Table S1 Compilation of exponents and contraction parameters of the radial deformation function together with multipole charges.

atom	ζ(bohr^{-1})	κ'	Q_{mp}	atom	ζ(bohr^{-1})	κ'	Q_{mp}
I				**II**			
Ca	4.16	1.00	1.3(3)	Li	2.42	1.00	0.66(20)
P	9.80	0.82(2)	0.05(9)	P	9.80	0.76(1)	-0.20(1)
O1	8.44	0.94(6)	-0.18(5)	O1	8.44	1.01(6)	-0.21(5)
O2	8.44	0.73	-0.34(3)	O2	8.44	0.73	-0.32(3)
O3	8.44	0.73	-0.33(3)	O3	8.44	0.73	-0.32(3)
C	5.96	0.87(3)	-0.61(11)	C	5.96	0.84(3)	-0.48(20)
H1	3.78	1.20	0.22(2)	H1	3.78	1.20	0.34(2)
H2	3.78	1.20	0.18(3)	H2	3.78	1.20	0.17(3)
H3	3.78	1.20	0.17(3)	H3	3.78	1.20	0.25(3)
H4	3.78	1.20	0.18(3)	H4	3.78	1.20	0.12(3)

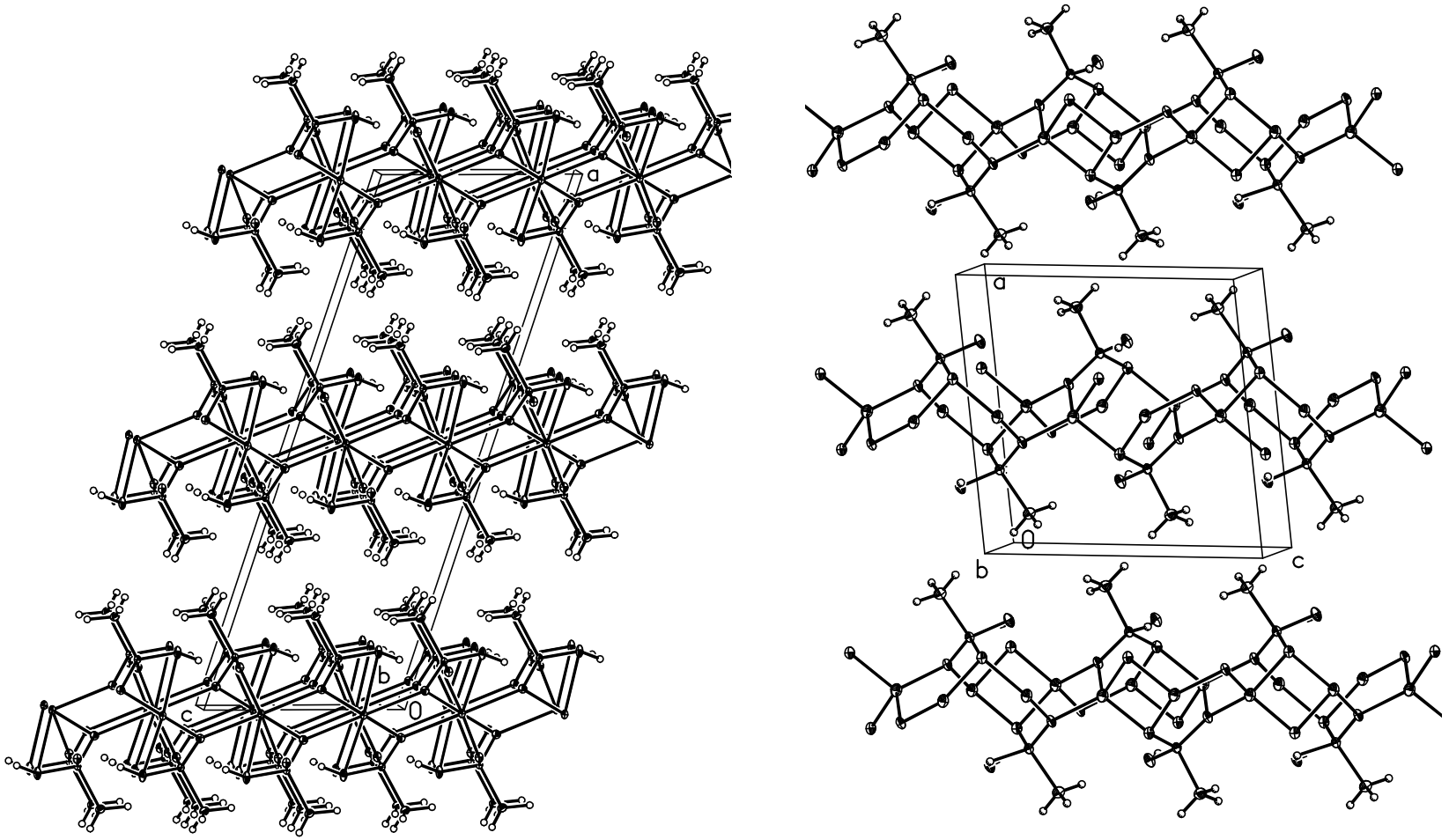
Table S2 Supplementary topological parameters for **I** and **II.**

	R_{ij}	d_1	d_2	$?_1$	$?_2$	$?_3$
I						
P-O1	1.5794	0.6354	0.944	-8.19	-7.46	30.33
P-O2	1.5124	0.6148	0.8976	-10.45	-9.98	41.02
P-O3	1.5163	0.6178	0.8985	-9.99	-9.55	39.46
O1-H1	1.0106	0.7703	0.2404	-37.75	-36.2	30.21
P-C	1.7896	0.6923	1.0973	-6.13	-5.65	8.1
C-H2	1.0909	0.6526	0.4383	-15.47	-14.99	9.92
C-H3	1.0901	0.6741	0.4161	-15.02	-14.99	11.72
C-H4	1.0901	0.6916	0.3985	-15.68	-15.44	12.36
O2-Ca	2.4044	1.217	1.1874	-0.85	-0.79	5.67
O2-Ca^{i}	2.3852	1.2064	1.1788	-0.93	-0.89	5.97
O3-Ca^{ii}	2.3749	1.2037	1.1712	-0.92	-0.9	6.02
H1-O3^{ii}	1.6276	0.552	1.0755	-3.93	-3.46	7.43
II						
P-O1	1.58	0.6328	0.9473	-7.86	-7.5	30.37
P-O2	1.507	0.6093	0.8977	-10.42	-9.84	44.79
P-O3	1.5214	0.6128	0.9086	-10.17	-9.65	41.81
O1-H1	1.022	0.7851	0.2369	-34.33	-33.26	26.67
P-C	1.7867	0.682	1.1047	-6.08	-5.78	9.54
C-H2	1.09	0.6995	0.3906	-15.81	-15.62	14.35
C-H3	1.091	0.7313	0.3597	-16.41	-16.14	14.71
C-H4	1.0902	0.6859	0.4043	-16.05	-15.66	13.5
O2-Li	1.9092	1.1827	0.7265	-1.36	-1.3	8.24
O2-Li^{iii}	1.929	1.1925	0.7365	-1.18	-1.12	7.57
O3-Li^{iv}	2.0421	1.2626	0.7795	-0.71	-0.67	4.97
O3-Li^{v}	1.9725	1.2217	0.7508	-1.03	-1	6.46
H1-O3^{vi}	1.6746	0.5665	1.108	-2.2	-1.77	7.73

The symmetry codes are taken from Table 4.

Table S3. Characteristics of selected natural bond orbitals in hydrogen methylphosphonate. The first item shows the composition, the other – occupation (lp –lone pair).

orbital	MPI	$MPCa_3$	MPII	$MPLi_4$
σ(P-O1)	$0.4512P(sp^{3.8})+0.8924O(sp^{1.67})$ 1.988	$0.4745P(sp^{3.51})+0.8803O(sp^{2.11})$ 1.986	$0.4588P(sp^{3.72})+0.8885O(sp^{2.19})$ 1.986	$0.4894P(sp^{3.20})+0.8720O(sp^{2.80})$ 1.986
σ(P-O2)	$0.5064P(sp^{2.47})+0.8623O(sp^{2.11})$ 1.987	$0.4511P(sp^{3.53})+0.8925O(sp^{1.38})$ 1.985	$0.5096P(sp^{2.51})+0.8604O(sp^{2.19})$ 1.985	$0.4799P(sp^{3.02})+0.8773O(sp^{1.68})$ 1.988
σ(P-O3)	$0.5066P(sp^{2.52})+0.8622O(sp^{2.12})$ 1.987	$0.4919P(sp^{2.79})+0.8707O(sp^{1.90})$ 1.984	$0.5034P(sp^{2.5})+0.8641O(sp^{2.02})$ 1.987	$0.4671P(sp^{3.21})+0.8842O(sp^{1.46})$ 1.987
σ(P-C)	$0.5836P(sp^{3.16})+0.8121C(sp^{3.07})$ 1.971	$0.6571P(sp^{2.13})+0.7538C(sp^{3.83})$ 1.963	$0.5742P(sp^{3.23})+0.8187C(sp^{2.88})$ 1.975	$0.6378P(sp^{2.34})+0.7702C(sp^{3.48})$ 1.969
lp(O1)	$sp^{1.59}$; 1.964	$sp^{1.32}$; 1.949	$sp^{1.11}$; 1.971	$sp^{0.89}$; 1.958
lp(O1)	p; 1.934	p; 1.890	p; 1.924	p; 1.894
lp(O2)	$sp^{0.47}$; 1.976	$sp^{0.73}$; 1.967	$sp^{0.46}$; 1.978	$sp^{0.60}$; 1.973
lp(O2)	p; 1.834	p; 1.901	p; 1.838	p; 1.886
lp(O2)	p; 1.830	p; 1.889	p; 1.830	p; 1.868
lp(O3)	$sp^{0.47}$; 1.977	$sp^{0.54}$; 1.968	$sp^{0.50}$; 1.977	$sp^{0.69}$; 1.973
lp(O3)	p; 1.846	p; 1.844	p; 1.842	p; 1.898
lp(O3)	p; 1.828	p; 1.840	p; 1.828	p; 1.887
σ^*(P-O1)	$0.8924P(sp^{3.83})-0.4512O(sp^{1.67})$ 0.223	$0.8803P(sp^{3.51})-0.4745O(sp^{2.11})$ 0.165	$0.8885P(sp^{3.72})-0.4588O(sp^{2.19})$ 0.216	$0.8720P(sp^{3.20})-0.4894O(sp^{2.80})$ 0.155
σ^*(P-O2)	$0.8623P(sp^{2.47})-0.5064O(sp^{2.11})$ 0.135	$0.8925P(sp^{3.53})-0.4511O(sp^{1.38})$ 0.167	$0.8604P(sp^{2.51})-0.5096O(sp^{2.19})$ 0.131	$0.8773P(sp^{3.02})-0.4799O(sp^{1.68})$ 0.135
σ^*(P-O3)	$0.8622P(sp^{2.53})-0.5066O(sp^{2.12})$ 0.134	$0.8707P(sp^{2.79})-0.4919O(sp^{1.90})$ 0.120	$0.8641P(sp^{2.50})-0.5034O(sp^{2.02})$ 0.133	$0.8842P(sp^{3.21})-0.4671O(sp^{1.46})$ 0.141
σ^*(P-C)	$0.8121P(sp^{3.16})-0.5836C(sp^{3.07})$ 0.171	$0.7538P(sp^{2.13})-0.6571C(sp^{3.84})$ 0.109	$0.8187P(sp^{3.23})-0.5742C(sp^{2.88})$ 0.180	$0.7702P(sp^{2.34})-0.6378C(sp^{3.48})$ 0.124



I **II**

Fig. S1. Packing diagram of calcium bis(hydrogen methyphosphonate) (**I**) and lithium hydrogen methylphosphonate (**II**)

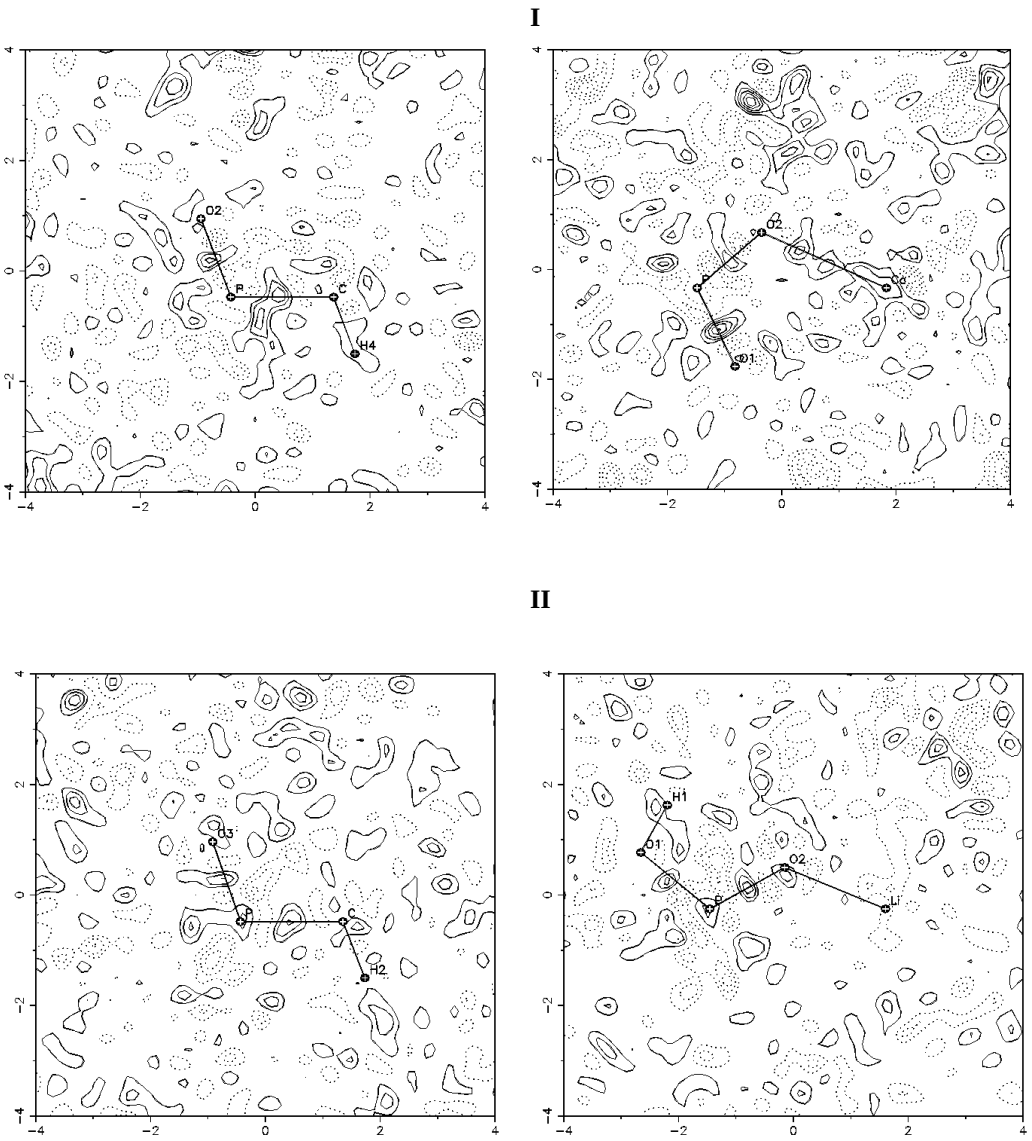


Fig. S2. Residual density maps for multipole refinements of **I** and **II**. The contour intervals are drawn at 0.05 e/Å^3; the positive contours are solid, the negative – dotted, the zero contours have been omitted. The scale is shown in Å and the sections are through the (P, M, O2) and (P, C, O3) planes, where M = Ca for **I** and Li for **II**.