An ab Initio Study of the P−C Bond Rotation in Phosphorus(V)-Stabilized Carbanions: The Phosphoryl versus Thiophosphoryl Group

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The potential energy surface for the P−C bond rotation in the *P*-methylthioxophosphonic diamide anion ($\mathbf{8}^-$) has been computed at MP4(SDQ)/6-31+G*//6-31+G*. An extensive basis set evaluation up to the MP4(SDTQ)/6-311+G**//MP2/6-311+G** level for four rotamers of $\mathbf{8}^-$ led to the selection of the above basis set for optimal performance. Results were compared to the previously studied and recomputed phosphoryl analog ($\mathbf{7}^-$). The experimentally determined higher P−C bond rotational barrier for the thio species is found by our calculations as well, and its roots can be traced by structural comparisons, an isodesmic equation, and NBO analysis. The isodesmic equation for the stabilization of a carbanion by the phosphoryl groups yields energies (P═O, −40, P═S, −47 kcal/mol) in the vicinity of those for the strongest carbanion-stabilizing heteroatomic groups (π acceptors like BH_2 or AlH_2). The NBO method indicates a stronger back-bonding from the oxygen lone pairs into the σ^* (P−N) orbitals than from those of sulfur. This effect destabilizes the ground state (GS) geometry in which the lone pair on carbon interacts with the same σ^* orbitals. Inclusion of molecules having substituents on phosphorus with a higher (fluorine) and a lower (hydrogen) electronegativity than nitrogen reveals a more general picture. With the electronegative substituents on phosphorus, the favorable carbon lone pair stabilization in the GS of the thio derivatives combines with similar stabilizing interactions for both chalcogen analogs in the TS's resulting in higher rotational barriers for the sulfur species. With electropositive substituents, the opposite effects are observed.

Introduction

Carbanions are arguably the most useful and versatile class of reactive intermediates for C−C bond construction.[1] Stabilization of these species by attachment of a heteroatom substituent at the carbanionic center greatly facilitates their handling and characterization and, most importantly, enhances their selectivity in subsequent reactions.[2] In recent years we have been involved in a broadly-based program on the structure, reactivity, and synthetic applications of phosphorus(V)-stabilized carbanions.[3] One of the more intriguing dimensions of this program has been the comparison of the structural and synthetic consequences of employing phosphoryl (P═O) versus thiophosphoryl (P═S) type anion-stabilizing groups. Insofar as our ultimate goal is the fundamental understanding of the relationship between structure and reactivity of phosphorus(V)-stabilized carbanions, we have undertaken the comparison of phosphoryl- and thiophosphoryl-stabilized anions by computational methods.

Background

Preparative. One of the most striking manifestations of the difference between phosphoryl- and thiophosphoryl-stabilized anions is in the stereoselectivity of their reaction with electrophilic agents in a chiral environment, Figure 1.[4] The diastereoselectivity depends on many factors including (1) the location of the lithium ion, (2) the conformation of the heterocycle, (3) the orientation of the carbanion substituents in the reactive conformation, and (4) the relative rates of P−C bond rotation and of the reactions.[6] Early working hypotheses[5a,7] were based on assumptions about theses factors which were derived from experimental findings in related systems.[2e,8] Only recently has a more detailed picture of the bonding and conformational characteristics of phosphorus-stabilized carbanions been available from the combined body of information including NMR studies,[9,10] X-ray analyses,[6,9a−c,10] and MO calculations.[6,10,11]

Structural. In examinations of solution and solid state structures of phosphoryl- and thiophosphoryl-stabilized anions, the differences between these families

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[1] (a) Hanack, M. *Methoden der Organischen Chemie (Houben-Weyl)*; G. Thieme Verlag: Stuttgart, New York, 1993; Vol. E 19d. (b) Snieckus, V. *Advances in Carbanion Chemistry*; Jai Press: Greenwich, CT, 1992; Vol. 1. (c) Trost, B. M.; Fleming, I. *Comprehensive Organic Synthesis*; Pergamon Press: Oxford, U.K., 1991; Vol. 1. (d) Brandsma, L.; Verkruijsse, H. *Preparative Polar Organometallic Chemistry 1*; Springer Verlag: Berlin, 1987. (e) Brandsma, L. *Preparative Polar Organometallic Chemistry 2*; Springer Verlag: Berlin, 1990.

[2] (a) Biellman, J.-F.; Ducep, J.-P. *Org. React.* **1982**, *27*, 1. (b) Krief, A. *Tetrahedron* **1980**, *36*, 2531. (c) Beak, P.; Reitz, D. B. *Chem. Rev.* **1978**, *78*, 275. (d) Werstiuk, N. H. *Tetrahedron* **1983**, *39*, 205. (e) Boche, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 277.

[3] Denmark, S. E.; Chen, C.-T.; Reed, R. A. *Adv. Carbanion Chem.*, in press.

[4] Denmark, S. E.; Chen, C.-T. *J. Am. Chem. Soc.*, in press.

[5] (a) Denmark, S. E.; Dorow, R. L. *J. Org. Chem.* **1990**, *55*, 5926. (b) Denmark, S. E.; Marlin, J. E. *J. Org. Chem.* **1991**, *56*, 1003. (c) Denmark, S. E.; Chatani, N.; Pansare, S. V. *Tetrahedron* **1992**, *48*, 2191. (d) Denmark, S. E.; Chen, C.-T. *J. Am. Chem. Soc.* **1992**, *114*, 10674. (e) Denmark, S. E.; Chen, C.-T. *J. Org. Chem.* **1994**, *59*, 2922.

[6] Cramer, C. J.; Denmark, S. E.; Miller, P. C.; Dorow, R. L.; Swiss, K. A.;Wilson, S. R. *J. Am. Chem. Soc.* **1994**, *116*, 2437.

[7] Denmark, S. E.; Marlin, J. E. *J. Org. Chem.* **1987**, *52*, 5742.

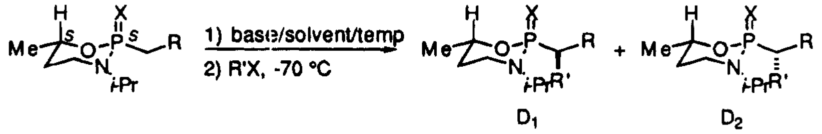
[8] (a) Bottin-Strzalko, T.; Seyden-Penne, J.; Pouet, M.-J.; Simonnin, M.-P. *J. Org. Chem.* **1978**, *43*, 4346. (b) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624. (c) Gais, H.-J.; Hellmann, G.; Günther, H.; Lopez, F.; Lindner, H. J.; Braun, S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1025. (d) Gais, H.-J.; Hellmann, G.; Lindner, H. J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 100.

[9] (a) Denmark, S. E.; Dorow, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 864. (b) Denmark, S. E.; Miller, P. C.; Wilson, S. R. *J. Am. Chem. Soc.* **1991**, *113*. 1468. (c) Denmark, S. E.; Swiss, K. A.; Wilson, S. R. *J. Am. Chem. Soc.* **1993**, *115*, 3826. (d) Denmark, S. E.; Swiss, K. A. *J. Am. Chem. Soc.* **1993**, *115*, 12195.

[10] Zarges, W.; Marsch, M.; Harms, K.; Haller, F.; Frenking, G.; Boche, G. *Chem. Ber.* **1991**, *124*, 861.

[11] Denmark, S. E.; Cramer, C. J. *J. Org. Chem.* **1990**, *55*, 1806.

0022-3263/95/1960-5867$09.00/0



R	X	R'X	solvent	additive	ratio $D_1 : D_2$	yield, %
Ph	O	MeI	THF	none	34 : 1	93
Ph	S	MeI	THF	none	>1000 : 1	98
Ph	O	BnBr	THF	none	17 : 1	89
Ph	S	BnBr	THF	none	>1000 : 1	93
MeO	S	MeI	THF	HMPA	16 : 1	84
MeO	S	MeI	Et_2O	PMDTA	1 : 11	93

Figure 1. Comparison of alkylation selectivities for P=O- versus P=S-stabilized anions.

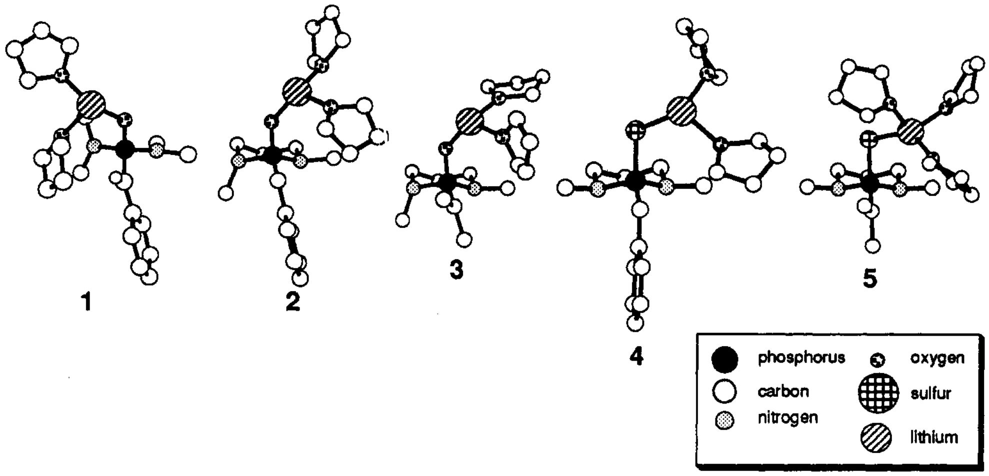


Figure 2. X-ray structures of P=O (**1**,[6] **2**,[9a] and **3**[9b]) and P=S (**4**[9c] and **5**[12]) stabilized anions.

of organolithium compounds are clearly manifest. The X-ray crystallographic structures of five lithiated oxo- and thioxophosphoryl diamide systems **1**–**5** exhibit an array of characteristic similarities (Figure 2): (1) the lithium cation is always bonded to the chalcogen on phosphorus and has no contact with the carbanion, (2) the carbanionic center is almost or completely planar, and (3) the carbanion is oriented parallel to the P=X bond (X = O, S) or nearly so.

These structures also illustrate important differences: (1) while **1-4** crystallize as dimers with two THF molecules on each lithium, **5** crystallizes as a tris-THF-solvated monomer,[12] (2) disposition of the *N*-methyl groups in the P=O species **2** and **3** are the same with one pseudoaxial and one pseudoequatorial group, and (3) in the P=S compounds **4** and **5** both *N*-methyl groups are equatorial. On the basis of extensive NMR studies, we have found the solution structures of these compounds to be similar to the solid state structures except that *both* P=S derivatives are monomeric in solution. No lithium–carbon contact is present in solution in any of the systems **1**–**5**.

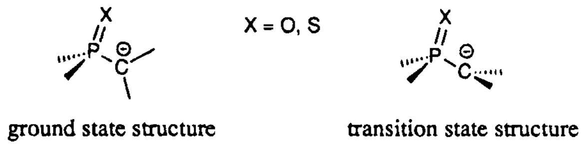


Figure 3. Anion orientations for GS and TS structures of phosphorus(V)-stabilized anions.

Variable temperature solution NMR experiments have also provided an activation barrier for the P–C bond rotation in the *P*-isopropyl phosphoryl compound **3** ($\Delta G^{\ddagger}$ (Me_2O) = 6.7 (± 0.6) kcal/mol)[6] and in the thiophosphoryl analog **5** ($\Delta G^{\ddagger}$ (THF) = 9.8 (± 0.3) kcal/mol).[6] This striking difference has been rationalized on the basis of hyperconjugative orbital interactions:[9c] the superior acceptor properties of the σ^* (P–N) over the σ^* (P=X) orbitals account for the parallel anion arrangement in the ground state (GS) structures (Figure 3). In the perpendicular orientation of the carbon lone pair in the transition state (TS) structures, the major stabilization derives from its overlap with the σ^* (P=X) which was argued to be inferior for P=S compared to P=O, thus yielding a higher rotational barrier for the thio analog. However, from the extended analysis reported herein, we will show that this orbital overlap is slightly better for P=S and that the difference in rotational barriers comes from differences in GS stabilities.

Theoretical. Stabilization of a carbanion through phosphorus substituents has attracted considerable theoretical interest. Early work was mainly concerned with ylides.[13] The origin of the favorable influence of second-row atoms on a carbanion could only be assessed with sufficiently large basis sets. In a landmark achievement, Schleyer, Houk, and co-workers attributed the stabiliza-

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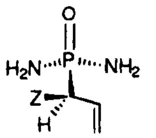
[12] Kranz, M.; Swiss, K. A.; Wilson, S. R.; Denmark, S. E. Submitted for publication.

tion effects to the easier polarizability and more electropositive character of second-row substituents and to improved negative hyperconjugation compared to first-row substituents.[14]

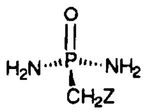
Stabilization of a carbanion by a phosphoryl group in the methylphosphine oxide anion has been shown by Streitwieser et al. at 3-21+G* to occur via electrostatic interactions with a strongly polar P=O bond.[15] The crystal structure of diethyl *P*-(α-lithiobenzyl)phosphonate led Boche et al. to calculate the minimum structures for the *P*-methylphosphonate anion and the *P*-methylphosphonic diamide anion at 6-31+G**//3-21G* + ZPE.[10] They found energy minima with a pseudoparallel and a pseudoperpendicular carbanion relative to the P=O bond for both anions, where the former orientation corresponds to the solid state arrangement of the diamide **2** shown above and the latter to that of the phosphonate.[10] The small energy difference between both minima (1.0 and 0.1 kcal/mol, respectively) convinced them that crystal packing forces were responsible for the experimentally observed preference.

Denmark and Cramer have carried out two very detailed studies of neutral, anionic, and lithiated *P*-allyl-[11] (**6**) and *P*-methylphosphonic diamides[6] (**7**) in which they addressed the energetics of P–C bond rotation. In accord with findings by Streitwieser et al.,[15] a high ionic character in the neutral species as well as in the deprotonated molecules is found. In the earlier paper, they concentrated on changes in hybridization and charge localization in the carbon chain upon deprotonation and coordination of the oxygen with lithium. In this and their later work, they suggested that the small basis set ($3\text{-}21G^{(*)}$) gives spuriously planar nitrogen atoms. At a higher level of theory ($6\text{-}31{+}G^{*(*)}$), the variable response of the significantly pyramidalized nitrogens gives rise to more than one energy minimum for a defined O=P–C–H dihedral angle.[6] The relative energies of the four stationary points for $\mathbf{7}^-$ depend on the degree of negative hyperconjugation between the carbon and nitrogen lone pairs and the σ^* orbitals accessible in the particular rotamer. The same model system $\mathbf{7}^-$ was then used to simulate computationally the crystal structures of **2** and **3** by constraining both amino groups to the solid state orientation. Having locked the P–N rotation, only one minimum and one TS is found upon P–C bond rotation and will be discussed in detail below. Coordination of lithium to the oxygen of the constrained model system does not dramatically change the geometries but raises the rotational barrier by about 1 kcal/mol.



6

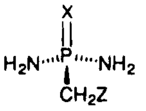
Z = H, anion, Li



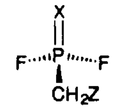
7

Z = anion

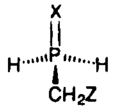
The striking reaction stereoselectivity and structural differences between the phosphoryl- and thiophosphoryl-based reagents stimulated our computational investigation into the origins of the experimental observations. The goals we set for this endeavor include the following: (1) to establish an appropriate basis set for these systems, (2) to scan the potential energy surface for the thiophosphoryl analog of $\mathbf{7}^-$ ($\mathbf{8}^-$), (3) to reevaluate the potential energy surface of $\mathbf{7}^-$, and finally (4) to trace the origin of the stabilizing effects in both compounds by analyzing their wavefunctions. To establish the observed interactions as general trends, the same wavefunction analysis has been performed for the oxo and thio analogs of **7** and **8** with more (fluorine, **9**, **10**) and less (hydrogen, **11**, **12**) electronegative phosphorus substituents.



7 X = O
8 X = S



9 X = O
10 X = S



11 X = O
12 X = S

Z = H, anion

A final word concerning the chemical bonding in phosphoryl and thiophosphoryl compounds. Gilheany very recently published a comprehensive review article about the bonding situation in phosphines, phosphine oxides and sulfides, and phosphonium ylides.[16] He cites experimental evidence for a strong, short, and polar P=O bond with a bond order of greater than 2 and a somewhat weaker and less polar P=S bond with a bond order less than 2.[17] The fortuitous correspondence between bond strength, bond order, and number of electron pairs exists only among second-row elements and is elusive for lower rows: the P=O bond may contain up to four electron pairs but has a bond strength/order of approximately 2.

Methods

Standard basis sets[18] incorporated into the GAUSSIAN 92 program[19] were employed on an SGI Power Challenge at the National Center of Supercomputing Applications at Urbana–Champaign. All geometries were fully optimized within the designated symmetry constraints with the restricted Hartree–Fock (RHF)[20] or the second order Møller–Plesset (MP2)[21] perturbation theory method. Further correction for electron correlation was introduced by single point calculations at the MP4 level. Analytical frequency analyses were carried out to characterize stationary points and to obtain zero point vibrational energies (ZPE), which were scaled by 0.89[22] to calculate the final energy estimates. The wavefunctions obtained at RHF/6-31+G* were analyzed with the natural bond orbital (NBO) method[23] included in GAUSSIAN 92. Hyperconjugative effects can be assessed by use of the second-order perturbation theory.[24] Although this procedure is known to overestimate

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(13) Gilheany, D. G. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley-Interscience: Chichester, U.K., 1993; Vol 3, Chapter 1.

(14) Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arat, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467.

(15) Streitwieser, A., Jr.; Rajca, A.; McDowell, R. S.; Glaser, R. *J. Am. Chem. Soc.* **1987**, *109*, 4184.

(16) Gilheany, D. G. *Chem. Rev.* **1994**, *94*, 1339.

(17) Gilheany, D. G. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley-Interscience: Chichester, U.K., 1992; Vol. 2, Chapter 1.

(18) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

(19) Gaussian 92, Revision E2 and G3. Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, M. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1992.

(20) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69.

(21) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Binkley, J. S.; Pople, J. A. *Int. J. Quant. Chem.* **1975**, *9*, 229.

(22) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quant. Chem.* **1979**, *13*, 225.

(23) (a) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO* Version 3.1. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(24) Tyrrell, J.; Weinstock, R. B.; Weinhold, F. *Int. J. Quant. Chem.* **1981**, *19*, 781.

stabilizing interactions, they closely parallel the energies attained by the more accurate Fock matrix deletion procedure.[25]

Results

Basis Set Evaluation for the *P*-Methylthioxophosphonic Diamide Anion (8$^-$). It has been established early-on that polarization functions on phosphorus[26] and diffuse functions for lone pairs (of either neutral species or anions)[27] are essential for generating reliable geometries. The effect of basis set size has previously been investigated for various P=O, P=S, and P–C-containing compounds.[14,28-31]

Relatively small structural changes have been noted for phosphinic acid in going from 4–31G* to 6-311G**.[29] A comprehensive basis set survey for phosphine oxide by Streitwieser et al. ranging from STO-3G* to 6-31G*(dd) (2 d-functions on phosphorus) establishes P=O bond contraction with polarization functions and bond lengthening with diffuse functions.[30] Optimization at the correlated level (MP2/6-311G**) yields little change compared to HF/6-31G* for the diatomic molecules PO and PS but a significant increase of the P–C bond length (0.04 Å) in PCH.[31] The effect of adding polarization and diffuse functions to the basis set (3-21G$^{(*)}$ to 6-31+G$^{*(*)}$) is reported to be only small in the *P*-methylphosphonic diamide anion; however, a change in the order of relative stabilities of the two local minima and, more significantly, in the pyramidalization of the carbanion occurs.[6]

Four of the stationary points (vide infra) on the potential energy surface of the *P*-methylthioxophosphonic diamide anion (**8**$^-$) have been optimized with several standard basis sets[18] at the Hartree–Fock and the correlated levels of theory (Tables 1 and 2, respectively). The largest change in structural parameters occurs between the 3-21G* and the 6-31G* basis (only the bond lengths increase in moving from the Pople basis sets to the Dunning–Hay D95+**). There are minor geometrical variations among the different correlated levels (Table 2). The HF/6-31+G* geometries agree well with those at the highest correlated level employed (MP2(FC)/6-311+G**), except for a persistently shorter P=S bond at the latter level which has previously been noted.[31] It thus seems appropriate to employ geometry optimizations at HF/6-31+G* for these kinds of compounds.

Various combinations of basis sets have been probed for calculating the energies of the four rotamers of **8**$^-$ (Table 3). Upon inclusion of electron correlation, the order of relative energies remains the same up to the highest level of theory employed (MP4(SDTQ)/6-311+G**//MP2(FC)/6-311+G**). Therefore, the MP4(SDQ)/6-31+G*//6-31+G* basis appears to be an optimal combination of computer-time efficiency and accuracy.

Table 1. Structural Parameters for Four Stationary Points of the *P*-Methylthioxophosphonic Diamide Anion (8$^-$) at Different Hartree–Fock Basis Set Levels (cf. Figure 7 for Graphics)

basis set (no. of basis fcts)	rel E	α (deg)	β (deg)	P–S (Å)	P–C (Å)	S–P–C (deg)	N–P–N (deg)
3-21G* (77)							
C_1 min	+2.2	74.0	91.8	2.004	1.663	116.2	95.5
C_s min	0.0	0.0	−106.4	2.026	1.682	130.2	112.0
C_s TS	+4.7	90.0	90.0	2.008	1.658	116.1	97.1
C_1 TS	+5.6	37.4	−101.4	2.018	1.672	123.5	102.0
6-31G* (95)							
C_1 min	0.0	73.4	99.9	2.015	1.674	116.4	94.1
C_s min	+0.3	0.0	−115.2	2.033	1.709	128.9	107.9
C_s TS	+1.5	90.0	90.0	2.023	1.665	116.5	95.8
C_1 TS	+3.1	32.6	−112.9	2.035	1.698	125.0	101.4
6-31+G* (115)							
C_1 min	0.0	73.1	97.8	2.016	1.685	116.3	94.7
C_s min	+0.1	0.0	−114.2	2.036	1.716	128.0	108.1
C_s TS	+1.4	90.0	90.0	2.025	1.677	116.2	96.3
C_1 TS	+3.0	34.6	−111.2	2.035	1.705	123.8	101.8
6-311+G** (162)							
C_1 min	+0.2	72.9	100.6	2.019	1.683	116.3	95.4
C_s min	0.0	0.0	−114.9	2.041	1.712	127.8	108.2
C_s TS	+1.5	90.0	90.0	2.027	1.673	116.1	96.6
C_1 TS	+3.2	34.0	−112.2	2.039	1.702	123.6	102.0
D95+** (146)							
C_1 min	+0.3	73.5	102.0	2.030	1.700	116.3	95.2
C_s min	0.0	0.0	−115.5	2.051	1.729	128.4	107.8
C_s TS	+1.8	90.0	90.0	2.039	1.689	116.3	96.6
C_1 TS	+3.0	33.8	−113.4	2.050	1.721	124.3	101.9

Table 2. Structural Parameters for Four Stationary Points of the *P*-Methylthioxophosphonic Diamide Anion (8$^-$) at Different Correlated Levels of Theory

basis set (no. of basic fcts)	rel E	α (deg)	β (deg)	P–S (Å)	P–C (Å)	S–P–C (deg)	N–P–N (deg)
MP2(FC)/6-31G* (95)							
C_1 min	0.0	71.9	104.9	2.007	1.681	116.4	91.8
C_s min	+1.4	0.0	−115.0	2.032	1.707	130.7	108.1
C_s TS	+2.3	90.0	90.0	2.017	1.667	116.8	93.8
C_1 TS	+3.5	33.4	−113.3	2.033	1.696	126.4	100.4
MP2(FC)/6-31+G* (115)							
C_1 min	0.0	73.1	103.7	2.004	1.695	116.4	92.4
C_s Min	+1.4	0.0	−113.5	2.029	1.715	129.5	107.6
C_s TS	+2.2	90.0	90.0	2.016	1.681	116.8	94.8
C_1 TS	+3.5	34.6	−111.0	2.028	1.704	125.1	101.0
MP2(FC)/6-311+G** (162)							
C_1 min	0.0	73.1	105.1	2.000	1.691	116.2	93.3
C_s min	+1.0	0.0	−115.2	2.025	1.713	129.3	107.4
C_s TS	+1.6	90.0	90.0	2.011	1.676	116.5	95.0
C_1 TS	+3.4	35.1	−112.5	2.024	1.701	124.9	101.0

Table 3. Relative Energies for Four *P*-Methylthioxophosphonic Diamide Anion Rotamers (8$^-$) at Different Basis Set Levels

	(C_1 min)	(C_s min)	(C_s TS)	(C_1 TS)
3-21G*	+2.2	0.0	+4.7	+5.6
6-31+G*	0.0	+0.1	+1.4	+3.0
6-311+G**	+0.2	0.0	+1.5	+3.2
MP2/6-31+G*//6-31+G*	0.0	+1.1	+2.0	+3.2
MP4(SDQ)/6-31+G*//6-31+G*	**0.0**	**+0.9**	**+1.8**	**+3.0**
MP4(SDTQ)/6-31+G*//6-31+G*	0.0	+1.0	+1.9	+2.9
MP2/6-31+G*//MP2(FC)/6-31+G*	0.0	+1.4	+2.2	+3.5
MP2/6-311+G**//MP2(FC)/6-311+G**	0.0	+1.0	+1.6	+3.4
MP4(SDTQ)/6-311+G**//MP2(FC)/ 6-311+G**	0.0	+1.0	+1.6	+3.3

Recalculation of the Stationary Points on the Potential Energy Surface of the *P*-Methylphosphonic Diamide Anion (7$^-$). The key attributes that characterize the carbanion geometry are its torsion with

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(25) Arnaud, R. *J. Comput. Chem.* **1994**, *15*, 1341.

(26) (a) Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1976**, *64*, 5142. (b) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(27) Chandrasekhar, J.;Andrade, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609.

(28) (a) Schmidt, M. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 1922. (b) Wang, P. Zhang, Y.; Glaser, R.; Reed, A. E.; Schleyer, P. v. R.; Streitwieser, A. *J. Am. Chem. Soc.* **1991**, *113*, 55.

(29) Ewig, C. S.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 1965.

(30) Streitwieser, A., Jr.; McDowell, R. S.; Glaser, R. *J. Compt. Chem.* **1987**, *8*, 788.

(31) Maclagan, R. G. A. R. *J. Phys. Chem.* **1990**, *94*, 3373.

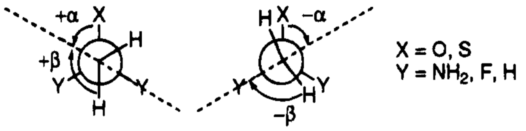


Figure 4. Definition for α and β angles (view along P–C bond).

respect to the P=X bond (α) and its degree of pyramidalization (β), Figure 4. These angles are defined by creating an imaginary reference plane which bisects the H–C–H angle. The angle α describes the torsion between the P=X axis and this plane ($|\alpha| \le 90°$). The angle β is defined between one of the carbanion hydrogens and the plane such that $|\beta| \ge 90°$. This way, (1) the hybridization of the carbanion is easily deduced from the limits, 90° = sp^2 and 120° = sp^3, and (2) an inversion of the carbanion is accompanied by a change in the sign of the β value. In Figure 5, two views of the minima and transition state structures and some structural parameters of 7^- at HF/6-31+G* are displayed. The rotamers shown in Figure 5 and their relative energies differ from those previously described[6] not only because of the slightly different basis sets employed for optimizations and single point calculations but rather due to an extensive survey of the potential energy surface and determination of the formerly neglected Hessian matrices.

In the current study, we found the same minima as Cramer et al.[6] However, there is a second C_s minimum with α = 0° (cf. Figure 4) which is 0.3 kcal/mol lower in energy than the one previously found and which has, surprisingly, the nitrogen lone pairs oriented parallel to the σ (P–N) bonds instead of the σ^* (P–N) orbitals. Additionally, the nitrogens of the newly found isomer are more strongly pyramidalized and the N–P–N angle is smaller than in the conformer reported by Cramer.[6] The favorable C_s minimum seems to have been located together with the global minimum by Boche et al. (3-21G*); however, they were unable to find a TS.[10] The α = 90° rotamer is not a stationary point on the 6-31+G* energy surface which has been tacitly assumed previously.[6] All three C_s-symmetric α = 90° conformers have been computed (both nitrogen lone pairs oriented parallel to the σ^* bond of P=O [6-31+G*: 0.0 kcal/mol], P–C [+ 5.8], and P–N [+ 6.4]), and they all exhibit two imaginary frequencies.

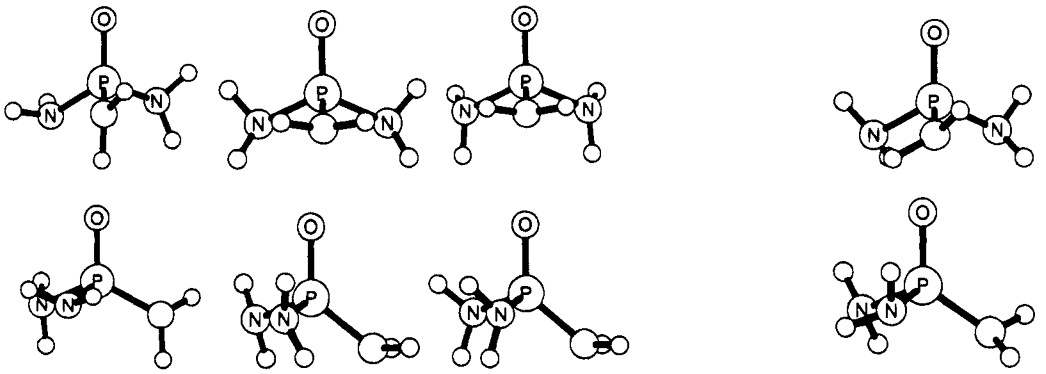
The energy and some structural parameters of the C_1 TS show the most significant deviations from the previously published data due to the different basis sets employed but the basic features remain unchanged and will be discussed below.

The strong pyramidalization of the nitrogens found in all three minima (sum of the angles at the nitrogens = 329–343°; (360° for planar, 328.5° for tetrahedral)) contrasts with the nearly planar nitrogens found in the X-ray crystal structure of **1** (see Figure 2).[6] We initially assumed that this is due to the different size of the substituents on nitrogen. However, computationally substituting the hydrogens in $\mathbf{6}^-$ with methyl groups has a considerable but not decisive effect on nitrogen pyramidality (Table 4). Computationally incorporating an allyl group (*anti* to P=O and *s-cis* to P–C) as a mimic for the benzyl moiety in **1** has virtually no effect on nitrogen pyramidality. If all four O–P–N–C dihedral angles are fixed at the experimental values in the otherwise unrestricted optimization (6-31+G*), the energy is 4.4 kcal/mol higher than in the freely optimized molecule (NIMAG = 0). Coordinating oxygen with one or two lithium atoms (the P–O–Li angles fixed at the experimental values), to simulate the lithium-bridged dimer found in the crystal structure of **1**, results in a significant flattening of one of the nitrogens (Σ angles at N: 352°). The difference between the freely optimized monolithium *P*-allyl compound and its analog with fixed O–P–N–C dihedral angles is diminished to 1.6 kcal/mol. The agreement of the computed dilithio geometry with the X-ray structure of **1** is remarkable. We propose that further solvation of the lithiums in the largest computational model results in a still-closer geometrical agreement (increase of the O–Li and decrease of the P–O distances). Overall, it seems to be the combination of steric effects (N–Me) and electronic effects (lithium coordination) that forces the nitrogens to be planar in **1**.

The Potential Energy Surface of the *P*-Methylthioxophosphonic Diamide Anion ($\mathbf{8}^-$). The structures for the 3-21G* rotational coordinate of $\mathbf{8}^-$ are shown in Figure 6. Upon rotation about the P–C bond in 15° increments starting from α = 0°, the relative energy increases to + 6.2 kcal/mol at α = 45° with little structural change within the molecule. The nitrogens remain essentially planar due to the insufficient basis set employed (vide infra). Further rotation flips one of the amino groups around the P–N bond by about 90° and is accompanied by a strong decrease in relative energy (to +2.8 kcal/mol for α = 60°). The planarization of the carbanion during this step (β = –102 to +91°; cf. Figure 4) contrasts with the pyramidalization of both nitrogens which is much stronger with larger basis sets (cf. Figure 7). The "propeller-like" arrangement of the lone pairs was found to arise from stabilizing interactions of carbon and nitrogen lone pairs with appropriate σ^* (P=O, P–N, or P–C) orbitals.[6] Both amino groups retain their orientation in the last two points on the reaction coordinate, which are fairly close in energy. The decrease in pyramidality of the carbanion (β = –106 to +91°) as well as the abrupt change in energy during the course of the rotation are well precedented in the oxo derivative ($\mathbf{7}^-$) computed at a similar level of theory (3-21G$^{(*)}$).[6] The major differences between $\mathbf{8}^-$ and $\mathbf{7}^-$ are that the decrease in energy appears earlier on the reaction coordinate (α = 45°) for $\mathbf{7}^-$ and that the relative energies are always larger in the thio analog.

In Figure 7, two views of the minima and TS's and selected structural parameters of $\mathbf{8}^-$ at HF/6-31+G* are displayed. There is one more stationary point than for $\mathbf{7}^-$ (α = 90°) but the order of relative energies is the same and the bond angles and dihedral angles of the different conformers are very similar to the oxo values.[6]

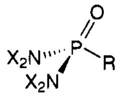
The lowest energy structure exhibits a slightly pyramidalized methylene group (β = 97.8°) arranged roughly gauche to the P=S bond (α = 73.1°). Of the nitrogen lone pairs, one is oriented parallel to the σ^* (P=S) orbital and the other one parallel to the σ^* (P–C). The minima with C_s symmetry (α = 0°) have features identical to those discussed above for the oxo analog: the lower energy structure has the nitrogen lone pairs pointing toward each other *and* shows a smaller N–P–N angle and a stronger pyramidalization of the nitrogens. The rotamer with C_s symmetry (α = 90°) is a true stationary point (NIMAG = 1) with the nitrogen lone pairs oriented parallel to the σ^* (P=S) orbital (parallel to σ^* (P–C): + 5.8 kcal/mol; to σ^* (P–N): + 6.4 at 6-31+G*; both NIMAG = 2). The C_1 TS structure is significantly higher



	Min. (C_1)	Min. (C_S)	Min (C_S)	TS (C_S)	TS (C_1)
rel. energy [kcal/mol]	**0.0**	**+ 0.53**	**+ 0.83**	(NIMAG=2)	**+ 2.51**
α [degree]	72.2	0.0	0.0	90.0	38.3
ß [degree]	104.0	-112.9	-112.0		-108.3
Σ angles at N [degree]	334/329	338/338	343/343		329/334
P-O [Å]	1.492	1.500	1.497		1.499
P-N [Å]	1.709 1.743	1.708 1.708	1.711 1.711		1.722 1.729
P-C [Å]	1.700	1.719	1.709		1.706
C-P-O [degree]	117.6	128.4	130.7		123.9
N-P-N [degree]	95.0	107.2	110.3		100.9

Figure 5. Stationary points for the *P*-methylphosphonic diamide anion ($\mathbf{7}^-$) at MP4(SDQ)/6-31+G*//6-31+G* + ZPE.

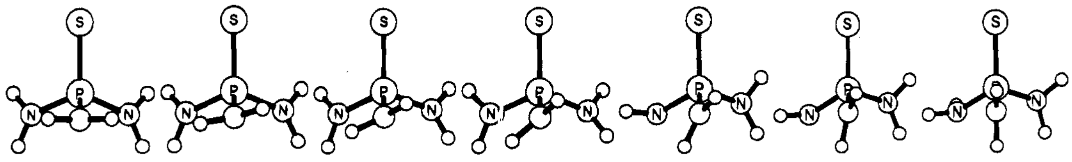
Table 4. Geometrical Parameters of $\mathbf{7}^-$ and its Higher Substituted Derivatives at 6-31+G* and of 1

	Δ E^a	Li−O (Å)	P−O (Å)	P−C (Å)	P−$N_{1/2}$ (Å)	O−P−C (deg)	N−P−N (deg)	H−C−P−O (deg)	ΣN_1, N_2 (deg)
X = H									
R = CH_2^{-b}			1.492	1.700	1.743 1.709	117.6	95.0	31.8	329, 334
X = Me									
R = CH_2^-			1.491	1.697	1.747 1.724	117.2	95.9	22.4	343, 346
R = allyl$^-$	0.0		1.487	1.729	1.721 1.705	113.7	98.6	13.2	345, 345
	(+ 4.4)^c		(1.487)	(1.726)	(1.705) (1.703)	(114.7)	(104.1)	(19.5)	(357, 359)
R = allyl$^-$/Li^{+d}	0.0	1.683	1.528	1.715	1.692 1.673	107.6	101.1	35.8	346, 350
	(+ 1.6)^c	(1.680)	(1.529)	(1.710)	(1.676) (1.673)	(108.7)	(106.8)	(41.8)	(357, 359)
R = allyl$^-$/Li$_2$(OH)$^{+d,e}$		1.846/48	1.539	1.699	1.706 1.667	108.7	100.5	22.5	345, 352
X-ray of 1		1.935	1.520	1.683	1.669 1.665	111.9	104.3	22.0	357, 359

[a] In kcal/mol. [b] C_1 min of Figure 1. [c] All four O−P−N−C dihedral angles are fixed at the values of **1**. [d] Lithium(s) is/are coordinated to oxygen, and the P−O−Li angles are fixed at the values of **1**. [e] OH^- is coordinated to both lithiums.

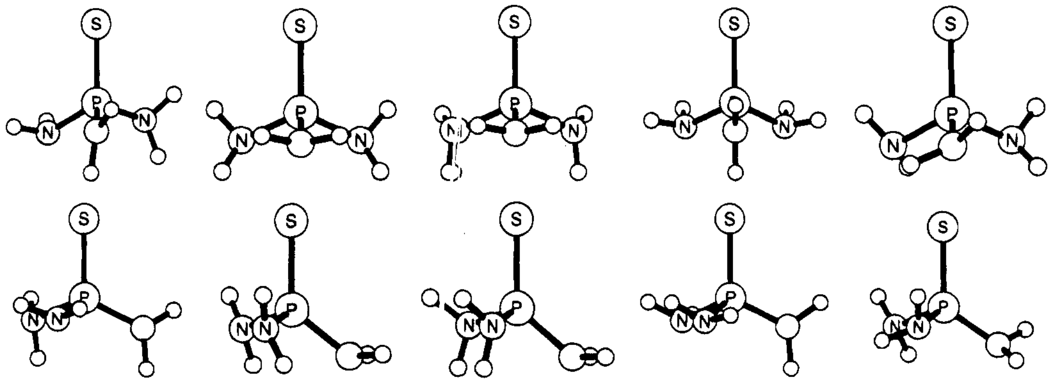
in energy than the other TS whereas Cramer et al.[6] found the reverse order of energy for the oxo analogs ($\mathbf{7}^-$) at their highest level of theory (MP3/6-31+G$^{*(*)}$//6-31+G$^{*(*)}$). The carbon lone pair of the C_1 TS of $\mathbf{8}^-$ is staggered to the σ (P−N) bond and the σ* (P═S) orbital. The nitrogen lone pairs are parallel to the bonding orbitals of the P−C and one P−N bond, respectively.

Comparison between the Chalcogen Analogs $\mathbf{7}^-$ and $\mathbf{8}^-$. (1) Energies. Both C_s minima as well as the TS (C_1) of $\mathbf{8}^-$ are higher in energy relative to the global minimum than they are in the oxo case ($\mathbf{7}^-$). The higher rotational barrier for $\mathbf{8}^-$ is in line with results from NMR experiments of nitrogen- and carbanion-substituted lithium salts of $\mathbf{7}^-$ and $\mathbf{8}^-$ in THF.[6,9] The small relative TS energy difference for our model systems $\mathbf{7}^-$ and $\mathbf{8}^-$ (0.3 kcal/mol) compared to the difference in free activation enthalpy for P−C bond rotation between **3** and **5** (3.1 kcal/mol) must be attributed to the attenuating effects of the freely rotating amino group lone pairs in $\mathbf{7}^-$ and $\mathbf{8}^-$.[6] We abstained from artificially constraining these groups but rather turned to cyclic systems where the nitrogens are built into a heterocycle. Preliminary results exhibit markedly higher TS energies for P═S than for P═O.[12] An increase in the rotational barrier by changing from the oxo to the thio derivative has been observed in related compounds. For example, rotation around the C_{sp^2}−N bond in tetramethylthiourea and in dimethylthioformamide is energetically more costly than in their oxo analogs (ca. 1.3 kcal/mol in either case), as determined both computationally[32] and experimentally.[33] Thioformamide has a 3.1 kcal/mol (MP4/6-31G** optimization) higher C−N rotational barrier than formamide,



rel. energy [kcal/mol]	**0.0**	**+ 0.91**	**+ 3.31**	**+ 6.21**	**+ 2.77**	**+ 2.23**	**+ 2.88**
α [degree]	0	15	30	45	60	75	90
ß [degree]	-106.4	-106.5	-106.2	-102.3	90.6	91.7	91.1
Σ angles at N [degree]	360/360	360/359	360/358	357/356	348/348	350/346	349/345

Figure 6. Rotational coordinate for the P–C bond in the *P*-methylthioxophosphonic diamide anion (8^-) at 3-21G*.



	Min. (C₁)	*Min. (Cs)*	*Min. (Cs)*	TS (*Cs*)	TS (*C₁*)
rel. energy [kcal/mol]	**0.0**	**+ 0.92**	**+ 1.32**	**+1.36**	**+ 2.76**
α [degree]	73.1	0.0	0.0	90.0	34.6
ß [degree]	97.8	-114.2	-113.4	90.0	-111.2
Σ angles at N [degree]	334/330	340/340	345/345	329/329	330/336
P-S [Å]	2.016	2.036	2.031	2.025	2.035
P-N [Å]	1.706 1.739	1.697 1.697	1.699 1.699	1.723 1.723	1.714 1.716
P-C [Å]	1.685	1.716	1.709	1.677	1.705
C-P-S [degree]	116.3	128.0	130.5	116.2	123.8
N-P-N [degree]	94.7	108.1	111.9	96.3	101.8

Figure 7. Stationary points for the *P*-methylthioxophosphonic diamide anion (8^-) at MP4(SDQ)/6-31+G*//6-31+G* + ZPE.

which was attributed to the more favorable nitrogen lone pair overlap with the π^* (C=S) orbital on the basis of second-order pertubation analysis.[34]

Schleyer et al. have determined the structures and stabilities of heteroatom-stabilized carbanions twice within a decade. Despite considerable improvement in the basis set quality, the stabilization of the methyl anion by the PH_2 group has barely changed: from −23.0 (MP2/6-31+G*//3-21+$G^{(*)}$)[28] to - 21.3 kcal/mol (QCISD(T)/6-31+G*//MP2/6-31+G* + ZPE)[35] for the isodesmic equation:

$$CH_3^- + CH_3PH_2 \rightarrow CH_4 + {}^-CH_2PH_2$$

The corresponding stabilization energies for 7^- and 8^- are as follows (the protonated forms **7H** and **8H** will be discussed below)

	6-31+G*	MP4(SDQ)/6-31+G *// 6-31+G* + ZPE
oxo	−39.4	−39.9 kcal/mol
thio	−48.4	−46.8 kcal/mol

The thioxophosphonic diamide group in 8^- is superior to the phosphonic diamide group in 7^- for anion stabilization. These values also suggest that the phosphondiamide is as strongly stabilizing for a negative charge on carbon as the most effective substituents included in the more recent study by Schleyer et al. (the π-acceptors BH_2, 54.0 and AlH_2, 44.9 kcal/mol).[35]

(2) Geometries. Considering the disparate anion-stabilizing properties of the P=X groups, the structural similarities between the rotamers of 7^- and 8^- are surprising. The sum of the angles at nitrogen (degree of pyramidalization) as well as the C–P=O and the N–P–N angles never deviate by more than 2°. Except for the C_1 minimum, the methylene group is slightly more pyramidalized in the rotamers of 8^-. The P–N bonds are always shorter in 8^- (vide infra) and the P–C bond is drastically shorter (0.015 Å) when the carbon lone pair is oriented perpendicular to the P=S axis (C_1 min) while in the parallel arrangements of the carbon lone pair, the P–C distances are similar in both.

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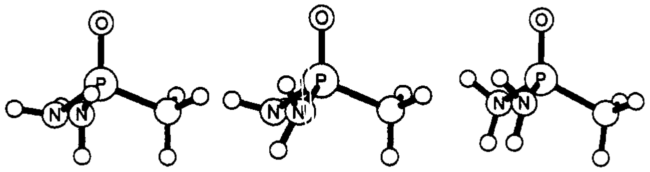
[32] Tóth, K.; Bopp, P.; Peräkylä, M.; Pakkanen, T. A.; Jancsó, G. *THEOCHEM* **1994**, *312*, 93.

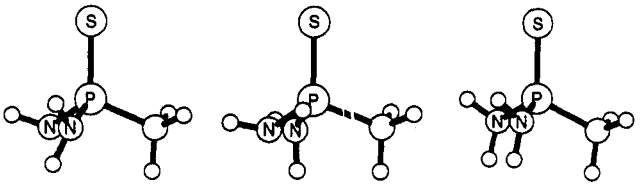
[33] (a) Drakenberg, T.; Dahlqvist, K.-I.; Forsén, S. *J. Phys. Chem.* **1972**, *76*, 2178. (b) Drakenberg, T. *J. Phys. Chem.* **1976**, *80*, 1023.

[34] Ou, M.-C.; Chu, S.-Y. *J. Phys. Chem.* **1995**, *99*, 556.

[35] El-Nahas, A. M.; Schleyer, P. v. R. *J. Comput. Chem.* **1994**, *15*, 596.



	Min. (C_1)	Min. (C_1)	Min (C_S)	X-ray
rel. energy [kcal/mol]	**0.0**	**+ 0.09**	**+ 2.58**	**structures[1]**
Σ angles at N [degree]	339/351	338/352	348/348	352 - 360
P-O [Å]	1.466	1.467	1.465	1.47 - 1.49
P-N [Å]	1.675 1.663	1.682 1.662	1.675 1.675	1.62 - 1.69
P-C [Å]	1.811	1.806	1.803	1.75 - 1.83[2]
C-P-O [degree]	112.4	113.4	117.2	107 - 112
N-P-N [degree]	100.2	102.9	111.8	103 - 107



	Min. (C_1)	Min. (C_1)	Min (C_S)	X-ray
rel. energy [kcal/mol]	**0.0**	**+ 0.06**	**+ 1.92**	**structures[3]**
Σ angles at N [degree]	336/351	337/352	348/348	341 - 360
P-S [Å]	1.956	1.954	1.952	1.93 - 1.96
P-N [Å]	1.688 1.664	1.681 1.664	1.676 1.676	1.63 - 1.69
P-C [Å]	1.811	1.816	1.809	1.77 - 1.85[2]
C-P-S [degree]	114.3	113.3	117.5	108 - 116
N-P-N [degree]	103.2	100.2	112.1	104 - 110

1) range of 5 X-ray structures from the Cambridge Crystallographic Database (ref. 36)

2) all carbons are sp^2 hybridized

3) range of 9 X-ray structures from the Cambridge Crystallographic Database (ref. 36)

Figure 8. Stationary points for the *P*-methylphosphonic (**7H**) and *P*-methylthioxophosphonic diamides (**8H**) at MP4(SDQ)/6-31+G*//6-31+G* + ZPE.

For comparison, the protonated forms **7H** and **8H** have been computed at the same levels of theory (Figure 8). For both derivatives, there are two energetically almost degenerate rotamers (ΔE < 0.1 kcal/mol) with one nitrogen lone pair always being parallel to the σ^* (P=X) bond and the other one oriented along the P−C bond axis with opposite senses of inversion of the NH_2 group in both rotamers. The degree of pyramidalization of the latter NH_2 groups is rather small (sum of angles at N: 351−2°). However, the good acceptor properties of the σ^* (P=X) bond allow for a strong overlap with the appropriate nitrogen lone pair rendering this nitrogen strongly pyramidalized (sum of angles at N: 336−9°) in both chalcogen analogs. The assumption that planar nitrogens in the propenylphosphondiamine is an 3-21G* artifact[11] is supported by our lower level calculations of **7H** and **8H**. The rotamer with both nitrogen lone pairs oriented to overlap with the appropriate σ^* (P−N) bonds is somewhat higher in energy (oxo: 2.6; thio: 1.9 kcal/mol). The geometrical characteristics around phosphorus are well within the range found in the X-ray structures of phosphonic and thioxophosphonic di(bisalkyl-)amides (Figure 8).[36] The experimentally larger N−P−N angles and stronger pyramidalization of the nitrogens may be attributed to the size of the methyl groups compared to the computationally employed hydrogens as demonstrated for the deprotonated P=O species (Table 4).

Upon deprotonation, the well-precedented[6,11,28] P−C bond shortening, P=X and P−N bond lengthening, and C−P=X angle widening occurs, but to a different extent in both analogs. In the thio case, the P−N bonds lengthen somewhat less, but more importantly, the P−C bond shortens 0.02 Å more (thio: Δr = 0.13; oxo: 0.11 Å) between the lowest energy structures of $\mathbf{8}^-$ and that of its protonated equivalent. This effect seems to be a consequence of the superior anion-stabilizing properties of the thiophosphoryl group as already manifested through the isodesmic reaction above. The cause for this effect will be discussed in the following section.

(3) NBO Analysis. Localization of the electron density using an orthogonalized atomic orbital basis yields a P−C and a P−X single bond with three lone pairs on the chalcogen and one on carbon, respectively, except for the C_s TS of $\mathbf{8}^-$ which exhibits a P=C double bond. This π bond and the corresponding π^* orbital are strongly involved in interactions with adjacent MO's, as are the carbon lone pairs of the other rotamers of $\mathbf{7}^-$ and $\mathbf{8}^-$. Whether a lone pair on carbon or a P=C double bond is formed by the NBO localization procedure depends on

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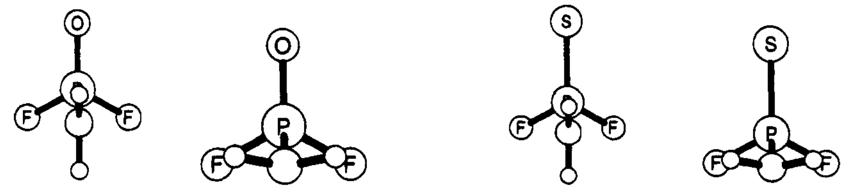
(36) A search of the Cambridge Crystallographic Database (version 3.21) revealed five X-ray structures related to **7H** (ref codes: DOKZEI, JISYIT, JISYOZ, OMAPBD, VIJNOR) and nine structures related to **8H** (ref codes: DODDIJ, JEXJUR, KETJAU, KICFEH, PAFKUC, VEZKIU, YAGLOH.



	Min. (C_S)	TS (C_S)	Min. (C_S)	TS (C_S)
rel. energy [kcal/mol]	**0.0**	**+ 5.61**	**0.0**	**+ 7.42**
α [degree]	90.0	0.0	90.0	0.0
ß [degree]	90.0	-113.4	90.0	-113.4
P-X [Å]	1.467	1.471	1.968	1.978
P-F [Å]	1.605 1.605	1.591 1.591	1.605 1.605	1.586 1.586
P-C [Å]	1.660	1.693	1.651	1.686
X-P-C [degree]	122.0	129.5	121.0	129.3
F-P-F [degree]	91.0	98.0	90.5	98.6 ·

Figure 9. Stationary points for the *P*-methylphosphonic ($\mathbf{9}^-$) and -thioxophosphonic difluoride anions ($\mathbf{10}^-$) at MP4(SDQ)/6-31+G*//6-31+G* + ZPE.

an arbitrarily fixed threshold in the NBO algorithm and does not affect the calculated atomic charges.

As might be anticipated from the similar structural parameters, the NBO analysis yields qualitatively the same results for both chalcogen derivatives. Electron delocalization is slightly larger in the oxo species as indicated by the total non-Lewis contributions (oxo: 1.27–32%; thio: 1.10–19%) as well as by the second-order perturbation theory analysis[24] (vide infra). The salient difference is a stronger π-type backbonding from the oxygen lone pairs into appropriate acceptor orbitals,[37] particularly σ^* (P–N), which leads to the ubiquitously longer P–N bonds in the oxo rotamers. The response of the P–C bond depends on several factors:

(1) In the C_1 minimum, the carbon lone pair delocalizes into both σ^* (P–N) orbitals (stronger into the more appropriately aligned one) to a greater extent in the thio analog, which manifests itself in a shorter P–C bond in $\mathbf{8}^-$ (0.015 Å). The lone pair back-bonding from oxygen and sulfur, respectively, into the σ^* (P–C) orbital is very similar in this rotamer.

(2) In both C_s minima, the overlap of the carbon lone pair with the σ^* (P=X) and, to a lesser extent, with the σ^* (P–N) orbitals is still stronger in the thio analog but to a smaller extent than in the C_1 minimum resulting in similar P–C bond lengths in the respective chalcogen rotamers.

(3) In the C_1 TS of the thio analog ($\mathbf{8}^-$), the carbon lone pair is more strongly pyramidalized and the axis through this lone pair is turned more toward the P=X axis than in the oxo case ($\mathbf{7}^-$) allowing for a better overlap with σ^* (P=X) in the former. Despite the superior oxygen lone pair back-bonding into the σ^* (P–C) orbital, P–C bond lengths of both analogs are quite similar.

The second-order perturbation theory analysis indicates that the carbon lone pair is stabilized best in the C_1 minimum and, there, better in the thio than in the oxo derivative.

The NBO atomic charges are almost identical among the different rotamers of each derivative and remain virtually the same for carbon ($\mathbf{7}^-$: −1.47; $\mathbf{8}^-$: −1.41) but differ considerably for phosphorus in $\mathbf{7}^-$ (+2.36) and $\mathbf{8}^-$ (+ 1.82). The overall picture that emerges from NBO analysis can be summarized as follows:

(1) The ionic component of the P–C bond is stronger in the oxo compared to the thio analog.

(2) This effect is countered by a strong oxygen lone pair back bonding which destabilizes the adjacent anionic charge on carbon.

(3) The combination of these effects result in a P–C bond length similar to that in the thio derivative for the C_s minima and the TS.

(4) The superior stabilization of a negative charge by sulfur compared to oxygen is evident in the C_1 minimum yielding a considerably shorter P–C bond length in the former case.

To establish a more general basis for rationalizing the relationship between electron distribution and carbanion stabilization, a simpler model system was chosen. Substituting fluorines for the amino groups eliminates the complicating effects of nitrogen lone pair reorientation due to the cylindrical electron distribution around the halogen atoms.

The *P*-Methylphosphonic ($\mathbf{9}^-$) and -thioxophosphonic Difluoride Anions ($\mathbf{10}^-$). For computation of the difluoride anions, the same computational level as for $\mathbf{8}^-$ has been chosen for consistency. Stationary points of $\mathbf{9}^-$ and $\mathbf{10}^-$ are shown in Figure 9. The structural data for $\mathbf{9}^-$ are the same as previously published.[6] The structures of the thio analog ($\mathbf{10}^-$) exhibit the same agreements with and deviations from those of $\mathbf{9}^-$ as found between $\mathbf{8}^-$ and $\mathbf{7}^-$. All four geometries in Figure 9 have C_s symmetry. The CH_2 group is parallel to the P=X axis in the GS structures and pseudoperpendicular in the TS structures with an identical degree of pyramidalization (67°) at carbon in both analogs. In going from the GS's to the TS's, the P–F bonds become shorter and the P=X and P–C bonds lengthen, both due to the change of carbon lone pair orientation.

Bond angles and dihedral angles are almost identical between both molecules while bond lengths vary in a characteristic pattern. The P–C bond is shorter in the GS of the thio case, which can, from NBO analysis, be assigned to a stronger back-bonding from the oxygen lone pairs into the σ^* (P–C) orbital. The NBO analysis generates P–C π bonds for both GS structures instead of carbon lone pairs, thus rendering a comparison of specific orbital interactions to previous NBO results moot. The P–F bond lengths are identical in the GS structures of $\mathbf{9}^-$ and $\mathbf{10}^-$ which correlates with the slight differences

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[37] π Bond energies (MP2/6-31G**) of P=O: 68.1 kcal/mol; P=S: 43.0. Leroy, G.; Temsamani, D. R.; Wilante, C.; Dewispelaere, J.-P. *THEOCHEM* **1994**, *309*, 113.

	Min. (C_S)	TS (C_1)	Min. (C_S)	TS (C_S)
rel. energy [kcal/mol]	**0.0**	**+ 6.49**	**0.0**	**+ 3.47**
α [degree]	0	84.1	0.0	90.0
ß [degree]	-112.5	-106.3	-115.2	90.0
P-X [Å]	1.503	1.498	2.033	2.019
P-H [Å]	1.407 1.407	1.417 1.428	1.396 1.396	1.413 1.413
P-C [Å]	1.720	1.709	1.726	1.692
X-P-C [degree]	128.2	119.4	128.7	118.3
H-P-H [degree]	100.9	95.0	100.9	94.9

Figure 10. Stationary points for the methylphosphine oxide (**11**$^-$) and sulfide anions (**12**$^-$) at MP4(SDQ)/6-31+G*//6-31+G* + ZPE.

between P-N distances in the lowest energy minima of **7**$^-$ and **8**$^-$.

P-Methylthioxophosphonic difluoride (**10H**) has previously been calculated.[38] Geometry changes upon deprotonation agree with those found for the diamide species.

In **9**$^-$ and **10**$^-$, NBO atomic charges are more positive on phosphorus (+2.62 and +2.10, respectively) than in **7**$^-$ and **8**$^-$ due to the more electronegative fluorines and almost identical on carbon (−1.48 and −1.43, respectively) yielding a relative difference between both atoms almost identical to that in **7**$^-$ and **8**$^-$.

The C_s symmetry of both TS's and the identical degree of carbon pyramidalization ($\beta = -111°$) allows for a better comparison than in the differing TS structures of **7**$^-$ and **8**$^-$. In both compounds, the carbon lone pairs exhibit similar delocalization into σ^* (P═X) orbitals. However, in the thio case, delocalization into the σ^* (P−F) bonds is stronger while back-bonding from the chalcogen lone pair into the σ^* (P−C) orbital is weaker. Both effects account for the shorter P−C bond in the thio analog.

In the TS structures, the stabilization effects for the carbanion are somewhat smaller than in **7**$^-$ and **8**$^-$. However, the negative charge must be comfortably accommodated in the GS's as supported by the considerable P−C bond length increase in going to the TS's ($\Delta r \approx 0.34$ Å) and the high rotational barriers for **9**$^-$ (+5.6 kcal/mol) and **10**$^-$ (+7.4 kcal/mol).

The favorable acceptor properties of the σ^* (P−N) or the σ^* (P−F) orbitals give rise to a carbanion GS orientation parallel to the P═X bond. If the stabilizing capability of these orbitals can be diminished below that of the σ^* (P═X) orbital, a perpendicular carbanion in the GS should result. The methylphosphine group was selected to probe this assumption.

The Methylphosphine Oxide (11$^-$**) and Sulfide Anions (12**$^-$**).** The geometries and selected parameters for the methylphosphine anions **11**$^-$ and **12**$^-$ are displayed in Figure 10. In contrast to the nitrogen- and fluorine-substituted derivatives, the phosphine GS structures have the pyramidalized carbanion pseudoperpendicularly oriented to the P═X group and parallel in the TS structures.[39] Streitwieser et al.[15] have computed **11**$^-$ at 3-21+G* and found the same C_s minimum structure. They briefly mention a geometry 5.4 kcal/mol higher in energy and with the CH_2 group parallel to the P═X axis. This C_s-symmetric 6-31+G* geometry of **11**$^-$ exhibits two imaginary frequencies and optimizes to a C_1 TS with the CH_2 group slightly rotated and a pyramidal carbon. All other structures in Figure 10 have C_s symmetry.

The opposite geometries in GS and TS structures entail a reversed order for the rotational barriers: the value for the oxo derivative **11**$^-$ is almost twice as high (+6.5 kcal/mol) as that for **12**$^-$ (+3.5 kcal/mol). The structural changes in going from the GS's to the TS's is reversed as well: the P═X and P−C bonds shorten while the P−H bonds lengthen. The third analogy among the previously discussed compounds is also reversed: The P−C distance is longer in the GS of **12**$^-$ than in that of **11**$^-$ but it shortens more in going to the TS of **12**$^-$ (Δr = 0.034 Å) than to that of **11**$^-$ (0.011 Å).

The GS NBO analyses reveal a similar chalcogen lone pair back bonding as in the comparable rotamers of **7**$^-$ and **8**$^-$.[40] For the first time, however, a stronger overlap of the carbon lone pair with the σ^* (P═O) instead of the σ^* (P═S) orbital is found, accounting for the shorter P−C distance in the GS of the oxo species **11**$^-$. In the TS's, the chalcogen lone pair back bonding is much stronger for **11**$^-$ than for **12**$^-$.

The exclusive carbon lone pair stabilizing effects are larger in **11**$^-$ in the GS and in **12**$^-$ in the TS. This is in full accord with rotational barrier heights and P−C bond distances.

Conclusion

Structures and energies for the different rotamers of the *P*-methylthioxophosphonic diamide anion (**8**$^-$) are very similar to those of the previously published oxophosphoryl analogs (**7**$^-$). The slightly higher activation barrier for P−C bond rotation in **8**$^-$ (2.8 vs 2.5 kcal/mol in **7**$^-$) follows the trend of NMR results for lithiated 1,3,2-diazaphosphorinane derivatives of **8**$^-$ and **7**$^-$ and reflects

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[38] 3-21G* or 6-31G* results (not specified), P═S, 1.87; P−F, 1.56; P−C, 1.78 Å. Chatterjee, K. K.; Durig, J. R. *Struct. Chem.* **1994**, *5*, 239.

[39] This reversal has been documented by the X-ray crystal structure of lithio-2-benzylphosphorinane 2-oxide: Swiss, K. A.; Wilson, S. R. Unpublished results from these laboratories.

[40] The longer P═X bonds in **11**$^-$ and **12**$^-$ compared to **7**$^-$−**10**$^-$ can be rationalized considering the lower positive charge on phosphorus in the phosphines (+1.66, +1.03, respectively, in the GS's); cf. ref 16.

the different stabilizing capabilities of both chalcogens. Inclusion of the difluoride and the phosphine systems into our study yields a consistent picture. With electronegative elements on phosphorus, the σ^* (P–N or P–F) orbitals become better π-acceptors and the σ^* (P=X) is raised in energy. Both effects lead to GS structures with the carbon lone pair perpendicular to the P=X axis. The reverse holds for the phosphine derivatives.

The greater electronegativity difference between phosphorus and oxygen leaves the phosphorus more positive in **7**$^-$. However, stronger oxygen lone pair back bonding into the σ^* (P–C) and σ^* (P–N) orbitals has a lengthening effect on the P–C bond and, more importantly, decreases carbon lone pair stabilization in its arrangement perpendicular to the P=O axis. It is thus a *diminished stabilization of the GS geometries in the oxo species* **7**$^-$ and **9**$^-$ that gives rise to the *lower* rotational barriers around the P–C bond in the oxo $P(NH_2)_2$ and PF_2 species. The combination of an *improved oxygen GS and sulfur TS stabilization* in the phosphine derivatives leads to the *higher* activation energy of the oxo species (**11**$^-$).

Locking the reorientation possibilities of the amino groups in **7**$^-$ has previously been shown to alleviate the stabilizing interactions in the TS structure thus leading to significantly higher rotational barriers.[6] Evaluation of larger molecules with more experimental relevance such as 1,3,2-diazaphospholidenes and -phosphorinanes provides for more rigid systems and is currently under investigation.[12]

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Supporting Information Available: Archive entries of the largest basis set optimizations for **8**$^-$ and of the optimized molecules in Figures 5–10 (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for orrdering information.

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