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The molecular structure of chloromethylphosphine, $CClH_2PH_2$, as determined by gas-phase electron diffraction and ab initio computations[☆]

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Abstract

The gas-phase structure of chloromethylphosphine, $CClH_2PH_2$, has been determined by electron diffraction employing constraints derived from ab initio computations at the CISD(fc)/6-31+G** level. At 293 K, the compound exists in two conformations, anti and gauche (phosphorus lone pair relative to the C–Cl bond); the mole fraction of the gauche conformer is 0.22(5). Important experimental structural parameters (r_g/pm, $\angle_\alpha$/deg) for the anti and gauche conformers, respectively, are (values without e.s.d.s indicate that the difference between the parameters for the two conformers was fixed at the theoretical value): r(C–P) = 186.3(3), 187.4; r(C–Cl) = 179.1(5), 179.0; r(P–H) = 141.5(4), 142.9; PCCl = 115.7(1), 107.8(5) [CISD(fc)/6-31+G** 116.5, 110.6]. The large difference between the PCCl angles in the conformers can be rationalised on the basis of overlaps between non-bonding and antibonding molecular orbitals.

1. Introduction

We have been studying the structure of phosphaethene [1–6], CH_2PH, using gas-phase electron diffraction (GED). This thermally fragile, highly reactive compound is generated in situ by dehydrochlorination of chloromethylphosphine, $CClH_2PH_2$, using calcium oxide [5]:

$$2CClH_2PH_2(g) + CaO(s) \xrightarrow{\Delta} CH_2PH(g) + CaCl_2(s) + H_2O(g)$$

Since it is very difficult to generate the phosphaethene free from contamination by chloromethylphosphine, it has been important at the outset to determine the structure of $CClH_2PH_2$ for an optimum analysis of the GED data.

Although the structures of a number of alkylphosphines [7], R_nPH_{3-n}, and alkylhalophosphines [7], R_nPX_{3-n}, have been determined in the gas phase, no structural studies have been reported for haloalkylphosphines, $CH_{3-n}X_nPH_2$. These classes of compounds present a number of potentially interesting structural features, such as the variation of r(C–P) with the substituents at C and P, the magnitude of the PCX angles, and the possibility that mixtures of conformers may exist.

[☆] Dedicated to Professor Yonezo Morino on his 87th birthday.
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Table 1
Nozzle-to-plate distances (mm), weighting functions (nm^{-1}), correlation parameters, scale factors, and electron wavelengths (pm) used in the electron diffraction study

Nozzle-to-plate distance	Δs	$s_{min.}$	sw_1	sw_2	$s_{max.}$	Correlation parameter	Scale factor k[a]	Electron wavelength[b]
259.76	2	20	40	140	164	0.434	0.776(5)	5.681
201.08	4	40	60	192	224	−0.382	0.813(9)	5.680

[a] Figures in parentheses are the estimated standard deviations.
[b] Determined by reference to the scattering pattern of benzene vapour.

The most complete structural determination has been reported by Durig and co-workers [8] for the trans and gauche conformers of ethylphosphine, $CH_3CH_2PH_2$. Particularly notable in this microwave (MW) study was the wide PCC angle in the trans conformer, 116.1(1)° compared to 110.5(1)° for the gauche confomer. The large difference was attributed to non-bonded repulsive interactions between the phosphino hydrogen atoms and the methylene or methyl hydrogen atoms. However, theoretical computations have shown that large deviations from regular tetrahedral CCX (X = Main-Group element) bond angles are due primarily to hyperconjugation effects [9]. It was therefore of interest to compare the structures of the conformers of chloromethylphosphine with those of ethylphosphine, the two molecules differing only in the replacement of a chlorine atom by a methyl group.

2. Experimental

2.1. Synthesis

Chloromethylphosphine was prepared by the reduction of 1-chloromethyldiphenylphosphonate, $ClCH_2P(O)(OPh)_2$. The method was used essentially that of Cabioch et al. [10], but modified such that a solution of $AlCl_2H$ in triglyme was employed as the reducing agent [11]. The sample was purified by fractional condensation in vacuo and its purity checked by reference to the ^1H NMR spectrum [12]. The ester was prepared by the reaction of chloromethylphosphonic dichloride (Aldrich), $ClCH_2P(O)Cl_2$, with phenol in the presence of triethylamine; it was purified by recrystallisation from an ether/cyclohexane mixture [5].

2.2. Electron-diffraction measurements

Electron-scattering intensities were recorded on Kodak Electron Image plates using the Edinburgh gas-diffraction apparatus operating at about 44.5 kV (electron wavelength about 5.7 pm) [13]. Originally, data were collected using a metal inlet system and nozzle; such data, however, did not refine well ($R_G \geqslant 0.14$) using the analysis described below. Since it seemed likely that the vapour had interacted with the metal surfaces, subsequent measurements were made using an all-glass inlet system originally designed for the study of digallane [14]. Nozzle-to-plate distances for the all-glass inlet nozzle were about 201 and 260 mm, yielding data in the s range 20–224 nm^{-1}; three long- and four medium-camera plates were selected for analysis. The sample and nozzle temperatures were about 273 and 293 K, respectively, during the exposure periods.

The scattering patterns of benzene were also recorded for the purpose of calibration; these were analysed in exactly the same way as those of the chloromethylphosphine so as to minimise systematic errors in the wavelengths and camera distances. Nozzle-to-plate distances, weighting functions used to set up the off-diagonal weight matrix, correlation parameters, final scale factors, and electron wavelengths for the measurements are collected together in Table 1.

The electron scattering patterns were converted into digital form using a computer-controlled Joyce–Loebl MDM6 microdensitometer with a scanning program described elsewhere [15]. The programs used for data reduction [15] and least-squares refinement [16] have ben described previously; the complex scattering factors employed were those listed by Ross et al. [17].

2.3. *Theoretical calculations*

All computations were carried out using the GAUSSIAN 92 package of programs [18] and standard procedures [19]. Geometries were optimised initially at the MP2(fu)/6-31+G** level of theory and analytical frequency calculations at this level were also performed to determine the nature of the stationary points. Geometries were subsequently reoptimised at CISD/6-31+G** and single point energy calculations at the QCISD/6-311+G(2df,p) level were performed employing these geometries. The relative energies were corrected by zero-point vibrational energies (ZPEs) calculated at MP2(fu)/6-31+G** and scaled by a factor of 0.93. Hence, the results quoted in the text refer to a final level of theory denoted as QCISD/6-311 + G(2df,p)//CISD/6-31+G** + 0.93.ZPE(MP2 (fu)/6-31+G**).

The natural population analysis [20] was performed for the HF/6-31+G** wavefunction employing the CISD/6-31+G** optimised geometries. Orbital contour plots show natural bond orbitals (NBOs) and energies of interaction have been estimated by a second-order perturbation theory analysis of the Fock matrix in the NBO basis.

3. Molecular model

On the basis of the ab initio calculations detailed below, the model used to define the atomic coordinates of chloromethylphosphine described a mixture of two conformers; with respect to the location of the phosphorus lone pair relative to the C–Cl bond, these are anti (a) and gauche (g) conformers (see Fig. 1). Assuming C_s symmetry for the anti conformer, the 15 parameters listed in Table 2 were chosen to define the structures of the two conformers using the atom numbering scheme shown in Fig. 1.

Table 2
GED structural parameters[a,b] for $CClH_2PH_2$

Parameter		
p_1	r(C–P)/r(C–C) (mean)	182.7(1)
p_2	r(C–P) (mean) – r(C–Cl) (mean)	7.8(8)
p_3	r(C–P) (g) – r(C–P) (a)	1.1(f)
p_4	r(C–Cl) (a) – r(C–Cl) (g)	2.0(f)
p_5	r(C–H)	112.6(4)
p_6	r(P–H)	138.4(4)
p_7	PCCl (mean)	111.8(2)
p_8	ΔPCCl = PCCl(a) – PCCl(g)	7.9(5)
p_9	HCH (mean)	108.4(f)
p_{10}	ΔHCH = HCH(a) – HCH(g)	–1.0(f)
p_{11}	ψ	–1.5(f)
p_{12}	CPH	96.8(f))
p_{13}	ClCPH(a)	48.3(f)
p_{14}	ClCPH(12) (g)	73.6(f)
p_{15}	Mole fraction of gauche conformer	0.22(5)

[a] Bond distances r_α^0 in pm, angles $\angle_\alpha$ in degrees.

[b] For definitions of parameters, see text. For atom numbering scheme, see Fig. 1. Figures in parentheses are the estimated standard deviations. f = fixed.

The heavy atoms were defined by four distance and two angle parameters: the average of the four C–P and C–Cl distances, p_1, the difference between the mean C–P and the mean C–Cl distances, p_2, the difference between the two C–P distances of the conformers, p_3, the analogous C–Cl difference, p_4, and the mean and difference of the PCCl angles, p_7 and p_8, respectively. Common C–H and P–H distances and CPH angle were assumed for both confomers. The HCH angles of the chloromethyl group were defined by a mean, p_9, and a difference, p_{10}, of the two angles. For the anti conformer, the angle ψ, p_{11}, defined the difference between the bisectors of the angles HCH and PCCl, a positive value denoting an increase in the Cl···H(6)/H(7) non-bonded distance. The ClCPH dihedral angles were given by p_{13} (a) and p_{14} (g), and p_{15} defined the mole fraction of the gauche conformer in the mixture. The asymmetry of the $CClH_2$ group in the gauche conformer, as indicated in the ab initio optimisation, was also incorporated into the model.

4. Results

4.1. *Refinement of the structure*

The radial distribution curve for chloromethylphosphine (Fig. 2) consists of four distinct peaks at

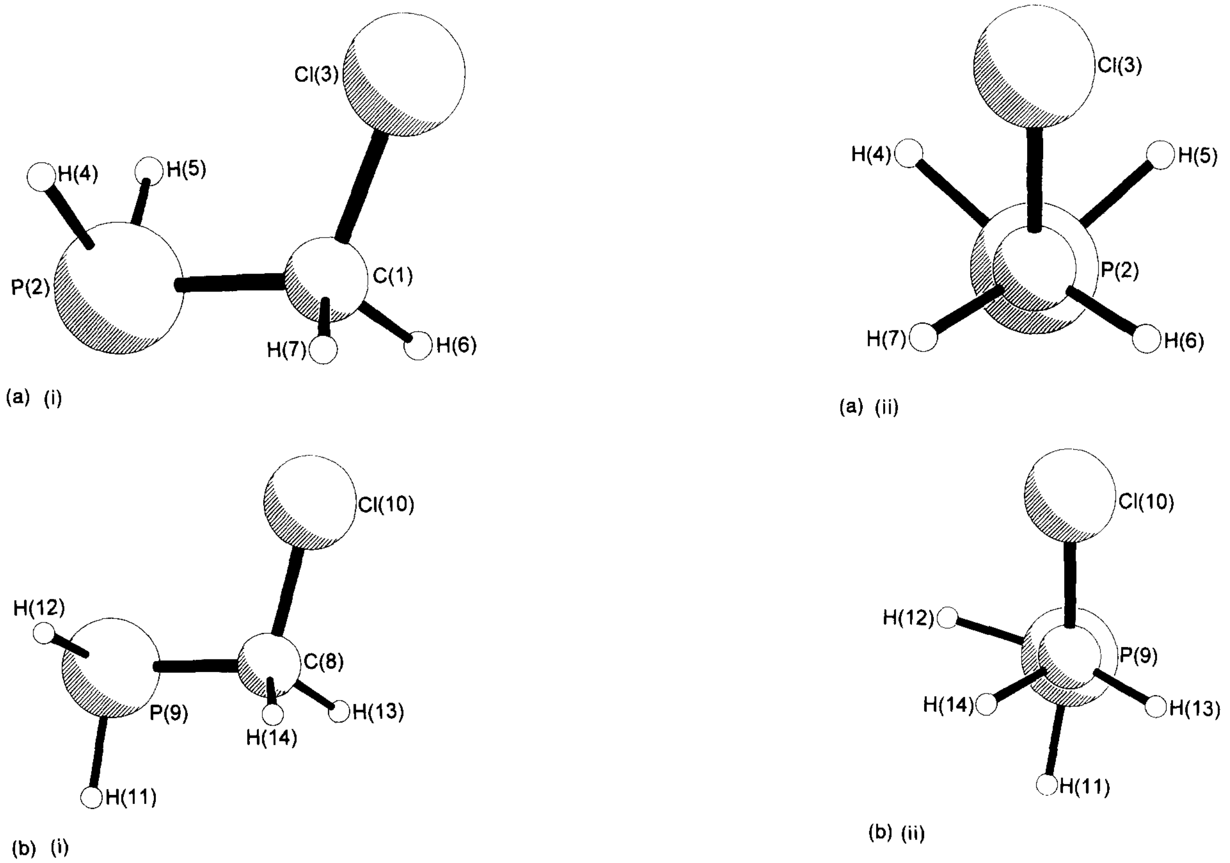


Fig. 1. Views of the $CClH_2PH_2$ conformers, (a) anti and (b) gauche, in the optimum refinement of the electron diffraction data: (i) perspective view and (ii) view along the C–P bond.

distances near 141, 182, 242 and 307 pm together with a shoulder at about 113 pm. The features at $r < 200$ pm correspond to scattering from bonded atom pairs in both conformers; the shoulder at about 113 pm is attributable to the C–H bonds, the peak at 141 pm to the P–H bonds and that at 182 pm to the C–P and C–Cl bonded pairs. The Cl(3) $\cdots$ H(6) and P(2) $\cdots$ H(6) non-bonded pairs of the anti conformer contribute mainly to the peak at 242 pm augmented by C $\cdots$ H and other Cl $\cdots$ H and P $\cdots$ H pairs from both conformers. Scattering from the non-bonded pairs Cl(3) $\cdots$ H(5) and P(2) $\cdots$ Cl(3) (anti) and P(9) $\cdots$ Cl(10) (gauche) accounts almost completely for the intense peak at 307 pm.

The set of starting parameters for the refinements was taken from the theoretical geometries optimised at the CISD/6-31+G** level. The starting values for the amplitudes of vibration (u) and the perpendicular amplitude corrections (K) were derived from the ab initio force field, computed at the MP2/6-31+G** level, using the program ASYM20 [21].

Of the 14 parameters defining the molecular geometries (Table 2), it was possible to refine six simultaneously. The value of the gauche mole fraction in the final refinement was determined by plotting the value of R_G for a series of refinements in which p_{15} was varied stepwise over the range 0.00–0.50. The resultant function was approximately quadratic in p_{15}, giving $p_{15} = 0.22(10)$ at the 95% confidence level [22], implying an e.s.d. of 0.05.

In addition, five groups of amplitudes of vibration could be refined simultaneously. Within each group, the ratios of amplitudes were fixed at the ab initio values. It was not possible to refine u_1(C–P)

Table 3
Interatomic distances (r_a in pm) and amplitudes of vibration (u in pm) for $CClH_2PH_2$ [a–c]

	Distance		Amplitude (GED)	Amplitude (calc.)[d]
Anti conformer				
r_1	C(1)–P(2)	186.2(3)	4.5(7)	5.2
r_2	C(1)–Cl(3)	179.0(5)	4.5(rf)	5.0
r_3	C(1)–H(6)	113.5(4)	8.1(7)	7.5
r_4	P(2)–H(4)	141.1(4)	7.6(5)	8.2
r_5	Cl(3) ··· H(6)	238.4(5)	10.7	10.6
r_6	C(1) ··· H(4)	245.4(3)	12.8 (3)	12.6
r_7	P(2) ··· H(6)	247.0(41)	11.5	11.3
r_8	P(2) ··· Cl(3)	308.9(13)	6.8(3)	7.3
r_9	Cl(3) ··· H(5)	306.2(23)	18.3 (tied to u_8)	19.8
Gauche conformer				
r_{10}	C(8)–P(9)	187.3(3)	4.5 (tied to u_1)	5.2
r_{11}	C(8)–Cl(10)	178.8(5)	4.4 (tied to u_2)	5.0
r_{12}	C(8)–H(13)	113.4(4)	8.1 (tied to u_3)	7.5
r_{13}	P(9)–H(11)	142.5(4)	7.7 (tied to u_4)	8.3
r_{14}	Cl(10) ··· H(14)	239.7(6)	10.7	10.6
r_{15}	Cl(10) ··· H(13)	240.3(6)	10.8	10.6
r_{16}	C(8) ··· H(11)	247.8(3)	13.2 (tied to u_5)	13.0
r_{17}	P(9) ··· H(13)	248.3(4)	11.5	11.6
r_{18}	P(9) ··· H(14)	253.7(4)	11.1	10.9
r_{19}	P(9) ··· Cl(10)	295.5(9)	7.5 (tied to u_8)	8.2
r_{20}	Cl(10) ··· H(12)	317.4(10)	24.7(f)	24.7
r_{21}	Cl(10) ··· H(11)	401.6(7)	11.8(f)	11.8

[a] For atom numbering scheme, see Fig. 1. Figures in parentheses are the estimated standard deviations.

[b] H ··· H non-bonded distances were also included in the refinements, but are not listed here; amplitudes of vibration were fixed at values derived from the theoretical force field.

[c] rf = refined then fixed; *f* = *fixed*.

[d] Amplitude calculated from the theoretical force field.

and u_2(C–Cl) simultaneously or as a tied group; in such cases the values refined were unrealistically small (< 3 pm). Refinement of u_2(C–Cl) alone gave a value of 4.5(7) pm, i.e. within one e.s.d. of the theoretical value, at which it was fixed. Attempts to refine other parameters or amplitudes led to either unreasonable values or large e.s.d.s. For example, the mean HCH angle, p_9, refined to a value of 104.7(30)° but the slight improvement in R_G was not significant at the 95% level [22].

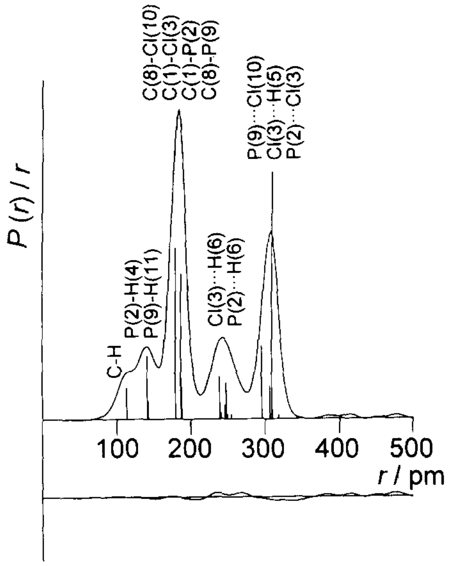


Fig. 2. Observed and final weighted difference radial distribution curves for $CClH_2PH_2$. Before Fourier inversion the data were multiplied by $s.\exp[(-0.000\,02s^2)/(Z_C - f_C)/(Z_P - f_P)]$.

Details of the structural parameters obtained in the optimum refinement are given in Table 2; the corresponding distances and amplitudes are collected in Table 3 and Cartesian coordinates are listed in Table 4. The most significant elements of the least-squares correlation matrix are shown in Table 5. The success of the final refinement, for which $R_G = 0.059$ ($R_D = 0.063$), may be assessed on the basis of the difference between the experimental and calculated radial distribution curves (Fig. 2). Fig. 3 offers a similar comparison between the experimental and calculated molecular scattering intensity curves.

4.2. Ab Initio and natural population analysis calculations

Four distinct conformations are possible for chloromethylphosphine. In addition to the anti and gauche conformers, these consist of a syn conformer (phosphorus lone pair eclipsing the C–Cl bond) with C_s symmetry and an eclipsed conformer (phosphorus lone pair eclipsing a C–H bond of the chloromethyl group) with C_1 symmetry. The geometries of all four conformers were optimised initially at the correlated MP2/6-31+G** level and the relative energies calculated at MP2/6-31+G**//MP2/6-31+G** (Table 6). At this level, both the syn and eclipsed conformers were found to have one imaginary frequency, identifying them as transition states. The anti and gauche conformers, with no imaginary frequencies, correspond to minima

Table 4
Atomic coordinates (pm) for $CClH_2PH_2$
(a) Electron diffraction refinement

Atom	x	y	z
(i) *Anti conformer*			
C(1)	000.0	000.0	000.0
P(2)	186.0	000.0	000.0
Cl(3)	−77.6	161.2	000.0
H(5)/H(4)	202.4	91.4	±102.7
H(6)/H(7)	−36.7	−55.1	±91.0
(ii) *Gauche conformer*			
C(8)	000.0	000.0	000.0
P(9)	187.1	000.0	000.0
Cl(10)	−54.6	170.1	000.0
H(11)	203.5	−135.4	−23.4
H(12)	203.5	38.9	−131.8
H(13)	−37.3	−50.3	93.5
H(14)	−44.4	−51.8	−89.5

(b) Ab initio [CISD(fc)/6-31+G** level] optimisation

Atom	x	y	z
(i) *Anti conformer*			
C(1)	000.0	000.0	000.0
P(2)	185.4	000.0	000.0
Cl(3)	−79.7	160.1	000.0
H(5)/H(4)	203.7	92.4	±103.8
H(6)/H(7)	−35.0	−53.3	±87.6
(ii) *Gauche conformer*			
C(8)	000.0	000.0	000.0
P(9)	186.5	000.0	000.0
Cl(10)	−62.9	167.2	000.0
H(11)	199.8	−137.7	−25.9
H(12)	203.0	39.5	−133.7
H(13)	−35.9	−48.2	90.1
H(14)	−42.5	−50.2	−85.9

on the potential energy surface. All the geometries were subsequently optimised at the higher CISD/6-31+G** level (Tables 4 and 7) and the relative energies calculated at the CISD/6-31+G**//CISD/6-31+G** level (Table 6). In addition, the importance of the level of theory in calculating the relative energies was investigated for the CISD/6-31+G** geometries. The results are given in Table 6.

A natural population analysis [20], giving NBOs, was performed for each conformer. This method provides an estimate of the stabilisation energy of donor–acceptor orbital interactions. The orbitals are assumed to be localised on either one centre (core of lone-pair orbitals), two centres (2c–2e bonding), or three centres (3c–2e bonding) and, as such, the electron density is not described completely as with a molecular orbital approach. In general, care must be taken when using this method since a large number of relatively small interactions ($\leqslant 9\,kJ\,mol^{-1}$) may be as significant as a small number of relatively large interactions.

Table 5
Least squares correlation matrix (×100) for $CClH_2PH_2$ [a]

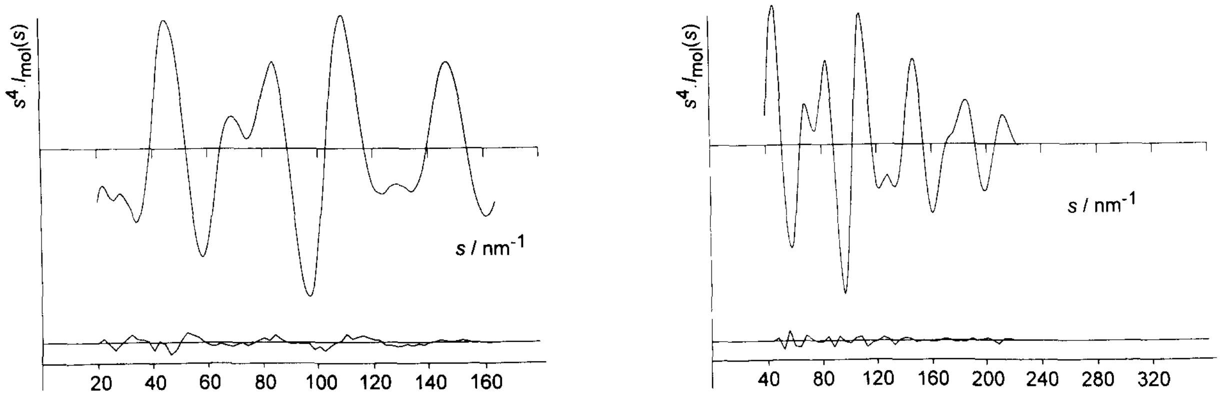
p_2	p_8	u_1	u_4	u_8	
−62		77			p_1
		−88	−60		p_2
	−87			72	p_7
				−84	p_8
			53		u_1
			59		u_3

[a] Only elements with absolute values ⩾50 are shown.

Considering the anti and gauche conformers only (the minima), the major interactions in the anti conformer occur (i) between the lone pair on phosphorus [lp(P)] and the antibonding sigma-type orbital of the C-Cl bond [σ*(C–Cl)], and (ii) between the lone pair on chlorine in the heavy-atom plane [lp(Cl)] and the antibonding sigma-type orbital of the C–P bond [σ*(C–P)]. These interactions are denoted (i) lp(P) $\rightarrow \sigma^*$(C–Cl) with interaction energy $E_i = 32.5\,kJ\,mol^{-1}$, and (ii) lp(Cl) $\rightarrow \sigma^*$(C–P) with $E_i = 22.9\,kJ\,mol^{-1}$, respectively, and are illustrated as contour plots in Fig. 4. For the gauche conformer, $E_i < 2.1\,kJ\,mol^{-1}$ for the interaction lp(P) $\rightarrow \sigma^*$(C–Cl) and $E_i = 15.6\,kJ\,mol^{-1}$ for the interaction lp(Cl) $\rightarrow \sigma^*$(C–P); the most significant interaction is $E = 17.9\,kJ\,mol^{-1}$ for σ(P–H) $\rightarrow \sigma^*$(C–Cl) and, in addition, $E_i = 15.5\,kJ\,mol^{-1}$ for lp(Cl) $\rightarrow \sigma^*$(C–H) and $13.8\,kJ\,mol^{-1}$ for lp(P) $\rightarrow \sigma^*$(C–H). Clearly, the lp(P) $\rightarrow \sigma^*$(C–Cl) interaction becomes very small for the gauche conformer, in which such orbitals are almost orthogonal to one another.

5. Discussion

In the gas phase at 293 K, chloromethylphosphine is present as a mixture of anti and gauche



(i) (ii)

Fig. 3. Observed and final weighted difference molecular scattering intensity curves for $CClH_2PH_2$. Nozzle-to-plate distances were (i) 259.8 and (ii) 201.1 mm.

conformers; the experimental mole fraction of the gauche conformer is 0.22(5).

The principal structural parameters derived from the ab initio computations (CISD/6-31+G**) are given in Table 7. The values defining the equilibrium geometry (r_e) are in good agreement with those refined from the electron-diffraction pattern (r_g). The theoretical relative energies at various levels of correlated theory (corrected for ZPE) for the different conformers are shown in Table 6. With increasing level, the difference between the anti and other conformers becomes slightly smaller. For the CISD/6-31+G** optimised geometry, the difference as calculated using single-point calculations (6-311+G(2df,p) basis) ranges from 4.5 kJ mol^{-1} at MP2 to 3.8 kJ mol^{-1} at QCISD, the highest level available to us. Assuming a Boltzmann distribution for the gas-phase mixture, and allowing for the double multiplicity of the gauche conformer, this implies a gauche mole fraction of 0.24–0.30. All of the values fall within two e.s.d.s of the experimentally determined parameter, 0.22(5).

The P–C distances determined for chloromethylphosphine (r_g = 186.3(3) pm (anti) and

Table 6

Theoretical relative energies[a] (kJ mol^{-1}) at various levels of theory for the conformations of $CClH_2PH_2$

Level of theory	Conformation[b]				% Gauche (293 K) in the mixture
	Anti	Gauche	Syn	Eclipsed	
MP2(fu)/6-31+G**//MP2(fu)/6-31+G**	0.0	5.7	13.1	15.6	16.0
Number of imaginary frequencies[c]	0	0	1	1	
CISD/6-31+G**//CISD/6-31+G**	0.0	4.8	11.9	14.4	22.0
MP2[d]	0.0	4.5	11.8	14.6	24.1
MP3[d]	0.0	4.1	11.0	14.4	27.1
MP4SDQ[d]	0.0	3.9	10.7	12.6	28.8
QCISD[d]	0.0	3.8	10.7	12.6	29.5

[a] Corrected for differences in zero-point vibrational energies (scaled by 0.93) as obtained by frequency calculations at the MP2(fu)/6-31+G** level.

[b] For definitions, see the text.

[c] 0 and 1 correspond to minima and transition states, respectively.

[d] Single-point energy calculations employing the 6-311+G(2df,p) basis set and geometries optimised at the CISD(fc)/6-31+G** level of theory (i.e. level 6-311+G(2df,p)//CISD(fc)/6-31+G**).

Table 7
A comparison of theoretical and experimental parameters for the conformers of $CClH_2PH_2$ [a]

	Theoretical $(r_e)^b$	GED$(r_g, \angle_\alpha)^c$
Anti conformer		
r[C(1)–P(2)]	185.4	186.3(3)
r[C(1)–Cl(3)]	178.8	179.1(5)
r[C(1)–H(6)]	108.3	114.1(4)[d]
r[P(2)–H(5)]	140.2	141.5(4)
∠PCCl	116.5	115.7(1)
∠PCH	108.9	109.1(f)
∠HCH	107.9	107.9(f)
∠CPH	97.5	96.8(f)
∠HPH	95.5	95.7(f
Gauche conformer		
r[C(8)–P(9)]	186.5	187.4[e]
r[C(8)–Cl(10)]	178.6	179.0[e]
r[C(8)–H(13)/H(14)]	108.3/108.2	114.0[e]
r[P(9)–H(11)/H(12)]	140.7/140.4	142.9[e]
∠PCCl	110.6	107.8(5)
∠PCH(13)/H(14)	109.3/113.2	109.4(f)/113.2(f)
∠HCH	108.9	108.9(f)
∠CPH(11)/H(12)	95.4/96.7	96.8(f
∠HPH	95.1	95.7(f)

[a] For atom numbering scheme, see Fig. 1.

[b] Geometry optimised at the CISD(fc)/6-31+G** level.

[c] Figures in parentheses are the estimated standard deviations; f = fixed.

[d] The C–H distance is defined by a shoulder in the radial distribution curve and may be subject to systematic errors.

[e] The difference between the gauche and anti distances was fixed at the theoretical value.

187.4(3) pm (gauche) are similar to those reported previously for simple methylphosphines: PH_2CH_3, 185.8(3) pm [7]; $PH(CH_3)_2$, 185.3(3) pm [7]; $P(CH_3)_3$, 184.4(3) pm [7]; $PH_2CH_2CH_3$, 186.2(2) pm (trans) and 186.4(2) pm (gauche) [8]. Only two structures containing the $CClH_2$–P moiety have been reported hitherto and for both the P–C bond length is poorly determined; namely, chloromethylphosphonic dichloride, $CClH_2POCl_2$, 186.2(19) pm [23] and chloromethyldichlorophosphine, $CClH_2PCl_2$, 186.0(20) pm [24]. The C–Cl bond distances in $CClH_2PH_2$ (179.1(5) pm (anti) and 179.0(5) pm (gauche)) are typical of other monohalogenated C(sp^3) systems such as $CClH_3$ (r_g = 178.3(2) pm) [25] but slightly longer than those found for $CClH_2P(O)Cl_2$ (176.9(6) pm) [23] and $CClH_2PCl_2$ (176.5(18) pm) [24]. This is as expected, if the $P(O)Cl_2$ and PCl_2 groups are assumed to be more electronegative than the PH_2 group.

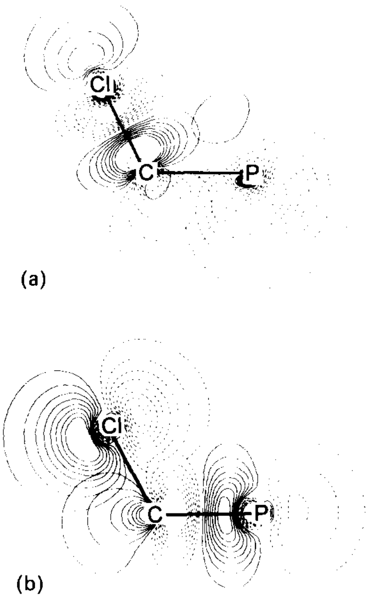


Fig. 4. Orbital contour plots for the anti conformer of $CClH_2PH_2$ showing the interactions (a) lp(P) → σ^*(C–Cl) and (b) lp(Cl) → σ^*(C–P). Dashed and solid lines denote different phases.

The most striking difference between the conformers of chloromethylphosphine is found for the ClCP angle. In the anti conformer this angle is 7.9(5)° (GED) (5.9° at CISD/6-31+G**) larger than in the gauche form. Such a large difference is not unprecedented; Durig and co-workers [8] recently determined (MW) the CCP angle in the trans form of $CH_3CH_2PH_2$ to be 5.6(1)° wider than in the gauche conformer. Such a difference has not, however, been determined before by electron diffraction.

Durig and co-workers [8] have rationalised the wide CCP angle in the trans conformer of ethylphosphine on the basis of non-bonded repulsive interactions between the phosphino hydrogen atoms and the methylene or methyl hydrogens. Whilst noting that similar interactions must also be considered for chloromethylphosphine, a natural population analysis [20] reveals that orbital interactions play an important role. The major stabilising interactions for the anti conformer are shown as contour plots in Fig. 4; these consist of

(a) lp(P) → σ*(C–Cl), and (b) lp(Cl) → σ*(C–P). In both cases, these interactions favour a widening of the ClCP angle. (Note that in (b) a narrowing of the ClCP angle is not favoured since a nodal plane passes through the C–P bond.) The lp(P) → σ*(C–Cl) interaction is inconsequential in the gauche conformer since the orbitals are almost orthogonal; in addition the lp(Cl) → σ*(C–P) interaction is computed to be much less important, relative to other interactions, than in the anti form.

The lp(P) → σ*(C–Cl) interaction, if considered alone, would lead to a shortening of *r*(C–P) and a lengthening of *r*(C–Cl), whilst the effect of the lp(Cl) → σ*(C–P) interaction would be the reverse. That *r*(C–P) is longer in the gauche than in the anti conformer is consistent with this expectation, the lp(P) → σ*(C–Cl) interaction being effectively absent for the gauche form. Both interactions widen the angle in the anti conformer, but the effects on the C–P and C–Cl bond lengths cancel one another. The commonly used explanation for the wide angle of lp(P) → σ*(C–Cl) hyperconjugation is only half the story.

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