oligomeric [$Cp_2Zr(H)Cl]_x$ (**8**) in 10 mL of toluene. The mixture is stirred for 2 h at room temperature. Solvent is then removed from the resulting clear dark-red solution in vacuo. The remaining residue is recrystallized from pentane to give 0.80 g (62%) of **9**: mp 68 °C (dec., DSC); ^1H NMR (benzene-d_6) δ 7.45 (s, 1 H, =CH), 7.19–7.16, 7.10–7.03 (m, 5 H, Ph), 5.74 (s, 10 H, Cp), 0.20 (s, 6 H, $GaMe_2$); ^{13}C NMR (benzene-d_6) δ 258.9 (Zr—C=), 146.8 ($^1J_{CH}$ = 154 Hz, = *C*H), 142.8 (ipso-C, phenyl), 129.0, 126.6, 126.3 (*C*H, phenyl), 111.5 ($^1J_{CH}$ = 173 Hz, Cp), –1.3 ($^1J_{CH}$ = 124 Hz, $GaMe_2$); IR (KBr) ν 1437 cm^{-1}, 1013, 801 (Cp), 1589 (C=C).

Exchange Reactions of Complexes 6a and 6b with Olefins. (a) Reaction of $Cp_2Zr(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_6H_8)(\mu\text{-}CH_3)GaMe_2$ (**6a**) with norbornene: A sample of **6a** (20 mg, 0.048 mmol) is dissolved in 0.7 mL of benzene-d_6. Norbornene (5 mg, 0.053 mmol) is added, and the progress of the reaction monitored by ^1H NMR spectroscopy. Trimethylgallium (^1H NMR δ –0.15, s) and the product **13** are formed. After 1 h at ambient temperature the reaction has almost gone to completion. The sealed NMR tube is opened. The volatile materials are removed from the orange-colored solution in vacuo, and the residue is washed with a small volume of cold pentane. A yellow solid of **13** is obtained (10 mg, 50% yield): mp 173 °C (dec., DSC). The identification as **13** was carried out spectroscopically: ^1H NMR (benzene-d_6) δ 5.89, 5.85 (each s, 5 H, Cp), 2.40 (m, 1 H), 2.33 (m, 1 H), 2.11 (m, 2 H), 1.67 (m, 4 H), 1.57 (m, 2 H), 1.46 (m, 4 H), 1.25 (m, 4 H); ^{13}C NMR (benzene-d_6) δ 181.0, 137.6 (olefinic C), 111.5 (Cp), 67.9, 51.9, 45.5, 40.1 (each *C*H), 36.6, 35.7, 34.5, 31.1, 29.9, 24.8, 24.5 (each *C*H_2).

(b) Reaction of $Cp_2Zr(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_6H_4)(\mu\text{-}CH_3)GaMe_2$ (**6b**) with ethylene: The complex **6a** (20 mg, 0.049 mmol) is dissolved in 0.6 mL of benzene-d_6. Ethylene is bubbled through the solution in a 5-mm NMR tube for 10 min. The NMR tube is then sealed, and the reaction is allowed to proceed for 1 h. An ^1H NMR spectrum revealed the presence of excess ethylene (s at δ 5.24) and the formation of the zirconaindane **14**: ^1H NMR (benzene-d_6) δ 7.05 (m, 4 H, C_6H_4), 5.86 (s, 10 H, Cp), 3.32 (pseudo-t, 2 H, CH_2), 1.29 (pseudo-t, 2 H, CH_2). After 36 h the formation of **15** as an additional reaction product was revealed by its ^1H NMR signals.

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Supplementary Material Available: Details of the X-ray crystal structure analysis of **6a** and **6b** including atomic coordinates and complete listings of bond lengths and angles (17 pages); listings of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

MM3 Molecular Mechanics Study of Alkylphosphines

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Abstract: The MM3 force field has been extended to cover alkylphosphines. The structures of eight alkylphosphines have been reproduced, as well as the known conformational equilibria, barriers to rotation, moments of inertia, and dipole moments. The vibrational spectra for these eight compounds have been studied and fit with a root mean square error of 34 cm^{-1}.

Introduction

The recently reported MM3 force field can accurately handle a wide range of organic functional groups, including saturated hydrocarbons,[1] alkenes,[2] aromatic hydrocarbons,[3] aliphatic amines,[4] amides and polypeptides,[5] alcohols and ethers,[6] aldehydes and ketones,[7] nitro compounds,[8] sulfides,[9] and disulfides.[10] The present work has centered on developing MM3 force field parameters to properly model alkylphosphines.

The extension of the earlier MM2 force field to treat most functional groups has been progressing since its introduction almost 15 years ago. Because of this effort the MM2 force field has been widely used. In time the MM3 force field will be able to treat as many classes of compounds as its predecessor. Due to the use of more complex potential functions and the addition of torsion–stretch and generic bend–bend interaction parameters, MM3 has the ability to reproduce vibrational spectra. This is one of the major innovations of MM3 over MM2. Reproducing the spectral data, as well as the inclusion of these additional terms, makes parameterization of the MM3 force field somewhat more complex than it was for MM2, but the additional parameters have been shown to be necessary in order to accurately reproduce the experimental vibrational data.[1]

As an initial step to the parameterization of biologically important phosphorus compounds, such as phosphates and nucleotides, we have studied alkylphosphines in order to develop a force field capable of calculating the structures, relative energies, and vibrational spectra of this class of compounds. The phosphine parameter set developed in this work, presented as Table I, has been optimized to reproduce structure, vibrational spectra, rotational barriers, moments of inertia, and dipole moments.[11] These parameters have been incorporated into the MM3(92) program.[12]

Methods

Experimental structural data were found in the literature for phosphine,[13] methylphosphine,[14,15] dimethylphosphine,[15] trimethylphosphine,[16]

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(11) All of the phosphine parameters that are included in the original MM3 program (MM3(91)) and indicated by a ** are carried over from preliminary work and are superseded by the parameters herein.

(12) A parameter set for use with MM3(91) is also available upon request from the authors.

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Table I. MM3(92)[a] Parameter Set for Alkylphosphines

Bond Stretching Parameters

bond	l_0 (Å)	k_s
P-H[b]	1.420	3.065
P-C	1.843	2.940

Angle Bending Parameters

atoms	k_θ	θ_0 (deg) type 1	θ_0 (deg) type 2	type 3
H-P-H	0.680	92.2	93.5	[c]
C-P-H	0.705	94.7	96.4	[c]
C-P-C	0.770	95.6	98.1	[c]
P-C-H	0.570	111.0	108.4	108.6
P-C-C	0.600	107.5	109.6	108.0

Torsional Parameters

atom types	V_1	V_2	V_3
H-P-C-H	0.000	0.000	0.290
C-P-C-H	0.000	0.000	0.410
H-P-C-C	–0.447	–2.612	0.560
P-C-C-H	0.000	0.000	0.305
C-P-C-C	–1.430	0.000	0.589

Electronegativity Correction Parameters

atom types defining bond	end of bond	attached atom	correction to l_0
C-P	C	C	+0.0025
C-H	C	P	–0.0030
C-P	P	H	+0.0070
C-C	C	P	0.0000

Torsion-Stretch Parameter

atoms defining bond	k_{tb}
C-P	0.1040

Dipole Parameters

atoms defining bond	bond moment
C-P	0.81
H-P	–0.53

[a] A parameter set for use with the MM3(91) program is also available upon request from the authors. [b] The atom types for the included atoms are P(25), C(1), and H(5). [c] For angles with type 25 as the central atom, no type 3 bending constant is possible.

ethylphosphine,[17] isopropylphosphine,[18] ethyldimethylphosphine,[19] and *tert*-butylphosphine.[20]

The experimental structures were entered into an MM3 data file and optimized using an initial parameter set utilizing the full matrix optimization scheme so as to obtain the vibrational frequencies, as well as the optimized structures. These calculated values were then entered into a spread sheet containing the experimental values, and the deviations were calculated between the experimental and MM3 values. The root mean square (rms) deviation of the bond lengths and bond angles was determined, as well as the rms deviation for all vibrational frequencies. Each parameter was then modified to obtain the best correlation with the reported experimental structures.

It was observed from earlier work that the stretching and bending parameters had the largest effect on the calculated structures and vibrational frequencies of the phosphine skeletons. Therefore, the initial approach was to alter only these parameters to optimize the structural and spectral correlation between experiment and molecular mechanics calculation. This made for a simplification of the parameterization process. When the best fit was achieved by altering only these parameters, the torsional, stretch–bend, torsion–stretch, and electronegativity correction terms (which have a lesser and more selective effect on the structure and vibrational frequencies) were then included to "fine tune" the calculations, so as to correctly reproduce the rotational barriers, energy differences between conformers, and moments of inertia. Bond dipole terms were added to properly compute the molecular dipole moments. Because of the small dipoles exhibited in this class of compounds, dipole–dipole interactions had no effect on the structures of any of the test molecules. Finally, as necessary, the entire phosphine parameter set was slightly adjusted to afford the best overall agreement between theory and experiment.

Table II. Comparison of Structural Data Obtained via Electron Diffraction and Microwave Spectroscopy

	electron diffraction	microwave	difference
	Bond Length		
methylphosphine[a]			
P–C	1.858	1.863	–0.005
C–H	1.094	1.093	0.001
P–H	1.423	1.414	0.009
dimethylphosphine			
P–C	1.853	1.853	0.000
C–H (long)	1.097	1.09	0.007
C–H (short)	1.097	1.086	0.011
P–H	1.445	1.418	0.027
trimethylphosphine			
P–C	1.846	1.841	0.005
C–H	1.091	1.09	0.001
		rms diff	0.011
	Bond Angles		
methylphosphine			
∠C–P–H	96.5	97.5	–1.0
dimethylphosphine			
∠C–P–C	99.2	99.76	–0.6
∠P–C–H	109.8	109.9	–0.1
∠C–P–H	96.5	96.5	0.0
trimethylphosphine			
∠C–P–C	98.6	99.1	–0.5
		rms diff	0.6

[a] Electron diffraction data for methylphosphine and dimethylphosphine taken from ref 15. Microwave data for methylphosphine is from ref 14, that for dimethylphosphine is from ref 23. Electron diffraction and microwave data for trimethylphosphine come from refs 16 and 34, respectively.

Results and Discussion

Structural Data. Since MM3 attempts to reproduce both the molecular structure and vibrational properties in the gas phase, ideally the structural data should be from gas-phase electron diffraction experiments, corrected for vibrational motion.[21] Much of the reported data, although taken from electron diffraction experiments, are reported as r_a values, which do not include vibrational corrections. If the vibrational corrections have been made, the structure is reported as the r_g values, upon which MM3 is based. The r_a numbers afford experimental bond lengths shorter than if the vibrational correction had been made. The size of these corrections are quite small, however, on the order of 0.002 Å,[22] and are often ignored. If no electron diffraction data are available, structures derived from microwave spectroscopy may also be substituted. It should be noted that the molecular geometries determined by these two methods are not equivalent. The bond lengths derived from the microwave data, usually reported as r_s values, tend to be somewhat shorter than those derived from electron diffraction data. Bond angles derived from microwave spectroscopy tend to be quite similar to those derived from electron

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diffraction, although for the set of compounds studied, they tend to be slightly larger. A comparison of these differences can be demonstrated where the structure of a compound has been determined by both electron diffraction and microwave experiments, as shown in Table II.

Overall, the experimental and MM3 calculated structures are in good agreement. Using the full set of experimental data for all eight compounds obtained from electron diffraction and microwave experiments, and including both the gauche and trans conformers of ethylphosphine and ethyldimethylphosphine, the rms error between 26 calculated and experimental bond lengths is 0.011 Å. The rms error between 35 calculated and experimental bond angles of this data set is 2.01°. It should be noted that these errors represent the results of the comparison of calculated structures to different types of experimental data of varying accuracy and represent a non-optimal data set. If, for example, the trans conformers of ethylphosphine and ethyldimethylphosphine, which could not be properly treated by MM3 (vide infra), are not included in the data set, the rms error for the modeled angles becomes 1.05°, a 48% improvement. Using this data set also improved the error in bond lengths 9%. Likewise, using only the compounds that have electron diffraction data gives rms errors of 0.96° for the bond angles and 0.010 Å for the bond lengths. These results are discussed on a compound by compound basis in the following sections.

The only systematic error readily evident concerns the C–H bond length of the methyl-substituted phosphines, where the calculated bond length is too long in all cases. This is necessitated in order to calculate correctly the stretching frequencies for substituted phosphines. MM3(91) neglected the effect of the electronegativity correction parameter on vibrational frequencies. As a result, the C–H stretching modes in these compounds, when geminal to a phosphorus atom, were calculated by MM3(91) to have frequencies that are systematically too low. The correction of this type of error in MM3(92) will be described in a subsequent publication.[24] In order to properly model the C–H bond lengths, the electronegativity correction parameter must be increased to an extremely large value of −0.016 Å, larger than even the value for a fluorine substituent. In addition, including this electronegativity correction term in MM3(92) has a significant effect on the C–H stretching frequencies, often calculating them to be >150 cm^{-1} too high. This new parameter set endeavors to strike a balance between the calculated structures and vibrational spectra. All of the C–H stretching frequencies are calculated slightly too high by MM3(92). The calculated C–H bond lengths are also slightly too long.[12]

IR Data. Infrared and/or Raman spectroscopy experiments have been reported for all of the compounds that were involved in the present work.[25] The comparison between calculated and experimental vibrational data was carried out on these eight compounds for a total of 315 vibrational frequencies. As with the structural data, MM3 attempts to reproduce gas-phase vibrational frequencies from both IR and Raman spectra. Vibrational modes that are observable in both IR and Raman conditions usually fall within a few wave numbers of each other, well within the error limits that we hope to achieve with MM3, and so can be used interchangeably. Vibrational data gathered from the liquid or solid phase can present problems due to shifts that occur in the spectrum in different phases. If liquid- and solid-phase data must be used, the liquid-phase data are generally preferable since they are free of crystal packing forces. Any use of nongas-phase data should be done with considerable caution.

Table III. Structural Data for Phosphine

	MM3	ED[a]	deviation
P–H	1.420	1.437 ± 0.004	−0.017
∠H–P–H	93.5	93.5	0.0

[a] Experimental data from ref 13.

Table IV. Vibrational Modes of Phosphine

vibrational assignment	symmetry	exptl[a]	MM3	deviation
P–H asym str	E	2328	2309	−19
P–H asym str	E	2328	2309	−19
P–H sym str	A_2	2323	2303	−20
P–H asym bnd	E	1122	1092	−30
P–H asym bnd	E	1122	1092	−30
P–H sym bnd	A_1	992	1064	72
			rms dev	37

[a] Experimental data from ref 25a.

Assignment of each of the vibrational frequencies to the normal modes from the associated eigenvector matrix can be a laborious task. The ability to take the numerical data and visualize the vibrational modes simplified this procedure enormously. In the present work, assignment of the MM3 vibrational data to normal modes was accomplished using the program VIBPLOT,[26] which is included with the MM3(92) package. This program utilizes an optional MM3 output file[27] containing the minimized structural coordinates and the vibrational eigenvector matrix. From these input data, VIBPLOT dynamically displays each of the vibrational modes of a compound on a MicroVAX or DECstation running DECwindows. This method allows easy assignment of most of the vibrational modes. Where there is significant mixing of the vibrations, a printed output of the eigenvector matrix can be used to determine the contributions to the normal modes.

If the experimental IR frequencies had been previously assigned to the normal modes, they were matched with the appropriate vibrations from VIBPLOT. In the vast majority of cases, the experimental assignments and those of VIBPLOT/MM3 were in agreement. A few of the experimentally assigned vibrations did not agree with the assignments given by MM3 and VIBPLOT. In these instances the parameter set was modified to try to reflect the experimental assignments where possible. In some cases it was necessary to reassign the experimental vibrations. Unless the vibrational assignments have been made unequivocally, which entails exhaustive isotopic substitution, there is some uncertainty inherent in the experimental assignment. Reassignment of experimental frequencies determined by other methods is not uncommon in the experimental literature, so where necessary, a few frequencies have been reassigned.

Overall, agreement between the calculated and experimental vibrational data was satisfactory. Fitting all the available spectroscopic data for all eight compounds (with separate calculations for the two conformers of the ethyl, ethyldimethyl, and isopropyl compounds) gave an overall rms error between calculated and experimental values of 34 cm^{-1}. For comparison, the basic set of hydrocarbons used to establish the alkane section of the MM3 force field showed an overall rms error of 35 cm^{-1} in the vibrational frequencies.

Phosphine. The structure of phosphine has been solved using electron diffraction by Bartell and Hirst.[13] The phosphine molecule is a unique case in this study, as there is only a single type of bond (P–H) and a single type of angle (H–P–H) present in the molecule (see Table III). This makes the fitting to experimental data trivial

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(27) MM3 must be instructed to output the optional vibrational data by using option 4 or 5 in the interactive input. This creates the optional output file VIBPLT.DAT

Table V. Strutural Data for Methylphosphine

	MM3	ED[a]	deviation	MW[b]	deviation
P–H	1.4205	1.423 ± 0.007	−0.003	1.414	
P–C	1.8574	1.858 ± 0.003	<−0.001	1.863	
C–H (av)	1.1089	1.094 ± 0.008	0.015	1.093	
∠P–C–H	110.16	109.6 ± 1	0.6		
∠H–P–H	92.75			93.38	−0.63
∠C–P–H	97.06			97.50	−0.44
∠H–C–H (av)	108.77			109.75	−0.96

[a] Electron diffraction data from ref 15. [b] Microwave data from ref 14.

Table VI. Vibrational Assignments for Methylphosphine

vibrational assignment	symmetry	IR gas[a]	MM3	deviation
C–H asym str	A''	3003	3014	11
C–H asym str	A'	2990	3012	22
C–H sym str	A'	2936	2908	28
P–H asym str	A''	2309	2305	−4
P–H sym str	A'	2305	2302	−3
$\mathrm{CH_3}$ asym bnd	A'	1435	1422	−14
$\mathrm{CH_3}$ asym bnd	A''	1429	1419	−10
$\mathrm{CH_3}$ sym bnd	A'	1296	1286	−10
$\mathrm{PH_2}$ sciss	A'	1092	1085	−7
$\mathrm{CH_3}$ wag	A''	1017	920	−97
$\mathrm{CH_3}$ wag	A'	978	917	−60
$\mathrm{PH_2}$ twist	A''	(696)	814	118
$\mathrm{PH_2}$ wag	A'	730	775	45
C–P stretch	A'	676	685	9
int torsion	A''	219	212	−8
			rms dev	45

[a] All the experimental IR values are from ref 25b. The value in parentheses is from the solid-phase data reported in the same reference.

if it is the only compound in the data set, but quite difficult if other compounds are considered. The P–H bond is calculated by MM3 to be too short; however, this deviation is necessary in order to properly reproduce the structures of alkylated phosphines, where the experimental P–H bond lengths range from 1.414 Å in methylphosphine, determined by microwave spectroscopy,[14] to 1.445 Å in dimethylphosphine, determined by electron diffraction.[15]

The bending vibrations of this molecule (see Table IV) cannot be properly reproduced as the only relevant variable is the H–P–H bending force constant. The degenerate pair of vibrations that appear at 1122 cm^{-1} in the experimental spectrum are calculated to be 1092 cm^{-1}, 30 cm^{-1} too low. The nondegenerate bending vibration at 992 cm^{-1} in the experimental spectrum is calculated to be too high by 72 cm^{-1}. Raising the value of the bending constant (k_Θ) causes all of the bending frequencies to increase. Likewise, lowering the value of k_Θ causes all of the bending frequencies to decrease, with no overall benefit. An H–P–H bend–bend interaction force constant of 0.275 has been found to correct these variations. Using this force constant in the calculations has no effect on the calculated structure or stretching vibrations. The bending modes are calculated at 1122 cm^{-1} and 1003 cm^{-1}, reducing the rms error to 14 wave numbers. Unfortunately this value cannot be included in the overall parameter set at present because MM3 employs a generic bend–bend interaction constant of the form H–X–H. Inclusion of a constant for this type of interaction also has a significant effect on the calculated results of the other phosphines included in this study, as well as all other types of compounds with this type of angle that have been previously examined.

Weston has shown that the splittings of the vibrational bands can be used to determine the barrier to inversion.[28] He estimated that the barrier to inversion of phosphine is 27.4 kcal mol^{-1}. MM3 calculates this barrier to be 20.91 kcal mol^{-1}, a 24% difference. Since MM3 uses a harmonic approximation for the spectroscopic calculation, the calculated inversion barriers are generally too low.

Table VII. Structural Data for Dimethylphosphine

	MM3	MW[a]	ED[a]	deviation[b]
P–H	1.4205	1.418[c]	1.445 ± 0.02	0.0025
P–C	1.8529	1.853	1.853 ± 0.003	−0.0001
C–H (av)	1.1088	1.088	1.097 ± 0.007	0.0118
∠C–P–H	96.2	96.5	(96.5)[d]	−0.3
∠P–C–H (av)	110.2	109.6	109.8 ± 0.7	0.4
∠C–P–C	99.8	99.76	99.2 ± 0.6	0.6

[a] The electron diffraction data are from ref 15. The microwave data are taken from ref 35. [b] In all the tables the deviation shown is the difference between the calculated MM3 values and the electron diffraction data where available. If no ED data are available for a particular structural feature, the microwave data are used. [c] Because of the exteme length of the P–H bond determined by electron diffraction this microwave value was used in the data analysis. [d] The C–P–H angle value is an assumed value.

Ammonia[29] has an experimental barrier to inversion of 5.77 kcal mol^{-1}, while MM3 calculates the barrier to inversion of ammonia to be 5.48 kcal mol^{-1}, an error of 5%.

Methylphosphine. In Table V, with the exception of the C–H bond length discussed above, the agreement between the calculated and experimental structures is very good, with all of the calculated structural values well within the uncertainties of the experimentally determined bond lengths and bond angles.

The $\mathrm{PH_2}$ twisting mode of this molecule is unobservable in the gas phase,[25b] and so solid-phase data had to be used. This assignment has the largest deviation of any vibrational mode in the molecule (vibrational assignments for methylphosphine are given in Table VI). It is conceivable that this mode is affected by crystal packing forces. If this mode is removed from the statistical analysis, the rms error of the vibrational fit for methylphosphine becomes 35 cm^{-1}, quite in line with the other compounds studied.

Insertion of the H–X–H bend–bend constant (0.275 md Å/rad^2 molecule) used to correct the phosphine vibrational calculations causes the calculated $\mathrm{CH_3}$ bending frequencies to rise from 1422, 1419, and 1286 cm^{-1} to 1466, 1463, and 1394 cm^{-1}, respectively. The lower frequency methyl wagging vibrational modes show a slight improvement with the inclusion of this term, but this is more than offset by the significantly larger deviations of the methyl bending vibrations. The rms deviation for this compound upon the incorporation of this term rises to 51 cm^{-1}, a value beyond our accepted range. Including this constant in the calculations of the remaining compounds in this study shows the same trend and will not be discussed for each compound individually. The generic H–X–H bend–bend interaction term from MM3 is carried over unchanged, because inclusion of the correction for the bend–bend interaction for phosphine is not transferable to other compounds of the class. It is unclear if the inclusion of a specific H–P–H bend–bend interaction term would make a significant improvement in these calculations. MM3 would have to be reprogrammed to include treatment of specific bend–bend interactions to determine if this is indeed the situation. This would create a new version of the already released MM3(92) program and so was not undertaken.

Dimethylphosphine. All of the calculated structural features in Table VII, with the exception of the P–H and C–H bond lengths, are within the uncertainties of the experimental values. The deviation of the C–H bond length has been discussed. The high experimental uncertainty of the P–H bond length arises from fitting the structure to the radial distribution curves of the electron diffraction experiment. The small P–H peak appears between the more intense C–H and P–C peaks and so cannot be well determined. The value obtained from this electron diffraction experiment is also significantly longer than any other experimentally determined P–H bond. The calculated bond length agrees more closely with the experimental value determined by microwave spectroscopy, which appears to be more in line with other experimentally determined P–H bond lengths. For these reasons, the value of 1.418 Å determined by microwave spec-

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Table VIII. Vibrational Assignments for Dimethylphosphine

vibrational assignment[a]	symmetry	IR gas[b]	MM3	deviation
(A′) C–H asym str	A′	2985	3014	29
(A′) C–H sym str	A′	2975	3014	29
(A″) C–H asym str	A″	2985	3014	39
(A″) C–H asym str	A″	2975	3013	38
(A″) C–H sym str	A′[c]	2923	2909	−14
(A′) C–H sym str	A″[c]	2918	2909	−9
(A′) P–H stretch	A′	2288	2304	16
(A′) C–H_3 asym def	A′	1447	1429	−18
(A″) C–H_3 asym def	A″	1443	1425	−18
(A′) C–H_3 asym def	A′	1434	1423	−12
(A″) C–H_3 asym def	A″	1434	1421	−14
(A′) C–H_3 sym def	A′	1297	1290	−7
(A″) C–H_3 sym def	A″	1284	1288	4
(A″) P–H bnd + CH_3 rock (22%)[e]	A″	1012	927	−85
(A′) CH_3 rock	A′	990	927	−63
(A″) C–H_3 rock + P–C str (11%)	A′[c]	986	921	−65
(A″) C–H_3 rock + P–C str (21%)	A″	954	909	−45
(A′) CH_3 rock	A″[c]	947	870	−77
(A′) P–H bnd + C–P str (16%)	A′	729	718	−11
(A″) P–C asym str	A″	703	699	−4
(A′) P–C asym str + C–P–C def (13%)	A′	660	663	3
(A′) C–P–C def	A′	261	264	3
CH3 torsion	A′	190.7	199	9
CH3 torsion	A″	188.8	178	−11
			rms dev	35 cm^{-1}

[a] Vibrational modes that contribute less than 10% to the mode have not been listed. The symmetries in parentheses are those assigned in ref 25c. [b] IR frequencies are from ref 25c. [c] These vibrational modes do not exhibit the same symmetry as those reported in the experimental paper. [d] In this and all other tables, the apparent differences in the deviations for some vibrational modes are due to round-off errors. [e] This vibration and the methyl rock just below are reversed in the MM3(92) assignment. The difference in the two modes is less than 1 cm^{-1}, however, and so no reassignment was made.

Table IX. Structural Data for Trimethylphosphine

	MM3	MW[a]	ED[a]	deviation
P–C	1.8456	1.841	1.846 ± 0.003	−0.0004
C–H (av)	1.1086	1.09	1.091 ± 0.006	0.0176
∠P–C–H	110.3		110.7 ± 0.5	−0.4
∠C–P–C	98.6	99.1	98.6 ± 0.3	0.0

[a] The microwave data is from ref 34. The electron diffraction data is from ref 16.

troscopy was used for the data analysis.

MM3 calculations satisfactorily reproduce the experimental spectrum of dimethylphosphine, with an rms deviation of 35 cm^{-1}. The largest deviations between the calculated and experimental vibrational modes (Table VIII) appear in those assigned to the C–H stretches and the methyl rocks. The experimental values of these modes have also been a source of uncertainty and have been assigned differently by a number of researchers.[25c,30,31] The experimental vibrational data that we used were taken from the most recent of these studies,[25c] but the fit to these bands and their symmetries is still not as good as desired. These four vibrational frequencies were reassigned using the calculated modes as a guide.

The four highest C–H stretching frequencies reported experimentally occur as two pairs at 2985 and 2975 cm^{-1}, each of these pairs having one vibrational mode of A′ species and one having A″ symmetry. MM3 calculates that the four highest frequencies will all lie between 3015 and 3014 cm^{-1}, with the highest two having A′ symmetry and the lower two A″ symmetry. Since the differences between the calculated and experimental frequencies were well within the deviation range, the experimental A′ and A″ pairs were retained and the ordering of the calculated frequencies was changed.

Table X. Vibrational Assignments for Trimethylphosphine

assignment	symmetry	experimental gas IR[a]	raman liq	MM3	deviation
CH_3 asym str	A1	2988		3017	29
CH_3 asym str	E	2978		3016	38
CH_3 asym str	E	2978	2969	3016	38
CH_3 asym str	E	2968	2954	3014	46
CH_3 asym str	E	2968		3014	46
CH_3 asym str	A2	2915		3013	
CH_3 sym str	A1	2900		2911	−4
CH_3 sym str	E	2900		2911	11
CH_3 sym str	E	2890	2894	2911	21
CH_3 asym bnd	A1	1441		1435	−6
CH_3 asym bnd	E	1430		1431	1
CH_3 asym bnd	E	1430		1431	1
CH_3 asym bnd	E	1416	1421	1428	12
CH_3 asym bnd	E	1416		1428	12
CH_3 asym bnd	A2	1325		1424	
CH_3 sym bnd	A1	1312	1312	1298	−14
CH_3 sym bnd	E	1297	1293	1294	−4
CH_3 sym bnd	E	1283		1294	11
CH_3 wag	A1		973	942	−31
CH_3 wag	E	952	948	927	−13
CH_3 wag	E	952		927	−13
P–C–H bnd	E	940		908	−27
P–C–H bnd	E	940		908	−27
CH_3 wag	A2	935		901	
P–C asym str	E	709	708	697	−12
P–C asym str	E	706		697	−9
P–C sym str	A1		653	647	−6
C–P–C sym bnd	A1		305	272	−33
C–P–C asym bnd	E		263	262	−1
C–P–C asym bnd	E		263	262	−1
CH_3 twist	E	248		217	−31
CH_3 twist	E	248		217	−31
CH_3 twist	A2	223[b]		192	−5
				rms dev	22

[a] Experimental data from refs 25d and e. [b] This "silent" vibrational mode was calculated from the microwave spectrum in ref 34.

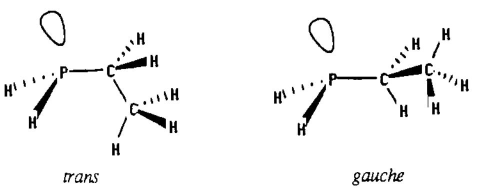

Figure 1. Conformations of ethylphosphine.

Trimethylphosphine. The geometry of trimethylphosphine has been determined by both electron diffraction[16] and microwave spectroscopy.[34] With the exception of the C–H bond length, the calculated molecular geometry is within the uncertainties of the experimentally obtained numbers (see Table IX).

The vibrational results for this compound, given in Table X, are quite good, with an rms deviation of only 22 cm^{-1}. This represents the closest agreement between calculated and experimental vibrational spectra of all the compounds in the study. This comparison requires none of the experimental modes to be reassigned, which may have to do with the small amount of mixing between the vibrational modes. Once again, the largest deviations between the calculated and experimental values appear in the modes assigned to the C–H stretching modes and the methyl wags. The vibrations in the A_2 symmetry group are not observed either by infrared or Raman spectroscopy and so could not be compared with the calculated vibrations. The A_2 torsional mode was determined via microwave spectroscopy.[34]

From the assignment of the vibrational frequencies by a number of methods for this compound, the variation of the vibrational

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Table XI. Structural Data for *trans*- and *gauche*-Ethylphosphine

	trans			gauche		
	MM3	MW[a]	deviation	MM3	MW[a]	deviation
P–H	1.4200	1.4230	–0.0030	1.4205	1.4153	0.0052
				1.4205	1.4169	00.36
P–C	1.8642	1.8465	0.0177	1.8646	1.8525	0.0121
C–C	1.5332	1.5334	–0.0002	1.5325	1.5355	–0.0030
∠H–P–H	94.61	92.89	1.72	92.18	92.68	–0.50
∠C–P–H	97.71	96.31	1.40	97.03	97.86	–0.82
				97.00	96.75	0.25
∠C–C–P	112.36	116.31	–3.95	110.90	110.65	0.25
∠P–C–H	108.37	106.68	1.69	109.23	111.48	–2.25
				108.55	106.93	1.62

[a] Experimental data from ref 17.

frequency in the solid, liquid, and gas phases can be demonstrated. Comparison of the gas-phase IR and Raman spectra known for ethylphosphine shows a much smaller difference in these two types of experiments.

Ethylphosphine. Durig and co-workers[17] have reported the structure of the gauche and trans conformers of ethylphosphine by studying a number of isotopically substituted species using microwave spectroscopy. They have determined that ethylphosphine exists as a 55:45 trans/gauche mixture with a predicted energy difference of 200 ± 100 cm^{-1} between the two conformers. A subsequent study of the vibrational spectrum of ethylphosphine by Durig et al.[25f] gave a value of 560 ± 60 cal mol^{-1}.

Durig has defined the two conformers as trans and gauche, referring to the relationship of the methyl group to the lone pair of the phosphorus (Figure 1). This nomenclature is retained here and is the same convention used to describe the conformers of ethyldimethylphosphine.

Aside from the torsion angle that differentiates them, the geometries of the two conformers of this compound are similar. The major difference appears in the C–C–P bond angle. In the trans conformer, this angle is experimentally determined to be 116.31°, and in the gauche conformer it is determined to be 110.65°.

With any one parameter set, MM3 cannot simultaneously reproduce the structures of both of these conformers correctly. A torsion–bend interaction term would be required to properly calculate this type of bond angle dependence on the torsion angle, and this type of parameter is not used in MM3 at the present time. Since both conformers could not be reproduced with a given set of parameters with any degree of accuracy, we chose to reproduce only one of the two conformers correctly, rather than average the error between the two, as was done with MM2.[32] Although the gauche conformer is slightly higher in energy, the experimentally reported structural angles seem to be closer to what one would intuitively expect. Therefore, we decided to fit the parameters to this conformer. The comparisons of the calculated MM3 structures to the experimental data are presented in Table XI.

MM3 is able to calculate the internal angles of the gauche conformer quite well but has considerable difficulty with the angles of the trans conformer. It is unclear why this is the case, but it may have to do with steric congestion brought about by error in calculating the C–C–P angle, which is calculated to be approximately 4° too small. If this angle were calculated properly, moving the methyl group further away from the phosphorus atom, it would partially relieve some of the induced crowding and possibly allow the other angles in the compound to relax. In the gauche conformer, the only angles that exhibit significant error are the P–C–H angles. MM3 calculates a difference between the two P–C–H angles that is too small. One way to correct for this is to make use of a smaller P–C–H force constant, allowing for a more flexible angle. However, if this is done for this compound, the rms vibrational error increases markedly. The error between the experimental and calculated values was minimized to give the best average agreement with the two P–C–H angles without sacrificing the vibrational comparison significantly.

The tables of vibrational data for the two conformers of this compound, as well as those of *tert*-butylphosphine and the two conformers each of isopropyl- and ethyldimethylphosphine have been submitted as Tables 18–24, and are available as supplementary material. Minor reassignments of the experimental spectral data are also discussed in the supplementary material on a compound by compound basis.

trans-Isopropylphosphine

gauche-Isopropylphosphine

Figure 2. Conformations of isopropylphosphine.

Table XII. Structural Data for *gauche*-Isopropylphosphine[a]

	MM3	MW[a]	deviation
P–C	1.8758	1.878	–0.0022
P–H[b]	1.4199[c]	1.414	0.0059
C–C[d]	1.5382	1.527	0.0112
C–C–P	109.7[c]	109.5	0.2
∠H–P–H[b]	94.1	93.4	0.7
∠C–P–H[b]	97.7	97.5	0.2
∠C–C–C[d]	110.5	111.8	–1.3

[a] Structure taken from ref 18. [b] Experimental value assumed to be the same as in methylphosphine. [c] Value expressed as the average of two unequal values. [d] Experimental value assumed to be the same as in isopropylamine.

The calculated and experimental vibrational spectra of the trnas conformer of ethylphosphine have an rms difference of 36 cm^{-1}, and the gauche conformer exhibits an rms difference of 35 cm^{-1}. This is not unreasonable, considering the fact that some of the structural features are not reproduced well. The symmetries of the vibrational modes are not reported in the literature and so cannot be compared to the calculated vibrations.

It should be noted that, with the exception of the torsional modes, the experimentally determined vibrations of the two conformers of ethylphosphine are reported to be the same. The calculated spectra of the two conformers have slightly different frequencies for the bending and stretching modes, as one would expect. The magnitude of these differences is, in most cases, well within the rms error between the calculations and experiment and so is considered negligible.

Isopropylphosphine. The microwave spectra for isopropylphosphine and the PD$_2$-substituted compound have been reported.[18] Like ethylphosphine, this compound also exists as a mixture of two conformers, trans and gauche, which refer to the positions of the phosphorus lone pair and the single hydrogen at the adjoining carbon. The two structures are shown as Figure 2. From these measurements a structure for the gauche conformer has been postulated. Due to the limited amount of isotopic substitution in this study, and the therefore limited information on the molecule, many of the structural parameters had to be assumed. The phosphino moiety was assumed to have the structure of methylphosphine, and the isopropyl group was assumed to have the same geometry as that of isopropylamine. Using these constraints and fitting to the observed moments of inertia, the experimentally determined structural parameters consist of the C–P bond distance and the C–C–P bond angle. The comparison of this proposed structure and that calculated by MM3 is shown in Table XII.

The computed structure is quite close to the empirical structure, with the exception of the C–C bond length, calculated more than 0.01 Å too long. This is not surprising, as the proposed structure uses an assumed bond length equal to that of isopropylamine, as well as being a measurement by microwave spectroscopy, typically somewhat shorter than MM3 values.

The experimental vibrational spectrum of isopropylphosphine is known for both the trans and gauche conformers of the molecule. Comparison of the calculated and experimental spectra gives an rms error of 33 cm^{-1} for the trans conformer and 37 cm^{-1} for the gauche conformer. The experimental assignments for the vibrations of the isopropyl moiety were guided by the assignment of Klaboe[33] for a series of isopropyl halides. Minor adjustments between the vibrational spectra of the halides and phosphines were

Table XIII. Structural Data for *trans*- and *gauche*-Ethyldimethylphosphine

	trans			gauche		
	MM3	ED[a]	deviation	MM3	ED[a]	deviation
P–C[b]	1.8472	1.848	−0.0008	1.8490	1.848	0.0010
C–C	1.5328	1.559	−0.0262	1.5330	1.559	−0.0260
∠Me–P–Et	101.9	99.6	2.3	99.1	99.6	−0.5
∠Me–P–Me	99.5	101.5	−2.0	98.5	101.5	−3.0
∠C–C–P	116.5	107.6	8.9	111.7	112.3	−0.6
∠P–C–H[c]	110.4	110.5	−0.1	110.3	110.5	−0.2

[a] Experimental data from ref 19. [b] Average value for all P–C bond lengths. [c] Only the angles of the P–CH_3 bond are considered in this measurement.

noted, and a decision was made to go with the MM3/VIBPLOT assignments. There are a total of 10 reassignments for the 66 vibrational modes of the two conformers. Justification for the reassignments is detailed in the supplementary material.

Ethyldimethylphosphine. Ethyldimethylphosphine has also been studied by Durig and co-workers.[19,25g] The structure has been determined by electron diffraction, and the IR and Raman spectra have been recorded and assigned. Durig and co-workers determined that in order to refine the fit of the experimental data to a proposed structure, some assumptions had to be made in order to simplify their analysis. With the exception of the P–C–C bond angle and the methyl torsional angle, all the structural parameters of the two conformers were assumed to be the same.[19] This is clearly not the case in the actual molecule. The P–C–C angle is reported to be 107.6° and 112.3° in the trans and gauche conformers, respectively. This behavior, where the gauche conformer has the wider angle, is the opposite of what occurs in ethylphosphine, where the trans conformer has the wider angle by more than 5°. If a graphical representation of the trans conformer is constructed using the reported structural parameters, the hydrogens of the ethyl group are within 1.5 Å of the hydrogens of the phosphorus methyls. This led us to question the accuracy of the reported structure of the trans conformer. All of the trial parameter sets that were used in the fitting process calculated the trans conformer to have the larger C–C–P angle of the two conformers. Considering the above suspicions about the structure of the trans conformer, we chose to use only the reported structure of the gauche conformer for the structural fit and parameterization.

The experimentally reported enthalpy difference (ΔH) between the gauche and trans conformers is 0.383 kcal mol^{-1}, with the gauche conformer being the more stable of the two. MM3 calculates the gauche conformer to be more stable by 0.573 kcal mol^{-1}. This behavior is the opposite of what occurs in the case of ethylphosphine, where the trans conformer is more stable. This can be attributed to the relative steric bulk of the groups attached to the phosphorus atom. In the ethyl compound the ethyl CH_3 group would rather be gauche to the two hydrogens and trans to the lone pair. Substituting methyl groups for the hydrogen atoms on the phosphorus atom causes the ethyl CH_3 to prefer to lie between one methyl and the lone pair, as opposed to being gauche to both of the methyl groups. The calculated and experimental structures of both conformers of ethyldimethylphosphine are shown in Table XIII.

For the reasons outlined above, we were unable to fit both conformations of ethyldimethylphosphine and so elected to concentrate on achieving a good representation of the gauche conformer. While the deviation of the P–C bond length is acceptable, the C–C bond length is calculated to be over 0.02 Å too short. The experimental C–C bond lengths for the other compounds in this study range from 1.527 Å in *gauche*-isopropylphosphine to 1.535 Å in *tert*-butylphosphine, with ethylphosphine having an intermediate value. Although all the other C–C lengths were derived from microwave spectroscopy, the differences between the r_s and r_a values should not be so large. Because correction of this error in ethyldimethylphosphine adversely affects the calculated moments of inertia for other compounds, it was deemed acceptable.

Table XIV. Structural Data for *tert*-Butylphosphine

	MM3	MW[a]	deviation
P–C	1.8825	1.896	−0.0135
C–C fixed	1.5396	1.535	0.0046
P–H fixed at PMe3	1.4198	1.414	0.0058
∠C–C–C fixed	110.0	108.5	1.5
∠H–P–H fixed	93.3	93.4	−0.1
∠C–P–H	97.7	95.7	2.0

[a] The microwave structural data are taken from ref 20.

Table XV. Rotational Barriers

	exptl barrier[a]	MM3 barrier	deviation	% deviation
methylphosphine[b]				
CH_3 rotation	1.959	1.4296	−0.529	−27.0
dimethylphosphine[c]				
CH_3 rotation	2.32	1.9367	−0.38	−16.5
trimethylphosphine[d]				
CH_3 rotation	2.6	2.4504	−0.15	−5.8
ethylphosphine[e]				
gauche–trans energy difference	0.6632	0.5478	−0.1154	−17.4
trans CH_3 rotation	3.74	3.0169	−0.72	−19.3
gauche CH_3 rotation	3.14	2.9697	−0.17	−5.4
trans to 60°	2.745	2.2786	−0.466	−17.0
trans to 180°	2.767	2.2843	−0.483	−17.4
gauche to 60°	2.082	1.7308	−0.351	−16.9
gauche to 180°	2.104	1.7365	−0.368	−17.5
isopropylphosphine[f]				
CH_3 rotation	4.3	3.3049	−1.0	−23.1
ethyldimethylphosphine[g]				
gauche–trans energy difference (liq)	0.383	0.4074	0.024	6.4
trans P–CH_3 rotation	2.56	2.5115	−0.05	−1.9
gauche P–CH_3 rotation	2.56	1.9942	−0.57	−22.1
trans C–CH_3 rotation	3.22	2.9902	−0.23	−7.1
gauche C–CH_3 rotation	3.22	2.8331	−0.39	−12.0
tert-butylphosphine[h]				
CH_3 rotation	3.81	3.6577	−0.15	−4.0
PH_2 rotation	2.79	2.9262	0.14	4.9

[a] All values in kcal mol^{-1}. [b] Data from ref 14. [c] Data from ref 25c. [d] Data from ref 34. [e] Data from ref 17. [f] This value is obtained by averaging the two values for methyl rotation in the gauche conformer with the single value for the trans conformer. Experimental data form ref 25i. [g] Data from ref 25g. [h] Data from ref 25h.

Comparison of the experimental and calculated vibrational spectra for the two conformers of this molecule gives rms deviations of 32 cm^{-1} for the trans conformer and 29 cm^{-1} for the gauche conformer. The assignment of the experimental IR and Raman spectra of ethyldimethylphosphine was not done definitively by isotopic substitution. Instead, the assignments were chosen from looking at the differences between the gas- and solid-phase spectra and by doing a normal coordinate analysis on the structure to obtain the amount of mixing between the vibrational modes. The normal coordinate analysis was carried out using structural parameters from microwave work on a variety of related phosphines. Lacking the definitive assignments obtained by isotopic substitution for these compounds, we have found that a larger proportion of the assignments do not agree with those afforded by the present calculations. The ordering of many of the calculated frequencies is different between the two conformers, whereas only nine of the 42 experimental frequencies are reported to be different in the experimental data.

***tert*-Butylphosphine.** Microwave spectra have been reported for *tert*-butylphosphine and the mono- and dideutero analogs substituted on the phosphorus atom.[20] Due to the limited amount of isotopic substitution, many of the structural parameters must be assumed. In the reported structure, the geometry around the phosphino group is assumed to be that of methylphosphine (P–H = 1.414 Å and ∠H–P–H = 93.4°). The *tert*-butyl group was assigned a structure with a C–C distance of 1.535 Å, a C–H

Table XVI. Moments of Inertia

compd and axis	exptl rotational constant (MHz)	moment of inertia ($\times 10^{-39}$ g·cm^2) exptl	MM3	deviation	% deviation
methylphosphine					
x	71873	1.1676	1.1859	0.0183	1.56
y	11791.6	7.1170	7.1239	0.0069	0.10
z	11678.7	7.1858	7.1893	0.0035	0.05
dimethylphosphine					
x	16071.87	5.2216	5.2656	0.0440	0.84
y	7018.19	11.9576	12.0292	0.0716	0.60
z	5403.61	15.5305	15.5821	0.0516	0.33
trimethylphosphine					
x	5816.24	14.4287	14.4814	0.0527	0.36
y	5816.24	14.4287	14.4814	0.0527	0.36
calcd from ^{13}C	3837.34	21.8696	22.3692	0.4996	2.28
trans-ethylphosphine					
x	25796.651	3.2532	3.4386	0.1854	5.70
y	5016.551	16.7288	16.2839	−0.4449	−2.66
z	4600.2982	18.2425	17.92	−0.3225	−1.77
gauche-ethylphosphine					
x	25572.273	3.2817	3.3047	0.0230	0.70
y	5126.27	16.3708	16.4935	0.1227	0.75
z	4658.047	18.0163	18.1124	0.0961	0.53
gauche-isopropylphosphine					
x	7633.34	10.9940	11.1074	0.1134	1.03
y	4243.36	19.7770	19.8853	0.1083	0.55
z	3045.84	27.5527	27.5879	0.0352	0.13
tert-butylphosphine					
x	4379.63	19.0832	19.3354	0.2522	1.32
y	2878.88	29.1506	29.3848	0.2342	0.80
z	2870.86	29.2320	29.4384	0.2064	0.71

distance of 1.090 Å, and a C–C–H angle of 109.9°. P–H and P–D bonds were assumed to have equal lengths for the least squares fit of the rotational constants of the three studied compounds to the proposed structures. Using these constraints a structure was proposed, and it is compared to the one calculated by MM3 in Table XIV.

Given that the experimental structure is only a rough approximation, dependent on the assumptions and the reliability of the least squares fit, the calculated MM3 structure is acceptable. It is noteworthy that the experimental paper reports that the P–C bond is relatively long in this compound. This is confirmed by MM3, where this bond is calculated to be 1.8825 Å, not as long as the 1.896 Å proposed by Durig et al.,[20] but longer than any other calculated P–C bond by almost 0.01 Å. The fit to the experimental vibrational spectrum is acceptable for this compound, with an rms error of 35 cm^{-1}.

Torsional Parameters. When a fairly good fit for the structure and the vibrational frequencies was achieved for each compound, the torsional parameters were then adjusted to reproduce the available experimental data. These parameters were chosen not only to fit the torsional vibrational modes of the compounds under investigation but also to attempt to reflect the experimentally determined rotational barriers as well. From previous parameterization efforts, it was known that fitting to the torsional vibrational frequencies afforded barriers to rotation that are on the whole too low. If the barriers to rotation are used as the primary source of experimental data for developing torsional parameters, the corresponding modes in the vibrational spectra are calculated consistently to be too high. Proper modeling of the barriers to rotation also creates difficulties in producing parameters for calculating heats of formation as well. (In the present study no extensive experimental data were found for heats of formation so this did not present a problem.) From microwave data the barriers to rotation for the methyl group were determined for methyl-,[13] dimethyl-,[25c] and trimethylphosphine.[34]

Methylphosphine has only one torsional parameter that defines the rotation of the methyl group, H–P–C–H (atom types 5–25–1–5). The V_3 constant was adjusted to give the best fit to the experimental data. Likewise, methyl rotation in trimethylphosphine only involves the C–P–C–H (atom types 1–25–1–5) torsional parameter. This V_3 constant was also adjusted in order to reproduce the experimental data. The rotation of the methyl group in the dimethyl compound is affected by both of these parameters, and so a compromise that offered the smallest average deviation among all three of these compounds was used.

The fitting of the rotational and vibrational data for the other compounds is somewhat more complex as more than one torsional parameter is involved in each of the rotations. The torsional parameters for ethylphosphine presented a challenge as the minimum energy conformation occurs when the methyl group is trans to the lone pair of the phosphorus atom. In this conformation the C–C–P–H torsion angle is 13°. Unlike MM2, MM3 does not explicitly treat lone pairs. This means that the rotational barriers must be treated using only the C–C–P–H torsional parameter. This required the use of V_1 and V_2 terms in order to get what is essentially a rotation with V_3 symmetry skewed by 47°. The results of the fits to the torsional vibrations can be seen in the previous section. The agreement between the observed and calculated rotational barriers and conformational energy differences is presented in Table XV. As expected, MM3 calculates energy barriers that are too low in comparison to the experimental data in the majority of cases. The computed barriers are on the average 0.3 kcal mol^{-1} too low. This is another artifact of using the harmonic approximation for the vibrational mode calculations.

Moments of Inertia

The moments of inertia for many of the compounds were known from the microwave data. The results for methylphosphine,[14] dimethylphosphine,[35] trimethylphosphine,[34] *tert*-butylphosphine,[20] the two conformers of ethylphosphine,[17] and *gauche*-isopropylphosphine[18] have been reported in the literature, and the comparison between these experimental values and those calculated by MM3 are shown as Table XVI.

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(35) Nelson, R. *J. Chem. Phys.* **1963**, *39*, 2382.

(36) Durig, J. R.; Cox, A. W., Jr. *J. Chem. Phys.* **1976**, *64*, 1930.

Table XVII. Dipole Moments of Alkylphosphines

compd	exptl value[a]	MM3 value	difference	% difference
methylphosphine[b]	1.100 ± 0.010	1.184	0.084	7.64
dimethylphosphine[c]	1.23 ± 0.01	1.247	0.017	1.38
trimethylphosphine[d]	1.192 ± 0.005	1.173	−0.019	−1.59
trans-ethylphosphine[e]	1.226 ± 0.005	1.184	−0.042	−3.43
gauche-ethylphosphine[e]	1.22 ± 0.07	1.186	−0.034	−2.79
gauche-isopropylphosphine[f]	1.23 ± 0.01	1.186	−0.004	−3.58
tert-butylphosphine[g]	1.17 ± 0.02	1.196	0.026	2.22

[a] All values are in D. [b] Data from ref 14. [c] Data from ref 25c. [d] Data from ref 34. [e] Data from ref 36. [f] Data from ref 25i. [g] Data from ref 25h.

The fits to the experimental moments of inertia are reasonable, with the exception of *trans*-ethylphosphine. This error can be attributed to the fact that the geometry is calculated poorly for this conformer. The average deviation for the entire set of compounds is 1.10%. If the data for *trans*-ethylphosphine is discounted the average error is reduced by almost half to 0.62%. This is within the acceptable limit that can be accounted for from the systematic differences induced by MM3 calculating values based on r_g and microwave spectra giving r_a values.

Dipole Moments. Dipole moments have been determined for a number of the compounds under investigation in this study, either by microwave spectroscopy, ab initio calculations, or both. The comparison of the experimental and calculated dipole moments is presented as Table XVII. The calculated and experimental dipole moments for the molecules where data are available agree quite well. All values agree to within 0.1 D.

Conclusions

An MM3 force field has been developed that can model the structures, vibrational spectra, moments of inertia, and dipole moments of alkylphosphines with reasonable accuracy. These parameters represent a starting point for the development of MM3 parameters for other, biologically important, phosphorus-containing moieties, including phosphates and nucleotides. The incorporation of a torsion-bend parameter in future versions of molecular mechanics would allow for a more accurate representation of the conformers of ethylphosphine. This more accurate structural modeling would also increase the accuracy of the calculations of the moments of inertia, as well as the dipole moments and the barriers to rotation of these compounds.

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Registry No. Phosphine, 7803-51-2; methylphosphine, 593-54-4; dimethylphosphine, 676-59-5; trimethylphosphine, 594-09-2; ethylphosphine, 593-68-0; isopropylphosphine, 4538-29-8; ethyldimethylphosphine, 1605-51-2; *tert*-butylphosphine, 2501-94-2.

Supplementary Material Available: Tables containing the comparisons between experimental and calculated vibrational assignments of *trans*- and *gauche*-ethylphosphine, *trans*- and *gauche*-isopropylphosphine, *trans*- and *gauche*-ethyldimethylphosphine, and *tert*-butylphosphine (13 pages). Ordering information is given on any current masthead page.

Probing Redox-Induced Molecular Transformations by Atomic-Resolution Scanning Tunneling Microscopy: Iodide Adsorption and Electrooxidation on Au(111) in Aqueous Solution

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Abstract: In-situ atomic-resolution scanning tunneling microscopy (STM) has been utilized on ordered Au(111) under electrode potential control in acidic aqueous solution to examine potential-dependent iodine adlayer structures formed by iodide electrooxidation as well as covalent electrosorption. In the potential region −0.3 to +0.4 V vs SCE, below where electrooxidation of solution iodide occurs, several distinct iodine adlayer structures were observed. At the most negative potentials, structures close to the hexagonal $(\sqrt{3} \times \sqrt{3})R30°$ ($\theta_I = 0.33$) pattern are evident. The registry between the adlayer and the substrate lattice was deduced in part from composite-domain images created by stepping the electrode potential so as to alter markedly the adsorbate coverage during acquisition of a given STM image. At potentials between −0.2 and +0.2 V, adlayer patterns progressively closer to the $(5 \times \sqrt{3})$ ($\theta_I = 0.4$) structure became increasingly prevalent. This features a diminution in the iodine spacing along two of the three iodine rows, with a corresponding ca. 5° shift from the $R30°$ direction. Above 0.2 V, the STM images indicate that predominant presence of more complex higher-coverage adlayers ($\theta_I \approx 0.44$) featuring long-range (19–22 Å) z corrugations rotated by 8–10° from the hexagonal iodine adlattice. These corrugations arise from periodic alterations in the iodine-binding site, necessitated by I–I distances that approach the van der Waals diameter. Above 0.3 V, however, polyiodide chains were also observed, featuring shorter (2.8–3.2 Å) I–I distances compatible with adsorbate–adsorbate chemical bonding; these increasingly distort the monomeric iodine superlattice structure. At the onset of solution iodide electrooxidation, at 0.45 V, *multilayer* iodine films were observed to form, consisting of polyiodide strands growing outward from a $(5 \times \sqrt{3})$ surface template. This STM spatial information is compared with structural data obtained previously from potential-dependent surface Raman spectra. The prospects of utilizing in-situ electrochemical STM to explore redox-induced surface molecular transformations are noted in the light of these findings.

The evolution of molecular-level structural techniques applicable directly to solid–liquid interfaces is having an increasingly profound impact on our fundamental understanding of electrochemical surface science.[1] Besides spectroscopic and diffraction methods,

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