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Article

Structural Changes, P–P Bond Energies, and Homolytic Dissociation Enthalpies of Substituted Diphosphines from Quantum Mechanical Calculations

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The molecular structures of the diphosphines $P_2[CH(SiH_3)_2]_4$, $P_2[C(SiH_3)_3]_4$, $P_2[SiH(CH_3)_2]_4$, and $P_2[Si(CH_3)_3]_4$ and the corresponding radicals $P[CH(SiH_3)_2]_2$, $P[C(SiH_3)_3]_2$, $P[SiH(CH_3)_2]_2$, and $P[Si(CH_3)_3]_2$ were predicted by theoretical quantum chemical calculations at the HF/3-21G*, B3LYP/3-21G*, and MP2/6-31+G* levels. The conformational analyses of all structures found the gauche conformers of the diphosphines with C_2 symmetry to be the most stable. The most stable conformers of the phosphido radicals were also found to possess C_2 symmetry. The structural changes upon dissociation allow the release of some of the energy stored in the substituents and therefore contribute to the decrease of the P–P bond dissociation energy. The P–P bond dissociation enthalpies at 298 K in the compounds studied were calculated to vary from –11.4 kJ mol^{-1} ($P_2[C(SiH_3)_3]_4$) to 179.0 kJ mol^{-1} ($P_2[SiH(CH_3)_2]_4$) at the B3LYP/3-21G* level. The MP2/6-31+G* calculations predict them to be in the range of 52.8–207.9 kJ mol^{-1}. All the values are corrected for basis set superposition error. The P–P bond energy defined by applying a mechanical analogy of the flexible substituents connected by a spring shows less variation, between 191.3 and 222.6 kJ mol^{-1} at the B3LYP/3-21G* level and between 225.6 and 290.4 kJ mol^{-1} at the MP2/6-31+G* level. Its average value can be used to estimate bond dissociation energies from the energetics of structural relaxation.

Introduction

The concept of bond energy has been useful in many areas of chemistry and thermochemistry. According to the classic definition of bond energy, the sum of the energies of all bonds in a compound is equal to the compound's atomization energy. Thus for a compound containing only similar bonds, such as methane, the calculation of the average C−H bond energy is straightforward and equals one-quarter of its atomization energy. For hypothetical vibrationless states at 0 K, the experimental atomization energy of methane is 1756 kJ mol^{-1},[1] and the C−H bond energy is thus 439 kJ mol^{-1}. The energies of other bonds, such as the C−C bond in ethane, can then be derived from the atomization energy of ethane using the value for the average C−H bond energy obtained for methane. In this way, the C−C bond energy in ethane is calculated to be 349 kJ mol^{-1}.[1] One might suppose that the bond dissociation energy, or in other words the observable energy of homolytic bond dissociation, of a compound would then be equal to the energy of that bond. However, this only holds for diatomic molecules. In polyatomic molecules, bond dissociation energies appear to differ from the energy content of the dissociating bonds. For example, the enthalpy of dissociation reaction of ethane, $C_2H_6 \rightarrow 2CH_3$, for hypothetical vibrationless states at 0 K, 399 kJ mol^{-1},[1] is not equal to the energy of the C−C bond calculated from atomization energies by following the formalism discussed above. It has been proposed that this is due to reorganization of the products, and thus usage of the concept of radical reorganization energy was suggested. The radical reorganization energy was calculated as the difference between the observed bond dissociation energy and the bond energy obtained by other methods (e.g., atomization energies, as described above), $2\Delta E_{\mathrm{reorg}}(\mathrm{X}) = \Delta E_{\mathrm{diss}} - D_0(\mathrm{X-X})$.[2]

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(1) The experimental atomization energies of methane and ethane and the enthalpy for homolytic dissociation of ethane into methyl radicals at 298 K were obtained using thermodynamic data from NIST Standard Reference Database Number 69, release March, 2003, http://webbook.nist.gov/chemistry. The standard enthalpies at 298 K were converted to those in the vibrationless state at 0 K by applying corresponding corrections calculated at the B3LYP/6-311+G** level.

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In our recent work, we have made an attempt to define the reorganization energy as the energy of structural relaxation of the fragments. This energy is calculated as the difference between the energies of the fragments retaining their in-molecule geometry and those of the corresponding free radicals. An X−X bond energy was defined on the basis of a simple mechanical analogy of two flexible balls connected by a spring as $D_0(\mathrm{X-X}) = \Delta E_{\mathrm{diss}} + 2\Delta E_{\mathrm{reorg}}(\mathrm{X}) + \Delta E(\mathrm{X-X})$, where $D_0(\mathrm{X-X})$ is the intrinsic energy content of the X−X bond corresponding to the dissociation energy of the unsubstituted X−X bond, ΔE_{diss} is the observable bond dissociation energy, $\Delta E_{\mathrm{reorg}}(\mathrm{X})$ is the energy of the structural relaxation of the fragments, and $\Delta E(\mathrm{X-X})$ is the energy of the distortion of the X−X bond in the compound with the substituents compared to the unsubstituted X−X bond.[3] The difference between this approach and the estimation of the bond energy by using the formula $D_0(\mathrm{X-X}) = \Delta E_{\mathrm{diss}} + 2\Delta E_{\mathrm{reorg}}(\mathrm{X})$ is that the former takes into account the energy of the distortion of the central bond, $\Delta E(\mathrm{X-X})$, and thus may be presumed to be more accurate. All these values can be estimated by quantum-mechanical calculations, and the results for the P−P bond energy in tetramethyldiphosphine and tetrasilyldiphosphine obtained from the parameters of homolytic dissociation of the P−P bond were found to be in agreement with the P−P bond energy computed by the classic approach through atomization energies.[3]

The small energies of structural relaxation in the cases of tetramethyldiphosphine and tetrasilyldiphosphine together with the high P−P bond energy result in large P−P bond dissociation energies in these compounds. The observation of spontaneous homolytic dissociation upon melting of tetrakis(disyl)diphosphine, $P_2\{CH[Si(CH_3)_3]_2\}_4$, suggests, however, that more crowded substituents and consequently bigger relaxation energies lead to a low dissociation energy of the P−P bond.[4]

In the present study, we have investigated the structures of derivatives of tetramethyldiphosphine and tetrasilyldiphosphine, increasingly loaded with sterically demanding substituents, concentrating on the relationships between the structural changes upon dissociation, their energetics, dissociation energies, and the P−P bond energies. Knowing the relationships between these quantities is important in designing new compounds with desired behavior under given conditions toward homolytic dissociation and the production of free radicals. The molecules studied, except tetrakis(trimethylsilyl)diphosphine, have not yet been synthesized, and their structures, determined by either theoretical or experimental techniques, have not been reported. The available experimental structural parameters for similar compounds are used for comparison with our theoretical results.

Theoretical Calculations

Gas-phase quantum mechanical calculations for the substituted diphosphines $P_2[CH(SiH_3)_2]_4$, $P_2[C(SiH_3)_3]_4$, $P_2[SiH(CH_3)_2]_4$, and $P_2[Si(CH_3)_3]_4$ as well as spin-unrestricted open-shell optimizations for the corresponding radicals $P[CH(SiH_3)_2]_2$, $P[C(SiH_3)_3]_2$, $P[SiH(CH_3)_2]_2$, and $P[Si(CH_3)_3]_2$ were made utilizing the Gaussian98 series of programs.[5] Initially, conformational analyses for all molecules were performed using molecular mechanics and employing the built-in universal force field (UFF).[6] The lowest-energy conformers from these calculations as well as several conformers with different torsional angles around the central P−P bond and the adjacent P−C or P−Si bonds were then optimized at the Hartree−Fock (HF) level employing the standard 3-21G* basis set[7] to ensure that the most stable conformers were found. Vibrational frequency analyses were performed at the HF level of theory for the lowest-energy conformers to confirm the nature of the computed stationary points as real minima (no imaginary frequencies) and to provide estimates of thermal energy corrections for calculation of standard enthalpies of dissociation, 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 the dissociation of the systems in question is small (in the region of 1.0 kJ mol^{-1}), and it was ignored in this study. The most stable structures were then fully optimized at the B3LYP/3-21G* level of theory.[8] The STABLE calculations on the optimized structures of the radicals were performed at the B3LYP/3-21G* level to confirm that the structures that had been obtained did indeed correspond to the lowest electronic states. The calculations at the B3LYP/3-21G* level had been shown to perform as well as the calculations employing the B3LYP functional with much larger basis sets for tetramethyldiphosphine and tetrasilyldiphosphine,[3] when the correction for basis set superposition error is applied. In addition, application of the

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Table 1. Selected Theoretical Parameters[a] (Bond Lengths in pm, Bond Angles and Dihedral Angles in degrees) and Absolute Energies (au) for the Computed Lowest-Energy Conformers of the Diphosphines and Corresponding Radicals with the Spin Density (SD) on Phosphorus

parameter	B3LYP/3-21G*	MP2/6-31+G*	parameter	B3LYP/3-21G*	MP2/6-31+G*
$P_2[CH(SiH_3)_2]_4$			$P_2[SiH(CH_3)_2]_4$		
P−P	223.4	221.6	P−P	222.7	221.4
P−C	190.2	188.4	P−Si	225.9	225.8
P−C	187.7	186.0	P−Si	225.6	225.1
(Si−C)$_{mean}$	190.3	190.2	(Si−C)$_{mean}$	189.1	188.6
(Si−C−P)$_{mean}$	112.3	112.7	(C−Si−P)$_{mean}$	110.2	109.7
C−P−C	105.4	106.1	i−P−Si	103.8	104.9
C−P−P−C	84.6	80.0	Si−P−P−Si	83.7	79.4
H−C−P−C	129.4	130.3	H−Si−P−Si	156.0	155.0
H−C−P−C	37.2	40.9	H−Si−P−Si	61.6	60.7
E	−3152.2499092	−3161.9447421	*E*	−2151.8116139	−2158.1124918
$P[CH(SiH_3)_2]_2$			$P[SiH(CH_3)_2]_2$		
P−C	187.4	185.8	P−Si	225.8	225.9
(Si−C)$_{mean}$	189.9	189.6	(Si−C)$_{mean}$	189.2	188.5
(Si−C−P)$_{mean}$	109.6	110.0	(C−Si−P)$_{mean}$	109.4	109.3
C−P−C	100.5	100.2	Si−P−Si	98.1	96.3
H−C−P−C	28.6	28.6	H−Si−P−Si	39.7	34.8
SD	0.9168	1.2842	SD	0.9646	1.1044
E	−1576.0941592	−1580.9325105	*E*	−1075.8611833	−1079.0063485
$P_2[C(SiH_3)_3]_4$			$P_2[Si(CH_3)_3]_4$		
P−P	223.8	228.3	P−P	222.5	221.2
P−C	192.2	190.6	P−Si	225.9	225.7
P−C	189.6	188.1	P−Si	226.4	225.6
(Si−C)$_{mean}$	191.5	191.5	(Si−C)$_{mean}$	189.4	188.8
(Si−C−P)$_{mean}$	113.5	113.6	(C−Si−P)$_{mean}$	110.3	110.2
C−P−C	112.7	112.6	Si−P−Si	109.4	110.9
C−P−P−C	89.9	89.1	Si−P−P−Si	103.5	104.7
Si−C−P−C	133.6	134.0	C−Si−P−Si	179.0	180.0
Si−C−P−C	175.1	177.5	C−Si−P−Si	176.4	170.0
E	−4309.2197086	−4322.570403	*E*	−2308.2811986	−2314.845276
$P[C(SiH_3)_3]_2$			$P[Si(CH_3)_3]_2$		
P−C	188.6	187.0	P−Si	226.3	226.4
P−C	188.6	187.0	(Si−C)$_{mean}$	188.9	188.8
(Si−C)$_{mean}$	190.7	190.5	(C−Si−P)$_{mean}$	109.7	110.0
(Si−C−P)$_{mean}$	110.9	110.8	Si−P−Si	104.0	103.4
C−P−C	113.3	113.6	C−Si−P−Si	162.1	162.2
Si−C−P−C	163.5	163.8	SD	0.9643	1.0616
Si−C−P−C	163.7	163.8	*E*	−1154.097961	−1157.3724663
SD	0.9249	1.0941			
E	−2154.5960801	−2161.2563057			

[a] For angle torsions, the smallest positive value for counterclockwise rotation is shown. For the X−P−P−X torsions, zero angle corresponds to doubly eclipsed conformation. For bond lengths and torsions the first values are for the groups closest to each other.

B3LYP/3-21G* method permits the full geometry optimizations to be performed with reasonable computational effort for such large systems as the series of molecules in the present study. The structures computed at the B3LYP/3-21G* level were then used to obtain electronic energies at the MP2 level[9] with only valence orbitals active and employing the 6-31+G* basis set.[10] These structures were then fully optimized at the MP2(FC)/6-31+G* level to judge the effects of the full optimizations at the higher level on the computed structural and thermodynamic parameters. Single-point energies of the halves of the molecules were also calculated at the corresponding levels of theory. In addition, the bond energies, as equilibrium values, were calculated for vibrationless states at 0 K. The basis set superposition error (BSSE) was estimated by full counterpoise correction at all the nonempirical levels of theory that were used.

Discussion

Molecular Geometries and Conformations. Selected parameters of the structures computed at the higher levels of theory are presented in Table 1 and the optimized structures are shown in Figure 1. The structures obtained from UFF and HF levels can be found in Supporting Information.

In general, the bond lengths and bond angles in the present theoretical structures of the diphosphines computed at the B3LYP/3-21G* level agree reasonably well with corresponding values computed at the MP2/6-31+G* level. A notable difference is observed, however, for the P−P bond in $P_2[C(SiH_3)_3]_4$. It is found to be shorter by 4.5 pm by the B3LYP/3-21G* calculations than predicted by the calculations at the MP2/6-31+G* level. The computed parameters at both the B3LYP/3-21G* and the MP2/6-31+G* level also show good agreement with available solid-state experimental

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Table 2. Uncorrected Theoretical Thermochemical Parameters, $\Delta E_{diss}/\Delta H_{diss}$,[a] with BSSE in Parentheses (kJ mol^{-1}), ΔS_{diss},[b] (J mol^{-1} K^{-1}) for Homolytic Dissociation of the P−P Bond in Substituted Diphosphines and Absolute Values of the Relaxation Energy of the Fragments, $2\Delta E_{reorg}$ (kJ mol^{-1})

parameter	molecular mechanics	HF/3-21G*	B3LYP/3-21G*	B3LYP/3-21G*//MP2/6-31+G*	MP2/6-31+G*
$P_2[CH(SiH_3)_2]_4 \rightarrow 2P[CH(SiH_3)_2]_2$					
$\Delta E_{diss}/\Delta H_{diss}$		73.3/62.1 (−42.8)	161.7/150.5 (−45.9)	208.8/197.6 (−54.7)	209.3/198.1 (−56.4)
ΔS_{diss}		247.9			
$2\Delta E_{reorg}$	60.0	45.5	46.2	43.7	42.0
$P_2[C(SiH_3)_3]_4 \rightarrow 2P[C(SiH_3)_3]_2$					
$\Delta E_{diss}/\Delta H_{diss}$		−45.1/−60.2 (−61.9)	72.3/57.3 (−68.6)	151.2/136.1 (−82.2)	151.7/136.6 (−83.8)
ΔS_{diss}		287.3			
$2\Delta E_{reorg}$	126.6	86.4	72.4	70.2	73.1
$P_2[SiH(CH_3)_2]_4 \rightarrow 2P[SiH(CH_3)_2]_2$					
$\Delta E_{diss}/\Delta H_{diss}$		151.7/143.4 (−47.7)	234.3/226.0 (−47.0)	261.7/253.4 (−44.9)	262.0/253.7 (−45.8)
ΔS_{diss}		220.1			
$2\Delta E_{reorg}$	14.2	12.5	9.2	9.8	11.8
$P_2[Si(CH_3)_3]_4 \rightarrow 2P[Si(CH_3)_3]_2$					
$\Delta E_{diss}/\Delta H_{diss}$		137.5/128.6 (−53.1)	223.9/215.0 (−54.9)	261.3/252.4 (−54.7)	263.5/254.6 (−56.7)
ΔS_{diss}		212.8			
$2\Delta E_{reorg}$	51.8	23.1	19.1	21.6	24.8

[a] ΔE_{diss} is the dissociation energy for vibrationless states at 0 K; ΔH_{diss} is the enthalpy of dissociation at 298 K. [b] ΔS_{diss} is the entropy change in the dissociation reaction at 298 K.

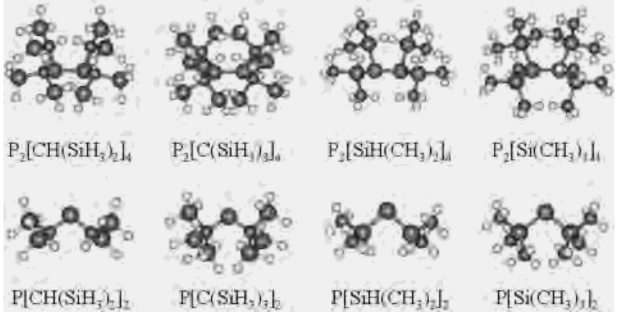

Figure 1. Optimized structures of diphosphines and corresponding radicals obtained at the MP2/6-31+G* level.

parameters in similar crowded diphosphines, such as $P_2\{CH[Si(CH_3)_3]_2\}_4$,[4] $P_2(C_6H_{11})_4$,[11] and $P_2[Si(CH_3)_2C(CH_3)_3]_4$.[12]

The bond lengths computed by molecular mechanics using the UFF appear to be, in general, within 3−6 pm of the corresponding parameters computed by HF, density functional theory (DFT), and MP2 methods, with poorer agreement for the C−P−C and Si−P−Si angles, which were found to be smaller in calculations employing molecular mechanics by up to 15°.

The conformations of the diphosphines studied in the present work were found to change considerably when going to HF, DFT, and MP2 methods from molecular mechanics. At the higher levels the lowest-energy conformers of all four diphosphines are gauche conformers possessing C_2 symmetry, similar to those observed in the solid state for $P_2\{CH[Si(CH_3)_3]_2\}_4$,[4] $P_2(C_6H_{11})_4$,[11] and $P_2[Si(CH_3)_2C(CH_3)_3]_4$.[12]

The main trends in the structural changes of the fragments upon dissociation are similar to those previously observed for tetramethyldiphosphine and tetrasilyldiphosphine.[3] The P−C or P−Si bonds in the radicals become slightly shorter and the C−P−C or Si−P−Si angles smaller. In addition, on average the Si−C bonds in the substituent groups in the radicals also shorten and the corresponding P−Si−C or P−C−Si angles decrease, relieving the accumulated strain. The lowest-energy conformers of all four radicals possess C_2 symmetry, and their conformations are similar to that observed for the bis(disyl)phosphido radical, $P\{CH[Si(CH_3)_3]_2\}_2$.[4]

In all cases, except the diphosphine $P_2[Si(CH_3)_3]_4$, there are also appreciable changes in conformation of the radicals compared to the corresponding parts of the diphosphines. The fragments of the diphosphines $P_2[CH(SiH_3)_2]_4$ and $P_2[SiH(CH_3)_2]_4$ possess C_1 local symmetry, and the local symmetry of the fragments of the diphosphine $P_2[C(SiH_3)_3]_4$ is close to C_s. In these diphosphines, the conformational change involves considerable rotation of one of the substituent groups to adopt the C_2 symmetry found in the corresponding radicals. The fragments of the $P_2[Si(CH_3)_3]_4$ diphosphine already have close to C_2 local symmetry and undergo little conformational change upon dissociation.

Dissociation. The results of thermochemical calculations for homolytic dissociation of the P−P bonds in the compounds studied are summarized in Table 2. The dissociation and reorganization energies computed at the MP2/6-31+G* level using the geometries optimized at the B3LYP/3-21G* level show good agreement with the results obtained in the full optimization of the structures at the MP2/6-31+G* level.

Comparisons of the P−P bond dissociation energies and the P−P bond lengths computed at the MP2/6-31+G* level show that in general a longer P−P bond results in lower dissociation energy. For instance, the longer P−P bond of 228.3 pm in $P_2[C(SiH_3)_3]_4$ compared to 221.6 pm in $P_2[CH(SiH_3)_2]_4$ is associated with a smaller bond dissociation energy, 67.9 kJ mol^{-1} compared to 152.9 kJ mol^{-1}. (The values of the dissociation energies are corrected for BSSE.) There are, however, exceptions. In $P_2[Si(CH_3)_3]_4$, the P−P bond length of 221.2 pm and bond dissociation energy of 206.8 kJ mol^{-1} are both smaller than the P−P bond length of 221.4 pm and bond dissociation energy of 216.2 kJ mol^{-1}

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in $P_2[SiH(CH_3)_2]_4$. A similar trend is observed in the results of the B3LYP/3-21G* calculations.

The reorganization energies of the two radicals that are formed, $2\Delta E_{\mathrm{reorg}}$, computed as the difference between energies obtained in the full optimization of the radicals and those obtained by single point calculations for the corresponding unrelaxed halves of the dissociating molecules, are also presented in Table 2. The calculations indicate direct correlation between the amount of energy stored in the ligands and the decrease in the dissociation energy for all systems in the present study.

The reorganization energies calculated using molecular mechanics reflect the trend in the energies found by HF, DFT, and MP2 methods, but the agreement between values is poor, especially for the larger reorganization energies observed for the $P_2[C(SiH_3)_3]_4$/$P[C(SiH_3)_3]_2$ system. The agreement on average may be improved by scaling the energies from molecular mechanics to those computed at higher levels. A linear equation fitting the absolute values of reorganization energies obtained by molecular mechanics to those found at the B3LYP/3-21G* level is $\Delta E(\mathrm{DFT}) = 0.576\Delta E(\mathrm{UFF}) + 0.3$ kJ mol^{-1}, with a mean standard deviation of 11 kJ mol^{-1}. A similar equation fitting the same values to those computed at the MP2/6-31G* level is $\Delta E(\mathrm{MP2}) = 0.556\Delta E(\mathrm{UFF}) + 2.8$ kJ mol^{-1}, with a mean standard deviation of 6 kJ mol^{-1}.

In our previous work, we have suggested a simple mechanical model for the energetics of bond dissociation on the basis of which the intrinsic energy of the dissociating bond can be estimated.[3] In this model, two identical flexible balls of undistorted radius r_0 are connected by a spring with undistorted length l_0. The equilibrium separation distance in this system is d.

$$\Delta E_{\mathrm{total}} = \Delta E(\mathrm{X{-}X}) + 2\Delta E_{\mathrm{reorg}}(\mathrm{X}) = \frac{f_{\mathrm{s}}(d - l_0)^2}{2} + f_{\mathrm{b}}\left(r_0 - \frac{d}{2}\right)^2 \quad (1)$$

$$D_0(\mathrm{X{-}X}) = \Delta E_{\mathrm{diss}} + 2\Delta E_{\mathrm{reorg}}(\mathrm{X}) + \Delta E(\mathrm{X - X}) \quad (2)$$

$$\frac{\Delta E(\mathrm{X{-}X})}{2\Delta E_{\mathrm{reorg}}(\mathrm{X})} = \frac{f_{\mathrm{b}}}{2f_{\mathrm{s}}} \quad (3)$$

Here, by use of the reorganization energies of the substituents, $\Delta E_{\mathrm{reorg}}(\mathrm{X})$ and the force constants for the P−P bond, f_{s}, and the substituents as a whole, f_{b}, the latter of which is, for this purpose, the derivative of the energy of the fragment with respect to the distance to its companion fragment, the energy of the distortion of the bond, $\Delta E(\mathrm{X - X})$, can be calculated from eq 3. The energy required to break the undistorted P−P bond, $D_0(\mathrm{P{-}P})$, can then be obtained from eq 2 using the dissociation energy ΔE_{diss}.

To apply this model, the harmonic force constants of the bond, f_{s}, and substituents as a whole, f_{b}, were calculated for the present series of diphosphines. In each case, several single-point energy calculations were performed, with different increasing P−P bond lengths in the vicinity of the fully optimized value, keeping the structure of the halves of the molecule fixed at that obtained in full structure optimization of the diphosphine. A harmonic quadratic potential was then fitted to the energies relative to that of the fully optimized structure. The quadratic term of this potential corresponds to the force constant of the P−P bond, f_{s}. Then the structures of the halves of the molecule were allowed to optimize at each point of the calculations, keeping the P−P bond length fixed. The difference of the relative energies at each fixed P−P distance obtained in these two series of calculations corresponds to the reorganization energy of the two substituents at that particular P−P distance. As the second derivative of the potential energy contribution from the two halves of the molecule, $f_{\mathrm{b}}(r_0 - d/2)^2$, relative to their separation distance d, is equal to $f_{\mathrm{b}}/2$, multiplying the quadratic term from the harmonic quadratic potential fit to these values by two thus gives the force constant, f_{b}, for each of the halves of the molecule. The results of these calculations at the B3LYP/3-21G* level are presented in Table 3. It should be noted that the values computed by the HF methods generally agree well with those from DFT, whereas the corresponding values obtained by molecular mechanics are appreciably different.

Table 3. Theoretical Harmonic Force Constants (kJ mol^{-1} pm^{-2}) for the P−P Bond, f_{s}, and the Substituents as a Whole, f_{b}, in the Substituted Diphosphines Computed at the B3LYP/3-21G* Level

parameter	$P_2[CH(SiH_3)_2]_4$	$P_2[C(SiH_3)_3]_4$	$P_2[SiH(CH_3)_2]_4$	$P_2[Si(CH_3)_3]_4$
f_{s}	0.0371	0.0335	0.0415	0.0373
f_{b}	0.0100	0.0155	0.0139	0.0134
$f_{\mathrm{b}}/2f_{\mathrm{s}}$	0.1348	0.2313	0.1675	0.1796

By use of the values of force constants and reorganization energies computed at the B3LYP/3-21G* level for the diphosphines $P_2[Si(CH_3)_3]_4$ and $P_2[C(SiH_3)_3]_4$ (Tables 2 and 3), the values for the P−P bond energies in these compounds are calculated as 191.5 and 92.8 kJ mol^{-1}, respectively. The P−P bond energy appears to be considerably smaller in $P_2[C(SiH_3)_3]_4$ than in $P_2[Si(CH_3)_3]_4$ in this calculation, with no apparent reason for such a diminution in this compound. To reach the same level of the bond energy (about 200 kJ mol^{-1}), greater reorganization energy for the $P[C(SiH_3)_3]_2$ radical would be required. One possible explanation for the greater stabilization of the radical could be that there is more electronic delocalization in $P[C(SiH_3)_3]_2$ than in $P[Si(CH_3)_3]_2$, which would make the $P[C(SiH_3)_3]_2$ radical more stable even without large structural changes. This, however, was ruled out on the basis of only minor differences between the spin-density distributions in the two radicals also presented in Table 1. The theoretical spin-density distribution suggests that the lone electron is located mainly on phosphorus with only a small degree of delocalization. According to the DFT calculations, the delocalization is higher in the cases of the $P[CH(SiH_3)_2]_2$ and $P[C(SiH_3)_3]_2$ radicals, as reflected by a smaller spin density on phosphorus. However, this slight difference does not seem to account for the substantial calculated diminution in the P−P bond energy. In the calculations at the MP2/6-31+G* level, however, the greatest delocalized electron density is found for the radical P[Si-

Table 4. The Energies Stored in the Parameters Vanishing during Dissociation, $2\Delta E_{\text{hidden}}$, Total Reorganization Energies,[a] $2\Delta E^{\text{total}}_{\text{reorg}}$, Energies Stored in the Central P−P Bond, ΔE(P−P), and the Theoretical P−P Bond Energies, D_0(P−P) Corrected for BSSE (kJ mol^{-1}) in the Substituted Diphosphines

parameter	molecular mechanics	HF/3-21G*	B3LYP/3-21G*	B3LYP/3-21G*//MP2/6-31+G*	MP2/6-31+G*
			$P_2[CH(SiH_3)_2]_4$		
$2\Delta E_{\text{hidden}}$	34.7	20.3	20.3	20.3	22.1
$2\Delta E^{\text{total}}_{\text{reorg}}$	94.7	65.8	66.5	64.0	64.1
ΔE(P−P)	7.7	8.9	9.0	8.6	8.6
D_0(P−P)		105.2	191.3	226.7	225.6
			$P_2[C(SiH_3)_3]_4$		
$2\Delta E_{\text{hidden}}$	187.5	105.4	105.4	105.4	107.1
$2\Delta E^{\text{total}}_{\text{reorg}}$	314.1	191.8	177.8	175.6	180.2
ΔE(P−P)	62.7	39.4	41.1	40.6	41.7
D_0(P−P)		124.2	222.6	285.2	290.4
			$P_2[SiH(CH_3)_2]_4$		
$2\Delta E_{\text{hidden}}$	14.1	5.5	5.5	5.5	10.6
$2\Delta E^{\text{total}}_{\text{reorg}}$	28.3	18.0	14.7	15.3	22.4
ΔE(P−P)	0.4	2.8	2.5	2.6	3.8
D_0(P−P)		124.8	204.5	234.7	242.4
			$P_2[Si(CH_3)_3]_4$		
$2\Delta E_{\text{hidden}}$	8.7	2.4	2.4	2.4	7.6
$2\Delta E^{\text{total}}_{\text{reorg}}$	60.5	25.5	21.5	24.0	32.4
ΔE(P−P)	5.1	4.6	3.9	4.3	5.8
D_0(P−P)		114.5	194.4	234.9	245.0

[a] $2\Delta E^{\text{total}}_{\text{reorg}} = 2\Delta E_{\text{hidden}} + 2\Delta E_{\text{reorg}}$.

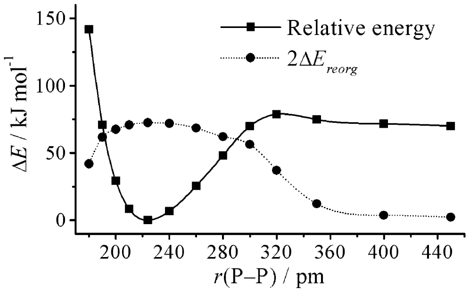

Figure 2. Potential energy curve (■) for homolytic dissociation of the P−P bond in the diphosphine $P_2[C(SiH_3)_3]_4$ and the reorganization energy, $2\Delta E_{\text{reorg}}$ (●), at different P−P distances computed at the B3LYP/3-21G* level of theory.

$(CH_3)_3]_2$, while calculations of the P−P bond energy for the $P_2[Si(CH_3)_3]_4$/$P[Si(CH_3)_3]_2$ system do not result in an unusually small value.

This suggests that there may be stronger effects influencing the bond energy than the degree of electronic delocalization in these series of molecules. To investigate the energetics of dissociation and the energetics of structural changes in the substituents, the potential energy curves for P−P bond dissociation were calculated for the diphosphines $P_2[C(SiH_3)_3]_4$ and $P_2[Si(CH_3)_3]_4$ at the B3LYP/3-21G* level; they are presented in Figures 2 and 3, respectively. Although the lowest-energy conformers of both diphosphines were calculated to have C_2 symmetry, the computations for $P_2[Si(CH_3)_3]_4$ were performed without any symmetry constraint, to investigate the influence of the changing P−P bond length on the overall structure of the molecule. However, the resulting structures retained their original C_2 symmetry, so the calculations for $P_2[C(SiH_3)_3]_4$ were performed taking advantage of the C_2 symmetry, thus greatly reducing the required amount of computational time. The energies stored in the substituents as compared to the optimized radicals at each point are also plotted.

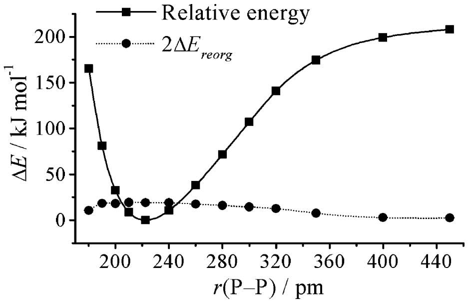

Figure 3. Potential energy curve (■) for homolytic dissociation of the P−P bond in the diphosphine $P_2[Si(CH_3)_3]_4$ and the reorganization energy, $2\Delta E_{\text{reorg}}$ (●), at different P−P distances computed at the B3LYP/3-21G* level of theory.

In a model based on the simple mechanical analogy of a spring (bond) attached to two identical flexible balls (substituents), as used in our previous work,[3] one would expect the energy stored in the substituents to increase with shortening of the central bond. Unexpectedly, the energy stored in the substituents, defined as the difference between the energy obtained in a single-point calculation of the halves of the diphosphines and the energies of fully optimized radicals, is found to change only slightly over a substantial interval of the central P−P bond length. It is even seen to decrease at shorter P−P distances, while the total potential energy rises sharply. This rise cannot be attributed to a change of potential energy of the P−P bond alone. An explanation may be found by analyzing the structural parameters around the phosphorus. In the diphosphines, there are structural parameters that have no meaning in the radical, such as, for example, the P−P−C and P−P−Si bond angles. As the P−P bond shortens, these angles undergo considerably larger changes than the corresponding C−P−C or Si−P−Si angles, as shown in Figures 4 and 5, thus accumulating some strain too.

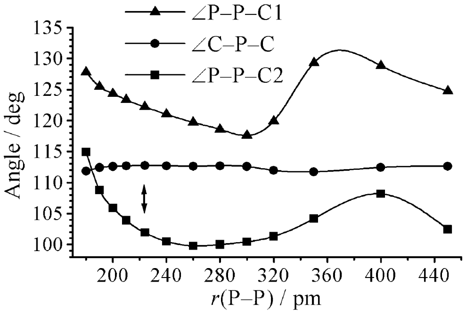

Figure 4. Variation of valence angles around the phosphorus in the diphosphine $P_2[C(SiH_3)_3]_4$ at different P−P distances during dissociation, as calculated at the B3LYP/3-21G* level. The arrow shows the position of the potential energy minimum.

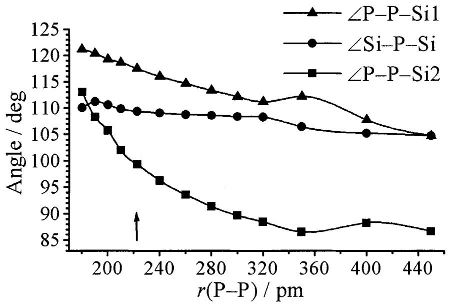

Figure 5. Variation of valence angles around the phosphorus in the diphosphine $P_2[Si(CH_3)_3]_4$ at different P−P distances during dissociation, as calculated at the B3LYP/3-21G* level. The arrow shows the position of the potential energy minimum.

However, as these angles, along with some other parameters, are missing in the radicals, allowing the lone electron on phosphorus to occupy the most favorable position, the total strain in the substituents, measured as the difference between the energy of the fragments retaining their in-molecule geometry and the energy of the fully optimized radicals, is thus underestimated.

This energy associated with the vanishing parameters can be most easily obtained from molecular mechanics as the difference between twice the energy of half of the diphosphine and the energy of the corresponding diphosphine. These values also contain the energy term corresponding to the stretching of the P−P bond itself. It is small, however, as the computed force constants for the P−P bond in Table 3 are in the region of 0.1 kJ mol^{-1} pm^{-1} and cannot be more than a few kJ mol^{-1}. The hidden energies stored in the parameters vanishing during dissociation for all four molecules in the present study are presented in Table 4. They are calculated using energies from molecular mechanics, with the contribution to the total potential energy due to the P−P bond stretch, assumed to be 5 kJ mol^{-1}, subtracted. These hidden energies are scaled by using the equations derived above for reorganization energies and utilized in estimation of the P−P bond energies. These energies confirm our assumption that the $P_2[CH(SiH_3)_2]_4$ and $P_2[C(SiH_3)_3]_4$ diphosphines are considerably more strained than is evident from comparison of the energies of the fragments and the optimized radicals. Larger hidden energies are obtained for the molecules $P[CH(SiH_3)_2]_2$ and $P[C(SiH_3)_3]_2$ for which small dissociation energies and relatively small reorganization energies are observed, while only small hidden energies are calculated for the molecules $P[SiH(CH_3)_2]_2$ and $P[Si(CH_3)_3]_2$. The P−P bond energies, D_0(P−P), are also presented in Table 4. They show less variation in this range of molecules, taking into account the uncertainty in estimation of the hidden energies, than the P−P bond dissociation energies and allow rationalization of their variations. The model using constant bond energy values allows estimation of experimentally observable bond dissociation energies utilizing the energies of structural relaxation, which may be obtained from methods not normally giving accurate bond dissociation energies, such as the HF method or even molecular mechanics, in large molecular systems. In addition, the energy of the distortion of the central bond, ΔE(X−X), is calculated to be rather large in some cases, e.g., 40.6 kJ mol^{-1} for $P[C(SiH_3)_3]_2$, and thus cannot be ignored in calculation of the bond energy. The suggested model takes into account this energy term, instead of just estimating the bond energy from dissociation and reorganization energies alone.

Conclusions

In the present series of compounds, correlation is observed between dissociation energy and the amount of relaxation energy stored in the substituents; the bigger the relaxation effect, the smaller the dissociation energy. There appears to be a weak correlation between the computed P−P bond force constants and the P−P bond dissociation energies, but there is not enough information to show whether this is significant.

The relaxation energy calculated as the difference between energies obtained in the full optimization of the radicals and those obtained by single point calculations for the corresponding unrelaxed halves of the dissociating molecules may not correspond to the total amount of strain in the molecule due to deformation of the substituents, as shown by the computed dissociation energy curves for the substituted diphosphines. Taking into account the hidden energy stored in the parameters vanishing during dissociation leads to all the intrinsic energies of P−P bond for the diphosphines studied falling within a smaller range. Little variation of the intrinsic P−P bond energy would be expected for these compounds, as their substituents have similar electronegativities.

The proposed model can be used to describe the relationship between bond dissociation energy and the amount of strain in the molecule by employing a constant intrinsic bond energy, at least in cases where there is no significant stabilization due to electronic effects. The model also allows identification of the major factors, such as larger relaxation energies, that lead to a lower dissociation energy of the P−P bond.

The compounds studied indicate, not surprisingly, that consecutive combination of two shorter bonds in the substituents (P−C, 188.4−186.0 pm, and C−Si, 190.2 pm, in $P_2[CH(SiH_3)_2]_4$) results in greater strain in the diphosphines than the combination of longer and shorter bonds (P−Si, 225.8−225.1 pm, and C−Si, 188.6 pm, in $P_2[SiH(CH_3)_2]_4$)

with approximately similar length of the central P−P bond as computed at the MP2/6-31+G* level.

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Supporting Information Available: The final Cartesian coordinates of the optimized structures of the lowest-energy conformers of the diphosphines and corresponding radicals obtained at the UFF, HF/3-21G*, B3LYP/3-21G*, and the MP2/6-31+G* levels of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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