

X-RAY AND SEMIEMPIRICAL (AM1) CALCULATION OF C₁₂H₁₁O₂P

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Abstract: The molecular structure of the title compound was studied by experimental and computational methods (X-ray and AM1). X-ray analysis shows the compound crystallizes in the monoclinic system, space group P 2₁/c. $a = 11.465(1)$, $b = 6.072(1)$, $c = 15.747(1)\text{Å}$, $\beta = 99.90(1)^\circ$. The molecular structure is not planar. There is a near-ideal tetrahedral coordination at the P atom. The crystal structure has very strong hydrogen bonds on the x-z plane. Using semiempirical (AM1) method the structure of stable conformers were determined and obtained geometries were compared with those found experimentally.

Keywords: X-Ray, Conformational analysis, AM1 method

C₁₂H₁₁O₂P'NİN X-IŞINI VE YARI-DENEYSSEL(AM1) HESAPLAMASI

Özet: Adı geçen bileşiğin moleküler yapısı deneysel ve hesaplama metodları (X-ışını ve AM1) ile incelendi. X-ışını analizi bileşiğin monoklinik sistemde ve P 2₁/c uzay grubunda kristallendiğini göstermektedir. $a = 11.465(1)$, $b = 6.072(1)$, $c = 15.747(1)\text{Å}$, $\beta = 99.90(1)^\circ$. Moleküler yapı düzlemsel değildir. P atomu etrafında ideal tetrahedrale yakın bir koordinasyon vardır. Kristal yapının x-z düzleminde çok güçlü hidrojen bağları vardır. Yarı-deneysel (AM1) metodu kullanılarak yapının kararlı formu tanımlandı. Gözlenen ve deneysel olarak bulunan geometriler karşılaştırıldı.

Anahtar Kelimeler: X-ışını, Konformasyon analizi, AM1 metod

1. Introduction

Phosphinic acids (C₁₂H₁₁O₂P) possess the ability to form strong hydrogen bonds in the solid state by virtue of the very electronegative oxygen atoms bound to an electropositive phosphor atom [1,2].

It is reported that Die Kristallstruktur von Diphenylphosphinsäure first crystallographic study about the title compound is at Chem. Ber. by Fenske et al. [3]. In this work, we discussed the results of the crystallographic and computational methods for diphenylphosphinic acid.

2. Experimental

2.1 Synthesis

The title compound reported in this work was prepared by the general method [4].

2.2 Computational Method

AM1 method [5] at the level of restricted Hartree-Fock (RHF) approach has been used for the molecular orbital calculations. The geometric structure and energy of the molecule can be calculated, by considering molecular mechanics, taking care of the mutual influences among all the atoms of the molecule. We optimized the geometry of the molecule by the MMP2 method for the molecular mechanics [6,7]. By optimization procedure, total energies of the molecule was calculated and its stable form was determined.

2.3 X-ray analysis

A summary of the crystallographic information is given in Table 1. The data was collected on a SMART CCD diffractometer using graphite-monochromated MoK α radiation with a detector distance of 4cm and swing angle of -35°. A hemisphere of the reciprocal space was covered by combination of three sets of exposures; each set had a different ϕ angle (0,88,180°) and each exposure of 30s covered 0.3° in ω . Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating thirty initial frames at the end of data collection and analysing the duplicate reflections, and was found to be negligible.

Table 1. Crystallographic data for C₁₂H₁₁O₂P.

Chemical formula	C ₁₂ H ₁₁ O ₂ P	
Molecular weight	218.18	
Crystal system, space group	Monoclinic, P 2 ₁ /c (No:14)	
Unit cell dimensions : a,b,c (Å)	a = 11.465(1), b = 6.072(1), c = 15.747(1)	
β (°)	99.90(1)	
Volume (Å ³)	V =1079.8(1)	
Z	4	
T(K)	293(2)	
F(000)	456	
Crystal size(mm)	0.32 x 0.28 x 0.22	
Crystal density (g.cm ⁻³) and μ (mm ⁻¹)	1.342, 0.23	
Absorption correction	Empirical using SADABS	
T _{max.} and T _{min.}	0.9512 / 0.9301	
$\lambda=0.71073\text{Å}$ (MoK α)	R _{int} =0.0704	
h , k , l	-15 / 11, -7 / 8 , -17 / 20	
θ range [°]	1.8 to 28.3	
Total reflections	7285	Unique data 2632 [I \geq 2 σ (I)]
Number of parameters	141	
R = 0.057	R _w = 0.149	
Goodness-of-fit on F ²	0.963	σ/Δ = 0.001
Residual electron density (eÅ ⁻³)	+0.54, -0.50	

The collected data were reduced by using the program SAINT [8] and empirical absorption correction was carried out by using the SADABS [9] program. The title compound was solved by direct methods SHELXS97 [10] and refined by full-matrix least-squares method SHELXL97 [11] on F².

The H atom of hydroxyl group was found in the difference Fourier map and allowed to refine with isotropic displacement parameters. The other H atoms attached to the phenyl rings were fixed geometrically and allowed to ride on their parent atoms.

The final conventional $R(F) = 0.057$ and $wR(F^2) = 0.149$ for $I \geq 2 \sigma(I)$ with weighting scheme, $w=1/[\sigma^2(F_o^2)+(0.0787P)^2]$.

3. Results and Discussion

In this study, $C_{12}H_{11}O_2P$ was solved by X-ray analysis method and its spatial parameters were refined. The atomic coordinates and equivalent isotropic displacement parameters with estimated standard deviations for the other atoms except H are listed in Table 2. An ORTEP-III [12] drawing of the title compound with atom numbering is shown in Figure 1. X-ray and computational results for geometrical parameters are given in Table 3.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $C_{12}H_{11}O_2P$.

Atom	x	y	z	U(eq)
P(1)	3388(1)	1064(1)	7500(1)	28(1)
O(1)	4025(1)	-645(3)	7067(1)	41(1)
O(2)	3851(2)	3443(3)	7490(1)	42(1)
C(1)	3376(2)	333(4)	8604(1)	31(1)
C(2)	2973(2)	1856(5)	9148(2)	48(1)
C(3)	2970(3)	1339(6)	10006(2)	64(1)
C(4)	3382(2)	-658(5)	10325(2)	55(1)
C(5)	3776(2)	-2178(5)	9796(2)	52(1)
C(6)	3768(2)	-1697(4)	8934(2)	43(1)
C(7)	1880(2)	1299(4)	6963(1)	30(1)
C(8)	1246(2)	3219(4)	7010(2)	45(1)
C(9)	79(3)	3375(6)	6603(2)	63(1)
C(10)	-441(2)	1612(7)	6145(2)	68(1)
C(11)	161(2)	-297(6)	6092(2)	59(1)
C(12)	1337(2)	-482(4)	6503(2)	43(1)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} (a_i^* a_j^*) (a_i a_j)$$

The conformational analysis of the molecule was made by the program PCMODEL [13]. With the obtained molecular geometry data, quantum calculations were made by using the AM1 approximation methods [14]. The highest occupied and the lowest unoccupied molecular orbital energies (HOMO : 4.51eV and LUMO : 4.63eV), the bond orders between the atoms and the electron density on the atomic orbitals, electronic energies and dipole moment (4.87 Debye) were calculated for title compound. A quantum-chemical calculation showed that the charges on atoms P1, O1 and O2 are 2.909, -1.176 and -0.846e⁻, respectively.

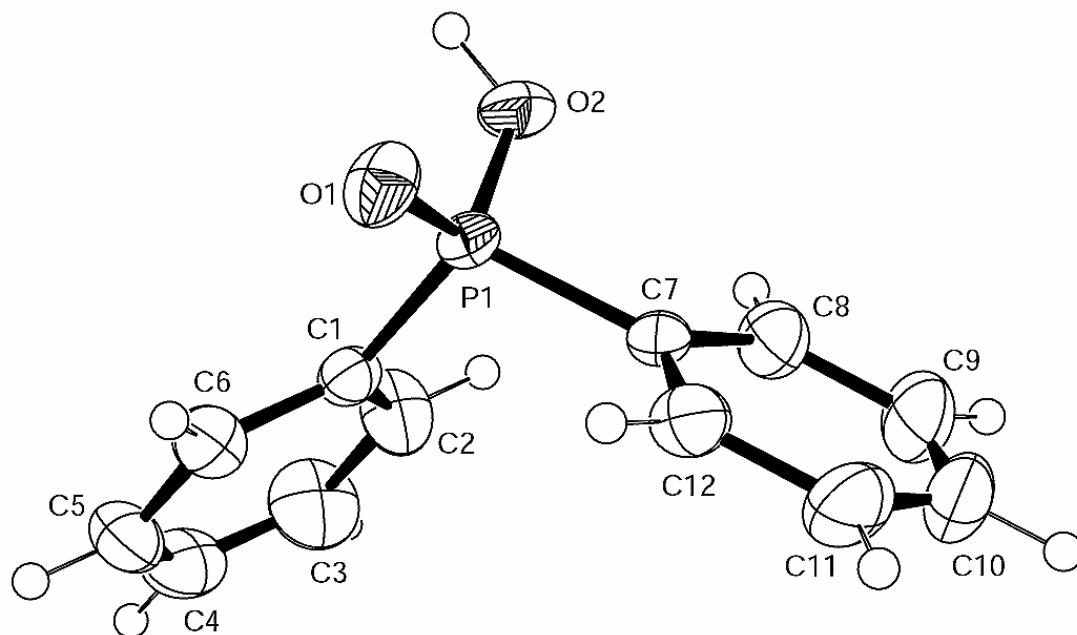


Figure 1. A view of the title compound showing the labelling of the non-H atoms. Thermal ellipsoids are shown at the 50% probability level.

Table 3. Geometric parameters for $C_{12}H_{11}O_2P$.

Bond lengths (Å)	X-Ray	AM1
P(1)-O(1)	1.500(3)	1.4640
P(1)-O(2)	1.540(2)	1.6198
P(1)-C(7)	1.795(2)	1.6169
P(1)-C(1)	1.795(2)	1.6163
C(1)-C(6)	1.383(3)	1.3958
C(1)-C(2)	1.393(3)	1.3930
C(2)-C(3)	1.387(4)	1.3936
C(3)-C(4)	1.366(4)	1.3963
C(4)-C(5)	1.371(4)	1.3963
C(5)-C(6)	1.387(4)	1.3928
C(7)-C(8)	1.383(3)	1.3970
C(7)-C(12)	1.388(3)	1.3922
C(8)-C(9)	1.384(4)	1.3931
C(9)-C(10)	1.369(5)	1.3962
C(10)-C(11)	1.359(5)	1.3966
C(11)-C(12)	1.396(3)	1.3929
Bond angles (°)		
O(1)-P(1)-O(2)	116.6(1)	105.3
O(1)-P(1)-C(7)	110.2(1)	115.2

O(2)-P(1)-C(7)	103.1(1)	105.9
O(1)-P(1)-C(1)	110.8(1)	116.3
O(2)-P(1)-C(1)	107.6(1)	105.5
C(7)-P(1)-C(1)	108.0(1)	107.8
C(6)-C(1)-C(2)	118.7(2)	119.5
C(6)-C(1)-P(1)	121.9(2)	118.8
C(2)-C(1)-P(1)	119.3(2)	121.7
C(3)-C(2)-C(1)	120.4(3)	120.5
C(4)-C(3)-C(2)	120.1(3)	119.6
C(3)-C(4)-C(5)	120.2(3)	120.2
C(4)-C(5)-C(6)	120.4(3)	119.6
C(1)-C(6)-C(5)	120.2(3)	120.5
C(8)-C(7)-C(12)	119.5(2)	119.4
C(8)-C(7)-P(1)	120.9(2)	118.2
C(12)-C(7)-P(1)	119.5(2)	122.3
C(7)-C(8)-C(9)	120.5(3)	120.4
C(10)-C(9)-C(8)	119.3(3)	119.7
C(11)-C(10)-C(9)	121.3(3)	120.2
C(10)-C(11)-C(12)	120.0(3)	119.6
C(7)-C(12)-C(11)	119.3(3)	120.6
Torsion angles (°)		
O(1)-P(1)-C(1)-C(6)	-8.3(2)	32.8
O(2)-P(1)-C(1)-C(6)	-136.8(2)	149.0
C(7)-P(1)-C(1)-C(6)	112.5(2)	-98.2
O(1)-P(1)-C(1)-C(2)	171.1(2)	-145.3
O(2)-P(1)-C(1)-C(2)	42.5(2)	-29.1
C(7)-P(1)-C(1)-C(2)	-68.2(2)	83.6
C(6)-C(1)-C(2)-C(3)	0.2(4)	1.2
P(1)-C(1)-C(2)-C(3)	-179.2(2)	179.3
C(1)-C(2)-C(3)-C(4)	1.1(5)	-0.4
C(2)-C(3)-C(4)-C(5)	-1.4(5)	-0.5
C(3)-C(4)-C(5)-C(6)	0.5(4)	0.5
C(2)-C(1)-C(6)-C(5)	-1.1(4)	-1.2
P(1)-C(1)-C(6)-C(5)	178.2(2)	-179.4
C(4)-C(5)-C(6)-C(1)	0.8(4)	0.4
O(1)-P(1)-C(7)-C(8)	-155.5(2)	-11.0
O(2)-P(1)-C(7)-C(8)	-30.3(2)	-126.9
C(1)-P(1)-C(7)-C(8)	83.4(2)	120.6
O(1)-P(1)-C(7)-C(12)	25.4(2)	167.5
O(2)-P(1)-C(7)-C(12)	150.6(2)	51.6
C(1)-P(1)-C(7)-C(12)	-95.7(2)	-60.8
C(12)-C(7)-C(8)-C(9)	0.0(4)	0.8
P(1)-C(7)-C(8)-C(9)	-179.1(2)	179.4
C(7)-C(8)-C(9)-C(10)	-0.6(4)	-0.5
C(8)-C(9)-C(10)-C(11)	1.0(5)	0.0
C(9)-C(10)-C(11)-C(12)	-0.7(5)	0.3
C(8)-C(7)-C(12)-C(11)	0.3(4)	-0.6
P(1)-C(7)-C(12)-C(11)	179.4(2)	-179.1
C(10)-C(11)-C(12)-C(7)	0.1(4)	0.0

In the crystal structure the very short P-O...O=P distance of 2.477(2)Å indicates a strong hydrogen bond as shown in Figure 2. [O2--H12O...O1(1-x,-0.5+y, 0.5-z)]. This arrangement is the more commonly found in the crystalline state for phosphonic or phosphonic acids; a dimeric form, forming an eighth-membered ring, is also seen [15,16]. The P=O and P-O distances are 1.500(3) and 1.540(2)Å, respectively. These values agree with the related compounds [17].

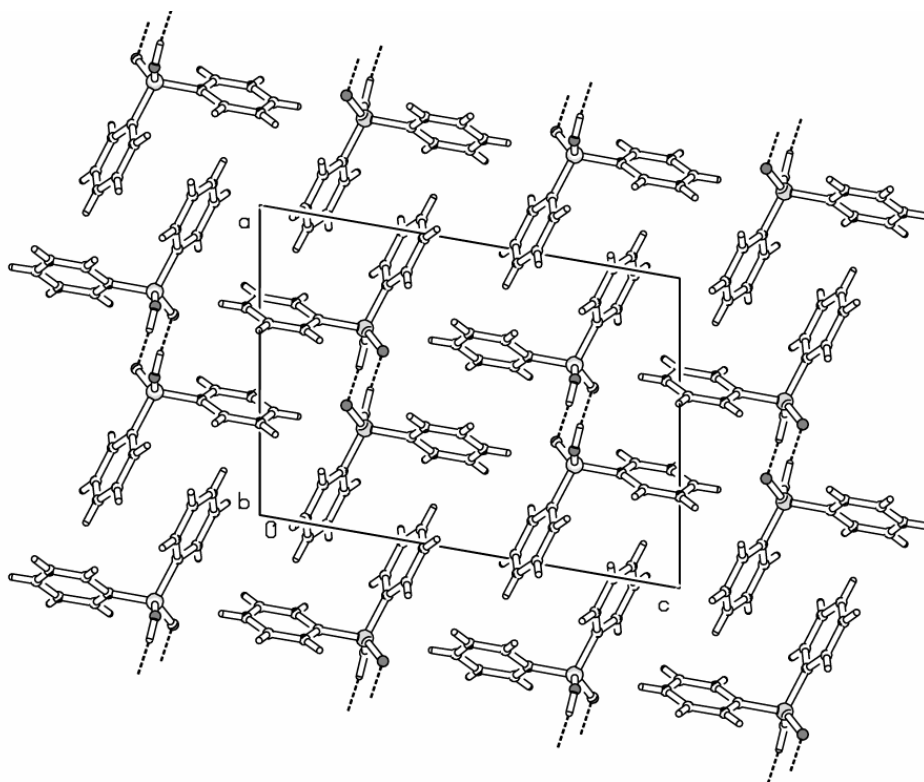


Figure 2. The packing diagram for the title compound along the b-axis. Hydrogen bonds are shown as dashed lines.

The average P-C distance is 1.795(2)Å. The mean O-P-C bond angle is 107.9(1)°, indicating tetrahedral coordination at the P atom. The C1-P1-C7 bond angle is 108.0(1)°. The dihedral angle between two phenyl rings is 70.4(1)°.

The geometry of the most stable conformation of the title compound was calculated using semiempirical (AM1) method. Calculated angles and bond lengths are almost identical to those found using X-ray analysis. But, the calculated torsion angles are different the ones of X-ray analysis. Because, in theoretical calculations, the only one molecule which its net charge is zero, was assumed in gas phase. Although, in solid phase, there are also the inter and intra molecular interactions. There exists a satisfactory agreement between experimental and calculated values.

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