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P–P bond cleavage; energetics and structural changes in tetramethyldiphosphine and tetrasilyldiphosphine from *ab initio* MO calculations†

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The molecular structures and conformations of tetramethyldiphosphine and tetrasilyldiphosphine and their corresponding dimethylphosphido and disilylphosphido radicals were computed by high-level *ab initio* molecular orbital calculations utilising a range of methods (HF, MP2, B3LYP) and different basis sets. The thermodynamic properties of the homolytic dissociation reaction were also calculated at the G2 level and compared with those computed by other theoretical methods. The results indicate that although the MP2/6-311+G* calculations are superior in reproducing experimental structural and high-level theoretical thermodynamic data, the thermodynamic properties computed using the B3LYP method with effective core potentials for Si and P or even with a small (3-21G*) basis set are on a par with calculations employing larger basis sets and more elaborate treatment of electron correlation at the MP2 level. This offers the possibility of quick reasonable estimation of thermodynamic properties of large dissociating systems. An estimation of bond energies based on the energetics of structural changes upon dissociation of the diphosphines gives values in agreement with the previously estimated P–P bond energies in organic compounds. The current *ab initio* calculations demonstrated the existence of two conformers of tetramethyldiphosphine, *gauche* and *anti*, with the *anti* form being more stable by 6.1 kJ mol^{-1} as computed at the MP2/6-311+G* level, in disagreement with the previous results of the electron diffraction structure investigation. This disagreement in the conformational composition and the large difference in computed and experimental values of the P–P–C angles indicate that the structure of tetramethyldiphosphine in the gas phase may need re-determination.

Introduction

Recently it has been found that tetrakis(disilyl)diphosphine, $P_2\{CH[Si(CH_3)_3]_2\}_4$, while having a strong P–P bond in the crystal, dissociates into bis-disilyl-phosphido radicals, $P\{CH[Si(CH_3)_3]_2\}_2$, on melting and exists in dissociated form both in the liquid and in the gas phase.[1]

According to X-ray crystallography the diphosphine has a P–P bond length of 231.0 pm,[1] only about 10 pm longer than the P–P bond observed in solid tetramethyldiphosphine, 221.2 pm.[2] However, the energy required for the observed modest lengthening of a P–P bond in the above example was calculated to be very small,[1] and such a small diminution of the usually relatively strong P–P bonds (bond energy of about 211 kJ mol^{-1})[3] does not seem to be the reason for the facile dissociation of the molecule. It has also been observed that the conformation of the fragments of the molecule changes considerably upon dissociation and it has been shown that the relaxation of the substituent ligands releases a substantial amount of energy, which contributes to the dissociation.[1]

Previous calculations on formic, fluoroformic, acetic, and trifluoroacetic acids and their dimers have indicated that the energetics of the structural changes upon dissociation/dimerisation may be responsible for up to a 10 kJ mol^{-1} difference between the hydrogen bond energy and the dissociation/dimerisation enthalpy.[4] Although in these cases there were not any substantial steric interactions between the parts of the associated dimers, the energy of structural distortion was due to electronic redistribution within the fragments upon dissociation/dimerisation. All these examples nevertheless add to the realisation of the importance of structural changes in understanding the thermochemistry of the dissociation/association processes.

In the present work we decided to investigate the structures and thermochemistry of homolytic dissociation of two substituted diphosphines, parent to the $P_2\{CH[Si(CH_3)_3]_2\}_4$/$P\{CH[Si(CH_3)_3]_2\}_2$ system, namely tetramethyldiphosphine and tetrasilyldiphosphine, as model compounds, monitoring structural and energetic changes in the dissociation reaction by *ab initio* calculations. A further aim was to identify the most effective theoretical method to evaluate the thermochemistry of homolytic dissociation, which could be applied to much larger systems.

The structure of the tetramethyldiphosphine had been investigated previously by several experimental methods yielding conflicting conclusions. An early investigation by infrared and Raman spectroscopy found that the molecule exists in pure *anti* form in the solid, whereas there is a mixture of *gauche* and *anti* conformers in the liquid, with the *gauche* structure slightly predominating.[5] A later gas-phase electron diffraction study at 170 °C found the experimental data to be consistent with a single distorted *anti* conformation of the molecule.[6] The observed 16° deviation from the *anti* form was attributed to the large-amplitude torsional motion about the central P–P bond. A study of the gas-phase IR spectrum resulted in the conclusion that the *gauche* conformer predominates over *anti* in the ratio 3 : 2.[7] The photoelectron spectrum

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† Electronic supplementary information (ESI) available: experimental and theoretical skeletal vibrational frequencies of *anti*/*gauche*-tetramethyldiphosphine and theoretical skeletal vibrations of *anti*/*gauche*-tetrasilyldiphosphine. See http://www.rsc.org/suppdata/dt/b2/b201904c/

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of tetramethyldiphosphine has been interpreted in terms of a mixture of 84% *anti* and 16% *gauche* conformers, in disagreement with the electron diffraction and IR results.[8] Variable temperature photoelectron spectra again indicated that the *anti* conformer of the molecule is more stable than the *gauche* conformer in the gas phase,[9] by 2.1 ± 0.4 kJ mol^{-1}. This energy difference corresponds to 50% of each conformer at the temperature of the electron diffraction experiment. A semi-empirical MNDO study of mass spectral fragmentation of tetramethyldiphosphine has suggested the existence of the *anti* form as the only conformer of the molecule,[10] in disagreement with the photoelectron and IR spectra.

In addition to studying the thermodynamics of homolytic dissociation in diphosphines, high-level *ab initio* calculations on tetramethyldiphosphine may help to resolve the above uncertainties in interpretation of different experimental data.

The structure of tetrasilyldiphosphine, although being a parent structure to the known tetrakis(trimethylsilyl)diphosphine,[11] has not been investigated by either theoretical or experimental techniques. We have used the available structural data for trisilylphosphine in the gas phase[12] and the crystal[13] for comparison with our theoretical structural parameters.

Ab initio calculations

Gas-phase *ab initio* molecular orbital calculations for tetramethyldiphosphine and tetrasilyldiphosphine as well as spin-unrestricted open-shell optimisations for the dimethylphosphido and disilylphosphido radicals were made utilising the GAUSSIAN 98 series of programs,[14] employing standard 3-21G,[15] 6-31G,[16] and 6-311G basis sets[17] also augmented by diffuse and polarisation functions on heavy atoms. The Lanl2DZ[18] effective core potential on Si and P atoms with the 6-31G* basis set on the first row atoms (further referred to as the ECP basis set) was also tested. A range of methods including HF, MP2 with only valence electrons active, DFT, and GAUSSIAN 2 were compared, but we have concentrated on the use of the DFT methods. Becke's three-parameter exchange functional[19] in combination with the Lee–Yang–Parr correlation functional,[20] B3LYP, was tested with different basis sets, as density functional theory offers quick and cost-effective methods for calculations of many types of chemical properties. The spin contamination in the open-shell calculations was removed by standard methods during the SCF procedure. Vibrational frequency analyses were performed at the corresponding levels of theory to confirm the nature of the computed stationary points as real minima (no imaginary frequencies) or transition states (one imaginary frequency) and to provide an estimation of thermal energy corrections for calculation of standard enthalpies of dissociation reactions, as well as reaction entropy changes. Although it is the usual practice to multiply the vibrational frequencies computed at the HF level by a factor of 0.92 and use these values in calculation of the thermal energy corrections, the effect of such correction on the calculated enthalpy of dissociation of the systems in question is very small (in the region of 0.5 kJ mol^{-1}) and it was ignored in this study. Single-point energies of the halves of the molecules were also calculated at the corresponding levels.

Potential energy curves for internal rotation about the central P–P bond were calculated for both P_2Me_4 and $P_2(SiH_3)_4$ at the HF/3-21G* level assuming different values for the C–P–P–C or Si–P–P–Si dihedral angles and optimising all other parameters. Zero values of the C–P–P–C or Si–P–P–Si angles correspond to the fully eclipsed conformation, when the P–C or P–Si bonds and lone pairs of electrons on neighbouring phosphorus atoms are eclipsing each other. The dihedral angles are positive when rotating clockwise. The minimum-energy structures and transition states were then fully optimised at the HF/3-21G* level and also computed at higher levels of theory, except MP2/6-311+G* and B3LYP/ECP, for which only the minima were optimised.

The basis set superposition error (BSSE) was estimated by full counterpoise correction for the lowest energy conformation of the diphosphines at all applied theoretical levels. The thermodynamic parameters were computed for the lowest energy conformers of the molecules. The bond energies, as equilibrium properties, were calculated for vibrationless states at 0 K.

Discussion

Molecular geometries

The main parameters of the computed structures of tetramethyldiphosphine, tetrasilyldiphosphine and the corresponding radicals are summarised in Tables 1 and 2.

The best agreement of the experimental electron diffraction[6] and theoretical P–P and P–C bond lengths in tetramethyldiphosphine is observed for those computed at the HF/3-21G* level, probably due to fortuitous cancellation of errors. The MP2/6-311+G* P–P bond appears slightly longer than the experimental, and there is continuous lengthening of this bond with increase of the basis set in computations using the DFT method with the B3LYP functional. The HF/3-21G* level, however, underestimates the P–P–C angle by about 16° compared to the experimental X-ray value,[2] while computations with a larger basis set and high-level methods reproduce the experimental values satisfactorily. The overall agreement between structural parameters including both bond lengths and bond angles is therefore best for the results obtained at the MP2/6-311+G* level. We should note that the gas-phase electron-diffraction value of the P–P–C angle is up to 3° larger than the computed one and the value from X-ray crystallography in the solid state.[2] This may be a consequence of description of the gas-phase mixture of two conformers with considerably different P–P–C angles by a single-conformer model in the original electron diffraction study.[6] The theoretical calculations predict one of the angles to be up to 7° larger in the *gauche* conformer than the corresponding angle in the *anti* conformer. Unexpectedly, the performance of the B3LYP method worsened with the increase of the basis set, with the closest agreement with the experimental data achieved in the calculations applying the smallest 3-21G* basis set.

Similar trends can be seen in the computed structures of tetrasilyldiphosphine, although selection of the method demonstrating the best agreement with experiment is hindered by the scarcity of relevant experimental data. The experimental P–Si bond lengths in trisilylphosphine[12,13] are closest to those predicted by the HF/3-21G* calculations in tetrasilyldiphosphine, although agreement with the Si–P–Si angles is the best for the results of the MP2/6-311+G* calculations.

As in the case of tetramethyldiphosphine the structure computed at the B3LYP/3-21G* level shows better agreement with the results of the time-consuming MP2/6-311+G* method than do the structures computed utilising the B3LYP functional with larger basis sets or employing the effective core potentials.

All theoretical methods agree, however, on the trends of changes in structural parameters between *anti* and *gauche* conformers of both tetramethyl- and tetrasilyl-diphosphines. When going from the *anti* to the *gauche* conformer the P–P bond shortens, with the amount of shortening being bigger in tetrasilyldiphosphine. The P–C or P–Si bonds become slightly longer, while all bond angles increase.

Dissociation is accompanied by the following structural changes. The P–C or P–Si bonds become slightly shorter, by less than 1 pm, and the C–P–C angle slightly smaller, by a few tenths of a degree. A more pronounced change is observed for the conformation of the substituent groups in the radicals as compared to the corresponding fragments of the diphosphines.

Table 1 Computed and experimental structural parameters (bond lengths in pm, angles in degrees) for tetramethyldiphosphine (*anti*/*gauche* conformers) and the dimethylphosphido radical

Parameter P$_2$Me$_4$	HF/3-21G*	HF/6-31G*	HF/6-311+G*	MP2/6-311+G*	B3LYP/ECP[a]	B3LYP/3-21G*	B3LYP/6-31G*	B3LYP/6-311+G*	Expt. gas[b]	Expt. solid[c]
P–P	220.8/219.4	222.2/220.9	222.8/221.8	221.8/221.0	225.7/224.1	223.1/221.7	225.2/223.6	225.7/224.5	219.2(9)	221.2(1)
P–C[d]	185.4/185.2	185.9/185.8	185.5/185.5	185.2/185.2	187.1/187.1	187.1/186.8	187.4/187.3	186.8/186.8	185.3(3)	183.8(1)
P–C	185.4/185.2	185.9/185.7	185.5/185.3	185.2/185.0	187.1/186.9	187.1/186.8	187.4/187.2	186.8/186.6	185.3(3)	183.8(1)
(C–H)$_{av}$	108.5/108.5	108.5/108.5	108.4/108.4	109.3/109.3	109.6/109.5	109.6/109.6	109.6/109.5	109.3/109.3	110.9(9)	—
C–P–C	99.1/99.9	99.5/100.2	99.7/100.3	98.8/99.1	98.9/99.7	98.2/99.2	98.8/99.6	98.8/99.6	99.6(10)	98.8(1)
P–P–C[d]	82.6/105.7	99.5/106.3	99.4/106.2	97.8/104.9	98.6/105.9	97.6/105.0	98.5/105.9	98.3/105.9	101.1(7)	98.3(1)
P–P–C	82.6/99.4	99.5/100.2	99.4/99.9	97.8/98.4	98.6/99.1	97.6/98.3	98.5/99.0	98.3/98.8	101.1(7)	98.3(1)
(P–C–H)$_{av}$	110.6/110.2	110.6/110.7	110.7/110.8	110.7/110.8	110.6/110.6	110.4/110.5	110.5/110.6	110.7/110.8	108.8(25)	—
C–P–P–C	180.0/72.6	180.0/75.3	180.0/76.4	180.0/73.3	180.0/74.5	180.0/71.2	180.0/74.0	180.0/75.2	164(23)	180.0
PMe$_2$										
P–C	185.2	185.8	185.3	184.8	186.5	186.4	186.8	186.1	—	—
(C–H)$_{av}$	108.6	108.6	108.5	109.4	109.7	109.7	109.7	109.4	—	—
C–P–C	98.6	98.8	98.9	97.5	98.6	98.0	98.4	98.4	—	—
(P–C–H)$_{av}$	110.7	110.8	110.8	110.9	110.9	110.7	110.8	111.0	—	—

[a] 6-31G* basis set on first row elements and Lanl2DZ on phosphorus. [b] Ref. 6. [c] Ref. 2. [d] The first line for the P–C and the P–P–C parameters corresponds to the P–C bonds located closer to each other, and the second line corresponds to the P–C bonds located further from each other in the tetramethyldiphosphine conformers.

Table 2 Computed structural parameters (bond length in pm, angles in degrees) for tetrasilyldiphosphine (*anti*/*gauche* conformers) and the disilylphosphido radical and experimental data for trisilylphosphine

Parameter P$_2$(SiH$_3$)$_4$	HF/3-21G*	HF/6–31G*	HF/6-311+G*	MP2/6-311+G*	B3LYP/ECP[a]	B3LYP/3-21G*	B3LYP/6-31G*	B3LYP/6-311+G*	Expt. gas[b]	Expt. solid[c]
P–P	223.9/220.8	224.6/221.7	225.1/222.7	224.6/222.1	228.2/225.2	226.8/223.9	228.2/225.2	228.4/225.7	—	—
P–Si[d]	225.3/224.6	226.4/226.0	226.8/226.6	225.2/225.3	227.6/227.3	225.9/225.3	227.6/227.4	227.8/227.5	224.8(3)	224.6(1)
P–Si	225.4/224.6	226.6/225.8	227.0/226.2	225.3/224.6	227.9/227.0	226.1/225.3	227.8/226.9	228.0/227.0	—	—
(Si–H)$_{av}$	147.4/147.4	147.4/147.4	147.4/147.4	148.2/148.2	148.4/148.4	148.6/148.6	148.7/148.7	148.4/148.4	148.5(10)	136(3)
Si–P–Si	99.4/103.5	99.5/104.0	98.7/103.0	96.5/100.5	97.0/101.5	96.6/100.4	96.7/101.1	96.7/100.9	96.5(5)	96.1(2)
P–P–Si[d]	103.4/110.1	103.9/110.8	103.1/110.6	100.8/109.4	101.7/110.0	100.6/108.8	101.1/109.9	101.0/109.9	—	—
P–P–Si	97.8/100.5	99.1/101.6	98.6/100.9	95.5/98.9	97.1/99.4	96.0/98.3	97.3/99.6	97.0/99.1	—	—
(P–Si–H)$_{av}$	109.5/109.5	109.5/109.6	109.4/109.5	109.3/109.4	109.7/109.8	109.7/109.8	109.8/109.9	109.6/109.7	110.9(14)	110.8(11)
Si–P–P–Si	159.3/90.1	161.0/86.4	162.3/85.4	162.3/82.1	162.7/85.9	163.9/90.0	166.1/83.4	166.0/84.0	—	—
P(SiH$_3$)$_2$										
P–Si	225.5	226.6	227.0	225.3	227.3	225.5	227.2	227.3	—	—
(Si–H)$_{av}$	147.5	147.5	147.5	148.2	148.6	146.2	146.6	148.6	—	—
Si–P–Si	99.5	99.4	98.3	94.5	96.6	97.0	96.6	96.4	—	—
(P–Si–H)$_{av}$	109.8	109.9	109.8	109.9	110.2	110.3	110.3	110.2	—	—

[a] 6-31G* basis set on first row elements and Lanl2DZ on phosphorus and silicon. [b] Parameters for P(SiH$_3$)$_3$ taken from ref. 12. [c] Parameters for P(SiH$_3$)$_3$ taken from ref. 13. [d] The first line for the P–Si and the P–P–Si parameters corresponds to the P–Si bonds located closer to each other, and the second line corresponds to the P–Si bonds located further from each other in the tetrasilyldiphosphine conformers.

Conformations

All levels of theory result in the *anti* conformer of P_2Me_4 with C_{2h} symmetry being more stable than the C_2 symmetry *gauche* conformer. There are three transition states on the potential energy curve to internal rotation about the central P–P bond in tetramethyldiphosphine, with the two lowest ones being equivalent. The higher transition state with all of the carbons eclipsing each other has C_{2v} symmetry, and the lower one, with C_2 symmetry, has two carbons close to eclipsing one another. The energy differences between *anti* and *gauche* conformers vary, depending on the basis set and method. The highest energy differences are computed at the MP2 and B3LYP levels with the 6-311+G* basis set, 6.1 and 5.4 kJ mol^{-1}, respectively. The experimental energy difference derived from the analysis of photoelectron spectra[9] is smaller, 2.1 ± 0.4 kJ mol^{-1}, and is more closely reproduced by lower levels of calculations. The best agreement of the experimental data on the energy difference between conformers is with the results of the computations at the HF/6-31G* level, 2.2 kJ mol^{-1}. Introduction of electron correlation and higher basis sets leads to a greater energy difference (Fig. 1).

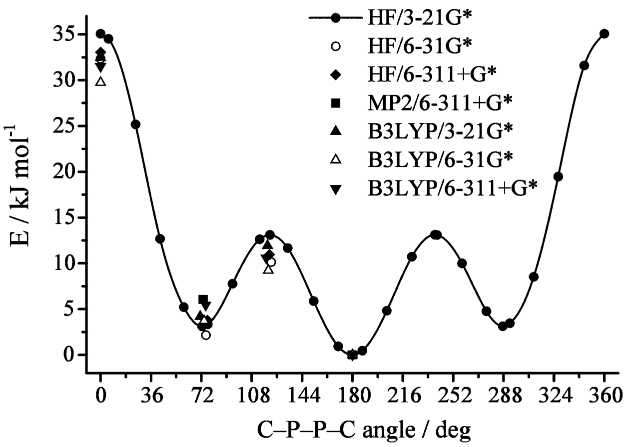

Fig. 1 Potential energy curve for internal rotation about the central P–P bond in tetramethyldiphosphine.

The relative stabilities of the conformers change with the substitution of the methyl groups by silyl groups in tetrasilyldiphosphine. The potential energy curve for internal rotation about the central P–P bond (Fig. 2) in this case has four minima (two pairs of identical minima) and four transition states, two of which are equivalent. The first minimum corresponds to a *gauche* conformation with C_2 symmetry as predicted by all computational methods. The symmetry of the doubly eclipsed, highest transition state on the potential energy curve was found to depend on the level of computations used. Calculations with small basis sets (HF/3-21G* and B3LYP/3-21G*) have predicted this structure to have C_{2v} symmetry, similar to that found for the corresponding transition state of tetramethyldiphosphine, while calculations with larger basis sets have resulted in a structure with C_2 symmetry. Another feature of tetrasilyldiphosphine is that the *anti* structure having C_{2h} symmetry is another transition state, although very low, and not a stable minimum as in the case of tetramethyldiphosphine. The stable minimum has a slightly bent *anti* conformation with C_2 symmetry, again predicted at all computational levels used. The relative stability of the two minima changes considerably when electron correlation is introduced at the B3LYP or MP2 level. The computations without inclusion of the electron correlation at the HF level predict the *gauche* conformation of tetrasilyldiphosphine to be more stable than the distorted *anti* conformer by about 6 kJ mol^{-1}. The distorted *anti* conformer becomes slightly more stable (by 1.2 kJ mol^{-1} at most at the MP2/6-311+G* level) than the *gauche* conformer with inclusion of the electron correlation into the computations.

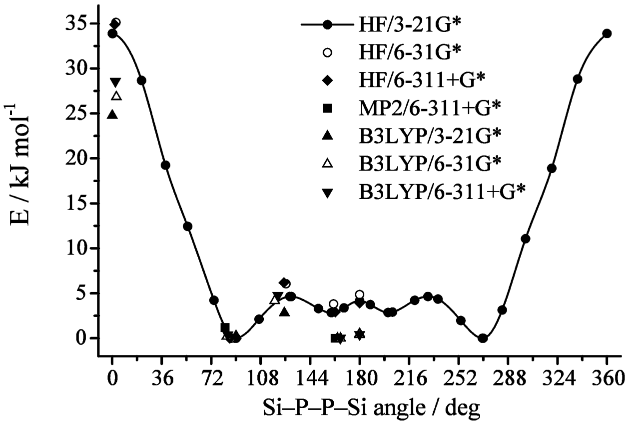

Fig. 2 Potential energy curve for internal rotation about the central P–P bond in tetrasilyldiphosphine.

Similar symmetry changes dependent on the basis set are observed for the $P(SiH_3)_2$ radical. While the dimethylphosphido radical is found to possess C_{2v} symmetry by all theoretical methods used in the present study, the symmetry of the structure of the disilylphosphido radical changes from C_{2v} to C_2 when going from 3-21G* to larger basis sets including the basis set with effective core potentials. The deviation from C_{2v} symmetry (indicated by the extent of the silyl group torsions) is highest at the MP2/6-311+G* level.

Vibrational spectra

Comparison of the experimental IR and Raman frequencies for the skeletal vibrations of tetramethyldiphosphine with the corresponding theoretical ones is presented in Table A of the ESI. The analysis has concentrated on the skeletal vibrations, as these vibrations play the predominant role in the dissociation of the P–P bond. The computed frequencies are generally in good agreement with the observations,[5,7] although there is a difference between the originally reported[5] assignment and that made on the basis of the computed spectra of tetramethyldiphosphine for the bending modes of the $C_2P–PC_2$ skeleton. The original assignment was made supposing that the scissoring motion should be at lower frequency than the wagging motion, based on the previous experience with molecules including the PC_3 fragment.[5] However, the computed vibrational spectra have shown that the picture is complicated by coupling of these two modes, although one of the computed scissoring modes is higher in frequency than one of the wagging modes for all levels of theory. In addition, one of the scissoring modes is computed to differ only slightly from the higher frequency twisting mode. This may result in peak overlap in the experimental spectra and complicate the analysis. Furthermore, the computed methyl torsional frequencies lie very close to the skeletal bending vibrations, making the assignment even more difficult. These discrepancies suggest that a more thorough vibrational analysis of the IR and Raman spectra of tetramethyldiphosphine may be necessary. The assignment of bending modes for the *gauche* conformer of tetramethyldiphosphine is rather complicated by vibrational coupling. Only the stretching and torsion modes presented in Table A show a small amount of coupling and so can be compared with the corresponding modes of the *anti* conformer of tetramethyldiphosphine.

In general, the P–C stretching vibrations computed at the B3LYP/6-311+G* level show closer agreement with the experimental frequencies, while the P–P stretching is better reproduced by the MP2/6-311+G* spectra. Although the magnitudes vary, all computed spectra agree on the trends of the changes in the vibrational frequencies observed experimentally when going from the *anti* to the *gauche* conformer of tetramethyldiphosphine. The P–C stretching frequencies do not change much (the computed difference is within 4 cm^{-1} for the higher level calculations), while there is a considerable decrease in the P–P stretching frequency, by 28 cm^{-1} as computed at the MP2/6-311+G* level, with the observed difference being 26 cm^{-1}. Surprisingly, this difference in stretching frequency is associated with a slight shortening (Table 1) of the P–P bond length in the *gauche* conformer as compared to that in the *anti* conformer.

The computed P–Si and the P–P stretching frequencies in tetrasilyldiphosphine are very similar and the analysis revealed coupling between these modes. Comparison of the stretching modes of the *gauche* and *anti* conformers of the tetrasilyldiphosphine and of these with corresponding modes of tetramethyldiphosphine is also not straightforward because of the vibrational coupling. The trends are, however, the same as for the conformers of tetramethyldiphosphine (Table B, ESI).

Dissociation

The dissociation enthalpies increase considerably with introduction of electron correlation, with the differences as large as 110 kJ mol^{-1} for tetramethyldiphosphine (Table 3) and 125 mol^{-1} for tetrasilyldiphosphine (Table 4), when going from the HF/6-311+G* level to the MP2/6-311+G* level of calculations. The change in the calculated reaction entropy is considerably smaller over the whole spectrum of the methods and it does not exceed 15 J mol^{-1} K^{-1}. A difference in entropy of this size would imply only a 4.5 kJ mol^{-1} change in the calculated Gibbs free energy of the reaction at 298 K, according to the equation $\Delta G = \Delta H - T\Delta S$. The highest dissociation enthalpies for both tetramethyldiphosphine and tetrasilyldiphosphine are computed utilising the G2 method. Although there is no direct experimental thermochemical data on the homolytic dissociation of tetramethyldiphosphine into dimethylphosphido radicals, indirect information about the energy of dissociation of the P–P bond in tetramethyldiphosphine may be obtained from the difference in experimental mass-spectral appearance potentials of $P_2Me_4^+$ and PMe_2^+ ions through the release of neutral PMe_2 radical.[10] This difference amounts to a rather high value of 443.8 kJ mol^{-1}, supporting the higher dissociation enthalpy computed at the G2 level or other levels including electron correlation, than that determined at the HF level.

For both molecules a gradual decrease in the dissociation enthalpy is observed with increase of the basis set using the B3LYP method (Tables 3 and 4), while the enthalpies of dissociation corrected for BSSE show less variation over the range of methods with electron correlations included. Values of 201.9, 189.5, 186.7, 189.8, and 188.9 kJ mol^{-1} for the dissociation enthalpy corrected for BSSE were computed at the MP2/6-311+G*, B3LYP/ECP, B3LYP/3-21G*, B3LYP/6-31G*, and B3LYP/6-311+G* levels of theory, respectively, for tetramethyldiphosphine. The corresponding values for tetrasilyldiphosphine are 205.3, 188.3, 185.8, 187.5, and 187.0 kJ mol^{-1}. The thermodynamic calculations at the B3LYP/ECP or even B3LYP/3-21G* levels thus show satisfactory performance, taking into account the amount of computational time required for other higher-level methods.

It has been realised that the experimentally observable enthalpy of dissociation, also called bond dissociation energy (ΔH_{diss}, BDE), of a compound X–Y does not necessarily resemble the actual energy content of the X–Y bond [bond energy, BE, D(X–Y)], because of the reorganisation of the radicals with the energy $\Delta E_{\mathrm{reorg}}$.[21] Various schemes have been proposed for direct calculation of bond energies,[21–23] from which reorganisation energies then can be derived according to the equation $\Delta E_{\mathrm{diss}} = D_0(\mathrm{X{-}Y}) + \Delta E_{\mathrm{reorg}}(\mathrm{X}) + \Delta E_{\mathrm{reorg}}(\mathrm{Y})$,[21] corresponding to the dissociation energy of the hypothetical vibrationless state of the molecule at 0 K. The origin of the

Table 3 Theoretical thermochemical parameters (ΔH_{diss}, with BSSE in parentheses/kJ mol^{-1}; ΔS_{diss}/J mol^{-1} K^{-1}) for the homolytic dissociation of the P–P bond in tetramethyldiphosphine at 298 K, P–P bond energy corrected for BSSE [D_0(P–P)/kJ mol^{-1}], energy of the P–P bond distortion [ΔE(P–P)/kJ mol^{-1}], and the energy of the relaxation of the fragments ($2\Delta E_{\mathrm{reorg}}$/kJ mol^{-1})

Parameter	HF/3-21G*	HF/6-31G*	HF/6-311+G*	MP2/6-311+G*	B3LYP/ECP[a]	B3LYP/3-21G*	B3LYP/6-31G*	B3LYP/6-311+G*	G2
ΔH_{diss}	132.9 (−30.0)	115.6 (−6.3)	116.5 (−7.4)	227.3 (−25.4)	194.7 (−5.2)	216.9 (−30.2)	196.6 (−6.8)	193.6 (−4.7)	256.1
ΔS_{diss}	184.3	182.0	181.5	186.5	186.8	179.3	184.7	185.9	182.0
$2\Delta E_{\mathrm{reorg}}$[b]	−2.5	−2.8	−2.8	−2.8	−2.9	−2.5	−2.8	−3.1	—
ΔE(P–P)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	—
D_0(P–P)	116.0	122.8	122.8	214.6	203.0	200.0	203.6	203.1	—

[a] 6-31G* basis set on first row elements and Lanl2DZ on phosphorus. [b] The reorganisation energy computed for two halves of the dissociating molecule.

Table 4 Theoretical thermochemical parameters (ΔH_{diss}, with BSSE in parentheses/kJ mol^{-1}; ΔS_{diss}/J mol^{-1} K^{-1}) for the homolytic dissociation of the P–P bond in tetrasilyldiphosphine at 298 K, P–P bond energy corrected for BSSE [D_0(P–P)/kJ mol^{-1}], energy of the P–P bond distortion [ΔE(P–P)/kJ mol^{-1}], and the energy of the relaxation of the fragments ($2\Delta E_{\mathrm{reorg}}$/kJ mol^{-1})

Parameter	HF/3-21G*	HF/6-31G*	HF/6-311+G*	MP2/6-311+G*	B3LYP/ECP	B3LYP/3-21G*	B3LYP/6-31G*	B3LYP/6-311+G*	G2
ΔH_{diss}	146.5 (−40.6)	119.6 (−11.9)	117.1 (−11.8)	242.5 (−37.2)	194.1 (−5.8)	224.0 (−38.2)	195.7 (−8.2)	194.8 (−7.8)	260.6
ΔS_{diss}	198.4	200.3	204.0	184.4	210.9	200.7	190.8	192.5	200.3
$2\Delta E_{\mathrm{reorg}}$[b]	−4.5	−5.4	−5.3	−3.4	−3.1	−2.9	−3.1	−2.6	—
ΔE(P–P)	0.3	0.4	0.4	0.3	0.2	0.2	0.2	0.2	—
D_0(P–P)	119.2	121.8	119.2	216.2	200.1	197.6	199.2	198.2	—

[a] 6-31G* basis set on first row elements and Lanl2DZ on phosphorus and silicon. [b] The reorganisation energy computed for two halves of the dissociating molecule.

reorganisation energies derived in this way has been left unexplained, however, for the majority of chemical compounds. Considering the P_2Me_4/PMe_2 and $P_2(SiH_3)_4/P(SiH_3)_2$ systems, because the structures of the fragments in the diphosphines are different from those in the free radicals, we can split the dissociation reaction into two hypothetical steps. In the first step, instantaneous breaking of the central bond produces two fragments, which retain the structure of those in the original molecules. This requires energy ΔE_{inst}. In the second step, relaxation of the two fragments releases $2\Delta E_{\text{reorg}}(X)$. The observed dissociation energy is therefore $\Delta E_{\text{diss}} = \Delta E_{\text{inst}} - 2\Delta E_{\text{reorg}}(X)$. A simple mechanical analogy of this process is a model consisting of two identical flexible balls with a force constant f_b, and undistorted radius r_0 connected through their centres by a spring with force constant f_s and undistorted length l_0. The force constant f_b corresponds to deformation of the ball along the direction of the connecting spring and has the same dimensions as the spring's force constant f_s. The undistorted length of the spring is smaller than twice the radius of the undistorted ball. In this case the spring becomes strained and the balls are also distorted. The total potential energy of the system of balls connected by the spring compared to the undistorted spring and balls is thus equal to the sum of potential energies stored in the balls and the spring:

$$E_{\text{total}} = \frac{f_s(d-l_0)^2}{2} + f_b\left(r_0 - \frac{d}{2}\right)^2 \qquad (1)$$

where d is the length of the distorted spring in the system. In the equilibrium

$$\frac{\partial E_{\text{total}}}{\partial d} = \left(f_s + \frac{f_b}{2}\right)d - f_s l_0 - f_b r_0 = 0 \qquad (2)$$

and thus the equilibrium distance d_{eq} is calculated as

$$d_{\text{eq}} = \frac{f_s l_0 + f_b r_0}{f_s + \dfrac{f_b}{2}} \qquad (3)$$

By knowing the equilibrium length of the spring the relationship of energies stored in the distorted spring and two distorted balls is then calculated by substituting d in eqn. (1) by the equilibrium distance obtained in eqn. (3):

$$\frac{E_{\text{spring}}^{\text{eq}}}{2E_{\text{ball}}^{\text{eq}}} = \frac{f_b}{2f_s} \qquad (4)$$

The energy required to break the distorted spring connected to the distorted flexible balls, $\Delta E_{\text{diss}} = E_{\text{inst}} - 2\Delta E_{\text{ball}}(X)$, can be related to the energy, $D_0(X\text{–}X)$, required to break the same undistorted spring, by the equation (see Fig. 3):

$$D_0(X\text{–}X) = \Delta E_{\text{diss}} + 2\Delta E_{\text{ball}}(X) + \Delta E_{\text{spring}} \qquad (5)$$

In relation to the diphosphines, the energy $D_0(P\text{–}P)$ represents the P–P bond energy content and $2\Delta E_{\text{ball}}(X)$ corresponds to the relaxation energy, $2\Delta E_{\text{reorg}}(X)$, of the fragments, as shown in Fig. 3. The reorganisation energy, in contrast to the previous definition,[21] is thus defined as the energy of structural changes, calculated as a difference between energies obtained in the full optimisation of the radicals and those obtained by single point calculations for the corresponding unrelaxed halves of the dissociating molecules. The same reorganisation energy may be obtained as the difference between the energy of dissociation of the optimised molecule into two isolated fragments retaining their in-molecule geometries and the dissociation energy of the molecule into two optimised structures, $\Delta E_{\text{inst}} - \Delta E_{\text{diss}}$ (Fig. 3). The calculation of the ΔE_{spring} term in the equation defining the bond energy content requires knowledge of the force constants of the spring (bond) as well as that of the balls (substituents as a whole). By using the geometries of tetramethyldiphosphine and tetrasilyldiphosphine optimised at the B3LYP/6-311+G* level, harmonic force constants of the P–P bond and the substituents in these molecules were calculated in the following way. First, several single-point energy calculations were performed at the B3LYP/6-311+G* level with different increasing P–P bond lengths close to the fully optimised values keeping the structure of the substituents at that obtained in full optimisation of the diphosphines. A harmonic quadratic potential was then fitted to the obtained relative energies compared to the fully optimised structures. The quadratic term of the potential corresponds to the P–P bond force constant f_s. Then the structures of the substituents were allowed to optimise at each point of the calculations keeping the P–P bond fixed. The difference of the relative energies at each fixed P–P distance obtained in these two calculations corresponds to the change in the reorganisation energy of the two substituents at the particular P–P distance. Twice the quadratic term from the harmonic quadratic potential fit to these values thus corresponds to the substituent's force constant f_b. By using the reorganisation energy and force constants for the P–P bond and the substituents, the energy of the distortion of the bond can be calculated from eqn. (4). The results of these calculations are presented in Table 5. The same ratio of the force constants was assumed for all methods involved in the study and the corresponding contributions of the energy stored in the P–P bond, $\Delta E(P\text{–}P)$, corresponding to ΔE_{spring}, were calculated. These results, the energies, required to break the undistorted P–P bond, $D_0(P\text{–}P)$, from eqn. (5) together with standard thermodynamic parameters of the dissociation reaction are summarised in Tables 3 and 4.

Table 5 Force constants (kJ mol^{-1} pm^{-2}) for the P–P bond, f_s, and for the substituents, f_b, and energies stored in the bond, $\Delta E(P\text{–}P)$, and the substituents, $2\Delta E_{\text{reorg}}$, (kJ mol^{-1}) for tetramethyldiphosphine and tetrasilyldiphosphine computed at the B3LYP/6-311+G* level

Parameter	f_s	f_b	$2\Delta E_{\text{reorg}}$	$\Delta E(P\text{–}P)$
$P_2(CH_3)_4$	0.0413	0.0027	3.1	0.1
$P_2(SiH_3)_4$	0.0371	0.0056	2.6	0.2

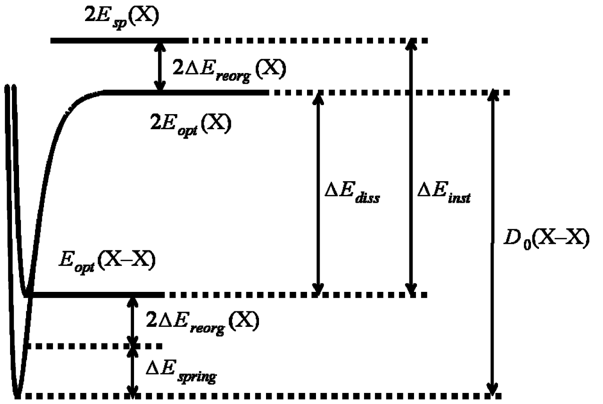

Fig. 3 Definition of the bond energy content $D_0(X\text{–}X)$ using the dissociation energy $\Delta E_{\text{diss}} = 2E_{\text{opt}}(X) - E_{\text{opt}}(X\text{–}X)$ and the energy of structural relaxation of the fragments $2\Delta E_{\text{reorg}}(X) = 2E_{\text{opt}}(X) - 2E_{\text{sp}}(X)$. E_{opt} and E_{sp} denote the energies obtained in the full optimisation and single-point energy calculations, respectively.

The P–P bond energy calculated by the above formalism at the MP2/6-311+G* level appears to be in reasonable agreement with that obtained by the classical approach based on the least-squares fitting of the bond energy terms to the atomisation energy of several compounds with P–P bonds,[3] 211 kJ mol^{-1}. The P–P bond in $P_2(SiH_3)_4$ appears to be slightly stronger, as suggested by both bond dissociation enthalpy and bond energy calculated by the proposed formalism at the MP2/6-311+G* level, although it does not coincide with a shorter bond. Instead, according to the MP2/6-311+G* computations, the P–P bond in the lowest energy conformer of $P_2(SiH_3)_4$ is about 3 pm longer than the P–P bond in the lowest energy conformer of P_2Me_4 (Tables 1 and 2). Although the values of the P–P bond energy are computed to be up to 19 kJ mol^{-1} smaller at the B3LYP level than at the MP2 level, they are still reasonable estimates, compared to the HF values. The B3LYP calculations predict a slightly stronger P–P bond in tetramethyldiphosphine than in tetrasilyldiphosphine.

Pyrolysis experiments[9] with tetramethyldiphosphine have indicated that the decomposition product, trimethylphosphine, appears at a temperature of about 260 °C. The equilibrium constant of homolytic dissociation obtained using the computed thermochemical parameters suggests, however, that the dissociation would not proceed to any detectable extent at this temperature. This may indicate that homolytic dissociation is not the first step in the mechanism of thermal decomposition of tetramethyldiphosphine, which most probably involves rearrangement mechanisms and may not be unimolecular.

Conclusions

The current *ab initio* calculations, which have shown that two conformers are present in the gas phase of tetramethyldiphosphine, are inconsistent with the previous electron diffraction results, which indicated the existence of a single *anti* conformer of the molecule. The calculations support the notion of the large-amplitude torsional motion about the central P–P bond in tetramethyldiphosphine. The calculated barriers to torsion are 13.1 and 31.6 kJ mol^{-1} as computed at the HF/3-21G* level. The higher levels of theory predict even lower barriers to torsion in tetramethyldiphosphine (Fig. 1). Although there is a general agreement between the computed and experimental structural parameters, a large difference is observed for the P–P–C angles (Table 1). This seems to be a consequence of the use of an inappropriate single-conformer model in the refinements based on the experimental electron diffraction data. These differences suggest that re-determination of the structure of tetramethyldiphosphine in the gas phase is necessary.

The results of MP2/6-311+G* thermochemical calculations for homolytic dissociation of tetramethyldiphosphine and tetrasilyldiphosphine are in closest agreement with the thermodynamic parameters computed by the G2 method. It has also been shown that the B3LYP method, utilising effective core potentials or even small basis sets, provides a reasonable estimate of the dissociation enthalpy, close to that achieved by far more expensive MP2 calculations. Reasonable estimates of the entropy change in the dissociation reaction of the title compounds are provided by fast HF calculations even with small basis sets. All these allow us to conclude that the B3LYP method with the effective core potentials or even the small 3-21G* basis set may be a reasonable method applicable to large dissociating systems containing similar fragments, such as tetrakis(disilyl)diphosphine.[1]

For the diphosphines studied here the proposed approach to calculation of bond energy content based on energetics of structural changes upon dissociation produces values in agreement with the classical approach, in which bond energies are derived from the atomisation energies of the compounds. The present approach will be also tested on more crowded diphosphines for comparison.

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