Crystal structure of 2-dimethoxy-phosphinyl-1,3-benzodithiole, $(C_6H_4S_2CH)PO(OCH_3)_2$

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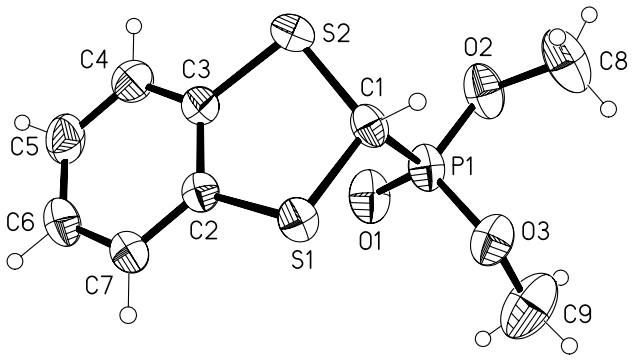
Received September 9, 2003, accepted and available on-line November 11, 2003; CCDC-No. 1267/1147



Abstract

$C_9H_{11}O_3PS_2$, monoclinic, $P12_1/n1$ (No. 14), a = 9.791(3) Å, b = 10.943(2) Å, c = 11.619(3) Å, β = 108.970(2)°, V = 1177.3 Å^3, Z = 4, $R_{gt}(F)$ = 0.035, $wR_{ref}(F^2)$ = 0.078, T = 293 K.

Source of material

The title compound can be easily produced by Michaelis-Arbuzov reaction [1,2]. Recrystallization from ethanol afforded colourless crystals suitable for X-ray analysis. ^{1}H-NMR spectrum shows a doublet signal at δ = 4.875–4.893 ppm (J = 5.2 Hz) assignable to 1-CH, a doublet signal at δ = 3.767–3.803 ppm (J = 9.8 Hz) assignable to POMe, and a multiple signal at δ = 7.0263–7.2616 ppm assignable to the four aryl hydrogen atoms.

Discussion

The title compound can be deprotonated with butyllithium in Witting Reaction to give phosphonate carbanion [1], which is high reactive with a variety of carbonyl compounds to produce alkenes especially large conjugation compounds. The distances between the two S atoms and the least-square plane of benzene ring are 0.065(4) Å and 0.069(4) Å, which are below 5% of C—C and C—S bond lengths. The dihedral angle between benzene ring plane and S1-C2-C3 plane is 2.1° and the dihedral angle between benzene ring plane and S2-C3-C2 plane is 2.2°. So it can be thought that the two S atoms are on the same plane with the benzene ring. The bond lengths of S1—C1, S1—C2, S2—C1 and S2—C3 are in the range 1.759 Å – 1.814 Å, which are longer than the value existing in strong conjugation system (1.735 Å – 1.800 Å, [3]), and shorter than the value of weak conjugation's bonds (1.77 Å – 1.84 Å, [4]). As seen from the dihedral angle of 29° between the C1-S1-S2 and S1-C2-C3-S2 planes, the five-membered C1-S1-C2-S2-C3 ring has an envelope-like conformation, and the methylene C1 atom has a distance of –0.523(2) Å to the least-square plane. They are smaller than those reported (35.0° and 0.627 Å, correspondingly [4]). The bond lengths of S—C (aryl) are shorter than that of S—C (ordinary) in all the mentioned three compounds (present work and [3,4]), and the bond lengths of S—C are not equal. Accordingly, a conclusion is obtained that the bond lengths are shortened along with the enhancing of conjugation effect.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.4 × 0.5 × 0.6 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.71 cm^{-1}
Diffractometer, scan mode:	Bruker P4, ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2739, 2075
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1817
$N(param)_{refined}$:	137
Program:	SHELXTL [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	0.1826	1.0495	0.7635	0.057
H(4A)	4*e*	–0.2320	0.7504	0.5693	0.082
H(5A)	4*e*	–0.3317	0.6249	0.6859	0.088
H(6A)	4*e*	–0.2482	0.6372	0.8972	0.077
H(7A)	4*e*	–0.0615	0.7725	0.9969	0.063
H(8A)	4*e*	0.4305	0.9942	0.5675	0.121
H(8B)	4*e*	0.3581	1.0658	0.6493	0.121
H(8C)	4*e*	0.5048	0.9975	0.7090	0.121
H(9A)	4*e*	0.5995	0.8881	1.0158	0.136
H(9B)	4*e*	0.5078	0.7680	0.9826	0.136
H(9C)	4*e*	0.5894	0.8170	0.8961	0.136

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	4*e*	0.09582(7)	0.95351(6)	0.90399(6)	0.0547(4)	0.0445(4)	0.0531(4)	–0.0045(3)	0.0229(3)	–0.0061(3)
S(2)	4*e*	–0.01102(8)	0.93930(7)	0.63803(6)	0.0661(5)	0.0635(5)	0.0524(4)	–0.0002(4)	0.0201(3)	0.0150(3)
P(1)	4*e*	0.29138(8)	0.85965(6)	0.77212(7)	0.0554(4)	0.0363(4)	0.0754(5)	–0.0028(3)	0.0313(4)	–0.0091(3)
O(1)	4*e*	0.2540(2)	0.7312(2)	0.7751(2)	0.073(1)	0.035(1)	0.116(2)	0.0014(9)	0.041(1)	–0.007(1)
O(2)	4*e*	0.3361(2)	0.8876(2)	0.6565(2)	0.088(2)	0.065(1)	0.091(2)	–0.017(1)	0.058(1)	–0.024(1)
O(3)	4*e*	0.4154(2)	0.9092(2)	0.8851(2)	0.055(1)	0.056(1)	0.089(2)	0.0034(9)	0.016(1)	–0.009(1)
C(1)	4*e*	0.1482(3)	0.9662(2)	0.7684(2)	0.056(2)	0.034(1)	0.059(2)	–0.003(1)	0.028(1)	0.001(1)
C(2)	4*e*	–0.0385(3)	0.8432(2)	0.8413(2)	0.046(1)	0.041(1)	0.052(1)	0.002(1)	0.019(1)	–0.000(1)
C(3)	4*e*	–0.0891(3)	0.8361(2)	0.7150(2)	0.049(1)	0.052(2)	0.052(1)	–0.001(1)	0.017(1)	0.005(1)
C(4)	4*e*	–0.1975(3)	0.7552(3)	0.6565(3)	0.061(2)	0.081(2)	0.057(2)	–0.014(2)	0.011(1)	–0.004(2)
C(5)	4*e*	–0.2563(3)	0.6817(3)	0.7254(3)	0.060(2)	0.075(2)	0.084(2)	–0.024(2)	0.021(2)	–0.011(2)
C(6)	4*e*	–0.2062(3)	0.6884(3)	0.8505(3)	0.064(2)	0.057(2)	0.081(2)	–0.010(1)	0.037(2)	0.003(2)
C(7)	4*e*	–0.0967(3)	0.7684(2)	0.9096(2)	0.055(2)	0.052(2)	0.057(2)	0.000(1)	0.025(1)	0.003(1)
C(8)	4*e*	0.4139(5)	0.9950(3)	0.6445(4)	0.137(4)	0.081(2)	0.118(3)	–0.028(2)	0.088(3)	–0.017(2)
C(9)	4*e*	0.5377(4)	0.8401(4)	0.9503(4)	0.073(2)	0.088(3)	0.154(4)	0.021(2)	0.003(2)	–0.024(3)

Acknowledgments. This work has been financially supported by the State Key Fundamental Research Fund (G199903305) and Fundamental Study Fund of Tsinghua University.

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