Ab Initio Studies on Organophosphorus Compounds. Part 2.[1] Monoanionic Methyl Methylphosphonate and Methyl Methylphosphinate and their Sulfur Analogues

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The molecular properties of nine monoanionic methyl methylphosphonate and methyl methylphosphinate and their sulfur analogues have been studied by *ab initio* molecular orbital methods. Molecular structures, dipole moments, stability, charge distributions and torsional barriers have been reported. The effects of sulfur and oxygen substitution have been compared. Energetics for model and hydrolysis reactions have been calculated for all the compounds up to the MP2/6-31G*//6-31G* level. Phosphonate compounds with $-OCH_3$ group were found to adopt an extended molecular backbone while $-SCH_3$ systems preferred bent conformations. Inclusion of the correlation corrections with 6-31G* basis set, instead of 3-21G(*) level, was found to have an effect on the calculated energetics of model reactions.

Phosphorus-containing compounds have an essential role in many biological processes. Because of their bioactive nature organophosphorus compounds are used for several purposes for example as medicines *e.g.* bisphosphonates,[2-4] fertilizers, pesticides and plant growth regulators. Lately many organophosphorus compounds have been taken as a subject of theoretical studies. Different molecular derivatives of phosphine oxide and sulfide have been reported to be studied by *ab initio* molecular orbital methods.[5-11] Acid or ester molecules[12-16] and simple oxoacids of phosphorus which can produce several anionic species in aqueous solutions have been investigated theoretically.[14,16-19] Polyphosphorous acids, anhydrides,[20-23] different phosphate,[24-26] phosphinate[24,27,28] and phosphonate[24,29] structures have also been studied. The bonds between phosphorus and some of the first and second row atoms (*e.g.* O, N, S) have been found to be preferentially dative bonds, which have some π-back bonding character.[17,22] The properties of those bond systems and substituent effects have been extensively studied.[30-32]

In the present work we have studied systematically the geometries and molecular properties of monoanionic methyl methylphosphonate and methyl methylphosphinate and their sulfur analogues. Nine compounds were collected for a detailed analysis from those methylphosphonates and methylphosphinates which have been investigated in the previous paper (Part 1).[1] Table 1 gives the definition of the studied compounds. Anionic charges have been included in the molecular structures. Selected compounds are all possible candidates of bioactive molecules. The molecular side chains with $-OH$ and $-SH$ in the previous study have been replaced by the $-O-CH_3$ or $-S-CH_3$ tails (Fig. 1). Molecular geometries, stability, charge distributions and torsional barriers have been investigated to find out the substituent effects of O or S. Calculated geometric results for $-X-CH_3$ type (X = O, S) compounds have been compared to the previously presented $-X-H$ systems.[1] Energetics of several model and hydrolysis reactions have been solved and compared with corresponding reactions in the previous study.[1]

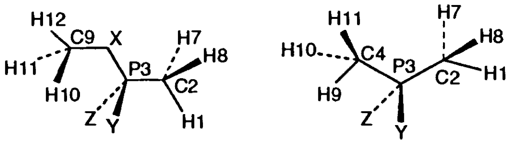
Computational Methods.—All *ab initio* molecular orbital calculations were performed with the GAUSSIAN 90 and 92 programs on an SGI 4D/35 computer. Standard 3-21G(*) and 6-31G* basis sets were used. The 3-21G(*) basis set includes five d-functions on phosphorus and sulfur atoms. The 6-31G* basis set has d-functions on all heavy elements. These basis sets have been found to predict reasonably well the energies, geometries and atomic charges of various phosphorus compounds and hypervalent molecules.[5,30,33] The d-functions of the basis sets have been observed to be essential for a proper description of phosphorus containing compounds.[5,15-20,22,30,33-36] The effects of electron correlation corrections were investigated with the second-order Møller–Plesset (MP2) perturbation theory. Molecular structures were optimized with 3-21G(*) and 6-31G* basis sets. After that single point procedures and frozen-core approximations were then used in MP2/3-21G(*)//3-21G(*) and MP2/6-31G*//6-31G* calculations.

Calculations and Results.—The selected geometrical parameters from the 6-31G* basis set calculations for different conformations are reported in Table 1. Total and relative energies of the optimized geometries for studied structures are presented in Table 2 with SCF and MP2 levels. Energies for CH_3OH/CH_3SH and H_2O/H_2S molecules were also calculated for further use in the model and hydrolysis reactions. Table 3 includes Mulliken charges for selected atoms and Table 4 presents model and hydrolysis reactions and energetics for different pairs of molecules.

Conformational Analyses and Optimized Geometries.—The starting point of the calculations was $CH_3P(O)_2OCH_3$ (**1**). Firstly two different conformational analyses were done to find out how the two torsional angles [Fig. 1(*a*) axes 1 and 2] should be considered. In the first analysis torsional angle 1, C–P–O–C, and 2, P–O–C–H, [Fig. 1(*a*)] were changed step by step and after every increment all the other parameters where optimized. The step size used was 30° and the range of rotation 360°. In the second analysis only the torsional angle 1 was rotated. Because both types of conformational analysis gave similar energy profiles for the rotation of C–P–O–C, it can be concluded that the methyl group can also find its optimal position during the simpler optimization procedure. Therefore the torsional angle C–P–X–C (1) in Fig. 1(*a*) was selected to be the only rotatable bond in the further calculations.

The conformational analyses were done for molecules **1**–**6** by changing the C–P–X–C torsional angles 360° in steps of 30°. The minima found in the analyses were used as starting structures in the later full optimizations. Energy and dipole moment profiles of torsional rotations for C–P–X–C backbones

Table 1 Selected geometric parameters for the monoanionic compounds calculated by 6-31G* basis



Structures **1–6** Structures **7–9**

Struct.	X	Y	Z	Bond length/pm *r*(P–X)	*r*(P–Y)	*r*(P–Z)	Bond angle/° (X–P–C2)	(Y–P–C2)	(C9–X–P)	Torsional angle/° (C9–X–P3–C2)	(H10–C9–X–P3)
C2–P(X)(Y)(Z)–C9											
1	O4	O5	O6	165.9	148.2	148.2	96.6	109.7	116.8	180.0	60.6
2	S4	O5	O6	217.0	147.7	148.0	101.9	108.6	101.6	82.1	165.9
3	O4	O5	S6	164.4	148.0	199.9	96.5	110.7	118.6	186.2	175.4
4a	S4	O5	S6	215.4	148.3	198.9	101.7	108.6	100.6	−80.6	195.8
4b	S4	O5	S6	215.7	148.0	199.4	101.5	109.3	104.9	75.0	173.5
5	O4	S5	S6	163.8	199.6	199.6	96.2	109.8	120.4	180.0	180.0
6a	S4	S5	S6	214.7	199.3	199.8	101.6	108.5	103.9	74.0	180.0
6b	S4	S5	S6	214.9	199.9	199.9	96.7	109.3	100.4	179.9	180.1
C4–P(Y)(Z)–C2				*r*(P–X)	*r*(P–Y)	*r*(P–Z)	(X–P–C2)	(Y–P–C2)	(C4–P–C2)	(C4–P3–C2–H1)	(H9–C4–P3–C2)
7	—	O5	O6	—	148.9	148.9	—	107.9	101.4	180.0	180.0
8	—	O5	S6	—	148.9	200.9	—	109.0	101.1	181.3	178.6
9	—	S5	S6	—	200.9	200.9	—	108.3	101.2	180.0	180.0

Labels **a** and **b** indicate minimum energy conformations 1 and 2. Minimum **a** is the lowest energy system from pairs **a**–**b**.

Table 2 Total and relative energies of the studied compounds calculated with 6-31G* and MP2/6-31G*//6-31G* basis sets

Struct.	[6-31G*] *E*/a.u.	E_R/kJ mol^{-1}	MP2 *E*/a.u.	E_R/kJ mol^{-1}
1	−644.638 34	—	−645.550 16	—
2	−967.287 04	—	−968.148 39	—
3	−967.293 32	—	−968.143 68	—
4a	−1289.939 79	0.0	−1290.739 75	0.0
4b	−1289.938 84	2.5	−1290.738 71	2.7
5	−1289.947 67	—	−1290.736 88	—
6a	−1612.595 81	0.0	−1613.333 89	0.0
6b	−1612.595 58	0.6	−1613.333 60	0.8
7	−569.753 33	—	−570.490 93	—
8	−892.413 64	—	−893.088 47	—
9	−1215.075 85	—	−1215.687 75	—
CH_3OH	−115.035 42		−115.344 94	
CH_3SH	−437.700 32		−437.952 34	
H_2O	−76.010 75		−76.195 96	
H_2S	−398.667 32		−398.788 21	

Table 3 Mulliken charges of selected atoms (6-31G*)

Struct.	X	Y	Z	X	Y	Z	P
C2–P(X)(Y)(Z)–C9							
1	O4	O5	O6	−0.741	−0.828	−0.828	1.428
2	S4	O5	O6	−0.301	−0.799	−0.812	1.286
3	O4	O5	S6	−0.735	−0.784	−0.795	1.245
4a	S4	O5	S6	−0.201	−0.775	−0.719	1.003
4b	S4	O5	S6	−0.208	−0.761	−0.727	0.999
5	O4	S5	S6	−0.709	−0.684	−0.684	0.929
6a	S4	S5	S6	−0.108	−0.614	−0.624	0.576
6b	S4	S5	S6	−0.127	−0.618	−0.618	0.570
7	—	O5	O6	—	−0.837	−0.837	1.342
8	—	O5	S6	—	−0.790	−0.795	1.109
9	—	S5	S6	—	−0.676	−0.676	0.728

are presented in Figs. 2 and 3. Both the energy profile and the dipole moments were calculated with the 3-21G(*) basis set. Rotational barriers of C–P–O–C molecules at $\tau = 0°$ changes from 32 to 39 kJ mol^{-1}, when the number of sulfur atoms increases from 0 to 2. The corresponding barriers of C–P–S–C molecules is from 46 to 37 kJ mol^{-1}. In the latter case the barrier is the lowest when the number of sulfur atoms is 2. At $\tau = 180°$ there is an energy minimum for X = O compounds $CH_3P(O)(S)OCH_3$ (**3**) and $CH_3P(S)_2OCH_3$ (**5**) (Fig. 1). The barrier in compound (**1**) is only 1.3 kJ mol^{-1} at $\tau = 180°$ and it vanishes when the 6-31G* basis set was used.

Compounds X = S have different rotational barriers in every case. $CH_3P(O)_2SCH_3$ (**2**) and $CH_3P(O)(S)SCH_3$ (**4**) have 16 kJ mol^{-1} barrier at $\tau = 180$ and 240° respectively (Fig. 3). $CH_3P(S)_2SCH_3$ (**6**) has two symmetrical 11 kJ mol^{-1} barriers when $\tau = 120$ and 240°. Similar general trends have been found

Table 4 Model reactions and energetics calculated by 3-21G(*) and 6-31G* basis sets

							E/kJ mol^{-1}							
	Pair	Reactants			Products		A	B	C	D	A′	B′	C′	D′
1	**2–1**	$CH_3P(O^-)(O)SCH_3$	+ 1a/b	→	$CH_3P(O^-)(O)OCH_3$	+ 1c/d	−84.6	−42.5	−49.0	−24.1	(−70.0)	(−20.7)	(−28.9)	(15.7)
2	**3–1**	$CH_3P(O^-)(S)OCH_3$	+ 1a/b	→	$CH_3P(O^-)(O)OCH_3$	+ 1c/d	−45.8	−26.0	−40.1	−36.5	(−31.1)	(−4.2)	(−19.9)	(3.3)
3	**4–1**	$CH_3P(O^-)(S)SCH_3$	+ 2a/b	→	$CH_3P(O^-)(O)OCH_3$	+ 2c/d	−137.3	−74.4	−98.7	−66.2	(−108.0)	(−30.7)	(−58.4)	(13.4)
4	**5–1**	$CH_3P(S^-)(S)OCH_3$	+ 2a/b	→	$CH_3P(O^-)(O)OCH_3$	+ 2c/d	−105.1	−53.7	−98.6	−73.8	(−75.8)	(−10.0)	(−58.2)	(5.8)
5	**6–1**	$CH_3P(S^-)(S)SCH_3$	+ 3a/b	→	$CH_3P(O^-)(O)OCH_3$	+ 3c/d	−196.1	−97.8	−161.4	−101.0	(−152.2)	(−32.2)	(−100.9)	(18.4)
6	**3–2**	$CH_3P(O^-)(S)OCH_3$		→	$CH_3P(O^-)(O)SCH_3$		38.8	16.5	9.0	−12.4				
7	**4–2**	$CH_3P(O^-)(S)SCH_3$	+ 1a/b	→	$CH_3P(O^-)(O)SCH_3$	+ 1c/d	−52.6	−31.9	−49.7	−42.1	(−52.6)	(−10.1)	(−29.5)	(−2.3)
8	**5–2**	$CH_3P(S^-)(S)OCH_3$	+ 1a/b	→	$CH_3P(O^-)(O)SCH_3$	+ 1c/d	−20.5	−11.2	−49.5	−49.7	(−5.8)	(10.6)	(−29.3)	(−9.9)
9	**6–2**	$CH_3P(S^-)(S)SCH_3$	+ 2a/b	→	$CH_3P(O^-)(O)SCH_3$	+ 2c/d	−111.5	−55.2	−112.4	−77.0	(−82.2)	(−11.5)	(−72.0)	(2.6)
10	**4–3**	$CH_3P(O^-)(S)SCH_3$	+ 1a/b	→	$CH_3P(O^-)(S)OCH_3$	+ 1c/d	−91.5	−48.4	−58.6	−29.8	(−76.8)	(−26.5)	(−38.5)	(10.0)
11	**5–3**	$CH_3P(S^-)(S)OCH_3$	+ 1a/b	→	$CH_3P(O^-)(S)OCH_3$	+ 1c/d	−59.3	−27.7	−58.5	−37.3	(−44.7)	(−5.9)	(−38.3)	(2.5)
12	**6–3**	$CH_3P(S^-)(S)SCH_3$	+ 2a/b	→	$CH_3P(O^-)(S)OCH_3$	+ 2c/d	−150.3	−71.7	−121.3	−64.6	(−121.0)	(−28.0)	(−81.0)	(15.0)
13	**5–4**	$CH_3P(S^-)(S)OCH_3$		→	$CH_3P(O^-)(S)SCH_3$		32.1	20.7	0.2	−7.5				
14	**6–4**	$CH_3P(S^-)(S)SCH_3$	+ 1a/b	→	$CH_3P(O^-)(S)SCH_3$	+ 1c/d	−58.8	−23.3	−62.7	−34.8	(−44.2)	(−1.5)	(−42.5)	(5.0)
15	**6–5**	$CH_3P(S^-)(S)SCH_3$	+ 1a/b	→	$CH_3P(S^-)(S)OCH_3$	+ 1c/d	−91.0	−44.0	−62.9	−27.3	(−76.3)	(−22.2)	(−42.7)	(12.5)
16	**8–7**	$CH_3P(O^-)(S)CH_3$	+ 1a/b	→	$CH_3P(O^-)(O)CH_3$	+ 1c/d	−22.2	−12.1	−30.1	−25.9	(−7.5)	(9.8)	(−10.0)	(13.9)
17	**9–7**	$CH_3P(S^-)(S)CH_3$	+ 2a/b	→	$CH_3P(O^-)(O)CH_3$	+ 2c/d	−65.0	−19.1	−76.1	−47.2	(−35.7)	(24.6)	(−35.8)	(32.4)
18	**9–8**	$CH_3P(S^-)(S)CH_3$	+ 1a/b	→	$CH_3P(S^-)(O)CH_3$	+ 1c/d	−42.8	−7.0	−46.0	−21.3	(−28.2)	(14.8)	(−25.8)	(18.5)

Basis sets used: (A and A′) = 3-21G(*), (B and B′) = 6-31G*, (C and C′) = MP2/3-21G(*)//3-21G(*), (D and D′) = MP2/6-31G*//6-31G*; a = CH_3OH, b = H_2O, c = CH_3SH and d = H_2S. Energies of hydrolysis reactions are in parentheses. Reaction pairs **3**–**2** and **5**–**4** are examples of isomerizations.

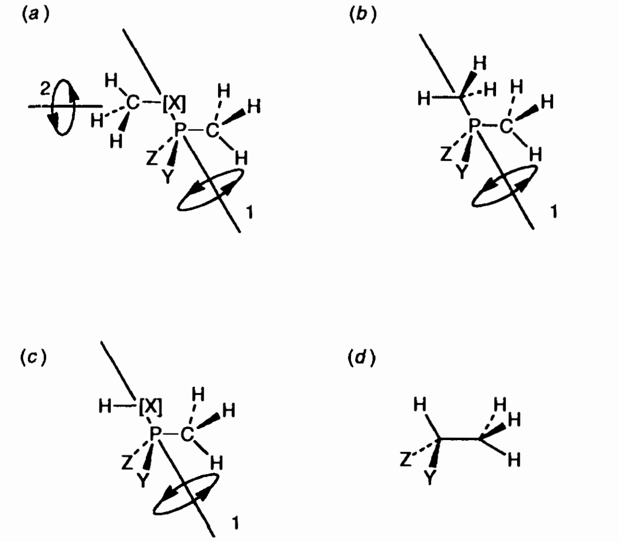


Fig. 1 Geometries and the rotatable torsional angles. (*a*) Methyl methylphosphonate. (X, Y, Z = O or S). Torsional angle 1 = C–P–X–C and torsional angle 2 = P–O–C–H. (*b*) Methyl methylphosphinate. Torsional angle 1 = C–P–C–H. (*c*) and (*d*) are structures from the previous paper.[1]

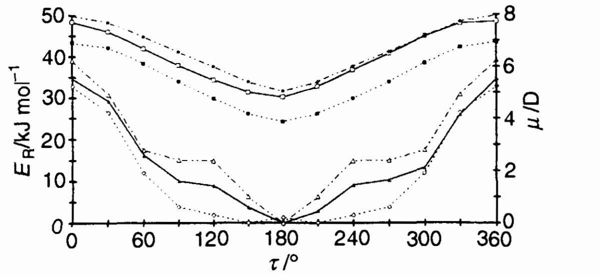


Fig. 2 Torsional energy (E_R/kJ mol^{-1}) and dipole moment (μ/D†) profiles of C–P–O–C type compounds. Structure **1**: energy ···◇···, dipole ···■···; structure **3**: energy ——▲——, dipole ——□——; structure **5**: energy –·· △ –··, dipole –·· ◇—··.

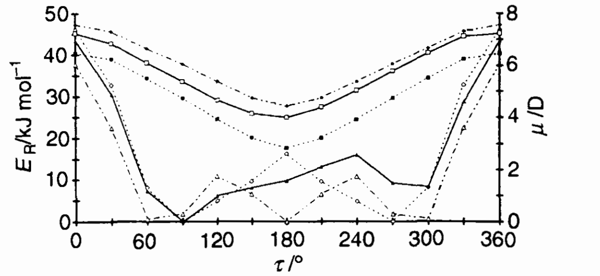


Fig. 3 Torsional energy (E_R/kJ mol^{-1}) and dipole moment (μ/D†) profiles of C–P–S–C type compounds. Structure **2**: energy ···◇···, dipole ···■···; structure **4**: energy ——▲——, dipole ——□——; structure **6**: energy —··△—··, dipole —···◆—··.

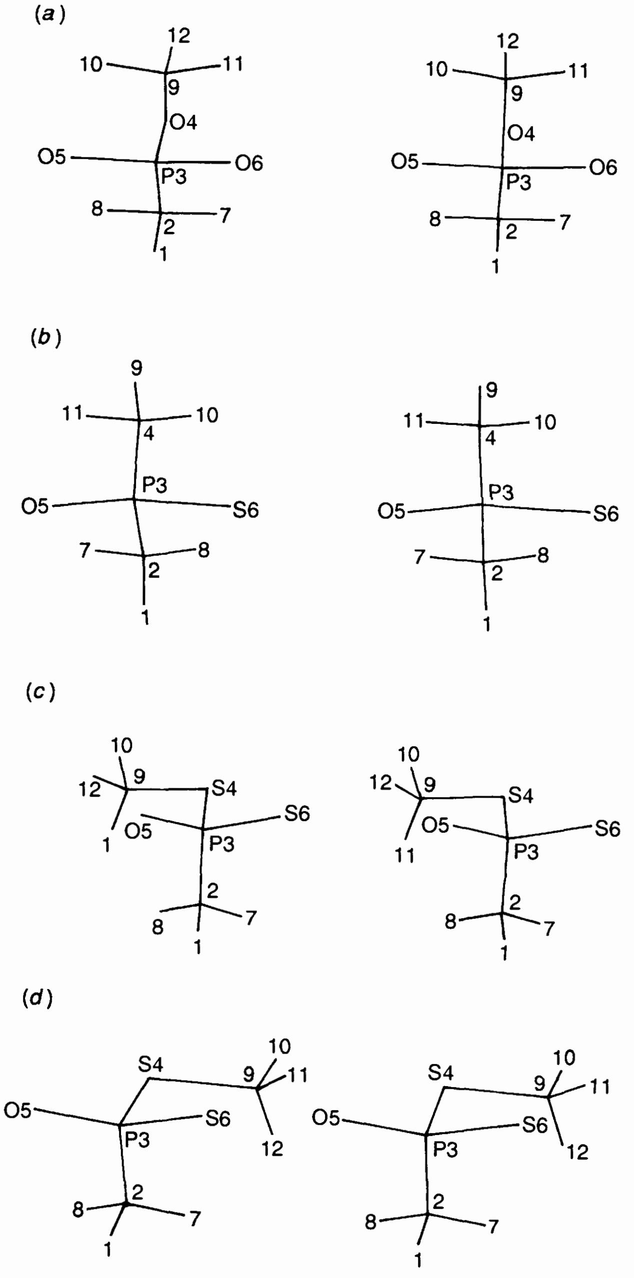


Fig. 4 Selected optimized compounds are presented as stereo pairs (6-31G*). (*a*) Structure **1**, (*b*) structure **8**, (*c*) structure **4** (energy minimum 1) and (*d*) structure **4** (energy minimum 2).

for energy profiles in $CH_3P(Z)(Y)XCH_3$ and earlier reported $CH_3P(Z)(Y)XH$ compounds.[1] The minimum energy geometry of $CH_3P(O)_2OCH_3$ (**1**) calculated with the 6-31G* basis set is presented in Fig. 4(*a*). The optimized geometries of **3** and **5** correspond to the geometry of **1**. Compound **4** has two minimum energy conformations where the methyl group is bent around the C–S–P–C torsional angle. Those orientations have been presented in Fig. 4, where the methyl group is (*c*) near oxygen and (*d*) near sulfur. The MP2/6-31G*//6-31G* level energy difference between the minima is only 2.7 kJ mol^{-1} and the location near the oxygen is the favoured one. The 6-31G(*) level calculations predict the same order for the stability and the energy difference of 2.5 kJ mol^{-1} is near the previously discussed MP2 value (Table 2). Molecule **2** has one minimum conformation with a torsional angle of 82°. Compound **6** has both the linear and bent molecular structures in relation to the torsional angle C–S–P–C. Energetically the most favourable one is the orientation where the methyl group is bent 74° around the C–S–P–C torsional angle towards the sulfur atom (Fig. 1). The energy difference between the conformations is 0.8 kJ mol^{-1} with MP2/6-31G*//6-31G* and 0.6 kJ mol^{-1} at the 6-31G(*) level (Table 2). The reason why the methyl group is bent close to the oxygen or the sulfur is the possibility of forming intramolecular hydrogen bond type interactions. Inside structure **2** the optimized 6-31G* interaction distance between O ··· H is 258 pm. Molecule **4** has two different bent conformations. Minimum orientation 1 has O ··· H distance 255 pm and minimum 2 has S ··· H distance 294 pm. Those conformations have been presented in Fig. 4 (*c*) and (*d*). Conformations **2**, **4**

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† 1 D = 3.335 64 × 10^{-30} C m.

and **6** all have intramolecular hydrogen bond interactions. The only difference between them is the second conformation of molecule **6**, which has the molecular backbone like the one presented in Fig. 4(*a*). In the optimized geometries of methyl methylphosphinates (**7**, **8**, **9** in Table 1) the methyl groups are in eclipsed conformations. The molecular structure **8** is shown as an example in Fig. 4(*b*).

It is well known that in the gas phase molecules usually prefer conformations which have the lowest dipole moments.[37] The minima in the dipole moment diagrams of $-O-CH_3$ compounds **1**, **3**, **5** (Fig. 2) coincide with the minima in the torsional profile. For $-S-CH_3$ compounds **2**, **4**, **6** (Fig. 3) the dipole moment diagrams are similar to the diagrams of $-O-CH_3$ compounds, but the conformations where the torsional angles C–P–S–C are bent towards oxygen or sulfur have different minima in the torsional energy profiles than those predicted by dipole moments. This difference is probably a result of the P–S and S–C bonds in $-S-CH_3$ being longer than the corresponding bonds in $-O-CH_3$ compounds, which makes the intramolecular hydrogen bonding interactions more favourable in $-S-CH_3$ than in $-O-CH_3$ compounds. The P–S and S–C bond lengths are about 49 and 43 pm longer than the corresponding bonds in the $-O-CH_3$ systems. In addition, the calculated data show $\mathbf{1} < \mathbf{3} < \mathbf{5}$ and $\mathbf{2} < \mathbf{4} < \mathbf{6}$ trends for the dipole moments, where the smallest moments have been found for the oxygen rich compounds. In phosphonates the C–O–P angles are 116.8, 118.6 and 120.4° for structures **1**, **3** and **5**. For the corresponding sulfur derivatives the C–S–P angles are 101.6, 104.9 and 103.9° for **2**, **4** and **6**, respectively. Thus, the angle C–X–P tends to straighten when the number of sulfur atoms increases. This is due to the greater spatial requirements of sulfur as compared to oxygen. The angle C–P–X is calculated to be 96.2–96.6° for X = O and 96.7–101.9° for X = S compounds. Merz and Kollman have reported earlier a value of 97.1° for the three oxygen systems.[38] In the phosphinate molecules, the C–P–C angles were calculated to be 101.1–101.4°.

The bond lengths reported in Table 1 show no clear differences in the molecules studied. When those results are compared to the previous values in the $CH_3P(Z)(Y)XH$ compounds,[1] the P–X distances are also similar indicating that the replacement of H with CH_3 has only a small local effect.

Mulliken charges calculated with the 6-31G* basis set are presented in Table 3. All substituents can be seen to have withdrawn electron density from phosphorus. When there are three oxygen atoms in the phosphonate molecule (**1**) phosphorus has the largest positive Mulliken charge value of 1.43. In the case of three sulfur atoms a charge of 0.57 is calculated for the phosphorus. The same trend was found for calculated phosphinate compounds as well.

Model and Hydrolysis Reactions.—The energetics of the model and hydrolysis reactions are presented in Table 4. Example reactions for pair **6–1** are:

Model reaction:

$$CH_3P(S^-)(S)SCH_3 + 3\,CH_3OH \longrightarrow CH_3P(O^-)(O)OCH_3 + 3\,CH_3SH$$

Hydrolysis reaction:

$$CH_3P(S^-)(S)SCH_3 + 3\,H_2O \longrightarrow CH_3P(O^-)(O)OCH_3 + 3\,H_2S$$

The energies of the most stable conformations of each molecule were used. In the model reactions there is a general trend that compounds with more sulfur are less stable. For example the model reaction 5, $CH_3P(S)_2SCH_3 + 3\,CH_3OH \rightarrow CH_3P(O)_2OCH_3 + 3\,CH_3SH$, is exothermic by −97.8 and −101.0 kJ mol^{-1}, at the 6-31G* and MP2/6-31G*//6-31G* levels, respectively. In the case of hydrolysis, the energy for the same pair of compounds changes from −32.2 to 18.4 kJ mol^{-1} when the electron correlation is taken into account at the 6-31G* level. From the results shown in Table 4 one can conclude that the inclusion of correlation corrections has an important effect on the energetics of the molecular reactions presented. The energies calculated as a reference for the pair **6–1** with the SCF/6-31 + G* basis set, which includes diffusion functions for the heavy atoms, are −96.6 kJ mol^{-1} for the model reaction and −18.2 kJ mol^{-1} for the hydrolysis reaction. Diffusion functions change the reaction energies only a little compared to 6-31G* values. The energies calculated at the MP2/3-21G(*)//3-21G(*) level differ significantly from the MP2/6-31G*//6-31G* values. Especially in the case of hydrolysis reactions this difference is significant both in absolute values and, more notably, in relative values too. In the hydrolysis reactions replacement of oxygen with sulfur gives a reverse effect on the stability compared to the model reactions: sulfur stabilizes the compounds compared with oxygen. The direction of the reactions is also changed. It must be emphasized that because the reaction energies are small, calculations at a higher level and the inclusion of zero-point energies can change the direction of the reactions. However, the qualitative conclusions presented here probably would not be affected by calculations at a higher level of theory.

When the energies at the 6-31G* level are compared with the corresponding results of the $CH_3P(Z)(Y)XH$ (X = O,S) compounds[1] the results are found to be similar. For example, the energy for reaction **3–1** $CH_3P(O)(S^-)OCH_3 + H_2O \rightarrow CH_3P(O)(O^-)OCH_3 + H_2S$ is −4.2 kJ mol^{-1}, when it is −3.3 kJ mol^{-1} for the analogous reaction of $CH_3P(Z)(Y)OH$ molecules. The energy difference for the previous pair **3–1** is only 0.9 kJ mol^{-1}. Pair **5–1** in Table 4 has an energy value −10.0 kJ mol^{-1} and that of the reaction with the –OH compound is −12.3 kJ mol^{-1}. In general it can be summarized that the $-O-CH_3$ group seems to exert only a small (1–3 kJ mol^{-1}) destabilizing effect on the energies of the model reactions relative to the OH group. The reason for this behaviour may be the electron donating nature of the methyl group in comparison with hydrogen.

Conclusions

In the present *ab initio* molecular orbital study the geometries and molecular properties of nine monoanionic methyl methylphosphonates and methyl methylphosphinates and their sulfur analogues have been investigated. Conformational analyses were made for the compounds and the rotational barriers were investigated. The phosphonates with the $-OCH_3$ group were found to adopt extended conformations. The compounds with $-SCH_3$ preferred bent molecular backbones with intramolecular hydrogen bonds. That the P–S (Δ = 49 pm) and S–C (Δ = 43 pm) bonds in the $-SCH_3$ analogues are longer than the corresponding P–O and O–C bonds in the $-OCH_3$ compounds is probably due to the intramolecular hydrogen bonds in the former case.

Model and hydrolysis reactions were calculated using basis sets up to the MP2/6-31G*//6-31G* level in order to compare the effects of O and S on the stability of the compounds. The inclusion of correlation corrections and the use of the 6-31G* instead of the 3-21G(*) basis set was found to affect results even qualitatively. In the model reactions the most stable phosphonate compound at the MP2/6-31G*//6-31G* level was $CH_3P(O)_2OCH_3$ (**1**) and the most unstable $CH_3P(S)_2SCH_3$ (**6**). However, in the hydrolysis reactions the order of stability is reversed: the compounds with sulfur were the most stable. The same relationship between the model and hydrolysis reactions was also found for phosphinates. Comparison with the energetics of the hydrolysis reactions of $CH_3P(Z)(Y)XH$ compounds[1] indicated that the methyl group causes a small 1–3 kJ mol^{-1} destabilizing effect as compared to hydroxy group.

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Paper 3/06750E
Received 11*th November* 1993
Accepted 7*th January* 1994