Supplementary Materials

Crystal structure, Raman spectroscopy and dielectric properties of new semi-organic crystals based on 2-methylbenzimidazole

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S1. Single crystal XRD results

Table S1. Results of refinement of the MBI-phosphate-1 structure (space group $P\bar{1}$ (N 2)) using single crystal XRD data. Atomic numbers Z, relative coordinates of atoms (x/a, y/b, z/c) and their isotropic temperature factors U are shown.

N	Atom	Z	x/a	y/b	z/c	$U_{eq/iso}$(Å^2)[a]
1	P1	15	0.46195(7)	0.80872(6)	0.06072(5)	0.03431(18)
2	P2	15	0.16324(7)	0.91062(7)	0.36794(6)	0.04084(19)
3	O4	8	0.48677(18)	0.91710(17)	0.14076(14)	0.0406(4)
4	O3	8	0.59151(18)	0.72889(19)	0.00377(15)	0.0471(5)
5	O2	8	0.3828(2)	0.87223(18)	-0.03235(16)	0.0456(5)
6	O1	8	0.3529(2)	0.70532(18)	0.12826(16)	0.0465(5)
7	O8	8	0.16634(19)	0.78762(19)	0.29563(16)	0.0494(5)
8	O6	8	0.1369(2)	0.8816(2)	0.49506(16)	0.0561(5)
9	O9	8	0.5918(2)	0.5663(2)	0.82096(18)	0.0577(6)
10	N1	7	0.8046(2)	0.6505(2)	0.10201(17)	0.0388(5)
11	H1	1	0,73585	0,67098	0,06707	0,047
12	N2A	7	0.4255(2)	0.5746(2)	0.66594(17)	0.0391(5)
13	H2A	1	0,48757	0,56474	0,70917	0,047
14	N2	7	0.9728(2)	0.6722(2)	0.19626(18)	0.0408(5)
15	H2	1	1,03051	0,70917	0,23239	0,049
16	N1A	7	0.2796(2)	0.6697(2)	0.56861(18)	0.0437(5)
17	H1A	1	0,23137	0,73178	0,53847	0,052
18	O7	8	0.0467(3)	1.0119(3)	0.34162(18)	0.0863(9)
19	C8	6	0.8582(2)	0.5206(3)	0.11855(19)	0.0358(5)
20	C3	6	0.9665(2)	0.5343(3)	0.17879(19)	0.0364(5)
21	C2A	6	0.3702(3)	0.6920(3)	0.6364(2)	0.0402(6)
22	C2	6	0.8760(3)	0.7387(3)	0.1486(2)	0.0406(6)
23	C7	6	0.8234(3)	0.3947(3)	0.0851(2)	0.0462(6)
24	H7	1	0,75086	0,38552	0,04457	0,055
25	C4	6	1.0451(3)	0.4221(3)	0.2075(2)	0.0486(7)
26	H4	1	1,11827	0,43088	0,24755	0,058
27	C6	6	0.9014(3)	0.2839(3)	0.1148(3)	0.0575(8)
28	H6	1	0,88062	0,19709	0,09431	0,069
29	C5	6	1.0104(3)	0.2971(3)	0.1743(3)	0.0581(8)
30	H5	1	1,0612	0,21917	0,19216	0,07
31	C1A	6	0.4028(4)	0.8276(3)	0.6735(3)	0.0616(8)
32	H1AB	1	0,36706	0,83547	0,75543	0,092
33	H1A	1	0,35828	0,89764	0,63295	0,092
34	H1A	1	0,50435	0,83787	0,65646	0,092
35	C1	6	0.8514(4)	0.8885(3)	0.1463(3)	0.0619(8)
36	H1A	1	0,86693	0,9215	0,06735	0,093
37	H1B	1	0,91632	0,93064	0,18552	0,093
38	H1C	1	0,75491	0,91097	0,18448	0,093
39	C8A	6	0.2753(3)	0.5307(3)	0.5543(2)	0.0407(6)
40	C3A	6	0.3687(3)	0.4701(3)	0.6169(2)	0.0384(6)
41	C4A	6	0.3881(3)	0.3292(3)	0.6207(2)	0.0550(7)
42	H4A	1	0,45016	0,28637	0,6629	0,066
43	C7A	6	0.1992(3)	0.4559(4)	0.4923(3)	0.0598(8)
44	H7A	1	0,1374	0,49793	0,44953	0,072
45	C6A	6	0.2189(4)	0.3175(4)	0.4966(3)	0.0747(10)

46	H6A	1	0,16888	0,26356	0,45622	0,09
47	C5A	6	0.3106(4)	0.2557(3)	0.5589(3)	0.0713(10)
48	H5A	1	0,32097	0,16073	0,55945	0,086
49	O5	8	0.3083(3)	0.9790(3)	0.3336(2)	0.0976(10)
50	H9A	1	0.585(3)	0.626(3)	0.879(2)	0.066(10)
51	H9B	1	0.609(4)	0.480(2)	0.851(3)	0.096(13)
52	H1D	1	0.283(3)	0.743(3)	0.187(2)	0.088(12)
53	H2B	1	0.433(4)	0.944(3)	-0.075(3)	0.101(14)
54	H7B	1	-0.025(3)	1.042(4)	0.401(3)	0.104(14)
55	H5B	1	0.360(4)	0.967(5)	0.258(2)	0.125(16)

[a]Equivalent isotropic temperature factors U_{eq} are shown for non-hydrogen atoms refined in an approximation of anisotropic temperature factor. For atoms of H, the isotropic temperature factors U_{iso} are shown

Symmetry codes:

x; y; z

-x; -y; -z

Table S2. Atomic displacement parameters for the MBI-phosphate-1(Å^2).

Ato	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P1	0.0349(3)	0.0342(3)	0.0360(3)	-0.0055(3)	-0.0119(3)	0.0001(3)
P2	0.0420(4)	0.0408(4)	0.0399(4)	-0.0109(3)	-0.0080(3)	0.0024(3)
O4	0.0439(10)	0.0406(10)	0.0395(9)	-0.0076(7)	-0.0118(8)	-0.0055(8)
O3	0.0407(10)	0.0562(11)	0.0464(10)	-0.0150(9)	-0.0134(8)	0.0090(9)
O2	0.0476(11)	0.0434(11)	0.0534(11)	0.0013(9)	-0.0272(9)	-0.0058(9)
O1	0.0530(12)	0.0340(10)	0.0494(11)	-0.0055(8)	-0.0018(9)	-0.0059(8)
O8	0.0395(10)	0.0530(11)	0.0550(11)	-0.0216(9)	-0.0044(9)	-0.0072(9)
O6	0.0585(12)	0.0693(13)	0.0409(10)	-0.0075(9)	-0.0166(9)	0.0284(10)
O9	0.0832(15)	0.0454(12)	0.0550(12)	-0.0106(10)	-0.0399(11)	0.0103(11)
N1	0.0325(11)	0.0493(13)	0.0370(11)	-0.0049(9)	-0.0126(9)	-0.0009(9)
N2A	0.0374(11)	0.0492(13)	0.0328(10)	-0.0037(9)	-0.0125(9)	0.0042(10)
N2	0.0358(11)	0.0487(13)	0.0410(11)	-0.0095(10)	-0.0138(9)	-0.0037(10)
N1A	0.0412(12)	0.0520(13)	0.0385(11)	-0.0044(10)	-0.0117(10)	0.0113(10)
O7	0.117(2)	0.0916(18)	0.0397(11)	0.0051(12)	-0.0058(13)	0.0630(16)
C8	0.0290(12)	0.0470(15)	0.0306(11)	-0.0043(10)	-0.0032(10)	-0.0038(11)
C3	0.0313(12)	0.0476(15)	0.0291(11)	-0.0039(10)	-0.0032(10)	-0.0026(11)
C2A	0.0377(13)	0.0484(15)	0.0335(12)	-0.0068(11)	-0.0051(11)	0.0020(11)
C2	0.0359(13)	0.0461(15)	0.0398(13)	-0.0068(11)	-0.0073(11)	-0.0011(11)
C7	0.0421(15)	0.0543(17)	0.0415(14)	-0.0102(12)	-0.0041(12)	-0.0119(13)
C4	0.0446(15)	0.0633(19)	0.0387(14)	0.0003(13)	-0.0118(12)	0.0064(13)
C6	0.064(2)	0.0492(17)	0.0547(17)	-0.0068(14)	0.0011(15)	-0.0131(15)
C5	0.067(2)	0.0506(18)	0.0505(17)	0.0056(14)	-0.0012(15)	0.0088(15)
C1A	0.077(2)	0.0512(18)	0.0557(18)	-0.0128(14)	-0.0094(16)	-0.0050(16)
C1	0.065(2)	0.0500(18)	0.074(2)	-0.0094(15)	-0.0212(17)	0.0017(15)
C8A	0.0349(13)	0.0536(16)	0.0327(12)	-0.0084(11)	-0.0042(10)	0.0003(11)
C3A	0.0366(13)	0.0458(15)	0.0302(12)	-0.0029(10)	-0.0012(10)	-0.0004(11)
C4A	0.0629(19)	0.0492(17)	0.0467(16)	0.0051(13)	0.0014(14)	0.0030(14)
C7A	0.0457(16)	0.085(2)	0.0518(17)	-0.0165(16)	-0.0129(14)	-0.0100(16)
C6A	0.075(2)	0.083(3)	0.065(2)	-0.0234(19)	-0.0034(19)	-0.031(2)
C5A	0.092(3)	0.0485(19)	0.065(2)	-0.0133(16)	0.007(2)	-0.0161(18)
O5	0.0832(18)	0.104(2)	0.0927(19)	-0.0644(16)	0.0292(15)	-0.0520(16)

Table S3. Bond lengths (Å) in MBI-phosphate-1 structure according to results of structure refinement using single crystal XRD data(Table S1).

P1-O4	1.4981(19)	N2A-C2A	1.312(3)	C2-C1	1.475(4)
P1-O3	1.485(2)	N2A-C3A	1.374(3)	C7-C6	1.368(4)
P1-O2	1.559(2)	N2-C3	1.377(3)	C4-C5	1.369(4)
P1-O1	1.563(2)	N2-C2	1.320(3)	C6-C5	1.385(5)

P2-O8	1.491(2)	N1A-C2A	1.323(3)	C8A-C3A	1.378(4)
P2- O6	1.489(2)	N1A-C8A	1.378(4)	C8A-C7A	1.377(4)
P2-O7	1.535(2)	C8-C3	1.386(3)	C3A-C4A	1.383(4)
P2-O5	1.539(3)	C8-C7	1.378(4)	C4A-C5A	1.378(5)
N1-C8	1.374(3)	C3-C4	1.378(4)	C7A-C6A	1.359(5)
N1-C2	1.321(3)	C2A-C1A	1.474(4)	C6A-C5A	1.368(5)

Table S4. Bond angles (°) in MBI-phosphate-1 structure according to results of structure refinement using single crystal XRD data (Table S1).

O4-P1-O2	110.14(11)	C2-N2-C3	108.9(2)	C6-C7-C8	116.4(3)
O4-P1-O1	109.74(11)	C2A-N1A-	108.7(2)	C5-C4-C3	116.8(3)
O3-P1-O4	115.40(11)	N1-C8-C3	106.5(2)	C7-C6-C5	122.0(3)
O3-P1-O2	110.08(12)	N1-C8-C7	131.7(2)	C4-C5-C6	121.6(3)
O3-P1-O1	107.75(12)	C7-C8-C3	121.7(2)	C3A-C8A-N1A	106.2(2)
O2-P1-O1	102.96(12)	N2-C3-C8	106.1(2)	C7A-C8A-N1A	131.4(3)
O8-P2-O7	108.40(14)	N2-C3-C4	132.5(2)	C7A-C8A-C3A	122.4(3)
O8-P2-O5	108.69(12)	C4-C3-C8	121.3(2)	N2A-C3A-C8A	106.4(2)
O6-P2-O8	114.66(13)	N2A-C2A-	109.4(2)	N2A-C3A-C4A	133.1(3)
O6-P2-O7	109.02(12)	N2A-C2A-	125.4(2)	C8A-C3A-C4A	120.5(3)
O6-P2-O5	107.43(15)	N1A-C2A-	125.2(3)	C5A-C4A-C3A	116.5(3)
O7-P2-O5	108.49(19)	N1-C2-C1	124.9(2)	C6A-C7A-C8A	116.8(3)
C2-N1-C8	108.8(2)	N2-C2-N1	109.6(2)	C7A-C6A-C5A	121.6(3)
C2A-N2A-C3A	109.2(2)	N2-C2-C1	125.5(2)	C6A-C5A-C4A	122.3(3)

Table S5. Hydrogen-bond geometry (Å,°) in MBI-phosphate-1 structure according to results of structure refinement using single crystal XRD data (Table S1).

Bonded	D-H…A	Angle, °	D…A, Å	D-H, Å	H…A, Å
$(MBI+H)^+$&water	N2A-H2A…O9	167.94(18)	2.659(4)	0.860(3)	1.812(3)
$(MBI+H)^+$&$H_2PO_4^-$	N1A-	169.69(18)	2.658(4)	0.860(3)	1.807(3)
$(MBI+H)^+$&$H_2PO_4^-$	N1-H1…O3	174.01(18)	2.625(4)	0.860(3)	1.768(3)
$(MBI+H)^+$&$H_2PO_4^-$	N2-H2…O8	174.30(18)	2.688(4)	0.860(3)	1.831(3)
water&$H_2PO_4^-$	O9-H9A…O3	171.2(9)	2.717(4)	0.90(3)	1.82(3)
water&$H_2PO_4^-$	O9-H9B…O1	165.2(10)	2.760(4)	0.93(3)	1.85(3)
$H_2PO_4^-$ &$H_2PO_4^-$	O2-H2B…O4	174.1(10)	2.614(4)	0.94(4)	1.68(4)
$H_2PO_4^-$ &$H_2PO_4^-$	O1-H1D…O8	172.2(8)	2.501(4)	0.93(4)	1.58(4)
$H_2PO_4^-$ &$H_2PO_4^-$	O5-H5B…O4	163.1(10)	2.617(5)	0.93(4)	1.71(4)
$H_2PO_4^-$ &$H_2PO_4^-$	O7-H7B…O6	170.4(10)	2.541(5)	0.92(5)	1.63(5)

Table S6. Results of refinement of the MBI-phosphate-2 structure (space group $P\bar{1}$ (*N* 2)) using single crystal XRD data. Atomic numbers *Z*, relative coordinates of atoms (*x*/*a*, *y*/*b*, *z*/*c*) and their isotropic temperature factors *U* are shown.

N	Atom	*Z*	*x*/*a*	*y*/*b*	*z*/*c*	$U_{eq/iso}$(Å^2)[a]
1	P1	15	0.65038(4)	0.47711(2)	0.32850(2)	0.02871(7)
2	P2	15	0.14346(4)	0.64935(2)	0.09433(2)	0.02725(6)
3	O8	8	-0.05087(12)	0.68034(8)	0.17307(6)	0.03333(15)
4	O4	8	0.63987(14)	0.36367(7)	0.41648(6)	0.03536(17)
5	O3	8	0.62083(13)	0.44881(9)	0.19787(6)	0.03870(18)
6	O6	8	0.25113(14)	0.76271(9)	0.11253(9)	0.0438(2)
7	O7	8	0.28586(13)	0.50867(8)	0.11702(8)	0.03978(17)
8	O5	8	0.08454(13)	0.65382(10)	-0.03880(7)	0.0426(2)
9	O2	8	0.86432(16)	0.50280(10)	0.33190(8)	0.0474(2)
10	O9	8	0.61453(15)	0.73800(11)	0.01939(10)	0.0491(2)
11	O1	8	0.48740(18)	0.61014(9)	0.36234(7)	0.0558(3)
12	N2	7	0.82891(15)	-0.12070(8)	0.34741(8)	0.03329(17)
13	H2	1	0,86564	-0,18995	0,30079	0,04
14	N1	7	0.73544(15)	0.08928(8)	0.40688(9)	0.03383(18)

15	H1	1	0,70235	0,17686	0,40472	0,041
16	C3	6	0.74445(16)	0.00902(9)	0.51083(9)	0.03023(17)
17	C8	6	0.80457(16)	-0.12622(9)	0.47291(9)	0.03016(17)
18	C2	6	0.78608(17)	0.00948(10)	0.31087(10)	0.03397(19)
19	C4	6	0.70725(18)	0.04185(12)	0.63272(11)	0.0384(2)
20	H4	1	0,66808	0,13166	0,65818	0,046
21	C7	6	0.8293(2)	-0.23520(11)	0.55457(11)	0.0391(2)
22	H7	1	0,86963	-0,32505	0,52922	0,047
23	C6	6	0.7903(2)	-0.20234(14)	0.67618(12)	0.0456(3)
24	H6	1	0,80327	-0,27204	0,73398	0,055
25	C1	6	0.7927(2)	0.05717(14)	0.18275(12)	0.0495(3)
26	H1A	1	0,88812	-0,01072	0,13483	0,074
27	H1B	1	0,83369	0,14055	0,17766	0,074
28	H1C	1	0,66045	0,07251	0,15295	0,074
29	C5	6	0.7319(2)	-0.06684(14)	0.71395(11)	0.0445(3)
30	H5	1	0,70893	-0,0493	0,79633	0,053
31	H1D	1	0.439(3)	0.613(2)	0.4421(14)	0.082(6)
32	H6A	1	0.384(2)	0.743(2)	0.0791(19)	0.087(7)
33	H9A	1	0.698(3)	0.739(2)	0.0777(15)	0.064(5)
34	H5A	1	0.186(2)	0.6152(17)	-0.0914(14)	0.054(5)
35	H9B	1	0.673(4)	0.669(2)	-0.037(2)	0.097(8)
36	H2A	1	0.871(3)	0.5630(19)	0.2787(17)	0.076(6)
37	H7A	1	0.412(3)	0.483(2)	0.154(2)	0.099(8)

[a]Equivalent isotropic temperature factors U_{eq} are shown for non-hydrogen atoms refined in an approximation of anisotropic temperature factor. For atoms of H, the isotropic temperature factors U_{iso} are shown

Symmetry codes:

x; y; z

-x; -y; -z

Table S7. Atomic displacement parameters for the MBI-phosphate-2 (Å^2).

Ato	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P1	0.03898(15)	0.02356(10)	0.01944(10)	-0.00064(7)	0.00257(9)	-0.00211(9)
P2	0.02550(12)	0.02957(11)	0.02508(10)	-0.00588(8)	0.00382(8)	-0.00525(9)
O8	0.0329(4)	0.0355(3)	0.0300(3)	-0.0070(2)	0.0095(3)	-0.0086(3)
O4	0.0507(5)	0.0220(3)	0.0284(3)	-0.0012(2)	0.0105(3)	-0.0043(3)
O3	0.0346(4)	0.0527(5)	0.0222(3)	-0.0083(3)	0.0013(3)	0.0002(3)
O6	0.0386(5)	0.0374(4)	0.0574(5)	-0.0094(3)	0.0063(4)	-0.0152(3)
O7	0.0360(4)	0.0327(3)	0.0480(4)	-0.0077(3)	-0.0081(3)	-0.0019(3)
O5	0.0342(4)	0.0604(5)	0.0261(3)	-0.0065(3)	0.0018(3)	0.0000(4)
O2	0.0566(6)	0.0524(5)	0.0406(4)	0.0137(4)	-0.0130(4)	-0.0265(4)
O9	0.0315(4)	0.0541(5)	0.0600(6)	-0.0049(4)	0.0012(4)	-0.0088(4)
O1	0.0851(8)	0.0322(4)	0.0281(3)	0.0035(3)	0.0133(4)	0.0182(4)
N2	0.0383(5)	0.0239(3)	0.0357(4)	-0.0065(3)	0.0002(3)	-0.0047(3)
N1	0.0387(5)	0.0211(3)	0.0396(4)	-0.0033(3)	-0.0008(3)	-0.0046(3)
C3	0.0289(4)	0.0240(3)	0.0369(4)	-0.0053(3)	-0.0013(3)	-0.0051(3)
C8	0.0298(4)	0.0237(3)	0.0360(4)	-0.0043(3)	-0.0017(3)	-0.0050(3)
C2	0.0360(5)	0.0273(4)	0.0373(5)	-0.0021(3)	-0.0008(4)	-0.0063(4)
C4	0.0376(6)	0.0359(5)	0.0401(5)	-0.0111(4)	0.0012(4)	-0.0065(4)
C7	0.0428(6)	0.0269(4)	0.0458(6)	0.0016(4)	-0.0037(5)	-0.0062(4)
C6	0.0487(7)	0.0433(6)	0.0432(6)	0.0071(5)	-0.0029(5)	-0.0104(5)
C1	0.0611(9)	0.0465(6)	0.0384(6)	0.0052(5)	-0.0012(5)	-0.0113(6)
C5	0.0451(7)	0.0514(6)	0.0358(5)	-0.0037(4)	-0.0005(5)	-0.0107(5)

Table S8. Bond lengths (Å) in MBI-phosphate-2 structure according to results of structure refinement using single crystal XRD data (Table S6).

P1-O4	1.4971(7)	P2-O6	1.5500(8)	N1-C3	1.3842(14)	C2-C1	1.4854(16)
P1-O3	1.5252(8)	P2-O7	1.5305(9)	N1-C2	1.3299(13)	C4-C5	1.3845(18)
P1-O2	1.5577(10)	P2-O5	1.5556(8)	C3-C8	1.3990(12)	C7-C6	1.3890(18)
P1-O1	1.5479(9)	N2-C8	1.3889(13)	C3-C4	1.3913(15)	C6-C5	1.4008(19)
P2-O8	1.5001(7)	N2-C2	1.3347(13)	C8-C7	1.3897(14)		

Table S9. Bond angles (°) in MBI-phosphate-2 structure according to results of structure refinement using single crystal XRD data (Table S6).

O4-P1-O3	114.73(5)	O6-P2-O5	109.56(5)	N2-C8-C7	131.89(9)
O4-P1-O2	107.52(5)	O7-P2-O6	110.59(5)	C7-C8-C3	122.00(10)
O4-P1-O1	111.76(5)	O7-P2-O5	107.35(5)	N2-C2-C1	125.10(10)
O3-P1-O2	107.90(5)	C2-N2-C8	108.96(8)	N1-C2-N2	109.38(9)
O3-P1-O1	105.96(5)	C2-N1-C3	109.19(8)	N1-C2-C1	125.52(10)
O1-P1-O2	108.81(6)	N1-C3-C8	106.36(8)	C5-C4-C3	116.17(10)
O8-P2-O6	107.94(5)	N1-C3-C4	131.89(9)	C6-C7-C8	116.22(10)
O8-P2-O7	114.44(5)	C4-C3-C8	121.75(10)	C7-C6-C5	121.66(11)
O8-P2-O5	106.83(5)	N2-C8-C3	106.11(8)	C4-C5-C6	122.20(11)

Table S10. Hydrogen-bond geometry (Å,°) in MBI-phosphate-2 structure according to results of structure refinement using single crystal XRD data (Table S6).

Bonded	D-H…A	Angle, °	D…A, Å	D-H, Å	H…A, Å
$(MBI+H)^+$&$H_2PO_4^-$	N1-H1…O4	173.96(12)	2.6997(12)	0.8600(9)	1.8429(8)
$(MBI+H)^+$&H_3PO_4	N2-H2…O8	169.26(11)	2.7691(13)	0.8600(10)	1.9195(9)
$H_2PO_4^-$&$H_2PO_4^-$	O1-	172.8(7)	2.5363(12)	0.918(18)	1.623(18)
H_3PO_4 & water	O6-	169.7(8)	2.5713(17)	0.93(2)	1.652(18)
water& H_3PO_4	O9-	158.3(7)	2.8850(16)	0.90(3)	2.03(3)
H_3PO_4& $H_2PO_4^-$	O5-	176.1(7)	2.5963(15)	0.887(19)	1.711(19)
water& H_3PO_4	O9-H9B…O7	156.4(9)	2.8748(16)	0.94(3)	1.99(3)
$H_2PO_4^-$& H_3PO_4	O2-	166.0(9)	2.6205(16)	0.84(3)	1.79(3)
H_3PO_4 & $H_2PO_4^-$	O7-	172.9(8)	2.4456(15)	0.95(3)	1.50(3)

Table S11. Results of refinement of the MBI-phosphite structure (space group $P2_1/c$ (N14)) using single crystal and powder XRD data. Atomic numbers Z, relative coordinates of atoms (x/a, y/b, z/c) and their isotropic temperature factors U are shown.

N	Atom	Z	x/a	y/b	z/c	$U_{eq/iso}$(Å²)[a]	x/a	y/b	z/c	$U_{iso}^{overall}$ (Å²)[b]
			Single crystal[c]: a = 17.1966(6) Å, b = 17.7098(7) Å, c = 6.9992(4) Å, β = 94.963(4)[c]				Powder[b]: a = 17.1966(3) Å, b = 17.7198(6) Å, c = 7.00895(8) Å, β = 94.878(2)[d]			
1	P1	15	0.08615(4)	0.51576(4)	0.30208(13)	0.0481(3)	0.0888(3)	0.5147(5)	0.2971(8)	0.095(2)
2	P2	15	0.48754(5)	0.90321(5)	0.32937(15)	0.0614(3)	0.4893(4)	0.9046(4)	0.3246(8)	0.095(2)
3	O6	8	0.16729(11)	0.54113(11)	0.2910(3)	0.0590(6)	0.1659(6)	0.5413(9)	0.2953(15)	0.077(2)
4	O7	8	07555(11)	0.44727(11)	0.4237(4)	0.0620(7)	0.0800(6)	0.4516(8)	0.4249(13)	0.077(2)
5	O5	8	0.03459(12)	0.58241(12)	0.3627(4)	0.0634(7)	0.0405(7)	0.5814(7)	0.3586(13)	0.077(2)
6	N1	7	0.30340(12)	0.29450(13)	0.5464(3)	0.0439(6)	0.3065(8)	0.2864(11)	0.5628(19)	0.060(3)
7	H1	1	0.352939	0.290575	0.574076	0,053	0.3530(53)	0.2940(79)	0.606(15)	0.10(1)
8	N4	7	0.22508(13)	0.67805(14)	0.3160(4)	0.0481(6)	0.2252(7)	0.6784(10)	0.3158(17)	0.061(3)
9	H4A	1	0.203144	0.634437	0.317647	0,058	0.1946(58)	0.6363(77)	0.334(14)	0.10(1)
10	N2	7	0.18943(12)	0.34386(14)	0.4804(4)	0.0470(6)	0.1905(8)	0.3366(11)	0.4865(16)	0.061(3)
11	H2	1	0.153172	0.376961	0.458416	0,056	0.1463(55)	0.3661(75)	0.458(13)	0.10(1)
12	N3	7	0.31403(15)	0.76379(15)	0.3109(4)	0.0552(7)	0.3210(7)	0.7662(9)	0.3033(19)	0.061(3)
13	H3	1	0.359075	0.784749	0.309163	0,066	0.3591(51)	0.8155(77)	0.319(15)	0.10(1)
14	O3	8	0.45518(13)	0.82647(13)	0.3007(4)	0.0799(8)	0.4622(7)	0.8303(8)	0.2924(14)	0.077(2)
15	O2	8	0.41922(14)	0.95952(15)	0.3415(5)	0.0874(9)	0.4273(6)	0.9539(8)	0.3504(15)	0.077(2)
16	O1	8	0.54656(14)	0.91287(14)	0.4940(4)	0.0856(9)	0.5419(7)	0.9131(7)	0.4998(16)	0.077(2)
17	O7	8	0.44635(15)	0.29530(18)	0.7231(5)	0.0974(11)	0.4475(6)	0.2933(8)	0.7284(13)	0.077(2)
18	C3	6	0.25207(15)	0.23456(16)	0.5182(4)	0.0400(7)	0.2563(9)	0.2325(13)	0.5203(22)	0.060(2)

19	C16	6	0.18658(17)	0.74672(16)	0.3176(4)	0.0444(7)	0.1883(9)	0.7428(12)	0.3189(24)	0.060(2)
20	C8	6	0.17909(15)	0.26662(17)	0.4758(4)	0.0417(7)	0.1801(9)	0.2598 (11)	0.4822(21)	0.060(2)
21	C11	6	0.24378(18)	0.80166(17)	0.3135(4)	0.0482(7)	0.2460(9)	0.8009(13)	0.3095(22)	0.060(2)
22	C2	6	0.26451(16)	0.35872(17)	0.5242(4)	0.0467(7)	0.2685(9)	0.3523(12)	0.5249(21)	0.060(2)
23	C10	6	0.30086(17)	0.6900(2)	0.3116(5)	0.0509(8)	0.3005(9)	0.6933(13)	0.3141(23)	0.060(2)
24	C4	6	0.26288(18)	0.15710(18)	0.5268(5)	0.0534(8)	0.2627(9)	0.1525(12)	0.5292(22)	0.060(2)
25	H4	1	0.311930	0.135771	0.555240	0,064	0.3066(62)	0.1305(74)	0.541(14)	0.10(1)
26	C15	6	0.10861(19)	0.7649(2)	0.3201(5)	0.0582(8)	0.1051(9)	0.7624(12)	0.3204(22)	0.060(2)
27	H15	1	0.070199	0.728126	0.324209	0,07	0.0702(56)	0.7277(73)	0.316(14)	0.10(1)
28	C7	6	0.11302(17)	0.2222(2)	0.4393(5)	0.0553(8)	0.1147(9)	0.2237(13)	0.4465(21)	0.060(2)
29	H7	1	0.063844	0.243213	0.410421	0,066	0.0639(56)	0.2431(74)	0.397(13)	0.10(1)
30	C12	6	0.2257(2)	0.87788(19)	0.3097(5)	0.0632(9)	0.2275(9)	0.8826(12)	0.3131(21)	0.060(2)
31	H12	1	0.263939	0.914941	0.307345	0,076	0.2693(57)	0.9108(77)	0.286(14)	0.10(1)
32	C6	6	0.1242(2)	0.1456(2)	0.4482(5)	0.0657(10)	0.1216(9)	0.1452(12)	0.4425(19)	0.060(2)
33	H6	1	0.081317	0.113973	0.424704	0,079	0.0813(53)	0.1148(68)	0.409(12)	0.10(1)
34	C5	6	0.1974(2)	0.1137(2)	0.4910(5)	0.0640(9)	0.1954(9)	0.1135(12)	0.4892(20)	0.060(2)
35	H5	1	0.202005	0.061353	0.495446	0,077	0.2047(58)	0.0614(82)	0.514(12)	0.10(1)
36	C1	6	0.2989(2)	0.43473(19)	0.5444(6)	0.0715(10)	0.3027(9)	0.4284(13)	0.5572(22)	0.060(2)
37	H1A	1	0.313121	0.445008	0.677465	0,107	0.3145(57)	0.4451(91)	0.677(13)	0.10(1)
38	H1B	1	0.261410	0.471443	0.494219	0,107	0.2646(54)	0.4697(83)	0.492(12)	0.10(1)
39	H1C	1	0.344452	0.437308	0.474588	0,107	0.3450(53)	0.4368(79)	0.476(13)	0.10(1)
40	C13	6	0.1481(2)	0.8953(2)	0.3098(5)	0.0705(10)	0.1491(9)	0.8971(12)	0.3136(22)	0.060(2)
41	H13	1	0.13316	0.945803	0.305311	0,085	0.1406(55)	0.9519(81)	0.307(14)	0.10(1)
42	C14	6	0.0913(2)	0.8404(2)	0.3163(5)	0.0696(10)	0.0896(9)	0.8400(11)	0.3181(21)	0.060(2)
43	H14	1	0.039441	0.855173	0.318142	0,084	0.0395(65)	0.8588(64)	0.307(13)	0.10(1)
44	C9	6	0.3600(2)	0.6298(2)	0.3066(6)	0.0750(11)	0.3610(9)	0.6274(11)	0.3058(22)	0.060(2)
45	H9A	1	0.336562	0.581903	0.330194	0,113	0.3541(54)	0.5719(80)	0.310(15)	0.10(1)
46	H9B	1	0.401875	0.639275	0.403541	0,113	0.4018(50)	0.6473(69)	0.387(14)	0.10(1)
47	H9C	1	0.380132	0.629125	0.182876	0,113	0.3857(52)	0.6358(71)	0.183(13)	0.10(1)
48	H5A	1	-0.002(2)	0.567(3)	0.444(6)	0.122(17)	0.0020(77)	0.5828(59)	0.4305(143)	0.10(1)
49	H7A	1	0.481(2)	0.255(2)	0.725(8)	0.126(17)	0.4783(65)	0.2586(75)	0.746(13)	0.10(1)
50	H7B	1	0.455(3)	0.328(2)	0.825(5)	0.126(18)	0.4629(65)	0.3237(66)	0.829(14)	0.10(1)
51	H2B	1	0.432(3)	1.005(2)	0.408(8)	0.16(2)	0.4439(54)	0.0016(92)	0.391(13)	0.10(1)
52	H1D	1	0.0532(19)	0.4992(19)	0.117(5)	0.078(10)	0.0659(51)	0.4830(91)	0.129(12)	0.10(1)
53	H2A	1	0.525(2)	0.922(2)	0.173(6)	0.112(14)	0.5099(77)	0.9175(62)	0.149(14)	0.10(1)

[a]Equivalent isotropic temperature factors U_{eq} are shown for non-hydrogen atoms refined in an approximation of anisotropic temperature factor. For atoms of H, the isotropic temperature factors U_{iso} are shown

[b]Isotropic temperature factor common for atoms of one sort

[c] The coordinates of hydrogen atoms except H1D and H2A were calculated from geometric consideration of the corresponding rigid groups (C(H), N(H), O(H), O(H, H), C (H, H, H)) and were not refined. Their temperature isotropic factors were also fixed at values equal to $1.2 \cdot U_{eq}$ for C(H) and N(H) groups and $1.5 \cdot U_{eq}$ for O(H), O(H, H), C (H, H, H) and were not refined (U_{eq} is the equivalent isotropic temperature atom of the non-hydrogen atom of the corresponding group). All non-refined parameters are given without e.s.d.s.

[d]At the first stages of the Rietveld refinement of the structure, the coordinates of the hydrogen atoms were recalculated from the coordinates of the atoms obtained using data from the single crystal and the refined unit cell parameters. At subsequent stages, the coordinates of hydrogen atoms were refined by imposing a restriction on the values of the distances M-H in the nearest coordination sphere of M atoms (M = P, O, N, C), assuming that these distances cannot deviate from the average values obtained from single crystal data by more than 0.1 Å

Symmetry codes:
x; y; z
-x; -y; -z
-x; y+1/2; -z+1/2
x; -y-1/2, z-1/2

Table S12. Atomic displacement parameters for the MBI-phosphite (Å²).

Ato	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P1	0.0365(4)	0.0439(5)	0.0636(6)	-0.0005(4)	0.0025(3)	0.0005(3)
P2	0.0473(5)	0.0550(6)	0.0802(7)	0.0079(5)	-0.0033(4)	-0.0063(4)
O6	0.0423(11)	0.0507(12)	0.0854(17)	0.0008(12)	0.0140(10)	-0.0018(9)
O4	0.0413(11)	0.0418(13)	0.1054(19)	0.0111(12)	0.0208(11)	0.0063(9)
O5	0.0528(12)	0.0469(13)	0.0930(19)	0.0150(12)	0.0206(12)	0.0116(10)
N1	0.0312(11)	0.0506(15)	0.0495(15)	-0.0016(12)	0.0005(10)	0.0034(10)
N4	0.0510(14)	0.0483(15)	0.0446(15)	0.0015(12)	0.0029(11)	-0.0102(11)
N2	0.0361(12)	0.0541(15)	0.0509(16)	0.0005(12)	0.0031(11)	0.0092(11)
N3	0.0541(15)	0.0564(17)	0.0548(18)	0.0011(13)	0.0029(12)	-0.0172(13)
O3	0.0549(13)	0.0547(15)	0.130(2)	-0.0057(15)	0.0074(14)	-0.0019(11)
O2	0.0636(15)	0.0611(16)	0.129(3)	-0.0050(17)	-0.0411(16)	0.0113(13)
O1	0.0616(14)	0.0638(16)	0.123(2)	-0.0064(15)	-0.0376(15)	0.0136(12)
O7	0.0568(15)	0.092(2)	0.136(3)	-0.052(2)	-0.0339(16)	0.0191(15)
C3	0.0379(14)	0.0509(18)	0.0312(15)	0.0002(13)	0.0034(11)	0.0002(12)
C16	0.0572(17)	0.0443(17)	0.0315(16)	0.0015(13)	0.0030(13)	-0.0043(14)
C8	0.0375(14)	0.0551(18)	0.0328(16)	0.0024(13)	0.0047(12)	0.0008(13)
C11	0.0565(17)	0.0530(19)	0.0347(17)	-0.0008(14)	0.0015(13)	-0.0085(15)
C2	0.0424(15)	0.0476(18)	0.0500(19)	-0.0054(14)	0.0026(13)	0.0032(13)
C10	0.0513(17)	0.056(2)	0.0461(19)	0.0023(15)	0.0054(14)	-0.0087(15)
C4	0.0550(18)	0.055(2)	0.050(2)	0.0044(16)	0.0030(15)	0.0051(15)
C15	0.0569(18)	0.063(2)	0.054(2)	0.0005(17)	0.0032(15)	-0.0026(16)
C7	0.0366(15)	0.078(2)	0.050(2)	0.0085(17)	0.0005(13)	-0.0072(15)
C12	0.083(3)	0.053(2)	0.053(2)	-0.0030(16)	0.0020(18)	-0.0128(18)
C6	0.062(2)	0.074(3)	0.061(2)	-0.0007(19)	0.0028(17)	-0.0275(19)
C5	0.076(2)	0.054(2)	0.062(2)	0.0001(17)	0.0073(18)	-0.0107(18)
C1	0.062(2)	0.053(2)	0.098(3)	-0.009(2)	-0.0005(19)	-0.0034(17)
C13	0.094(3)	0.054(2)	0.062(2)	-0.0009(18)	-0.001(2)	0.011(2)
C14	0.070(2)	0.070(3)	0.068(3)	-0.002(2)	0.0040(19)	0.008(2)
C9	0.057(2)	0.072(3)	0.095(3)	0.000(2)	0.006(2)	-0.0001(18)

Таблица S13. Selected distances in MBI-phosphite structure according to results of structure refinement, using single crystal and powder XRD data (Table S11).

Distance		Single crystal[a]	Powder[b]	Distance		Single crystal[a]	Powder[b]
P1-	H1D	1.40(3)	1.34(10)	C7-	H7	0.930(3)	0.98(10)
	O6	1.475(2)	1.41(1)		C6	1.369(5)	1.40(3)
	O4	1.503(2)	1.45(2)		C8	1.387(4)	1.30(2)
	O5	1.557(2)	1.53(1)		H6	1.992(4)	2.02(12)
	H5A	1.9866(8)	2.19(12)		C3	2.417(4)	2.45(2)
P2-	H2A	1.35(4)	1.33(11)		C5	2.418(5)	2.40(3)
	O3	1.476(2)	1.41(2)		N2	2.527(4)	2.39(3)
	O1	1.478(3)	1.47(1)	C12-	H12	0.930(3)	0.91(11)
	O2	1.549(3)	1.40(1)		C13	1.370(5)	1.37(2)
	H2B	1.9797(9)	1.96(15)		C11	1.385(5)	1.48(3)
O6-	P1	1.475(2)	1.41(1)		H13	1.993(3)	1.93(12)
	H4A	1.768(2)	1.77(13)		C14	2.409(5)	2.49(2)
	H1D	2.35(3)	2.25(11)		C16	2.420(4)	2.57(3)
	O5	2.487(3)	2.35(2)		N3	2.527(4)	2.62(3)
	O4	2.524(3)	2.40(2)	C6-	H6	0.930(3)	0.89(10)
	H1B	2.398(2)	2.45(11)		C7	1.369(5)	1.40(3)
	N4	2.621(3)	2.63(2)		C5	1.390(5)	1.40(2)

O4-	P1	1.502(2)	1.45(1)		H5	2.014(4)	2.09(13)
	H5A	1.762(2)	1.90(12)		H7	2.021(4)	2.01(12)
	H2	1.826(2)	1.90(12)		C8	2.341(5)	2.27(3)
	H1D	2.33(3)	2.14(9)		C4	2.409(5)	2.45(2)
	H5A	2.466(2)	2.69(11)		C3	2.714(4)	2.80(3)
	O5	2.523(3)	2.43(2)	C5-	H5	0.929(4)	0.95(14)
	O6	2.524(3)	2.40(2)		C4	1.369(5)	1.36(2)
	O5	2.570(3)	2.73(2)		C6	1.390(5)	1.40(2)
	N2	2.685(3)	2.79(2)		H6	2.010(3)	1.99(9)
O5-	H5A	0.820(3)	0.87(12)		H4	2.020(3)	1.94(11)
	P1	1.557(2)	1.53(2)		C3	2.340(5)	2.36(3)
	H1D	2.30(3)	2.44(13)		C7	2.418(5)	2.40(3)
	O6	2.487(3)	2.35(2)		C8	2.729(5)	2.61(3)
	O4	2.523(3)	2.43(2)	C1-	H1C	0.959(4)	0.97(10)
	O4	2.570(3)	2.73(2)		H1A	0.960(4)	0.90(10)
O3-	P2	1.476(2)	1.41(2)		H1B	0.961(3)	1.06(12)
	H3	1.816(2)	1.82(9)		C2	1.472(5)	1.48(3)
	H7A	1.916(2)	1.91(13)		N1	2.485(4)	2.52(3)
	H2A	2.29(4)	2.05(11)		N2	2.488(4)	2.54(3)
	O2	2.457(3)	2.31(2)		H1	2.719(3)	2.55(13)
	O1	2.505(3)	2.41(2)		H2	2.726(3)	2.93(10)
	N3	2.676(3)	2.69(2)	C13-	H13	0.930(4)	0.98(14)
	O7	2.757(4)	2.70(2)		C12	1.370(5)	1.37(2)
O2-	H2B	0.820(3)	0.93(15)		C14	1.382(5)	1.44(3)
	P2	1.549(3)	1.40(1)		H14	2.004(4)	2.00(11)
	H2A	2.34(4)	2.19(12)		H12	2.023(4)	2.11(10)
	O3	2.457(3)	2.31(2)		C11	2.335(5)	2.39(3)
	O1	2.494(4)	2.27(2)		C15	2.410(5)	2.51(3)
	O1	2.583(4)	2.62(2)		C16	2.713(5)	2.82(3)
O1-	P2	1.478(3)	1.47(1)	C14-	H14	0.930(4)	0.92(11)
	H2B	1.772(3)	1.70(15)		C15	1.370(5)	1.40(3)
	H7B	2.047(3)	2.00(11)		C13	1.382(5)	1.44(3)
	H2A	2.24(4)	2.48(10)		H13	2.004(4)	2.17(14)
	H2B	2.487(2)	2.38(13)		H15	2.022(4)	2.02(13)
	O2	2.494(4)	2.27(2)		C16	2.332(5)	2.42(3)
	O3	2.505(3)	2.41(2)		C12	2.409(5)	2.49(2)
	O2	2.583(4)	2.62(2)		C11	2.713(5)	2.78(2)
	H4	2.633(3)	2.76(11)	C9-	H9A	0.960(4)	0.99(14)
	O7	2.869(4)	2.85(2)		H9B	0.960(4)	0.94(9)
O7-	H7A	0.850(3)	0.82(12)		H9C	0.961(4)	1.00(10)
	H7B	0.851(3)	0.91(11)		C10	1.476(5)	1.57(3)
	H1	1.839(3)	1.77(9)		N4	2.479(5)	2.51(2)
	N1	2.654(3)	2.60(2)		N3	2.502(4)	2.55(3)
	O3	2.757(4)	2.70(2)		H4A	2.706(4)	2.89(10)
N1-	H1	0.860(2)	0.84(9)	H5A-	O5	0.820(3)	0.87(12)
	C2	1.323(2)	1.35(3)		O4	1.762(2)	1.90(12)
	C3	1.384(4)	1.30(3)		P1	1.9866(8)	2.19(12)
	N2	2.160(3)	2.20(2)		O4	2.466(2)	2.69(11)
	C8	2.208(3)	2.25(2)	H1-	N1	0.860(2)	0.84(9)
	C1	2.485(4)	2.52(3)		O7	1.839(3)	1.77(9)
	C4	2.532(4)	2.50(3)		C2	1.950(3)	1.83(10)

	O7	2.654(3)	2.60(2)		C3	2.007(3)	2.03(11)
N4-	H4A	0.860(2)	0.93(13)		H7A	2.3977(1)	2.38(14)
	C10	1.324(4)	1.32(2)		H7B	2.4286(1)	2.41(14)
	C16	1.385(4)	1.31(3)		C1	2.719(3)	2.55(14)
	N3	2.158(4)	2.27(2)	H4A-	N4	0.860(2)	0.93(13)
	C11	2.213(4)	2.20(3)		O6	1.768(2)	1.77(13)
	C9	2.479(4)	2.51(2)		C10	1.951(3)	2.10(11)
	C15	2.527(4)	2.55(2)		C16	2.008(3)	1.89(14)
	O6	2.621(3)	2.63(3)	H2-	N2	0.860(2)	0.93(11)
N2-	H2	0.860(2)	0.93(11)		O4	1.826(2)	1.90(12)
	C2	1.327(3)	1.37(2)		C2	1.957(3)	2.13(9)
	C8	1.380(4)	1.37(3)		C8	2.006(3)	1.97(13)
	N1	2.160(3)	2.21(2)	H3-	N3	0.860(3)	1.09(12)
	C3	2.220(4)	2.17(3)		O3	1.816(2)	1.82(9)
	C1	2.488(4)	2.54(3)		C10	1.955(3)	2.39(13)
	C7	2.527(3)	2.39(3)		C11	2.008(3)	1.96(9)
	O4	2.685(4)	2.80(2)		C12	2.825(3)	2.55(10)
N3-	H3	0.860(3)	1.09(12)	H2B-	O2	0.820(3)	0.93(15)
	C10	1.326(4)	1.34(3)		O1	1.772(3)	1.70(15)
	C11	1.383(4)	1.43(2)		P2	1.9797(9)	1.96(15)
	N4	2.158(4)	2.27(2)		O1	2.487(2)	2.38(13)
	C16	2.217(4)	2.33(2)		H2B	2.5573(1)	2.36(13)
	C9	2.502(4)	2.55(3)	H7B-	O7	0.851(3)	0.91(11)
	C12	2.527(4)	2.62(3)		H7A	1.3881(1)	1.33(17)
	O3	2.676(3)	2.69(2)		O1	2.047(3)	2.00(11)
C3-	N1	1.384(4)	1.30(3)		H1	2.4286(1)	2.41(14)
	C4	1.385(4)	1.42(3)	H7A-	O7	0.850(3)	0.82(12)
	C8	1.386(4)	1.40(2)		H7B	1.3881(1)	1.33(17)
	H1	2.007(3)	2.03(11)		O3	1.916(3)	1.91(13)
	H4	2.035(3)	2.00(13)		H1	2.3977(1)	2.38(14)
	C2	2.210(4)	2.14(3)	H4-	C4	0.930(3)	0.85(11)
	N2	2.220(4)	2.17(3)		C5	2.020(4)	1.94(11)
	C5	2.340(5)	2.36(3)		C3	2.035(3)	2.00(13)
	C7	2.417(4)	2.45(2)		H5	2.3123(1)	2.13(16)
	C6	2.714(4)	2.80(3)	H15-	C15	0.930(3)	0.86(11)
C16-	C15	1.381(4)	1.48(2)		C14	2.022(4)	2.02(13)
	N4	1.385(4)	1.31(3)		C16	2.033(3)	2.05(10)
	C11	1.386(4)	1.43(3)		H14	2.3106(1)	2.38(17)
	H4A	2.008(3)	1.89(14)	H7-	C7	0.930(3)	0.98(10)
	H15	2.033(3)	2.05(10)		C6	2.021(4)	2.01(12)
	C10	2.211(4)	2.12(2)		C8	2.037(3)	2.06(10)
	N3	2.217(4)	2.33(2)		H6	2.3097(1)	2.29(18)
	C14	2.332(5)	2.42(3)	H12-	C12	0.930(3)	0.91(11)
	C12	2.420(4)	2.57(3)		C13	2.023(4)	2.11(10)
	C13	2.713(5)	2.82(3)		C11	2.037(3)	2.00(14)
C8-	N2	1.380(4)	1.37(3)		H13	2.3119(1)	2.35(14)
	C3	1.386(4)	1.40(2)	H6-	C6	0.930(3)	0.89(10)
	C7	1.387(4)	1.30(2)		C7	1.992(4)	2.02(12)
	H2	2.006(3)	1.97(13)		C5	2.010(4)	1.99(9)
	H7	2.037(3)	2.06(10)		H5	2.2905(1)	2.38(14)
	C2	2.202(4)	2.24(3)		H7	2.3097(1)	2.29(18)

	N1	2.208(3)	2.25(2)		H1D	2.49(3)	2.35(17)
	C6	2.341(5)	2.27(3)	H5-	C5	0.929(4)	0.95(14)
	C4	2.424(4)	2.38(3)		C4	1.995(3)	1.90(14)
	C5	2.729(5)	2.61(3)		C6	2.014(4)	2.09(12)
C11-	N3	1.383(4)	1.43(2)		H6	2.2905(1)	2.38(14)
	C12	1.385(5)	1.48(3)		H4	2.3123(1)	2.13(16)
	C16	1.386(4)	1.43(3)	H1A-	C1	0.960(4)	0.90(10)
	H3	2.008(3)	1.96(9)		H1B	1.5677(1)	1.56(13)
	H12	2.037(3)	2.00(14)		H1C	1.5677(1)	1.55(14)
	C10	2.208(4)	2.12(3)		C2	2.007(3)	2.08(14)
	N4	2.213(4)	2.20(3)	H1B-	C1	0.961(3)	1.06(12)
	C13	2.335(5)	2.39(3)		H1C	1.5676(1)	1.51(14)
	C15	2.419(5)	2.53(2)		H1A	1.5677(1)	1.56(13)
	C14	2.713(5)	2.78(2)		C2	2.007(3)	2.09(15)
C2-	N1	1.323(4)	1.35(3)		O6	2.398(2)	2.45(11)
	N2	1.327(3)	1.37(2)	H1C-	C1	0.959(4)	0.97(10)
	C1	1.472(5)	1.48(3)		H1B	1.5676(1)	1.51(14)
	H1	1.950(3)	1.83(11)		H1A	1.5677(1)	1.55(14)
	H2	1.957(3)	2.13(10)		C2	2.008(3)	2.04(12)
	H1A	2.007(3)	2.08(14)	H13-	C13	0.930(4)	0.98(14)
	H1B	2.007(3)	2.09(15)		C12	1.993(3)	1.93(12)
	H1C	2.008(3)	2.04(12)		C14	2.004(4)	2.17(14)
	C8	2.202(4)	2.24(3)		H14	2.2812(1)	2.40(16)
	C3	2.210(4)	2.13(3)		H12	2.3119(1)	2.35(14)
C10-	N4	1.324(4)	1.32(2)	H14-	C14	0.930(4)	0.92(11)
	N3	1.326(4)	1.34(3)		C15	1.992(4)	2.04(11)
	C9	1.476(5)	1.57(3)		C13	2.004(4)	2.00(11)
	H4A	1.951(3)	2.10(11)		H13	2.2812(1)	2.40(16)
	H3	1.955(3)	2.39(13)		H15	2.3106(1)	2.38(17)
	H9C	2.011(3)	2.06(10)	H9A-	C9	0.960(4)	0.99(14)
	H9B	2.011(3)	1.95(9)		H9B	1.5676(1)	1.64(17)
	H9A	2.011(3)	2.34(14)		H9C	1.5676(1)	1.57(17)
	C11	2.208(4)	2.12(3)		C10	2.011(3)	2.34(14)
	C16	2.211(4)	2.12(3)	H9B-	C9	0.960(4)	0.94(9)
C4-	H4	0.930(3)	0.85(11)		H9A	1.5676(1)	1.64(17)
	C5	1.369(5)	1.36(2)		H9C	1.5677(1)	1.45(13)
	C3	1.385(4)	1.42(3)		C10	2.011(3)	1.95(9)
	H5	1.995(3)	1.90(13)	H9C-	C9	0.961(4)	1.00(10)
	C6	2.409(5)	2.45(2)		H9A	1.5676(1)	1.57(17)
	C8	2.424(4)	2.38(3)		H9B	1.5677(1)	1.45(13)
	N1	2.532(4)	2.49(3)		C10	2.011(3)	2.06(10)
C15-	H15	0.930(3)	0.86(11)	H1D-	P1	1.40(3)	1.34(10)
	C14	1.370(5)	1.40(3)		O5	2.30(3)	2.44(13)
	C16	1.381(4)	1.48(2)		O4	2.34(4)	2.14(9)
	H14	1.992(4)	2.04(11)		O6	2.35(3)	2.25(11)
	C13	2.410(5)	2.51(3)	H2A-	P2	1.35(4)	1.33(11)
	C11	2.419(5)	2.53(2)		O1	2.24(4)	2.48(10)
	N4	2.527(4)	2.55(2)		O3	2.29(4)	2.05(11)
					O2	2.34(4)	2.19(12)

[a]E.s.d.s of distances are calculated taking into account the e.s.d.s of the atoms and unit cell parameters. In case of distances with hydrogen atoms, coordinates of which were calculated without refinement (i.e.

excluding H1D and H2A), only e.s.d.s of coordinates of non-hydrogen atoms and the e.s.d.s of the unit cell parameters were used for calculation of the e.s.d.s of corresponding distances
[b]E.s.d.s of distances are calculated taking into account the e.s.d.s of the atoms and unit cell parameters.

Table S14. Bond angles (°) in MBI-phosphite structure according to results of structure refinement using single crystal XRD data (Table S11).

O6-P1-O4	115.96(12)	C4-C3-C8	122.0(3)	N2-C2-C1	125.3(3)
O6-P1-O5	110.32(12)	N4-C16-	106.0(3)	N4-C10-N3	109.1(3)
O4-P1-O5	110.96(13)	C15-C16-	132.1(3)	N4-C10-C9	124.6(3)
O3-P2-O2	108.75(14)	C15-C16-	121.9(3)	N3-C10-C9	126.4(3)
O3-P2-O1	115.97(16)	N2-C8-C3	106.8(2)	C5-C4-C3	116.3(3)
O1-P2-O2	110.83(16)	N2-C8-C7	132.0(3)	C14-C15-	116.0(3)
C2-N1-C3	109.5(2)	C3-C8-C7	121.3(3)	C6-C7-C8	116.3(3)
C10-N4-	109.4(2)	N3-C11-	106.4(3)	C13-C12-	115.9(3)
C2-N2-C8	108.8(2)	N3-C11-	131.8(3)	C7-C6-C5	122.3(3)
C10-N3-	109.2(2)	C12-C11-	121.8(3)	C4-C5-C6	121.7(3)
N1-C3-C8	105.7(2)	N1-C2-N2	109.2(3)	C12-C13-	122.2(3)
N1-C3-C4	132.2(3)	N1-C2-C1	125.5(3)	C15-C14-	122.3(4)

Table S15. Hydrogen-bond geometry (Å,°) in MBI-phosphite structure according to results of structure refinement using single crystal XRD data (Table S11).

Bonded	D-H…A	Angle, °	D…A, Å	D-H, Å	H…A, Å
$(MBI+H)^+$&water	N1-H1…O7	157.41(18)	2.655(4)	0.860(3)	1.840(3)
$(MBI+H)^+$&$H_2PO_3^-$	N4-H4A…O6	170.9(2)	2.621(4)	0.860(3)	1.768(2)
$(MBI+H)^+$& $H_2PO_3^-$	N2-H2…O4	177.3(3)	2.686(3)	0.860(3)	1.826(2)
$(MBI+H)^+$& $H_2PO_3^-$	N3-H3…O3	178.1(2)	2.676(4)	0.860(3)	1.816(3)
$H_2PO_3^-$& $H_2PO_3^-$	O5-H5A…O4	170(5)	2.576(4)	0.93(5)	1.65(4)
$H_2PO_3^-$& $H_2PO_3^-$	O2-H2B…O1	175(5)	2.581(4)	0.95(5)	1.64(4)
water & $H_2PO_3^-$	O7-H7B…O1	166(4)	2.869(5)	0.92(4)	1.97(4)
water & $H_2PO_3^-$	O7-H7A…O3	173(5)	2.756(4)	0.93(4)	1.83(4)

S2. Powder XRD

Main details of powder XRD experiments are described in the text of the paper. There are some extended details are presented. Additionally to the XRD measurements described in the paper text, the MBI-phosphite powder without milling was measured for comparison as well.

To correct the zero offset of the detector ($\Delta 2\theta_{zero}$) and displacement of the sample surface from the plane of focus ($\Delta 2\theta_{displ}$), additional measurements of the sample powder were carried out in the mixture with certified standard silicon powder Si640d (NIST, USA). Using Si reflections as internal standards, unit cell parameters of the powders were determined. The correction shifts of the XRD patterns were obtained, utilizing the 2θ angle positions of the Bragg reflections of the samples calculated on the base of the unit cell parameters as external standards. In further refinement cycles, the values of the unit cell parameters changes in the limits of two estimated standard deviations (e.s.d.s) only and the refined values of the angular correcting shits were nearly zero.

The model XRD patterns were simulated and fitted to the experimental ones by means of the Rietveld program *TOPAS* [31]. For the reflection profile fitting a modified Thompson-Cox-Hastings pseudo-Voigt (TCHZ) model [32,33] was chosen considering best results obtained by use of different profile models adopted in the *TOPAS*. For description of the emission spectrum of the Cu-K_α radiation, the Berger model of the five spectral lines [34] was utilized, as recommended for better quality of the fitting of the reflection profiles in the Manual of the program *TOPAS* [31] for diffractometers equipped with a metal filter of the $K_ß$ radiation. Background contribution was refined using Chebyshev's polynomial of 6st order [31].

First, the calculation and fitting of the theoretical powder XRD patterns to the experimental ones were performed by means of whole powder pattern decomposition technique according to Le Bail [36]. No whole structural model is necessary in this method. Only space group and values of the unit cell parameters from single crystal investigations are utilized. Good quality of the fitting (Fig. 6) and low values of the agreement factors reached in Le Bail method (Table S16) evidence the correctness of the unit cells metric and symmetry of the MBI-phosphate 1 and MBI-phosphite determined in single crystal investigations.

At next stage, to check the single crystal structure models, the theoretical powder XRD patterns were fitted to the experimental ones by means of the Rietveld method [35]. The unit cell parameters refined in Le Bail fitting (Table S16) were used as start values in Rietveld refinement. As primary data for Rietveld refinement of the structure, the atomic coordinates determined in corresponding single crystal investigations (Tables S1, S11) were used.

E.s.d.s calculated in Rietveld programs tend to be underestimated due to serial correlations. After finishing the fittings, checking for serial correlations and calculation of the coefficient $m_{\text{e.s.d.}}$ for correction of the e.s.d.s by multiplication is carried out by means of the program *RietEsd* [40], written on the basis of Bérar's procedure [39].

S2.1 MBI-phosphate-1

Table S16. Unit cell parameters obtained by means of intermediate (Le Bail method) and final (Rietveld technique) refinement of MBI-phosphate-1 and MBI-phosphite, using the powder XRD data, and reached agreement factors. Results from single crystal investigations are shown for comparison.

	Single crystal	Powder (Le Bail)	Powder (Rietveld)	Single crystal	Powder (Le Bail)	Powder (Rietveld)
compound	MBI-phosphate-1 (space group $P\bar{1}$)			MBI-phosphite (space group $P2_1/c$)		
T_{meas}(K)	293	296	296	293	296	296
a (Å)	9.574(9)	9.6759(2)	9.6819(3)	17.1996(6)	17.1959(3)	17.1974(3)
b(Å)	9.779(9)	9.8298(4)	9.8265(20)	17.7098(7)	17.7164(5)	17.7198(6)
c (Å)	11.796(10)	11.8080 (3)	11.8038 (5)	6.9992(4)	7.01112(8)	7.01193(8)
α (°)	88.294(18)	89.097(3)	88.984(16)	90	90	90
β(°)	78.07(2)	78.251(1)	78.147(2)	94.963(4)	94.873(2)	94.878(2)
γ(°)	87.646(19)	87.398(3)	87.371(20)	90	90	90
R_{wp} (%)		8.39	12.57	-	8.38	9.72
R_p (%)	-	5.40	8.71	-	5.59	6.95
cR_{wp} (%)	-	5.27	4.98	-	4.70	4.14
cR_p (%)	-	3.76	3.93	-	3.42	3.37
R_B (%)	4.61/11.49[a]	1.34[c]	4.34[c]	6.05/14.26[d]	0.73[f]	1.83[f]
	6.09/12.50[b]			11.74/17.01[e]		
$m_{\text{e.s.d}}$	-	2.54	4.10	-	2.71	3.24

[a] factors R_1/wR_2 (or, respectively, R_F/R_w in other designation) for 3225 reflections with intensity $I \geq 2\sigma(I)$

[b] factors R_1/wR_2 (or, respectively, R_F/R_w in other designation) for all 4131 reflections

[c] for all 815 reflections in 2θ range 5.70°-66.51° of the powder XRD pattern

[d] factors R_1/wR_2 (or, respectively, R_F/R_w in other designation) for 2784 reflections with intensity $I \geq 2\sigma(I)$

[e] factors R_1/wR_2 (or, respectively, R_F/R_w in other designation) for all 4857 reflections
[c] for all 1517 reflections in 2θ range 5.00°-85.50° of the powder XRD pattern

Due to small amount of the material necessary for investigations by other methods, MBI-phosphate-1 powder was not grinded and was used for XRD pattern recording as is. As a result, there is a strong influence of the effects of the preferred orientation of crystallites in the powder. Without taking into account the influence of the preferred orientation, the use of the structural model of Table S1 does not give a good fit of the theoretical diffractogram to the measured one (R_{wp} = 39.17%). The Bragg factor characterizing the agreement of experimental and calculated integral intensities of the XRD reflections is also too high (R_B = 54.66%). These agreement factors are obtained after refinement of background parameters, angular correcting shits and unit cell parameters.

Reflections with Miller indices *hkl* = 101, 202 showed increased intensity. The introduction of a preferred orientation in the March-Dollase model [33, 37] with direction [101] partially reduced the effect of texture. The second direction of the preferred orientation of crystallites in the March-Dollase model [102] was determined by selection of possible crystallographic directions considering the lowest *R*-factor values reaching R_{wp} = 21.45% and R_B = 9.21%. The residual effect of the effect of the preferred orientation of the powder crystallites in other crystallographic directions was taken into account by refining the parameters of the model of spherical harmonics of the 8th order [38] resulting in R_{wp} = 13.07% and R_B = 5.09%. Final refinement of the obtained parameters of the preferred orientation according to the March-Dollase model with the directions [101] and [102] gave the values of $r_{[101]}$ = 0.072(1), $r_{[102]}$ = 0.19(1), the percentage contribution of the texture with the direction [102] $f_{[102]}$ = 0.92(1).

At the last stage of the fit, overall isotropic temperature factors of atoms were refined ($U_{iso}^{overall}$ = 0.013(8) Å^2, 0.091(8) Å^2, 0.020(10) Å^2, 0.058(6) Å^2 and 0.119(51) Å^2 for atoms P, O, N, C and H, respectively), which resulted in the decrease of the R_{wp} factor on~0.5% and the R_B on ~0.7% (Table S16). Due to difficulties for obtaining the reliable interatomic distances after refinement of the atomic coordinates caused by high influence of the effect of the preferred, the atomic coordinates of the MBI-phosphate-1 determined by means of single crystal investigation were not refined from the XRD powder data.

S2.2 MBI-phosphite

The MBI-phosphite was grinded thoroughly. As a result, the influence of the effect of the preferred orientation was considerably reduced. Reached agreement factors by use the structure model presented in Table S11 resulted in reduced values of agreement factors R_{wp} = 25.22% and R_B = 20.78% after refinement of the background parameters, angular correcting shits and unit cell parameters (for the not-milled 'as is' MBI-phosphite powder R_{wp} = 71.73%, R_B = 62.35%).

However, the effect of preferential orientation was not completely avoided. Some reflections showed increased intensity compared to the calculated structural model. Setting two directions of preferred orientation ([110] and [100]) on the March-Dollase model [33,37] led to an improvement in the agreement factors to R_{wp} = 14.86%, R_B = 9.17%. The remaining effect of the texture effect with other directions of preferred orientation was removed by refining the parameters of the texture model with spherical harmonics of the 8th order, which led to a further decrease in the values of the agreement factors (*Rwp* = 11.45%, R_B = 4.47%). Further including in the refinement cycles the overall temperature factors of the atoms results in R_{wp} = 10.99%, R_B = 4.03%.

At subsequent stages, the coordinates of non-hydrogen atoms were refined. The coordinates of the hydrogen atoms were recalculated from those determined on the single crystal, taking into account the refined parameters of the unit cell. At the final stage, they were refined by imposing restrictions on the values of the M-H distances in the nearest coordination sphere of M atoms (M = P, O, N, C), assuming that these distances cannot deviate from the average values obtained from single crystal data by more than 0.1 Å.

S2.3 Powder XRD. Results

Calculated Bérar's coefficients $m_{e.s.d}$ together with values of the unit cell parameters of the MBI-phosphate 1 and MBI-phosphite, finally refined by means of Le Bail and Rietveld methods, are presented in Table S16. In the same Table S16 are summarized agreement factors, reached in the refinements (weighted profile factor R_{wp}, profile factor R_p, corrected for background weighted profile factor cR_{wp} and profile factor cR_p(correspondingly, R_{wp}' and R_p' in designation of *TOPAS*) as characteristics of the quality of the XRD pattern fitting, and Bragg factor R_B as an indicator of the quality of the structure refinement, see, for example, [31,33] for definition of the factors). As well, the unit cell parameters and agreement factors according to MBI-phosphate-1 and MBI-phosphite single crystal data are presented in Table S16 for comparison.

Good Rietveld fit quality of both powder XRD patterns is graphically illustrated in Fig. 6 of the main text of the paper. The relative coordinates and overall isotropic temperature factors of atoms of MBI-phosphite refined by Rietveld method from powder data are given in Table S11. The calculated selected interatomic distances are given in Table S13.

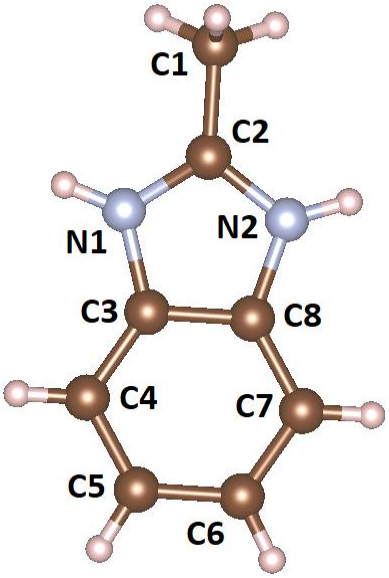
S3. Bond lengths and angles of MBI molecule in crystals with and without protonation.

Table S17.

Crystal	Bond N1-C2 (Å)	Bond C2-N2 (Å)	Bond N1-C2-N2 (°)	Bond C3-N1-C2 (°)	Bond C2-N2-C8 (°)
MBI*	1.339	1.335	112.7	106.1	106.3
MBI-phosphate-2	1.323	1.335	109.38	109.2	109.0
MBI-phosphite (cation #1)	1.323	1.327	109.2	109.5	108.8(2)
MBI-phosphite (cation #2)	1.326	1.324	109.1	109.2	109.4
MBI-phosphate-1 (cation #1)	1.321	1.320	109.6	108.8	108.9
MBI-phosphate-1 (cation #2)	1.323	1.312	109.4	108.7	109.2

* - data from Ref. [42]

Figure S1. Structure of cation $(MBI+H)^+$. Atom numbering correspond to Table S17.



S4. Elemental analysis.

Table S18. Experimental and calculated elemental composition of the new crystals.

	MBI-phosphite (C16 H24 N4 O7 P2)		MBI-phosphate-2 (C8 H16 N2 O9 P2)	
Element	Experiment, at.%	Calculation, at.%	Experiment, at.%	Calculation, at.%
C	49.45	45.50	37.26	29.09
N	15.36	13.27	9.32	8.48
O	29.69	26.54	41.91	43.64
p	5.50	14.69	11.51	18.79
Σ	100	100	100	100