0.649 Å^{-1}, orange-brown hexagonal plates ($0.25 \times 0.5 \times 0.5$ mm^3), 8091 measured reflections, 4746 unique, ($R_{int} = 0.030$), R values ($I > 2\sigma I$): $R1 = 0.0346$, $wR2 = 0.0640$, all data: $R1 = 0.0588$, $wR2 = 0.0713$. Diffractometer: Enraf-Nonius CAD4T with rotating anode ($Mo_{K\alpha}$, $\lambda = 0.71073$ Å). Structure solution with Patterson methods (DIRDIF-96).[14] Structure refinement with SHELXL-97 against F^2,[15] 330 parameters, no restraints. Nonhydrogen atoms were refined with anisotropic temperature parameters, hydrogen atoms were refined freely with isotropic temperature parameters. Absorption correction with Psi-scans ($\mu = 1.911$ mm^{-1}, 76–98% transmission). Structure graphics were performed with the program PLATON,[16] and the symmetry was checked. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101 009. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Differences Between Gas-Phase and Solid-State Molecular Structures of the Simplest Phosphonium Ylide, $Me_3P=CH_2$**

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Dedicated to Professor Hubert Schmidbaur

There is still no reliable structural determination of the simplest isolable phosphonium ylide $Me_3P{=}CH_2$. This is surprising as ylides are very important reagents in chemistry,[1, 2] and $Me_3P{=}CH_2$ was first prepared in a pure form by Schmidbaur and Tronich in 1968.[3] The main focus of structural investigations of ylides has been the coordination at the carbanion center, which is between tetrahedral and trigonal-planar geometries but not necessarily planar. The degree of flattening is dependent on the electronic nature of the substituents.[2] We have now observed substantial differences between the ab initio calculated geometry of trimethylmethylenephosphorane, $Me_3P{=}CH_2$, and the structure determined by gas-phase electron-diffraction (GED) in 1977.[4] Moreover, a crystal structure determination has resulted in a geometry compatible with neither of these two structures.

The original GED geometry from 1977 was determined under the assumption of local C_3 symmetry for the $C{=}PMe_3$ unit, whereas our new calculations employed theory up to the MP2/6-311G* level and consistently show a global minimum having C_s symmetry (Table 1). Assuming this symmetry for the model used in the GED analysis, we have reanalyzed the data collected in 1977[1] (see Figure 1 and Table 1). A refinement in the lower symmetry of C_s was feasible with our recently developed improved method of GED analysis (SARACEN,[5] which is a natural extension of Bartell's "predicate value" and Schäfer's MOCED method).[6] This avoids the use of simplifying, but unjustified fixed constraints, but instead employs information calculated by ab initio methods as flexible restraints. Thus, based on the sum of our experimental and theoretical knowledge, SARACEN provides us with improved geometries and better estimates of errors. The result for $Me_3P{=}CH_2$ is a substantially improved fit on the experimental intensities relative to the old refinement,[1] and the agreement between refined and calculated

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Table 1. Bond lengths [Å] and angles [°] determined by electron diffraction (GED), ab initio calculations,[a] and single crystal X-ray diffraction (XRD) of $Me_3P=CH_2$.[b]

Parameter	GED	MP2/6–311G*		XRD
	$r_a/<_a$	minimum	TS	
P1–C2	1.656(2)	1.677	1.667	1.678(2)
P1–C5	1.837(6)	1.849	1.813	1.791(2)
P1–C9	1.809(3)	1.817	1.832	1.808(1)
C2-P1-C5	122.4(7)	123.9	110.3	110.7(1)
C2-P1-C9	111.4(13)	110.4	117.5	115.69(6)
C5-P1-C9	101.0(20)	101.7	104.8	105.40(7)
C9-P1-C13(C9′)108.3(14)	107.4	100.5	102.9(1)	
P1-C2-H3/4	118.2(18)	117.0	119/121.6	111(2)/118(3)
H3-C2-H4	115.7(20)	116.1	119.3	118(3)
C5-P1-C2-H3/4	±73.9(30)	±72.2	180/0.0	180/40.9

[a] Global minimum and transition state of PCH_2 inversion. [b] In all methods the model had C_s symmetry.

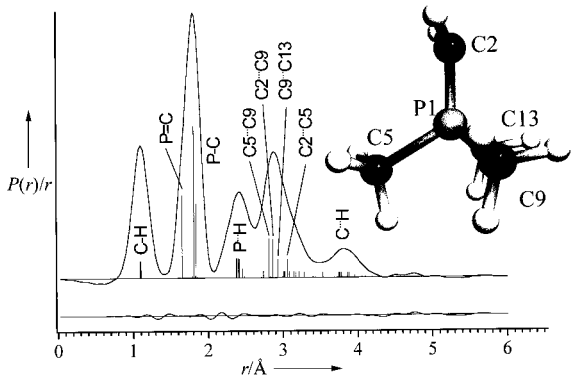

Figure 1. Molecular structure of $Me_3P=CH_2$, and experimental and difference radial distribution and difference curves from the gas-phase electron diffraction refinement. The position of interatomic distances are indicated as vertical lines and assigned.

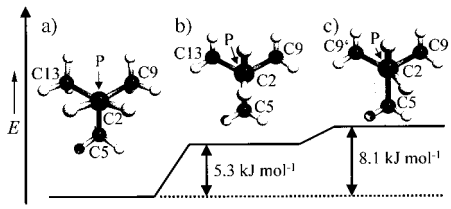

Figure 2. Different orientations of the CH_2 group in $Me_3P=CH_2$ relative to the plane of symmetry (vertical) as shown by a view along the P=C bond (the disordered H position is drawn as a faded circle).

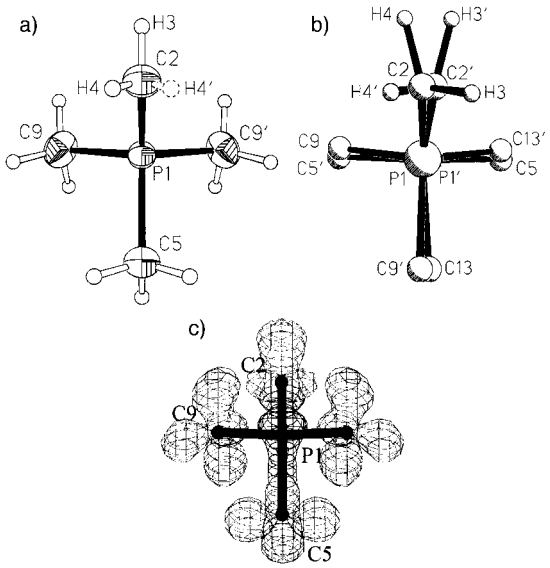

Figure 3. a) Molecular structure of $Me_3P=CH_2$ in the crystal. Labels H4 and H4a mark the positions of the disordered ylidic H atoms. b) One of the rejected disorder models for an alternative interpretation of the crystallographic results.[12] c) Difference Fourier map as calculated after anisotropic refinement of the P and C positions with contours shown at the 0.43 e $Å^{-3}$ level.

geometry strongly supports the prediction of the ab initio calculations, justifying the use of calculated restraints.

In the gas phase, the PCH_2 unit is oriented perpendicular to the mirror plane and has a pyramidal geometry, in which the plane of the CH_2 group is at an angle of 27.4(58)° to the P=C bond.[8] This compares well with an angle of 26° in $Ph_3P=CH_2$,[9] which has so far served as the reference structure for phosphonium ylides. The unique C2=P-C5 angle is much larger (122.4(7), calcd 123.9°) than the other two C=P-C angles (111.4(13)°, calcd 110.4°). This discrepancy should be compared to the large differences between the C=P-N angles in $(Me_2N)_3P=CH_2$.[10] This large deviation from local C_3 symmetry leads to two different $P-C_{methyl}$ bond lengths: P–C5 is about 0.03 Å longer than the two symmetry-equivalent P–C bonds.

In the crystal the $Me_3P=CH_2$ molecule adopts a strikingly different geometry[11] to that in the gas phase (Figures 2 and 3). A crystallographic plane of symmetry passes through the molecules, but one of the ylidic hydrogen atoms is located out of the plane (a disordered position resulting from crystal symmetry, Figure 2c), whereas the other is in the plane. The in-plane angle C2=P1-C5 is as much as 11.7° smaller in the crystal (110.7(1)°) than in the gas phase, whereas both symmetry-equivalent out-of-plane C=P-C angles (115.69(6)°) are larger in the solid state than in the gas phase (111.4(13)°). The orientation of the CH_2 group can be taken as a reference for structural comparison: The CH_2 group is bent towards C5 in the gas phase and towards C9 in the solid state (Figure 2). The differences between core angles in the two phases are thus (gas →solid) 122.4° →115.7, 111.4 →115.7, and 111.4 →110.7, which represent a pronounced deviation of the solid-state geometry from the ground state. This deviaton also affects the P-C-P angles which are 101.0, 101.0, and 108.3° in the gas phase, but 105.4, 105.4, and 102.9° in the crystal. Hence the whole molecule is distorted. The torsional angles describing the positions of the ylidic H atoms (C5-P1-C2-H3/4: 180/40.9°), however, are very similar to those found in the crystal structure of $Ph_3P=CH_2$.[9]

We have also tried to rationalize the unexpected crystal structure in terms of two disordered interpenetrating molecules that are close to the gas-phase geometry but related to one another by reflection or an approximate 120° rotation, as depicted in Figure 3b. However, careful consideration of the anisotropic displacement parameters (ADP) and of the well-determined hydrogen positions make the presence of such disorder improbable, although it cannot be excluded completely at present.[12]

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We were surprised to realize that the geometry of the PC_4 unit in the solid state is very close to that of a transition state computed for rotation–inversion of the ylidic CH_2 group (Table 1); this was obtained by restricting the ylidic H atoms to in-plane positions in C_s symmetry (Figure 2b). This transition state is 5.3 kJ mol^{-1} higher in energy than the calculated ground state. Optimization of the geometry (MP2/6-311G*) with the heavy-atom skeleton angles fixed at the crystal structure values led also to a PCH_2 unit lying in the plane of symmetry, while fixing the torsion angles describing the ylidic H positions to the solid-state values and relaxing the rest of the geometry led to almost the ground-state geometry. Under the action of both constraints (core angles and H-torsion angles as in the crystal) the energy increases by another 2.8 kJ mol^{-1} relative to the transition state, which provides us with an estimate of 8.1 kJ mol^{-1} for the energy difference between a free molecule of $Me_3P{=}CH_2$ and one placed in the crystal lattice. This is about the magnitude of deformation energies that can be compensated for by intermolecular forces in crystal lattices.

The crystal structure seems thus to be similar to a transition state (see Table 1 for a comparison of geometries) with ylidic H atoms distorted away from a planar arrangement of the PCH_2 unit. The packing of the molecules does not show any pronounced intermolecular contacts and thus the sum of small interactions must be responsible for the large distortion of the solid-state structure from the ground-state geometry.

The work presented in this paper shows how carefully structural results from one phase (or method) alone need to be interpreted. Only a combination of methods can provide us with realistic pictures of molecular structures. The omnipresent intermolecular forces in crystals should not be underestimated; in this case there are no intermolecular contacts that would normally be described as significant, yet the structural changes on crystallization are profound.

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[7] The experimental details for the electron diffraction experiment have been described.[4] Detailed description of parameter definition and applied restraints can be found in the supporting information. An alternative model with planar CH_2 group refines the structure with a significantly higher *R*g.

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[11] A solid–liquid equilibrium was established at 285 K in a sample held in a capillary o.d. 0.16 mm. A single crystal grew on cooling at 1 K h^{-1}. Crystal system monoclinic, space group $P2_1/m$ (the model is essentially unrefinable in the space group $P2_1$), $Z=2$, $a=6.0864(11)$, $b=7.6153(15)$, $c=6.4565(20)$ Å, $\beta=92.551(20)^\circ$, $V=298.96$ Å^3 at 120 K, cell from 46 reflections (θ range 15–19°). Diffractometer: Stoe-Stadi 4 with Oxford-Cryosystems cryostat, $Mo_{K\alpha}$-radiation, graphite monochromator, $2\theta_{max}=55^\circ$, ω scan with on-profile fitting, 739 independent reflections [$R_{int}=0.04$, 651 with $F_0>4\sigma(F_0)$] and solved with direct methods (SIR92, A. Altomare, M. C. Burla, M. Camelli, G. Cascarano, C. Giacovazzo, G. Polidori, and A. Guagliardi, *J. Appl. Cryst.* **1994**, *29*, 435); refinement: CRYSTALS version 10 (D. J. Watkin, C. K. Prout, J. R. Curruthers, P. W. Betteridge, Oxford, 1997) non-hydrogen atoms with anisotropic thermal displacement parameters, hydrogen atoms (located in difference Fourier maps) isotropically. Weighting scheme: Chebychev polynomial; 55 parameters, $R(F)$ (obs.) = 0.030, $wR(F)=0.032$, maximum residual electron density 0.39 and −0.24 e Å^{-1}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100730. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (Fax: (+44) (1223)-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[12] For the consideration of possible disorder in the crystal, the GED geometry has been taken as a reference. If the positions C5/C13′, C5′/C13 and H3/H3′ (see Figure 3b) are averaged to give $C5_{av}$, $C5'_{av}$ and $H3_{av}$, the following geometry is obtained: P1=$C2_{av}$ 1.656, P1–$C9_{av}$ 1.791, P1–$C5_{av}$ 1.808 Å, C2-P1-$C9_{av}$ 110.7, C2-P1-$C5_{av}$ 115.7, C9-P1-$C5_{av}$ 105.4, C5-P1-$C5'_{av}$ 102.9, H3-C2-$H4_{av}$ 118, H4-C2-$H4'_{av}$ 71°. These values are close to those observed in the crystal structure. However, the large distances between the disordered atom positions before averaging (e.g. C5-C13′) should be reflected in the experimental ADP's, which should thus be markedly elongated for $C5_{av}$ and $C5'_{av}$. This is not observed and the direction of this elongation does not coincide with the longest axis of the ADP's. Moreover, TLS (translation, libration, and screw) analysis shows the ADP's to be consistent with molecular libration as a rigid body, thus excluding contamination from alternative atomic positions.
An alternative model was generated from fitting the atom pairs P1/P1′, C2/C2′, C5/13′, C9/C5′, and C13/C9′of two gas phase geometries by a least square procedure (Figure 3b) and averaging the positions of these pairs. The resulting geometry is essentially the same as the above average structure. This model could be rejected on the basis of the well-located hydrogen positions of the CH_2 unit (Figure 3c), as the model suggests both H-positions are clearly off the mirror plane of the disordered heavy-atom skeleton. We are grateful to Prof. R. Boese and the other referees of this paper, who drew our attention to these disorder models, which clearly needed to be considered before drawing the conclusions outlined in this paper.

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