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Molecular structure and conformational preferences of trimethylphosphite, $P(OCH_3)_3$, as a free molecule and as a ligand in d-block metal complexes†

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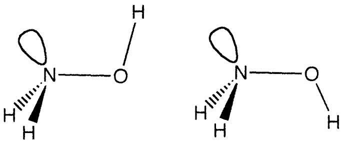
Free $P(OCH_3)_3$ has been studied by gas electron diffraction (GED) and DFT calculations at the B3PW91/6-311+G* level. Each conformer is characterised by three dihedral angles $\tau(COPlp)$ where *lp* denotes the direction of the electron lone pair on the P atom; assumed to lie in a plane containing the P–O bond and bisecting the opposing OPO angle. DFT calculations indicate that the most stable conformer is an *anti,gauche*$^+$, *gauche*$^+$ (ag^+g^+) conformer characterised by the angles $\tau_a = (COPlp)\ -173$, $\tau_b = 54$ and $\tau_c = 41°$. It is followed by an ag^-g^+ conformer at $\Delta E = 6.3$ kJ mol^{-1}, an aa^+g^+ conformer at $\Delta E = 6.6$ kJ mol^{-1}, and a $g^+g^+g^+$ conformer at $\Delta E = 10.4$ kJ mol^{-1}. The calculated standard free energies at 298.15 K indicate that the mole fractions in the gas phase at this temperature are $\chi(\pm ag^+g^+) = 73\%$, $\chi(ag^-g^+) = 16\%$, $\chi(\pm aa^+g^+) = 10\%$ and $\chi(\pm ag^+g^+g^+) = 1\%$; GED data indicate that the mole fractions of the more stable conformers at room temperature are $\chi(\pm ag^+g^+) = 78(13)\%$, $\chi(ag^-g^+) = 9(11)\%$ and $\chi(\pm aa^+g^+) = 14(21)\%$. Natural Bond Orbital (NBO) analysis of the wavefunctions suggest that while bond distances and valence angles are determined by anomeric effects, the relative stabilities of the four conformers are not determined by such effects alone. Examination of the crystal structures of 287 complexes where one or more $P(OCH_3)_3$ units are coordinated to a d-block transition metal M, shows that in the 523 crystallographically independent $MP(OCH_3)_3$ fragments 46% of the trimethylphosphite units adopt a $\pm ag^+g^+$ conformation, 19% an ag^-g^+ conformation and 30% a $\pm aa^+g^+$ conformation. It is suggested that the increased number of $\pm aa^+g^+$ conformers and decreased number of $\pm ag^+g^+$ conformers relative to the gas phase, as well as the folding back of the *gauche* ligands are due to interligand repulsion in the transition metal complexes. Structure optimisation of F_2POMe by DFT calculations at the B3PW91/6-311+G* level indicate that the most stable conformation is *anti*, while the energy of a *gauche* conformer is about 15 kJ mol^{-1} higher. NBO analysis of the wavefunctions indicate that the relative stabilities of the two conformers as well as the differences between bond distances and valence angles may be determined by anomeric effects.

Introduction

The main object of this article is to describe the molecular structure and conformations adopted by trimethylphosphite in the gas phase and how the structure and conformational preferences are modified in crystalline complexes of $P(OMe)_3$ with transition metals. In order to increase our understanding of the conformations adopted by the free molecule we also include the results of a computational study on F_2POMe.

The simplest molecule containing a single bond between a Group 15 element and and oxygen, *i.e.* hydroxylamine, has been studied by *ab initio* molecular orbital calculations.[1,2] The global energy minimum was found for the form **1a**, a second, local energy minimum for the form **1b** (Scheme 1). The energy of the latter was, however, computed to be about 40 kJ mol^{-1} above **1a** at the HF/DZ level.

The relative orientation of the two ends of the molecule may be described by the dihedral angle $\tau(HONlp)$ where *lp* denotes the direction of the electron lone pair on the N atom which is assumed to lie in a plane containing the N–O bond and bisecting the HNH valence angle. According to the nomenclature rules of IUPAC, $\tau(HONlp)$ should be defined as 0° in **1a** and 180° in **1b**.[3] We refer to **1a** as a *syn*, and **1b** as an *anti* conformer. A microwave study later confirmed the *syn* structure; no indications were found for the presence of other conformers.[4]



1a *syn* **1b** *anti*

Scheme 1

The prototypical molecule containing a single P–O bond, dimethylmethoxyphosphane or Me_2POMe, has two conformers in the gaseous or liquid phases.[5,6] The major conformer in the gas phase is a near *syn* conformer where the C–O bond is close to eclipsing the electron lone pair on the phosphorus atom. The second conformer in which the C–O bond is *anti* to the lone pair on P becomes more abundant in the liquid and is the only conformer in the solid state. Durig and Xiao have recorded the IR spectra of Me_2POMe in liquid xenon and krypton at temperatures ranging from −55 to −150 °C and determined the *anti* minus near *syn* enthalpy difference to be 4.7 ± 0.6 kJ mol^{-1}, while quantum chemical calculations at the MP2/6-31G(d) level indicate an electronic energy difference of 5.0 kJ mol^{-1}.[7]

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† Dedicated to Professor L. V. Vilkov, Moscow State University, on the occasion of his 70th birthday.

However, when the two methyl groups on the phosphorus atom in Me_2POMe are replaced by more electronegative substituents, the conformational equilibrium shifts; infrared and Raman spectra of gaseous and solid F_2POMe as well as the Raman spectra of the liquid indicate the exclusive presence of an *anti* conformer in all phases.[8] The structure of this *anti* conformer has been determined by microwave spectroscopy[9] and gas electron diffraction.[10] MP2/6-31G* calculations indicate that the energy of two degenerate *gauche* conformers (**1c**) is about 19 kJ mol^{-1} higher.[8] No structure parameters for the *gauche* conformers were reported, but the dihedral angle $\tau(COPlp)$ is presumably in the neighbourhood of 60°. Similarly the IR spectra of $C1_2POMe$ dissolved in liquid xenon and Raman spectra of the gas show that the only conformer present is the *anti*; quantum chemical calculations at the MP2/6-31G* level indicate that the energy of a near *syn* conformer is at least 15 kJ mol^{-1} higher.[11]

Very little appears to be known about the conformational preferences of trimethylphosphite, $P(OMe)_3$. Extrapolation based on the conformational properties of Me_2POMe suggests that the equilibrium conformation may be characterised by three methoxy groups in *syn* or near *syn* orientations relative to the electron lone pair on the phosphorus atom. The symmetry of such conformers might be C_3, or even C_{3v}. The electronegativity of O is, however, intermediate between those of F and Cl, and extrapolation based on the structures of $C1_2POMe$ and and F_2POMe suggests that all methoxy groups might be found in *anti* orientations, again resulting in C_3 or C_{3v} symmetry. Neither can models with methoxy groups in different orientations be ruled out. Indeed, an early study of the gas phase IR spectrum of trimethylphosphite, $P(OMe)_3$, led to the tentative conclusion that "the symmetry could be less than C_{3v} or C_3".[12] Gas electron diffraction data recorded at room temperature was found to be consistent with molecular models of C_3 symmetry and with the methoxy groups in *gauche* orientations relative to the P electron lone pair, but it was stated that the true conformation could not be established and that the gas might consist of more than one conformer.[13] Finally, *ab initio* calculations at the HF/6-31G** level led to the identification of two stable conformers, one with C_3 symmetry and all methoxy groups in *gauche* orientations, the other with C_1 symmetry, two MeO groups in *gauche* and the third in an *anti* orientation.[14] Structure optimisation at the MP2/6-31G** level indicated that the C_1 conformer was the more stable by about 18 kJ mol^{-1}.[14]

Density functional theory calculations

All DFT calculations were carried out at the B3PW91/6-311+G* level using the Gaussian 98 program system.[15] Structure optimisation of the *anti* conformer of F_2POMe was carried out under C_s, optimisation of the *gauche* without imposition of symmetry. Calculation of the molecular force fields confirmed that the optimal structures thus obtained correspond to minima on the potential energy hypersurface. Structure optimisation of $P(OMe)_3$ without imposition of symmetry led to the identification of two non-degenerate minima; structure optimisation under C_s or C_3 symmetry followed by calculation of the force field led to the identification of two more.

The molecular force field of each $P(OMe)_3$ conformer in Cartesian displacements was used to calculate root-means-square vibrational amplitudes (l) and vibrational correction terms $D = r_a - r_a$ at the temperature of the electron diffraction experiment using a program written by A. V. Belyakov.

Gas electron diffraction

NMR-grade $P(OCH_3)_3$ of stated purity better than 99% was purchased from Aldrich and used without further purification. GED data were recorded on the Balzers KDG2 unit at the University of Oslo[16] with an all-glass inlet system at room temperature and an accelerating potential of 42 kV. Diffraction patterns were recorded on a Kodak Electron Image Plate. The electron wavelength was calibrated against the bond distance in benzene. Exposures were made with nozzle-to-plate distances of about 50 and 25 cm. Optical densities were recorded on a commercial Agfa Arcus II scanner and the data processed as described elsewhere.[17] Atomic scattering factors were taken from ref. 18. Experimental backgrounds were drawn as least-squares adjusted polynomials to the difference between the total experimental intensity and molecular intensities calculated from the best geometrical model using a program written by A. V. Belyakov.

Structure refinements were based on data from six plates for each distance. The experimental intensity data extended from 2.6 to 15.4 $Å^{-1}$ (50 cm) and from 4.6 to 29.4 $Å^{-1}$ (25 cm), both curves with an increment of 0.2 $Å^{-1}$.

Least-squares structure refinements were carried out with a modified version of the program KCED25 (G. Gundersen, S. Samdal, H. M. Seip and T. G. Strand, Department of Chemistry, University of Oslo, 1981). Weight matrices were diagonal, the 50 cm data were assigned unit, the 25 cm data half weight. Estimated standard deviations calculated by the program were multiplied by a factor of three to include added uncertainty due to data correlation and non-refined vibrational amplitudes as well as an estimated scale uncertainty of 0.1%.

The three mean P–O, O–C and C–H bond distances were refined as independent parameters; differences between chemically equivalent but symmetry inequivalent bond distances (*e.g.* P–O distances) in the same conformer or between chemically equivalent bond distances in different conformers were fixed at the values indicated by the DFT calculations. Similarly the mean valence angles ∠OPO, ∠POC and ∠OCH were refined as independent parameters, while the difference between chemically similar but symmetry inequivalent angles were fixed at calculated values. The three dihedral angles characterising the predominant ag^+g^+ conformer were refined as independent parameters, while the dihedral angles in the other conformers were fixed at the values obtained from the DFT calculations. Methyl groups were fixed in staggered orientations. Finally we refined the mole fractions of the $\pm ag^+g^+$ and ag^-g^+ conformers while the mole fraction of the $\pm aa^+g^+$ conformer was calculated as the difference $\chi(\pm aa^+g^+) = 1 - \chi(\pm ag^+g^+) - \chi(ag^-g^+)$; the mole fraction of the less stable $\pm g^+g^+g^+$ conformer was assumed equal to zero as indicated by the DFT calculations. The mean P–O and O–C root-mean-square vibrational amplitudes were refined, other amplitudes were fixed at the calculated values. The total number of independent parameters refined was thus fifteen, including two scale factors. The final R-factor was $R = \sqrt{[\Sigma\, w(I_{obs} - I_{calc})^2/\Sigma w(I^2_{obs})]} = 0.038$.

The final set of structure parameters for the predominant ag^+g^+ conformer are listed in Table 3. Observed and calculated radial distribution curves are compared in Fig. 4.

Results and discussion

Conformational preferences and anomeric effects in F_2POMe

Density functional theory calculations on F_2POMe were carried out in order to explore the structure and conformational preferences of a A_2POMe fragment where A is an electronegative element, in a simpler molecule than $P(OMe)_3$.

Structure optimisation of F_2POMe led to the identification of two distinct conformers, the most stable of them being the *anti* conformer of C_s symmetry sketched in Fig. 1A or C. The bond distances and valence angles of this conformer are in reasonable agreement with those obtained by microwave spectroscopy[9] or gas electron diffraction[10] (see Table 1). Like the MP2/6-31G* calculations published by Durig and Robb,[8] our DFT calculations also indicate the existence of two degenerate minima corresponding to two enantiomeric *gauche*

Table 1 Structure parameters[a] of F_2POMe determined by microwave (MW) spectroscopy,[14] gas electron diffraction (GED)[15] and density functional theory (DFT) calculations at the B3PW91/6-311+G* level

	MW	GED	DFT	
Conformer	*anti*	*anti*	*anti*	*gauche*
Bond distances				
P–F	1.591(6)	1.595(4)	1.627	1.604/1.621[b]
P–O	1.560(15)	1.574(4)	1.601	1.618
O–C	1.446(5)	1.446(2)	1.432	1.438
Valence angles				
OPF	102.2(10)	101.6(1)	100.7	95.6/100.5[c]
FPF	94.8(6)	94.8(1)	94.8	96.9
POC	123.7(5)	123.9(1)	126.1	120.3
Dihedral angles				
COP*lp*	180	180	180	40.5
COPF	—	—	±48.5	171.7/−90.5[d]
Relative energies				
ΔE	—	—	0	14.9

[a] Distances in Å angles in degrees, relative energies ΔE in kJ mol^{-1}. [b] P–F(1)/P–F(2). [c] OPF(1)/OPF(2). [d] τ(COPF(1))/τ(COPF(2)). For numbering of the F atoms in the *gauche* conformer see Fig. 1.

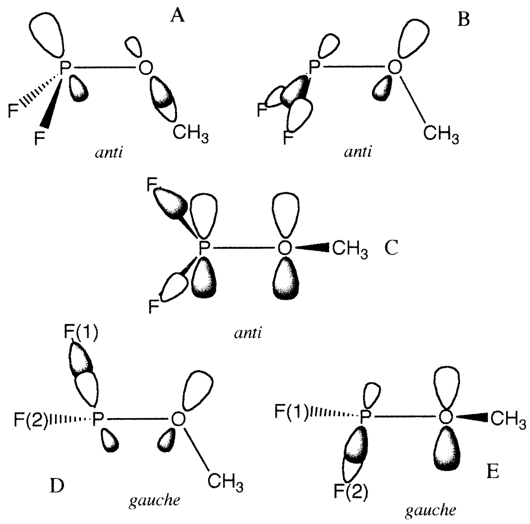

Fig. 1 Anomeric effects in the *anti* and *gauche* conformers of F_2POMe. The symmetry of the *anti* conformer is C_s and the molecule is depicted with the symmetry plane coinciding with (A or B), or perpendicular to the plane of the paper (C). Delocalisation of the P *lp* into the C–O antibonding orbital (A), delocalisation of the σ*lp* on O into the symmetric three-centre PF_2 antibonding orbital (B), and of the π*lp* on O into the asymmetric three-centre PF_2 antibonding orbital (C). The less stable *gauche* conformer has C_1 symmetry. In D the P–F(1) bond, in E the P–F(2) bond, is very nearly in the plane of the paper. Delocalisation of the σ*lp* on O into the antibonding P–F(1) orbital (D) and of the O π*lp* into the P–F(2) antibonding orbital (E).

conformers of C_1, symmetry at higher energy (see Fig. 1D or E). Bond distances, valence angles and dihedral angles of the *gauche*$^+$ conformer are listed in Table 1.

We have previously suggested that the equilibrium conformers of aminophosphanes, A_2PNMe_2, are stabilised by anomeric effects, *i.e.* through delocalisation of the electron lone pair on the N atom into antibonding P–A orbitals,[19,20] and decided therefore to analyse such effects in F_2POMe by Natural Bond Orbital (NBO) analysis[21] (see Fig. 1 and Table 2). Such analysis of the wavefunction of the *anti* conformer indicates that anomeric delocalisation of the electron lone pair on the phosphorus atom into the antibonding σ^*(O–C) orbital stabilises this conformer by about 24 kJ mol^{-1}. The delocalisation energy is expected to reach maximum values when the dihedral angle τ(*lp*POC) =180 or 0°, and to be at a minimum when this angle is about 90°; in the *gauche* conformer where τ(*lp*POC) = 41° it is reduced to about 6 kJ mol^{-1}. *lp*P $\longrightarrow$ σ^*(O–C) donation is expected to elongate the O–C bond and enlarge the POC valence angle, and the O–C bond is indeed calculated to be 0.6 pm longer and the POC angle 6° larger in the *anti* than in the *gauche* conformer.

The relative orientation of the PF_2 and OMe fragments in the *gauche* conformer is such that the direction of the π*lp* on the O atom is nearly coplanar with the P–F(2) and nearly perpendicular to the P–F(1) bond. As a consequence the π*lp*O $\longrightarrow$ σ^*(PF(2)) stabilisation energy is about 61, while the π*lp*O $\longrightarrow$ σ^*(PF(1)) energy is only 5 kJ mol^{-1}. The former represents the strongest anomeric stabilisation of this conformer. It is gratifying to note that the P–F(2) bond is calculaed to be about 2 pm longer than the P–F(1) bond and that ∠OPF(2) is calculated to be about 5° larger than ∠OPF(1). In the *anti* conformer the π*lp* on the O atom interacts equally with both P–F bonds; delocalisation into the asymmetric three-centre PF_2 antibonding orbital stabilises this conformer by 76 kJ mol^{-1}. Like the anomeric delocalisation of the *lp* on P, the delocalisation of the π*lp*O stabilises the *anti* conformer relative to the *gauche*.

The σ*lp* on the O atom is more tightly bound than the π*lp* and the anomeric delocalisation energies are much lower (see Table 2). Unlike the delocalisation of the π*lp*O, delocalisation of the π*lp* stabilises the *gauche* more than the *anti* conformer. In sum anomeric delocalisation of the three lone pairs *lp*P, σ*lp*O and σ*lp*O along the P–O bond stabilises the *anti* conformer by 116 and the *gauche* conformer by about 100 kJ mol^{-1}. The difference between these stabilisation energies, 15.8 kJ mol^{-1}, is approximately equal to the *gauche* minus *anti* electronic energy difference, ΔE =14.9 kJ mol^{-1}. Delocalisation of each of the three lone pairs is expected to strengthen and thus shorten the P–O bond, and we note that the P–O bond distance for the *anti* conformer is indeed calculated to be about 2 pm shorter than in the *gauche*. The results of the NBO analysis are thus entirely consistent with the assumption that both the conformational stabilities and bond distances and valence angles in the two conformers are determined by anomeric effects.

The molecular structure and conformational preferences of $P(OMe)_3$ by DFT calculations and gas electron diffraction

DFT calculations at the B3PW91/16–311+G* level led to the identification of four non-degenerate minima on the potential energy surface, corresponding to four distinct molecular conformations. A ball-and-stick model of the most stable conformer is shown in Fig. 2. The less stable conformers are sketched in Fig. 3. Relative electronic energies at 0 K and relative standard enthalpies and Gibbs free energies at 298.15 K are listed in Table 3 together with bond distances, valence angles and dihedral angles. In the following we shall characterise each conformer through the three dihedral angles τ(COP*lp*),

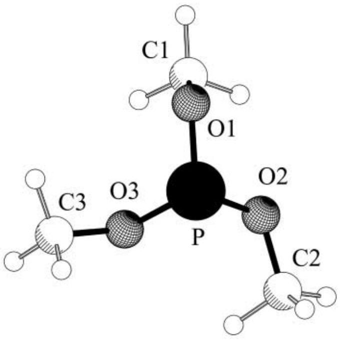

Fig. 2 A ball-and-stick model of the most stable (ag^+g^+) conformer of $P(OMe)_3$.

Table 2 Anomeric effects in the *anti* and *gauche* conformers of F_2POMe and within each O_2POMe fragment in the ag^+g^+ conformer of $P(OMe)_3$; dihedral angles (τ/°) and $lp \longrightarrow \sigma^*$ delocalisation energies ($\Delta\varepsilon$/kJ mol^{-1}) obtained by NBO analysis

F_2POMe	$\tau(lpPOC)$	$\Delta\varepsilon(lpP\longrightarrow\sigma^*(O–C))$	$\tau(\sigma lpOPF)$	$\Delta\varepsilon(\sigma lpO\longrightarrow\sigma_s^*(PF_2))$	$\tau(\pi/lpOPF)$	$\Delta\varepsilon(\pi lpO\longrightarrow\sigma^*(PF_2))$	$\Sigma\Delta\varepsilon$
anti	180	24.1	±131	8.1 + 8.1 = 16.2	±41	38.0 + 38.0 = 76.0	116.3
gauche	41	5.6	−8/89	26.1 + 3.0 = 29.1	82/−1	4.9 + 60.9 = 65.8	100.5

$(MeO)_2POMe$	$\tau(lpPOC)$	$\Delta\varepsilon(lpP\longrightarrow\sigma^*(O–C))$	$\tau(\sigma lpOPO')$	$\Delta\varepsilon(\sigma lpO\longrightarrow\sigma_s^*(PO'))$	$\tau(\pi lpOPO')$	$\Delta\varepsilon(\pi lpO\longrightarrow\sigma^*(P–O'))$	$\Sigma\Delta\varepsilon$
$O'_2PO(1)C(1)$	173	23.5	−135/127	5.0 + 5.1 = 10.1	−45/37	23.2 + 37.7 = 60.9	94.5
$O'_2PO(2)C(2)$	54	5.9	108/4	0.0 + 25.7 = 25.7	18/−87	41.7 + 0.0 = 41.7	73.4
$O'_2PO(3)C(3)$	41	5.4	88/12	2.8 + 19.7 = 22.5	−2/78	41.8 + 5.4 = 47.2	75.1

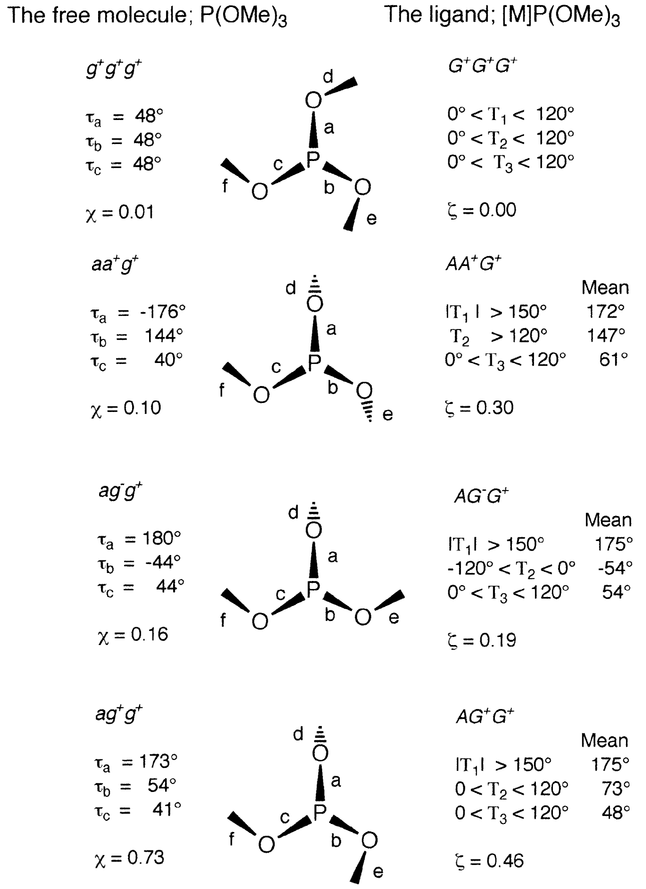

Fig. 3 Molecular conformations of $P(OMe)_3$. Left: dihedral angles and mole fractions (χ) in the gas phase predicted by DFT calculations. Right: average dihedral angles and incidences (ζ) obtained by analysis of the crystal structures of transition metal complexes.

where *lp* is the direction of the electron lone pair on the phosphorus atom; this lone pair is assumed to lie in a plane containing the P–O bond and bisecting the OPO valence angle in the opposing $P(OMe)_2$ fragment.

In the most stable or equilibrium conformer the three dihedral angles are 173, 54 and 41° corresponding to *anti*, *gauche*$^+$ and *gauche*$^+$ orientations of the methoxy groups. This conformer, which has C_1 symmetry, is optically active, and the enantiomer with dihedral angles, −173, −54 and −41° would, of course, be equally stable. Optical enantiomers are indistinguishable by gas electron diffraction. In the following we shall refer to the racemic mixture of ag^+g^+ and ag^-g^- as $\pm ag^+g^+$. The next higher potential energy minimum corresponds to an ag^-g^+ conformer of C_s symmetry with one dihedral angle of 180° and the remaining two equal to ±44° (see Fig. 3). Note that the two *gauche* methoxy groups are pointing away from each other. This ag^-g^+ conformer is not optically active.

The third conformer has C_1 symmetry and dihedral angles equal to −176, 144 and 40°. This conformer, which we denote by aa^+g^+, is optically active, we shall refer to the racemic mixture as $\pm aa^+g^+$. The calculated energy difference between the ag^-g^+ and aa^+g^+ conformers is too small to allow us to conclude which conformer is in fact the more stable.

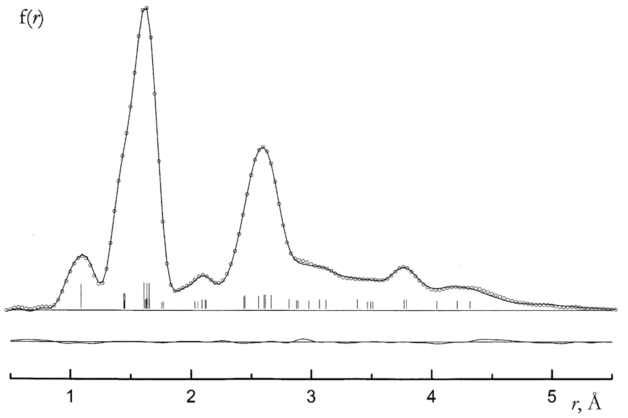

Fig. 4 Above: experimental (dots) and calculated (lines) radial distribution curves of $P(OMe)_3$. Artificial damping constant k = 0.0025 Å^2. Below: difference curve.

Finally optimisation under C_3 symmetry leads to the identification of a fourth stable conformer with three dihedral angles equal to +48°. We denote the racemic mixture of the $g^+g^+g^+$ conformer and its $g^-g^-g^-$ enantiomer as $\pm g^+g^+g^+$, This conformer is, however, considerable less stable than the other three.

Calculated free energies at 298 K (see Table 3) yield the following mole fractions for the gas phase at room temperature, $\chi(\pm ag^+g^+ = 0.73$, $\chi(ag^-g^+) = 0.16$, $\chi(\pm aa^+g^+) = 0.10$, and $\chi(\pm g^+g^+g^+) = 0.01$. Least-squares structure refinements to gas electron diffraction data recorded at room temperature were based on the assumption that $\chi(\pm g^+g^+g^+)$ was zero. The electron diffraction data confirm that the $\pm ag^+g^+$ conformer is indeed the most stable with a mole fraction equal to 0.78(13). The mole fractions of the ag^-g^+ and $\pm aa^+g^+$ conformers are much smaller and not significantly larger than zero; the probability that the ag^-g^+ conformer is present in the gas is only about 75%, and the probability that the $\pm ag^-g^+$ conformer is present barely greater than 50%. The experimental P–O bond distances are about 0.02 Å shorter than calculated, the experimental C–O distances about 0.02 Å longer whilst the experimental valence angles are not significantly different from those calculated. The experimental values obtained for the dihedral angles of the ag^+g^+ conformer are rather inaccurate, but not significantly different from the calculated ones. The dihedral angles of the less stable conformers were fixed at calculated values.

The results of NBO analysis of anomeric effects in the ag^+g^+ conformer are presented in Table 2. It is seen that the anomeric stabilisation energy due to donation of the P *lp* into the O–C antibonding orbital of the *anti* methoxy group is very similar to that computed for the *anti* conformer of F_2POMe, while the *lp*P ⟶ σ*(O–C) stabilisation energies computed for the two *gauche*

Table 3 First four columns; non-degenerate minima on the potential energy surface of $P(OMe)_3$ obtained by DFT calculations at the B3PW91/6-311+G* level; relative electronic energies at 0 K (ΔE); relative standard enthalpies (ΔH°), relative standard free energies (ΔG°) and mole fractions (χ) in the gas phase at 298 K; bond distances, valence angles and dihedral angles. Fifth column; mole fractions of the conformers; bond distances, valence angles and dihedral angles of the predominant, ag^+g^+, conformer obtained by least-squares refinement to the gas electron diffraction data

	DFT					
Conformer (symmetry)	ag^+g^+ (C_1)	ag^-g^+ (C_s)	aa^+g^+ (C_1)	$g^+g^+g^+$ (C_3)	GED	
ΔE/kJ mol^{-1}	0[a]	6.3	6.6	10.4	$\chi(\pm ag^+g^+)$[b]	0.78(13)
ΔH°_{298}/kJ mol^{-1}	0	6.0	6.3	10.1	$\chi(ag^-g^+)$	0.09(11)
ΔG°_{298}/kJ mol^{-1}	0	3.8	4.9	10.2	$\chi(\pm aa^+g^+)$[b]	0.14(21)
χ	0.73[b]	0.16	0.10[b]	0.10[b]	$\chi(\pm g^+g^+g^+)$[b]	[0]
					ag^+g^+ (C_1)	
Bond distances/Å	r_e	r_e	r_e	r_e	r_a	
P–O(1) (a)	1.626	1.643	1.644	1.644	1.609(4)	
P–O(2) (b)	1.649	1.651	1.634	1.644	1.632(4)	
P–O(3) (c)	1.668	1.651	1.670	1.644	1.651(4)	
O(1)–C(1) (d)	1.431	1.429	1.424	1.422	1.451(10)	
O(2)–C(2) (e)	1.421	1.422	1.426	1.422	1.441(10)	
O(3)–C(3) (f)	1.422	1.422	1.421	1.422	1.442(10)	
C–H (mean value)	1.094	1.093	1.093	1.093	1.090(4)	
Valence angles/°	$\angle_e$	$\angle_e$	$\angle_e$	$\angle_e$	$\angle_\alpha$	
O(1)PO(2) (ab)	97.4	102.5	105.0	97.9	98.2(9)	
O(2)PO(3) (bc)	95.8	92.6	96.5	97.9	96.1(9)	
O(1)PO(3) (ac)	103.5	102.5	101.4	97.9	103.8(9)	
PO(1)C(1) (ad)	123.6	123.2	126.7	118.8	121.6(12)	
PO(2)C(2) (be)	118.9	117.7	128.3	118.8	116.9(12)	
PO(3)C(3) (cf)	118.2	117.7	117.9	118.8	116.2(12)	
OCH (mean value)	109.2	109.4	109.6	109.7	113(3)	
Dihedral angles/°	τ_e	τ_e	τ_e	τ_e	τ_α	
τ_a = C(1)O(1)P*lp* (da*lp*)	173.2	180.0	−175.5	48.0	174(2)	
τ_b = C(2)O(2)P*lp* (eb*lp*)	54.0	−44.0	143.8	48.0	37(5)	
τ_c = C(3)O(3)P*lp* (fc*lp*)	41.4	44.0	40.4	48.0	35(5)	
C(1)O(1)PO(2) (dab)	44.8	47.8	49.3	−82.5	45(3)	
C(1)O(1)PO(3) (dac)	−53.2	−47.8	−50.8	178.4	−54(3)	
C(2)O(2)PO(3) (ebc)	−72.2	−168.3	19.5	−82.5	−84(6)	
C(2)O(2)PO(1) (eba)	−176.7	88.2	−84.3	178.4	171(6)	
C(3)O(3)PO(1) (fca)	−92.0	−88.2	−84.6	−82.5	−93(7)	
C(3)O(3)PO(2) (fcb)	168.4	168.3	168.6	178.4	167(7)	

[a] The electronic energy of the ag^+g^+ conformer is $E = -686.713366$ au. [b] Racemic mixture.

methoxy groups are similar to that computed for the *gauche* conformer of F_2POMe. As expected the POC valence angle of the *anti* MeO group is about 5° larger than that computed for the *gauche*.

The anomeric stabilisation energies resulting from donation of σ or π electron lone pairs on O into antibonding orbitals of the opposing PO'_2 fragment are significantly smaller than those calculated for the corresponding conformer of F_2POMe, but we note that the pattern is the same; delocalisation of the σ*lp* favours the *gauche* while delocalisation of the π*lp* favours the *anti* conformation. Moreover the strongest anomeric effects are associated with π*lp*O ⟶ σ*(P–O′) delocalisations. The bond distances and valence angles of the central PO_3 frame are difficult to rationalise since the anomeric delocalisation of each of the six electron lone pairs on the oxygen atoms will shorten one P–O bond and elongate one or two others, and increase one or two OPO valence angles. We note however, that anomeric delocalisation of three lone pairs along the P–O(1) bond stabilises the conformer by about 95 kJ mol^{-1} while the stabilisation due to delocalisations along the P–O(2) and P–O(3) bonds are about 20 kJ mol^{-1} smaller; as in F_2POMe we find that the stronger total anomeric delocalisation is associated with the shorter bond. If we limit ourselves to consideration of the strongest anomeric effects, *i.e.* to π*lp*O ⟶ σ*(P–O) delocalisations, the O(1)PO(2) angle is expected to be opened by delocalisation of π*lp*O(1) and the O(2)PO(3) angle is expected to be opened by delocalisation of π*lp*O(2), while O(1)PO(3) is expected to be enlarged by both π*lp*O(1) and π*lp*O(3) delocalisations. And indeed, the O(1)PO(3) angle is calculated to be about 7° larger than the other two.

Calculated P–O and C–O bond distances and OPO and POC valence angles in the three less stable conformers are equally consistent with the results obtained by NBO analysis of anomeric effects.

The DFT calculations on F_2POMe indicate that the equilibrium conformation of a methoxyphosphane in which the phosphorus atom carries two additional electronegative substituents is *anti* with τ(COP*lp*) = 180°, while the energy of a *gauche* conformer with τ(COP*lP*) = 80° is about 15 kJ mol^{-1} higher. It is gratifying to note that the energy of the least stable conformer of $P(OMe)_3$, in which all methoxy groups are *gauche*, is calculated to be about 10 kJ mol^{-1} higher than the energy of the most stable conformer in which one methoxy group has been rotated into an *anti* conformation, but why is the equilibrium conformation not characterised by two or three methoxy groups in the *anti* orientation?

One possible reason may be that the distance between the methyl groups of two or three *anti* MeO fragments would be sufficiently small to lead to significant steric repulsion; rigid rotation of the three methoxy groups in the $g^+g^+g^+$ conformer into *anti* orientations would lead to C···C distances shorter than 2.60 Å, much smaller than twice the accepted van der Waals diameter of a methyl group (4.00 Å). The dihedral angles in the aa^+g^+ conformer does indeed indicate that there is significant repulsion between the Me groups: the C(2)O(2)P*lp* angle has been reduced from 180 to 144° while the O(1)C(1) fragment has been rotated about 7° in the opposite direction. Nevertheless the NBO analysis indicates that the anomeric stabilisation of the aa^+g^+ conformer is greater than that of the ag^+g^+. So, even though bond distances and valence angles in each conformer are consistent with the anomeric effects indicated by NBO analysis, the relative energies of the four conformers are not determined by anomeric effects alone.

Conformational properties of P(OMe)$_3$ in transition metal complexes

Coordination of trimethylphosphite to a d-block metal centre might, if accompanied by back donation of dπ electrons from the metal atom into antibonding σ*(P–O) orbitals, reduce the anomeric stabilisation of the *anti* orientation of methoxy groups relative to the *gauche*. Steric congestion and repulsion between ligands to the metal atom might, on the other hand, lead to destabilisation of the sterically more demanding conformations, first and foremost the $g^+g^+g^+$ but also the ag^+g^+ and ag^-g^+ conformations, relative to the aa^+g^+ conformation. A search of the Cambridge Structural Database (March 1999 version)[22] yielded 287 ordered structures containing one or more P(OMe)$_3$ units coordinated to a transition metal atom M (in Groups 3 through 11) which in turn contained 523 crystallographically independent MP(OMe)$_3$ fragments. Each independent fragment is characterised by three dihedral angles T(COPM). Since the P–M bond presumably is formed through donation of the electron lone pair on the P atom, these dihedral angles should be roughly equivalent to the dihedral angles τ(COP*lp*) used to characterise the conformers of the free molecule. The dihedral angles in each molecule were ordered according to their magnitude and numbered in such a way that

$$|T_1| > |T_2| > |T_3|$$

In a normal investigation by X-ray crystallography no attempt is made to distinguish between an optically active fragment characterised by the three angles T_1, T_2, T_3 and its optical isomer characterised by $-T_1$, $-T_2$, $-T_3$. We chose therefore—when necessary—to change the signs of the three dihedral angles in such a manner that the smallest angle, T_3, is always positive.

A preliminary examination of the material showed that in all fragments except three at least one methoxy group was approximately *anti* the coordinate P–M bond with $|T_1| > 150°$. These three exceptional fragments were removed from the sample.[23] The variation of the remaining 520 values of T_1 is indicated by the histogram in Fig. 5; they clearly cluster around 180°, positive values of T_1 being somewhat more numerous than negative. Since signs were fixed by requiring T_3 to be positive, this means that there is a small positive correlation between the signs of T_1 and T_3. In the following we shall refer to ligands characterised by dihedral angles $|T_1| > 150°$ as *anti* represented by a capital *A* to underline the distinction between the gaseous molecule and the ligand in a crystalline complex.

A scatterplot of the dihedral angles T_2 and T_3 in the 520 MP(OMe)$_3$ ligand fragments is shown in Fig. 6. In the following we shall refer to fragments in which T_2 and T_3 both fall in the range between 0 and 120° (and in which $|T_1|$ is greater than 150°) as *anti,gauche*$^+$*,gauche*$^+$ or AG^+G^+. Our sample contains 240 such fragments which may be regarded as more or less distorted versions of the most stable, ag^+g^+ conformer of the free molecule. The average values for the three dihedral angles in these molecules were $|T_1| = 176$, $T_2 = 73$ and $T_3 = 48°$. The largest dihedral T_1 angle may be associated with the corresponding dihedral angle τ_a in the isolated molecule. At first sight one might be tempted to associate T_2 with τ_b and T_3 with τ_c. It should be realised, however, that while τ_b and τ_c are defined in terms of the three-dimensional structure of the molecule, T_2 and T_3 are defined through their relative magnitudes. Since in the ag^+g^+ conformer of the free molecule $\tau_b > \tau_c$ it might be assumed that this difference will be retained in the distorted ligands in the solid state, but this may not be so in every instance. What can be stated is that the *average* of the two *gauche* dihedral angles in the crystalline complexes is 61° compared to 48° in the gaseous ag^+g^+ conformer. Finally we define the incidence of AG^+G^+ conformations in the crystalline environment as $\zeta = 240 : 520 = 0.46$ as compared to a gas phase mole fraction of 0.73; it would appear that the $\pm ag^+g^+$ conformer has been both destabilised and deformed by interligand repulsions.

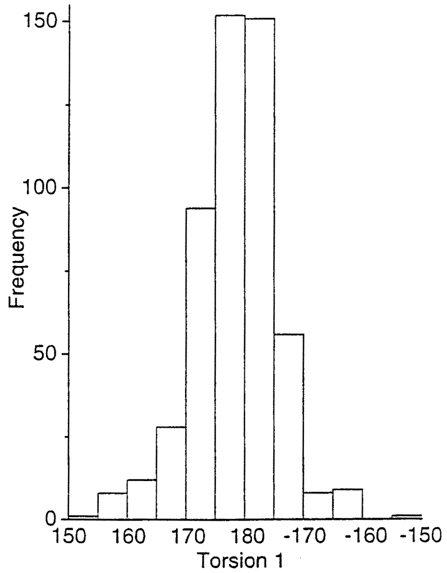

Fig. 5 A histogram showing the variation of the largest dihedral angle T_1(COPM) in 520 crystallographically independent MP(OMe)$_3$ fragments, M = transition metal in Groups 3 through 11.

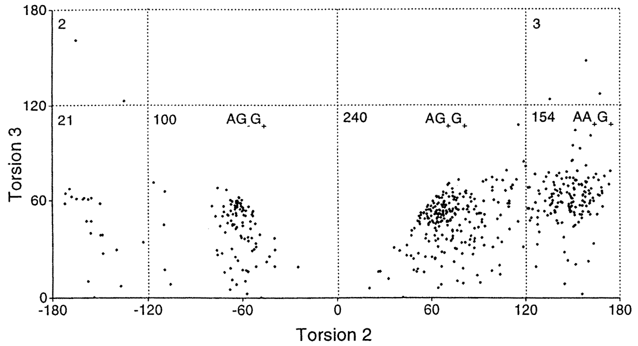

Fig. 6 Scatterplot of the second largest and smallest dihedral angles (T_2 and T_3 respectively) in 520 crystallographically independent MP(OMe)$_3$ fragments, M = d-block transition metal. Note that the signs have been defined in such a way that T_3 is always positive.

In a similar way we refer to the 100 fragments with $-120° < T_2 < 0°$ and $0° < T_3 < 120°$ as AG^-G^+. These fragments were all examined visually to make sure that the conformation corresponded to the ag^-g^+ conformer of the free molecule rather than the non-existent conformer ag^+g^- in which the two *gauche* methoxy groups would be pointed towards rather than away from each other. The average values of the dihedral angles of the AG^-G^+ conformers were $|T_1|, = 176$, $T_2 = -64$ and $T_3 = 43°$ and the incidence of AG^-G^+ conformations ζ 0.19, very similar to the gas phase mole fraction $\chi(ag^-g^+) = 0.16$. The average magnitude of the dihedral angles of the two *gauche* fragments (54°) is, however, about 10° larger than in the gas phase.

Finally we refer to the 154 ligands characterised by dihedral angles $|T_1| > 150°$, $120° < T_2 < T_1$, and $0° < T_3 < 120°$ as AA^+G^+. The average values of the three dihedral angles are $|T_1| = 172$, $T_2 = 147$ and $T_3 = 61°$. In this case we may confidently identify these dihedral angles with τ_a, τ_b and τ_c in the aa^+g^+ conformer of the free molecule.

As we have defined the three conformers AG^+G^+, AG^-G^+ and AA^+G^+ and they cover less than 10% of the entire molecular configuration space. The total number of fragments which fall inside the designated ranges is 492, or more than 94% of the crystallographically independent MP(OMe)$_3$ fragments. Only *one* MP(OMe)$_3$ fragment has been found to assume a distorted $G^+G^+G^+$ conformation.[23,24]

In Fig. 3 we compare the dihedral angles and mole fractions of the conformers of the free molecule in the gas phase at room temperature with the incidence (ζ) and dihedral angles characterising the conformations adopted by P(OMe)$_3$ as a ligand in transition metal complexes. It is seen that the stability of the AG^+G^+ conformation appears to be smaller, the stability of the AG^-G^+ conformation relatively unaltered, and the stability of the sterically less demanding AA^+G^+ conformation relatively greater in the crystalline complexes. At the same time the average dihedral angles of the *gauche* methoxy groups in each conformation has increased by 10° to 20°.

While this manuscript was in preparation, Smith and Coville reported a study of Tolman cone angles of 316 crystallographically independent MP(OMe)$_3$ fragments from the Cambridge Structural Database.[27] A histogram of the resulting cone angles showed a binodal distribution with two peaks of relative areas 1 : 2 centred at about 117° and 131° respectively. The first peak was assigned to ligands with two methoxy groups in *anti* and one in a *gauche* orientations, the second to ligands with two groups in *gauche* and one group in *anti* orientations. Smith and Coville did not distinguish between ag^+g^+ and ag^-g^+ conformers. The manner in which the cone angles were defined is, however, such that the relative orientation of the two *gauche* methoxy groups should be irrelevant. If the smaller peak at lower cone angle is assumed to represent the conformer which we have described as AA^+G^+ and the larger peak at higher cone angle to represent the AG^+G^+ and AG^-G^+ conformers, there is very good agreement between their results and ours. Smith and Coville observe that "the metal–ligand environment appears to play a role in establishing the observed phosphite conformations". This is certainly correct; in the free molecule in the gas phase at room temperature the combined mole fractions of low cone angle conformations is 0.10, in the crystalline complexes the incidence is three times higher. And even when the P(OMe)$_3$ ligand retains two methoxy groups in *gauche* orientations, these methoxy groups are typically folded back from the metal atom by some 10 or 20° relative to the gas phase, thus reducing the steric requirements of the trimethylphosphite ligand. But even though the effect of the crystalline environment is clear to see, it is not decisive; the combined incidence of the sterically more demanding AG^+G^+ and AG^-G^+ conformers is still about 65%.

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