Ab Initio Studies on Organophosphorus Compounds. Part 1. Monoanionic Methylphosphonate and Methylphosphinate and their Nitrogen and Sulfur Analogues

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The effects of sulfur and nitrogen substituents on the properties of 23 different analogues of monoanionic methylphosphonates and methylphosphinates have been investigated by an *ab initio* method with 3-21G(*) and 6-31G* basis sets. Conformational analyses were performed on all compounds with rotational bonds and the relative energies of conformers were studied. The effects of nitrogen and sulfur substituents were compared in terms of geometries, charge distributions and torsional barriers. In addition, the total energy changes of model reactions between the analogues were investigated. On the basis of the model reactions the most stable compounds were methylphosphonte (**1**), methylphosphonamidate (**7**) and methylphosphindithioate (**20**).

Many organophosphorus compounds with phosphonic and phosphinic acid moieties and their sulfur and nitrogen analogues are biologically active compounds. Various groups of them have found applications as pesticides, plant growth regulators and, increasingly, in human medicine.[1,2] In spite of their importance, there has been a lack of systematic theoretical studies for the purpose of elucidating the effects of different substituents on their molecular properties. Earlier *ab initio* studies on the related compounds have primarily dealt with parent phosphonic and phosphinic acids and their esters.[3,4] Some halogen and amino analogues have also been studied.[5–8] Phosphinic [$H_2P(O)OH$], phosphinothioic [$H_2P(O)SH$] and phosphinodithioic [$H_2P(S)SH$] acids and their anions have previously been investigated in detail by Boatz and Gordon.[9]

In this work we have systematically studied the properties of monoanionic sulfur and nitrogen analogues of methylphosphonate (**1**, **2**–**14**) and methylphosphinate (**15**, **16**–**25**) (Table 1) by *ab initio* molecular orbital methods. Compounds were selected to cover all sulfur and nitrogen analogues which have practical importance as candidate bioactive compounds. Calculations were performed on the molecules in their monoanionic form, because phosphonic and phosphinic acid groups have been found to be deprotonated in physiological conditions.[10] The properties of the anionic species and the effect of different substituents were compared in terms of geometries, charge distributions and torsional barriers. Moreover, the stability of different isomeric forms and of related compounds were compared with the help of total energy comparisons and model reactions.

Computational Methods.—*Ab initio* molecular orbital calculations were carried out with the GAUSSIAN 90 program[11] on SGI 4D/35 and VAX-6420 computers. All optimizations were done using the default gradient procedure and 3-21G(*) or 6-31G* basis sets. The 3-21G(*) basis set contains five d-type functions on second row elements only. The 6-31G* basis set includes d-functions on all heavy atoms. Basis sets with polarization functions were selected because these functions have been shown to be essential in determining the properties of second row elements.[12] The 3-21G(*) and 6-31G* basis sets have been found to give reasonable energies, geometries and charge distributions for compounds similar to those studied in this work, and reproduce a number of subtle geometrical features of hypervalent molecules.[3,5,13–16] Conformational analysis was performed following the procedures explained below using the 3-21G(*) basis set. Final optimisations and energy comparisons were done using the 6-31G* basis set. The effect of electron correlation on some model reactions was investigated by employing the second-order Møller–Plesset (MP2) perturbation correction. 6-31G* geometries (MP2/6-31G*//6-31G*) and frozen-core approximation was used in MP2 calculations.

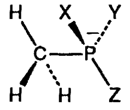
Results and Discussion

Geometries and Mulliken Charges.—In Table 1 selected bond lengths and angles of the molecules studied are summarised. Calculated total energies of the optimised structures are presented in Table 2.

The calculated bond lengths of the P–X and P–Y bonds in XPY groups (X and Y = O, S), where the anionic charge is delocalised, are only slightly longer than the experimental values of the double bonds in substituted phosphine oxides (1.475–1.520 *vs.* 1.44–1.48 Å)[5,17] and phosphine sulfides (1.987–2.065 *vs.* 1.87–1.96 Å).[15,17] With the 6-31G* basis set calculated P=O (1.465 Å) and P=S (1.954 Å) bond lengths in H_3PO and H_3PS[18] are in the range of the experimental values above and are shorter than our calculated bond lengths for the monoanionic species. The reference values for P=O and P=S double bonds are 1.45 and 1.92 Å, and for P–O and P–S single bonds, 1.56 and 2.10 Å.[19] The experimental values of 1.544 Å[20] and 1.539 Å[21] for substituted P=NH bonds, as well as the calculated (6-31G*) value of 1.548 Å in H_3PNH, are also slightly shorter than our calculated P=NH bond lengths (1.564–1.582 Å) in monoanionic species. It must be noted that these experimental values for P=NH are taken from compounds with bulky substituents and for that reason are possibly not good reference values. The above analysis of bond lengths indicates a substantial double bond character for P–O, P–S and P–NH bonds in the anionic species of this work.

In this context we have used the term double bond to describe the multiple bonds between phosphorus and O, S and N atoms although the electronic structures of these bonds are more complicated. The bonds have been found to be dative bonds, augmented with some π-bonding. The properties of these bonds

Table 1 Selected geometric parameters of the compounds studied, calculated using 6-31G*



				Bond length/Å				Angle/°		
Compound	X	Y	Z	P–C	P–X	P–Y	P–Z	X–P–C	Y–P–C	Z–P–C
1	O	O	OH	1.832	1.477	1.486	1.656	108.2	109.1	99.8
2	O	O	SH	1.832	1.475	1.476	2.189	108.7	108.3	101.1
3	O	S	OH	1.826	1.476	2.007	1.644	109.2	109.7	99.2
4	O	S	SH	1.833	1.480	1.987	2.168	108.8	108.5	100.9
5	S	S	OH	1.824	1.994	1.994	1.642	110.2	110.2	96.7
6	S	S	SH	1.836	1.992	1.994	2.156	108.5	180.0	100.9
7	O	O	NH_2	1.835	1.487	1.487	1.732	108.0	108.0	101.5
8	O	NH	OH	1.836	1.485	1.582	1.650	107.4	112.2	97.5
9	O	NH	NH_2	1.828	1.494	1.581	1.744	110.1	104.5	100.6
10	O	S	NH_2	1.830	1.486	2.008	1.723	108.8	108.0	101.5
11	O	NH	SH	1.824	1.482	1.564	2.226	110.8	104.8	100.3
12	S	NH	OH	1.821	2.022	1.565	1.659	110.6	105.6	99.5
13	S	NH	SH	1.825	2.000	1.568	2.201	110.3	105.1	100.0
14	S	NH	NH_2	1.823	2.021	1.578	1.735	109.7	105.4	100.6
15	O	O	H	1.843	1.486	1.486	1.421	108.2	108.2	98.7
16	O	OH		1.889	1.515	1.708		104.0	95.0	
17	O	S	H	1.837	1.487	2.003	1.407	109.4	108.0	98.7
18	O	SH		1.879	1.500	2.330		104.6	93.8	
19	S	OH		1.865	2.055	1.685		102.8	97.3	
20	S	S	H	1.837	2.004	2.004	1.400	108.7	108.7	99.2
21	S	SH		1.866	2.044	2.199		103.3	96.6	
22	O	NH	H	1.834	1.494	1.582	1.429	110.5	104.1	97.9
23	O	NH_2		1.881	1.520	1.786		105.0	92.7	
24	S	NH	H	1.830	2.017	1.581	1.415	110.0	105.6	97.8
25	S	NH_2		1.860	2.065	1.761		103.5	95.4	

Table 2 Calculated (6-31G*) total energies of the compounds

Compound	Energy/a.u.	Compound	Energy/a.u.
1	−605.615 42	**14**	−888.537 12
2	−928.256 04	**15**	−530.705 14
3	−928.270 75	**16**	−530.661 82
4	−1250.908 13	**17**	−853.366 46
5	−1250.923 90	**18**	−853.319 98
6	−1573.564 25	**19**	−853.345 85
7	−585.766 11	**20**	−1176.029 87
8	−585.725 63	**21**	−1176.001 89
9	−565.874 69	**22**	−510.815 96
10	−908.423 36	**23**	−510.811 51
11	−908.370 09	**24**	−833.482 63
12	−908.385 27	**25**	−833.501 46
13	−1231.026 87		

and the effects of different substituents have been extensively studied earlier.[5,15,16,22–28]

It can be seen from Table 1 that there is a clear trend of increasing P–C bond lengths in the series of MeP(X)Y (**16**, **18**, **19**, **21**, **23**, **25**), MeP(X)(Y)H (**15**, **17**, **20**, **20**, **24**) and MeP(X)(Y)Z (**1**–**14**). In the first member of this series phosphorus has a lone-pair, in the second one the lone-pair is used in bonding with hydrogen and in the last member it is used in bonding with an electronegative substituent. It is also obvious from Table 1 that the bond angles of P^V compounds are larger than the angles of P^{III} compounds. Similar changes in the P–C bond lengths are seen, for example, for the series of $(Me)_3P$, $(Me)_3PS$ and $(Me)_3PO$ and in the P–F and P–Cl bonds for the two series of CX_3P, CX_3PS and CX_3PO (X = Cl, F).[23] It can also be seen that a more electronegative group R leads to a smaller angle R–E–R in group 5 compounds ER_3 (E = N, P, As, *etc*.).[14]

These changes in bond lengths and angles have been interpreted[14] in terms of the valence-shell electron-pair repulsion theory: reduced bond lengths and larger angles are predicted as the electron pair of phosphorus (the lone-pair in P^{III} compounds) is increasingly drawn away by a more electronegative atom.

The charges of selected atoms obtained from Mulliken population analysis are presented in Table 3. Each of the substituents withdraws electrons from phosphorus. The amount of the withdrawn electrodensity is consistent with the electronegativities (O > N > S > H). Also, the magnitudes of formal charges on X and Y substituents (X, Y = O, S, NH, NH_2) follow the expected trend. The charges on oxygen, nitrogen and carbon are notably more unaffected on different substituents than sulfur.

Conformational Analysis and Torsional Barriers.—Conformational analysis were performed on all studied molecules with rotatable bonds (except methyl groups) using the 3-21G(*) basis set. For molecules with one rotational bond, conformational analyses were performed by rotating the torsional angle [C–P–X(Y)(Z)–H] 360° with steps of 30°. In each step only the torsional angle was fixed and the rest of the molecule was fully optimized. For molecules with two rotational bonds the rotating step was selected to be 60° in order to keep the computational task feasible. NH_2-groups were rotated with both torsional angles fixed at the same time in steps of 30° or 60° as explained above. The difference in torsional angles of the hydrogens in the NH_2-groups was selected to be that found in the fully optimised structure of each of the molecules. The results of the conformational analysis were presented graphically and each determined minima was then fully optimised using the 6-31G* basis set in order to find the conformation with minimum energy. Relative energies of all conformers determined and the corresponding values of torsional angles are summarised in Table 4.

For compounds with an NH_2-group it was characteristic that only one final conformation was found for the group, although

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

	Charge				
Compound	C	P	X	Y	Z
1	−0.722	1.406	−0.811	−0.852	−0.873
2	−0.716	1.271	−0.797	−0.796	−0.486
3	−0.718	1.229	−0.763	−0.826	−0.861
4	−0.710	0.976	−0.756	−0.710	−0.379
5	−0.707	0.898	−0.683	−0.683	−0.823
6	−0.686	0.556	−0.605	−0.611	−0.288
7	−0.711	1.378	−0.843	−0.843	−1.042
8	−0.711	1.318	−0.815	−1.056	−0.871
9	−0.696	1.269	−0.841	−1.022	−1.040
10	−0.705	1.189	−0.795	−0.817	−1.037
11	−0.699	1.137	−0.794	−0.973	−0.495
12	−0.693	1.088	−0.820	−0.952	−0.863
13	−0.683	0.803	−0.697	−0.931	−0.386
14	−0.680	1.043	−0.806	−0.979	−1.033
15	−0.720	1.240	−0.838	−0.838	−0.241
16	−0.698	0.815	−0.926	−0.903	
17	−0.718	1.001	−0.792	−0.791	−0.165
18	−0.706	0.685	−0.844	−0.589	
19	−0.684	0.608	−0.876	−0.887	
20	−0.697	0.617	−0.676	−0.676	−0.084
21	−0.673	0.307	−0.767	−0.409	
22	−0.702	1.117	−0.837	−1.016	−0.240
23	−0.688	0.713	−0.920	−1.021	
24	−0.691	0.849	−0.785	−0.978	−0.163
25	−0.668	0.485	−0.871	−1.008	

when the rotation was performed as explained above, two minima were located. When the final total optimatisation was performed, the minima had converted to the same one, in which the NH bonds tended to be *syn* to PX and/or PY bonds.

Torsional profiles of C–P–Z–H of **1**, **3**, **5** and **2**, **4**, **6** are presented in Figs. 1 and 2. The torsional barriers for these compounds at $\tau = 0°$ are in the range of 24–32 kJ mol^{-1}. At $\tau = 0°$ the Z–H (Z = O, S) bond and methyl-group are in the *syn* position. At $\tau = 180°$ the torsional barriers for compounds with an SH-group (**2**, **4**, **6**) are 7–12 kJ mol^{-1} (Fig. 2), but for compounds with an OH-group (**1**, **3**, **5**) the barriers are missing or, in the case of **1**, is only 2 kJ mol^{-1} (Fig. 1). This partially reflects the higher bond dipole of the OH than the SH bond and thus the higher tendency to arrange dipoles in an antiparallel manner in OH compounds compared to SH compounds. Torsional angles tend to have minimum values when Z–H and P–X or P–Y bonds are in a *syn* position. An explanation for this may be an intramolecular hydrogen bonding-type interaction between the hydrogen and X or Y atoms (X, Y = O, S, NH). In **23** and **25**, where there is only one electronegative atom bonded to phosphorus in addition to an NH_2-group, the other H atom of the NH_2-group is as expected in a *syn* position to the electronegative atom, and the other is *anti* to the methyl group and has a torsional angle of *ca.* 180°. In minimum structures the values of C–P–N–H torsional angles are near 180°, but for compounds with O attached to P in addition to NH (**8**, **9**, **22**) the *syn* conformations ($\tau = 80°$) are energetically quite close. For sulfur-substituted compounds (**12**, **13**, **14**, **24**) this conformer is missing possibly due to steric repulsion of the S atom.

Table 4 Calculated (6-31G*) relative energies and values of torsional angles of the conformers

Compound	Rotational group	Torsional angle/°^{a}	Relative energy/kJ mol^{-1}
1	OH	114.4	
2	SH	82.4	
3	OH	126.1	
4a	SH	280.0	0.0
4b	SH	81.1	0.7
5	OH	180.0	
6a	SH	79.5	0.0
6b	SH	180.0	6.6
7	NH_2	120.4 (239.3)	
8a	NH/OH	109.9 (130.6)	0.0
8b	NH/OH	173.2 (253.1)	1.2
8c	NH/OH	308.5 (161.4)	15.2
9a	NH_2/NH	234.2 (113.6)/167.0	0.0
9b	NH_2/NH	123.8 (241.1)/75.6	1.5
10	NH_2	120.6 (241.0)	
11a	NH/SH	175.7/271.6	0.0
11b	NH/SH	174.6/77.3	0.2
12a	NH/OH	166.8/247.8	0.0
12b	NH/OH	309.0/208.0	19.9
13a	NH/SH	167.9/76.9	0.0
13b	NH/SH	168.1/274.9	1.1
14	NH_2/NH	235.2 (113.7)/160.7	
16	OH	83.6	
18a	SH	64.9	0.0
18b	SH	192.5	0.4
19	OH	83.7	
21a	SH	70.1	0.0
21b	SH	267.0	7.1
21c	SH	189.7	7.5
22a	NH	171.1	0.0
22b	NH	83.8	3.4
22c	NH	308.0	14.7
23	NH_2	72.4 (186.2)	
24a	NH	161.4	0.0
24b	NH	308.9	23.3
25	NH_2	74.7 (190.3)	

[a] The value of the torsional angle of the other hydrogen of NH_2 is in parentheses. Only the other value is shown for symmetric molecules.

Table 5 Energetics for isomerisations (6-31G*)

Reaction			Energy/kJ mol^{-1}
1	**2** $MeP(O)_2SH^-$	→ **3** MeP(O)(S)OH	−38.6
2	**4** $MeP(O)(S)SH^-$	→ **5** $MeP(S)_2OH^-$	−41.4
3	**8** $MeP(O)(NH)OH^-$	→ **7** $MeP(O)_2NH_2^-$	−106.3
4	**11** $MeP(O)(NH)SH^-$	→**10** $MeP(O)(S)NH_2^-$	−139.9
5	**11** $MeP(O)(NH)SH^-$	→**12** $MeP(S)NH)OH^-$	−39.9
6	**12** $MeP(S)(NH)OH^-$	→**10** $MeP(O)(S)NH_2^-$	−99.9
7	**16** $MeP(O)OH^-$	→**15** $MeP(O)_2H^-$	−113.7
8	**18** $MeP(O)SH^-$	→**17** $MeP(O)(S)H^-$	−122.0
9	**18** $MeP(O)SH^-$	→**19** $MeP(S)OH^-$	−67.9
10	**19** $MeP(S)OH^-$	→**17** $MeP(O)(S)H^-$	−54.1
11	**21** $MeP(S)SH^-$	→**20** $MeP(S)_2H^-$	−73.5
12	**23** $MeP(O)NH_2^-$	→**22** $MeP(O)(NH)H^-$	−11.7
13	**24** $MeP(S)(NH)H^-$	→**25** $MeP(S)NH_2^-$	−49.4

Energetics of Isomerisation.—The isomerisation reactions and energies are summarised in Table 5. On the basis of these results we can find three trends. (*a*) $MeP(OH)(X)S^-$ (X, Y = O, S, NH) species are more stable than their $MeP(O)(X)SH^-$ isomers (reactions 1,2, 5, 9). (*b*) $MeP(X)(Y)NH_2^-$ (X, Y = O or S) species are more stable than their MeP(X) $(YY)NH^-$ isomers (reactions 3, 4, 6). (*c*) $MeP(X)(Y)H^-$ (X, Y = O or S) species are more stable than their $MeP(YH)X^-$ isomers (reactions 7, 8, 10, 11). Isomeric pairs 12 and 13 with NH_2-groups show the opposite behaviour with respect to the most stable isomer: the isomer $MeP(O)(NH)H^-$ is more stable than $MeP(O)NH_2^-$ by 11.7 kJ mol^{-1} (reaction 12), but $MeP(S)NH_2^-$ is 49.4 kJ mol^{-1} more stable than $MeP(S)(NH)H^-$ (reaction 13). In point (*c*) one reason for the high preference of $MeP(X)(Y)H^-$ isomers over $MeP(YH)X^-$ must be the delocalisation of the anionic charge: in $MeP(YH)X^-$ species the charge is mostly located on one atom (X), but in $MeP(X)(Y)H^-$

Table 6 Energetics for model reactions (6-31G*)

	Reaction		Energy/kJ mol^{-1} [a]
1	**3** $MeP(O)(S)OH^- + H_2O$	$\rightarrow$ **1** $MeP(O)_2OH^- + H_2S$	-3.3
2	**5** $MeP(S)_2OH^- + 2H_2O$	$\rightarrow$ **1** $MeP(O)_2OH^- + 2H_2S$	-12.3
3	**5** $MeP(S)_2OH^- + H_2O$	$\rightarrow$ **3** $MeP(O)(S)OH^- + H_2S$	-9.0
4	**6** $MeP(S)_2SH^- + 3H_2O$	$\rightarrow$ **1** $MeP(O)_2OH^- + 3H_2S$	-54.9
5	**6** $MeP(S)_2SH^- + 2H_2O$	$\rightarrow$ **3** $MeP(O)(S)OH^- + 2H_2S$	-51.6
6	**6** $MeP(S)_2SH^- + H_2O$	$\rightarrow$ **5** $MeP(S)_2OH^- + H_2S$	-42.6
7	**7** $MeP(O)_2NH_2^- + H_2S$	$\rightarrow$ **10** $MeP(O)(S)NH_2^- + H_2O$	-1.8
8	**9** $MeP(O)(NH)NH_2^- + H_2O$	$\rightarrow$ **7** $MeP(O)_2NH_2^- + NH_3$	-170.7
9	**9** $MeP(O)(NH)NH_2^- + H_2S$	$\rightarrow$ **10** $MeP(O)(S)NH_2^- + NH_3$	-172.5
10	**9** $MeP(O)(NH)NH_2^- + 2H_2S$	$\rightarrow$ **13** $MeP(S)(NH)SH^- + NH_3 + H_2O$	-33.2
11	**9** $MeP(O)(NH)NH_2^- + H_2S$	$\rightarrow$ **14** $MeP(S)(NH)NH_2^- + H_2O$	-15.4
12	**13** $MeP(S)(NH)SH^- + 2H_2O$	$\rightarrow$ **7** $MeP(O)_2NH_2^- + 2H_2S$	-137.5
13	**13** $MeP(S)(NH)SH^- + H_2O$	$\rightarrow$ **10** $MeP(O)(S)NH_2^- + H_2S$	-139.3
14	**14** $MeP(S)(NH)NH_2^- + 2H_2O$	$\rightarrow$ **7** $MeP(O)_2NH_2^- + H_2S + NH_3$	-155.4
15	**14** $MeP(S)(NH)NH_2^- + H_2O$	$\rightarrow$ **10** $MeP(O)(S)NH_2^- + NH_3$	-157.1
16	**14** $MeP(S) (NH)NH_2^- + H_2O$	$\rightarrow$ **13** $MeP(S)(NH)SH^- + NH_3$	-17.8
17	**15** $MeP(O)_2H^- + H_2S$	$\rightarrow$ **17** $MeP(O)(S)H^- + H_2O$	$-12.4\ (-12.0)$
18	**15** $MeP(O)_2H^- + 2H_2S$	$\rightarrow$ **20** $MeP(S)_2H^- + 2H_2O$	$-30.4\ (-28.8)$
19	**17** $MeP(O)(S)H^- + H_2S$	$\rightarrow$ **20** $MeP(S)_2H^- + H_2O$	$-17.9\ (-16.8)$
20	**22** $MeP(O)(NH)H^- + H_2O$	$\rightarrow$ **15** $MeP(O)_2H^- + NH_3$	$-164.8\ (-161.4)$
21	**22** $MeP(O)(NH)H^- + H_2S$	$\rightarrow$ **17** $MeP(O)(S)H^- + NH_3$	$-177.3\ (-173.5)$
22	**22** $MeP(O)(NH)H^- + 2H_2S$	$\rightarrow$ **20** $MeP(S)_2H^- + NH_3 + H_2O$	$-195.2\ (-190.2)$
23	**22** $MeP(O)(NH)H^- + H_2S$	$\rightarrow$ **25** $MeP(S)NH_2^- + H_2O$	-75.9
24	**25** $MeP(S)NH_2^- + 2H_2O$	$\rightarrow$ **15** $MeP(O)_2H^- + NH_3 + H_2S$	-88.9
25	**25** $MeP(S)NH_2^- + H_2O$	$\rightarrow$ **17** $MeP(O)(S)H^- + NH_3$	-101.4
26	**25** $MeP(S)NH_2^- + H_2S$	$\rightarrow$ **20** $MeP(S)_2H^- + NH_3$	-119.3

[a] MP2/6-31G*//6-31G* energies in parentheses.

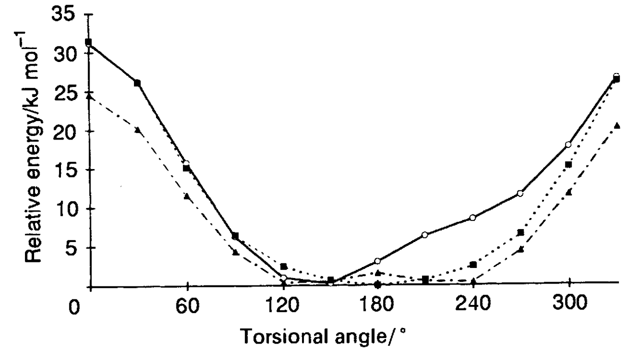


Fig. 1 Torsional profiles of C–P–O–H of compounds **1** (▲), **3** (○) and **5** (■) using 3-21G(*)

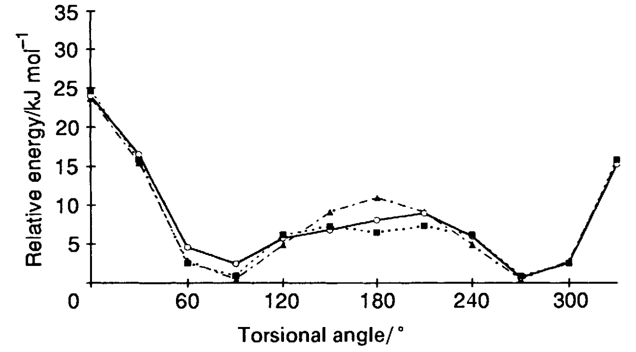


Fig. 2 Torsional profiles of C–P–S–H of compounds **2** (▲), **4** (○) and **6** (■) using 3-21G(*)

species it is delocalised on two atoms (X and Y). This effect also partially explains the difference between the isomerisation energies of $MeP(OH)O^- \rightarrow MeP(O)_2H^-$ (reaction 7) and its neutral counterpart $MeP(OH)(OH) \rightarrow MeP(O)(OH)H$. In the latter reaction the energy has been calculated (6-31G*) to be -35.1 kJ mol^{-1} [1,5] and in the former reaction it is -113.7 kJ mol^{-1}.

Model Reactions.—Energetics for model reactions are summarised in Table 6. In the case of a molecule with isomers, only the most stable one is taken into account. In the reactions of P^V compounds (reactions 1–16), the molecules with oxygens are the most stable and consecutive substitutions with sulfur and nitrogen make molecules less stable. The P^{III} compounds with sulfur are, on the other hand, more stable than their oxygen analogues. It is also noticeable that energy differences between oxygen and sulfur analogues are always comparatively small: *e.g.* in reaction 1 the difference is 3.3 kJ mol^{-1}, in reaction 2 it is 12.3 kJ mol^{-1} and in reaction 4 it is 54.9 kJ mol^{-1} in favour of the oxygen analogue. On the contrary, the reactions between nitrogen analogues and oxygen or sulfur analogues strongly favour the latter compounds (ΔE = 100–200 kJ mol^{-1}). On the basis of the model reactions the most stable compounds are methylphosphonate (**1**), methylphosphonamidate (**7**) and methylphosphindithioate (**20**). It must be remembered that because we are neglecting zero-point vibration and electron correlation corrections, there may be errors in the energies of model reactions and also in the isomerisation energies compared to calculations at the higher level of theory. However, earlier results of comparable isomerizations suggest that 6-31G* reproduces well the results including the electron correlation.[9,15,18,24,29] Also, the energies of some phosphinate model reactions calculated at the MP2/6-31G*//6-31G* level (Table 6) show that the neglect of electron correlation has only a small effect on energies of the model reactions. The energies with and without MP2 correction reported in Table 6 are within 5 kJ mol^{-1}.

Conclusions

In the present *ab initio* study we have elucidated the effects of sulfur and nitrogen substituents on the properties of 23 different monoanionic methylphosphonate and methylphosphinate analogues. Conformational analyses were performed on all compounds with rotational bonds and torsional barriers were investigated. The relative stabilities of related compounds were compared with the help of model reactions. The study gives clear indications of relative stabilities of isomers and preferred conformations of the compounds. The most stable compounds were found to be methylphosphonate (**1**), methylphosphonamidate (**7**) and methylphosphindithioate (**20**). P^V compounds with oxygen bound to phosphorus were generally the most stable analogues and consecutive substitutions by sulfur and nitrogen made these compounds less stable. The sulfur analogues of P^{III} compounds were found to be the most stable. The compounds with P=NH groups were calculated to be the most unstable analogues.

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