Ab Initio and PM3-MO Calculations of Lithiophosphonates†

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Geometries of methylphosphonic acid, the methylphosphonate anion (**1a**), and its monolithiated isomers **2-6**, $[H_2CP(O)(OH)_2]Li$, have been calculated by *ab initio* (MP2(full)/6-31+G*//MP2(full)/6-31+G*) and semiempirical (MNDO and PM3) methods. *d* Functions are not involved in the stabilization of **1a** (NBO-analysis). **1a** turns out to be configuratively slightly more stable than sulfone-stabilized carbanions, but shows a significantly lower rotational barrier. For sulfone- and phosphonate-containing anions our investigation predicts some of the highest methyl stabilization energies found so far. MP4(sdtq)/6-31+G*//MP2(full)/6-31+G* calculations, with inclusion of the ZPE correction, on the lithiated isomers show that structure **2** (Li^+ in contact with the anionic carbon and the doubly bonded oxygen) is most stable. Two pairs of isomers (**3/4** and **5/6**) lie only 4–8 kcal/mol above the global minimum **2**. The PM3 results are in very good agreement with the energetic ordering obtained from ab initio calculations. MNDO, however, fails to reproduce these data. PM3 shows deficiencies in the estimation of some specific bond lengths of **1a** which are conserved in the lithiated counterparts. PM3 and MNDO were used to simulate a polymeric X-ray structure of $\{[PhCHP(O)(OEt)_2]Li \cdot 2\ DABCO\}_\infty$. The Li–X distances of the calculated subunit is described much better by PM3 than by MNDO. Finally, a PM3 study was carried out in order to predict the dimeric structure of lithiophosphonates for a variety of substituents. For typical *aliphatic* Horner–Emmons reagents $[R^1R^2CP(O)(OR)_2]Li$, a dimeric eight-ring structure is predicted to be preferred over a four-membered ring isomer; the latter was found for a monoaromatic-substituted representative (R^1 = Ph, R^2 = H) by X-ray analysis.

Introduction

Metalated (especially lithiated) derivatives of several phosphorus compounds are known to be the reactive intermediates in variations[1] of the Wittig reaction.[2] These carbonyl olefinations, the Wadsworth–Emmons[3] and Horner-Emmons[4] reactions, take advantage of anions of phosphonic esters and phosphine oxides: In general, both nucleophiles are more reactive toward carbonyl compounds than comparable Wittig-type ylides.

Further, the well-known stabilization of carbanionic centers by adjacent phosphorus groups[5] has given rise to many experimental studies.[6] But despite their synthetic importance, only little theoretical work has been done in the field of the lithiated phosphorus(V) compounds. 3-21G(*)[7] ab initio calculations are reported for the methylphosphonate anion by Boche[8] and for several phosphonic diamide anions by Denmark and Cramer.[5g,9] Although structural properties are known from the determination of X-ray structures[8,10] and cryoscopic measurements, to the best of our knowledge, no theoretical work has been published dealing with *lithiated* phosphonates. Therefore, this investigation is intended to (a) gain insight in the gas phase structures of phosphonate anions and their monolithiated species by using the most simplified representatives, $[H_2CP(O)(OH_2)]Li$, which allow the application of advanced ab initio basis sets, (b) estimate the influence of *d*-functions in stabilizing phosphonate anions and their configurative stability, (c) assess comprehensively the reliability of the relatively new lithium parameters for PM3[11] by comparing PM3 and MNDO with ab initio results, (d) simulate the X-ray structure of a polymeric DABCO-complexed lithiophosphonate by calculating the repeating unit semiempirically, and finally, (e) to predict the structures of lithiophosphonates $[R^1R^2CP(O)(OR)_2]Li$ in the condensed phase under inclusion of different complexing (solvent) molecules.

Method

Ab initio calculations were performed using the Gaussian 92[12] program package. Semiempirical calculations were run using the program MOPAC6/PC.[13] All geometries were com-

† This paper is dedicated to Prof. Dr. h. c. H.-J. Bestmann on the occasion of his 70th birthday.

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pletely optimized at the MNDO,[14] PM3,[15] HF/6-31G*,[16] HF/6-31+G*,[17] and MP2(full)/6-31+G* (including Møller–Plesset electron correlation[18] in the framework of full second order) levels and characterized as minima, saddle points, etc. by calculation of vibrational frequencies. *Ab initio* energy calculations were performed on the MP2(full)/6-31+G* geometries using the 6-31+G* basis set (MP4(sdtq) level). Zero point energies were scaled by 0.91.[19] Absolute and relative energies are given in Tables 2 and 3.

Results and Discussion

The Methylphosphonate Anion, $[H_2CP(O)(OH)_2]^-$. We calculated two structures which differ in the nature of negative hyperconjugation[20] (**1a**, $n_C-\sigma^*_{P-O}$ interaction; **1b**, $n_C-\sigma^*_{P=O}$ interaction, Figure 1). These minima are separated by only 1.01 kcal/mol in favor of **1a**. The small energy difference indicates a slightly more effective interaction of the carbon lone pair (n_C) with the antibonding σ^*-orbital of the P-O bonds than with that of the P=O bond. This is further supported by an NBO analysis,[21] based on an MP2(full)/6-31+G* geometry, which confirms qualitatively the predominance of the $n_C-\sigma^*_{P-O}$ interaction.

This finding is in agreement with results of preceding investigations on this and related anions: Boche reported two minima for the $[H_2CP(O)(OH)_2]^-$ system on a much lower level of theory (6-31+G**//3-21G*) with an almost identical energetic separation.[8] For the phosphonic diamide anion, $[H_2CP(O)(NH_2)_2]^-$, two minimum structures (within 1.5 kcal/mol) have been calculated by Cramer and Denmark.[5g] The reported C–P bond rotation barriers are in both cases very low (less than 4 kcal/mol). However, electron correlation lowers the energy difference between the diamide structures by about 0.5 kcal/mol. The same influence was found in the course of our study.

This removal of a proton from methylphosphonic acid (Table 1) and the therefore increased hyperconjugation in the anion causes three major structural changes in **1a**: the lengthening of both the P=O (+0.026 Å) and P–O (+0.055 Å) bonds and the shortening of the C–P bond (−0.093 Å).

The carbanionic center is pyramidal with the hydrogens bent out of plane by 39.6° as indicated by the dihedral angle P–HCH in Table 1. The energy difference between the pyramidal minimum **1a** and the planar structure **1c** is calculated to be 0.97 kcal/mol. This difference is slightly higher than the energy needed for planarization of sulfone-stabilized carbanions, which is only about 0.5 kcal/mol.[22] Therefore, anionic carbons are configuratively slightly more stable when stabilized with a phosphonate than with a sulfone group. An NBO analysis predicts the *d* character on phosphorus in the σ bond orbitals for both minima to be always less than 2%—too low to be of any significance.

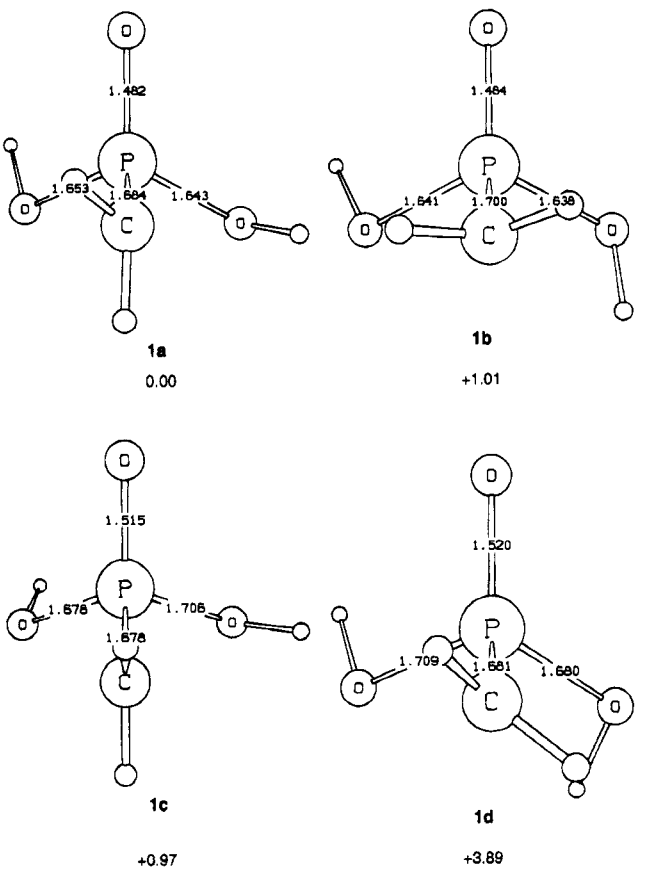

Figure 1. Bond lengths (Å) and relative energies (kcal/mol) of methylphosphonate anions; ab initio results (MP2(sdtq)/6-31+G*//MP2(full)6-31+G*, ZPE-corrected).

The barrier for the rotation of the C–P bond was estimated by calculation of a reaction coordinate of this rotation (HF/6-31G*) and optimization of the highest and lowest point, resulting in the global minimum **a** and the transition structure **1d**. The latter reveals one imaginary frequency and lies 3.30 kcal/mol above **a**, again in good agreement with the earlier computational work.[5g,8] Compared with the analogous sulfone-stabilized anions, this barrier is significantly lower.[22] Estimation for the rotational hindering of carbanions with sulfur- and phosphorus-containing groups from NMR experiments gives values lower than 8 kcal/mol (P) and 10–16 kcal/mol (S). The carbon lone pair in phosphonates can be stabilized at almost all angles (three equally good acceptors), whereas for the sulfones only one effective configuration exists.

We also determined the methyl stabilization energies (MSE)[23] for both the sulfur- and the phosphorus-containing anions according to the equation $CH_3^- + CH_3X \rightarrow$

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Table 1. Selected Bond Lengths (Å), Bond and Dihedral Angles (deg) of Phosphonic Acid and Its Methyl Anion

	phosphonic acid						methyl phosphonate anion				
	6-31G*	6-31+G*	MP2/ 6-31+G*	PM3	MNDO		6-31G*	6-31+G*	MP2/6-31+G*	PM3	MNDO
P–O_1	1.458	1.460	1.494	1.463	1.504	P–O_1	1.482	1.484	1.518	1.507	1.515
P–O_2	1.596	1.595	1.629	1.689	1.613	P–O_2	1.653	1.648	1.689	1.750	1.643
P–C	1.790	1.790	1.787	1.780	1.801	P–O_3	1.643	1.640	1.678	1.744	1.638
O_1–P–C	118.8	118.6	119.6	123.0	119.3	P–C	1.684	1.693	1.694	1.576	1.657
O_1–P–O	113.0	113.0	113.7	111.9	110.5	O_1–P–C	119.8	119.5	120.0	127.5	123.1
						O_1–P–C–H_1	178.0	177.9	177.1	169.4	168.8
						O_1–P–C–H_2	38.1	35.5	36.7	−6.2	−4.6
						P–(HCH)	140.5	142.8	140.4	176.0	172.9

Table 2. Energies[a] and Total Energies[b]

species	PM3[a] (NIMAG)[c]	MNDO[a] (NIMAG)[c]	6-31G*// 6-31G*[b]	6-31+G*// 6-31+G*[b]	MP2(full)/6-31+G*// MP2(full)/6-31+G*[b]	MP4(sdtq)/6-31+G*// MP2(full)/6-31+G*[b]	ZPE[d] (NIMAG)[e]
$(HO)_2P(O)CH_3$	−209.10 (0)	−152.80 (0)	−606.172 363	−606.183 174	−607.006 521	−607.028 804	48.13 (0)
1a	−205.48 (0)	−148.98 (0)	−605.536 278	−605.563 498	−606.402 971	−606.423 265	38.84 (0)
1b			−605.534 537	−605.561 951	−606.401 911	−606.422 252	39.25 (0)
1c	−204.05 (1)	−146.74 (1)	−605.533 249	−605.561 024	−606.400 611	−606.420 770	38.14 (1)
1d	−204.36 (1)	−147.31 (1)	−605.528 498	−605.556 176	−606.395 659	−606.416 011	38.11 (1)
2	−199.55 (0)	−173.22 (0)	−613.052 053	−613.062 006	−613.868 591	−613.917 775	41.03 (0)
3	−193.64 (0)	−161.01 (0)			−613.855 270	−613.904 860	41.11 (0)
4	−195.51 (0)	−164.52 (0)	−613.038 546	−613.049 766	−613.861 051	−613.910 335	41.11 (0)
5	−196.50 (0)	−137.37 (0)	−613.033 716	−613.046 929	−613.857 849	−613.907 098	41.08 (0)
6	−195.00 (0)	−137.60 (0)	−613.037 579	−613.051 432	−613.861 024	−613.910 219	41.11 (0)

[a] Energies in kcal/mol. [b] Total energies in au (= 627.51 kcal/mol). [c] Number of IMAGinary freqencies. [d] Zero point energies in kcal/mol (6-31+G* calculations). [e] Number of IMAGinary freqencies (6-31+G* calculations).

Table 3. Relative Energies[a]

species	PM3	MNDO	6-31G*// 6-31G*	6-31+G*// 6-31+G*	MP2(full)/6-31+G*// MP2(full)/6-31+G*	MP4(sdtq)/6-31+G*// MP2(full)/6-31+G*	corr[b]
1a	+0.0	+0.0	+0.0	+0.0	+0.0	+0.0	**+0.0**
1b			+1.09	+0.97	+0.67	+0.64	**+1.01**
1c	+1.41	+2.24	+1.90	+1.55	+0.82	+1.57	**+0.96**
1d	+1.10	+1.67	+4.88	+4.59	+4.59	+4.55	**+3.89**
2	+0.0	+0.0	+0.0	+0.0	+0.0	+0.0	**+0.0**
3	+5.91	+12.21			+8.36	+8.10	**+8.17**
4	+4.04	+8.70	+8.48	+7.68	+4.73	+4.67	**+4.74**
5	+3.05	+35.86	+11.51	+9.46	+6.74	+6.70	**+6.74**
6	+4.55	+35.62	+9.08	+6.64	+4.75	+4.74	**+4.81**

[a] Energies in kcal/mol. [b] Zero point energy corrected, see ref 19.

$CH_4 + CH_2X^-$ and compared these *ab initio* results (MP2(full)/6-31+G*//MP2(full)/6-31+G* + ZPE-(6-31+G*)-correction) with known MSEs.[24] Carbanions are better stabilized by second-row (15–25 kcal/mol) than by first-row elements (−5 to 10 kcal/mol). This is due to the more electropositive character, the more effective negative hyperconjugation, and the greater polarizability of the second-row groups.[24,25] Our findings predict MSEs of 51.1 kcal/mol for X = SO_2CH_3, 46.4 kcal/mol for X = P(O)-$(OH)_2$, 41.9 kcal/mol for X = $P(OH)_2$ and 23.1 kcal/mol for X = PH_2, some of the highest values for MSEs found so far. Not unexpectedly, the magnitude of stabilization of phosphorus-containing groups increases with increasing oxidation state.

A comparison of the MP2(full)/6-31+G* calculated geometries of **1a** and its uncharged precursor with those obtained from semiempirical methods is given in Table 1: The above-mentioned small influence of phosphorus *d* functions in stabilizing carbanions justifies the application of the semiempirical methods for energies, but, however, their effect on structures is well-known.[26] In the following we assess the reliability of PM3 and MNDO in reproducing geometries (Table 1). Although PM3 claims to be distinctly superior to MNDO because of the improved description of hypervalent molecules,[22,27] in the case of the phosphonic acid and its anion PM3 fails severely to reproduce some bond lengths. For example, the P–O single bonds are calculated about 0.06 Å too long compared with *ab initio* results. The most striking failure, however, is the estimation of the P–C^- bond. PM3 gives a bond length which is 0.12 Å too short. In contrast, MNDO calculates the geometries of both neutral and anionic species in reasonable agreement with the *ab initio* results. Another difference is the near planarity of the CH_2 moiety in the most stable conformation, **1a**, predicted by PM3 and MNDO. Nevertheless, severe semiempirical deficiencies, especially of MNDO, have been observed in the case of energy calculations of methyllithiophosphonates, which are discussed in the following section.

Methyllithiophosphonates, $[H_2CP(O)(OH)_2]Li$. The energy surface of the methyllithiophosphonate isomers was first explored with PM3. The resulting five struc-

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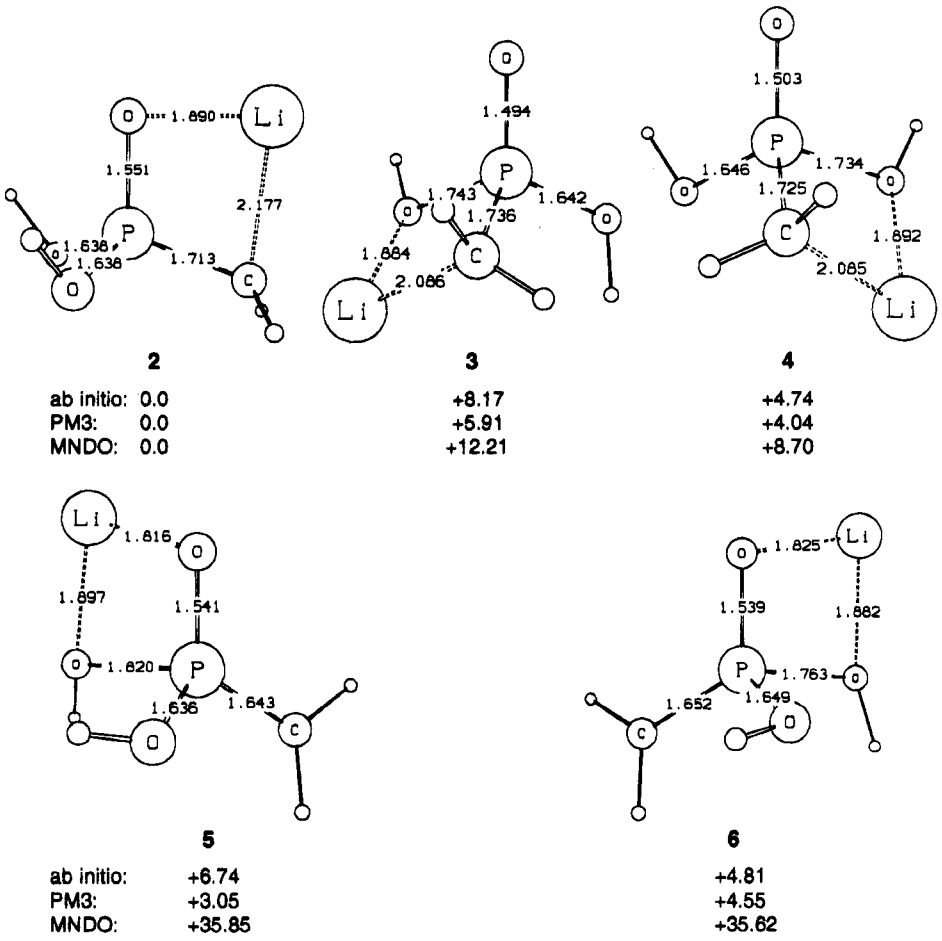

	2	3	4
ab initio:	0.0	+8.17	+4.74
PM3:	0.0	+5.91	+4.04
MNDO:	0.0	+12.21	+8.70

	5	6
ab initio:	+6.74	+4.81
PM3:	+3.05	+4.55
MNDO:	+35.85	+35.62

Figure 2. Bond lengths (Å) and relative energies (kcal/mol) of methyllithiophosphonate; *ab initio* (MP2(sdtq)/6-31+G*//MP2-(full)6-31+G*, ZPE-corrected) and semiempirical results.

tures were then optimized at the MP2(full)/6-31+G* level to give the minima **2**–**6**, and their relative energies were estimated with MP4(sdtq)/6-31+G*//MP2(full)/6-31+G* single point calculations (Figure 2). Apart from the global minimum, **2**, in which the lithium cation coordinates to the carbanion and the oxygen of the P=O bond, two pairs of isomers exist. These pairs have a common lithium contact to one oxygen of a P–O bond. For the isomers **3**/**4**, lithium coordinates to the carbanionic center; in the case of the other pair (**5**/**6**) a Li–O=P contact was found. The two isomers of a pair differ only in the orientation of the hydrogen atom of the "free" hydroxyl group: it can be aligned *syn* and *anti* relative *to the lithium cation* with the latter position being energetically preferred. The use of electron correlation methods is essential: Structure **3** cannot be localized at the HF level; it transforms into **4** during the optimization. All five species are close in energy with the two isomeric pairs **3**/**4** and **5**/**6** lying 4.74 and 8.17 kcal/mol above **2**, separated only by 3.5 kcal/mol.

In accordance with the *ab initio* results, both semiempirical methods find structure **2** to be the global minimum. Further, PM3 predicts—in agreement with the foregoing *ab initio* calculations—the isomers **3**–**6** to lie within a small energetic interval, that is within 2.9 kcal/mol (3.0–5.9 kcal/mol above **2**). Only compound **5** is calculated to be slightly too stable. The MNDO results for relative energies are far less reliable: Though the pair **3**/**4** lies a little too high (still within an acceptable accuracy of the methods used), the stability of the pair with two oxygen–lithium contacts is severely underestimated (about 30 kcal/mol).

The latter results seem to be a consequence of the well-known overestimation of Li-C interaction.[28] Obviously, MNDO is not suited for mechanistic studies on lithiophosphonates or related systems in which small energetic effects can be decisive.

Compared with the anion **1a**, addition of a lithium cation to one of the possible coordination centers results always in a significant lengthening of the corresponding bonds (Table 4): the C–P distance is extended by 0.03 Å, whereas the P–O and P=O bonds are lengthened by 0.07 and 0.03 Å, respectively. A "free" P–O bond is reduced by 0.04 Å. Though PM3 shows some deficiencies in the description of the "lithium-free" molecules, it reproduces these structural changes better than MNDO. Further, PM3—not MNDO—finds Li–O and Li–C distances which are almost identical with the ab initio results.

Comparison of PM3 Results with an X-ray Structure of a Lithiophosphonate. To test the reliability of the PM3 method in predicting geometries of larger systems, we calculated the repeating structural subunit (Figure 3) of a crystalline polymeric lithiophosphonate. The determination of the first solid state structure of a lithiated phosphonate was performed previously by Boche.[8] Diethyl (α-lithiobenzyl)phosphonate forms a dimeric substructure with a central Li–O–Li–O segment. The remaining two coordination positions of the lithium cation are saturated with DABCO molecules. A Li^+ contact exists to a nitrogen of a DABCO molecule. These units form a network using the second nitrogen of

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Table 4. Selected Bond Lengths (Å) and Bond and Dihedral Angles (deg) of Lithiated Methylphosphonates

2	6-31G*	6-31+G*	MP2/6-31+G*	PM3	MNDO
P=O_1	1.513	1.514	1.551	1.577	1.544
P–O_2	1.602	1.600	1.638	1.695	1.612
P–O_3	1.602	1.600	1.638	1.694	1.611
P–C	1.716	1.716	1.713	1.656	1.842
Li–O_1	1.855	1.848	1.890	1.875	2.066
Li–C	2.153	2.167	2.176	2.164	2.005
Li–P	2.397	2.405	2.421	2.408	2.583
C–P–O_1	111.2	111.0	112.0	112.1	103.7
P–C–H	113.8	114.0	113.8	118.7	109.2
C–P–O_1–Li	0.2	0.4	−0.3	0.0	0.0
P–(HCH)	130.9	131.0	131.0	139.5	119.0

3	6-31G*[a]	6-31+G*[a]	MP2/6-31+G*	PM3	MNDO
P=O_1			1.494	1.465	1.495
P–O_2			1.743	1.804	1.664
P–O_3			1.642	1.700	1.618
P–C			1.736	1.672	1.830
Li–O_2			1.883	1.869	2.143
Li–C			2.086	2.087	1.953
Li–P			2.639	2.643	2.748
C–P–O_1			127.6	130.2	125.3
P–C–H			111.4	118.0	107.7
C–P–O_2–Li			0.1	−5.9	−4.4
P–(HCH)			124.5	137.8	117.4
C–P–O_3–H			28.8	25.7	4.2
O_1–P–O_3–H			174.5	174.9	150.6

4	6-31G*	6-31+G*	MP2/6-31+G*	PM3	MNDO
P=O_1	1.464	1.466	1.503	1.472	1.499
P–O_2	1.686	1.684	1.734	1.801	1.662
P–O_3	1.606	1.606	1.646	1.702	1.615
P–C	1.728	1.728	1.725	1.663	1.836
Li–O_2	1.898	1.895	1.892	1.869	2.145
Li–C	2.067	2.075	2.085	2.085	1.950
Li–P	2.596	2.603	2.620	2.635	2.745
C–P–O_1	128.2	128.8	130.6	131.7	127.8
P–C–H	111.3	111.6	111.8	117.3	107.1
C–P–O_2–Li	6.9	9.8	10.4	3.2	1.9
P–(HCH)	125.0	125.6	124.7	137.3	115.5
C–P–O_3–H	147.5	147.1	149.2	161.4	153.1
O_1–P–O_3–H	3.3	2.6	2.8	12.2	6.4

5	6-31G*	6-31+G*	MP2/6-31+G*	PM3	MNDO
P=O_1	1.508	1.508	1.541	1.567	1.542
P–O_2	1.751	1.741	1.820	1.803	1.701
P–O_3	1.600	1.600	1.636	1.695	1.610
P–C	1.630	1.637	1.643	1.521	1.634
Li–O_1	1.782	1.776	1.816	1.801	1.962
Li–O_2	1.891	1.896	1.897	1.899	2.138
Li–P	2.494	2.499	2.538	2.688	2.804
C–P–O_1	122.3	122.5	112.5	131.0	122.9
P–C–H	119.8	120.0	119.8	124.2	118.5
O_1–P–O_2–Li	8.3	7.9	8.2	8.0	6.3
P–(HCH)	−175.3	−175.7	−178.5	−178.6	−172.1
C–P–O_3–H	150.1	156.0	147.4	169.8	131.0
O_1–P–O_3–H	67.4	62.2	70.3	18.9	57.3

6	6-31G*	6-31+G*	MP2/6-31+G*	PM3	MNDO
P=O_1	1.507	1.506	1.539	1.560	1.539
P–O_2	1.711	1.705	1.763	1.795	1.686
P–O_3	1.611	1.609	1.649	1.704	1.616
P–C	1.636	1.644	1.652	1.528	1.633
Li–O_1	1.788	1.780	1.824	1.806	1.954
Li–O_2	1.883	1.892	1.882	1.901	2.167
Li–P	2.492	2.495	2.532	2.667	2.802
C–P–O_1	120.9	121.0	120.8	129.7	123.4
P–C–H	120.3	120.3	119.5	124.6	118.6
O_1–P–O_2–Li	−0.4	−0.1	0.6	−1.3	0.5
P–(HCH)	170.3	170.9	162.4	179.6	174.2
C–P–O_3–H	−44.5	−44.1	−42.9	−7.2	−26.3
O_1–P–O_3–H	95.1	95.4	96.6	142.4	114.2

[a] Geometry optimizable only at MP2 level.

DABCO as "connectors". The carbanionic [$PhCH^-$] centers are not involved in the coordination pattern of the lithium cations. Our PM3 and MNDO simulation of this

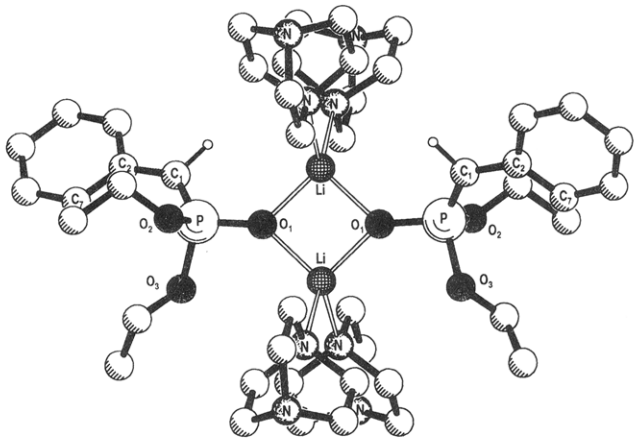

Figure 3. PM3-calculated subunit of the X-ray structure of $\{[C_6H_5CHP(O)(OC_2H_5)_2]Li{\cdot}DABCO\}_\infty$.

Table 5. Selected Geometrical Properties of Simulated X-ray Structure of $\{[PhHCP(O)(OEt)_2]Li \cdot DABCO\}_\infty$

	X-ray	PM3	MNDO
distances (Å)			
Li–O_1	1.99(2)	1.963	2.250
Li–C_1	3.89(2)	3.780	3.773
Li–N	2.12(2)	2.386	2.512
P–O_1	1.511(6)	1.592	1.546
P–O_2	1.610(7)	1.717	1.620
P–O_3	1.609(8)	1.726	1.629
P–C_1	1.64(1)	1.594	1.689
C_1–C_2	1.44(2)	1.415	1.423
Bond angle (deg)			
Li–O_1–Li	90.6(8)	87.4	88.4
O_1–Li–O_{1a}	89.4(9)	92.6	91.7
O_1–P–O_2	105.4(4)	102.9	101.8
O_1–P–C_1	122.7(5)	117.5	114.6
P–C_1–C_2	127.8(9)	131.0	133.1
H_1–C_1–P	117(5)	115.5	107.2
H_1–C_1–C_2	113(5)	113.5	119.7
Dihedral angle (deg)			
Li–O–Li–O	0(8)	0.2	0.0
C_7–C_2–C_1–P	13(2)	3.4	5.7
C_7–C_2–C_1–H_1	176(5)	179.0	177.5

polymeric structure is restricted to the dimeric subunit (Table 5 and Figure 3).

Both methods find the essential features of that structure. It can be clearly seen that PM3 is superior to MNDO for the reproduction of all the Li–X distances. Nevertheless, the already-mentioned weaknesses of the semiempirical methods, mainly for the phosphonate distances, remain.

These results confirm the previously reported applicability of PM3 for the simulation of large organolithium compounds in the crystalline state.[11,22,29]

Further Isomers of Dimeric Lithiophosphonates, $\{[R^1R^2CP(O)(OR)_2]Li\}_2$. There is no reason to assume that the DABCO coordinated polymeric material investigated by X-ray analysis is a suitable model for the understanding of the structural manifold of solvated and solid lithiophosphonates. There is a dearth of information because of experimental difficulties: For example, in THF solution at −108 °C, the dimer of [PhCHP(O)-$(OEt)_2$]Li was generated after reaction of $PhCH_2P(O)$-$(OEt)_2$ with *n*-BuLi.[30] However, no additional structural properties of that dimer were reported, probably due to the instability of the lithiated compound in the course of drying.

(29) Koch, R. Dissertation, Erlangen, 1994.

(30) The dimeric character of this species in THF was determined cryoscopically, compare ref 8.

Therefore, calculations may allow decisive interpretations. We thus extended our investigation to a variety of complexed species, $\{[RCHP(O)(OH)_2]Li\}_2 \cdot 4(Solv)$, in which Li–C and/or further Li–O contacts are possible. Due to the MNDO-inherent overestimation of the C–Li interaction, the improvement of PM3 concerning this detail, and the better description of the relative energies of lithiated phosphonates (Figure 2), such a study is restricted to the PM3 method.

Starting from various plausible structures with different substituents R, the eight membered ring systems with Li–C contacts result to be more stable than the four membered ring isomers, which correspond with the X-ray structure. Isomers with only lithium, phosphorus, and oxygen ring atoms are less important; they lie about 10 kcal/mol higher in energy than the related carbon containing counterparts.

In the case of the benzylanion species (R = Ph; **7a**,**b**, Figure 4), this trend is expressed by somewhat small energy differences, i.e., for the unsolvated (−10.5 kcal/mol) and the solvated examples (Solv = H_2O: −8.5 kcal/mol, Solv = NH_3: −5.8 kcal/mol). The C–Li distances in **7b** are found to be in the typical range for standard carbon-lithium contacts, i.e., in the interval between 2.097 and 2.162 Å.

The relative stability of the eight-membered isomer increases significantly in the case of the parent substructure (R = H, compounds **8a**,**b**): The unsolvated four-membered ring dimer **8a** can only be calculated by imposing symmetry restrictions to the central Li–O–Li–O segment[31] —it otherwise collapses into a structure similar to the final eight-membered ring, **8b**, which turns out to be 35.5 kcal/mol more stable. Again, simulation of solvation of the lithium cations effects the relative stabilization: The NH_3 coligands and the H_2O counterparts stabilize the eight-membered ring (−32.4 kcal/mol and −33.4 kcal/mol, relative to **8a**). Analysis of a possible thermal vibrational effect (using the THERMO routine in MOPAC) reveals no significant difference in the thermal contributions of both ring systems.

Therefore, for typical *aliphatic* and sterically not too congested Horner–Emmons reagents, $[R^1R^2CP(O)(OR)_2]$-Li, the PM3 calculations predict—with great reliability—the exclusive existence of eight-ring dimers in solution. For monoaromatic substituted examples this PM3-calculated trend is based on relatively small energy differences and therefore less convincing.

(31) The central four-membered Li–O–Li–O ring system was held planar (D_{2h} symmetry).

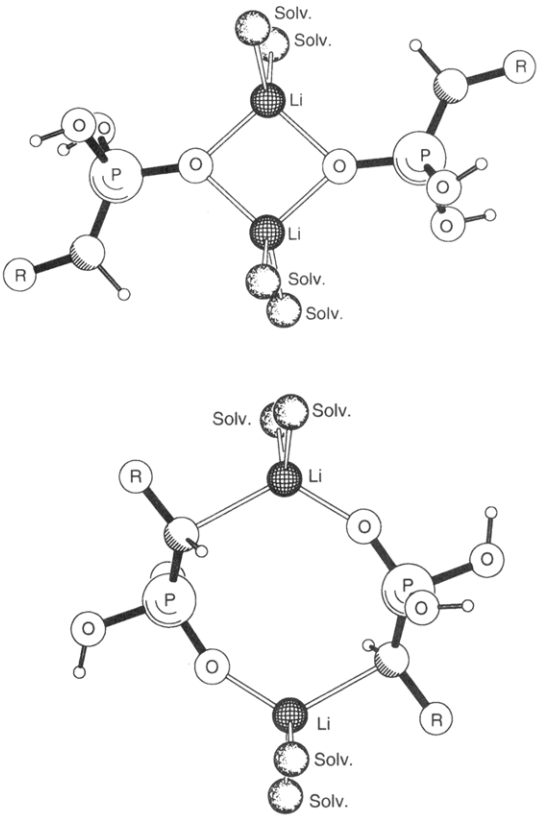

Figure 4. Four-membered (**7a**: R = Ph; **8a**: R = H) and eight-membered ring isomers (**7b**: R = Ph; **8b**: R = H) of $\{[RHCP(O)(OH)_2]Li\}_2$.

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