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Intra- and Intermolecular Hydrogen Bonding in 2-Phosphinylphenol: A Quantum Chemical Study

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A computational study of 2-phosphinylphenol has been carried out to investigate intramolecular hydrogen bond formation and its consequences in the rest of the molecule. This is an extension of both our synthetic work on organophosphorus derivatives of diphenyl ether and our experimental and computational structure analyses of salicylaldehyde, 2-nitrophenol, and related molecules. Full optimization of the 2-phosphinylphenol geometries was carried out both at the HF/6-31+G** level and, to include electron correlation, at the MP2/6-31G* level. The stabilization energy of the intramolecular hydrogen bonding in 2-phosphinylphenol (28.4 kJ/mol by isodesmic calculation) is smaller than that of the intermolecular hydrogen bonding in the dimer of 2-phosphinylphenol, also computed in this work to be 59.1 kJ/mol per hydrogen bond from the counterpoise interaction energy or 57.4 kJ/mol by BSSE-corrected isodesmic calculation. The closure of the six-membered ring with the intramolecular hydrogen bond apparently introduces energy-costing constraints. The geometrical changes in 2-phosphinylphenol accompanying the formation of the hydrogen bond are similar to those observed in 2-nitrophenol and salicylaldehyde, characterized as resonance-assisted hydrogen bonding. In addition to the lowest energy monomer with the hydrogen bond, two further stable minima of higher energy with no hydrogen bonding were found for 2-phosphinylphenol.

Introduction

Hydrogen bond formation is often the key interaction in both intramolecular and intermolecular interactions. Its understanding carries the potential of correlating structure with chemical properties and of designing molecules with desired characteristics.

Phosphine oxides are potential systems for hydrogen bond formation. It was the unexpected formation of bis(2-hydroxyphenyl)phenylphosphine 10-oxide in the reaction of 10-phenyl-10*H*-phenoxaphosphine 10-oxide with either sodium hydroxide or potassium *tert*-butoxide[2] that prompted our interest in studying intramolecular interactions between nearby hydroxy and phosphoryl groups. The ^{31}P NMR chemical shift of this product, which is downfield from that of triphenylphosphine oxide by 24 ppm,[3] suggested to us hydrogen bonding between the hydroxy and phosphoryl groups. As a first step, a model compound, 2-phosphinylphenol, $2\text{-}H_2P(O)C_6H_4OH$, was chosen to investigate the possibility of hydrogen bond formation by quantum chemical calculation.

Intramolecular hydrogen bonding in simple ortho-substituted derivatives of benzene, such as 2-nitrophenol[4] and salicylaldehyde,[5] has been investigated recently. It seemed to be a natural continuation of these studies to include phosphorus derivatives in this series. In addition to detecting hydrogen bonding, we found it of great interest to determine and understand the structural consequences of hydrogen bond formation in the rest of the molecule.

There have been indications in the literature of the possibility of *intermolecular* hydrogen bond formation in phosphine oxides, either in a dimeric molecule[6] or in a polymeric chain[7] in crystals. To see the possibility of this intermolecular hydrogen bond formation and its stability compared with the intramolecular hydrogen bond, we also computed the geometry of a dimer of 2-phosphinylphenol.

Computational Methods

All calculations were carried out using the Gaussian 94 program.[8] Since 2-phosphinylphenol may exist in different conformations, the potential energy surface of the molecule was scanned in order to find all stable minima. Five minimum structures were found, all of which have been further explored. Full geometry optimizations were carried out for all five structures at the standard HF/6-31G* level using the Berny optimization algorithm as implemented in Gaussian 94. These structures together with their HF optimized geometrical parameters are shown in Figure 1. Harmonic vibrational frequencies were calculated analytically for each of these optimized structures in order to determine if any of them corresponded to saddle points. Since all of these conformers except conformer C refined to geometries with almost perfect C_s symmetry, this symmetry was supposed for the frequency calculations for these four structures.

Conformers A, B, and C appeared to be true minima on the potential energy surface, and they were further investigated. Their structures were also fully optimized at the HF/6-31+G** level. Further geometry optimizations were carried out at the correlated level with the smaller basis set (MP2/6-31G*) in the frozen core approximation. These MP2 geometries are shown in Figure 2. Single-point calculations were carried out for the

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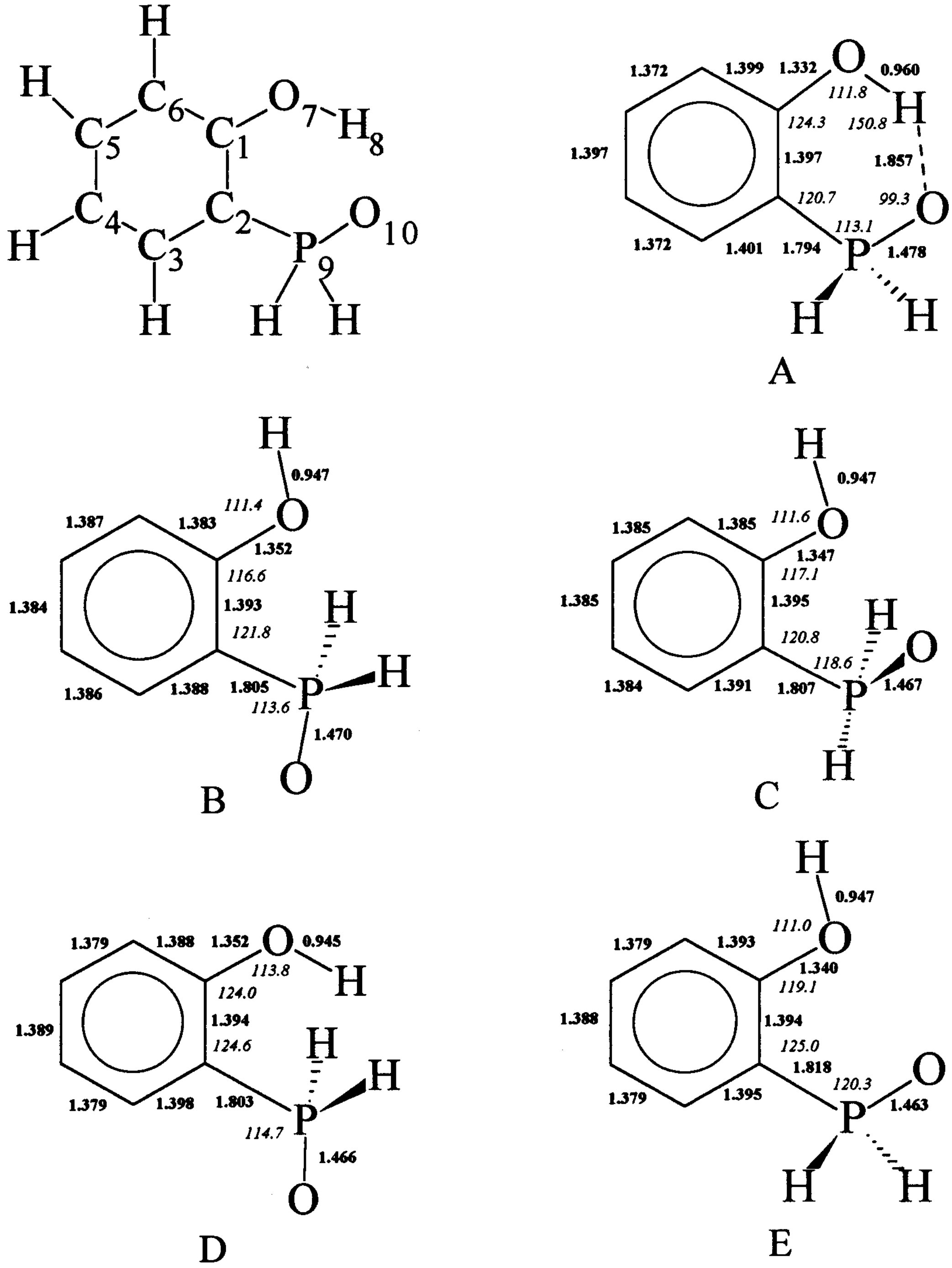


Figure 1. Numbering of atoms in conformer A and five minimum energy structures of 2-phosphinylphenol monomer with their HF/6-31G* optimized geometrical parameters. Conformers A, B, and C are true minima, while D and E are transition-state structures. Bond lengths (Å) are indicated in boldface, bond angles (deg) in italics.

larger basis set (MP2/6-31+G**//HF/6-31+G**). Finally, the geometry of the most stable conformer (A) was also optimized at the MP2/6-31+G** level. The ab initio absolute energies for these calculations are summarized in Table 1, with the energy differences of all conformers compared to the most stable conformer A. It appears that the inclusion of the extra polarization and diffuse functions decreases somewhat the energy differences between conformers A with B and C, respectively.

Two of the five conformers (D and E, see Figure 1) are transition structures with one imaginary frequency for each. They were not optimized further at higher levels, but their energies were also calculated using second-order perturbation theory based on the HF geometries (MP2/6-31G*//HF/6-31G*); see Table 1. The energy differences of the various conformers change somewhat with inclusion of electron correlation with either basis set applied.

To interpret geometrical changes in conformer A compared to its parent molecules, phenol and phenylphosphine oxide, their geometries have also been fully optimized at all levels of calculation used here. The observed structural trends were the same at all levels; therefore only the MP2/6-31G* results will be given.

Since the possibility of intermolecular hydrogen bond formation in related 2-phosphorylated phenols has arisen before,[6,7] the geometry of the dimer of 2-phosphinylphenol was also fully optimized at the HF/6-31G* level. The dimer's geometrical parameters are given in Figure 3. The geometry converged to

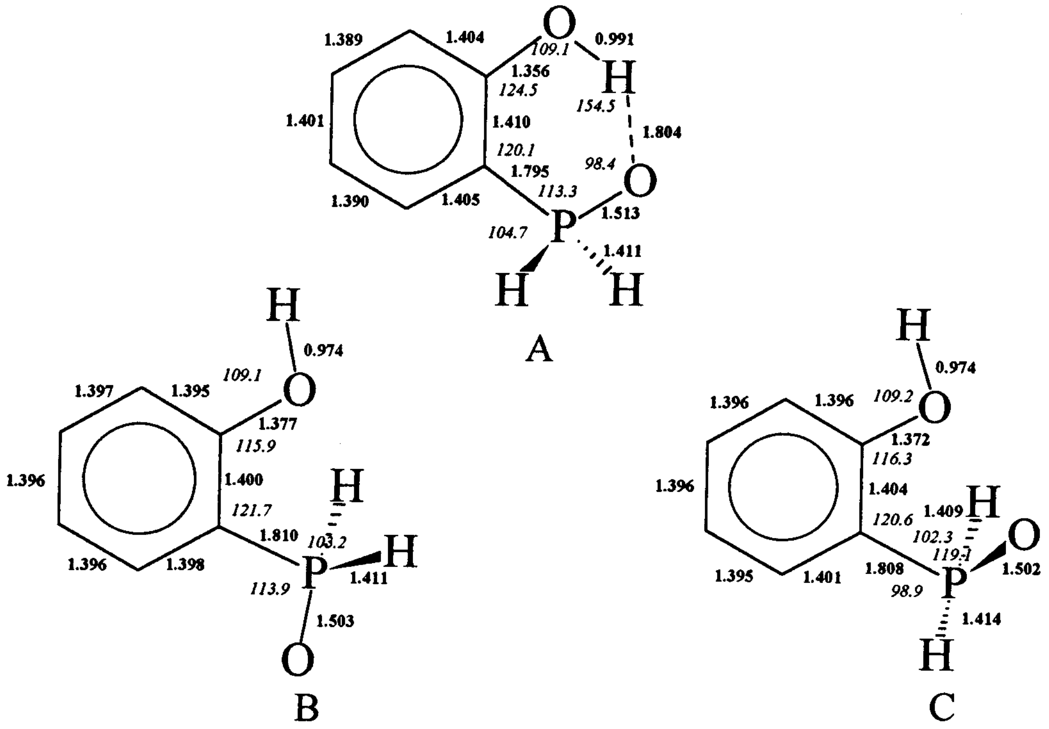


Figure 2. The MP2/6-31G* geometries of conformers A, B, and C of 2-phosphinylphenol. Bond lengths (Å) in boldface; bond angles (deg) in italics.

TABLE 1: Ab Initio Absolute Energies (au) of Conformer A of 2-Phosphinylphenol and Energy Differences (kJ/mol) between Other Forms and Conformer A at Different Levels of Calculation[a]

conformer	HF/6-31G*	HF/6-31+G**	MP2//HF/6-31G*	MP2/6-31G*	MP2//HF/6-31+G**	MP2/6-31+G**
A	−721.734 79	−721.765 72	−722.952 70	−722.957 02	−723.043 25	−723.047 18
B	15.4	13.0	18.7	19.2	15.2	
C	28.5	27.6	26.8	27.0	23.8	
D	37.5		38.7			
E	49.0		48.9			
dimer[b]	−61.0		−88.2			

[a] Without zero point vibrational energy corrections. [b] Compared to two molecules of A.

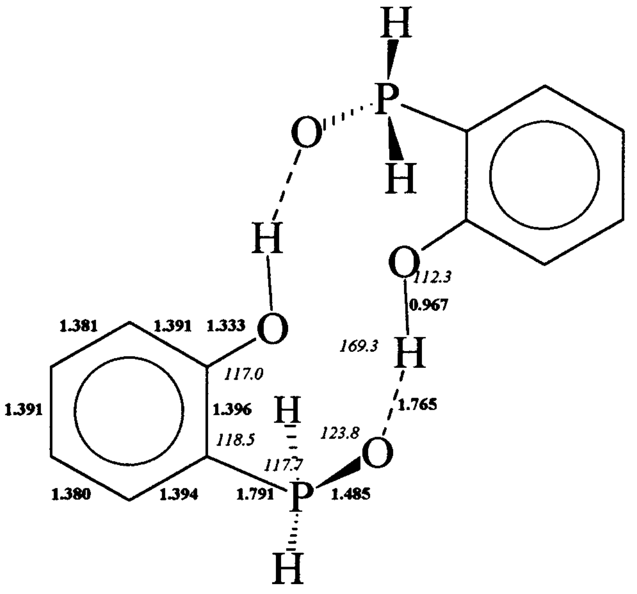


Figure 3. Shape and geometrical parameters of dimeric 2-phosphinylphenol computed at the HF-6-31G* level. Bond lengths are in angstroms, bond angles in degrees. The molecule has C_i symmetry.

a structure with almost perfect C_i symmetry, and this symmetry was assumed for the frequency calculation. This C_i-symmetry dimer turned out to be a stable minimum. Its energy was also calculated with single-point calculation at the correlated MP2/6-31G*//HF/6-31G* level. We note that this may be only one of the stable dimer structures since the full potential energy surface was not scanned.

The electron density was calculated with Spartan 4.0[9] at the HF/6-31G* level for the previously optimized geometry of conformer B for reasons to be discussed later. Slices of the electron density were generated from it using Spartan's graphical interface.

Results and Discussion

Comparison of Different Conformers. Five conformations of the monomeric form of 2-phosphinylphenol were found as stationary points on the potential energy surface. Vibrational analyses showed that conformers A, B, and C are minima, while D and E are saddle points. The structure with an intramolecular hydrogen bond, conformer A, is the global minimum. It is lower in energy than B and C by 18.7 and 26.8 kJ/mol, respectively, and it is more stable than the transition-state structures D and E by 38.7 and 48.9 kJ/mol. Here and hereafter the MP2/6-31G*//HF/6-31G* energies are considered.

Obviously the order of these energies is determined by the relative orientation of the polar OH and PO groups. In the highest energy structure E the oxygens are facing each other, 2.973 Å apart (compared with 3.00 Å, twice the van der Waals radius of oxygen). The other transition structure, D, has the

TABLE 2: Geometrical Parameters of Conformer A at Different Levels of Calculation[a]

	HF/6-31G*	HF/6-31+G**	MP2/6-31G*	MP2/6-31+G**
C1−C2	1.397	1.398	1.410	1.411
C2−C3	1.401	1.402	1.405	1.407
C3−C4	1.372	1.374	1.390	1.392
C4−C5	1.397	1.398	1.401	1.402
C5−C6	1.372	1.374	1.389	1.391
C1−C6	1.399	1.400	1.404	1.405
C1−O7	1.332	1.332	1.356	1.359
O7−H8	0.960	0.956	0.991	0.985
C2−P	1.794	1.797	1.795	1.799
P═O	1.478	1.481	1.513	1.518
P−H	1.392	1.394	1.411	1.403
O10···H8	1.857	1.867	1.804	1.803
O7···O10	2.735	2.737	2.732	2.723
C1−C2−C3	119.3	119.2	119.7	119.7
C2−C3−C4	121.5	121.5	120.9	120.9
C3−C4−C5	118.6	118.6	119.1	119.1
C2−C1−C6	119.1	119.2	118.9	119.1
C1−C6−C5	120.4	120.4	120.6	120.5
C4−C5−C6	121.1	121.0	120.7	120.7
C2−C1−O7	124.3	124.3	124.5	124.3
C1−O7−H8	111.8	112.4	109.1	109.6
C1−C2−P	120.7	120.8	120.1	120.2
C2−P═O	113.1	112.9	113.3	112.9
C2−P−H	105.5	105.7	104.7	105.1
P═O···H	99.3	99.6	98.4	98.8
O7−H8···O10	150.8	150.0	154.5	154.2

[a] Distances in angstroms, angles in degrees. For numbering of atoms see Figure 1.

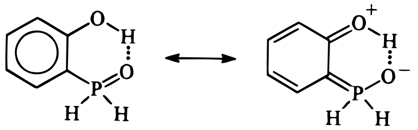
hydrogens of the polar groups facing each other. The imaginary frequency in each case represents a torsion of one of these groups, namely, that of the hydroxy group in D and the rotation of the phosphinyl group in E.

Conformers B and D differ only in the orientation of the hydroxy group, so the energy difference between the two conformers, 20.0 kJ/mol, can be taken as the rotational barrier of the OH group in 2-phosphinylphenol when the phosphinyl group is oriented with the oxygen anti to the hydroxy group. Similarly, conformers B and E differ only in the orientation of the phosphinyl group; thus, their energy difference, 30.2 kJ/mol, can be considered as the highest barrier on the rotational potential curve of the phosphinyl group when the hydrogen of the hydroxy group is anti to the phosphoryl group. The internal rotation potential of the phosphinyl group is a more complicated curve since there is an intermediate minimum corresponding to conformer C.

The repulsion of the oxygens in E seems a likely cause for both its high energy and its large O−C−C, C−C−P, and C−P−O bond angles relative to the corresponding angles in the parent molecules, phenol and phenylphosphine oxide, and also relative to the other conformers. Formation of conformer C from E through a 77.9° rotation around the C−P bond appears to relieve some of the oxygen−oxygen repulsion. The arrangement of the polar groups seems favorable in conformer B, for which the calculated O−C−C and C−C−P bond angles are within 1° of those in the parent molecules. The C−P−H bond angles are increased by 0.7° or 0.4°, and the C−P−O angle is decreased correspondingly by 1.4° or 1.3° relative to phenylphosphine oxide at the HF and MP2 level, respectively.

Geometry of Conformer A. The geometrical parameters of the most stable *monomeric* conformer of 2-phosphinylphenol, A (Figure 1), at different levels of computation are shown in Table 2. The results show that inclusion of the extra polarization functions on all elements and of the diffuse function on the heavy elements does not have an appreciable effect on the parameters at either the HF or the correlated level. The hydrogen bond lengthens somewhat from 1.857 to 1.867 Å at the HF level, while it remains essentially the same, 1.804 vs 1.803 Å, at the MP2 level. Concerning the MP2 vs HF geometries, the bond lengths show the usual lengthening in the MP2 structures compared to the HF ones. On the other hand, the hydrogen bond gets appreciably shorter, by about 0.05−0.06 Å, as compared with the HF calculations.

SCHEME 1



Intramolecular Hydrogen Bonding. The intramolecular hydrogen bond in conformer A, the absolute minimum, should be the decisive factor in stabilizing this form. Scheme 1 suggests that a contribution of the *o*-quinonoid resonance form should enhance this stabilizing effect. When comparing the geometry of 2-phosphinylphenol with phenol and with phenylphosphine oxide, all the geometrical changes are consistent with the importance of this *o*-quinonoid form. The comparison with the two parent molecules shows a shortening of the P−C bond (0.014 Å), a lengthening of the P−O bond (0.011 Å), and a lengthening of the O−H bond (0.017 Å), all at the MP2/6-31G* level. The changes of all the C−C bond lengths of the benzene ring are also consistent with the shift toward the *o*-quinonoid form. Thus, 2-phosphinylphenol represents a beautiful example of what has become known as resonance-assisted intramolecular hydrogen bonding.

This effect has been observed previously in similar systems, such as salicylaldehyde[4] and 2-nitrophenol.[5] It is of interest to compare their geometries and the amount of changes that occurred in their structures with the relevant parent molecules. Figure 4 shows these structures with the changes in their geometrical parameters compared to the respective parent molecules, all at the MP2/6-31G* level. The hydrogen bond distance in conformer A of 2-phosphinylphenol, 1.804 Å, is about the same as that in salicylaldehyde, 1.803 Å, both being somewhat longer than the one in 2-nitrophenol, 1.766 Å. It is noteworthy that in 2-phosphinylphenol, with 3d- but not 3p-orbital availability for π bonding, all the effects observed in molecules with first-row substituents still appear.

An often observed[10] indication of hydrogen bonding is the decrease of the OH stretching frequency. Our frequency calculations show that while the OH stretching frequency is the same in conformers B and C (and even in the transition-state structure E, and only slightly higher in D), it decreases in conformer A by 254 cm^{-1} (at the HF/6-31G* level), in accordance with the weakening of the O−H bond due to hydrogen bond formation, and is consistent with the appreciable lengthening of this bond.

In our previous work isodesmic calculations have been helpful in evaluating the stabilization of molecules resulting from hydrogen bonding.[11,12] Consider the following isodesmic equation:

$$C_6H_5OH + C_6H_5P(O)H_2 \rightarrow C_6H_6 + 2\text{-}H_2P(O)C_6H_4OH$$

From the MP2/6-31G*//HF/6-31G* energies of benzene, phenol, and phenylphosphine oxide we calculated the hypothetical energy of 2-phosphinylphenol were there no effect of interactions between the hydroxy and phosphinyl groups (zero energy

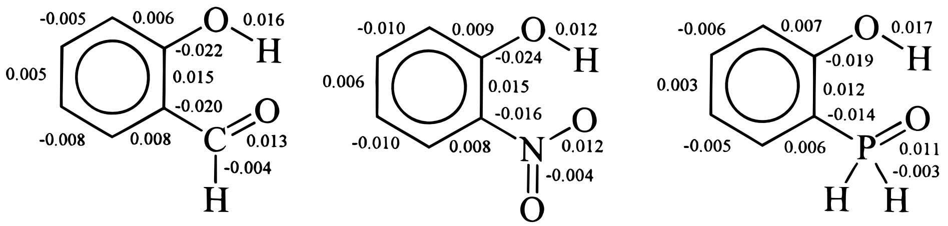
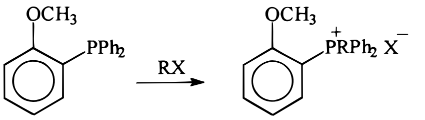


Figure 4. Salicylaldehyde, 2-nitrophenol, and 2-phosphinylphenol geometries, MP2/6-31G* level. Geometrical changes (Å) compared to the respective parent molecules are indicated.

change for the isodesmic reaction). The energy of conformer A is 28.4 kJ/mol lower than the energy of this hypothetical molecule.

To compare this hydrogen bond strength with similar systems, we have carried out an HF/6-31G* calculation of the change in energy on formation of a hydrogen-bonded complex between H_2O and H_3PO. The MP2/6-31G*//HF/6-31G* value was calculated to be −38.7 kJ/mol. Since there is a danger of introducing basis set superposition error (BSSE) in such comparisons,[13,14] we carried out counterpoise calculations in order to remove this possible error and obtained an interaction energy of −23.2 kJ/mol. Thus the hydrogen bond seems to be a little stronger in conformer A than in the water/phosphine oxide complex, as expected on different counts. Phenols are more acidic than water, and replacement of a hydrogen in a phosphine oxide by a phenyl group results in a more basic, that is, better hydrogen bonding phosphoryl group.[15] Furthermore, the resonance effect described above should enhance the intramolecular hydrogen bond. At the same time, the closure of the six-membered ring with the intramolecular hydrogen bond introduces energy-costing geometrical changes. The hydrogen bond length is in accordance with this in being shorter in conformer A than in the complex (1.86 vs 2.05 Å). Note that the P−O−H and the O−H−O angles of 99° and 151° in conformer A are not far from those in the complex (100° and 142°).

Conformer B. Conformer B is of interest to us because it relates to the experimental observation of a rate acceleration in the reaction of arylphosphines with alkyl halides when the aryl groups have methoxy groups ortho to the phosphorus.[16]



This rate enhancement suggests an energy-lowering interaction between the oxygen and the phosphorus in the transition state of this reaction.

Conformer B, which we view as a model for this transition state, is only 18.7 kJ/mol higher in energy than A, even though B lacks the hydrogen bond. Since the bond angles and bond distances in B are very similar to those of the parent molecules, phenol and phenylphosphine oxide, there is no indication of resonance interaction between the hydroxy and phosphinyl groups. The isodesmic calculation shows a stabilization of 9.7 kJ/mol for this molecule and this is attributed to either a favorable through-space effect resulting from the relative orientation of the polar OH and PO groups or to a long-range overlap of orbitals on the hydroxy oxygen and the phosphorus, as suggested by McEwen et al.[16] Since we have examined the electron density distribution using Spartan 4.0[9] and we find little evidence of a long-range bond, we conclude that the through-space effect is the stabilizing factor. A similar effect should operate between solvent molecules and the transition-state structure in the reaction of McEwen et al.,[16] and in fact their detailed kinetic studies show that a less negative entropy of activation is the main cause of the enhanced rate of reaction of the 2-methoxyphenylphosphines. Apparently fewer solvent molecules are involved in the transition-state complex of this reaction because the methoxy group takes the place of one or more solvent molecules.

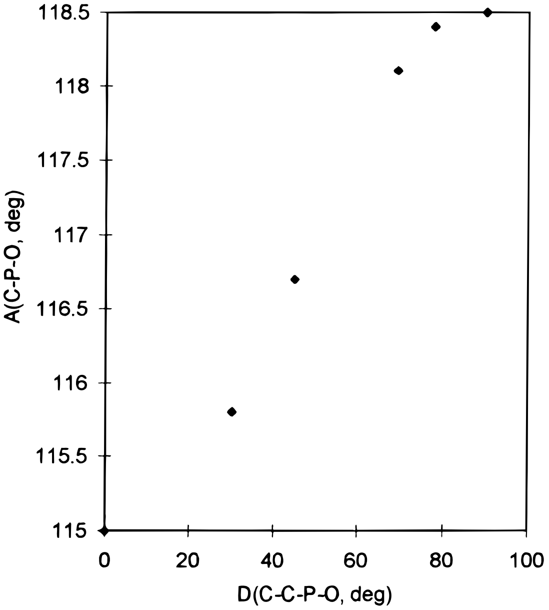


Figure 5. Variation of the C−P−O angle of phenylphosphine oxide with the C−C−P−O dihedral angle at the HF/6-31G* level.

Conformer C. Unlike the parent phenylphosphine oxide and the other four conformers, which have the phosphoryl group in the plane of the ring, conformer C has the PO group out of the plane by 78°. It also has a larger C−P−O bond angle, which may appear to result from repulsion between the two oxygens; however, this angle increases even in phenylphosphine oxide when the phosphoryl is rotated out of the plane of the ring. We have carried out a series of calculations on phenylphosphine oxide with a series of fixed dihedral angles and have obtained the results shown in Figure 5. They confirm the suspected effect on the C−P−O angle, which we attribute to repulsion between the π electrons of one side of the ring and the phosphoryl group when it is rotated out of the plane of the ring. There is a similar effect on the C−P−H angle, except that this angle decreases somewhat when the C−P−O angle increases.

The isodesmic calculation does not indicate much interaction between the groups in conformer C. There is only 1.6 kJ/mol of stabilization.

Dimer. Since experimental results on 2-diphenylphosphinylphenol and related molecules indicate that in the solid state and in solution there are intermolecular hydrogen bonds,[6,7,17] we thought it important to check the stability of the dimeric form of 2-phosphinylphenol. The geometry found is shown in Figure 3 together with its parameters from an HF/6-31G* level calculation. The geometry of the dimer was fully optimized without any constraint and it has C_i symmetry. Comparison with the monomer conformers reveals that it has two monomeric units with geometries closely resembling that of conformer C, since each unit has the PO group rotated 69° out of the plane of the adjacent benzene ring. The dimer has a shorter intermolecular hydrogen bond, 1.765 Å, compared to the intramolecular hydrogen bond in conformer A of 1.857 Å (HF/6-31G* level for both), which may be taken as an indication of a stronger bond. A further indication of the stronger intermolecular hydrogen bond in the dimer compared with the intramolecular hydrogen bond in conformer A is the 125 cm^{-1} decrease of the OH stretching frequency.

According to an isodesmic calculation of the dimer formation, it is 145.0 kJ/mol more stable than 2 mol of the hypothetical monomer, or 72.5 kJ/mol per hydrogen bond. Since the two units of the dimer are very similar in their geometry to conformer C, it is worthwhile to compare their energies. This gives a 141.7 kJ/mol stabilization energy for the dimer compared with 2 mol of C, or 70.8 kJ/mol per hydrogen bond, a value which is similar to the results of the isodesmic calculation. By the counterpoise method the dimer interaction energy is 118.2 kJ/mol, or 59.1 kJ/mol per hydrogen bond. Thus, the dimer has two very strong hydrogen bonds per molecule, much stronger than in the water−phosphine oxide complex, as expected.

To determine the amount of BSSE in comparisons of the dimer energy with the energies of other monomer conformers, we performed an MP2/6-31G*//HF/6-31G* computation on the monomer with the geometry of half the dimer using only the monomer basis set. The energy of this form of the monomer was found to be 15.1 kJ/mol greater than that of half the dimer, computed as in the counterpoise method with the full dimer basis set. The BSSE to be subtracted in comparisons of the dimer with 2 mol of various monomer conformers is thus 30.2 kJ/mol. For example, the above isodesmic calculation of the dimer formation can be corrected to $145.0-30.2 = 114.8$, or 57.4 kJ/mol per hydrogen bond, a value near that of the counterpoise interaction energy of 59.1 kJ/mol. We note that half the dimer with only the monomer basis set is 3.3 kJ/mol higher in energy than conformer C, even though the difference in their geometries may seem negligible. Apparently, with relatively large molecules small geometrical changes may bring about significant energy differences.

After BSSE subtraction, the dimer is found to be 58.1 kJ/mol more stable than 2 mol of the intramolecularly hydrogen bonded conformer A. Comparison of the bond distances in the dimer and in conformer A reveals less contribution of a quinonoid resonance form in the dimer than in A. We note that the hydrogen bond formation in the dimer is less restricted than the *intra*molecular hydrogen bond formation, and we observe that the O−H···O−P atoms are not in one plane as they are in A. The H−O−P angle is 24.5° larger in the dimer than in A, and the hydrogen bond is more linear, the O−H···O angle being 169.3° in the dimer compared to 150.8° in A.

Conclusions

1. Medium strength intramolecular hydrogen bonding occurs in 2-phosphinylphenol, accompanied by appreciable structural changes in the rest of the molecule as compared with the parent phenol and phenylphosphine oxide.
2. Comparison with salicylaldehyde and 2-nitrophenol shows similarity in the hydrogen bonding in all three systems. Thus in 2-phosphinylphenol phosphorus 3d orbitals may be playing a similar role to that of the carbon and nitrogen 2p orbitals in the other two systems in the hydrogen bonding.
3. The contributions of the quinonoid resonance form and the intramolecular hydrogen bonding seem to be reinforcing each other in 2-phosphinylphenol, just as in salicylaldehyde and 2-nitrophenol, and for all three the description “resonance-assisted hydrogen bonding” seems appropriate.
4. The dimer of 2-phosphinylphenol has two strong hydrogen bonds, the energy of each being 59.1 kJ/mol at the MP2/6-31G*//HF/6-31G* level by the counterpoise method or 57.4 kJ/mol by BSSE-corrected isodesmic calculation. It is found to be 58.1 kJ/mol lower in energy than 2 mol of the intramolecular hydrogen bonded conformer after subtraction of 30.2 kJ/mol of BSSE. The intermolecular hydrogen bond formation is geometrically less confined in the dimer than in the monomer.

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