Unprecedented Structures for PLi_5, SLi_4, and SLi_6

Colin J. Marsden

Department of Inorganic Chemistry, The University of Melbourne, Parkville, Victoria, 3052 Australia

Theoretical calculations have shown that PLi_5, SLi_4, and SLi_6 challenge conventional notions of molecular structure and bonding.

There has been recent interest in the theoretical exploration of lithium chemistry. While a formal analogy may be drawn between the ns^1 electronic structures of H and Li, there are of course very substantial differences in their overall chemical behaviour. Stoicheiometries and structures have been reported for CLi_6,[1] OLi_4,[2] and $SiLi_4$[3] which bear no resemblance to analogous hydrogen-containing compounds. I now describe a theoretical study of some lithium derivatives of P and S. These compounds have not yet been considered in the literature, and their structures are predicted to be even more remarkable than those of their N and O counterparts. PLi_5 has C_{4v} symmetry, SLi_6 has D_{3d} symmetry, but a definitive structural prediction is not yet possible for SLi_4, which has almost degenerate C_{2v} and C_{3v} isomers. All three 'hyperlithiated' compounds are predicted to be thermodynamically stable both to atomisation and to loss of Li_2, by substantial margins, but are probably less stable than the elements in their standard states.

Geometry optimisations were performed using the Gaussian 86 program[4] and the 3-21G(*) basis. Vibrational frequencies were calculated with this basis from analytical SCF second derivatives for each stationary point located. Better estimates of final molecular energies were obtained with the non-standard 6-31G(*) basis (which does not contain d functions on Li) at theoretical levels up to MP4SDQ. The success of theoretical methods of this type in predicting molecular structures is impressive, and they give at least semiquantitatively useful estimates of reaction energies.[5] Geometrical parameters for the various stationary points of PLi_5, SLi_4, and SLi_6 are displayed in Figure 1. Absolute energies are reported in Table 1 and relative energies are presented in Table 2.

Two stationary points were located for PLi_5. The C_{4v} isomer (**1**) is a true minimum, whose lowest vibrational mode is at 56 cm^{-1} (a_1), but the D_{3h} structure (**2**) has an e′ imaginary bending motion at 50i cm^{-1}, which is an in-plane motion of the equatorial atoms leading to (**1**) *via* a C_{2v} pathway. Isomer (**1**) is slightly but consistently more stable than (**2**) at all levels of theory used here. All other phosphoranes studied to date, either by experimental or theoretical methods, have a trigonal

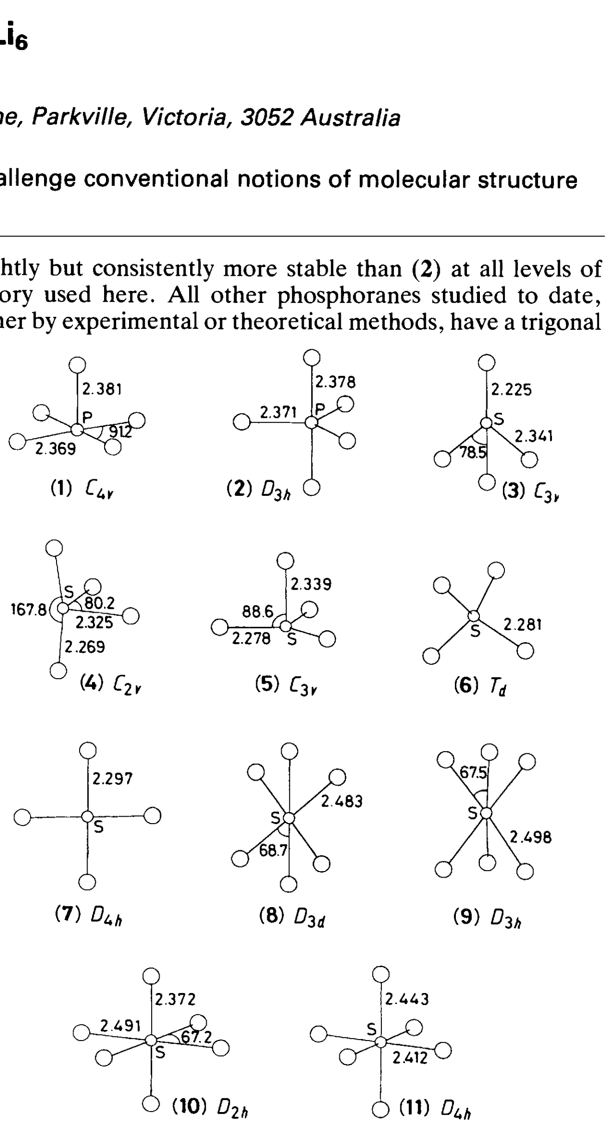

Figure 1. Optimized HF/3-21G(*) geometries of isomers of PLi_5, (**1**), (**2**); SLi_4, (**3**)—(**7**); and SLi_6, (**8**)—(**11**). Bond lengths in Å, angles in degrees.

Table 1. Energies of PLi_n and SLi_n molecules (−atomic units).

Species		Point group	3-21G(*)// 3-21G(*)	Z.P.E.[a]	6-31G(*)//3-21G(*)				
					RHF/	MP2/	MP3/	MP4DQ/	MP4SDQ/
PLi_3		C_{3v}	361.300 80	11.8 (0)	363.071 23	363.205 85	363.214 80	363.214 85	363.217 61
PLi_5	**(1)**	C_{4v}	376.136 69	18.1 (0)	377.996 01	378.164 42	378.175 37	378.172 88	
	(2)	D_{3h}	376.135 35	17.0 (2)	377.994 55	378.164 02	378.174 61	378.171 76	
SLi_2		$D_{\infty h}$	410.537 78	8.1 (0)	412.474 34	412.601 61	412.611 92	412.612 28	412.613 50
SLi_4	**(3)**	C_{3v}	425.362 92	14.6 (0)	427.388 82	427.547 21	427.563 31	427.564 59	427.566 18
	(4)	C_{2v}	425.361 62	13.9 (1)	427.387 38	427.549 43	427.564 76	427.565 06	427.566 74
	(5)	C_{3v}	425.360 33	13.3 (2)	427.385 98	427.548 67	427.563 85	427.563 98	427.565 58
	(6)	T_d	425.358 85	12.5 (3)	427.382 96	427.548 10	427.561 71	427.560 42	427.561 92
	(7)	D_{4h}	425.346 23	12.8 (2)	427.372 12	427.540 52	427.555 24		
SLi_6	**(8)**	D_{3d}	440.151 87	21.0 (0)	442.271 07	442.452 55	442.476 13	442.480 16	
	(9)	D_{3h}	440.148 49	20.6 (1)	442.268 44	442.450 57	442.474 05	442.478 08	
	(10)	D_{2h}	440.133 66	18.0 (2)	442.253 56	442.441 96	442.464 51	442.467 30	
	(11)	D_{4h}	440.111 41	22.5 (3)	442.229 47	442.426 21	442.447 80		

[a] Zero-point vibrational energy, unscaled, in kJ mol^{-1}, at HF/3-21G(*). Numbers of imaginary vibrational frequencies are given in parentheses for each stationary point.

Table 2. Relative energies and binding energies of PLi_n and SLi_n molecules (kJ mol^{-1}).

Species		3-21G(*) //3-21G(*)	6-31G(*)//3-21G(*)				
			RHF/	MP2/	MP3/	MP4DQ/	MP4SDQ/
PLi_5	**(1)**	0.0	0.0	0.0	0.0	0.0	
	(2)	3.5	3.8	1.1	2.0	2.9	
Δ_1[a]		−175.0	−153.5	−201.6	−190.4	−176.9	
SLi_4	**(3)**	0.0	0.0	5.8	3.8	1.2	1.5
	(4)	3.4	3.8	0.0	0.0	0.0	0.0
	(5)	6.8	7.5	2.0	2.4	2.8	3.0
	(6)	10.7	15.4	3.5	8.0	12.2	12.7
	(7)	43.8	43.8	23.4	25.0		
Δ_2[b]		−146.7	−126.4	−173.3	−170.1	−163.1	−164.0
SLi_6	**(8)**	0.0	0.0	0.0	0.0	0.0	
	(9)	8.9	6.9	5.2	5.5	5.5	
	(10)	47.8	46.0	27.8	30.5	33.8	
	(11)	106.2	109.2	69.2	74.4		
Δ_3[c]		−51.7	−41.8	−56.0	−54.4	−63.9	

[a] Energy of PLi_5 compared to sum of (PLi_3 + Li_2). [b] Energy of SLi_4 compared to sum of (SLi_2 + Li_2). [c] Energy of SLi_6 compared to sum of (SLi_4 + Li_2).

bipyramidal structure, apart from a class containing bidentate chelating ligands with internal ring systems.[6] Indeed, of all MX_5 species, where M is a main group element and X monodentate, only $SbPh_5$[7] and $InCl_5^{2-}$[8] are known to have square pyramidal structures, and 'packing factors' may well be influential for these solid-state cases, since a trigonal bipyramidal structure is predicted[9] by *ab initio* methods for AlF_5^{2-}.

The occupied valence orbitals for **(1)** are $6a_1^2 3e^4 7a_1^2 8a_1^2$, which may be contrasted with $4a_1^2 2e^4 5a_1^2 1b_2^2$ in PH_5 if C_{4v} symmetry is imposed. Orbital $8a_1$ in **(1)** is bonding between adjacent lithium atoms, but P–Li antibonding. Another C_{4v} stationary point for PLi_5 was found inadvertently, corresponding to the $a_1^2 \rightarrow b_1^2$ HOMO → LUMO excitation. This second C_{4v} state is a transition state, and lies 233 kJ mol^{-1} above **(1)** at the 3-21G(*)SCF level. PLi_5 is predicted to be substantially more stable than (PLi_3 + Li_2), as reported in Table 2. The atomisation energy of PLi_3 is calculated to be 416 kJ mol^{-1} [MP4DQ/6-31G(*)//3-21G(*)], but since solid phosphorus and metallic lithium lie some 820 kJ mol^{-1} below ($P_{(g)}$ + 3 $Li_{(g)}$), it is probable that PLi_5 is unstable relative to solid phosphorus and metallic lithium. However, its preparation is not necessarily precluded by thermodynamic instability.

No fewer than *five* different stationary points were located for SLi_4. Only one of these is a true minimum at 3-21G(*). Interestingly, this isomer **(3)** has C_{3v} symmetry. I believe that there is no precedent for an MX_4 species to have a C_{3v} ground state. It is remarkable that three other isomers of SLi_4 lie within 11 kJ mol^{-1} of **(3)** at 3-21G(*), especially given the enormous changes in molecular geometry evident in Figure 1. SLi_4 clearly has exceptional fluxional character. It should be noted that only one stationary point, of T_d symmetry, has been reported for OLi_4.[2] The relative energies of **(3)**, **(4)**, and **(5)** change as more exact theoretical methods are used (see Table 2). Isomer **(4)** is apparently stabilized over **(3)** by correlation effects, though since geometry optimisation was not undertaken with correlated wavefunctions this conclusion is tentative for the moment. Although it is not yet possible to predict with confidence which structure is adopted by SLi_4, there can be no doubt that it is more thermodynamically stable than (SLi_2 + Li_2).

Four different stationary points were located for SLi_6, of which only one, **(8)**, is a true minimum. Isomer **(8)** is the most stable isomer of SLi_6 at all levels of theory used here. I know of no other MX_6 molecule with a D_{3d} ground state, with the probable exception of OLi_6[10] for which vibrational frequencies have apparently not been calculated. The single D_{3h} imaginary vibrational frequency of 66i cm^{-1} for (**9**) is an a″ mode which rotates one 'eclipsed' Li_3 prismatic face relative to the other, to give the 'staggered' D_{3d} isomer (**8**).

The non-octahedral structure of SLi_6 may appear surprising, but can be traced to a Jahn–Teller distortion. Octahedral SLi_6 would have the valence orbital configuration $4a_{1g}{}^2 3t_{1u}{}^6 5a_{1g}{}^2 4t_{1u}{}^2$; the 'extra' valence bonding a_{1g} and t_{1u} orbitals which are possible in SLi_6 but not in SH_6 involve Li 2p orbitals. SLi_6 is predicted to have significant thermodynamic stability compared to (SLi_4 + Li_2), but no structure was found for SLi_8 lying below (SLi_6 + Li_2). Inspection of Figure 1 shows that many of the structures reported here may be regarded as containing triangular $Li_3{}^+$ fragments. Note that the closest Li · · · Li separation is 2.803 Å in (**8**) and 2.972 Å in (**3**) compared to 3.055 Å in $Li_3{}^+$ (3-21G/SCF calculations).

While the theoretical methods used here work well for 'standard' molecules,[5] they may be less applicable to unusual cases. Preliminary MCSCF and MRCI calculations have revealed that while PLi_3 and SLi_2 are reasonably well described by a single reference calculation, the 'hyperlithiated' species have more complex electronic structures with Hartree–Fock reference coefficients of about 0.93 (PLi_5), 0.94 (SLi_4), and 0.89 (SLi_6). A multireference approach will therefore probably be necessary to give a definitive theoretical description of these hyperlithiated compounds. Work is continuing in this area.

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References

1 P. v. R. Schleyer, E.-U. Würthwein, E. Kaufmann, T. Clark, and J. A. Pople, *J. Am. Chem. Soc.*, 1982, **104**, 5839.

2 P. v R. Schleyer, E.-U. Würthwein, and J. A. Pople, *J. Am. Chem. Soc.*, 1983, **105**, 5930.

3 P. v. R. Schleyer and A. E. Reed, *J. Am. Chem. Soc.*, 1988, **110**, 4453.

4 M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. J. Defrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fleuder, and J. A. Pople, Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 1987.

5 W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, 'Ab Initio Molecular Orbital Theory,' Wiley, New York, 1986.

6 R. A. Holmes, 'Penta Coordinated Phosphorus I,' Monograph 175, American Chemical Society, Washington, D.C., 1980, and references cited therein.

7 P. J. Wheatley, *J. Chem. Soc.*, 1964, 3718.

8 D. S. Brown, F. W. B. Einstein, and D. G. Tuck, *Inorg. Chem.*, 1969, **8**, 14.

9 C. J. Marsden, to be submitted for publication.

10 P. v. R. Schleyer, 'New Horizons of Quantum Chemistry,' eds. P.-O. Löwdin and B. Pullman, Reidel, Dordrecht, The Netherlands, 1983, pp. 95—109.