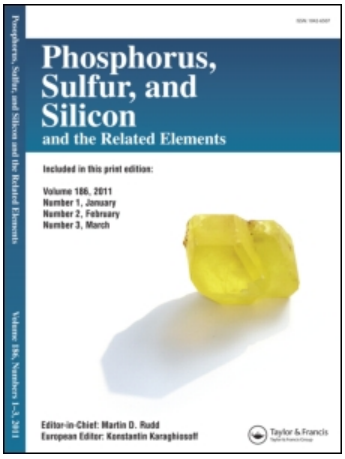

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Resolution, Crystal Structure And Absolute Configuration Of The Enantiomers Of Aminophenylmethanephosphonous Acid Hydrate

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RESOLUTION, CRYSTAL STRUCTURE AND ABSOLUTE CONFIGURATION OF THE ENANTIOMERS OF AMINOPHENYLMETHANEPHOSPHONOUS ACID HYDRATE

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Enantiomers of aminophenylmethanephosphonous acid have been obtained by resolution of the racemic acid using optically active isomers of 1-phenylethylamine. The crystal and molecular structures of the enantiomers of the acid monohydrate ($C_7H_{10}PO_2N \cdot H_2O$) have been determined by single-crystal X-ray diffraction method. The crystals are monclinic, of space grup $P2_12_12_1$ and $Z = 4$. Cell constants: $a = 5.410(2)$ Å, $b = 6.603(2)$ Å, $c = 25.061(5)$ Å for (+)-(R)-enantiomer and $a = 5.414(2)$ Å, $b = 6.602(2)$ Å, $c = 25.056(5)$ Å for (−)-(S)-enantiomer. The structures solved by direct method have been refined to final $R = 0.033$ and $R = 0.029$ respectively.

Key words: Aminophenylmethanephosphonous acid, enantiomers, resolution, X-ray study, crystal structure, absolute configuration.

INTRODUCTION

Aminophosphonates, defined as phosphorus analogues of amino acids, may act as their antagonists and thus interfere with various metabolic processes. Therefore, the chemistry of aminophosphonates continues to attract much interest and provides a wide variety of biologically active compounds. 1-Aminoalkanephosphonous acids containing monobasic group may be considered as closer analogues of amino acids than their phosphonic counterparts but only few methods for the preparation of free 1-aminoalkanephosphonous acids have been reported in the literature till now. The most general one, known since 1948, relies on addition of compounds containing P-H moiety to imines.[1] Baylis, Campbell and Dingwall had further developed this method by using the acid-labile N-protecting group starting from diphenylmethylimines.[2] This allowed to obtain several non-substituted aminophosphonous acids, analogues of natural amino acids. The acids exhibited

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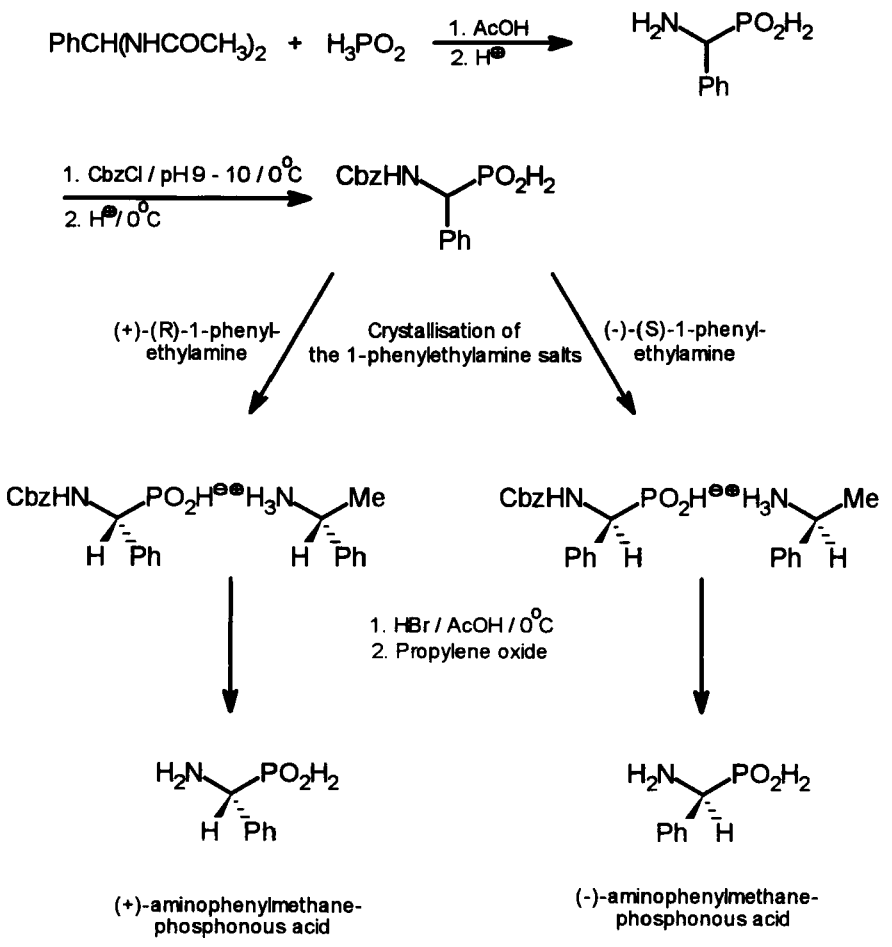
biological activities as antibacterial agents, fungicides and herbicides.[3–5] In the same laboratory, another synthetic strategy was also developed. It was accomplished by the C-alkylation of a suitably protected aminomethanephosphonous acid.[6] In 1978 Khomutov and Osipova applied the addition reaction of hypophosphorous acid to corresponding oximes for this purpose.[7] The obtained compounds were shown to act as inhibitors of t-RNA synthetases.[8,9]

1-Aminoarylmethanephosphonous acids (1-aminobenzylphosphonous acids) are of interest as potential effectors of plant growth characteristics. Tyka and Hägele described a convenient method for their preparation by means of amidoalkylation of H_3PO_2 using N,N'-arylmethylidenebisamides followed by hydrolysis.[10] Maier and Diel also synthesized a series of these compounds and found that they exhibited antifungal activities.[11] None of the aminoarylmethanephosphonous acids has been resolved into enantiomers so far but the crystal and molecular structure of racemic aminophenylmethanephosphonous acid was described.[12]



SCHEME I Resolution of the enantiomers of aminophenylmethanephosphonous acid.

TABLE I
Crystallographic data and details of refinement

	(+)-(R)-Aminophenyl-methanephosphonous acid	(-)-(S)-Aminophenyl-methanephosphonous acid
Chemical formula	$C_7H_{12}NO_3P$	$C_7H_{12}NO_3P$
Molecular weight	189.2	189.2
Cell constants		
a(Å)	5.410(2)	5.414(2)
b(Å)	6.603(2)	6.602(2)
c(Å)	25.061(5)	25.056(5)
V(Å^3)	895.2	895.6
Space group	$P2_12_12_1$	$P2_12_12_1$
Z	4	4
F(000)	400	400
T(K)	297	297
D_m(Mg/m^3) ($C_6H_6/CHCl_3$)	1.40(1)	1.40(1)
D_c(Mg/m^3)	1.403(1)	1.403(1)
Radiation	Cu K_α (λ=1.5418Å)	Cu K_α (λ=1.5418Å)
μ(cm^{-1})	24.80	24.80
Reflection determinig the lattice		
2θ range(°)	20<2θ<26	20<2θ<26
2θ maximum(°)	164	164
Number of standard reflections	3(100 ref.)	3(100 ref.)
Variation in standard reflections(%)	3	3
Number of reflexions		
Collected	2250	2233
Observed(I>3 σ(I))	1811	1807
Number of variables	157	157
R	0.033	0.029
R_w	0.037	0.032
S	2.891	2.047
w	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$
Δ/σ(for non-H atoms)	0.01	0.01
Δ/σ(for H atoms)	0.04	0.04
$\Delta\rho$	0.35	0.32

In this paper we report the resolution, crystal structure and the absolute configuration determination of both enantiomers of aminophenylmethanephosphonous acid. The purpose of this work was to obtain optically active phosphinate precursors for the synthesis of phosphono peptides by the Atherton-Todd approach.

RESULTS AND DISCUSSION

Resolution

The racemic aminophenylmethanephosphonous acid was obtained via amidoalkylation of hypophosphorous acid.[10] The N-benzyloxycarbonyl derivative was prepared by its acylation with benzyl chloroformate in aqueous alkaline solution. The enantiomers were separated by recrystallisation of diastereomeric salts of (+)-(R)- or (−)-(S)-1-phenylethylamine with the N-benzyloxycarbonylaminophenylmethanephosphonous acid to constant melting point and specific rotation similarly as reported earlier.[2] Acid hydrolysis afforded optically pure enantiomeric aminophenylmethanephosphonous acids (Scheme I).

The details of the crystal data collection and the refinements are given in Table I. The solution methods and the details of the absolute configuration determination are also described in the experimental part.

TABLE II

Final atomic coordinates and equivalent isotropic thermal parameters with estimated standard deviations in parentheses

	(+)-(R)-Aminophenylmethanephosphonous acid				(-)-(S)-Aminophenylmethanephosphonous acid			
Atom	x	y	z	B_{eq}(Å^2)	x	y	z	B_{eq}(Å^2)
P	0.0723(1)	0.2373(1)	0.4102(1)	1.83(2)	-0.0723(1)	-0.2374(1)	-0.4102(1)	2.11(2)
O(1)	0.1389(4)	0.1176(2)	0.4590(1)	2.75(7)	-0.1393(3)	-0.1168(2)	-0.4590(1)	3.03(6)
O(2)	-0.1957(3)	0.2523(3)	0.3953(1)	2.90(7)	0.1954(3)	-0.2525(2)	-0.3953(1)	3.12(6)
O(W)	0.5684(4)	-0.0931(2)	0.4555(1)	2.78(7)	-0.5692(3)	0.0929(2)	-0.4556(1)	3.07(6)
N	0.4470(4)	0.4929(3)	0.4418(1)	1.91(7)	-0.4465(4)	-0.4940(2)	-0.4419(1)	2.20(6)
C(1)	0.1966(4)	0.4958(3)	0.4177(1)	1.62(8)	-0.1954(4)	-0.4964(3)	-0.4176(1)	1.89(7)
C(2)	0.1906(4)	0.6079(3)	0.3648(1)	1.60(8)	-0.1894(4)	-0.6085(3)	-0.3650(1)	1.88(7)
C(3)	-0.0060(4)	0.7360(3)	0.3543(1)	2.31(9)	0.0061(4)	-0.7358(3)	-0.3544(1)	2.55(8)
C(4)	-0.0219(5)	0.8371(4)	0.3059(1)	2.88(10)	0.0219(5)	-0.8375(3)	-0.3056(1)	3.22(9)
C(5)	0.1618(5)	0.8084(4)	0.2670(1)	2.90(10)	-0.1596(5)	-0.8084(3)	-0.2672(1)	3.24(10)
C(6)	0.3550(5)	0.6799(4)	0.2774(1)	2.72(10)	-0.3543(5)	-0.6814(4)	-0.2775(1)	3.09(9)
C(7)	0.3714(5)	0.5792(4)	0.3263(1)	2.28(9)	-0.3716(4)	-0.5795(3)	-0.3262(1)	2.53(8)
H(P)	0.209(4)	0.160(3)	0.367(1)	2.4(6)	-0.206(4)	-0.159(3)	-0.365(1)	3.3(5)
H(1W)	0.417(5)	-0.012(3)	0.459(1)	3.4(6)	-0.440(5)	0.023(3)	-0.458(1)	3.9(6)
H(2W)	0.648(7)	-0.007(5)	0.439(1)	10.3(10)	-0.682(6)	-0.002(4)	-0.438(1)	8.2(10)
H(1N)	0.440(9)	0.491(6)	0.493(1)	12.8(10)	-0.439(7)	-0.451(4)	-0.483(1)	10.2(10)
H(2N)	0.568(5)	0.412(4)	0.420(1)	4.8(7)	-0.570(4)	-0.415(3)	-0.424(1)	3.5(6)
H(3N)	0.495(6)	0.646(4)	0.439(1)	6.3(9)	-0.513(5)	-0.675(4)	-0.444(1)	7.8(9)
H(1)	0.094(5)	0.555(3)	0.442(1)	2.3(5)	-0.089(4)	-0.562(3)	-0.442(1)	2.3(4)
H(2)	-0.144(5)	0.734(4)	0.380(1)	5.7(8)	0.156(4)	-0.745(3)	-0.382(1)	3.2(5)
H(3)	-0.156(5)	0.944(4)	0.304(1)	3.7(7)	0.151(5)	-0.939(4)	-0.301(1)	4.2(6)
H(4)	0.215(6)	0.873(5)	0.226(1)	8.1(10)	-0.168(4)	-0.864(4)	-0.230(1)	5.2(7)
H(5)	0.494(5)	0.664(4)	0.248(1)	3.4(6)	-0.493(6)	-0.663(4)	-0.250(1)	4.8(6)
H(6)	0.498(5)	0.502(3)	0.332(1)	3.2(6)	-0.508(4)	-0.501(3)	-0.331(1)	3.3(5)

$$B_{eq} = 1/3\Sigma_{ij}B_{ij}a_i^*a_j^*a_i a_j$$

TABLE III

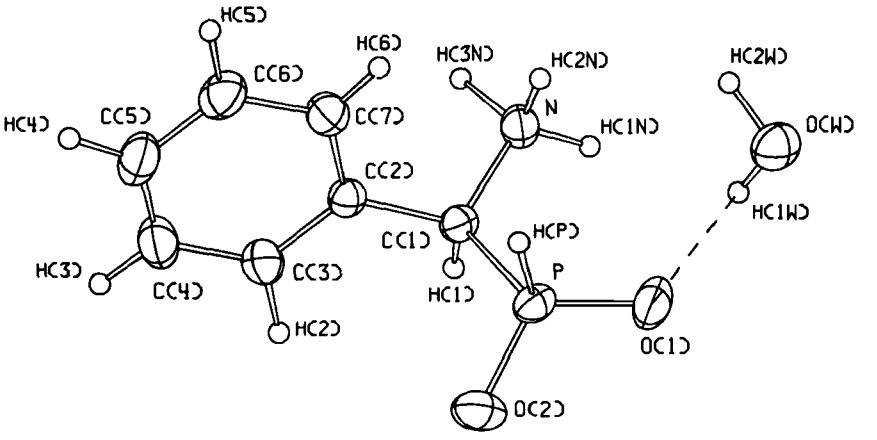
Anisotropic thermal parameters with estimated standard deviations in parentheses

(+)-(R)-Aminophenylmethanephosphonous acid						
Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	1.83(2)	1.47(2)	2.20(2)	-0.25(2)	0.41(2)	0.06(1)
O(1)	3.23(9)	2.27(6)	2.74(6)	0.12(7)	0.64(6)	0.97(5)
O(2)	1.87(8)	2.74(7)	4.09(7)	-0.42(7)	-0.03(6)	-0.38(6)
O(W)	2.78(8)	1.98(6)	3.59(7)	-0.09(7)	0.29(7)	-0.04(6)
N	2.02(8)	1.59(6)	2.12(6)	-0.14(7)	-0.39(6)	0.17(5)
C(1)	1.67(9)	1.57(7)	1.63(7)	-0.12(7)	0.13(6)	0.01(5)
C(2)	1.78(9)	1.23(7)	1.80(7)	-0.17(7)	-0.02(7)	0,02(5)
C(3)	2.18(11)	1.99(8)	2.74(8)	0.34(8)	-0.04(7)	0.24(7)
C(4)	3.10(13)	2.15(9)	3.40(10)	0.23(9)	-0.82(9)	0.71(8)
C(5)	3.47(13)	2.62(9)	2.60(9)	-0.71(10)	-0.69(9)	0.85(7)
C(6)	2.75(12)	3.40(11)	2.02(8)	-0.59(10)	0.09(8)	0.41(7)
C(7)	1.95(10)	2.69(9)	2.19(8)	0.30(9)	0.11(7)	0.26(7)
(-)-(S)-Aminophenylmethanephosphonous acid						
Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{13}
P	2.13(2)	1.74(1)	2.45(2)	-0.25(2)	0.40(1)	0.05(1)
O(1)	3.69(8)	2.43(5)	2.96(6)	0.22(6)	0.61(5)	0.95(5)
O(2)	2.00(7)	3.04(6)	4.33(6)	-0.37(6)	-0.07(5)	-0.36(6)
O(W)	3.12(7)	2.24(5)	3.85(6)	-0.18(7)	0.36(6)	-0.03(5)
N	2.38(8)	1.97(5)	2.24(5)	-0.11(6)	-0.44(5)	0.22(5)
C(1)	1.83(8)	1.83(6)	2.00(6)	-0.04(6)	0.14(6)	0.01(5)
C(2)	2.07(8)	1.55(6)	2.01(6)	-0.15(6)	-0.05(6)	0.00(5)
C(3)	2.53(10)	2.21(7)	2.92(8)	0.20(7)	-0.06(6)	0.20(6)
C(4)	3.31(12)	2.56(8)	3.78(9)	0.24(8)	-0.84(8)	0.81(7)
C(5)	4.01(12)	2.99(8)	2.73(8)	-0.81(9)	-0.70(8)	0.92(7)
C(6)	3.34(12)	3.70(10)	2.21(7)	-0.56(9)	0.23(7)	0.41(6)
C(7)	2.38(9)	2.93(7)	2.28(7)	0.26(8)	0.15(6)	0.29(6)

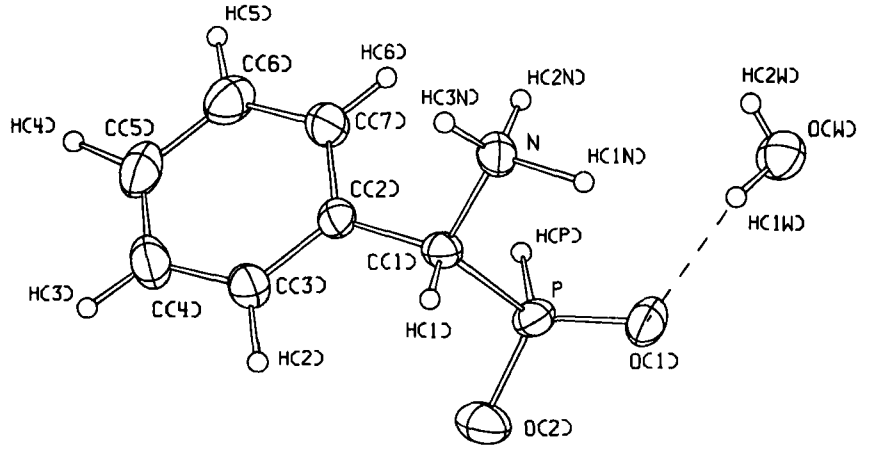
The temperature factor is of the form $T = exp[-1/4(B_{11}h_a^{2*2} + B_{22}k_b^{2*2} + B_{33}l_c^{2*2} + 2B_{12}hka^*b^* + 2B_{23}klb^*c^* + 2B_{13}hla^*c^*)]$.

Final atomic parameters and the anisotropic thermal parameters are listed in Tables II and III. Perspective views of the enantiomers of aminophenylmethanephosphonous acid are shown in Figure 1. Interatomic distances and bond angles are given in Tables IV and V.

The molecules of (+) and (−)-aminophenylmethanephosphonous acid exist as zwitterions with the nitrogen atoms of the amino groups protonated and the phosphonous groups negatively charged. The H(P) atoms are bound directly to the phosphorus atoms. The P—H(P) bond lengths of 1.41(2) Å and 1.44(2) Å are longer than the P—H(P) distance 1.52(2) Å in racemic aminophenylmethanephosphonous acid.[12] The O atoms of the phosphonous groups are in resonance with each other



(-)-(S)-Aminophenylmethanephosphonous acid



(+)-(R)-Aminophenylmethanephosphonous acid

FIGURE 1 Perspective view of the enantiomers of aminophenylmethanephosphonous acid.

as indicated by the bond lengths P—O(1) and P—O(2) which are 1.501(2) Å, 1.500(2) Å and 1.504(2) Å, 1.500(2) Å, respectively (Figure 1).

The conformation of the tittle compounds are determined by the torsion angles as given in Table VI.

The O(2) atoms are in *trans* position to N atoms and O(1) and H(P) atoms are in synclinal positions to N atoms. However, the phenyl rings are nearly perpendicular to the phosphonous groups.

The crystal structures are stabilized by the intermolecular hydrogen bonds involving the amino groups, oxygen atoms of the phosphonous groups and the water molecules. Interatomic distances and bond angles of the hydrogen bonds are given in Table VII.

TABLE IV

Bond lengths [Å] with estimated standard deviations in parentheses

Bond	(+)-(R)-Amino-phenylmethane-phosphonous acid	(-)-(S)-Amino-phenylmethane-phosphonous acid	Bond	(+)-(R)-Amino-phenylmethane-phosphonous acid	(-)-(S)-Amino-phenylmethane-phosphonous acid
P - O(1)	1.501(2)	1.504(1)	P - H(P)	1.41(2)	1.44(2)
P - O(2)	1.500(2)	1.500(2)	O(W) - H(1W)	0.98(3)	0.84(2)
P - C(1)	1.845(2)	1.845(2)	O(W) - H(2W)	0.83(4)	0.98(3)
N - C(1)	1.483(3)	1.489(2)	N - H(1N)	1.29(3)	1.07(3)
C(1) - C(2)	1.518(3)	1.513(3)	N - H(2N)	1.01(3)	0.96(2)
C(2) - C(3)	1.384(3)	1.378(3)	N - H(3N)	1.04(3)	1.25(3)
C(2) - C(7)	1.386(3)	1.398(3)	C(1) - H(1)	0.91(2)	0.94(2)
C(3) - C(4)	1.385(3)	1.396(3)	C(3) - H(2)	0.99(3)	1.07(2)
C(4) - C(5)	1.406(4)	1.390(3)	C(4) - H(3)	1.01(3)	0.97(2)
C(5) - C(6)	1.371(4)	1.372(3)	C(5) - H(4)	1.14(3)	1.01(2)
C(6) - C(7)	1.398(3)	1.397(3)	C(6) - H(5)	1.07(3)	1.02(3)
			C(7) - H(6)	0.87(3)	0.91(2)

TABLE V

Bond angles [°] with estimated standard deviations in parentheses

Bond angle	(+)-(R)-Amino-phenylmethane-phosphonous acid	(-)-(R)-Amino-phenylmethane-phosphonous acid	Bond angle	(+)-(R)-Amino-phenylmethane-phosphonous acid	(-)-(R)-Amino-phenylmethane-phosphonous acid
O(1) - P - O(2)	118.0(1)	118.1(1)	C(1) - P - H(P)	103(1)	103(1)
O(1) - P - C(1)	108.5(1)	108.7(1)	C(1) - N - H(1N)	112(2)	111(2)
O(2) - P - C(1)	108.4(1)	108.2(1)	C(1) - N - H(2N)	112(2)	117(1)
P - C(1) - N	111.2(1)	111.2(1)	C(1) - N - H(3N)	101(2)	106(1)
P - C(1) - C(2)	110.8(1)	111.0(1)	C(2) - C(1) - H(1)	111(1)	109(1)
N - C(1) - C(2)	112.4(2)	112.4(2)	C(2) - C(3) - H(2)	116(2)	120(1)
C(1) - C(2) - C(3)	118.8(2)	118.9(2)	C(2) - C(7) - H(6)	121(2)	124(1)
C(1) - C(2) - C(7)	121.7(2)	121.6(2)	C(3) - C(4) - H(3)	115(1)	118(1)
C(2) - C(3) - C(4)	120.6(2)	120.6(2)	C(4) - C(3) - H(2)	122(2)	119(1)
C(2) - C(7) - C(6)	120.1(2)	119.6(2)	C(4) - C(5) - H(4)	138(2)	129(1)
C(3) - C(2) - C(7)	119.5(2)	119.4(2)	C(5) - C(4) - H(3)	125(1)	122(1)
C(3) - C(4) - C(5)	119.9(2)	119.8(2)	C(5) - C(6) - H(5)	118(1)	121(1)
C(4) - C(5) - C(6)	119.3(2)	119.8(2)	C(6) - C(5) - H(4)	102(2)	111(1)
C(5) - C(6) - C(7)	120.6(2)	120.7(2)	C(6) - C(7) - H(6)	119(2)	117(1)
O(1) - P - H(P)	108(1)	109(1)	C(7) - C(6) - H(5)	122(1)	118(1)
O(2) - P - H(P)	110(1)	108(1)	H(1W) - O(W) - H(2W)	97(3)	102(2)
P - C(1) - H(1)	104(1)	106(1)	H(1N) - N - H(2N)	124(2)	109(2)
N - C(1) - H(1)	107(1)	107(1)	H(1N) - N - H(3N)	95(2)	103(2)
			H(2N) - N - H(3N)	108(2)	110(2)

TABLE VI

Selected torsion angle [°] with estimated standard deviations in parentheses

Torsion angle	(+)-(R)-Aminophenylmethanephosphonous acid	(-)-(S)-Aminophenylmethanephosphonous acid
O(1) - P - C(1) - N	40.4(2)	-40.3(2)
O(2) - P - C(1) - N	169.7(2)	-169.7(2)
H(P) - P - C(1) - N	-73.8(7)	75.8(6)
O(1) - P - C(1) - C(2)	166.2(2)	-166.1(1)
O(2) - P - C(1) - C(2)	-64.5(2)	64.5(2)
H(P) - P - C(1) - C(2)	52.1(8)	-50.8(6)
P - C(1) - C(2) - C(3)	96.7(3)	-96.7(2)
P - C(1) - C(2) - C(7)	-80.8(2)	80.6(2)
N - C(1) - C(2) - C(3)	-138.2(3)	138.2(3)
N - C(1) - C(2) - C(7)	44.3(3)	-44.6(2)

TABLE VII

Atom distances [Å] and angles [°] of hydrogen bonds with estimated standard deviations in parentheses

Hydrogen bond	(+)-(R)-Aminophenylmethanephosphonous acid				(-)-(S)-Aminophenylmethanephosphonous acid			
D - H ··· A	D - H	H ··· A	D ··· A	α_{DHA}	D - H	H ··· A	D ··· A	α_{DHA}
N - HN(1) ··· O(1)^{i}	1.29(3)	1.76(4)	2.791(2)	132(3)	1.07(3)	1.86(3)	2.790(2)	142(3)
N - HN(2) ··· O(2)^{ii}	1.01(3)	1.77(3)	2.760(3)	167(2)	0.96(2)	1.81(2)	2.769(2)	175(2)
N - HN(3) ··· OW^{iii}	1.04(3)	1.82(3)	2.832(2)	162(2)	1.25(3)	1.59(3)	2.828(2)	170(2)
OW - HW(1) ··· O(1)	0.98(3)	1.73(3)	2.710(3)	173(2)	0.84(2)	1.87(2)	2.709(2)	175(2)
OW - HW(2) ··· O(2)^{ii}	0.83(3)	2.20(4)	3.018(2)	170(3)	0.98(3)	2.08(3)	3.018(2)	160(2)
Symmetry code	(i):	0.5 + x	0.5 - y	1 - z	(i):	-0.5 + x	-0.5 - y	-1 - z
	(ii):	1 + x	y	z	(ii):	-1 + x	y	z
	(iii):	x	1 + y	z	(iii):	x	-1 + y	z

EXPERIMENTAL

Resolution

Aminophenylmethanephosphonous acid.[10] Aminophenylmethanephosphonous acid was prepared by amidoalkylation of anhydrous hypophosphorus acid with phenylmethylidene-bisacetamide in acetic acid followed by hydrolysis. The crude product was recrystallised from water. Yield: 70%; mp: 240–242°C (lit. mp: 242–243°C).

N-benzoxycarbonylaminophenylmethanephosphonous acid. 4 N NaOH was added to the mixture of 34.2 g (0.2 mol) of aminophenylmethanephosphonous acid and 500 ml of water to make the acid soluble and to adjust the pH to 9–10. After cooling the solution to 0°C, 34.2 g(0.2 mol) of benzyl chloroformate were added dropwise to the stirred solution during 1 hour. The pH was maintained at 9–10 for 6 hours by periodical addition of 4N NaOH at 0°C. For the next 12 hours stirring was continued at room temperature. The mixture was washed with ether. The aqueous layer was poured into a mixture of 120 ml of water, 80 ml of concentrated HCl and 400 g of ice. The separated solid was filtrated, washed with water and dried. The crude acid was recrystallised from ethyl acetate. Yield: 68%; mp: 145–147°C.

1-Phenylethylamine salts of N-benzoxycarbonylaminophenylmethanephosphonous acid. 6.1 g (0.05 mol) of (+)-(R)-1-phenylethylamine in 20 ml of ethanol was added dropwise to a refluxing solution of 15.2 g (0.05 mol) of N-benzoxycarbonylaminophenylmethanephosphonous acid in 100 ml of ethanol. The separated salt was recrystallised several times from ethanol until a constant melting point: 209–210°C was achieved. Specific rotation: $[\alpha]_D^{20} = +24.2°$ (1% solution in ethanol). Using the above procedure (−)-(S)-1-phenylethylamine salt of N-benzoxycarbonylaminophenylmethanephosphonous acid was obtained; mp: 207–208°C, $[\alpha]_D^{20} = -24.0°$ (1% solution in ethanol).

Enantiomers of aminophenylmethanephosphonous acid. 4.3 g (0.01 mol) of the diastereomeric salt was stirred with 2.7 g (0.015 mol) of 45% HBr solution in acetic acid at 0°C for 1 hour. Volatile products were removed under reduced pressure. The residue was dissolved in 20 ml of ethanol and the product precipitated by addition of propylene oxide. The solid was filtrated, washed with ethanol and ether and the crude product was recrystallised from water (+)-Aminophenylmethanephosphonus acid was obtained from (+)-(R)-1-phenylethylamine salt. Specific rotation $[\alpha]_D^{20} = +12.0°$ (2% solution in 1.0 N NaOH). (−)-Aminophenylmethanephosphonous acid was obtained from (−)-(S)-1-phenylethylamine salt, $[\alpha]_D^{20} = -11.8°$ (2% solution in 1.0 N NaOH).

Structure

Colorless crystals of enantiomers of aminophenylmethanephosphonous acid were obtained by recrystallization from water and were used for the data collection. The densities were measured by flotation in the chloroform/benzene mixture. The space groups and approximate unit-cell dimensions were determined from rotation and the Weissenberg photographs. The diffraction data was measured on a KM4 κ-axis computer-controlled four-circle diffractometer with the graphite-monochromated Cu K_α radiation.[13] The diffracted intensities were corrected for the Lorentz and polarization effects, but not for absorption or extinction.

The structures were solved by direct method with the SHELXS-86 program[14] and refined by the full-matrix least-square method, using the SYNTEX XTL/XTLE structure determination system,[15] adopted for calculation on the IBM PC/AT computer. All non-hydrogen atoms were refined with anisotropic thermal parameters. A difference Fourier map clearly afforded the positions of the hydrogen atoms and their positional parameters were incorporated into subsequent refinement cycle. Refinement to convergence led to R = 0.033 and R_w = 0.037 for (+)-(R)-enantiomer, and R = 0.029 and R_w = 0.032 for (−)-(S)-enantiomer. Neutral atomic scattering factors were taken from the *International Tables for X-ray Crystallography*.[16] The scattering factors for non-H atoms were corrected for real and imaginary components.

The absolute configurations of (+) and (−)-aminophenylmethanephosphonous acid were determined by examination of the Friedel pairs of all reflections using Cu K_α. The refinement of the parameters for the inverted structures gave R = 0.042 and R_w = 0.045 for (+)-enantiomer, and R = 0.039 and R_w = 0.039 for (−)-enantiomer, respectively. Thus, it appeared that (+)-enantiomer had the configuration R and (−)-enantiomer the configuration S.

The structure of (+)-(R)-enantiomer was also solved using Mo K_α radiation (λ = 0.71069 Å) with 2505 collected reflections (1987 for $I > 3\sigma(I)$ and led to final R = 0.032 and R_w = 0.39.

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