

PHYSICAL
CHEMISTRY

Geometry of a Strong Hydrogen Bond As Determined by Gas-Phase Electron Diffraction: The Cyclic Dimer of Dimethylphosphinic Acid

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Presented by Academician V.V. Lunin March 18, 2003

Received March 21, 2003

As shown earlier, phosphorus acids, including dimethylphosphinic acid $\text{Me}_2\text{P}(=\text{O})\text{OH}$ (**1**) and its derivatives, are strongly associated due to $\text{O}-\text{H}\cdots\text{O}=\text{P}$ hydrogen bonding [1–4]. The structure of associates depends substantially on the phase state of the substance. X-ray and neutron diffraction show that, in crystals, these acids generally form infinite helical chains (see, e.g., [5]), in contrast to carboxylic acids, which crystallize mainly as cyclic dimers. IR spectroscopy [1–4] and DFT calculations at the B3LYP/6-31+G** level [6] imply the prevalence of cyclic dimers of the $\text{R}_2\text{P}(=\text{O})\text{OH}$ and $(\text{RO})_2\text{P}(=\text{O})\text{OH}$ acids in the gas phase. The enthalpies of dimerization obtained from measurements of their gas-phase IR spectra in the temperature range 400–650 K are equal to 25–50 kcal mol⁻¹ (12–25 kcal mol⁻¹ per $\text{O}-\text{H}\cdots\text{O}=\text{P}$ hydrogen bond in the cyclic dimer) [1–4]. These values are the highest among the known enthalpies for hydrogen bonds formed by neutral molecules and are comparable to covalent bond energies. It turned out that the parameters of the broad $\nu(\text{O}-\text{H})$ band in the IR spectra of these dimers differ from those of the carboxylic acid dimers; i.e., the hydrogen bonds in phosphorus acid dimers have a specific experimental manifestation [3]. Structural studies of this problem should provide a deeper understanding of the nature and physicochemical manifestations of strong noncovalent interactions.

Existing notions of H-bond geometry are mainly based on the results of X-ray and neutron diffraction studies in crystals. However, studies with electron diffraction in the gas phase (GED), whose conditions exclude the influence of molecular environment or packing factors, are especially valuable for elucidating how the geometrical parameters characterizing a strong hydrogen bond depend on the properties of partner

molecules. Over three decades ago, the GED method was applied for the study of dimers of the simplest carboxylic acids [7, 8]. Although the potentialities of this method increased later on, no other publications on direct gas-phase studies of hydrogen-bonded structures have appeared. In this work, the structure of cyclic dimer **1** ($\text{Me}_2\text{P}(=\text{O})\text{OH}$)₂ (Fig. 1) has been studied by gas-phase electron diffraction at a temperature of 433 K.

The electron diffraction patterns were obtained on a modified EG-100M instrument with the use of an accelerating voltage of 50 kV. Their optical densities were measured on an MFS-12000CX scanner calibrated by a photometric wedge. Primary processing of the scanned information was carried out as described in [9]. Structural analysis was performed within harmonic approximation with consideration of nonlinear kinematic effects at the first-order level of perturbation theory (*h1*) [10, 11]. The experimental molecular scattering intensity function $sM^{\text{exp}}(s)$ with the argument s ranging from 4.00 to 35.25 Å⁻¹ was used. For the transition from the internuclear distances of the r_{h1} structure to the r_e parameters of the equilibrium structure, the anharmonic corrections were calculated using the first-order level of perturbation theory [12].

The number of peaks of the experimental radial distribution curve $f(r)$ (Fig. 2) is considerably smaller than the number of internuclear distances in dimer **1**. Therefore, it is virtually impossible to uniquely resolve the overlapping contributions without invoking some additional information. Experimental [1, 2] and quantum-chemical ([6] and this work) estimates of the dimerization energy show that the presence of monomer **1** is negligible and that it cannot be detected under GED experiment conditions. In contrast to the B3LYP/6-31+G** calculations performed earlier [6], our data obtained at the RHF/6-311G** level of theory showed that the equilibrium form of dimer **1** corresponds to the point group C_2 (Table 1). This allowed us to decrease the number of molecular model parameters to be refined in

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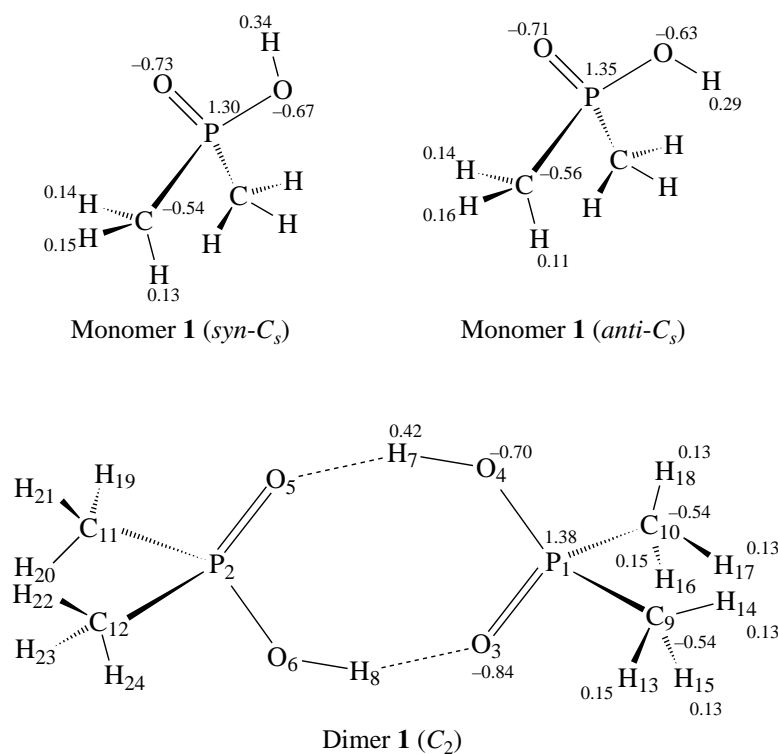


Fig. 1. Mulliken atomic charges calculated at the RHF/6-311G** level of theory for equilibrium conformations of the monomer (*syn-C_s* and *anti-C_s*) and cyclic dimer of **1** (*C₂*). The numbering of atoms for the dimer of **1** is given.

the course of GED data analysis. Since it is impossible to reliably determine experimentally the donor O–H bond length in polyatomic structures such as **1**, we were forced to fix the difference between this parameter and the varied C–H bond length at the value obtained in the RHF/6-311G** calculation. The calculated nonzero dipole moment shows that the equilibrium form of the H-bonded eight-membered ring deviates from planarity (*C_{2h}* symmetry). Although the difference in total energy between the *C₂* and *C_{2h}* forms, which is only about 0.5 kcal mol⁻¹, testifies to significant conformational flexibility of the cyclic system, the small-amplitude harmonic approach used in analysis at the *h1* level proved to be sufficient for reliable description of the fragment containing H-bonds. Thus, the maximum increase in spectroscopically calculated mean vibrational amplitude parameters $u_{ij, h1}$ as compared to $u_{ij, h0}$ values, without taking into account nonlinear kinematic effects, does not exceed 0.01 Å at the GED experiment temperature of 433 K. The mean amplitudes and vibrational corrections were calculated using the scaled quantum-chemical force field at the RHF/6-311G** level.

The results of structural analysis (the $r_{ij, h1}$ and $r_{ij, e}$ parameters) and theoretical estimates of bond lengths and most bond angles in dimer **1** are in good agreement (Table 1). The most remarkable deviation, in the case of

the CPC angle, may be explained by insufficient informativeness of the experimental $f(r)$ curve for distances above 4.2 Å (Fig. 2) involving the C atoms of the peripheral Me substituents and by inadequacy of the *h1* approximation used for these distances. The Newman projection of the experimentally obtained conformation

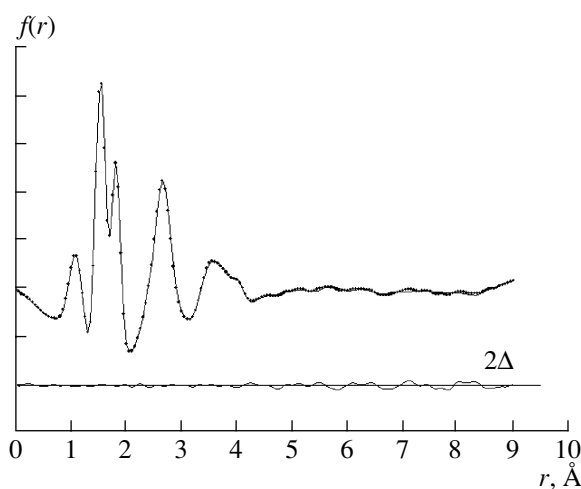


Fig. 2. Experimental (points) and theoretical (solid) radial distribution curves $f(r)$ and the difference curve (Δ) for cyclic dimer **1**. The artificial damping constant is $b = 0.001853 \text{ \AA}^2$.

Table 1. Results of gas-phase electron diffraction analysis ($T = 433$ K) and quantum-chemical calculations for the cyclic dimer ($\text{Me}_2\text{P}(=\text{O})\text{OH}$)₂

Parameter ^a	Experiment		Calculation	
	r_{h1} (C_2) ^b	r_e (C_2)	RHF/6-311G** (C_2)	B3LYP/6-31+G** (C_1) [6]
Distance, Å				
P ₁ =O ₃	1.497(3)	1.496	1.477	1.519
P ₁ -O ₄	1.573(4)	1.563	1.570	1.597
P ₁ -C ₉	1.806(4)	1.799	1.798	1.816
P ₁ -C ₁₀	1.811(4)	1.803	1.802	1.822
C-H _{av}	1.109(3)	1.091	1.084	
P ₁ ...P ₂	4.174(11)	4.121	4.171	
Bond angle, deg				
C ₉ -P ₁ =O ₃	108.8(21)		113.4	
C ₁₀ -P ₁ =O ₃	108.6(21)		111.7	
C ₉ -P ₁ -O ₄	103.2(17)		103.2	
C ₁₀ -P ₁ -O ₄	97.4(20)		106.1	
C ₉ -P ₁ -C ₁₀	119.7(10)		107.4	107.2
O ₄ -P ₁ =O ₃	119.5(5)		114.4	115.2
P ₁ -O ₄ -H ₇	116.5(17)		115.1	114.2
P ₁ =O ₃ ...H ₈	120.7(13)		134.0	
Dipole moment, D	–	–	1.37	
Total energy, au	–	–	-1140.857784	-1144.66116
ZPE, ^c au	–	–	0.203903	0.19027
Convergence factor R_{total} , % ^d	2.99		–	–

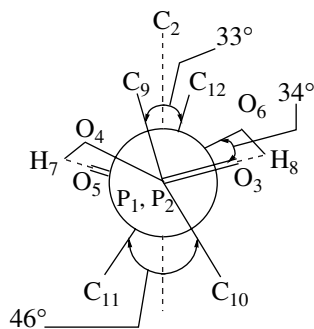
^a The numbering of the atoms is shown in Fig. 1.

^b The estimates of total experimental errors given in parentheses include the least-squares standard deviations and scale uncertainties.

^c Zero-point vibrational energy.

^d $R = 100 [\sum_j \omega_{jj} \Delta_j^2 / \sum_j \omega_{jj} (s_j M^{\text{exp}}(s_j))^2]^{1/2}$, where $\Delta_j = s_j M^{\text{exp}}(s_j) - K s_j M^{\text{theor}}(s_j)$ with an identity matrix of weight factors.

of the molecular skeleton of dimer **1** along the P...P direction and the dihedral angles characterizing this conformation are given in Scheme 1.

**Scheme 1.**

The phosphorus fragments of dimer **1** are arranged so that the C(9) and C(12) atoms of the peripheral Me

groups on one side of the ring lie farther from each other than the C(10) and C(11) atoms located on the other side of the ring. In each of the fragments, dimerization causes a turn of the O–H bond by less than 30° in comparison with the most stable, *syn-C_s*, form of monomer **1** (Fig. 1). The atoms of the O₄-P₁=O₃...H₈ chain are virtually coplanar (the dihedral angle is 6(1)°).

Since the gas-phase structure of monomer **1** has not been studied, the experimental estimates of changes in principal bond lengths upon dimerization can be obtained by comparison with the thermal average $r_{ij,g}$ parameters of related compounds, trimethylphosphine oxide $\text{Me}_3\text{P}=\text{O}$ [13] and trimethyl phosphate $(\text{MeO})_3\text{P}=\text{O}$ [14] (it is known [10] that the $r_{ij,h1}$ and $r_{ij,g}$ parameters for the chemical bonds nearly coincide). In dimer **1** (Table 1), the phosphoryl P–O bond is 0.02 Å longer than those in the $\text{Me}_3\text{P}=\text{O}$ (1.476(2) Å) and $(\text{MeO})_3\text{P}=\text{O}$ (1.477(6) Å) molecules, whereas the sin-

Table 2. Dimerization energies and geometrical parameters of the H-bonded fragments for cyclic dimers of dimethylphosphinic (**1**), formic (**2**), and acetic (**3**) acids obtained by experimental methods and quantum-chemical RHF, MP2, and B3LYP calculations

Parameter*	1				2			3		
	calculation		experiment		calculation [15]**		experiment [7]	calculation [15]**		experiment [8]
	RHF	B3LYP [6]	r_{h1}	r_e	RHF	MP2	r_a	RHF	MP2	r_a
Dimerization energy,										
$-\Delta E, \text{kcal mol}^{-1}$	21.9	23.2	24(6) [1, 2]		15.3	18.4	14 [2]	15.5	19.0	14.2 [2]
Distance, Å										
O–H	0.969	1.019	0.99	0.99	0.963	0.994	1.036(17) 1.058(17)***	0.962	0.994	1.03 (accepted)
–H...O(=X)	1.702	1.555	1.84(2)	1.72	1.831	1.706		1.819	1.694	
–O...O(=X)	2.657	2.571	2.81(2)	2.69	2.789	2.699	2.703(7) 2.722(7)***	2.779	2.688	2.684(10)
Angle, deg										
–OHO(=X)	167.7		164(3)		173.6	178.9	180 (accepted)	175.8	179.2	180 (accepted)

* X = P, C.

** Calculated with the use of the 6-31G** basis set; basis sets used in other calculations are given in the text.

*** The distance obtained for the deuterated dimer (HC(=O)OD)₂.

gle P–O bond is about 0.01 Å shorter than the analogous bond in (MeO)₃P=O (1.580(2) Å). This corresponds to electron-density transfer from the hydroxyl hydrogen atom in one of the monomer fragments to the phosphoryl oxygen atom in the other one, which follows from the change of Mulliken atomic charges upon dimerization (Fig. 1).

Quantum-chemical RHF calculations show that strengthening of the H-bond in cyclic dimer **1** as compared to the dimers of the simplest carboxylic acids entails not only a significant increase in the dimerization energy (which is in agreement with the experiment), but also noticeable changes in geometrical parameters of these bonds (Table 2). Contrary to expectations, however, the calculated elongation of donor O–H bonds in going from cyclic dimers of formic (**2**) and acetic (**3**) acids to dimer **1** is relatively small. The principal difference is the significant shortening of the =O...H bond in **1** (by 0.10–0.15 Å), which actually dictates the shortening of the –O...O= distance as well. The experimental verification of the computational results is impeded because the interpretation of GED data for **2** and **3** [7, 8], performed within the framework of the r_a structure without consideration of vibrational effects, is insufficiently reliable.

The P=O and P–O bond lengths in the helical chains formed by monomer **1** molecules in crystal ($r_{ij,\alpha}$ 1.495(4) and 1.559(4) Å as determined by X-ray diffraction [5]) are slightly different from our data for cyclic dimer **1** in the gas phase (Table 1). In the crystal, the –O...O= distance, reflecting the strength of the H-bond ($r_{ij,\alpha}$ 2.479(5) Å [5]), is significantly shorter than that for dimer **1** in the gas phase (Table 2). This confirms the conclusion based on IR spectroscopic study [4] that the transition from a gas to a solid sample leads to the strengthening of the H-bond.

ACKNOWLEDGMENTS

We are grateful to Prof. B.I. Zhilinskii for his assistance with quantum-chemical calculations.

This work was supported by the Russian Foundation for Basic Research (project nos. 02–03–32106 and 03–03–32272).

REFERENCES

1. Denisov, G.S. and Tokhadze, K.G., *Dokl. Akad. Nauk*, 1994, vol. 337, no. 1, pp. 54–56 [*Dokl. Phys. Chem.* (Engl. Transl.), vol. 337, nos. 1–3, pp. 117–119].
2. Asfin, R.E., Denisov, G.S., and Tokhadze, K.G., *J. Mol. Struct.*, 2002, vol. 608, pp. 161–168.

3. Asfin, R.E., Denisov, G.S., Poplevchenkov, D.N., *et al.*, *Pol. J. Chem.*, 2002, vol. 76, no. 9, pp. 1223–1231.
4. Tokhadze, K.G., Denisov, G.S., Wierzejewska, M., and Drozd, M., *J. Mol. Struct.*, 1997, vol. 404, pp. 55–62.
5. Giordano, F. and Ripamonti, A., *Acta Crystallogr.*, 1967, vol. 22, no. 5, pp. 678–682.
6. Gonzalez, L., Mo, O., Yanez, M., and Elguero, J., *J. Chem. Phys.*, 1998, vol. 109, no. 7, pp. 2685–2693.
7. Almeningen, A., Bastiansen, O., and Motzfeldt, T., *Acta Chem. Scand.*, 1969, vol. 23, no. 8, pp. 2848–2864; 1970, vol. 24, no. 2, pp. 747–748.
8. Derissen, J.L., *J. Mol. Struct.*, 1971, vol. 7, pp. 67–80, 81–88.
9. Atavin, E.G. and Vilkov, L.V., *Prib. Tekh. Eksp.*, 2002, vol. 6, pp. 27–30.
10. Sipachev, V.A., *Advances in Molecular Structure Research*, Greenwich: JAI Press, 1999, vol. 5, pp. 263–311.
11. Sipachev, V.A., *J. Mol. Struct.*, 2001, vol. 567/568, pp. 67–72.
12. Sipachev, V.A., *Struct. Chem.*, 2000, vol. 11, nos. 2/3, pp. 167–172.
13. Wilkins, C.H., Hagen, K., Hedberg, L., *et al.*, *J. Am. Chem. Soc.*, 1975, vol. 97, no. 22, pp. 6352–6358.
14. Oberhammer, H., *Z. Naturforsch., A: Phys. Sci.*, 1973, vol. 28, no. 7, pp. 1140–1143.
15. Borisenko, K.B., Bock, C.W., and Hargittai, I., *J. Mol. Struct., Theochem.*, 1995, vol. 332, pp. 161–169.