An Electron Diffraction Determination of the Molecular Structure of Hexamethylcarbodiphosphorane in the Gas Phase

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The molecular structure of hexamethylcarbodiphosphorane, $(CH_3)_3P=C=P(CH_3)_3$, in the gas phase has been determined by electron diffraction. Principle bond lengths (r_a) are: P – C, 181.4(3) pm, P = C, 159.4(3) pm; C – H, 108.9(4) pm. The angles between the P – C (methyl) bonds are 101.4(3)°, and the apparent P = C = P angle is 147.6(5)°. The single structure that fits the experimental data closest has C_2 overall symmetry, but an even closer fit is obtained if free rotation about the P = C bonds is assumed. This and other evidence indicates that the molecule is probably a symmetric top, and that the P = C = P unit is linear in the average structure, with shrinkage caused by a low frequency bending vibration giving rise to the apparent non-linearity.

Bestimmung der Molekülstruktur von Hexamethylcarbodiphosphoran in der Gasphase durch Elektronenbeugung

Die Molekülstruktur von Hexamethylcarbodiphosphoran, $(CH_3)_3P=C=P(CH_3)_3$, wurde in der Gasphase durch Elektronenbeugung bestimmt. Die hauptsächlichen Bindungslängen (r_a) sind P – C = 181.4(3) pm, P = C = 159.4(3) pm, C – H = 108.9(4) pm. Die Winkel zwischen den P – C-(Methyl)-Bindungen betragen 101.4(3)°, der scheinbare P = C = P-Winkel 147.6(5)°. Die einzige fixierte Struktur, die die beste Anpassung an die Meßdaten ergibt, hat die Gesamtsymmetrie C_2, doch wird für ein Modell mit freier Drehbarkeit um die P = C-Achse eine noch bessere Übereinstimmung gefunden. Daraus und aus anderen Hinweisen kann geschlossen werden, daß das Molekül einen symmetrischen Kreisel bildet und daß die P = C = P-Einheit in der gemittelten Struktur linear ist. Die beobachtete Schrumpfung geht danach auf eine sehr niedrige Beugungsfrequenz zurück, die zur scheinbaren Nichtlinearität führt.

Introduction

A study of the structure of trimethyl(methylene)phosphorane [1] indicated that the P = C-(methylene) bond is very short, corresponding to a bond order of at least 2, and that the methylene carbon atom can therefore be regarded as having sp² hybridisation and a probable planar arrangement of its bonds to phosphorus and hydrogen. It is therefore possible that a carbon atom bonded to two phosphorus trialkyl groups would have sp hybridisation,

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[1] *E. A. V. Ebsworth, T. E. Fraser*, and *D. W. H. Rankin*, Chem. Ber. **110**, 3494 (1977).

the PCP unit being linear. Crystalline hexaphenylcarbodiphosphorane has two mole-
cules in the unit cell, with PCP angles of 143.8(6) and 130.1(6)° [2]. In the ketene
$Ph_3P = C = C = O$ [3] the $P = C = C$ angle is 145.5(7)°, while in the analogous thioketene [4]
the corresponding angle is 168.0(7)°. Moreover, the related ion $[Ph_3P = N = PPh_3]^+$
in most compounds has $P = N = P$ angles ranging from 134.6 to 141.8° [5, 6], depending
on the counter anion; in one case, $[Ph_3P = N = PPh_3]^+$ $[V(CO)_6]^-$, the PNP unit is
crystallographically linear [7]. This evidence suggests that in these systems there is only
a small energy change involved in bending the chain by some 40−50° from the linear
configuration. Thus it is to be expected that in the gas phase, free from packing constraints,
hexamethylcarbodiphosphorane [8] might well have a linear PCP unit, but that a large
amplitude bending vibration would give rise to a large shrinkage effect, making the chain
appear bent when studied by electron diffraction. However, if the average structure, rather
than the structure determined from average distances, is in fact linear, the molecule is a
symmetric top, and the orbitals available for π bonding, phosphorus d, and carbon p
orbitals, are all members of degenerate pairs. In contrast to the situation in allenes, there
should be no electronic barrier to rotation about the double bonds.

We present here the results of a study of the gas phase structure of hexamethylcarbodi-
phosphorane, and our interpretation of them in the light of the possibilities outlined
above.

Molecular Models

Two models were used to describe the molecular geometry of hexamethylcarbodi-
phosphorane, $(CH_3)_3P = C = P(CH_3)_3$, during least squares refinements. In both of them,
the two $(CH_3)_3P = C$ units were assumed to be identical, with overall C_3 symmetry, and
local C_{3v} symmetry for each PCH_3 group. Geometrical parameters for this part were the
$P − C$, $P = C$, and $C − H$ bond lengths, the angles $C = P − C$ and $P − C − H$, and the twist
angle of the methyl groups, defined to be zero when one $C − H$ bond was *trans* to the
$P = C$ bond. In one model, there were two further geometrical parameters, the angle
$P = C = P$, and a twist angle. The latter was defined as the angle by which each $(CH_3)_3P$
group was twisted away from the position in which one $P − C$ bond was *cis* to the further
$P = C$ bond. Thus with zero twist the overall molecular symmetry was C_{2v}. The two end
groups could be given twists of the same sign, giving overall C_2 symmetry, or of opposite
sign, giving C_s symmetry. In the second model, the $P = C = P$ angle was defined in the same
way, but instead of defining a twist angle and considering a single fixed conformation,
free rotation about the $P = C$ bonds was assumed. To do this, twist angles were defined for
one $P − C$ bond at each end of the molecule, and all possible combination of these, from
10 to 350° in steps of 20°, were considered. In this way, 9 different long $P \cdots C$ distances
were calculated, but no less than 162 long $C \cdots C$ distances were involved, and an even

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[3] *J. J. Daly* and *P. J. Wheatley*, J. Chem. Soc. **1966**, 1703.

[4] *J. J. Daly*, J. Chem. Soc. A **1967**, 1913.

[5] *J. K. Ruff, R. P. White*, and *L. F. Dahl*, J. Am. Chem. Soc. **93**, 2159 (1972), and references therein.

[6] *H. B. Chin, M. B. Smith, R. D. Wilson*, and *R. Bau*, J. Am. Chem. Soc. **96**, 5285 (1974).

[7] *R. D. Wilson* and *R. Bau*, J. Am. Chem. Soc. **96**, 7601 (1974).

[8] [8a] *O. Gasser* and *H. Schmidbaur*, J. Am. Chem. Soc. **97**, 6281 (1975). − [8b] *H. Schmidbaur,
O. Gasser*, and *M. S. Hussain*, Chem. Ber. **110**. 3501 (1977), preceding.

greater number of $C \cdots H$ and $H \cdots H$ distances, and it seemed sensible to reduce these numbers to save computing time and space. For the $C \cdots C$ distances, the total range, from about 360 to 590 pm, was divided into 10 pm intervals and all those falling into one interval were replaced by a single composite "distance", being the weighted mean of its components, and having the appropriate total weight. The amplitudes of vibration for these distances represented the contributions to the real amplitudes arising from vibrations other than the torsion/internal rotation. For the $C \cdots H$ and $H \cdots H$ distances, even this method seemed to be unnecessarily complex, and these were therefore calculated assuming the same fixed conformation as was found using the first model.

Results

The results of the best refinements using the two models are listed in table 1 as refinements A and B, respectively. Errors quoted in this table are estimated standard deviations, obtained in the least squares analysis, increased to allow for systematic errors. In both refinements, all geometrical parameters were included, and as many amplitudes of vibration as would refine satisfactorily. For the rotation model, these included the two types of C(P)C amplitude, constrained to be equal, and the "framework" amplitude of vibration, excluding effects due to torsion or internal rotation, of the long $P \cdots C$ distances.

Table 1. Molecular parameters of $(CH_3)_3P = C = P(CH_3)_3$

	Refinement A		Refinement B	
	Distance (pm)	Amplitude (pm)	Distance (pm)	Amplitude (pm)
Independent distances (r_a)				
$r1$ (P=C)	161.1(5)	5.6(8)	159.4(3)	6.9(8)
$r2$ (P−C)	181.4(3)	5.5(5)	181.4(3)	6.1(4)
$r3$ (C−H)	109.3(5)	7.6(7)	108.9(4)	7.4(7)
Dependent distances[a]				
$d4$ (C···C)	283.8(30)	7.6(9)	280.6(16)	7.9(8)
$d5$ (C···C)	289.6(31)		290.4(20)	
$d6$ (P···H)	241.9(19)	11.6(7)	240.5(18)	11.3(6)
$d7$ (P···P)	306.7(24)	8.0 (fixed)	306.0(22)	7.8(11)
$d8$ (P····C)	382−447	14.1(13)	383−449	12.2(11)[b]
(C···C)	406−565	20.9(18)	365−585	22.5 (fixed)
Angles (degrees)				
<1 (P=C=P)	144.3(6)		147.6(5)	
<2 (C=P−C)	115.4(6)		116.7(4)	
<3 (P−C−H)	110.1(8)		109.3(9)	
<4 (methyl twist)[c]	37.7(18)		36.3(11)	
<5 (C_3P twist)[c]	31.4(6)		Free rotation	
R_G	0.131		0.113	
R_D	0.077		0.066	

[a] Many $C \cdots H$ and $H \cdots H$ distances were included in refinements, but are not listed here.
[b] "Framework" amplitude, refined for the group of $P \cdots C$ distances. See text.
[c] For definition, see text.

The best value for the corresponding parameters for the long C $\cdots$ C distances was found earlier to be 22.5 pm, but this was not refined further. The least squares correlation matrix for refinement B is given in table 2.

Table 2. Least squares correlation matrix for refinement B, multiplied by 100

| r1	r2	r3	<1	<2	<3	<4	u1	u2	u3	u4	u6	u7	u8	-1	k2	k3	
100	-54	-5	-62	29	7	15	7	-20	-10	-34	4	1	-4	-25	-42	-21	r1
	100	-7	41	-14	24	-47	-2	19	7	24	-2	5	1	24	33	14	r2
		100	14	-19	-24	22	-19	2	4	5	-13	-5	8	3	8	3	r3
			100	-62	-2	-25	-7	24	10	17	-12	-41	6	24	38	21	<1
				100	-30	-24	-3	-4	4	-51	13	21	12	-1	-5	-6	<2
					100	-90	28	-5	-16	17	-27	-8	-14	-11	-23	-8	<3
						100	-25	-10	8	-16	27	16	10	-5	-1	-4	<4
							100	39	-12	11	-1	5	-4	11	5	4	u1
								100	29	25	4	16	9	65	58	25	u2
									100	10	11	11	8	40	35	11	u3
										100	-5	50	-13	23	38	27	u4
											100	9	0	26	8	-14	u6
												100	-2	17	22	14	u7
													100	10	13	6	u8
														100	51	18	k1
															100	31	k2
																100	k3
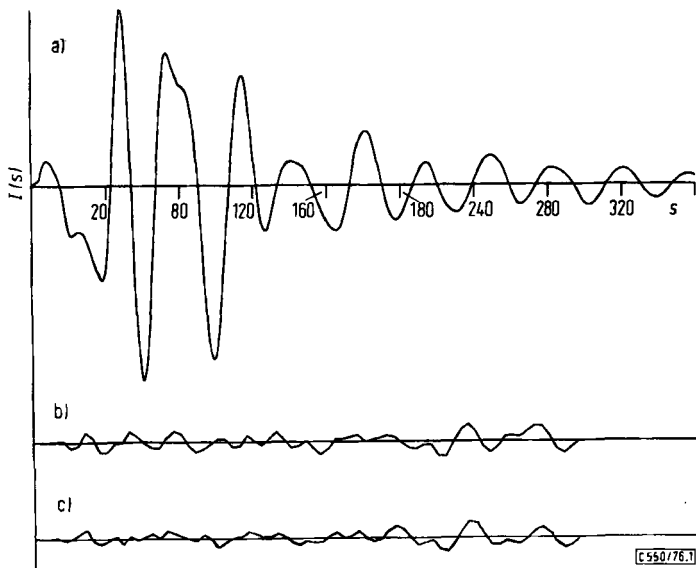
Fig. 1. Combined molecular scattering intensity curves: a) experimental, b) weighted difference, refinement A, c) weighted difference, refinement B
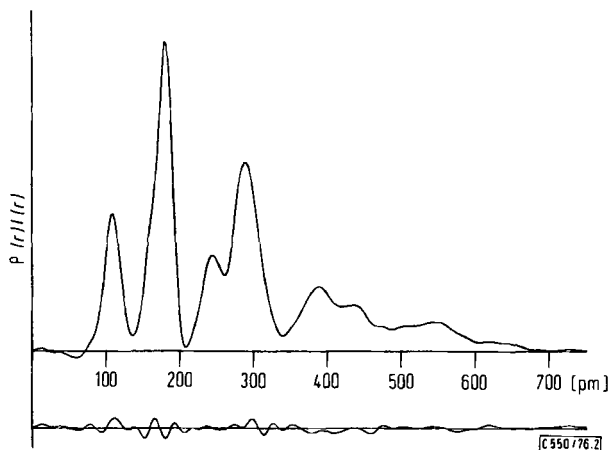
Fig. 2. Radial distribution curve, $P(r)/r$, and difference curve for refinement B. Before Fourier
inversion, the data were multiplied by: $s \cdot \exp[-0.00002\, s^2/(z_P - f_P)(z_C - f_C)]$

With the fixed conformation model, there was one more geometrical parameter, and so
amplitudes of vibration were not so easily refined. In this case, the amplitudes associated
with long $P \cdots C$ and $C \cdots C$ distances include a contribution from the torsional vibrations,
and so larger values were obtained. With this model, the lowest R factor (R_G) obtained was
0.131 compared with 0.113 using the free rotation model. The molecular scattering inten-
sities and final weighted differences for refinements A and B are shown in Fig. 1. The radial
distribution curve, $P(r)/r$, and difference curve for refinement B, are shown in Fig. 2.

Discussion

The parameters of the $C_3P=C$ skeletons of the two halves of hexamethylcarbodi-
phosphorane are very much as expected, when compared with corresponding parameters
for trimethyl(methylene)phosphorane[1]. Thus the $P=C$ distance is reduced from 164.0(6)
to 159.4(3) pm, just as in the corresponding phenyl compounds, for which the change is
from 166.1(8)[9] to 163.1(3) pm[2]. This shortening is consistent with a change of carbon atom
hybridisation from sp^2 to sp. The $C=P-C$ angle $[116.7(4)°]$ corresponds to a $C-P-C$
angle of 101.4°, not much wider than that $[99.1(2)°]$ in trimethylphosphine itself[10]. The
$P-C$ distances in the two phosphoranes are very similar, 181.4(3) and 181.5(3) pm, but
they are considerably shorter than the equivalent distance in trimethylphosphine,
184.1(3) pm.

All parameters associated with the $(CH_3)_3P=C$ groups are in excellent agreement with those for
corresponding parameters reported for trimethylphosphine oxide and sulfide[11], including those
involving hydrogen atom positions. These positions are much more reliably determined in the
present study than in the work on trimethyl(methylene)phosphorane, as possible systematic
errors arising from choice of methylene group parameters are avoided. As the agreement with

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

trimethylphosphine oxide and sulfide results was so good, the possibility of free rotation of methyl groups was not considered, as this had been found in the earlier work not to improve the fit of theoretical and experimental data.

The most interesting results of the present study are concerned with the relative positions and motions of the two $(CH_3)_3P=C$ units. In both refinements, A and B, the PCP angle is very wide, 147.6(6)°, in the preferred set of parameters. It should be emphasized that this angle is the one that gives the best fitting set of time-averaged interatomic distances (r_a), and that it is not necessarily the angle in the average structure of either the ground vibrational state of the molecule, or the vibrational states populated at the temperature of the experiment.

In carbon suboxide [12, 13], a linear molecule with a low frequency (63 cm^{-1}) for the CCC bending vibration, the apparent CCC angle, determined by electron diffraction, is only 158° and silyl isocyanate has an apparent SiNC angle of 151.7(12)° when studied by electron diffraction [14], although a microwave study [15] shows unequivocally that the ground state molecule is a symmetric top, with an SiNC angle of 180°.

Thus shrinkages large enough to make a linear system appear to be bent by 30° or more are well established, and we present two pieces of evidence to support the hypothesis that the present system may be similar. Firstly, in the linear $[Ph_3P=N=PPh_3]$ cation, the P=N bonds are 153.9(2) pm long [7], compared with 157−158 pm in the same ion in situations where the PNP angle is 137−142° [5, 6]. A P=C bond of the same order as the short P=N bond would be approximately 159 pm long − almost exactly the same as is found in the carbodiphosphorane. Secondly, in a linear $R_3P=C=PR_3$ system, all the orbitals that could be involved in π-bonding are members of degenerate pairs, and there can be no electronic barrier to rotation about the P=C bonds. In a bent system the degeneracy would be lifted, and the electronic contribution to the barrier would in principle be expected to increase as the angle decreases. Theoretical calculations have shown that the barrier to rotation about the P−C bond in the hypothetical H_3PCH_2 should be very small [16, 17]. Most 6-fold barriers are small. In bent R_3PCPR_3, the barrier to rotation about the P−C bonds would be 3-fold. From the ratio of the R factors for our refinements B and A, and tabulated values for such ratios [18], we can reject, at the 99% confidence level, the single conformation model of refinement A. The radial distribution curve, P(r), and difference curves for refinements A and B (Fig. 3) show how the free rotation model is superior. We conclude that rotation about the double bonds is effectively unrestricted; this would be most consistent with a model in which the average structure of the P=C=P chain were linear, at least for the vibrational states populated at the temperature of the experiment.

[12] M. Tanimoto, K. Kuchitsu, and Y. Morino, Bull. Chem. Soc. Jpn. 43, 2776 (1970).
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[17] J. Absar and J. R. van Wazer, J. Am. Chem. Soc. 94, 2382 (1972) (Ab-initio).
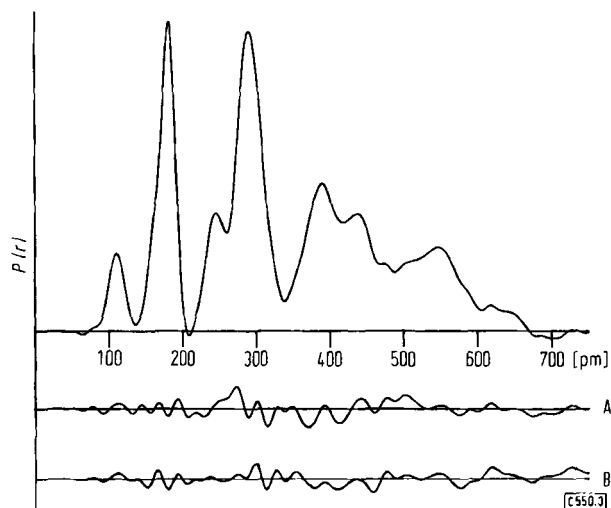[18] W. C. Hamilton, Acta Crystallogr. 18, 502 (1965).

Fig. 3. Radial distribution curve, P(r), and difference curves for refinements A (fixed conformation) and B (free rotation). The curves were obtained in the same way as those of Fig. 2
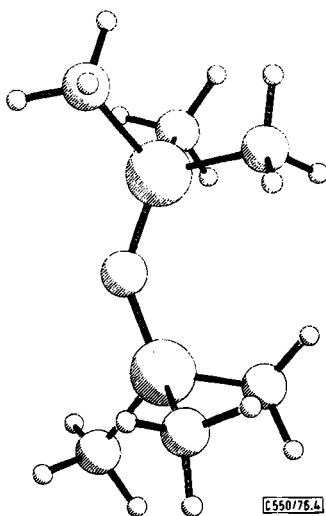

Fig. 4. Molecular model of $(CH_3)_3P=C=P(CH_3)_3$

If the $P=C=P$ unit is linear, then to account for the observed apparent angle, the PCP bending frequency, which is unknown, must be low, probably about 80 cm^{-1}. This is not unreasonable, by analogy with carbon suboxide[12, 13], which also has a central carbon atom with two double bonds, and a π-system derived from degenerate pairs of orbitals, in which the CCC bending frequency is 63 cm^{-1}. Similarly, the wide range of PNP and PCP angles in $Ph_3P=C=PPh_3$[2] and $[Ph_3P=N=PPh_3]$ cation[5, 6, 7] indicate that there is very little energy change involved in

bending the central chains by $40 - 50°$ from the linear structures, and the triboluminescence of hexaphenylcarbodiphosphorane has been attributed to a phase change associated with a change of PCP angle [19]. Thus it seems probable that in all these structures, the potential well for the bending coordinate is fairly flat-bottomed, rising steeply at about $130 - 140°$, when the phosphorus atoms get close to each other. Indeed, it may well be this easy flexibility, leading to ease of packing into a lattice, that accounts for the remarkable properties of $[Ph_3P = N = PPh_3]^+$, which is used for stabilising reactive anions.

It should be noticed that hexamethylcarbodiphosphorane is iso-electronic with hexamethyldisiloxane. This molecule has an SiOSi angle, determined by electron diffraction [20], of $148(3)°$, but there is uncertainty about the SiOSi bending frequency, and the extent of shrinkage effects. The possibility cannot be excluded that this disiloxane also has a linear average structure for the SiOSi group.

Finally, it should be noted that in the $P = C = P$ bending vibration of hexamethylcarbodiphosphorane, the atom that moves most is the central carbon atom. If this movement takes place without much relative movement of the two phosphorus atoms, then the $P = C$ distance would change in the course of the vibration, but the $P \cdots P$ distance would change relatively little. Our results show a surprisingly large amplitude of vibration, 6.9(8) pm, for the $P = C$ atom pair, and an unusually small value, 7.8(11) pm, for the $P \cdots P$ pair, although the latter value is correlated with $C \cdots C$ amplitudes of vibration. These two observations therefore provide further evidence that this molecule is a symmetric top, but with a large amplitude bending vibration.

Experimental Part

A sample of hexamethylcarbodiphosphorane was prepared from difluorotrimethylphosphorane by the route that has been described previously [8a], and purified by fractional distillation. Its purity was checked spectroscopically.

Electron diffraction scattering data were recorded photographically on Kodak Electron Image Plates using a Balzers' KD.G2 diffraction apparatus, and were converted to digital form with a Joyce-Loebl automatic microdensitometer. During experiments the temperature of the sample and inlet system were maintained at 350 K. Camera heights of 250 mm (3 plates), 500 mm (3 plates) and 1000 mm (3 plates) were used, giving data over a total range of 10 to 296 nm^{-1} in the scattering variable, s. The electron wavelength, 5.661(5) pm, was determined from the diffraction pattern of gaseous benzene.

An ICL 4-75 computer at the Edinburgh Regional Computing Centre was used for all calculations, with our usual data reduction [21] and least squares refinement [22] programmes. Weighting points used in setting up the off-diagonal weight matrix, together with correlation parameters and scale

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factors, are given in Table 3. In all calculations, the scattering factors of *Schäfer, Yates*, and *Bonham*[23] were used.

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

Camera height mm	Δs nm^{-1}	s_{min} nm^{-1}	sw nm^{-1}	sw_2 nm^{-1}	s_{max} nm^{-1}	p/h	Scale factor
250	4	72	87	282	296	0.4193	0.417(14)
500	2	24	29	142	152	0.4687	0.747(12)
1000	1	10	11.5	76	78	0.4978	0.603(15)

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