Chem. Ber. **110**, 3494–3500 (1977)

The Molecular Structure of Trimethyl(methylene)phosphorane in the Gas Phase, Determined by Electron Diffraction

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Received December 30, 1976

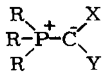
The molecular structure of trimethyl(methylene)phosphorane, $(CH_3)_3P=CH_2$, in the gas phase has been determined by electron diffraction. Principal distances are $r_a(P-C) = 181.5(3)$, $r_a(P=C) = 164.0(6)$ pm; and the angles between the P–C(methyl) bonds are 101.6(5)°. These parameters lead to a value for the order of the highly polar P–C(methylene) bond of about 2.0.

Die Molekülstruktur von Trimethyl(methylen)phosphoran in der Gasphase aus einer Elektronenbeugungsuntersuchung

Die Molekülstruktur von Trimethyl(methylen)phosphoran, $(CH_3)_3P=CH_2$, in der Gasphase wurde durch Elektronenbeugung bestimmt. Wichtigste Atomabstände r_a sind $P-C = 181.5(3)$ und $P=C = 164.0(6)$ pm. Die Valenzwinkel zwischen den P–C(Methyl)-Bindungen betragen 101.6(5)°. Diese Parameter ergeben für die stark polare P=C(Methylen)-Bindung eine Bindungsordnung von etwa 2.0.

Introduction

Compounds of the type R_3PCXY have attracted widespread interest, but particular attention has been paid to the nature of the phosphorus-carbon bond. This bond has orders of 1 and 2 in the extreme formal structures, **1** and **2**, and evidence from various sources has been used to ascertain how the electronic structures of particular compounds can be described relative to the extremes. Thus the values of $^1J(CH)$(methylene) in trialkyl(methylene)phosphoranes (ca. 150 Hz)[1] suggest that the orbital hybridisations of the carbon atoms are close to sp^2, and form **2** is appropriate. On the other hand, the low frequency chemical shift of the methylene protons has been interpreted[1] as indicating that there is a negative charge on the methylene carbon atom, giving increased shielding of the protons. This fits better with the ylide form, **1**. The assigned frequency of 1006 cm^{-1} for the "P=C stretching mode" in trimethyl(methylene)phosphorane has been used to



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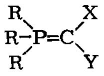

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[1] [1a] *H. Schmidbaur* and *W. Tronich*, Chem. Ber. **101**, 595 (1968). – [1b] *H. Schmidbaur*, *W. Buchner*, and *D. Scheutzow*, ibid. **106**, 1651 (1973).

calculate a force constant of 5.59 mdyne $Å^{-1}$ for the stretching of the bond, and from this a bond order of 1.65 was derived[2].

Structural data have been obtained for many compounds of the type Ph_3PCXY in the solid phase. In these, the length of the central bond ranged from 175[3] to 166[4] pm for triply connected carbon: these bond lengths indicate P—C bond orders of between 1.4 and 2.0. There is little variation in P—C(phenyl) bond lengths in this series of compounds, but the angles between the three P—C bonds are smallest in the compounds with the shortest P—C(methylene) bonds.

In view of the wide range of crystal structures that has been determined, it is remarkable that no gas phase structures of R_3PCXY compounds have been reported. However, the derivatives in which R = Ph are not very volatile, and the analogous compounds in which R = Me are harder to handle, being highly reactive, and have only been isolated relatively recently[1]. Consequently, it seemed worthwhile to us to undertake a study of trimethyl(methylene)phosphorane, and to obtain information about its structure in the gas phase free from crystal packing constraints. Such a study is also very important in the light of recent theoretical calculations on ylides, predominantly on the hypothetical molecule $H_3P{=}CH_2$[5–7]. We present here the results of the study.

Molecular Model

During refinements of the structure of trimethyl(methylene)phosphorane a model was used in which it was assumed that the three $P{-}CH_3$ groups had local C_{3v} symmetry,

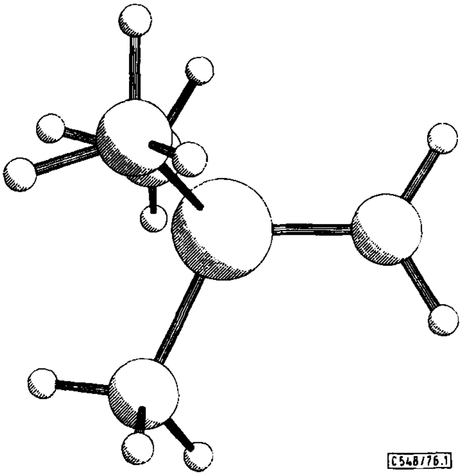

Fig. 1. Molecular Model of $(CH_3)_3P{=}CH_2$

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[5] *R. Hoffmann, D. B. Boyd*, and *S. Z. Goldberg*, J. Am. Chem. Soc. **92**, 3929 (1970).

[6] *I. Absar* and *J. R. van Wazer*, J. Am. Chem. Soc. **94**, 2382 (1972).

[7] [7a] *K. A. Ostoja-Starzewski, H. tom Dieck*, and *H. Bock*, J. Organomet. Chem. **65**, 311 (1974). — [7b] *K. A. Ostoja-Starzewski, W. Richter*, and *H. Schmidbaur*, Chem. Ber. **109**, 473 (1976).

and that the whole molecule apart from the methylene hydrogen atoms had C_3 symmetry. The $P-CH_2$ group was assumed to have C_{2v} local symmetry. With these constraints, the molecular geometry was defined by two P−C and two C−H bond lengths, PCH angles for the methyl and methylene groups, the twist angle of the methyl groups, defined as zero when one CH bond was *trans* to the P−C(methylene) bond, and the twist angle of the methylene group, defined as zero when the CH_2 plane also contained one P−C-(methyl) bond (Fig. 1).

Refinement and Results

The three geometrical parameters defining the skeletal structure, and three of the four amplitudes of vibration involving heavy atoms, all refined satisfactorily. These heavy atom distances account for the large peaks in the radial distribution curve (Fig. 2) at about 180 and 290 pm. The other substantial peaks in the radial distribution curve, at about 110, 240, and 380 pm, are due mainly to distances involving methyl hydrogen atoms. Thus it was possible to refine the C−H distance and PCH angle, and CH and $P\cdots H$ amplitudes of vibration, for the methyl groups. In addition, the twist angle of the groups was found by doing refinements with this angle and the methylene twist angle fixed at different values, and comparing the *R* factors obtained. One group of non-bonded $C\cdots H$ amplitudes of vibration was also refined. No parameters relating to the geometry of the methylene group were refined, as all the relevant peaks in the radial distribution curve coincided with more intense peaks representing distances associated with methyl hydrogen atoms. The refined values for the parameters associated with the methyl groups may therefore be slightly dependent on the assumed parameters for the methylene group: the quoted errors for these parameters have been increased to allow for this.

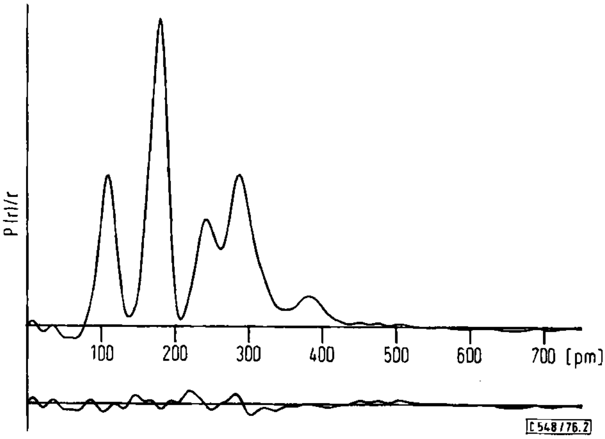

Fig. 2. Radial distribution curve, P(*r*)/*r*, for $(CH_3)_3P=CH_2$. Before Fourier inversion the data were multiplied by $s \cdot \exp[-0.00002\, s^2/(z_P - f_P)(z_C - f_C)]$

The parameters obtained in the best refinement, which converged to give R_G 0.13 and R_D 0.10, are listed in Table 1. Errors quoted in this table are estimated standard deviations, obtained in the least squares analysis, increased to allow for systematic errors and the effects of the constraints of the molecular model. The least squares correlation matrix for this refinement is given in Table 2. Observed and final weighted difference intensity curves are shown in Fig. 3a – c.

Table 1. Molecular parameters for $(CH_3)_3P=CH_2$

	Distance [pm]	Amplitude [pm]
Independent distances		
*r*1 (P=C)	164.0(6)	5.3(8)
*r*2 (P–C) (methyl)	181.5(3)	6.2(4)
*r*3 (C–H) (methyl)	109.9(5)	7.9(7)
*r*4 (C–H) (methylene)	106.0 (fixed)	7.1 (tied to *u* 3)
Dependent distances[a]		
*d*5 (C···C)	281.2(34)	11.5(10)
*d*6 (C···C)	294.0(57)	
*d*7 (P···H) (methyl)	241.3(30)	11.6(6)
*d*8 (P···H) (methylene)	244.9(40)	
*d*9 (C···H)[b]	374–396	17.8(16)
*d*10 (C···H)[b]	277–342	15.0 (fixed)
Angles (degrees)		
1 (C=P–C)	116.5(6)	
2 (P–C–H) (methyl)	109.3(4)	
3 (P=C–H) (methylene)	128 (fixed)	
4 (methyl twist)[c]	17 (see text)	
5 (methylene twist)[c]	0 (fixed)	

[a] Many H···H distances, not listed here, were included in the refinement.

[b] C···H distances fell into two ranges. The limits of those ranges, and the amplitudes of vibration for individual distances, are given here.

[c] For definition, see text.

Table 2. Least squares correlation matrix multiplied by 100

*r*1	*r*2	*r*3	<1	<2	*u*1	*u*2	*u*3	*u*5	*u*7	*u*9	*k*1	*k*2	*k*3	
100	31	–10	15	–23	–23	–31	–26	–40	–20	–4	–52	–38	–7	*r*1
	100	–6	12	–42	–14	1	1	0	1	13	2	12	9	*r*2
		100	–36	2	4	10	–3	28	–9	4	12	9	3	*r*3
			100	–72	–11	–10	1	–74	–13	–8	–12	–6	–1	<1
				100	4	–7	–2	36	24	–11	0	–17	–15	<2
					100	70	17	27	12	11	42	38	12	*u*1
						100	35	36	20	16	71	56	16	*u*2
							100	15	24	2	53	30	34	*u*3
								100	17	14	42	42	19	*u*5
									100	2	39	16	–10	*u*7
										100	14	19	13	*u*9
											100	53	12	*k*1
												100	18	*k*2
													100	*k*3

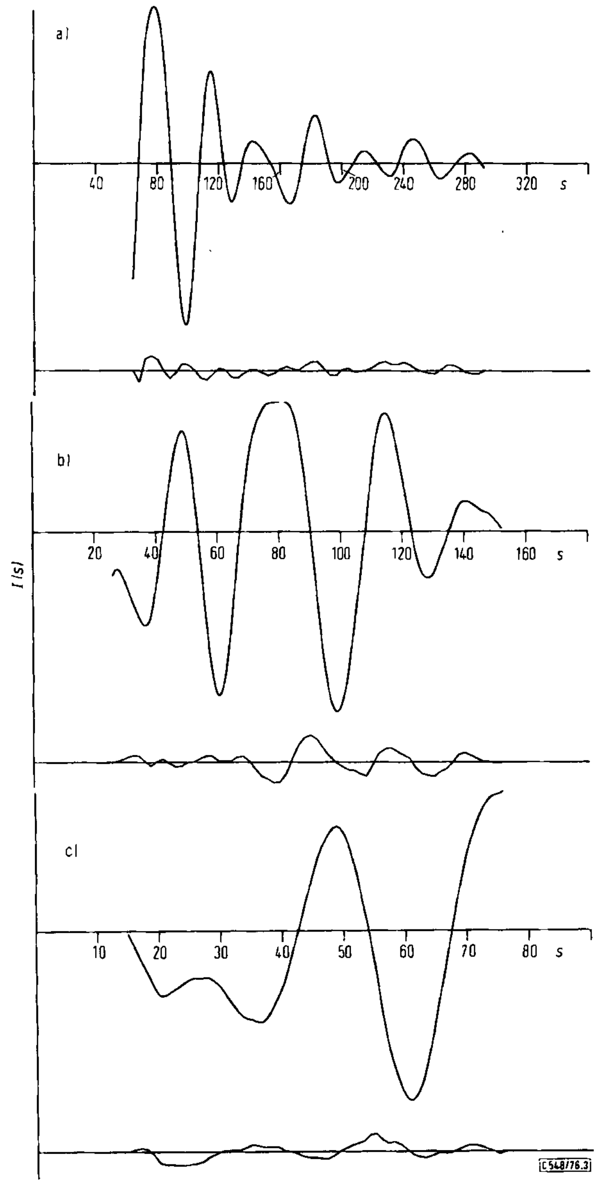

Fig. 3. Observed and final weighted difference molecular scattering intensities, obtained with nozzle-to-plate distances of a) 250, b) 500, and c) 1000 mm

Discussion

In comparison with trimethylphosphine, trimethyl(methylene)phosphorane has short P – C(methyl) bonds [181.5(3) instead of 184.1(3) pm][8] and wide angles [101.6(5) instead

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[8] *D. R. Lide* and *D. E. Mann*, J. Chem. Phys. **29**, 914 (1958).

of 99.1(2)°] between these bonds. These are differences that are frequently observed between 3- and 4-coordinated phosphorus compounds, as, for example, in PF_3 [9] and PF_3O [10]. The corresponding parameters for trimethylphosphine oxide [180.9(2) pm and 104.1(8)°] and trimethylphosphine sulfide [181.8(2) pm and 104.5(3)°] [11] are very close to those that we have determined.

The P–C(methylene) bond length of 164.0(6) pm is the shortest P–C distance involving a 3-coordinate carbon to be reported. This corresponds to a bond order of about 2.1, if one takes single, double, and triple bond distances to be 187, 166, and 153 pm, respectively – values derived from *Pauling*'s covalent radii [12], with electronegativity corrections. There is also considerable distortion of the four bonds to phosphorus, away from a regular tetrahedral arrangement. Three CPC angles are 101.6°: the other three are 116.5°. This is consistent with the correlation between distortion of the phosphorus tetrahedron and shortening of the unique P–C bond in methylene-triphenylphosphorane derivatives that was mentioned above. There is no indication from these results as to the size of the P–C(methylene) bond dipole.

The methyl hydrogen atoms positions are reasonably well defined, and bond lengths and angles are as expected. The methylene hydrogen atoms positions unfortunately could not be determined. In particular, it was not possible to establish the planarity of the $P{=}CH_2$ group, although this would be expected in terms of our interpretation of the short P=C distance as implying sp^2 hybridisation of the carbon atom.

We thank Professor *H. Schmidbaur* and Dr. *O. Gasser* for providing the sample and experimental details. Professor *D. W. J. Cruickshank* and Dr. *B. Beagley* for the provision of experimental facilities, and Mrs. *V. Ulbrecht* for assistance in obtaining electron diffraction data. We thank the *Science Research Council* for a Research Studentship (T. E. F.) and the *North Atlantic Treaty Organisation* for a research grant.

Experimental Part

A sample of trimethyl(methylene)phosphorane was prepared by the reaction of trimethyl(trimethylsilylmethylene)phosphorane with trimethylsilanol [1], and was purified by fractional condensation. Its purity was checked spectroscopically.

Electron diffraction scattering intensities were recorded photographically on Kodak Electron Image Plates, using a Balzers' KD.G2 diffraction apparatus at the University of Manchester Institute of Science and Technology. Data were obtained in digital form using a Joyce-Loebl automatic microdensitometer. The sample was maintained at 325 K and the nozzle at 347 K during exposures. Three camera heights were used, 250 mm (2 plates), 500 mm (2 plates) and 1000 mm (1 plate), giving data over a range of 15 to 292 mm^{-1} in the scattering variable, *s*. The electron wavelength, determined from the diffraction pattern of gaseous benzene, was 5.672 ± 0.002 pm.

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[10] *T. Moritani, K. Kuchitsu*, and *Y. Morino*, Inorg. Chem. **10**, 344 (1971).

[11] *C. J. Wilkins, K. Hagen, L. Hedberg, Q. Shen*, and *K. Hedberg*, J. Am. Chem. Soc. **97**, 6352 (1975).

[12] *L. Pauling*, The Nature of the Chemical Bond, 3rd ed., Cornell University Press, Ithaca, New York 1960.

All calculations were carried out on an ICL 4-75 computer at the Edinburgh Regional Computing Centre, using established data reduction [13)] and least squares refinement [14)] programme. Weighting points used in setting up the off-diagonal weight matrix are given in Table 3, together with correlation parameters and scale factors. In all calculations, the complex scattering factors of *Schäfer*, *Yates*, and *Bonham* [15)] were used.

Table 3. Weighting functions, scale factors, and correlation parameters

Camera height mm	Δs nm^{-1}	s_{min} nm^{-1}	sw_1 nm^{-1}	sw_2 nm^{-1}	s_{max} nm^{-1}	p/h	scale factor
250	4	64	68	284	292	0.4611	0.704(19)
500	2	26	29	144	152	0.4975	0.728(16)
1000	1	15	18.5	72	76	0.4999	0.503(25)

[13)] *D. M. Bridges, G. C. Holywell, D. W. H. Rankin,* and *J. M. Freeman,* J. Organomet. Chem. **32**, 87 (1971).

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[15)] *L. Schäfer, A. C. Yates,* and *R. A. Bonham,* J. Chem. Phys. **55**, 3055 (1971).

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