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Primary Phosphines Studied by Gas-Phase Electron Diffraction and Quantum Chemical Calculations. Are They Different from Amines?

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The molecular structures of allyl-, allenyl-, propargyl-, vinyl-, ethynyl-, phenyl-, benzyl-, and chloromethyl- phosphine have been determined from gas-phase electron diffraction data employing the SARACEN method. The experimental geometric parameters are compared with those obtained using ab initio calculations performed at the MP2 level using both Pople-type basis sets and the correlation-consistent basis sets of Dunning. The structure and conformational behavior of each molecule have been analyzed and, where possible, comparisons made to the analogous amine. For systems with multiple conformers, differences in the CCP bond angle of ~5° between conformers are common. Trends in the key parameters are identified and compared with those found in similar systems.

Introduction

Primary phosphines are poorly represented in the literature and are less widely used by chemists than secondary or tertiary phosphines. This is generally attributed to some undesirable properties; they are toxic, air sensitive, often pyrophoric and foul smelling. Despite this such compounds have many potential applications[1] and are interesting from a structural perspective. Previous microwave (MW) spectroscopic studies of alkylphosphines have shown the P−C bond length to vary greatly,[2] with values including 183.4 pm in cyclopropylphosphine[3] and 189.6 pm in $(CH_3)_3CPH_2$,[4] although no e.s.d.'s were quoted. A similar range of bond lengths is found when strongly electronegative fluorine atoms are substituted for either the methyl or phosphino hydrogen atoms in methylphosphine, with a P−C length of 182.0 pm for CH_3PF_2[5] (no e.s.d. reported) and 190.0(6) pm for CF_3PH_2,[6] both using MW spectroscopy. Primary phosphines also display interesting conformational behavior that is often quite different to that of their nitrogen analogues. For example, while propargylamine has a C_s conformation that is lower in energy than C_1 by around 6 kJ mol^{-1}, propargylphosphine consists of roughly equal amounts of C_s and C_1 conformers.[7,8] Such differences are attributed to the more diffuse P lone pair and the longer, less polar, P−H bonds. For primary phosphines with more than one conformation, significant structural differences have previously been noted between the various conformers. For example, in chloromethylphosphine ∠Cl−C−P was found to be 115.7(1)° in the *anti* conformer and 107.8(5)° in the *gauche*, when determined using gas-phase electron diffraction.[9] This difference was rationalized by considering the nature of the overlap between non-bonding and antibonding molecular orbitals for each conformer. A similar difference in bond angles between different conformations was also observed in a MW spectroscopic study of ethylphosphine.[2]

A number of primary phosphines have been studied by MW spectroscopy but very few complete experimental structures have ever been determined. The GED structures of eight primary phosphines (allyl-, allenyl-, propargyl-, vinyl-, ethynyl-, chloromethyl-, phenyl-, and benzyl-phosphine) are presented in this paper. Allylphosphine,[10] allenylphosphine,[11]

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(1) Brynda, M. *Coord. Chem. Rev.* **2005**, *249*, 2013–2034.
(2) Groner, P.; Johnson, R. D.; Durig, J. R. *J. Chem. Phys.* **1988**, *88*, 3456–3464.
(3) Dinsmore, L. A.; Britt, C. O.; Boggs, J. E. *J. Chem. Phys.* **1971**, *54*, 915–918.
(4) Li, Y. S.; Cox, A. W.; Durig, J. R. *J. Mol. Spectrosc.* **1978**, *70*, 34–40.
(5) Codding, E. G.; Creswell, R. A.; Schwendeman, R. H. *Inorg. Chem.* **1974**, *13*, 856–859.
(6) Wang, I. Y. M.; Brott, C. O.; Cowley, A. H.; Boggs, J. E. *J. Chem. Phys.* **1968**, *48*, 812–817.
(7) Cervellati, R.; Caminati, W.; Esposti, C. D.; Mirri, A. M. *J. Mol. Spectrosc.* **1977**, *66*, 389–398.
(8) Demaison, J.; Guillemin, J.-C.; Møllendal, H. *Inorg. Chem.* **2001**, *40*, 3719–3724.
(9) Brain, P. T.; Rankin, D. W. H.; Robertson, H. E.; Downs, A. J.; Greene, T. M.; Hoffman, M.; Schleyer, P. V. R. *J. Mol. Struct.* **1995**, *352*, 135–144.
(10) Møllendal, H.; Demiason, J.; Guillemin, J.-C. *J. Phys. Chem. A* **2002**, *106*, 11481–11482.
(11) Møllendal, H.; Demaison, J.; Petiprez, D.; Wlodarczak, G.; Guillemin, J.-C. *J. Phys. Chem. A* **2005**, *109*, 115–121.

propargylphosphine,[8] vinylphosphine,[12] and ethynylphosphine[13] have been studied using MW spectroscopy before but full structures were not determined. Chloromethylphosphine[9] and phenylphosphine[14] have been studied previously by GED but we have now refined the structures using modern techniques. The structure of benzylphosphine is studied for the first time. The structures of methylphosphine,[15] ethylphosphine,[2] and cyclopropylphosphine[3] have been determined in previous studies and will be used for comparison. The systematic study of α,β and β,γ unsaturated alkenyl- and alkynyl-phosphines and arylphosphines offers an excellent opportunity to assess the structural effects and bonding trends in primary phosphines as a function of the substitutent. As a result of the structural information obtained, trends in key parameters such as the P−C bond length and the C−C−P bond angles are identified, and are compared with rules devised for similar systems.[16]

Experimental Section

Syntheses. The starting materials lithium aluminum hydride, aluminum trichloride, diethyl vinylphosphonate, dichlorophenylphosphine, diethyl benzylphosphonate, and tetraethyleneglycol dimethyl ether (tetraglyme) were all purchased from Aldrich. All the experiments at atmospheric pressure were performed under nitrogen.

The preparations of allylphosphine (**1**),[17] propargylphosphine (**2**),[18] allenylphosphine (propadienylphosphine) (**3**),[19] vinylphosphine (**4**),[20] benzylphosphine (**5**),[21] chloromethylphosphine (**6**),[22,23] ethynylphosphine (**7**),[24] and phenylphosphine (**8**)[21] have already been reported. In several cases the published syntheses have been partially modified in this work. The exact experimental procedures used to synthesize compounds **1**−**8** are given in the Supporting Information.

Computational Methods. Calculations were performed for all compounds studied using the resources of the NSCCS[25] and the EaStCHEM RCF[26] using the Gaussian 03 program.[27] All MP2 methods were frozen core (fc).

Geometry Optimizations. An extensive search of the torsional potential of each compound was undertaken at the RHF/3-21G* level[28−30] to locate all minima. Geometry optimizations were conducted at the RHF[31] and MP2[32] levels of theory using both the Pople-type basis sets (6-31G*[33−35] and 6-311G*[36,37]) and the correlation-consistent basis sets of Dunning.[38−42] The optimized structures of the compounds studied, along with the atomic numbering schemes, are shown in Figures 1 and 2.

Frequency Calculations. Analytic second derivatives[43,44] of the energies with respect to nuclear coordinates were calculated at the MP2/6-311++G** level for each compound both to confirm the nature of the minima found by the optimization and for use with the SHRINK program.[45]

Gas-Phase Electron Diffraction (GED) Measurements. Data were collected for all the compounds studied using the Edinburgh gas electron diffraction apparatus.[46] For each molecule, an accelerating voltage of about 40 kV (electron wavelength ca. 6.0 pm) was used. Scattering intensities were recorded on Kodak Electron Image films. Sample and nozzle temperatures and nozzle-to-film distances for each compound can be found in the Supporting Information, along with the weighting points for the off-diagonal weight matrices, correlation parameters, scale factors and electron wavelengths. The electron wavelengths were determined from the scattering patterns of benzene vapor, recorded immediately before or after the compound patterns and analyzed in exactly the same way to minimize systematic errors in wavelengths and camera distances. The scattering intensities were measured using an Epson Expression 1680 Pro flatbed scanner and converted to optical densities as a function of the scattering variable, *s*, using an established program.[47]

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(12) Drean, P.; Le Guennec, M.; Lopez, J. C.; Alonso, J. L.; Denis, J. M.; Kreglewski, M.; Demaison, J. *J. Mol. Spectrosc.* **1994**, *166*, 210–223.

(13) Cohen, E.; McRae, G. A.; Goldwhite, H.; Stefano, S. D.; Beaudet, R. A. *Inorg. Chem.* **1987**, *26*, 4000–4003.

(14) Naumov, V. A.; Tafipol'skii, M. A.; Samdal, S. *Russ. J. Gen. Chem.* **2003**, *73*, 896–902.

(15) Noble-Eddy, R.; Masters, S. L.; Rankin, D. W. H.; Wann, D. A.; Khater, B.; Guillemin, J.-C. *Dalton Trans.* **2008**, 5041–5047.

(16) Mastryukov, V. S.; Boggs, J. E.; Durig, J. R. *J. Mol. Struct.* **2001**, *567−568*, 101–106.

(17) Serre, S. L.; Guillemin, J.-C.; Kárpáti, T.; Soos, L.; Nyulászi, L.; Veszprémi, T. *J. Org. Chem.* **1998**, *63*, 59–68.

(18) Guillemin, J.-C.; Malagu, K. *Organometallics* **1999**, *18*, 5259–5263.

(19) Guillemin, J.-C.; Savignac, P.; Denis, J.-M. *Inorg. Chem.* **1991**, *30*, 2170–2173.

(20) Cabioch, J.-L.; Denis, J.-M. *J. Organomet. Chem.* **1989**, *377*, 227–233.

(21) Horner, L.; Hoffmann, H.; Beck, P. *Chem. Ber.* **1958**, *91*, 1583–1588.

(22) Cabioch, J.-L.; Pellerin, B.; Denis, J.-M. *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, *44*, 27–32.

(23) Margules, L.; Demaison, J.; Sreeja, P. B.; Guillemin, J.-C. *J. Mol. Spectrosc.* **2006**, *238*, 234–240.

(24) Albrand, J. P.; Anderson, S. P.; Goldwhite, H.; Huff, L. *Inorg. Chem.* **1975**, *14*, 570–573.

(25) EPSRC National Service for Computational Chemistry Software. URL: http://www.nsccs.ac.uk.

(26) EaStCHEM Research Computing Facility (http://www.eastchem.ac.uk/rcf). This facility is partially supported by the eDIKT initiative (http://www.edikt.org).

(27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision C.02; Gaussian, Inc. ; Wallingford, CT, 2004.

(28) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939–947.

(29) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797–2803.

(30) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J . Am. Chem. Soc.* **1982**, *104*, 5039–5048.

(31) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69–89.

(32) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618–622.

(33) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261.

(34) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222.

(35) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163–168.

(36) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639–48.

(37) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650–654.

(38) Woon, D. E.; Dunning, T. H. Jr. *J. Chem. Phys.* **1993**, *98*, 1358–1371.

(39) Kendall, R. A.; Dunning, T. H. Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796–6806.

(40) Dunning, T. H. Jr. *J. Chem. Phys.* **1989**, *90*, 1007–1023.

(41) Peterson, K. A.; Woon, D. E.; Dunning, T. H. Jr. *J. Chem. Phys.* **1994**, *100*, 7410–7415.

(42) Wilson, A.; Mourik, T. v.; Dunning, T. H. Jr. *J. Mol. Struct., THEOCHEM* **1996**, *388*, 339–349.

(43) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *166*, 275–280.

(44) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *166*, 281–290.

(45) Sipachev, V. A. *J. Mol. Struct., THEOCHEM* **1985**, *121*, 143–151.

(46) Huntley, C. M.; Laurenson, G. S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1980**, 954–957.

(47) Fleischer, H.; Wann, D. A.; Hinchley, S. L.; Borisenko, K. B.; Lewis, J. R.; Mawhorter, R. J.; Robertson, H. E.; Rankin, D. W. H. *Dalton Trans.* **2005**, 3221–3228.

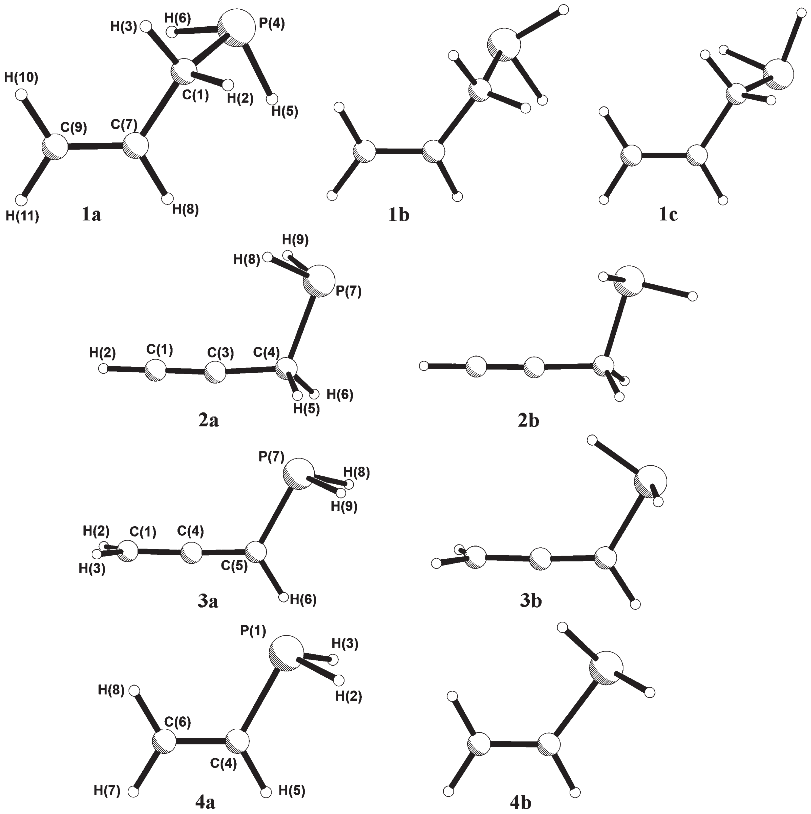

Figure 1. Molecular structures of the relevant conformations of allylphosphine (**1a**−**c**), propargylphosphine (**2a**,**b**), allenylphosphine (**3a**,**b**) and vinylphosphine (**4a**,**b**).

Data reduction and least-squares refinements were carried out using the ed@ed v2.4 program,[48] employing the scattering factors of Ross et al.[49]

Results

Ab Initio Calculations. Selected parameters for the optimized geometries of all compounds studied at the MP2/6-311++G** and MP2/aug-cc-pVTZ levels of theory are given in Table 1. A complete set of structural parameters for each compound is given in the Supporting Information. Where frequency calculations were available the relative abundance of each conformer was calculated using ΔG, but where frequency calculations were prohibitively expensive, ΔE was used.

GED Refinements. The starting parameters for the r_{h1} refinements[45] were taken from the theoretical geometries optimized at the MP2/6-311++G** level for each molecule. A theoretical Cartesian force field was obtained at this level and converted into a force field described by a set of symmetry coordinates using the SHRINK program,[45] which generated both the amplitudes of vibration (u_{h1}) and the curvilinear corrections (k_{h1}). All relevant geometric parameters and vibrational amplitudes were then refined. Flexible restraints were employed during the refinements using the SARACEN method.[50−52] The success of the final refinements can be assessed on the basis of the radial-distribution curves and the molecular-scattering intensity curves, which are shown in the Supporting Information, along with full lists of refined parameters. With the exception of allenylphosphine, for which R_G = 12.7%, R_G for the refinements ranged from 6.9% to 9.7%. A summary of the most important parameters is given in Table 1. The Supporting Information also contains the interatomic distances and the corresponding amplitudes of vibrations, least-squares correlation matrices, and experimental coordinates from the GED analyses.

Allylphosphine (1). A potential-energy surface (PES) scan around ϕC−C−C−P and ϕC−C−P−H revealed five stable conformations, two of which were discarded as they were calculated to be much higher in energy. This result is consistent with the conformations previously identified.[10] In the three lowest energy conformers ϕC−C−C−P is *anticlinal*, whereas it is *synperiplanar* in the two higher energy conformers. It is likely that the *synperiplanar* configuration is higher in energy because of increased steric repulsion between the phosphino group and the vinyl group. The remaining three conformers (**1a**−**c**) all possess C_1 symmetry and differ in the orientation of the PH_2 group. In **1a** the two CCPH dihedral angles are ± *synclinal*, in **1b** they are approximately −*synclinal*

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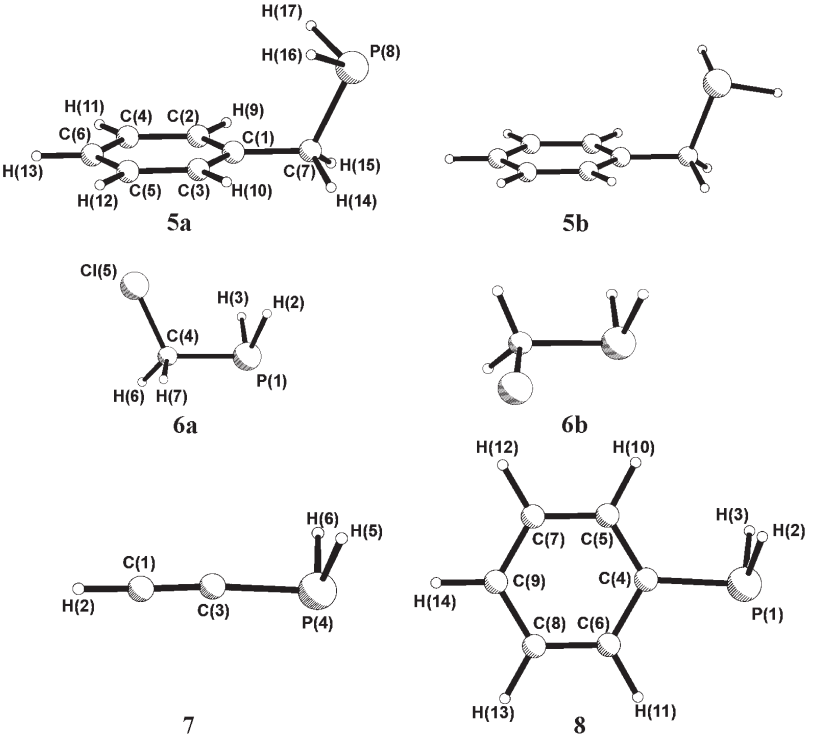
(48) Hinchley, S. L.; Robertson, H. E.; Borisenko, K. B.; Turner, A. R.; Johnston, B. F.; Rankin, D. W. H.; Ahmadian, M.; Jones, J. N.; Cowley, A. H. *Dalton Trans.* **2004**, 2469–2476.

(49) Ross, A. W.; Fink, M.; Hilderbrandt, R. In *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, Netherlands, 1992; Vol. *C*, p 245.

(50) Blake, A. J.; Brain, P. T.; McNab, H.; Miller, J.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H.; Robertson, H. E.; Smart, B. A. *J. Phys. Chem.* **1996**, *100*, 12280–12287.

(51) Brain, P. T.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1996**, 4589–4596.

(52) Mitzel, N. W.; Rankin, D. W. H. *Dalton Trans.* **2003**, 3650–3662.



5a **5b** **6a** **6b** **7** **8**

Figure 2. Molecular structures of the relevant conformations of benzylphosphine (**5a**,**b**), chloromethylphosphine (**6a**,**b**), ethynylphosphine (**7**), and phenylphosphine (**8**).

and *antiperiplanar*, and in **1c** are approximately +*synclinal* and *antiperiplanar*. All three conformers have the same statistical weight. On the basis of the ab initio calculations, electron-diffraction refinements were carried out using a model containing the three lowest energy conformers. The model was described using relevant bond lengths, bond angles, and dihedral angles and where two or more distances were close together the average and differences were used. A more detailed description of the model used, along with parameter descriptions for allylphosphine and all other compounds studied, is given in the Supporting Information. Initial refinements using the three-conformer model showed that the ratio of **1b** to **1c** was poorly defined, and so it was decided to fix the ratio of the abundances **1b**/**1c** at the ab initio value of **1b**/**1c** = 0.50. This behavior can be explained by considering the differences between the three conformers. At first glance the three lower energy conformations of allylphosphine appear to differ mainly in the orientation of the phosphino group. However, as the positions of these hydrogen atoms only influence the H···C and H···H distances, they are unlikely to be well resolved. Of greater importance is that for **1a** ∠C−C−P is around 115° while for **1b** and **1c** it is around 110° and therefore it is likely that the majority of the information about conformational ratios will come from the P(4)···C(7) distance and, to a lesser extent the P(4)···C(9) distance. In the MP2/6-311++G** calculations for **1a** *r*P(4)···C(7) is 283.7 pm and *r*P(4)···C(9) is 383.5 pm, for **1b** these distances are 277.0 and 372.1 pm, respectively, and for **1c** are 276.1 and 375.3 pm, respectively. As the distances for **1b** and **1c** are similar, while the distances for **1a** are distinct, it would be expected that the GED refinement would predict the ratio of **1a** to the total of **1b** + **1c** well, but that the abundances of 1b and **1c** themselves would be poorly determined.

Propargylphosphine (**2**). Propargylphosphine exists in two conformations,[8] one with C_s symmetry (**2a**), with the two C−C−P−H dihedral angles ±*synclinal*, and a C_1 conformer (**2b**), with one ϕC−C−P−H approximately *antiperiplanar* and the other approximately *synclinal*. **2b** has a statistical weight twice that of **2a**. The GED refinement was carried out using a model containing both conformers.

Allenylphosphine (**3**). Allenylphosphine has previously been shown by MW spectroscopy to have two conformations.[11] The first conformer (**3a**) possesses C_s symmetry, with the two C−C−P−H dihedral angles being ±*anticlinal*. The second conformer (**3b**) has C_1 symmetry with one ϕC−C−P−H close to *synperiplanar* and the second approximately *anticlinal*. Again, **3b** has a statistical weight twice that of **3a**. When the data for allenylphosphine were refined using a model containing both conformers, the amount of **3b** in the refinement fell to 0%. The *R* factor for this refinement is higher than for all the others, suggesting the presence of an impurity in the sample. The results of the refinement and the structure of **3a** are presented here, although it should be noted that the results are not expected to be precise or intended to offer any information on the relative energies of **3a** and **3b**.

Vinylphosphine (**4**). Vinylphosphine displays the same conformational behavior as allenylphosphine.[12] Both **4a** and **4b** were included in the refinement.

Benzylphosphine (**5**). A two-dimensional PES scan around ϕC−C−C−P and ϕC−C−P−H was conducted to locate all PES minima. A contour plot of the scan is shown in the Supporting Information (Figure SF1). The

Table 1. Selected Geometrical Parameters of the Studied Compounds, Including Experimental Values and Those Obtained at the MP2/6-311++G** (A) and MP2/aug-cc-pVTZ (B) Levels of Theory[a]

Allylphosphine

	1a			**1b**			**1c**		
parameter	GED	A	B	GED	A	B	GED	A	B
rP−C	187.5(1)	186.9	187.0	188.0(2)	187.4	187.5	187.7(1)	187.1	187.2
rP−H[b]	142.2(15)	141.2	141.5	142.2(15)	141.3	141.6	142.2(15)	141.2	141.4
∠H−P−H	94.2(10)	94.1	93.4	94.2(10)	94.1	93.4	94.9(10)	94.8	94.1
∠C−P−H[b]	96.9(10)	96.4	96.7	96.7(10)	96.7	97.1	96.9(10)	96.9	97.1
$r\mathrm{C}_{\alpha}-\mathrm{C}_{\beta}$	152.1(4)	149.6	148.9	152.4(4)	149.9	149.3	152.4(4)	149.9	149.3
$r\mathrm{C}_{\beta}-\mathrm{C}_{\gamma}$	135.7(7)	134.3	133.7	135.7(7)	134.2	133.6	135.7(7)	134.2	133.6
∠P−C−C	114.0(2)	114.5	114.2	109.3(10)	109.9	109.3	108.9(5)	109.5	109.1
∠C−C−C	122.9(8)	124.3	124.4	122.9(8)	124.5	124.5	122.9(8)	124.0	124.1
%[c]	79(4)	66.3	69.9[d]		11.9	8.6		21.8	21.5

Propargylphosphine

	2a			**2b**		
parameter	GED	A	B	GED	A	B
rP−C	187.1(2)	187.3	187.4	187.5(2)	187.7	187.8
rP−H[b]	141.6(6)	141.0	141.3	141.6(6)	141.2	141.5
∠H−P−H	94.2(10)	94.8	93.5	94.2(10)	94.3	93.7
∠C−P−H[b]	96.6(10)	96.2	96.3	96.2(10)	96.0	96.3
$r\mathrm{C}_{\alpha}-\mathrm{C}_{\beta}$	145.4(3)	145.6	145.1	145.7(3)	145.9	145.3
$r\mathrm{C}_{\beta}-\mathrm{C}_{\gamma}$	120.6(4)	122.0	121.7	120.7(3)	122.0	121.6
∠P−C−C	113.6(2)	114.9	114.4	108.5(5)	110.2	109.3
∠C−C−C	176.0(7)	179.2	179.5	176.0(11)	179.2	177.4
%[c]	68(5)	64.4[d]	58.7	32(5)	35.6[d]	41.3

Allenylphosphine

	3a			**3b**		
parameter	GED	A	B	GED	A	B
rP−C	183.6(2)	183.6	183.5		183.5	183.5
rP−H[b]	142.9(6)	141.3	141.6		141.2	141.4
∠H−P−H	92.4(10)	93.2	92.7		95.0	94.2
∠C−P−H[b]	97.7(9)	96.6	97.0		97.0	97.1
$r\mathrm{C}_{\alpha}-\mathrm{C}_{\beta}$	131.6(2)	131.5	130.9		131.6	131.1
$r\mathrm{C}_{\beta}-\mathrm{C}_{\gamma}$	131.6(2)	131.5	131.1		131.4	130.9
∠P−C−C	120.0(4)	120.4	119.4		124.2	123.5
∠C−C−C	177.6(7)	179.4	178.6		179.1	178.4
%[c]	100	66.8[d]	58.6	0	33.2[d]	41.4

Vinylphosphine

	4a			**4b**		
parameter	GED	A	B	GED	A	B
rP−C	182.9(1)	183.1	183.0	182.4(2)	182.5	182.5
rP−H[b]	141.2(7)	141.2	141.5	141.2(7)	141.2	141.4
∠H−P−H	94.2(10)	93.7	92.8	95.0(10)	95.3	94.5
∠C−P−H[b]	97.1(9)	97.1	97.5	97.2(9)	97.3	97.1
$r\mathrm{C}_{\alpha}-\mathrm{C}_{\beta}$	134.3(3)	134.3	133.8	134.3(3)	134.4	133.8
$r\mathrm{C}_{\beta}-\mathrm{C}_{\gamma}$						
∠P−C−C	119.1(4)	120.6	120.1	126.8(3)	125.5	125.3
∠C−C−C						
%[c]	65(5)	58.0	64.5	35(5)	42.0	35.5

Benzylphosphine

	5a			**5b**		
parameter	GED	A	B	GED	A	B
rP−C	188.1(2)	187.3	187.2	188.3(2)	187.4	187.3
rP−H[b]	143.0(8)	141.2	141.5	143.0(8)	141.4	141.6

Table 1. Continued

Benzylphosphine

	5a			**5b**		
parameter	GED	A	B	GED	A	B
$\angle$H−P−H	94.0(10)	94.0	93.2	94.0(10)	94.3	93.9
$\angle$C−P−H^b	96.0(10)	96.2	96.2	96.0(10)	96.8	97.1
$r\mathrm{C}_\alpha-\mathrm{C}_\beta$	150.8(4)	150.2	149.6	151.2(4)	150.6	150.0
$r\mathrm{C}_\beta-\mathrm{C}_\gamma$	138.7(6)	140.4	139.8	138.6(6)	140.4	139.8
$\angle$P−C−C	116.8(6)	115.0	114.4	111.8(5)	109.8	108.6
$\angle$C−C−C	119.7(2)	120.8	120.7	119.7(2)	120.7	120.7
%^{c}	33(11)	41.2	51.3	67(11)	58.8	48.7

Chloromethylphosphine

	6a			**6b**		
parameter	GED	A	B	GED	A	B
rP−C	186.8(6)	185.2	185.2	187.9(6)	186.4	186.3
rP−H^b	142.7(5)	140.8	141.2	142.7(5)	141.2	141.5
$\angle$H−P−H	94.7(10)	95.0	94.2	94.7(10)	94.8	93.7
$\angle$C−P−H^b	97.0(9)	96.8	96.5	97.0(9)	95.5	95.7
$r\mathrm{C}_\alpha-\mathrm{C}_\beta$						
$r\mathrm{C}_\beta-\mathrm{C}_\gamma$						
$\angle$P−C−C						
$\angle$C−C−C						
%^{c}	84(3)	74.6	64.2	16(3)	25.4	35.8

Ethynylphosphine

	7		
parameter	GED	A	B
rP−C	178.5(1)	177.8	177.5
rP−H^b	142.4(4)	141.0	141.3
$\angle$H−P−H	94.0(10)	95.2	94.0
$\angle$C−P−H^b	96.4(6)	96.8	96.8
$r\mathrm{C}_\alpha-\mathrm{C}_\beta$	121.9(2)	122.5	122.0
$r\mathrm{C}_\beta-\mathrm{C}_\gamma$			
$\angle$P−C−C	175.5(23)	169.7	173.4
$\angle$C−C−C			

Phenylphosphine

	8		
parameter	GED	A	B
rP−C	183.8(3)	184.4	184.3
rP−H^b	141.5(3)	141.2	141.5
$\angle$H−P−H	94.6(10)	94.1	93.2
$\angle$C−P−H^b	96.8(9)	97.3	97.4
$r\mathrm{C}_\alpha-\mathrm{C}_\beta$	139.9(4)	140.7	140.1
$r\mathrm{C}_\beta-\mathrm{C}_\gamma$	139.2(3)	139.9	139.3
$\angle$P−C−C	124.2(7)	123.6	123.3
$\angle$C−C−C	120.7(3)	120.7	120.7

[a] All distances in pm and angles in deg. See Figures 1 and 2 for atom numbering. [b] An average value was used when a molecule had no symmetry and the H atoms bonded to the P were nonequivalent. [c] Unless otherwise stated the abundances were calculated using ΔG for A and ΔE for B. [d] ΔE was used.

scan revealed two minima differing mainly in the orientation of the phosphino group. It also shows that there is no significant rotation of the benzene ring and so it is not necessary to construct a dynamic model. Conformer **5a** has C_s symmetry, with a mirror plane through the P(8), C(7), C(6), and C(1) atoms, and the two ϕC−C−P−H ±*synclinal*. In **5b** the symmetry is broken, although the phosphine does not move far from the mirror plane present in **5a** and the ring is still very close to having C_s symmetry. The main difference in **5b** is the rotation of the phosphino group such that one ϕC−C−P−H is approximately *anti-periplanar* and the other approximately *synclinal*.

Chloromethylphosphine (6). Chloromethylphosphine has two conformations with different Cl−C−P−H dihedral angles.[9] **6a** has C_s symmetry with the Cl−C−P−H dihedrals ±*synclinal*, whereas the second conformer, **6b**, has C_1 symmetry, with one of the two dihedral angles being close to *antiperiplanar* and the other close to *synclinal*.

Ethynylphosphine (7). PES scans revealed that ethynylphosphine (**7**) exists as a single conformer of C_s symmetry, consistent with the previous study.[13] The data were refined using a model containing eight parameters.

Phenylphosphine (8). Previous studies of phenylphosphine (**8**) suggested that the phosphino hydrogens were staggered either side of the phenyl ring.[14] Scans about ϕC−C−P−H were conducted at various levels of theory and are shown in the Supporting Information (Figure SI1). Although the lowest energy structure was always found to have a C−C−P−H dihedral angle of approximately 50°, the PES curve in each case was quite flat and the barrier to rotation was low, suggesting that the molecule is close to free rotation at the experimental temperature. When the PH_2 group rotates the structure differs mainly in the positions of the hydrogen atoms, with changes in ∠C−C−P of, at most, a couple of degrees. A dynamic model was created using a sine-wave-like barrier parametrized with a single parameter (barrier height), but this model did not offer an improved fit over a model using a single C_s conformer, and the barrier height could not be refined. This is to be expected as, assuming the ∠C−C−P does not change dramatically, the P−H and C(4)···H distances will vary little as the group rotates. Only non-bonded distances between the phosphino hydrogen atoms and the ring atoms change significantly, and such distances are very weakly scattering. It was therefore decided to ignore the rotation and use a model containing a single C_s conformer.

Discussion

The molecular structures of a number of primary phosphines have been investigated in the gas phase by GED supplemented by ab initio calculations via the SARACEN method.[50−52] An independent theoretical investigation of the structures was also undertaken.

Allylphosphine (1). The experimental structure of allylphosphine is generally in good agreement with the theoretical structures. The P−C bond length is 187.5(1) pm for the most abundant conformer (**1a**) and is slightly longer than those calculated at the highest levels of theory (186.9 and 187.0 pm by MP2/6-311++G** and MP2/aug-cc-pVTZ, respectively). The C−C and C=C bond lengths are also slightly longer than those calculated, at 152.1(4) and 135.7(7) pm for **1a** compared to calculated values in the range 148.9−150.8 and 131.6−135.2 pm. As found in previous studies of similar molecules,[16] a large difference in ∠C−C−P is found between different conformers, with that in **1a** consistently larger than in **1b** and **1c** by ~5°. The P−C bond length is also slightly shorter in **1a** than in **1b** and **1c**. The experimental abundance of **1a** of 79(5)% lies slightly above the calculated values, which range from 51% to 70%. The abundance of **1b** and **1c** combined was therefore 21(5)% but it was not possible to refine the abundance of **1b** relative to **1c**. The conformational behavior of allylphosphine is quite different to that of allylamine, for which four conformers have been identified.[53−56]

Propargylphosphine (2). Again good agreement is found between the experimental structure and the theoretical structures. The experimental *r*P−C for **2a** of 187.1(2) pm compares well to the calculated values of 187.3 and 187.4 pm at the MP2/6-311++G** and MP2/aug-cc-pVTZ levels, respectively. This bond length is very close to that found in allylphosphine, in which phosphorus is also bonded to an sp^3-hybridized carbon. The experimental *r*C−C for **2a** is also in good agreement with calculations, while *r*C≡C is a little shorter by experiment [120.6(4) pm] than the high-level theory predicts (122.0 and 121.7 pm by MP2/6-311++G** and MP2/aug-cc-pVTZ, respectively), although it is consistent with the range of calculated distances, which vary from 118.7 to 123.6 pm. For **2a** the calculated ∠C−C−C varies from 178.1 to 179.9°. The experimental value is a little smaller at 176.0(7)°. As with the other systems exhibiting multiple conformers, a large difference was found in ∠C−C−P with **2b** having a value around 5° narrower than **2a**. The values of ∠C−C−P for both **2a** and **2b** were slightly smaller by experiment than theory predicted. The experimental value is 113.6(2)° for **2a**, while the smallest angle predicted by theory is 114.4° at the MP2/aug-cc-pVTZ level. For **2b** the experimental and smallest ab initio values are 108.5(5) and 109.3°, respectively. Small differences between **2a** and **2b** were also found for *r*P−C, which is 0.4(1) pm longer in **2b**, and for *r*C−C, which is 0.3 pm longer in **2b**. The experimental abundance of **2a** is 68(5)%, which is slightly larger than values predicted by calculation, which vary from 45 to 64%. The same two conformations are found in the amine analogue,[7] but the analogous conformer to **2a** is significantly lower in energy than the conformer that resembles **2b**. This is probably because of increased repulsion between the nitrogen lone pair and C≡C, which destabilizes the amine **2b** conformation, and also because of an increased attraction between the amino hydrogen atoms and the triple bond because of the higher electronegativity of N, which stabilizes **2a**.

Allenylphosphine (3). Despite the worse-than-usual *R* factor and the inability to refine the structure of the second conformer, the refined structure of **3a** matches the theoretical structures very well. It must be noted, however, that both the ab initio results and a previous MW study[11] suggest that **3a** and **3b** should be present in a ratio of roughly 2:1 and so modeling a single conformer is not realistic. For the refinement with **3a** only, the P−C bond length is found to be 183.6(2) pm by experiment with the theoretical values varying from 182.8 to 185.4 pm and the highest level calculations predicting 183.6 and 183.5 pm. Calculations suggested that any difference between the two C=C bond lengths was small, and less than the anticipated experimental error. This was reflected in the refined values with both C=C distances refining to 131.6(2) pm. This compares well to calculated values, which are 131.5 and 131.0 pm at the MP2/6-311++G** and MP2/aug-cc-pVTZ levels. As with propargylphosphine, the refined C−C−C angle of 177.6(7)° was a little narrower than calculations suggested. Again, calculations predicted that ∠C−C−P

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(53) Roussy, G.; Demaison, J.; Barriol, J.; Rudolph, H. D. *J. Mol. Spectrosc.* **1971**, *38*, 535–544.

(54) Botskor, I.; Rudolph, H. D.; Roussy, G. J. *J. Mol. Spectrosc.* **1974**, *52*, 457–484.

(55) Botskor, I.; Rudolph, H. D.; Roussy, G. J. *J. Mol. Spectrosc.* **1974**, *53*, 15–36.

(56) Botskor, I.; Rudolph, H. D. *J. Mol. Spectrosc.* **1978**, *71*, 430–435.

varied between the two conformers, with the value in **3b** around 4° larger than in **3a**. The refined value of ∠C−C−P for **3a** was 120.0(4)°, which is consistent with the calculated values. The amine analogue, allenylamine, has been synthesized using flash vacuum pyrolysis[57] but has never been structurally characterized.

Vinylphosphine (4). The structure and conformational behavior of vinylphosphine is very similar to that of allenylphosphine. The experimental P−C bond length of 182.9(1) pm for **4a** is close to that found in allenylphosphine and is consistent with the values obtained from theoretical calculations. The experimental rC−C [134.3(3) pm] is also consistent with the calculated values and is, as expected, significantly longer than rC−C in allenylphosphine. The calculated ∠C−C−P for **4a** ranges from 120.1 to 121.6°, while for **4b** the angles range from 125.3 to 126.2°. The experimental values lie a little outside of these ranges, being 119.1(4) and 126.3(8)° for **4a** and **4b**, respectively, corresponding to a slightly larger than calculated difference between ∠C−C−P in the two conformers. The experimental abundance of **4a**, 65(5)%, is in good agreement with the theoretical abundances. The nitrogen analogue, vinylamine, is found entirely in a conformation resembling **4b**.[58−60]

Benzylphosphine (5). A search of the available literature revealed little previous work concerning this compound, and none relating to its structure. The conformational behavior of benzylphosphine (**5a** and **5b**, see Figure 2) is analogous to that of propargylphosphine (**2a** and **2b**, see Figure 1), so that the two systems are virtually identical apart from the $-C_6H_5$ and −C≡C−H fragments. The most stable conformation, **5a**, has ϕC−C−P−H ±*synclinal*. This conformation is most likely to be stabilized either because of a favorable interaction between the phosphino hydrogen atoms and the ring system (a weak intramolecular hydrogen bond) or because this conformation minimizes repulsion between the lone pair of electrons and the ring. The P−C bond lengths in this molecule are the longest encountered in this study, with the value for **5a** being 188.1(2) pm. This is around 4σ away from the highest level ab initio calculations (187.2 and 187.3 pm calculated using MP2/6-311++G** and MP2/aug-cc-pVTZ, respectively), and no obvious reason for this discrepancy can be found; in similar systems in this study the agreement between the theoretical and experimental values of P−C is much better. The P−C bond length in **5b** was found to be 188.3(2) pm. As with the other systems with multiple conformations, a difference of around 5° in ∠C−C−P was found between **5a** and **5b**. ∠C−C−P was found to be 117.0(6)° for **5a** and 111.8(5)° for **5b**, both of which are larger ($\sim 3-4\sigma$) than the highest level calculations suggest. **5a** and **5b** are calculated to be very close in energy, with **5a** slightly lower in energy in all but two of the calculations that use ΔG. The experimental abundance of **5a** is 33(11)% which, because of the large uncertainty, is consistent with most of the calculations. Benzylamine is also found to exist in two conformers.[61] The lower energy conformer in benzylamine is analogous to **5a** with the second conformer being similar to **5b**, but with the C−C−C−N dihedral angle rotated by around 50°.

Chloromethylphosphine (6). The GED structure of chloromethylphosphine has previously been published[9] and will not be discussed here in detail. The previous study used an r_g refinement with some parameters fixed. The new refinement, using the SARACEN method,[50−52] gives an r_{h1} structure with all relevant parameters refining. The results of the new refinement are generally comparable to the old refinement within experimental error. The major differences in the new refinement are that the ∠Cl−C−P angles in **6a** and **6b** are 0.5 and 0.9° narrower, respectively, with the e.s.d.'s being 0.1 and 0.7°, respectively. The previously determined abundance of **6b** was 22(5)% and in the new refinement it is 16(3)%. Both values are consistent with the abundances calculated ab initio, which vary widely from 16 to 46%. Comparison with the nitrogen derivative cannot be performed since only the more stable isomeric form of chloromethylamine, the iminium salt, has been characterized.[62]

Ethynylphosphine (7). The P−C bond length in ethynylphosphine is the shortest encountered in this study, with an experimental value of 178.5(1) pm. This is significantly larger than that found for the highest level calculations (177.8 and 177.0 pm by MP2/6-311++G** and MP2/aug-cc-pVQZ, respectively) but is consistent with the range of bond lengths found at lower levels of theory. An earlier experimental study found the distance to be 177.4(5) pm, although some parameters were fixed.[13] Of particular interest is any deviation from linearity of ∠C−C−P. Analogous compounds have been found to have Y−C≡X angles that are well away from 180°. For example, ∠P−C≡N in F_2PCN is 171.2(8)°.[63] Such large distortions are difficult to explain in a consistent manner, although it appears that the effect is caused by the interaction of the lone pair with the triple bond, as similarly large deviations from linearity are found when Y = N or P and X = C or N.[13] The uncertain nature of this angle in the present case is reflected in the calculated values, with the lowest value being 169.1° at the MP2/6-31G* level and the highest 177.0° at the HF/3-21G* level. The experimental value of 175.5(23)° compares with the larger calculated values, but the large uncertainty makes it difficult to draw firm conclusions. The previous study of this compound found the angle to be 173(2)°.[13] All other experimental parameters, including rC≡C of 121.9(2) pm, were close to both the calculated values and to those found in the previous study. Ethynylamine has never been characterized by GED or MW spectroscopy but has been studied using photoelectron spectroscopy.[64]

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(57) Hakiki, A.; Ripoll, J.-L.; Thuillier, A. *Tetrahedron Lett.* **1984**, *25*, 3459–3460.

(58) Hamada, Y.; Hashiguchi, K.; Tsuboi, M.; Koga, Y.; Kondo, S. *J. Mol. Spectrosc.* **1984**, *105*, 93–104.

(59) Hamada, Y.; Sato, N.; Tsuboi, M. *J. Mol. Spectrosc.* **1987**, *124*, 172–178.

(60) McNaughton, D.; Robertson, E. G. *J. Mol. Spectrosc.* **1994**, *163*, 80–85.

(61) Melandri, S.; Maris, A.; Favero, P. G.; Caminati, W. *Chem. Phys. Chem.* **2001**, *2*, 172–177.

(62) Bohme, H.; Viehe, H. G. *Iminium Salts in Organic Chemistry*; John Wiley & Sons: New York-London, 1979.

(63) Lee, P. L.; Cohn, K.; Schwendeman, R. H. *Inorg. Chem.* **1972**, *11*, 1917–1920.

(64) Wentrup, C.; Briehl, H.; Lorencak, P.; Vogelbacher, U. J.; Winter, H. W.; Maquestiau, A.; Flammang, R. *J. Am. Chem. Soc.* **1988**, *110*, 1337–1343.

Table 2. P−C Bond Lengths in Primary Phosphines

	C_α hybridization	rP−C/pm	
		experimental	MP2/6-311++G**
Propargylphosphine	sp^3	187.1(2)	187.3
Benzylphosphine	sp^3	188.1(2)	187.3
Allylphosphine	sp^3	187.4(1)	186.9
Ethylphosphine[a]	sp^3	186.2[b]	185.8
Methylphosphine[c]	sp^3	185.72(6)	185.6
Chloromethylphosphine	sp^3	186.8(6)	185.2
Phenylphosphine	~sp^2	183.8(3)	184.4
Allenylphosphine	sp^2	183.6(2)	183.6
Cyclopropylphosphine[d]	sp^2 [e]	183.4[b]	182.9
Vinylphosphine	sp^2	182.9(1)	183.1
Ethynylphosphine	sp	178.5(1)	177.8

[a] Ref 2. [b] No e.s.d.'s were reported. [c] Ref 11. [d] Ref 3. [e] According to the Walsh orbital description.

Phenylphosphine (8). Phenylphosphine has been studied previously, and so the results will not be discussed in detail. The structural parameters obtained are consistent with the previous work, but the parameters from this study generally have smaller e.s.d.'s. Our approach, an r_{h1} refinement using the SARACEN method to refine all relevant parameters, is expected to provide more reliable parameters than the previous r_a refinement with fixed parameters. With the exception of rC−H, all parameters in the current study are close to those given by the highest level calculations. The distance rP−C is found to be 183.8(3) pm, compared to 184.3 pm at the MP2/aug-cc-pVTZ level, and the larger of the two C−C−P angles is 124.2(7)°, which is consistent with the larger calculated angles. In the previous refinement these (r_a) values were 183.3(6) pm and 120.2(30)°. Aniline has been studied previously and found to adopt a C_s configuration with both amino hydrogen atoms on the same side of the ring.[65]

P−C Bond Lengths. The structures of methylphosphine,[15] ethylphosphine,[2] and cyclopropylphosphine[3] have been studied previously. For comparison the key structural parameters for these systems are listed in Table 2 along with the parameters from this study. The range of bond lengths spans ~10 pm, with propargylphosphine, benzylphosphine, and allylphosphine being the longest and ethynylphosphine the shortest. The general trend is that, as expected, the bond is longest when the α carbon (C_α) is sp^3 hybridized and gets progressively shorter for sp^2 and sp hybridization. This shortening is consistent with that found for a C−C bond in analogous environments and can be explained either by hyperconjugation[66] or by the interaction between the lone pair on P and the C−C π-system leading to the formation of resonance structures. For example, in vinylphosphine (and similarly for other sp^2-hybridized systems) the resonance structure $H_2C^-{-}CH{=}P^+H_2$ is possible, and for ethynylphosphine, $HC^-{=}C{=}P^+H_2$, such a resonance structure is not possible if carbon is sp^3 hybridized. The more subtle changes in bond lengths for molecules with the same C_α-hybridization appear to be related to an interaction between P and C_β. The results suggest that the P−C bond length is longer when a π-system exists at the β position, and that the bond length is longer if there is a more extensive π-system, for example rP−C is longer in propargylphosphine than in allylphosphine. It has previously been shown that the P lone pair interacts strongly with a π-system at the β position,[17] and so this trend in bonding appears to be indicative of repulsion between the phosphorus lone pair and any π-system at the β position.

Table 3. Conformational Differences in P−C Bond Length (ΔrP−C) and Differences in C−C−P Angle (Δ∠C−C−P) for Various Phosphines at the MP2/6-311++G** Level of Theory[a]

	ΔrP−C/pm	Δ∠C−C−P/deg
Allylphosphine[b]	−0.5	4.6
Propargylphosphine	−0.4	4.7
Allenylphosphine	−0.1	−3.8
Vinylphosphine	0.6	−4.9
Benzylphosphine[b]	−0.1	5.2
Chloromethylphosphine	−1.2	6.0[c]
Ethylphosphine[d]	−0.4	5.1

[a] Differences defined as the more stable conformer minus the less stable conformer. [b] For allylphosphine with 3 conformers the difference was defined as **1a**-**1b** and for benzylphosphine, in which the energy of the two conformers is ambiguous, it was defined as **5a**-**5b**. [c] Angle is Δ∠Cl−C−P. [d] Ref 2.

Structural Changes. The structural changes between systems with two or more conformations are shown in Table 3.

A previous study suggested a rule for similar systems in which the most stable conformer should have the shortest bond and the smallest bond angles.[16] In general the higher energy conformer will be more sterically crowded leading to longer bonds and wider angles. Six of the seven molecules have a shorter bond length in the more stable conformer. The exception is vinylphosphine, in which the lower energy conformer has a longer bond (182.9(1) pm) than the higher energy conformer (182.4(1) pm). It is somewhat surprising that this behavior in vinylphosphine is different to that of allenylphosphine, despite the molecules being so similar. Five of the seven systems, including all those with an sp^3-hybridized C_α, show a larger bond angle in the more stable conformation. The two exceptions are the two systems in which C_α is sp^2 hybridized, for which the lower energy conformation has a narrower C−C−P angle. In the two sp^2-hybridized systems the P−H bonds point away from the C=C bond while most of the sp^3 systems have the

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(65) Schultz, G.; Portalone, G.; Romando, F.; Domenicano, A.; Hargittai, I. *Struct. Chem.* **1996**, *7*, 59–71.

(66) Chou, K.-t.; Zhou, G.-d.; Chen, W. *Fundamentals of structural chemistry*; World Scientific: River Edge, NJ, 1993.

P−H bonds pointing toward the C−C bond. It is likely that in the sp^3 systems the lower energy conformation is favored because this minimizes repulsion from the phosphorus lone pair but that this conformation necessitates a larger C−C−P angle to accommodate the P−H bonds. In the higher energy conformations of the sp^3 systems the PH_2 group is rotated and so the C−C−P angle relaxes.

Conclusion

The gas-phase structures of a series of primary phosphines have been determined using gas-phase electron diffraction and compared to the structure predicted using quantum chemical calculations. The C−P bond length was found to vary by around 10 pm across the systems studied with the general trend being that the longest bond is found when C_α is sp^3 hybridized and the shortest when sp hybridized. For compounds with multiple conformers, differences were found between the conformations, with changes in rC−P of ~0.5 pm and in ∠C−C−P of ~5° being common. Many of the phosphines studied display different conformational behavior when compared to analogous amines. The amines most similar to their phosphine analogues are propargylamine, which exists in the same conformations as propargylphosphine albeit in a different ratio, and vinylamine, which exists solely as one of the two conformers of vinylphosphine. The other systems show greater variations. Benzylphosphine shares one conformation with benzylamine but both molecules have a unique second conformer, and while in phenylphosphine both H atoms are staggered with respect to the ring in aniline, they both lie to the same side of the ring. Allylamine, with four conformers, displays even more complex conformational behavior than that found in allylphosphine. Unfortunately for the remaining three compounds a direct comparison is not possible: allenylamine and ethynylamine have not been structurally characterized and chloromethylamine is found as the more stable isomeric iminium salt.

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Supporting Information Available: Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.