RESEARCH ARTICLE

Synthesis, Crystallographic Characterization and Density Functional Study of Novel Spoke-Molecular Tetravent ethyltriphenylphosphorous Dibromide

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Abstract: A novel molecular tetravent ethyltriphenylphosphorous dibromide ((C_6H_5)$_3$PCH$_2$Br$_2$) has been synthesized in toluene and has been characterized by single crystal x-ray crystallography. Theoretical studies have been conducted utilizing DFT(B3LYP/6-311+G(d,p) level of theory both in gas phase and solution using diverse solvents. Potential surface energy calculations revealed the existence of the tetravalent diionic form as a global minimum except in dimethylsolfoxide where our adduct is more stable. Calculations showed that the Br-Br bond distance is in quadratic variation with the medium dielectric constant. The unusual Br-Br lengthen is reasonably rationalized in terms of charge transfer of electron density from the π clouds in phenyl moieties to the σ* of the dibromine entity. The average harmonic oscillator index of aromaticity of the complex are found suffering a deviation from unity.

Keywords: Organophosphorous, X-ray, DFT, AHOMA, Hardness

Introduction

Organophosphorous halogen compounds (OPHCs) have distracted chemists intentions for decades due to its important role in organic chemistry as synthetic reagents, bond cleavage reagents and displacement ones. A vast number of OPHCs of the formula *R3PX2* and *R3PEX2* [*R= alkyl, aryl; E=P, Se, S, As, Sb, Bi; X$_2$=Cl$_2$, Br$_2$, I$_2$, ICl, IBr*] have been prepared[1-9]. These compounds in the solid state are found crucially dependent on the nature of the solvent used in the synthesis process[10]. Compounds of the formula *R$_3$PX$_2$; [R= Ph, Me, n-octyl, n-hexyl, n-butyl X=Cl, Br, I]* and compounds of the formula[11-13] *Ph$_3$PXY; (XY=Br$_2$, I$_2$, IBr)* that have been prepared in acetonitrile, dichloromethane or in nitrobenzene[14-16] are ionic with tetrahedral geometry and the correct form will be *[R$_3$PX]$^+$Y*.

Extensive studies on the compounds of the formula *R$_3$EX$_2$ (R$_3$=Ph$_3$, PhMe$_2$, Me$_3$; E=P, As; X$_2$= Br$_2$[17], I$_2$[17,18] IBr[16]* that isolated from diethyl ether solution which is relatively weak

polar solution leads to the formation of another geometrical structure of these compounds which is a four co-ordinate molecular spoke structure of the formula R_3E-X-X in the solid state as it has been proved by x-ray crystallographic studies. In CDCl$_3$ solution, which is a highly polar solvent, all the compounds ionise completely to form $[R_3PX]^+X^-$. Further series of linear spoke molecular structure of stochiometry[19] R_3PI_2 [R_3=(o-$MeOC_6H_4)_3$, (o-$MeOC_6H_4)_2Ph$, (o-$MeOC_6H_4)Ph_2$, (p-$FC_6H_4)_2Ph$, (p-$FC_6H_4)Ph_2$, (p-CH_2=$CHC_6H_4)Ph_2$, (CH_2=$CHCH_2)_2Ph_2$, ($C_6H_{11})Ph_2$, ($PhCH_2CH_2)_3$ or ($Me_2N)_3$] have been synthesised in diethyl ether. It is found that all of these compounds ionize in the highly polar CDCl$_3$ solution. Nevertheless, the compounds $(Me_2N)_3PI_2$ and $(CH_2$=$CHCH_2)_2PhPI_2$ proved to be ionic in the solid state which is in contradict to the four co-ordinate molecular geometry of the compounds R_3PI_2 that have been already mentioned.

A molecular trigonal bipyramidal compounds were identified as in the case[20] of R_3PF_2 (R = Ph, Me, Et, or nBu), Ph_3AsBr_2[19]. R_3PCl_2 [R=$(C_6F_5)_3$ or $(C_6F_5)Ph_2$] compounds having molecular five coordinate trigonal bipyramidal geometries were prepared in diethyl ether and crystallography identified by Godfrey and co-workers[14]. $(C_6F_5)_3PCl_2$ exhibited a trigonal-bipyramidal geometry, while $(C_6F_5)Ph_2PCl_2$ showd a significant distortion due to asymmetry of the equatorial groups around P atom. It is found that the molecular trigonal bipyramidal pentavalent molecular geometry of Ph_3PCl_2 dominant in solvents of low polarity, but converts into an ionic form in highly polar solvents[14].

In addition to the influence of the nature of the solvent used in synthesis the nature of the R group bound to the E metal has a fundamental effect on the structure of the dihalogen compounds. This impact could be touched easily if R is varied while both of E and X_2 are maintained unchanged in the dihalogen compounds. For example[19,21], R_3AsBr_2 compounds adopted the trigonal-bipyramidal structure when R=Ph, whereas the structure of the Me isomer is the molecular linear spoke charge transfer of tetrahedral geometry of the formula[19] Me_3As-Br-Br. It was accounted that the acidity of the E group is responsible for this behaviour. A pentavalent molecular geometry is more likely with increasing the acidity of ER_3, $i.e.$ the probability of preparing the trigonal-bipyramidal structure is enhanced in the presence of a suitably acidic tertiary phosphine. A similar situation is observed for the dichloro adducts[14,21-23], R_3PCl_2 being ionic with the formula $[R_3PCl]^+Cl^-$ when the alkyl group is methyl, n-propyl or isopropyl, whereas the trigonal bipyramidal geometrical structures are adopted when $[R_3$= $(C_6F_5)_3$ or $Ph_2(C_6F_5)]$[24].

The nature of the substituents not only, significantly, affect the geometrical structure of $OPHC$, but also affect each of the E-E', E-X, E'-X and X-X bond lengths[24]. For example, the (I-I) bond length in Ph_3P-I-I is 316.1 pm[17] while the same bond in $PhMe_2P$-I-I is 340.9 pm[25] and it is 333.2 pm in case[26] of t-Bu_3PI_2. Another example, the P-Se, Se-Br_1 and Se-Br_2 bond lengths in $(C_6H_{11})_3PSeBr_2$ are 227.1 pm, 256.8 pm and 256.6 pm respectively, whereas the P-Se, Se-Br_1, $SeBr_2$ bond lengths in $(Me_2N)_3PSeBr_2$ are 226.2 pm, 260.2 pm and 254.4 pm respectively[1].

Adducts of the formulas Ph$_3$PRBr; [R=Ph, Me, Et or C$_5$H$_9$] and Ph$_3$PRCl; R=Bu were recently isolated and crystallography identified by Burgess et al. However[27], compounds of the formula ArPRX$_2$ have not received that remarkable attention. Compounds of the formula[28] $[Ph_3PCH_2Br]^+Br^-$ and$[Ph_3PCH_2I]^+I^-$ as a di-ionic[29] molecular entities have been successfully prepared. Bromomethyltriphenylphosphonium bromide plays an import roll in organic synthesis. It is an essential reagent for carbon-carbon bond formation in Wittig reaction[30]. It is also used as starting material in synthesis of benzyldiphenylphosphine oxide which in turn and with other reagents, can be used for alkenes synthesis[31].

In this study the possibility of preparing compounds of the formula Ar_3PRX_2; $R=CH_2$, $X_2=Cl_2$, Br_2 will be examined and then will be theoretically investigated employing the density functional theory to shed the light on their geometries and electronic properties.

Experimental

The synthesis of the title compound has been accomplished in a similar manner to the one has been reported in the literature[31], prepared by the reaction of 10 mmol (2.62 g) triphenylphosphine and 10 mmol (1.74 g) dibromomethane under reflux in toluene and a white needle crystals were separated.

X-ray single crystal data were collected at 230 K using graphite monochromated Mo-Kα (λ=0.7107A°) radiation on a Bruker SMART APEX CCD diffractometer. Data reduction was carried out using SAINT[32] and the structure was solved using SHELXS-97[33] and showed that there are two molecules in the asymmetric unit. Full matrix refinement on F^2 was performed with SHELXL-97[33] and all calculations were carried out using the SHELXTL package[33]. The non-H atoms were refined anisotropically and H atoms were included in calculated positions, except for those bonded to N, which were found by Difference Fourier Methods and refined isotropically. It was necessary to collect the data at 230, since flash freezing to 100 K caused the crystal to break up. The crystal data are summarized in Table 1 and a plot of molecule **3** of the structure is shown in Figure 1.
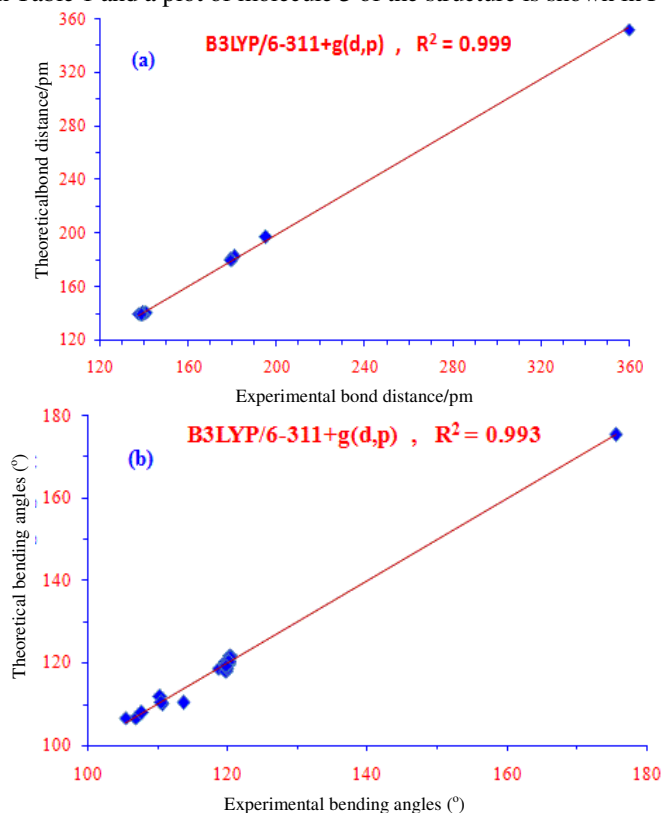
Figure 1. Correlation graphs of the calculated DFT geometrical parameters and the experimental ones; (a) bond distances and (b) bending angles of the title compound

Table 1. Crystal data and structure refinement of bromomethyltriphenylphosphonium bromide

Parameter		Synthesized compoud
Empirical formula		$C_{19}H_{17}Br_2P$
Formula weight		436.12
Crystal color		Colorless
Crystal size, mm^3		0.15x0.12x0.05
Crystal system		Monoclinic
Space group		P2(I)/n
	a (Å)	10.3077(2)
	b (Å)	14.0568(3)
Unit	c (Å)	12.4893(2)
cell dimensions	α, deg	90
	β, deg	105.152(1)
	γ, deg	90
V (Å^3)		1746.71(6)
Z		4
D, g cm^{-3}		1.404
F, 000		576
μ MoKα, mm^{-1}		4.73
T, K		150
λ, Å		0.71073
Absorption coefficient, mm^{-1}		0.104
Absorption correction: multi-scan		3431 reflections with
Range of h, j, k		-15/16, -14/14, 13/12
θ min/max (deg)		1.65 to 28.28
R, int		0.044
Completeness to theta = 25.00		100.0 %
reflections collected/unique/		10923/3077 [R(int)=0.0562]
Data/restraints/parameters		4002/1.07/268
GOF on F^2		0.946
Final R indices [I > 2σ(I)] R$_1$, wR$_2$		0.028 , 0.065
R indices (all data) R$_1$, wR$_2$		0.0675 , 0.1040
Δρ$_{min}$, Δρ$_{max}$		-0.58eÅ-3, 0.48 eÅ^{-3}
Max. and min. transmission		0.9794 and 0.9693
Extinction coefficient		0.0211(19)
Refinement method		Full-matrix least-squares on F^2

Computational details

The title compounds was initially fully optimized in the gas phase with no geometrical constrains at the density functional of Becke three-parameters hyprid functional of Lee, Yang and Parr[34,35] (DFT/B3LYP) in combination with the sophisticated 6-311+G(d,p) basis set in which diffused functions have been added for all atoms while polarized ones have been added to the heavy ones. Extra different basis sets were employed on phosphrous and bromine moieties in attempt to assign the most convenient basis set for each of P and Br to be used in this study. It is found that the sophisticated standard Dunning's correlation consistent quadruple-zeta augmented basis set with diffuse functions[36], aug-ccpV(Q+d)Z could be satisfactorily employed for the phosphorous moieties to account for any diffusion

of the charge densities. Previous studies conducted by Martin *et al.* and others[37-39] confirmed the necessity of employing such tight diffused functions in case of elements of the third period in periodic table. The ground state nature of each compound is examined by analytical vibrational frequency calculations conducted using second-derivative computations at the same level of theory. Energies, energies of frontier orbitals, aromaticity indicies, global softnesses and global hardnesses were calculated at the single point energy calculations with the DFT(B3LYP)/6-311++G(3d,3p) level of theories. The optimized gaseous wavefunctions were then taken as the input for calculations in solution by using the Conductor-Like Polarized Continuum Model (CPCM) of Barone[40] and Cossi[41] which is based on the polarizable Continuum Model (PCM) of Tomassi and co-workers[42-46] at B3LYP/6-311++G(3d,3p)// B3LYB/6-311+G(d,p) level of theory in dimethyl sulfoxide in attempt to account for the unusual length of the Br-Br bond distance predicted by the experimental single X-ray crystallography. Extrabasis sets were used for the phosphorous moieties.

All calculations were performed with the Gaussian 09 package[47]. Gauss View[48] and Chemcraft[49] programs were used for visualization of structures while[50] Mercury 3 was used for visualization and analysis of crystal structure.

Results and Discussion

Basis set

Different bases functions were used for P and Br atoms while C and H atoms were optimized at the 6-311+g(d,p) basis functions. Table 2 presents the bases functions employed at the gas phase and liquid state for the P and Br moieties at seven different jobs, the linear correlation factor of plotting the calculated geometrical (bond lengthy and bond angles) parameters versus the corresponding observed x- ray ones and the predicted Br-Br bond lengths in pm.

Table 2. The basis functions used for Br and P moieties in $(C_6H_5)_3PCH_2Br_2$, the regression and the estimated Br-Br bond distance in each job

	Job	atom	Basis function	R^2/(Bond length)	R^2/(Bending angle)	d_{Br-Br} / pm
Gas phase	1	P Br	Aug-cc-pvqz+d	0.903	0.991	270.8
	2	P Br	cc-pvqz+d 6-311g(d,p)	0.899	0.979	271.4
	3	P Br	Aug-cc-pvqz+d 6-311+g(d,p)	0.907	0.989	273.1
	4	P Br	Aug-cc-pvqz+d Lanl2dz	0.909	0.980	272.6
	5	P Br	6-311+g(d,p)	0.893	0.977	270.9
Solution	6	P Br	6-311+g(d,p)	0.999	0.984	351.7
	7	P Br	Aug-cc-pvqz+d 6-311+g(d,p)	0.999	0.993	352.3

The best correlation factors in cases of bond distances are obtained with jobs 2 and 4 (R^2= 0.907 and 0.909) respectively where job 4 showed better representation of the distance parameters with 0.002 correlation factor increment. Nevertheless, job 3 proved to be more reliable in terms of the bending angle parameters due to 0.009 correlation factor increment.

One would came to the result that the basis sets employed in the calculation conducted in job 3 would give better representation of predicting geometrical parameters. As a result of that, the basis sets 6-311+g(d,p) would be used for the entire molecule while the quadruple-zeta augmented basis set with diffuse function (aug-cc-pvqz+d) could be taken as an excellent one for calculation of P atom in the study. The validity of this basis set choice is strengthened by the calculation in solution where an excellent correlation between the calculated and observed parameters were obtained; 0.999 and 0.993 for the bond distances and bending angles respectively as it is clear from Figures 1a and 1b. It would be fair enough to recommend such basis set combinations in theoretical investigation of family of such compounds. Bond distances and bending angles predicted at the aforementioned bases sets at the specified level of theories are recorded in supplementary materials; Table 3 and Table 4 respectively.

Molecular structure

Preparation of the novel product Bromomethyltriphenylphosphonium bromide **3** was effected through a condensation reaction of triphenylphosphine **1** and dibromomethane **2** under reflux in toluene (Scheme 1). The formation of **3** was confirmed by x-ray crystallography.

**Table 3.** Experimental and theoretical bond distances of $(C_6H_5)_3PCH_2Br_2$

Bond Distance	X-Ray	Job (1)	Job (2)	Job (3)	Job (4)	Job (5)	Job (6)	Job (7)
C1-P1	1.805(2)	177.3	177	177.3	177.2	178.4	184.1	182.6
C1-Br1	1.951(2)	216.9	219.1	217.2	216.5	219.5	196.9	197
C2-C7	1.388(3)	140.2	140	140	140.2	140	140.1	140.2
C2-C3	1.402(3)	140	140.1	139.1	140.4	140	140.3	140.3
C2-P1	1.794(2)	180.4	180.4	180.5	180.1	181.7	181	179.6
C3-C4	1.383(4)	139.2	139	139.1	139.2	139.1	139.1	139.1
C4-C5	1.383(4)	139.3	139.4	139.4	139.7	139.3	139.5	139.5
C5-C6	1.383(4)	139.4	139.2	139.3	139.5	139.3	139.3	139.4
C6-C7	1.392(3)	139	139.2	139.3	139.5	139.2	139.3	139.3
C8-C9	1.388(3)	140	140	140	140.3	139.9	140.1	140.2
C8-C13	1.392(3)	140.3	140.3	140.4	140.4	140.3	140.4	140.5
C8-P1	1.790(2)	182.1	182.1	182	181.8	183.3	181.6	180.3
C9-C10	1.386(4)	139.3	139.3	139.5	139.4	139.4	139.3	139.2
C10-C11	1.378(4)	139.2	139.2	139.2	139.6	139.2	139.4	139.4
C11-C12	1.375(4)	139.5	139.5	139.6	139.7	139.5	139.5	139.5
C12-C13	1.389(4)	139	139	139	139.4	139	139.2	139.1
C14-C15	1.391(3)	140	140.2	140.3	140.4	140.1	140.1	140.2
C14-C19	1.407(3)	140.5	140.5	140.4	140.8	140.4	140.4	140.5
C14-P1	1.792(2)	180.8	180.8	180.8	180.6	182	181.4	180.1
C15-C16	1.392(3)	139.3	139.3	139.3	139.5	139.3	139.5	139.3
C16-C17	1.389(4)	139.3	139.3	139.4	139.5	139.3	139.3	139.3
C17-C18	1.384(3)	139.3	139.4	139.4	139.7	139.4	139.3	139.5
C18-C19	1.385(3)	139.1	139.1	139.2	139.3	139.1	139.3	139.1
Br-Br	359.7(3)	270.8	271.4	273.1	272.6	270.9	351.7	352.3
R^2		0.903	0.899	0.907	0.909	0.893	0.999	0.999

Table 4. Experimental and theoretical bending angles of $(C_6H_5)_3PCH_2Br_2$

Bond Angle	X-Ray	Job (1)	Job (2)	Job (3)	Job (4)	Job (5)	Job (6)	Job (7)
P1-C1-Br1	110.32(12)	113.7	113.4	110.5	110.3	114.4	114.6	113.6
C7-C2-C3	119.7(2)	119.8	119.8	119.8	119.9	120	120.1	119.9
C7-C2-P1	121.69(17)	120.2	120.2	120.3	120.6	120.1	120.1	120.3
C3-C2-P1	118.52(18)	120	120	120	119.5	120	119.7	118.7
C4-C3-C2	119.6(2)	120	119.9	119.9	119.9	119.8	119.7	119.8
C5-C4-C3	120.7(2)	120.1	120.2	120.2	120.1	120.2	120.2	120.1
C4-C5-C6	119.8(2)	120.1	120.1	120.1	120.2	120.1	120.2	120.2
C5-C6-C7	120.3(2)	120.2	120	120	120	120.1	120.2	120.1
C2-C7-C6	119.9(2)	119.9	120	120	119.9	119.9	119.7	119.8
C9-C8-C13	120.1(2)	119.3	119.3	119.4	119.5	119.5	120.1	119.8
C9-C8-P1	121.82(18)	121.8	121.8	121.8	121.4	121.7	119.7	120.4
C13-C8-P1	117.84(18)	118.9	118.9	118.8	119.1	118.8	120.2	119.8
C10-C9-C8	119.5(2)	120.1	120.1	120.1	120.1	120	119.7	119.9
C11-C10-C9	120.3(2)	120.2	120.2	120.2	120.2	120.3	120.2	120.2
C12-C11-C10	120.4(2)	120	120	120	120	120	120.2	120.1
C11-C12-C13	120.1(3)	120.1	120.1	120.1	120	120.1	120.2	120.2
C12-C13-C8	119.6(2)	119.7	120.3	120.3	120.2	120.1	119.7	119.8
C15-C14-C19	120.3(2)	120.3	119.7	120	119.8	119.9	120	119.8
C15-C14-P1	121.22(17)	121	121	120.5	119.7	120.9	120.1	120.3
C19-C14-P1	118.51(17)	119.3	119.3	119.8	120.5	119.1	119.9	119.9
C14-C15-C16	119.4(2)	119.8	120	120.1	120	119.9	119.8	119.9
C17-C16-C15	120.2(2(	120.3	120.1	120.1	120.1	120.1	120.2	120.2
C18-C17-C16	120.4(2)	120.1	120.1	120	120.1	120.1	120.1	120.1
C17-C18-C19	120.2(2)	120.1	120.4	120.4	120.4	120.4	120.2	120.2
C18-C19-C14	119.4(2)	120	119.8	119.7	119.7	119.6	119.7	119.8
C8-P1-C14	109.93(10)	110.9	107.8	107.5	107.9	107.7	110.3	110.6
C8-P1-C2	111.68(10)	110.7	107.2	109.4	107.1	107.1	110	110.3
C14-P1-C2	106.55(11)	109.1	109.1	109.5	109.7	108.9	110.5	106.9
C8-P1-C1	106.55(11)	107.9	111.1	109.8	110.9	111.4	105.9	105.4
C14-P1-C1	110.27(11)	110.6	110.5	110.7	110.5	110.4	110.4	110.5
C2-P1-C1	107.83(11)	107.3	111	110.9	110.6	111.1	109.6	107.7
C1-Br1-Br2	175.39(7)	179	179.1	176	179.1	178.8	179.4	175.5
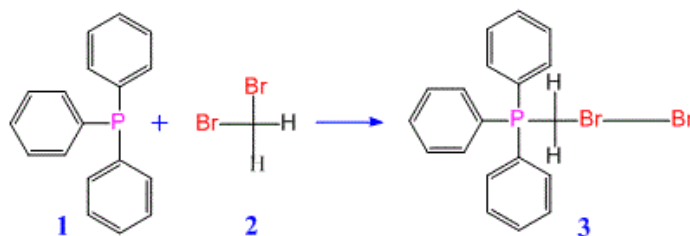
Scheme 1. Synthesis of Bromomethyltriphenylphosphonium bromide

The three dimensional geometrical structure of **3** is displayed in Figure 2a and b 2a represents the experimental x-ray crystal structure with the numbering scheme while 2b displays the optimized geometrical structure as predicted by the DFT(B3LYP)/6311+G(d,p) level of theory in the gaseous phase.
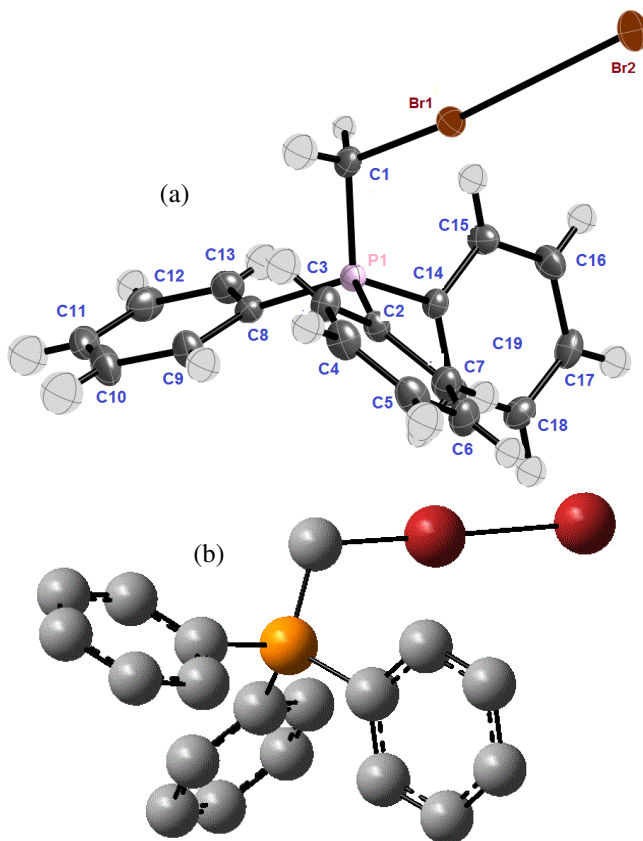
Figure 2. (a) The experimental geometric structure of the title compound at the unit cell with the numbering scheme (b) the theoretical geometrical structure as predicted by B3LYP/6-311+G(d,p) level of theory. Hydrogen atoms were omitted in 1b for clarity.

The crystal structure and the theoretical DFT(B3LYP) studies showed that the title compound existed as a solid molecular four-coordinate, tetrahedral geometrical structure, around the phosphorus central atom. The Br-Br moiety adopts a co-linear spoke structure, making an experimental angle 175.39(7)$^{\circ}$ with the carbon center of the methylene group. The phenyl moieties are in the well known dorsal structure. The Br-Br bond 3.597(3) Å in our compound is considerably lengthened with respect to that in a molecule Br_2 (1.9 Å), but still within bonding distance when compared to the van der Waals radius of Br_2 (4.2 Å) molecule. The extended Br–Br bond length in such charge transfer complex is expected, since the LUMO in dibromine is antibonding molecular orbital. Transfer of electron density into this orbital will therefore destabilize the dibromine entity and lead to an increased bond length. Many isoelectronic molecular complexes with long dihalogen or inter halogen bonding interactions have been successfully prepared and studied. The d_{I-I} was found 2.881(2), 2.962(2) and 2.985(2) for R_3PseI_2; [R=Ph, Me_2N, or Et_2N], respectively[1]. Adducts of the form $R_3PS-I-X$; [R=Ph, Me_2N, or C_6H_{11}] with X=I, Br or CI have been isolated and were crystallography characterized. The x-ray bonding distance, d_{I-X}, in $(Me_2N)_3PS-I-I$ is 2.856(1) Å. The d_{I-Br} in $Ph_3PS-I-Br$ was found 2.832(6) Å, is longer than that of the solid IBr (2.52 Å)[3].

The predicted DFT(B3LYP) geometrical parameters, *viz.* bond distances and bending angles in the gas phase within the assigned basis set are in very well agreement with the single x-ray observations of the same parameters. The squared correlation coefficients are 0.903 and 0.991 for the bond distances and bending angles, respectively. The main discrepancies between the gas phase calculations and the observed x-ray crystallography is substantially exist in the Br-Br bond distance. The observed Br-Br bond length is 359.7(3) pm while the calculated one in the gas phase is 270.8 pm. Obviously, the DFT-bases sets employed in gas phase calculations are failed to account very well for the unusual length of the observed Br-Br bond distance.

Energy

Calculations showed that the title compound **3** is ground state on the potential energy surface (PFS) whether in the gas phase or in solution due to inexistence of virtual vibrational modes of frequencies. In addition to the molecular tetravalent spoke molecular structure of the title compound, an ionic pair tetravalent geometrical structure has been elucidated in the potential energy surface calculations conducted in the gas phase, Figure 3.
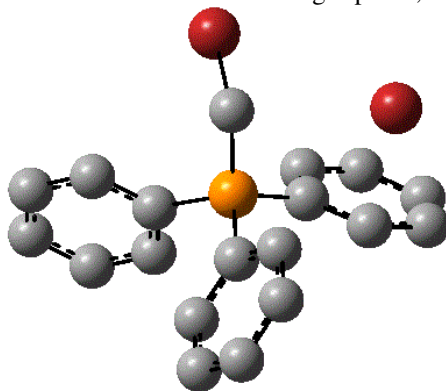
Figure 3. A tetravalent ionic form of bromomethyltriphenylphosphonium bromide as predicted by DFT(B3LYP)/6-311+G(d,p) level of theory. Hydrogens are omitted for clarity

Energy calculations in the gas phase predicted by DFT(B3LYP)/6-311++G(3d,3p)// B3LYP/6-311+g(d,p) showed that the molecular spoke synthesized form is less stable than the di-ionic global ground state form of the title compound by 16.85 Kcalmol^{-1}. Calculations conducted at the R$_3$PseR$_2$ complexes; R= H, Me, Et, N(CH$_3$)$_2$, N(C$_2$H$_5$)$_2$, Ph or C$_6$H$_{11}$, showed that the T-shaped molecular geometries of these complexes are more stable than the molecular spoke ones[51]. Gas phase theoretical investigations on Ph$_3$PX$_2$ complexes; X is Br or Cl, reflected that the charge transfer spoke geometry is the global minima in the case of X = Br while it's a local minimum when X = Cl. The global minimum in the case of X = Cl corresponds to the ion pairs tetrahedral geometrical structure.

Solvent effect

The gas phase predicted wave functions were used as the input wavefunctions in solvent simulations. CPCM model utilizing DFT(B3LYP) functional with the basis set 6-311+g(d,p) was used in the study for the entire molecules in the presence of the highly polar dielectric dimethylsulfoxide (DMSO) solvent . Extrabasis set (aug-cc-pvqz+d) was used on P atom. An excellent correlation was found between the observed and the calculated geometrical parameters as it is already shown in Table 2. Solvent calculations accounts very well for the

unusual length of the Br-Br bond distance (d_{Br-Br}). The difference in the Br-Br bond distance has been eliminated from 86.6 pm in the gas phase to 7.4 pm in DMSO solvent. The study extended to include many solvents, *viz.*, toluene, acetonitrile, dichloromethane and diethylether to investigate the influence of solvent dielectric constant (ε) on d d_{Br-Br}. Calculations showed that the d_{Br-Br} is fairly well quadratically varied with ε. The variation of d_{Br-Br} with ε is represented by the relation; $d_{Br-Br}=0.01\varepsilon^3-046\varepsilon^2+12.20\varepsilon+271.8$; $R^2=0.937$. Deviation from the observed d_{Br-Br} has been remarkably reduced in the presence of solvents with high ε; DMSO and acetonitrile. These results are found in accordance with the average harmonic oscillator index of aromaticity (AHOMA).

AHOMA is calculated using the formula $AHOMA = \dfrac{1}{N}\sum_{i=1}^{N}\left(1-\dfrac{\alpha}{n}\sum\left(R_{opt}-R_i\right)^2\right)$

where R_i is the ith C-C bond distance in the benzene ring within the studied molecule, R_{opt} is the optimum C-C bond in benzene (168.8 Å), $\alpha=257.7$ is the normalized factor that guarantees that HOMA of aromatic compound approaches 1 and of its Kekul´e nonaromatic structure approaches 0 and n is the number of C-C bonds in only one benzene ring[52]. Table 5 displays the AHOMAs and the relative deviations of 3 from unity in the gas phase, in solution in the presence of solvents that aforementioned and x-ray prediction as well. Relative deviations is calculated using the equation: $\mathrm{relative\,deviation} = \dfrac{1}{N}\left(\sum_{i=1}^{N}\left|\dfrac{1-AHOMA}{1}\right|X100\right)$, where N is the number of benzene rings

in the molecular formula of the titled compound.

Table 5. The prediction of AHOMA and the corresponding relative deviation

Medium	X-Ray	gas	DMSO	CH_2Cl_2	$(CH_3CH)_2O$	Toluene	acetonitrile
HOMA	0.9859	0.9847	0.9753	0.9752	0.9755	0.9768	0.9751
%Relative deviation	1.41±0.29	1.53±0.66	2.47±0.13	2.48±0.09	2.45±0.12	2.32±0.29	2.46±0.15

Calculations showed that the largest value of HOMA is associated with the gas phase calculations where the shortest d_{Br-Br} is noticed. The longest d_{Br-Br} is obtained with DMSO, acetonitrile and dichloromethane, solvents with the highest dielectric constants. Apparently, the calculated AHOMA of the phenyl moieties within our respected complex experienced a slight reduction and thus small relative deviation from unity as it must be for a benzene ring. Reduction of AHOMA of the phenyl moieties in the titled compound could be rationalized in terms of charge transfer of electron density from the PPh$_3$ moiety to the lowest unoccupied untibonding molecular orbital in dibromine. As a consequence of that, the dibromine entity will be destabilized. The Br-Br bond order would be reduced, leading to an increase in the Br-Br bond distance.

Global hardnesses η and global softnesses S of the molecular form Ph$_3$PCH$_2$Br-Br and ionic form [Ph$_3$PCH$_2$Br]$^+$ Br$^-$ of Ph$_3$PCH$_2$Br$_2$ have been expressed in terms of energies of frontier orbitals; the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), where the global softness is the reciprocal of the global hardness, such that; $\eta = \dfrac{1}{S} = \dfrac{(E_{LUMO}-E_{HOMO})}{2}$, where E_{HOMO} and E_{LUMO} are the energies of the highest occupied and lowest unoccupied molecular orbitals,

respectively. The calculated η and S in the gaseous phase of the molecular spoke and ionic forms in addition to the energies of frontier orbitals in electron volts (eV) are reported in Table 6.

Table 6. Energies of frontier orbitals, global hardness and global softness, all in eV

Structure	E_{HOMO}	E_{LUMO}	η	σ	χ
Spoke	-5.1038	-2.1911	2.9127	0.3433	-7.2949
ionic	-4.8809	-2.2403	2.6406	0.3787	-7.1212

The hardness of the spoke form is relatively larger than that of the ionic form while the ionic form is softer than the molecular form. Since softness and hardness can be employed to examine relative reactivity of substances[53], one would assume that the ionic form is more likely reactive than the spoke one. That's might shed the light on the fact that the di-ionic form has been prepared long time before the spoke one and amazingly employed as it is aforementioned.

Conclusion

A novel charge transfer tetravalent molecular spoke adduct of the formula $(C_6H_5)_3PCH_2Br_2$ has been prepared and theoretically studied by using DFT(B3LYP) both in gas phase and in solution where CPCM model was employed. Its molecular geometry has been crystallographically identified. Theoretical geometrical parameters were found in very well correlations with the corresponding observed ones in all media involved in the study. Potential surface energy and energy calculations reflected that the theoretical di-ion form of the titled compound is almost more stable in all studied media except in DMSO. The Br-Br bond distance has been found quadratically varied with the medium dielectric constant. The average harmonic oscillator index of aromaticity accounted for the remarkable Br-Br bond length elongation in terms of charge transfer from the phenyl moieties to the lowest unoccupied anti bonding $\sigma^*_{(4pz)}$ orbital of the Br-Br entity. Electronic hardness and softness parameters reflected the possibility of the ionic form to be more reactive than the spoke structure. Besides, the necessity of having diffused functions in phosphorous calculations has been confirmed.

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