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Acta Cryst. (1994). C50, 1165–1169

Methyl (2-Methoxycarbonylbenzoyl)triphenylphosphoranylideneacetate and its Ethanolate Complex

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(*Received* 29 *March* 1993; *accepted* 6 *December* 1993)

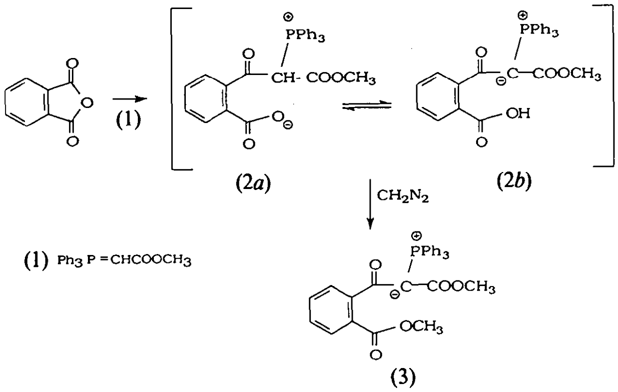
Abstract

Two different crystals of the compound methyl (2-methoxycarbonylbenzoyl)triphenylphosphoranylideneacetate, $C_{30}H_{25}O_5P$ (I) and $C_{30}H_{25}O_5P.0.5C_2H_6O$ (II), were studied by X-ray diffraction. The second crystal contains a molecule of ethanol close to an inversion centre. The solvent molecule is disordered on two positions and is involved in hydrogen bonding with the O atom of a carbonyl group. In crystal (I), the P—C(phenyl) distances vary from 1.808 (6) to 1.819 (5) Å, while the fourth P—C bond is shorter, at 1.759 (4) Å. In crystal (II), the P—C(phenyl) distances are 1.811 (6)–1.817 (6) Å and the fourth P—C bond is also shorter, at 1.763 (6) Å. These values suggest a multiple nature for the P—C bond. A high-field methoxy signal observed in the NMR spectrum was attributed to the shielding magnetic anisotropic effect of the phenyl rings of the PPh_3 group.

Comment

Enol lactones are found in many marine and terrestrial organisms and a large number of natural and synthetic compounds bearing this functionality exhibit interesting and useful biological properties (Pattenden, 1978). The most direct approach to the synthesis of enol lactones is through a Wittig condensation of suitably substituted cyclic anhydrides with stabilized phosphoranes. Although a number of such reactions have been reported (Chopard, Hudson & Searle, 1965; Doyle & Massy-Westropp, 1982, and references therein; Knight & Pattenden, 1975, 1979; Kayser & Breau, 1988, 1989; Breau & Kayser, 1989), the mechanism and the factors controlling the regio- and stereoselectivity have not been systematically investigated until recently (Kayser, Hatt & Hooper, 1991, 1992, Kayser, Hatt, Yu & Hooper, 1993).

During low-temperature NMR studies of the condensations between phthalic anhydride and the stabilized phosphorane methyl triphenylphosphoranylideneacetate (1), a high-field methoxy signal at 2.982 p.p.m. was observed. Trapping with CH_2N_2 gave the product (3), which confirmed the existence of an unstable addition product (2*a*), apparently in equilibrium with (2*b*). The trapped compound (3) showed two methoxy signals: the new methoxy ester signal at 3.826 p.p.m. and the previously noted high-field signal at 3.016 p.p.m. (Kayser *et al.* 1991).



To understand the reason for the high-field methoxy ester signal, the crystal structure of compound (3) was determined.

The results of the two crystal structure determinations have shown that both crystals correspond to the same compound. Crystal (II) contains a molecule of solvent (ethanol), while no solvent was detected in crystal (I). The NMR spectra of the mixture have shown that the crystals containing ethanol are present in a smaller quantity (~25%). Labeled diagrams of the two crystals are shown in Figs. 1 and 2. The two structures are very similar except for the conformation in the crystalline state around C(8). This is evident from Figs. 1 and 2. This difference is caused by the presence of hydrogen bonds in crystal (II), involving O(1) and the ethanol molecule.

The P—C(phenyl) distances are normal and vary from 1.808 (6) to 1.819 (5) Å for (I) and from 1.811 (6) to 1.817 (6) for (II), while the fourth bond P—C(8) is shorter: 1.759 (4) for (I) and 1.763 (6) Å

Acta Crystallographica Section C
ISSN 0108-2701 ©1994

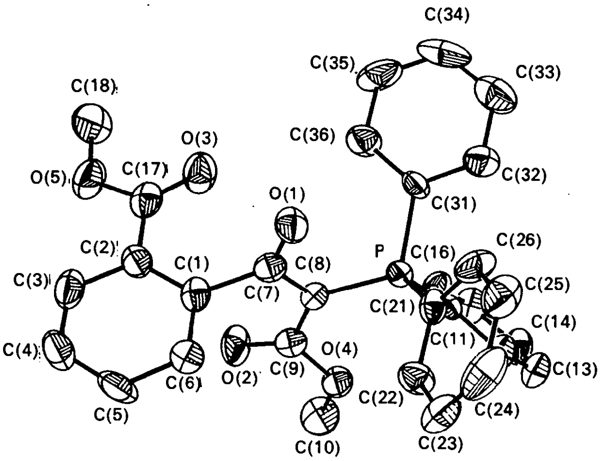


Fig. 1. Labelled diagram of (I).

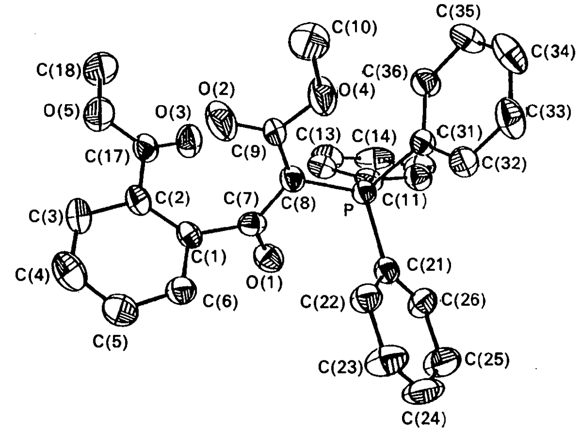


Fig. 2. Labelled diagram of (II).

for (II). These results are similar to those obtained for the crystal structure of Ph_3P-$C(CO_2Et)$-CO-CH_2-CH_2-COOH by Abell, Clark & Robinson (1988), who attributed the shorter distance to the multiple nature of the P—C bond. They assigned the phosphorane structure in both solution and the solid state rather than that of a phosphonium salt. Other structures (Cameron, Duncanson, Freer, Armstrong & Ramage, 1975) have been reported showing similar results. For $Ph_3P{:}CH_2$, the P—CH_2 bond distances are much shorter: 1.662 (8) and 1.659 (8) Å (Bart, 1969). The angles around the P atom are close to the tetrahedral value. The angles C(8)—P—C(Ph) are slightly larger [average 112.0 (2) for (I) and 112.1 (2)° for (II)] than the C(Ph)—P—C(Ph) values [average 106.6 (2) for (I) and 106.3 (3)° for (II)], which is in agreement with the hypothesis of multiple bonding for the P—C(8) bond. In both crystals (I) and (II), the P—C(8)—C(7) angle is much smaller [111.4 (4) and 110.7 (4)°, respectively] than the P—C(8)—C(9) angle [126.2 (4) and 126.2 (4)°, respectively], while the angle C(7)—C(8)—C(9) is 122.2 (4) and 122.8 (5)°, respectively. All these values are close to those reported by Abell *et al.* (1988).

The atoms P, C(7), C(8) and C(9) are planar, as shown by the torsion angles (Table 2). The weighted best planes through the four atoms have been calculated (deposited material). The four atoms O(1), O(2), O(4) and C(10) are also in the same plane. The C(7)—O(1) bond length is indentical for the two crystals [1.237 (6) for (I) and 1.232 (6) Å for (II)], even if O(1) in crystal (II) is involved in hydrogen bonding with the ethanol molecule.

The four atoms of the methyl ester group on C(2) (except H) are in the same plane as the phenyl ring. The deviations of these atoms from the weighted best plane calculated through C(1)–C(6) are: C(17) 0.005 (5) and 0.089 (8), O(3) 0.059 (4) and 0.418 (6), O(5) −0.084 (4) and −0.170 (6), C(18) −0.122 (7) and −0.008 (9) Å, for crystals (I) and (II), respectively. This planarity would extend the aromaticity of the phenyl ring. The dihedral angle between the phenyl ring [C(1)–C(6)] and the plane through P, C(7), C(8) and C(9) is 85.3 (2) for (I) and 73.0 (2)° for (II).

The packing diagrams of the molecules in the crystals are part of the deposited material. No hydrogen bond is expected in compound (I). Therefore, the molecules are held together only by van der Waals forces. The ethanol molecule in crystal (II) is disordered on two positions around an inversion centre. The bond distances are C(19)—C(19)′ 1.567 (17) and O(6)—C(19) 1.423 (15) Å, while the angle O(6)—C(19)—C(19)′ is 107.0 (9)°. Hydrogen bonding involving the ethanol molecule with one of the other O atoms would be expected. The distance O(6)···O(1) is 2.841 (9) Å with a favorable C(19)—O(6)···O(1) angle of 120.7 (7)°. This hydrogen bond is responsible for the different conformation in the two crystals around C(8).

The methoxy group [O(4)—C(10)H_3] is located directly above the three phenyl rings of the PPh_3 substituent. It can be concluded, therefore, that the high-field methoxy signal at 3.016 p.p.m. is due to the shielding magnetic anisotropic effect of the phenyl rings. A similar structural feature was observed in the crystal structure of a phosphorane resulting from the condensation of succinic anhydride with a related ylide ethyl(triphenylphosphoranylidine) acetate (Abell *et al.*, 1988).

Experimental

The compound was synthesized as described by Kayser *et al.*, (1991). The product was first recrystallized in ethanol and later in methanol. Crystals suitable for X-ray diffraction were isolated.

Crystal (I)

Crystal data

$C_{30}H_{25}O_5P$
$M_r = 496.50$
Monoclinic
$P2_1/c$
$a = 9.796\ (4)$ Å
$b = 22.623\ (12)$ Å
$c = 13.863\ (5)$ Å
$\beta = 122.89\ (3)°$
$V = 2580\ (2)$ Å^3
$Z = 4$
$D_x = 1.278$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 15 reflections
$\theta = 15\text{-}25°$
$\mu = 0.14$ mm^{-1}
$T = 295$ K
Rectangular plate
$0.35 \times 0.21 \times 0.10$ mm
Colourless

Data collection

Syntex $P\bar{1}$ diffractometer
$2\theta/\theta$ scans
Absorption correction: none
5397 measured reflections
5096 independent reflections
1470 observed reflections $[I \geq 2.5\sigma(I)]$
$R_{\text{int}} = 0.04$

$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 27$
$l = -14 \rightarrow 14$
3 standard reflections monitored every 97 reflections intensity variation: <2%

Refinement

Refinement on F
$R = 0.053$
$wR = 0.043$
$S = 1.10$
1470 reflections
325 parameters
All H-atom parameters refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.08$
$\Delta\rho_{\max} = 0.13$ e Å^{-3}
$\Delta\rho_{\min} = -0.09$ e Å^{-3}
Atomic scattering factors from Cromer & Liberman (1970)

Crystal (II)

Crystal data

$C_{30}H_{25}O_5P.0.5C_2H_6O$
$M_r = 519.53$
Triclinic
$P\bar{1}$
$a = 10.562\ (5)$ Å
$b = 10.459\ (5)$ Å
$c = 13.161\ (5)$ Å
$\alpha = 88.18\ (4)°$
$\beta = 72.46\ (4)°$
$\gamma = 71.76\ (4)°$
$V = 1313.5\ (11)$ Å^3
$Z = 2$
$D_x = 1.313$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 15 reflections
$\theta = 14\text{-}25°$
$\mu = 0.14$ mm^{-1}
$T = 295$ K
Square plate
$0.288 \times 0.288 \times 0.115$ mm
Colourless

Data collection

Syntex $P\bar{1}$ diffractometer
$2\theta/\theta$ scans
Absorption correction: none
4930 measured reflections
4656 independent reflections
2167 observed reflections $[I \geq 2.8\sigma(I)]$
$R_{\text{int}} = 0.046$

$\theta_{\max} = 25°$
$h = 0 \rightarrow 12$
$k = -11 \rightarrow 12$
$l = -15 \rightarrow 15$
3 standard reflections monitored every 97 reflections intensity variation: <3%

Refinement

Refinement on F
$R = 0.076$
$wR = 0.074$
$S = 1.86$
2167 reflections
343 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F) + 0.0006F^2]$
$(\Delta/\sigma)_{\max} = 0.09$
$\Delta\rho_{\max} = 0.42$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Crystal (I)				
P	0.5801 (2)	0.1045 (1)	0.2968 (1)	0.0234 (5)
O(1)	0.8019 (4)	0.1796 (1)	0.4717 (3)	0.0330 (15)
O(2)	0.7513 (5)	0.0157 (2)	0.5888 (3)	0.0415 (17)
O(3)	0.6762 (4)	0.1706 (2)	0.6368 (3)	0.0516 (20)
O(4)	0.6458 (4)	−0.0174 (1)	0.4099 (3)	0.0382 (16)
O(5)	0.8254 (5)	0.1677 (2)	0.8279 (3)	0.0590 (20)
C(1)	0.9433 (6)	0.1175 (2)	0.6337 (4)	0.0302 (20)
C(2)	0.9488 (6)	0.1329 (2)	0.7332 (4)	0.0325 (21)
C(3)	1.0932 (7)	0.1236 (2)	0.8397 (4)	0.0441 (24)
C(4)	1.2282 (7)	0.1003 (3)	0.8473 (4)	0.0462 (23)
C(5)	1.2222 (7)	0.0843 (2)	0.7492 (4)	0.0420 (22)
C(6)	1.0799 (6)	0.0936 (2)	0.6426 (4)	0.0353 (21)
C(7)	0.8038 (6)	0.1305 (2)	0.5116 (4)	0.0284 (20)
C(8)	0.6955 (5)	0.0842 (2)	0.4427 (4)	0.0227 (19)
C(9)	0.7006 (6)	0.0261 (2)	0.4892 (4)	0.0302 (20)
C(10)	0.6225 (8)	−0.0742 (2)	0.4457 (5)	0.0540 (24)
C(11)	0.4381 (6)	0.0469 (2)	0.2065 (4)	0.0257 (19)
C(12)	0.4456 (6)	0.0189 (2)	0.1217 (4)	0.0383 (20)
C(13)	0.3302 (7)	−0.0226 (2)	0.0534 (4)	0.0430 (22)
C(14)	0.2090 (7)	−0.0373 (2)	0.0724 (4)	0.0415 (21)
C(15)	0.2024 (6)	−0.0105 (2)	0.1577 (4)	0.0446 (22)
C(16)	0.3161 (6)	0.0324 (2)	0.2243 (4)	0.0332 (20)
C(17)	0.8032 (7)	0.1591 (2)	0.7254 (4)	0.0402 (21)
C(18)	0.6922 (9)	0.1914 (3)	0.8324 (5)	0.0621 (27)
C(21)	0.7138 (6)	0.1193 (2)	0.2474 (4)	0.0293 (20)
C(22)	0.8385 (6)	0.0791 (2)	0.2790 (4)	0.0338 (21)
C(23)	0.9473 (6)	0.0880 (2)	0.2459 (4)	0.0497 (22)
C(24)	0.9344 (7)	0.1373 (2)	0.1846 (5)	0.0600 (24)
C(25)	0.8141 (7)	0.1779 (2)	0.1541 (5)	0.0466 (23)
C(26)	0.7023 (7)	0.1685 (2)	0.1848 (4)	0.0390 (21)
C(31)	0.4436 (6)	0.1663 (2)	0.2649 (4)	0.0266 (19)
C(32)	0.3384 (7)	0.1831 (2)	0.1526 (4)	0.0423 (22)
C(33)	0.2233 (7)	0.2268 (3)	0.1243 (5)	0.0484 (23)
C(34)	0.2155 (7)	0.2535 (3)	0.2101 (6)	0.0546 (24)
C(35)	0.3194 (8)	0.2370 (3)	0.3214 (6)	0.0632 (23)
C(36)	0.4355 (7)	0.1933 (2)	0.3519 (5)	0.0355 (21)
Crystal (II)				
P	0.2359 (2)	0.8936 (2)	0.1584 (1)	0.0305 (5)
O(1)	0.2529 (4)	0.6753 (4)	0.2795 (3)	0.0450 (8)
O(2)	−0.1540 (5)	0.9297 (5)	0.3365 (4)	0.0747 (8)
O(3)	−0.0097 (5)	0.6108 (4)	0.2271 (4)	0.0531 (8)
O(4)	−0.0727 (5)	1.0675 (5)	0.2274 (4)	0.0595 (8)
O(5)	−0.2102 (5)	0.5926 (5)	0.3362 (4)	0.0644 (8)
O(6)	0.4242 (8)	0.5055 (8)	0.3925 (7)	0.0850 (8)
C(1)	0.0336 (6)	0.7197 (5)	0.4079 (5)	0.0336 (8)
C(2)	−0.0699 (6)	0.6612 (6)	0.4158 (5)	0.0370 (8)
C(3)	−0.1507 (6)	0.6345 (6)	0.5146 (5)	0.0442 (8)
C(4)	−0.1221 (7)	0.6635 (6)	0.6057 (5)	0.0538 (8)
C(5)	−0.0201 (6)	0.7207 (6)	0.6005 (5)	0.0497 (8)
C(6)	0.0587 (6)	0.7485 (6)	0.5016 (5)	0.0423 (8)
C(7)	0.1302 (6)	0.7495 (6)	0.3062 (5)	0.0354 (8)
C(8)	0.0886 (6)	0.8647 (5)	0.2501 (5)	0.0339 (8)
C(9)	−0.0549 (6)	0.9534 (6)	0.2764 (5)	0.0359 (8)
C(10)	−0.2097 (6)	1.1578 (6)	0.2467 (6)	0.0652 (8)
C(11)	0.3273 (6)	0.7683 (6)	0.0468 (5)	0.0368 (8)
C(12)	0.2845 (6)	0.6559 (6)	0.0425 (5)	0.0419 (8)
C(13)	0.3502 (6)	0.5635 (6)	−0.0436 (5)	0.0506 (8)

C(14)	0.4538 (7)	0.5834 (7)	−0.1279 (5)	0.0598 (8)
C(15)	0.4931 (6)	0.6968 (7)	−0.1276 (5)	0.0544 (8)
C(16)	0.4242 (6)	0.7908 (6)	−0.0408 (5)	0.0451 (8)
C(17)	−0.0939 (6)	0.6211 (6)	0.3171 (5)	0.0416 (8)
C(18)	−0.2373 (7)	0.5420 (7)	0.2477 (6)	0.0693 (8)
C(19)	0.4447 (8)	0.5583 (9)	0.4825 (7)	0.1149 (9)
C(21)	0.3542 (6)	0.9068 (6)	0.2297 (5)	0.0344 (8)
C(22)	0.2913 (6)	0.9625 (6)	0.3351 (5)	0.0433 (8)
C(23)	0.3738 (7)	0.9850 (7)	0.3923 (6)	0.0624 (8)
C(24)	0.5142 (7)	0.9479 (7)	0.3468 (6)	0.0680 (8)
C(25)	0.5799 (7)	0.8937 (7)	0.2425 (5)	0.0621 (8)
C(26)	0.4961 (6)	0.8725 (6)	0.1843 (5)	0.0451 (8)
C(31)	0.1922 (6)	1.0517 (5)	0.0953 (5)	0.0322 (8)
C(32)	0.2079 (6)	1.1654 (6)	0.1334 (5)	0.0429 (8)
C(33)	0.1632 (7)	1.2879 (6)	0.0893 (5)	0.0552 (8)
C(34)	0.1001 (7)	1.2936 (6)	0.0107 (5)	0.0586 (8)
C(35)	0.0873 (6)	1.1804 (6)	−0.0287 (5)	0.0509 (8)
C(36)	0.1332 (6)	1.0593 (6)	0.0140 (5)	0.0436 (8)

Table 2. *Selected geometric parameters* (Å, °)

Crystal (I)

P—C(8)	1.759 (4)	C(17)—O(5)	1.330 (7)
P—C(11)	1.819 (5)	O(4)—C(10)	1.439 (7)
P—C(21)	1.808 (6)	O(5)—C(18)	1.443 (10)
P—C(31)	1.817 (6)	C(8)—C(7)	1.425 (7)
C(7)—O(1)	1.237 (6)	C(8)—C(9)	1.454 (7)
C(9)—O(2)	1.211 (6)	C(7)—C(1)	1.518 (7)
C(17)—O(3)	1.211 (7)	C(2)—C(17)	1.493 (9)
C(9)—O(4)	1.351 (6)		

C(8)—P—C(11)	112.2 (2)	C(8)—C(9)—O(4)	113.4 (4)
C(8)—P—C(21)	109.8 (2)	O(1)—C(7)—C(1)	117.2 (5)
C(8)—P—C(31)	114.1 (2)	O(2)—C(9)—O(4)	121.5 (5)
C(11)—P—C(21)	108.3 (2)	C(9)—O(4)—C(10)	116.0 (4)
C(11)—P—C(31)	101.4 (2)	C(7)—C(1)—C(2)	125.6 (5)
C(21)—P—C(31)	110.7 (2)	C(7)—C(1)—C(6)	114.5 (5)
P—C(8)—C(7)	111.1 (4)	C(1)—C(2)—C(17)	120.4 (5)
P—C(8)—C(9)	126.2 (4)	C(3)—C(2)—C(17)	120.9 (5)
P—C(11)—C(12)	122.8 (4)	C(2)—C(17)—O(3)	125.0 (5)
P—C(11)—C(16)	117.4 (4)	C(2)—C(17)—O(5)	112.7 (5)
P—C(21)—C(22)	116.9 (4)	O(3)—C(17)—O(5)	122.3 (5)
P—C(21)—C(26)	124.1 (4)	C(17)—O(5)—C(18)	118.3 (5)
P—C(31)—C(32)	119.2 (4)	C(1)—C(2)—C(3)	118.7 (5)
P—C(31)—C(36)	120.5 (4)	C(2)—C(3)—C(4)	121.2 (5)
C(7)—C(8)—C(9)	122.2 (4)	C(3)—C(4)—C(5)	120.1 (6)
C(8)—C(7)—O(1)	122.3 (5)	C(4)—C(5)—C(6)	119.4 (5)
C(8)—C(7)—C(1)	119.9 (4)	C(5)—C(6)—C(1)	121.0 (5)
C(8)—C(9)—O(2)	125.1 (5)	C(6)—C(1)—C(2)	119.5 (5)

P—C(8)—C(7)—C(1)	164.5 (4)	C(1)—C(7)—C(8)—C(9)	−7.8 (8)
P—C(8)—C(7)—O(1)	−6.1 (7)	C(2)—C(17)—O(5)—C(18)	178.5 (5)
P—C(8)—C(9)—O(2)	163.2 (4)	C(1)—C(2)—C(17)—O(3)	2.6 (9)
P—C(8)—C(9)—O(4)	−18.2 (7)	C(1)—C(2)—C(17)—O(5)	−176.1 (5)
C(2)—C(1)—C(7)—O(1)	−84.8 (7)	C(3)—C(2)—C(17)—O(3)	−177.0 (6)
C(2)—C(1)—C(7)—C(8)	104.0 (6)	C(3)—C(2)—C(17)—O(5)	4.3 (8)
C(6)—C(1)—C(7)—O(1)	88.6 (6)	O(3)—C(17)—O(5)—C(18)	−0.2 (8)
C(6)—C(1)—C(7)—C(8)	−82.5 (6)		

Crystal (II)

P—C(8)	1.763 (6)	C(17)—O(5)	1.307 (9)
P—C(11)	1.811 (6)	O(4)—C(10)	1.409 (7)
P—C(21)	1.813 (8)	O(5)—C(18)	1.432 (10)
P—C(31)	1.817 (6)	C(8)—C(7)	1.413 (8)
C(7)—O(1)	1.232 (6)	C(8)—C(9)	1.449 (7)
C(9)—O(2)	1.198 (8)	C(7)—C(1)	1.509 (8)
C(17)—O(3)	1.231 (7)	C(2)—C(17)	1.491 (10)
C(9)—O(4)	1.327 (8)	O(6)—C(19)	1.423 (15)
		C(19)—C(19′)	1.567 (17)

C(8)—P—C(11)	114.4 (3)	C(8)—C(9)—O(4)	115.0 (5)
C(8)—P—C(21)	108.9 (3)	O(1)—C(7)—C(1)	116.4 (5)
C(8)—P—C(31)	113.1 (3)	O(2)—C(9)—O(4)	120.0 (5)
C(11)—P—C(21)	110.5 (3)	C(9)—O(4)—C(10)	118.5 (5)
C(11)—P—C(31)	103.8 (3)	C(7)—C(1)—C(2)	126.6 (6)
C(21)—P—C(31)	105.6 (3)	C(7)—C(1)—C(6)	114.9 (6)
P—C(8)—C(7)	110.7 (4)	C(1)—C(2)—C(17)	120.0 (5)
P—C(8)—C(9)	126.2 (4)	C(3)—C(2)—C(17)	118.3 (6)
P—C(11)—C(12)	119.9 (4)	C(2)—C(17)—O(3)	123.3 (7)
P—C(11)—C(16)	120.9 (5)	C(2)—C(17)—O(5)	113.2 (5)
P—C(21)—C(22)	115.9 (5)	O(3)—C(17)—O(5)	123.4 (7)
P—C(21)—C(26)	123.8 (5)	C(17)—O(5)—C(18)	117.6 (5)
P—C(31)—C(32)	120.6 (5)	C(1)—C(2)—C(3)	121.6 (6)
P—C(31)—C(36)	119.0 (5)	C(2)—C(3)—C(4)	118.2 (7)
C(7)—C(8)—C(9)	122.8 (5)	C(3)—C(4)—C(5)	121.4 (6)
C(8)—C(7)—O(1)	120.5 (5)	C(4)—C(5)—C(6)	119.9 (7)
C(8)—C(7)—C(1)	122.6 (4)	C(5)—C(6)—C(1)	120.4 (7)
C(8)—C(9)—O(2)	125.0 (6)	C(6)—C(1)—C(2)	118.4 (5)
		C(19)—C(19′)—O(6)	107.0 (9)

P—C(8)—C(7)—C(1)	163.9 (6)	C(1)—C(7)—C(8)—C(9)	−9.0 (11)
P—C(8)—C(7)—O(1)	−8.7 (9)	C(2)—C(17)—O(5)—C(18)	174.8 (5)
P—C(8)—C(9)—O(2)	177.5 (6)	C(1)—C(2)—C(17)—O(3)	15.4 (8)
P—C(8)—C(9)—O(4)	−1.7 (9)	C(1)—C(2)—C(17)—O(5)	−167.3 (5)
C(2)—C(1)—C(7)—O(1)	−106.4 (8)	C(3)—C(2)—C(17)—O(3)	−162.6 (5)
C(2)—C(1)—C(7)—C(8)	80.7 (8)	C(3)—C(2)—C(17)—O(5)	14.6 (7)
C(6)—C(1)—C(7)—O(1)	70.0 (7)	O(3)—C(17)—O(5)—C(18)	2.4 (9)
C(6)—C(1)—C(7)—C(8)	−102.9 (8)		

The recrystallized product showed, under the microscope, two different shapes of crystals. One crystal of each type was selected after examination under a polarizing microscope for homogeneity. Other information on crystallographic measurements and structure resolution is given by Melanson & Rochon (1975). Corrections were made for Lorentz-polarization effects and the anomalous-dispersion terms of P were included in the calculations (Cromer, 1965; *International Tables for X-ray Crystallography*, 1974, Vol. IV). The structures were solved using direct methods with a Nicolet *SHELXTL* system (Sheldrick, 1984). Other non-H atoms were located by structure factors and Fourier-map calculations. Two residual peaks close to an inversion centre were observed for crystal (II); these could be assigned to a molecule of solvent, either methanol or ethanol - the NMR spectrum of compound (II) showed the presence of ethanol. Occupancy factors were 1 for C(19) and 0.5 for O(6). Most H-atom positions were located; others were calculated with C—H = 0.96 Å. In the last series of cycles, the refinement [by block diagonals for (I) and by block cascade procedure (*SHELXTL*) for (II)] included the coordinates and isotropic displacement parameters of the H atoms. The calculations were performed on a Cyber 860 [for (I)] using programs already described (Melanson & Rochon, 1975) and with a Nicolet *SHELXTL* system.

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data, along with packing diagrams have been deposited with the IUCr (Reference: CD1055). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1994). **C50**, 1169–1171

2,2′-Azinodimethyldiphenol, $C_{14}H_{12}N_2O_2$

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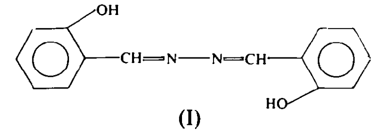
(*Received* 5 *July* 1993; *accepted* 3 *December* 1993)

Abstract

The X-ray single-crystal structure determination of the title compound reveals a *trans* planar structure in which the molecules stack in columns parallel to the *c* axis of the unit cell. Each molecule contains intramolecular O···N hydrogen bonds [2.611 (6) Å].

Comment

Proton transfer, accompanied by a configurational change of the π-electron structure, is one of the key reactions in many proposals for molecular-electronic devices. Schiff base compounds undergo photochromism and thermochromism in the solid state by proton transfer from the hydroxyl O atom to the imine N atom, which may be reversible. Molecular switches may also be based on proton transfer. In the molecular systems, with proton transfer, the charge transport occurs through overlapping intermolecular π orbitals. The electrical properties depend heavily on the intermolecular interactions. Thus, a thermochromic Schiff base may be a candidate for construction of a novel type of conductive organic material in which the proton motion is essentially correlated to the electron conduction (Hadjoudis, Vittorakis, Moustakali-Mavridis, 1987; Inabe, 1991). These phenomena may be related to the molecular packing in the lattice (Bregman, Leiserowitz & Schmidt, 1964). In this paper, the structure of the title compound, (I), is described.



(I)

The molecular geometry is illustrated in Fig. 1. The molecule is located on the centre of inversion so that only one half of the molecule is crystallographically independent. The N—C(7) [1.285 (7) Å] and N—N′ [1.386 (9) Å] distances indicate that these correspond to double and single bonds, respectively. Although the bond length O—H(O) is typical of a hydroxyl group, the distance between the O and N atoms, which are intramolecularly hydrogen bonded, is 2.611 (6) Å, and is comparable to those observed for thermochromic *N*,*N*′-disalicylidene-1,6-pyrenediamine [2.614 Å (Inabe, Hoshino, Mitani & Maruyama, 1989)] and photochromic 2-chloro-*N*-salicylideneaniline [2.609 Å (Bregman, Leiserowitz & Osaki, 1964)]. The O—C(1) bond length [1.364 (8) Å] is in the range observed for other *N*-salicylideneanilines (Inabe, Hoshino, Mitani & Maruyama, 1989; Bregman, Leiserowitz & Osaki, 1964; Bregman, Leiserowitz & Schmidt, 1964). The torsion angles N—C(7)—C(6)—C(1) [−2.61 (7)°] and N—C(7)—C(6)—C(5) [179.51 (7)°] indicate that the molecule is practically planar. The maximum deviation from the mean plane is 0.016 Å for non-H atoms. The molecules stack tightly to form columns

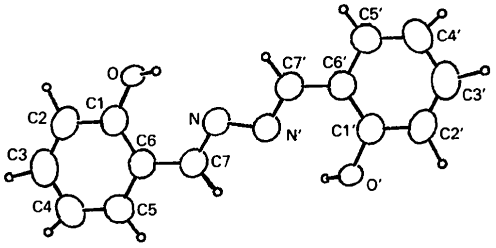


Fig. 1. A view of the title molecule with the atomic numbering scheme.

Acta Crystallographica Section C
ISSN 0108-2701 ©1994