(Benzene-1,3,5-triyl)tris[phosphine] ($C_6H_3(PH_2)_3$) and (Benzene-1,3,5-triyl)tris[phosphonic Acid] ($C_6H_3[P(O)(OH)_2]_3$). Absence of Hydrogen Bonding in Solid Primary Phosphines

by **Stephan A. Reiter**, **Bernd Assmann**, **Stefan D. Nogai**, **Norbert W. Mitzel**, and **Hubert Schmidbaur***

Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstrasse 4, D-85747 Garching

The prolonged photo-*Arbuzov* reaction (3 weeks, Hg lamp) of 1,3,5-trichloro-benzene with a large excess of trimethyl phosphite (as a solvent) at 50° gives moderate yields of dimethyl (3,5-dichlorophenyl)phosphonate (**1**; 14.5%), tetramethyl (5-chloro-1,3-phenylene)bis[phosphonate] (**2**; 35.4%), and hexamethyl (benzene-1,3,5-triyl)tris[phosphonate] (**3**; 30.1%). The products can be separated by fractional distillation. Acid hydrolysis of the esters gives almost quantitative yields of the corresponding phosphonic acids **4**–**6**. Reduction of the esters **1**–**3** by $LiAlH_4$ in tetrahydrofuran affords the primary phosphines (3,5-dichlorophenyl)phosphine (**7**; 46.5%), (5-chloro-1,3-phenylene)bis[phosphine] (**8**; 34.5%) and (benzene-1,3,5-triyl)tris[phosphine] (**9**; 25.2% yield). In the crude reduction products from **2** (preparation of **8**) and from **3** (preparation of **9**), (3-chlorophenyl)phosphine and (1,3-phenylene)bis[phosphine], respectively, are observed as by-products. All compounds are characterized by standard analytical, spectroscopic, and (for **1**, **7**, and **8**) structural techniques. The arrangement of the molecules in the crystal structures of **7** and **8** suggest that H-bonding between the primary aryl*phosphines* is virtually insignificant for the packing of the components. This is in marked contrast to the importance of H-bonding for the supramolecular chemistry of aryl*amines*. The new primary polyphosphines and polyphosphonic acids are to be employed in the construction of extended arrays.

Introduction. – Aryl*phosphines* play an important role in many areas of contemporary chemistry. Tertiary phosphines Ar_3P are the most prominent class of ligands for transition metals, and their complexes are used as homogeneous catalysts in a large variety of reactions [1]. They are also the base chemicals for many reagents in organic synthesis including phosphonium salts [2], phosphonium ylides [2–4], phosphine boranes [2][5], and phosphine oxides and sulfides [2]. Secondary phosphines Ar_2PH are less common in catalysts and also as reagents, but their P–H group offers an additional functionality for the design of more sophisticated substitution patterns and for oxidation products. Finally, primary phosphines $ArPH_2$ are the least developed series of arylphosphines with still very limited areas of application [6–8]. However, their potential as synthons is even greater owing to two reactive P–H functions in addition to the nucleophilic/donor center at the P-atom.

Only a relatively small number of primary arylphosphines has been prepared and fully characterized [9–11], and this is particularly true for aromatic hydrocarbons with more than one primary phosphine function [6][12–23]. For benzene itself, the complete set of primary phosphines has the general formula $C_6H_n(PH_2)_{6-n}$ comprising a total of 12 species, of which only less than half are known (*Fig. 1*).

Current interest in advanced materials with tailored structures and properties has attracted increasing attention to polyphosphinoarenes with a rigid skeleton, on which new structural motifs can be built readily and selectively. In our own studies, recent

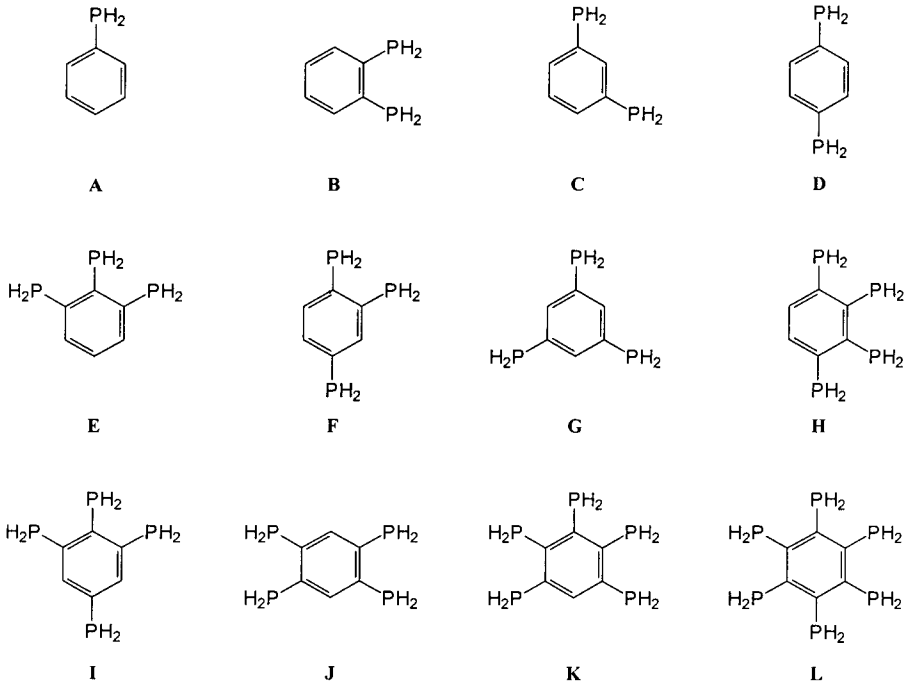


Fig. 1. *Polyphosphino-substituted benzene molecules* **A**–**L**. Only **A**–**D** and **J** are known.

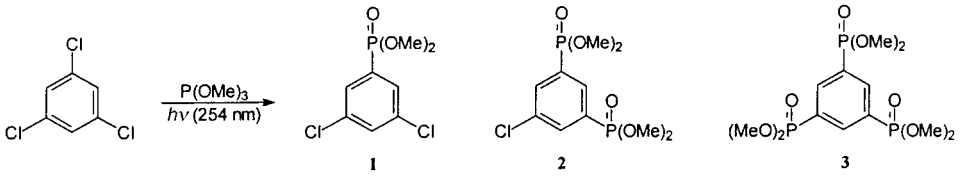
work focused on phosphine-supported gold clusters [24], with initial work on PH_3 [25–30], $Ph-PH_2$ [30–33], 1,2- [34] and 1,4-$C_6H_4(PH_2)_2$ [35], and secondary phosphines [36][37] as nucleation centers for cluster growth. In the present work, we report the preparation of the corresponding (benzene-1,3,5-triyl)tris[phosphine] (=1,3,5-triphosphinobenzene), which will be used both as a polyfunctional donor as well as for the construction of one- and two-dimensional networks.

The synthetic strategies employed are based on previous investigations, mainly the photo-*Arbuzov* reaction [6][12][38]. The methods were adapted to the challenge posed by the multiphosphination of benzene, which was previously accomplished in only isolated cases [6][12–21].

Preparative Results. – For all reactions, 1,3,5-trichlorobenzene served as the starting material. Preliminary experiments with the trifluoro, tribromo, and triiodo analogues showed that there is no advantage in using these more expensive reactants. Thus, 1,3,5-$C_6H_3Cl_3$ was dissolved in an excess of trimethyl phosphite (molar ratio 1:5) and irradiated by UV light (Hg, 254 nm, 700 W) for 3 weeks at 50° (*Scheme 1*). Unreacted $(MeO)_3P$ and its *Arbuzov* isomerization product $(MeO)_2P(O)Me$ were removed by distillation *in vacuo* and the residue subjected to fractional distillation *in vacuo*. Typically, the product distribution of this particular experiment was 14.5% yield of dimethyl (3,5-dichlorophenyl)phosphonate (**1**), 35.4% of tetramethyl (5-chloro-1,3-phenylene)bis[phosphonate] (**2**), 30.1% of hexamethyl (benzene-1,3,5-triyl)tris-

[phosphonate] (**3**), and some nonvolatile residue. Shorter reaction times gave only slightly higher yields of **1**, but much lower yields of **2** and **3**. Longer reaction times, on the other hand, did not give more satisfactory yields of **2** and **3**, but led instead to more extensive decomposition and to the generation of more *Arbuzov* rearrangement $(MeO)_3P \rightarrow (MeO)_2P(O)Me$.

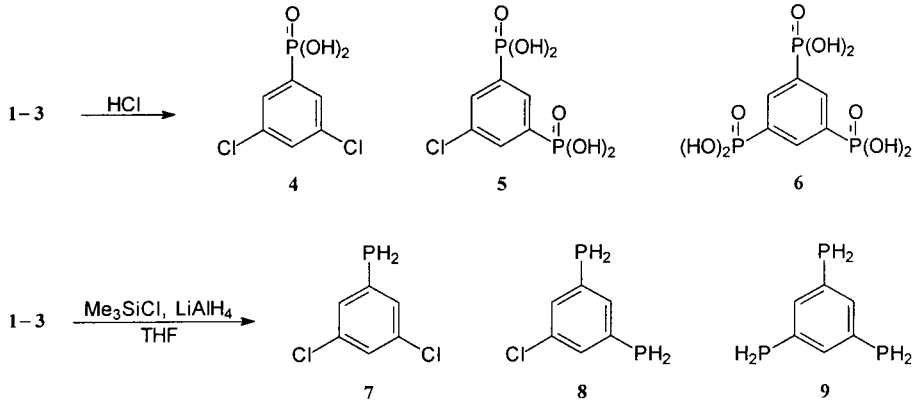
Scheme 1. *Photo*-Arbuzov *Reaction: Preparation of the Phosphonic Acid Esters* **1**–**3**



All three products **1**–**3** were obtained as colorless, viscous liquids, stable well above 210°. Compound **1** could be crystallized upon quenching with liquid N_2 and annealing by warming to room temperature, and from single crystals its structure could be determined (see below). Compounds **2** and **3** solidified in a glassy state upon cooling and remelted upon warming. No crystals could be obtained. The three esters are soluble in most common organic solvents. The NMR spectra ($CDCl_3$) showed the expected set of resonances, and the mass spectra and elemental analyses confirmed the proposed composition.

Ester hydrolysis of **1**–**3** with concentrated aqueous hydrochloric acid under reflux afforded the corresponding phosphonic acids **4**–**6** in almost quantitative yields (*Scheme 2*). The colorless, crystalline dichloro compound **4** was described previously, and its melting point [39] was confirmed. The present synthesis is much more convenient than the process used earlier [39]. Compounds **4** and **5** were obtained as thin needles or colorless plates (resembling boric acid), respectively. The needles and plates were too thin for a single-crystal structure determination. Surprisingly, the most symmetrical compound **6** could not be crystallized from any of the solvents tested. Complete evaporation of the solvents (H_2O, MeOH, EtOH, ^{i}PrOH *etc.*) yielded **6** as a

Scheme 2. *Preparation of the Phosphonic Acids* **4**–**6** *and Primary Phosphines* **7**–**9**

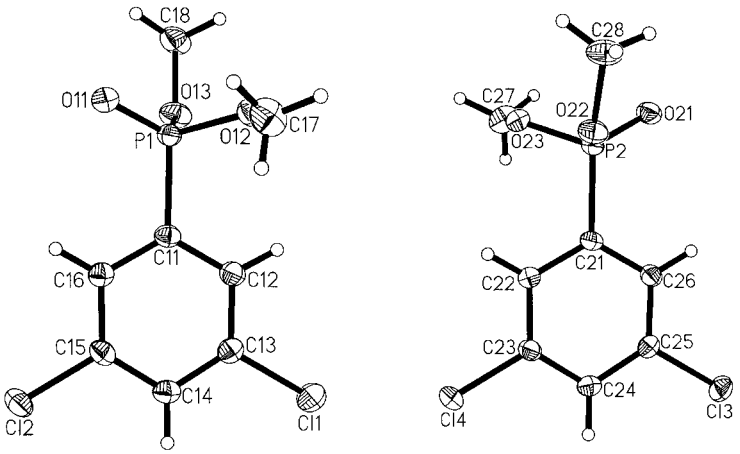


white powder. All three phosphonic acids **4**–**6** are soluble in highly polar organic solvents like dimethylsulfoxide, and the NMR spectra were in agreement with the inferred composition, as were mass spectra and elemental analyses.

$LiAlH_4$ Reduction of the three phosphonic acid esters **1**–**3** in tetrahydrofuran mediated by the addition of stoichiometric quantities of chlorotrimethylsilane [6][12] gave acceptable yields (46.5, 34.5, and 25.2%, resp.) of the corresponding phosphines **7**–**9** (*Scheme 2*). Alkaline hydrolytic workup followed by vacuum distillation furnished the products as colorless mobile liquids. The mono- and dichloro compounds **7** and **8** solidified on cooling to 21 and $-13°$, respectively, and the crystals could be used for structure determinations. Compound **9** solidified as a glass when chilled in liquid N_2, but no crystals could be grown and no melting point could be determined. Not unexpectedly, all three phosphines have an extremely unpleasant odor, are very sensitive to oxidation, and ignite when exposed to air after spreading on filter paper. The liquids are miscible with most common organic solvents and do not react with water, alcohols, or chlorocarbons ($CHCl_3$, CH_2Cl_2) at room temperature. Solutions in $CDCl_3$ showed ^{1}H-, ^{13}C-, and ^{31}P-NMR chemical shifts in full agreement with the structural patterns and idealized C_s (**7**), C_{2v} (**8**), and C_{3h} symmetry (**9**). Extensive coupling of the H- and P-atoms leads to the corresponding *multiplets* with second-order splitting. The EI-MS exhibited the molecular ions in high abundance, and elemental analyses confirmed the molecular formulae. The band assignments in the IR spectrum (KBr plates) of liquid **7** were supported by quantum-chemical calculations [40–42]. P–H Stretching, bending, and torsional frequencies were located at 2295.6, 1099.6, 860.4, and 817.9 cm^{-1}, respectively (see *Exper. Part*). Because of the extreme sensitivity of **8** and **9**, the results of vibrational spectroscopic studies were satisfactory for only **7**. Traces of oxidation by-products could not be excluded in the case of **8** and **9**. The quality of the products **7**–**9** was checked by GC/MS analysis. Crude products (prior to careful redistillation) were found to contain (3-chlorophenyl)phosphine (preparation of **8**), readily identified by its MS, and the known [15] (1,3-phenylene)bis[phosphine] (preparation of **9**), which clearly result from reductive cleavage of C–P bonds.

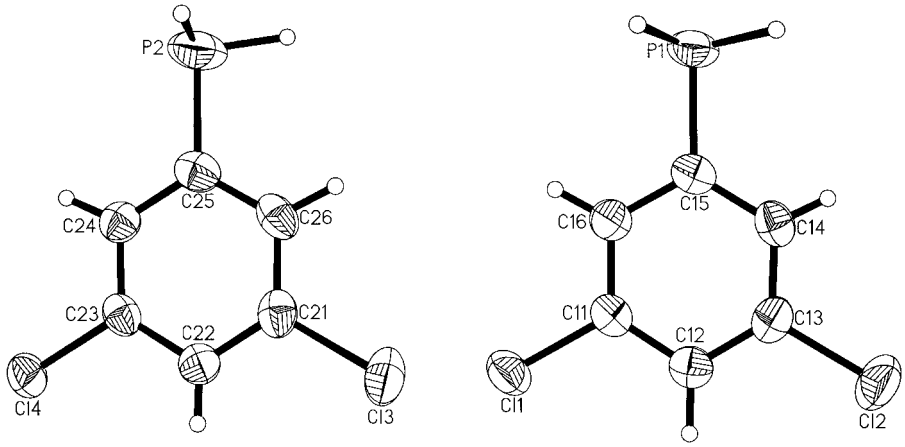
Crystal and Molecular Structures. – Crystals of dimethyl (3,5-dichlorophenyl)-phosphonate (**1**) are monoclinic, space group $P2_1/n$, with $Z = 8$ formula units in the unit cell. The asymmetric unit contains two independent molecules **I** and **II** of very similar geometry (*Fig. 2*). Each phosphonate group has the standard tetrahedral configuration with one short P=O bond (1.466(1) and (1.465(2) Å, resp.), two longer P–O bonds (1.571(1) and 1.573(1), and 1.566(2) and 1.577(1) Å, resp.), and one P–C bond (1.796(2) and 1.794(2) Å, resp.). The angles at the P-atoms are in the rather large range from 102.12(7) (between MeO groups) to 116.24(9)° (between MeO and O=). The preferred conformation, *i.e.*, the rotation of the Ph group around the P–C axis, brings the P=O groups closer to the phenyl plane than the P–O groups: O(11)–P(1)–C(11)–C(16) 21.7(2)°, O(21)–P(2)–C(21)–C(26) 21.1(2)°. The dichlorophenyl groups show no irregularities.

Monophosphine **7** was crystallized from the melt (orthorhombic, space group $Pca2_1$, $Z = 8$). The asymmetric unit contains two independent molecules **III** and **IV** with very similar geometries (*Fig. 3*). In the lattice, the molecules are stacked in two different columns, one for molecule **III** and the other for molecule **IV** (*Fig. 4*). Surprisingly, in



I **II**

Fig. 2. *The two independent molecules* **I** *and* **II** *in the crystals of compound* **1** (ORTEP, 50% probability ellipsoids, arbitrary radii for H-atoms) *with atomic numbering*. Selected bond lengths [Å] and angles [°] with standard deviations in parantheses: P(1)–C(11) 1.794(2), P(1)–O(11) 1.465(2), P(1)–O(12) 1.577(1), P(1)–O(13) 1.566(2), Cl(1)–C(13) 1.736(2), Cl(2)–(15) 1.735(2); P(2)–C(21) 1.796(2), P(2)–O(21) 1.466(1), P(2)–O(22) 1.571(1), P(2)–O(23) 1.573(1), C(13)–C(25) 1.737(2), C(14)–C(23) 1.736(2); C(11)–P(1)–O(11) 113.86(9), C(11)–P(1)–O(12) 105.44(8), C(11)–P(1)–O(13) 103.02(8), O(11)–P(1)–O(12) 114.53(8), O(11)–P(1)–O(13) 116.24(9), O(12)–P(1)–O(13) 102.26(8); C(21)–P(2)–O(21) 113.84(8), C(21)–P(2)–O(22) 102.61(8), C(21)–P(2)–O(23) 105.65(8), O(21)–P(2)–O(22) 115.70(8), O(21)–P(2)–O(23) 115.36(8), O(22)–P(2)–O(23) 102.12(7).



III **IV**

Fig. 3. *The two independent molecules* **III** *and* **IV** *in the crystals of compound* **7** (ORTEP, 50% probability ellipsoids, arbitrary radii for H-atoms) *with atomic numbering*. Selected bond lengths [Å] and angles [°]: P(1)–C(15) 1.794(3), Cl(1)–C(11) 1.747(3), Cl(2)–C(13) 1.765(3), P(2)–C(25) 1.802(3), Cl(3)–C(21) 1.755(3), Cl(4)–C(23) 1.744(3); C(14)–C(15)–P(1) 121.2(2), C(16)–C(15)–P(1) 118.7(2), C(24)–C(25)–P(2) 120.5(2), C(26)–C(25)–P(2) 120.1(2).

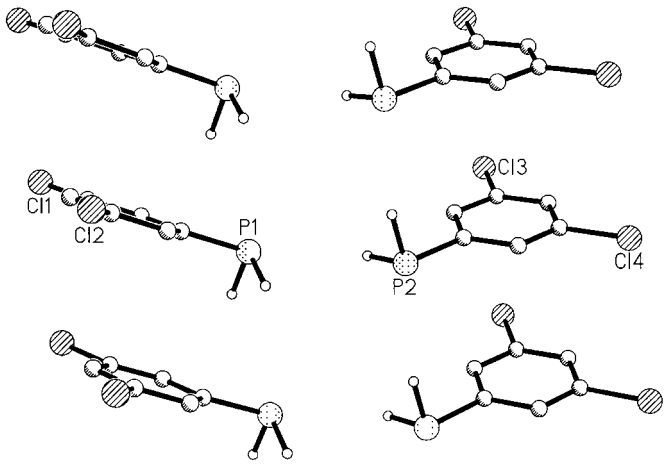


Fig. 4. *Stacking of the two independent molecules* **III** *and* **IV** *in separate columns in the crystals of compound* **7** (arbitrary radii). The contacts between the PH_2 groups in and between the columns are too large to allow significant H-bonding.

each column, the individual units are placed above each other with the Cl-atoms above Cl-atoms, and the phosphino groups above phosphino groups. Between the columns, the closer contacts are between phosphino groups. This positioning could suggest either weak intermolecular P–H···P H-bonds or P···P closed-shell interactions. A close inspection of the molecular geometry at the P-atoms shows, however, that the geometry is neither in favor of quasi-linear P–H···P H-bonds nor of direct P···P contacts. In fact, the nonbonding P···P distances (3.8 Å) are well beyond the sum of the *Van der Waals* radii, and the orientation of the P–H bonds is not directed towards the partner P-atom (*Fig. 4*).

Bis[phosphine] **8** was crystallized from the melt (triclinic, $P\bar{1}$, $Z=2$). The crystal quality and, hence, the data set obtained were not fully satisfactory. Therefore, H-atoms were placed into calculated positions at the C-atoms and not refined. Likewise, the H-atoms attached to the P-atoms were introduced at fixed distances and angles (based on literature data [43] and on quantum-chemical calculations [40–42]), but refined regarding their conformational orientation (*i.e.*, the rotation about the P–C bonds). With these constraints, an acceptable model was obtained as shown in *Fig. 5*. The monomers of **8** are organized in pairs as shown in *Fig. 6*, with the components related by a center of inversion. The closest contact between the monomers is between the PH_2 groups, but the exceedingly long distances rule out significant H-bonding: P(2)–H(22) 1.360(5), P(1)···H(22A) 2.880,P(1)···P(2A) 4.211 Å, with an angle P(1)–H(22A)··· P(2A) of 166.1°.

The literature contains virtually no reference data for P–H···P H-bonds, because only very few structures of primary phosphines have been determined, and the results were not indicative of H-bonding. An example in case is the crystal structure of mesitylphosphine (=(2,4,6-trimethylphenyl)phosphine) [43], where the closer intermolecular contacts are between PH_2 and Me groups and not between PH_2 groups. For this mesityl compound with its *ortho* substituents, steric hindrance may play a role, but

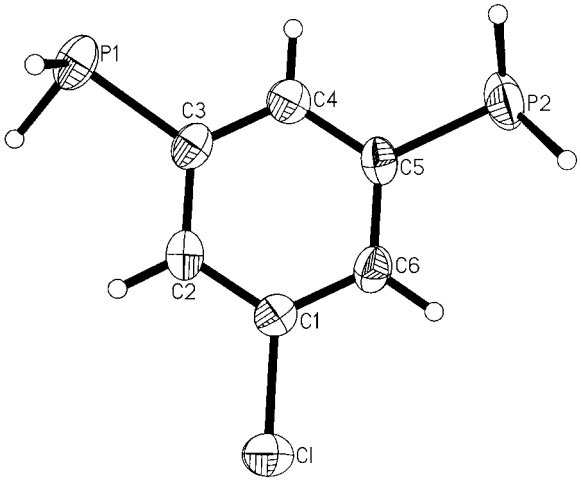


Fig. 5. *Molecular structure of compound* **8** *in the crystal* (ORTEP, 50% probability ellipsoids, arbitrary radii for H-atoms) *with atomic numbering*. Selected bond lengths [Å] and angles [°]: P(1)–C(3) 1.830(3), P(2)–C(5) 1.823(3), Cl–C(1) 1.737(3), C(2)–C(3)–P(1) 121.9(2), C(4)–C(3)–P(1) 118.9(2), C(4)–C(5)–P(2) 120.7(2), C(6)–C(5)–P(2) 120.1(2).

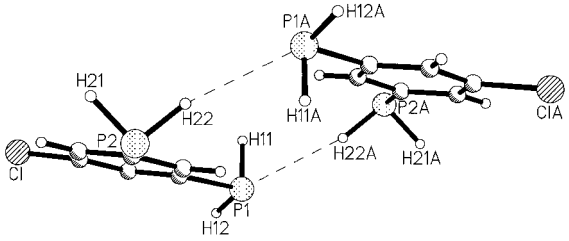


Fig. 6. *A pair of symmetry-related* (C_i) *molecules in the crystals of compound* **8** *with numbering of the P-bound H-atoms.* The contacts between the dimers (P(1)···P(2) *ca.* 4.2 Å) are too long for significant H-bonding.

the environment of the PH_2 group is still sufficiently open to allow closer approach of the functional groups were there significant attractive interaction. Primary arylphosphines with even more bulky substituents than 2,4,6-trimethylphenyl are to be excluded from the present discussion, because intermolecular contacts are ruled out by steric effects [44–46].

Therefore, the structures of the two primary phosphines presented in this study indicate that H-bonding between primary arylphosphines $ArPH_2$ has only a very minor influence – if any – on the supramolecular chemistry. This is obviously true even for cases where strongly electronegative substituents such as Cl-atoms in 3- and 3,5-position, respectively, enhance the acidity (but reduce the basicity) of the phosphino groups. It should further be noted that there are also no conspicuously short intermolecular contacts between PH_2 groups and Cl-atoms.

Conclusions. – The present investigation shows that aryl-substituted primary mono-, bis-, and tris[phosphines] are accessible *via* a rather convenient photo-*Arbuzov* route

from the corresponding chlorobenzenes and trimethyl phosphite. The phosphonate esters generated in this reaction can be hydrolyzed by strong acid to give the corresponding phosphonic acids, or reduced by $LiAlH_4$ to give the phosphines in acceptable yields. Analytical, spectroscopic, and structural studies confirm the proposed compositions and structures for representative compounds.

Since only one primary arylphosphine (mesitylphosphine) has been structurally characterized to date [43], the structures of the new compounds provide important reference data. Perhaps most interesting is the observation that H-bonding plays no significant role in the mode of packing in the crystals of the new phosphines **7** and **8**. There is evidence neither for short and directional P–H···P bonding nor for closed-shell P···P interactions typically found for the heavier congeners of phosphorus, *vic.* arsenic, antimony, and bismuth [47]. The results are in agreement with findings for mesitylphosphine [43], for which no conspicuous contacts between the primary phosphino groups were detected. It should be noted that the crystal structures of phenylphosphine and other simple arylphosphines are still unknown. The low boiling point (−87.7°) and low enthalpy of vaporization of PH_3 (3.49 kcal/mol) are also indicative of exceedingly weak intermolecular forces between these PH_3 molecules.

Future work will be directed towards the synthesis of even more highly phosphinated benzenes including the elusive (benzenehexayl) hexakis[phosphine] ($C_6(PH_2)_6$). It should be noted that benzenehexathiol $C_6(SH)_6$ [48][49] and hexasilylbenzene $C_6(SiH_3)_6$ [50][51] have already been prepared. The gap between these two isoelectronic analogues presents a preparative challenge for further studies.

Experimental Part

1. *General.* All starting materials are commercially available. For the photo-*Arbuzov* reaction, an all-quartz fall-film photoreactor (*Normag N 9356*) with a Hg high-pressure lamp (*Original Hanau TQ 718/N 9380*, 254 nm, 700 W) was used. High-temperature/high-vacuum distillations of the primary phosphines were carried out in a 'Kugelrohr' apparatus (*Büchi*), all other experiments in conventional glass apparatus which was dried and flushed with N_2 prior to use. M.p. and decomposition temp.: glass capillaries immersed in an *Electrothermal-IA-9200* device (*Kleinfeld Labortechnik*). Standard equipment was employed for all other analytical and spectroscopic investigations. IR: in cm^{-1}. NMR: δ in ppm, J in Hz. MS: m/z.

2. *Photo*-Arbuzov *Reaction: Phosphonic Acid Esters* **1**–**3**. A soln. of 1,3,5-trichlorobenzene (80 g, 0.44 mol) in trimethyl phosphite (250 ml, 2.12 mol) is placed in the quartz reactor (see above) and irridiated with UV light for 3 weeks at 50° (thermostat). Excess trimethyl phosphite and volatile reaction products are distilled off in a vacuum to leave a yellow-brown viscous oil. Fractional distillation gives some unreacted trichlorobenzene at 120–130°/0.05 Torr, followed by **1** at 160° (16.24 g, 14.5%), **2** at 180° (51.17 g, 35.4%), and **3** at 210° (53.27 g, 30.1%). All three products are obtained as colorless, oily liquids at 20°, of which only **1** crystallizes after quenching in liq. N_2 and annealing by slow warming to r.t.

Dimethyl (3,5-Dichlorophenyl)phosphonate (**1**): ^{1}H-NMR ($CDCl_3$, 20°): 7.47 (*m*, H–C(2), H–C(6)); 7.34 (*m*, H–C(4)); 3.60 (*d*, J = 11.3, 2 MeO). ^{13}C-NMR ($CDCl_3$, 20°): 135.27 (*d*, J = 22.1, C(1)); 132.17 (*d*, J = 2.8, C(3), C(5)); 131.55 (*s*, C(4)); 129.59 (*d*, J = 10.1, C(2), C(6)); 52.69 (*d*, J = 5.5, 2 MeO). ^{31}P-NMR ($CDCl_3$, 20°): 17.46 (*s*). EI-MS (70 eV): 253 ($[M-1]^+$), 224 ($[M-MeO]^+$), 146 ($[M-PO(OMe)_2]^+$). Anal. calc. for $C_8H_9Cl_2O_3P$ (255.04): C 37.68, H 3.56; found: C 37.34, H 3.48.

Tetramethyl (5-Chloro-1,3-phenylene)bis[phosphonate] (**2**): ^{1}H-NMR ($CDCl_3$, 20°): 7.94 (*m*, H–C(2)); 7.82 (*m*, H–C(4), H–C(6)); 3.67 (*d*, J = 11.0, 4 MeO). ^{13}C-NMR ($CDCl_3$, 20°): 135.48 (*dd*, J = 23.9, 14.7, C(4), C(6)); 135.35 (*t*, J = 3.7, C(5)); 132.66 (*t*, J = 10.1, C(2)); 130.26 (*dd*, J = 90.3, 14.7, C(1), C(3)); 52.89 (*m*, 4 MeO). ^{31}P-NMR ($CDCl_3$, 20°): 17.74(*s*). EI-MS (70 eV): 327 ($[M-1]^+$), 297 ($[M-MeO]^+$), 234 ($[M-PO_3Me]^+$), 220 ($[M-PO(OMe)_2]^+$). Anal. calc. for $C_{10}H_{15}ClO_6P_2$ (328.63): C 36.55, H 4.60; found: C 36.12, H 4.21.

Hexamethyl (Benzene-1,3,5-triyl)tris[phosphonate] (**3**): ^{1}H-NMR ($CDCl_3$, 20°): 8.35 (*m*, H–C(2), H–C(4), H–C(6)); 3.70 (*d*, *J* = 12.2, 6 MeO). ^{13}C-NMR ($CDCl_3$, 20°): 138.50 (*m*, C(2), C(4), C(6)); 129.01 (*dt*, *J* = 192.0, 13.2, C(1), C(3), C(5)); 53.13 (*m*, 6 MeO). ^{31}P-NMR ($CDCl_3$, 20°): 18.15 (*s*). EI-MS (70 êV): 401 ($[M-1]^+$), 371 ($[M-MeO]^+$), 308 ($[M-PO_3Me]^+$, 294 ($[M-PO(OMe)_2]^+$). Anal. calc. for $C_{12}H_{21}O_9P_3$ (402.21): C 35.83, H 5.26; found: C 35.28, H 5.14.

3. *Ester Hydrolysis: Phosphonic Acids* **4**–**6**. Each of the esters **1**–**3** is dissolved in conc. HCl soln. (37%) and heated under reflux for 10 h. On cooling, **4** and **5** crystallize from the reaction mixture, and **6** is obtained as a white powder on complete evaporation of the solvent.

(3,5-Dichlorophenyl)phosphonic Acid (**4**): From **1** (2.20 g, 8.63 mmol) and conc. HCl soln. (50 ml), 1.94 g (99.1%) of **4**. M.p. 189–190° ([39]: 188–190°). ^{1}H-NMR ((D_6)DMSO, 20°): 10.76 (br. *s*, 2 OH); 7.77 (*s*, H–C(4)); 7.56 (*dd*, *J* = 13.2, 1.8, H–C(2), H–C(6)). ^{13}C-NMR ((D_6)DMSO, 20°): 138.69 (*d*, *J* = 177.6, C(1)); 134.19 (*d*, *J* = 20.8, C(2), C(6)); 130.24 (*d*, *J* = 2.3, C(4)); 128.68 (*d*, *J* = 10.0, C(3), C(5)). ^{31}P-NMR ((D_6)DMSO, 20°): 8.72 (*s*). CI-MS: 226 (M^+). Anal. calc. for $C_6H_5Cl_2O_3P$ (226.98): C 31.75, H 2.22, Cl 31.24, P 13.65; found: C 31.72, H 1.90, Cl 29.30, P 13.70.

(5-Chloro-1,3-phenylene)bis[phosphonic Acid] (**5**): From **2** (3.00 g, 9.13 mmol) and conc. HCl soln. (50 ml), 2.43 g (97.7%) of **5**. M.p. 240° (dec.). ^{1}H-NMR ((D_6)DMSO, 20°): 10.76 (br. *s*, 4 OH); 7.93 (*t*, *J* = 12.4, H–C(2)); 7.71 (*m*, *AA′XX′*, H–C(4), H–C(6)). ^{13}C-NMR ((D_6)DMSO, 20°): 137.00 (*m*, *AXX′*, C(1), C(3)); 132.98 (*t*, *J* = 18.1, C(2)); 131.97 (*m*, *AXX′*, C(4), C(6)); 130.97 (*t*, *J* = 10.0, C(5)). ^{31}P-NMR ((D_6)DMSO, 20°): 9.99 (*s*). CI-MS: 192 ($[ClC_6H_4PO(OH)_2]^+$). Anal. calc. for $C_6H_7ClO_6P_2$ (272.52): C 26.44, H 2.59, Cl 13.01, P 22.73; found: C 26.59, H 2.61, Cl 12.07, P 22.09.

(Benzene-1,3,5-triyl)tris[phosphonic Acid] (**6**): From **3** (3.00 g, 7.46 mmol) and conc. HCl soln. (50 ml), 2.31 g (97.4%) of **6**. M.p. 240° (dec.). ^{1}H-NMR ((D_6)DMSO, 20°): 10.19 (br. *s*, 6 OH); 8.10 (*t*, *J* = 13.0, H–C(2), H–C(4), H–C(6)). ^{13}C-NMR ((D_6)DMSO, 20°): 134.72 (*m*, *AXX′*$_2$, C(2), C(4), C(6)); 133.08, (*m*, *AX′*$_2$, C(1), C(3), C(5)). ^{31}P-NMR ((D_6)DMSO, 20°): 11.73 (*s*). CI-MS: 238 ($[C_6H_4(PO(OH)_2)_2]^+$). Anal. calc. for $C_6H_9O_9P_3$ (318.05): C 22.66, H 2.85, P 29.22; found: C 21.88, H 3.40, P 29.13.

4. *Ester Reduction: Primary Phosphines* **7**–**9**. *(3,5-Dichlorophenyl)phosphine* (**7**). Chlorotrimethylsilane (5.27 g, 48.51 mmol) is slowly added to a suspension of $LiAlH_4$ (1.84 g, 48.49 mmol) in THF (30 ml) at −78°. The mixture is allowed to warm to r.t. and stirred for 2 h. Subsequently, a soln. of **1** (4.11 g, 16.12 mmol) in THF (30 ml) is added with stirring at −35°, and stirring is continued for 36 h at r.t. The mixture is then quenched with H_2O (30 ml) followed by 2M aq. NaOH (30 ml), the aq. layer washed with Et_2O (2 × 30 ml), the combined org. phase dried ($MgSO_4$) and evaporated, and the residue submitted to bulb-to-bulb distillation at *ca*. 130°/1 mbar: 1.34 g (46.5% of **7**. M.p. 21°. IR (liquid film): 2296, 1557, 1424, 1402, 1381, 1140, 1100, 1071, 860, 818, 801, 665. ^{1}H-NMR ($CDCl_3$, 20°): 7.34 (*dd*, *J* = 6.3, 1.6, H–C(2), H–C(6)); 7.26 (*m*, H–C(4)); 3.98 (*d*, *J* = 202.6, PH_2). ^{13}C-NMR ($CDCl_3$, 20°): 134.90 (*d*, *J* = 5.6, C(3), C(5)); 132.98 (*d*, *J* = 13.7, C(1)); 132.21 (*d*, *J* = 16.1, C(2), C(6)); 128.23 (*s*, C(4)). ^{31}P-NMR ($CDCl_3$, 20°): −120.67 (*s*). EI-MS (70 eV): 178 (M^+), 143 ($[M-Cl]^+$). Anal. calc. for $C_6H_5Cl_2P$ (178.99): C 40.26, H 2.82, Cl 39.61, P 17.30; found: C 40.54, H 3.13, Cl 39.02, P 16.81.

(5-Chloro-1,3-phenylene)bis[phosphine] (**8**). As described for **7**, from $LiAlH_4$ (10.40 g, 274.0 mmol), Me_3SiCl (29.80 g, 274.3 mmol), and **2** (15.00 g, 45.65 mmol) in THF (300 ml): 2.78 g (34.5%) of **8**. M.p. −13°. B.p. 89°/1 mbar. ^{1}H-NMR ($CDCl_3$, 20°): 7.43 (*t*, *J* = 6.4, H–C(2)); 7.35 (*d*, *J* = 6.6, H–C(4), H–C(6)); 3.93 (*d*, *J* = 202.9, 2 PH_2). ^{13}C-NMR ($CDCl_3$, 20°): 138.12 (*t*, *J* = 15.3, C(2)); 134.18 (*t*, *J* = 5.7, C(5)); 133.56 (*d*, *J* = 15.1, C(4), C(6)); 131.35 (*dd*, *J* = 11.9, 5.2, C(1), C(3)). ^{31}P-NMR ($CDCl_3$, 20°): −121.89 (*s*). EI-MS (70 eV): 176 (M^+), 143 ($[M-PH_2]^+$). Anal. calc. for $C_6H_7ClP_2$ (176.52): C 40.83, H 4.00, Cl 20.08, P 35.09; found: C 41.54, H 4.20, Cl 19.17, P 32.55.

In the crude reduction product obtained from **2**, *(3-chlorophenyl)phosphine* was detected. EI-MS (70 eV): 144 (M^+).

(Benzene-1,3,5-triyl)tris[phosphine] (**9**). As described for **7**, from $LiAlH_4$ (8.49 g, 223.8 mmol), Me_3SiCl (24.31 g, 223.8 mmol), and **3** (10.00 g, 24.86 mmol) in THF (200 ml): 1.09 g (25.2%) of **9**. B.p. *ca*. 45°/1 mbar. ^{1}H-NMR ($CDCl_3$, 20°): 7.51 (*t*, *J* = 6.8, H–C(2), H–C(4), H–C(6)); 3.91 (*d*, *J* = 201.9, 3 PH_2). ^{13}C-NMR ($CDCl_3$, 20°): 140.02 (*t*, *J* = 15.3, C(2), C(4), C(6)); 129.51 (*dt*, *J* = 10.9, 4.7, C(1), C(3), C(5)). ^{31}P-NMR ($CDCl_3$, 20°): −122.49 (*s*). EI-MS (70 eV): 174 (M^+), 141 ($[M-PH_2]^+$). Anal. calc. for $C_6H_9P_3$ (174.06): C 41.40, H 5.21, P 53.39; found: C 41.53, H 5.43, P 52.98.

In the crude reduction product obtained from **3**, *(1,3-phenylene)bis[phosphine]* was detected. EI-MS (70 eV): 142 (M^+), 109 ($[M-PH_2]^+$).

5. *X-Ray Crystallography.* Crystals of suitable quality and size of compounds **1** and **7** were mounted under a steady stream of cooled N_2 (−25°) on the ends of quartz fibers in *F06206R* oil and used for intensity data collection on a *Nonius DIP-2020* diffractometer, employing graphite-monochromated MoK_α radiation. A single

crystal of **8** was grown *in situ* in a capillary by slowly cooling the melt after establishing a solid/liquid equilibrium and selecting a suitable seed crystal (others removed by local melting). Intensity data of **8** were collected on a *Nonius Turbo-CAD4* diffractometer employing graphite-monochromated MoK_α radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference-*Fourier* syntheses and refined by full-matrix least-squares calculations on F^2 (SHELXL-97). The thermal motion was treated anisotropically for all non-H-atoms. The C-bonded H-atoms of **1** and **7** were found and refined isotropically, those of **8** were calculated and allowed to ride on their parent atoms with fixed isotropic contributions. All P-bonded H-atoms were introduced at fixed distances and angles (based on literature data and on quantum-chemical calculations), but refined regarding their conformational orientation (*i.e.*, the rotation about the P–C bonds). Further information on crystal data, data collection and structure refinement are summarized in the *Table*. Thermal parameters and tables of interatomic distances and angles have been deposited with the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDS-174183, 174184, and 174172 (**1**, **7**, and **8**, resp.).

Table 1. *Crystal and Structure-Solution Data for Compounds* **1**, **7**, *and* **8**

	1	**7**	**8**
Empirical formula	$C_8H_9Cl_2Ot_3P$	$C_6H_5Cl_2P$	$C_6H_7ClP_2$
M	255.02	178.97	176.51
Crystal system	monoclinic	orthorhombic	triclinic
Space group	$P2_1/n$	$Pca2_1$	$P\bar{1}$
a/Å	6.6786(1)	17.2695(3)	4.1069(5)
b/Å	25.4857(4)	3.9585(1)	9.163(2)
c/Å	9.7596(2)	22.1769(5)	11.325(2)
α/°	90	90	75.35(2)
β/°	95.2790(4)	90	85.95(1)
γ/°	90	90	81.86(1)
U/Å^3	2149.47(6)	1516.04(6)	407.9(1)
ρ_{calc}/g cm^{-3}	1.576	1.568	1.437
Z	8	8	2
T/K	133	133	193
Refls. measured	50934	47515	6621
Refls. unique	4933 ($R_{int} = 0.054$)	3150 ($R_{int} = 0.043$)	2334 ($R_{int} = 0.0736$)
Refined parameters/restraints	325/0	204/11	95/10
R_1 ($I \geq 2\sigma(I)$)	0.0340	0.0332	0.0663
wR_2	0.0810	0.0774	0.1878
Weighting scheme[a])	$a = 0.0229$	$a = 0.0320$	$a = 0.1122$
	$b = 2.0629$	$b = 0.4127$	$b = 0.1284$
Contribution of one specimen to the racemic twin (BASF)		0.42(7)	
σ_{fin}(max/min)/eÅ^{-3}	0.467/ – 0.332	0.369/ – 0.237	0.666/ – 0.457

[a]) Fractional contribution of the twin component.

This work was supported by the *Fonds der Chemischen Industrie*, *Deutscher Akademischer Austauschdienst*, and *Volkswagenstiftung*.

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Received November 19, 2001