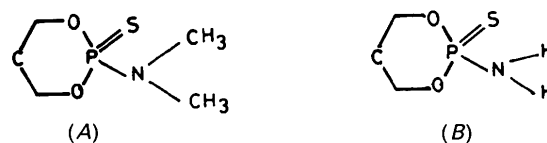


Fig. 2. Comparison of the phosphorine ring with different substitution at the N atom.

Table 3. Comparison of bond lengths (Å) and angles (°) in six- and seven-membered rings

	P=S	P—C	P—N	P—O	O—P—O	O—P—C	O—P—N	O—P—S	S—P—N	C—P—O
(I) (six)*	1.924 (2)	1.771 (5)	—	1.581 (3) 1.582 (3)	103.4 (1)	102.9 (2) 103.4 (2)	—	114.6 (1) 114.4 (1)	—	116.0 (2) 115.7 (3)
(II) (six)*	1.919 (3)	—	1.616 (8)	1.601 (4) 1.601 (4)	101.5 (5)	—	104.3 (2)	114.6 (2)	115.8 (3)	116.0 (2)
(III) (seven)*	1.925 (1)	1.771 (3)	—	1.595 (2) 1.587 (2)	105.1 (9)	102.3 (1)	—	113.8 (1) 114.1 (1)	117.6 (1)	118.7 (1) 118.9 (2)
(IV) (seven)*	1.923 (2)	—	1.612 (5)	1.591 (4) 1.587 (4)	103.6 (2)	—	104.2 (3) 102.4 (3)	114.2 (3) 114.7 (2)	116.1 (1)	119.4 (4) 120.4 (3)
(V) (seven)	1.924 (2)	—	1.492 (3)	1.624 (2)	100.8 (1)	—	109.6 (2)	113.9 (2)	120.8 (2)	118.1 (2)

Notes: (I) 2-Thiono-2,5,5-trimethyl-1,3,2-dioxaphosphorinane. (II) 2-Thiono-2-N-dimethylamino-5,5-dimethyl-1,3,2-dioxaphosphorinane. (III) 3-Thiono-3-methyl-1,5-dihydro-2,4,3-benzodioxaphosphepin. (IV) 3-Thiono-3-N-dimethylamino-1,5-dihydro-2,4,3-benzodioxaphosphepin. (V) Title compound.

* Grand & Roberts (1978).

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Structural Investigations of Benzo[c]cinnoline Derivatives. III. Structure of 2-Fluorobenzo[c]cinnoline

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Abstract. C₁₂H₇N₂F, $M_r = 198.20$, monoclinic, $C2/c$, $a = 11.296(4)$, $b = 8.471(3)$, $c = 18.889(2)$ Å, $\beta = 98.83(2)^\circ$, $V = 1786.0(2)$ Å³, $Z = 8$, $D_m = 1.45$, $D_x = 1.474$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54180$ Å, $\mu(\text{Cu } K\alpha) = 8.284$ cm⁻¹, $F(000) = 816$, $T = 293$ K, $R = 0.051$ for 1378 observed unique reflections [$I \geq 3\sigma(I)$]. The rings in the benzo[c]cinnoline skeleton are close to planar with dihedral angles of $0.45(7)$ – $1.17(8)^\circ$. The F atom is located $0.004(3)$ Å from the least-squares plane of the benzenoid ring.

Introduction. Benzo[c]cinnoline and some of its derivatives have mutagenic (Leary, Lafleur, Liber & Bleemann, 1983), antirheumatic (Matter, 1957; Erlenmeyer, 1958) and carcinogenic (Ashby, Styles & Paton, 1980) physiological activities. They have also been used as bleach catalysts in the processing of photograph silver-dye bleach materials (Jan, 1980). The structures of benzo[c]cinnoline (van der Meer, 1972), 1-morpholinobenzo[c]cinnoline (Hökelek, Watkin, Kılıç & Tüzün, 1990), 1- and 3-piperidinobenzo[c]cinnoline (Hökelek, Kılıç & Tüzün, 1991a) and 2- and 4-pyrrolidinobenzo[c]cinnoline (Hökelek, Kılıç & Tüzün, 1991b) have previously been reported. The structure determination of the title compound was undertaken to study the effects of changing the types and positions of the substituents.

Experimental. The title compound was dissolved in ethanol. The clear solution was cooled slowly at

room temperature. In about two days, yellow rod-shaped crystals were obtained. Experimental data, the method used to solve the structure and other related data and procedures are given in Table 1. Non-H atoms were included with anisotropic displacement parameters. Since difference syntheses did not clearly show the positions of the H atoms they were placed in calculated positions at a distance of 1.079 Å from the corresponding C atoms with coordinates and isotropic displacement parameters taken as 1.3 times the corresponding displacement parameters of the connecting non-H atoms.

Discussion. The final coordinates and equivalent isotropic thermal parameters are given in Table 2.* The molecular structure with the atom-numbering scheme is shown in Fig. 1. Bond lengths and angles are given in Table 3. The benzo[c]cinnoline skeleton is close to, but not exactly, planar, as can be seen from the dihedral angles $\alpha-\beta = 1.17(8)$, $\alpha-\gamma = 0.50(7)$ and $\beta-\gamma = 0.45(7)^\circ$ between rings α (C8, C9, C10, C11, C12, C13), β (C5, N6, N7, C8, C13, C14) and γ (C1, C2, C3, C4, C5, C14) in Fig. 1.

* Lists of observed and calculated structure factors, anisotropic thermal parameters, H-atom parameters, and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53665 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.