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A quantum chemical study on structure of 1,2-bis(diphenylphosphinoyl)ethane and phenol cocrystal

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Abstract

The cocrystal of 1,2-bis(diphenylphosphinoyl)ethane (DPPEO) with phenol (1:1) were studied theoretically with AM1, PM3, MNDO and MINDO/3 semi-empirical methods to elucidate its structure. The bond lengths and angles from theoretical studies of molecule DPPEO/phenol (1:1) were found to be as expected. Theoretical results, concerning with intermolecular van der Waals forces in cocrystal, were compared with the previously obtained experimental data and AM1 results were found to be the best fit for bond lengths and angles of DPPEO/phenol.

Keywords: Hydrogen bonding; Cocrystal; X-ray diffraction; Quantum chemical studies; Semi-empirical methods; van der Waals forces

1. Introduction

As the phosphine oxides are an excellent hydrogen bond acceptor, they can form large, high quality crystals when cocrystallized with a variety of hydrogen bond donors. This is a procedure that was promoted as a crystallization aid for compounds that do not crystallize well on their own [1]. There are a few examples of hydrogen bonded complexes for triphenylphosphine oxide (TPPO) and alcohols (diphenylmethanol) [2] or phenols [3–5]. Although the hydrogen bond geometry is very similar in all of the TPPO cocrystals with phenols, which consists of a single linear bond, TPPO/phenol is different. The material was prepared from a 1:1 mixture of the components, but isolated as a 2:3 TPPO/phenol cocrystal [6]. We have previously reported a theoretical study on geometries of (+)-(*R*)-2,2-bis(diphenylphosphinoyl)-1,1′-binaphthyl and its cocrystal with hydroquinone [7]. The phosphine oxide in the present study, 1,2-bis(diphenylphosphinoyl)ethane (DPPEO), produced 1:1 complex with phenol. The traditional X-ray diffraction techniques and theoretical studies allow the determination of the positions of the atoms in the compounds under study for suitable systems [8–10]. The continuous increase in development of the computer technology and in turn with tremendous development in sophistication of software, which are suitable to apply in structure–reactivity relations [11,12], reaction mechanism [13–15], corrosion [16–18] and in some biological processes [19,20], has tempted us to study the structure of the title compound to search the parallelism of the computed results with the experimental ones. We had compared the results, for bond lengths and bond angles as well as hydrogen bonding in the cocrystal of DPPEO and phenol, between quantum chemical results in the gas phase and X-ray structural studies. The data from previous X-ray structural study were kindly provided by one of us [21].

2. Method of calculation

Theoretical calculation were carried out at the Restricted Hartree–Fock level using MINDO/3, MNDO,

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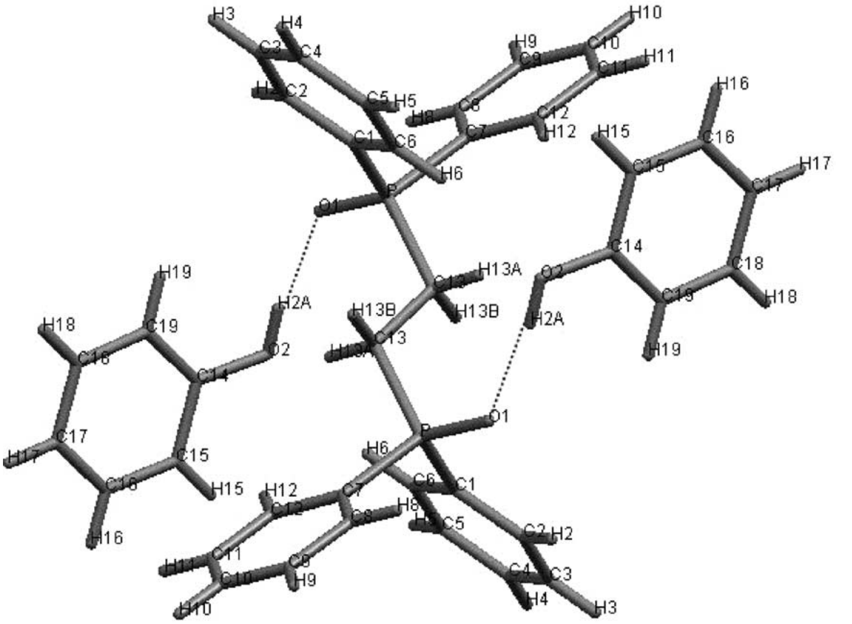

Fig. 1. The structure of DPPEO/phenol.

PM3 and AM1 semi-empirical SCF-MO methods in the MOPAC 7.0 program [22], implemented on an Intel Pentium Pro. 400 MHz computer. Initial estimates for the geometries of all were obtained by a molecular mechanics program (CS Chemoffice Pro for Windows) [23], followed by full optimization of all geometrical variables (bond lengths, bond angles and dihedral angles), without any symmetry constraint, using the semi-empirical MINDO/3, MNDO, PM3, AM1 quantum chemical methods in the MOPAC 7.0 program. The molecular plots for the cocrystal of DPPEO/phenol and the van der Waals contacts in cocrystal were produced by MERCURY program from Cambridge Crystallographic Data Centre (CCDC) [24,25].

3. Results and discussion

Cocrystals of the DPPEO/phenol, suitable for single crystal X-ray diffraction, were grown as colourless blocks from light petroleum (bp 60–80 °C)/dichloromethane. The compound crystallises in the centrosymmetric monoclinic space group *P2₁/c*, with two formula units per unit cell. There is a single crystallographically distinct residue in

Table 1
The difference between selected bond lengths and angles of two halves of the molecule obtained from quantum chemical calculations for DPPEO/phenol

	AM1	AM1[a]	|Δ|	PM3	PM3[a]	|Δ|	MNDO	MNDO[a]	|Δ|	MINDO/3	MINDO/3[a]	|Δ|
Bond lengths (Å)												
P–O1	1.476	1.571	0.095	1.488	1.490	0.002	1.520	1.520	0	1.537	1.536	0.001
P–C7	1.628	1.598	0.030	1.822	1.818	0.004	1.770	1.770	0	1.878	1.874	0.004
P–C1	1.625	1.625	0	1.815	1.824	0.009	1.768	1.769	0.001	1.874	1.878	0.004
P–C13	1.654	1.654	0	1.852	1.847	0.005	1.827	1.826	0.001	1.895	1.885	0.010
O2–H2A	0.978	1.809	0.831	0.953	0.956	0.003	0.949	0.949	0	0.951	0.950	0.001
H2A···O1	2.045	2.045	0	2.290	2.214	0.076	2.928	2.911	0.017	2.814	2.845	0.031
O2···O1	2.904	2.904	0	3.222	3.169	0.053	3.811	3.836	0.025	3.666	3.691	0.025
			0.137[b]			0.022[b]			**0.006**[b]			0.011[b]
Angles (°)												
O1–P–C1	113.4	112.1	1.3	114.6	113.2	1.4	112.6	112.4	0.2	108.9	111.2	2.3
O1–P–C13	112.1	112.4	0.3	114.6	114.5	0.1	109.5	109.9	0.4	112.3	110.1	2.2
C1–P–C13	106.2	105.8	0.4	103.3	104.8	1.5	105.7	107.8	2.1	108.1	108.3	0.2
O1–P–C7	111.9	112.3	0.4	113.7	113.7	0	110.1	110.3	0.2	110.2	110.3	0.1
C1–P–C7	108.2	107.2	1	104.5	104.8	0.3	106.2	105.9	0.3	110.4	108.2	2.2
C7–P–C13	104.5	106.6	2.1	104.9	105.0	0.1	112.7	110.4	2.3	107.0	108.7	1.7
O2–H2A....O1	146.5	145.6	0.9	165.9	176.5	10.6	155.3	164.9	9.6	149.6	149.1	0.5
			0.9[b]			2.0[b]			2.2[b]			1.3[b]

[a] Data for second half of the cocrystal, |Δ| = abstract values of difference between two halves of the cocrystal.

[b] Mean values for |Δ|.

Table 2
Mean values of selected bond lengths and angles obtained from quantum chemical calculations and obtained from previous experimental study for DPPEO/phenol

	AM1[a]	% (a)	PM3[a]	% (b)	MNDO[a]	% (c)	MINDO/3[a]	% (d)	Exp. [21]
Bond lengths (Å)									
P–O1	1.524	2.488	1.489	0.134	1.520	2.219	1.537	3.362	1.487(3)
P–C7	1.613	10.139	1.820	1.393	1.770	1.393	1.876	4.513	1.795(4)
P–C1	1.625	9.370	1.820	1.506	1.769	1.339	1.876	4.629	1.793(4)
P–C13	1.654	8.264	1.850	2.607	1.827	1.331	1.890	4.825	1.803(4)
O2–H2A	1.394	70.000	0.955	16.463	0.949	15.732	0.951	15.976	0.820
H2A···O1	2.045	10.541	2.252	21.730	2.920	57.838	2.830	52.973	1.850
O2···O1	2.904	9.050	3.196	20.015	3.824	43.597	3.679	38.152	2.663
		17.1[b]		**9.1**[b]		17.6[b]		17.8[b]	
Angles (°)									
O1–P–C1	112.75	0.850	113.90	1.878	112.50	0.626	110.05	1.565	111.8(2)
O1–P–C13	112.25	0.045	114.55	2.094	109.70	2.228	111.20	0.891	112.2(2)
C1–P–C13	106.00	0.935	104.05	2.757	106.75	0.234	108.20	1.121	107.0(2)
O1–P–C7	112.10	0.268	113.70	1.699	110.20	1.431	110.25	1.386	111.8(2)
C1–P–C7	107.70	0.186	104.65	2.651	106.05	1.349	109.30	1.674	107.5(2)
C7–P–C13	105.55	0.612	104.95	1.177	111.55	5.038	107.85	1.554	106.2(2)
O2–H2A....O1	146.05	14.088	171.20	0.706	160.10	5.824	149.35	12.147	170.0
		2.4[b]		**1.9**[b]		2.4[b]		2.9[b]	

% (a) $=(|\mathrm{AM1}-\mathrm{Exp}|/\mathrm{Exp})\times 100$, % (b) $=(|\mathrm{PM3}-\mathrm{Exp}|/\mathrm{Exp})\times 100$, % (c) $=(|\mathrm{MNDO}-\mathrm{Exp}|/\mathrm{Exp})\times 100$, % (d) $=(|\mathrm{MINDO/3}-\mathrm{Exp}|/\mathrm{Exp})\times 100$.

[a] Mean values for two halves of the molecule.

[b] Mean values for the difference of theoretical and experimental results.

the asymmetric unit with the two halves of the DPPEO molecule being symmetry related. The asymmetric unit contains half of the DPPEO molecule and one phenol molecule. The molecular structure of the 1:2 cocrystal of DPPEO/phenol is shown in Fig. 1.

The geometries of the DPPEO molecule and the phenol molecules were found to be similar to the literature data [6]. Selected bond lengths and angles in the DPPEO are similar to those in TPPO in the 2:3 complex of TPPO with phenol [6]. There are two identical, symmetry related, almost linear, hydrogen bonds from each phenol molecule to the oxygen of the phosphine oxide.

All these experimental results were confirmed in the present study (Tables 1–4). The molecule (DPPEO/phenol) in gas phase was studied with MINDO/3, MNDO, PM3 and AM1 semi-empirical methods at

Table 3
The difference between selected bond lengths and angles of two halves of the molecule obtained from quantum chemical calculations for DPPEO/phenol with van der Waals contacts

	AM1	AM1[a]	$\lvert\Delta\rvert$	PM3	PM3[a]	$\lvert\Delta\rvert$	MNDO	MNDO[a]	$\lvert\Delta\rvert$	MINDO/3	MINDO/3[a]	$\lvert\Delta\rvert$
Bond lengths (Å)												
P–O1	1.482	1.482	0	1.537	1.534	0.003	1.537	1.535	0.002	1.541	1.538	0.003
P–C7	1.622	1.622	0	1.870	1.872	0.002	1.869	1.872	0.003	1.875	1.878	0.003
P–C1	1.622	1.622	0	1.869	1.871	0.002	1.868	1.871	0.003	1.875	1.877	0.002
P–C13	1.653	1.653	0	1.887	1.878	0.009	1.886	1.877	0.009	1.890	1.882	0.008
O2–H2A	0.978	0.978	0	0.914	0.999	0.085	0.930	0.971	0.041	0.955	0.951	0.004
H2A···O1	2.063	2.064	0.001	2.758	2.824	0.066	2.758	2.824	0.066	2.759	2.825	0.066
O2···O1	2.931	2.931	0	3.623	3.770	0.147	3.640	3.746	0.106	3.663	3.732	0.069
			0.000[b]			0.045[b]			0.033[b]			0.022[b]
Angles (°)												
O1–P–C1	112.5	112.4	0.1	112.2	110.5	1.7	111.2	110.3	0.9	111.1	110.3	0.8
O1–P–C13	110.8	110.8	0	107.8	109.9	2.1	107.8	109.8	2.0	107.9	109.7	1.8
C1–P–C13	105.6	107.9	2.3	108.0	110.5	2.5	108.0	110.5	2.5	108.0	110.5	2.5
O1–P–C7	112.4	112.5	0.1	110.0	110.5	0.5	110.0	110.4	0.4	110.0	110.5	0.5
C1–P–C7	107.5	107.4	0.1	108.0	107.6	0.4	108.0	107.6	0.4	107.6	107.6	0
C7–P–C13	107.8	105.5	2.3	112.4	108.1	4.3	112.4	108.2	4.2	112.1	108.1	4.0
O2–H2A....O1	146.8	146.7	0.1	158.1	158.3	0.2	158.5	158.9	0.4	158.2	159.8	1.6
			0.714[b]			1.671[b]			1.543[b]			1.600[b]

[a] Data for second half of the cocrystal, $|\Delta|$ = abstract values of difference between two halves of the cocrystal.

[b] Mean values for $|\Delta|$.

Table 4
Mean values of selected bond lengths and angles obtained from quantum chemical calculations with van der Waals contacts and obtained from previous experimental study for DPPEO/phenol

	AM1[a]	% (a)	PM3[a]	% (b)	MNDO[a]	% (c)	MINDO/3[a]	% (d)	Exp. [21]
Bond lengths (Å)									
P–O1	1.482	0.336	1.536	3.295	1.536	3.295	1.540	3.564	1.487(3)
P–C7	1.622	9.638	1.871	4.234	1.871	4.234	1.877	4.568	1.795(4)
P–C1	1.622	9.537	1.870	4.294	1.870	4.294	1.876	4.629	1.793(4)
P–C13	1.653	8.319	1.883	4.437	1.882	4.382	1.886	4.603	1.803(4)
O2–H2A	0.978	19.268	0.957	16.707	0.951	15.976	0.953	16.220	0.820
H2A···O1	2.064	11.568	2.791	50.865	2.791	50.865	2.792	50.919	1.850
O2···O1	2.931	10.064	3.697	38.828	3.693	38.678	3.698	38.866	2.663
		9.8[b]		17.5[b]		17.4[b]		17.6[b]	
Angles (°)									
O1–P–C1	112.45	0.581	111.35	0.403	110.75	0.939	110.70	0.984	111.8(2)
O1–P–C13	110.80	1.248	108.85	2.986	108.80	3.030	108.80	3.030	112.2(2)
C1–P–C13	106.75	0.234	109.25	2.103	109.25	2.103	109.25	2.103	107.0(2)
O1–P–C7	112.45	0.581	110.25	1.386	110.20	1.431	110.25	1.386	111.8(2)
C1–P–C7	107.45	0.047	107.80	0.279	107.80	0.279	107.60	0.093	107.5(2)
C7–P–C13	106.65	0.424	110.25	3.814	110.30	3.861	110.10	3.672	106.2(2)
O2–H2A....O1	146.75	13.676	158.20	6.941	158.70	6.647	159.00	6.471	170.0
		2.4[b]		2.6[b]		2.6[b]		2.5[b]	

% (a) = (|AM1 − Exp|/Exp) × 100, % (b) = (|PM3 − Exp|/Exp) × 100, % (c) = (|MNDO − Exp|/Exp) × 100, % (d) = (|MINDO/3 − Exp|/Exp) × 100.

[a] Mean values for two halves of the molecule.

[b] Mean values for the difference of theoretical and experimental results.

20 °C at which the experimental values were obtained [21].

Table 1 lists the gas phase computation results for MINDO/3, MNDO, PM3 and AM1 semi-empirical methods. There are two different results for each theoretical study in gas phase for the two halves of the molecule, although they are symmetric in solid state. Deviations from symmetry between the same method indicates MNDO and AM1 give better accord for selected bond lengths and angles, respectively (Table 1).

Table 2 lists the mean values of the same theoretical results and previously obtained experimental results [21].

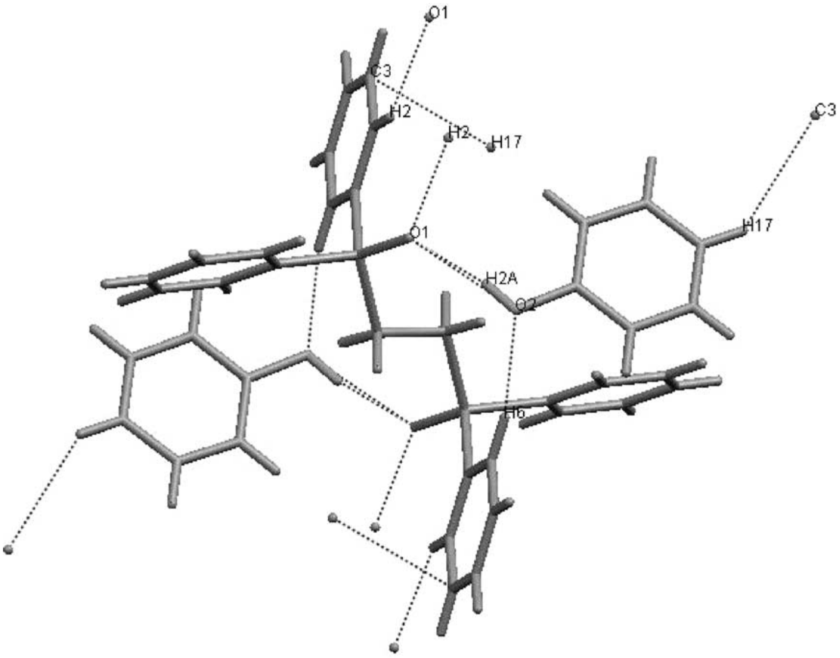

Fig. 2. van der Waals interactions of DPPEO/phenol.

Among the applied methods, PM3 seems to give better results for both bond lengths and angles of DPPEO/phenol, suggested with the mean values for percentage of difference between theoretical and experimental results (Table 2).

In solid state, there is a van der Waals contact (2.517 Å) in molecule between oxygen atom (O2) of phenol residue and hydrogen atom (H6) of one of the phenyl groups located at the opposite half of the phosphine oxide. There are also intermolecular contacts from O1 to H2 (2.403 Å), C3 to H17 (2.897 Å) (Fig. 2) among the neighbour cocrystals. Table 3 lists the theoretical results regarding with van der Waals interaction in molecule (O2···H6), which have different from the study performed without these forces. Among the applied methods, AM1 showed the best outcome for symmetry of the two halves of the cocrystal (Table 3) and gave better results for selected bond lengths and angles for DPPEO/phenol cocrystal (Table 4). Since the theoretical methods used in this study has the limit of allowed number of atoms of 100, intermolecular contacts between the neighbour cocrystals could not be investigated. This probably caused significant elongation of hydrogen bond length (H2A···O1) and related bond lengths of O2···O1 and O2–H2A in all calculations.

4. Conclusion

All available hydrogen bond donors and acceptors are involved forming hydrogen bonds in the cocrystal. This is in accord with the Etter rules that in the solid state all available acidic hydrogen atoms participate in hydrogen bonds [26]. The crystal structure of the cocrystal DPPEO/phenol has been thoroughly examined previously and it revealed that there are no apparent holes in the packing diagram due to dense packing behaviour in the lattice [21]. There are short contacts among molecules and in molecules in the unit cell ranging 2.4–2.9 Å. Comparable results were obtained between experimental and theoretical studies for the bond lengths and angles. On concerning van der Waals interactions in cocrystal for computing, AM1 gave better results for both bond lengths and angles for DPPEO/phenol. Small differences for the bond lengths and angles between theoretical and experimental results might be due to the phase differences.

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