not H bonded B_{eq} is ≈12·2 Å^2. The dihedral angles between the planes of the nitro groups and the phenyl ring are also noticeably different; N(1)O(2)O(3) makes an angle of 13·61 (5)° with the C(1)–(6) ring, N(2)-O(4)O(5) makes 7·56 (5)°, and N(3)O(6)O(7) makes 5·67 (5)°.

The bond lengths (Table 2) result from the superposition of the two disordered picric acid molecules, and it is probable that the precise positioning of the naphthalene molecules is likewise affected. Unsuccessful attempts were made to separate the two arrangements, including full-matrix least-squares refinement, but no progress was made along these lines, and the results presented are the best interpretation which can be made at present. To try to improve the resolution of the atomic parameters, two additional complete sets of intensity data were collected on the diffractometer using Mo $K\alpha$ radiation, and also a considerable amount of photographic data on the Weissenberg camera, but the quite large variations in values of F led to the belief that no two crystals used had the same proportion of disorder and the results presented here are for one particular crystal only under one particular set of experimental conditions, and these are not necessarily reproducible.

Proton transfer of the type postulated and the ability of nitro groups to abstract H atoms have already been envisaged in an investigation of the structure of picric acid (Soriano-Garcia, Srikrishnan & Parthasarathy, 1978).

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Structure of α-(Isopropylamino)salicylphosphonic Acid Hemihydrate, $C_{10}H_{16}NO_4P.0{\cdot}5H_2O$

By W. Sawka-Dobrowolska

Institute of Chemistry, University of Wrocław, 14 *Joliot-Curie* 50–383 *Wrocław, Poland*

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Abstract. $M_r = 254{\cdot}2$, monoclinic, $C2/c$, $a = 24{\cdot}686$ (4), $b = 6{\cdot}257$ (1), $c = 18{\cdot}629$ (3) Å, $\beta = 123{\cdot}60$ (2)°, $V = 2396{\cdot}7$ Å^3, $Z = 8$, $D_m = 1{\cdot}41$ (1), $D_x = 1{\cdot}41$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}24$ mm^{-1}, $F(000) = 1080$, $T = 293$ K, $R = 0{\cdot}041$ for 1736 reflexions. The title compound exists as a zwitterion and adopts a *trans* conformation with the P—C—N—C torsion angle 179·5 (2)°. The coordination around P is distorted tetrahedral with normal P—O bond lengths. There is intermolecular, and possibly intramolecular, hydrogen bonding in the structure.

Introduction. The present structural investigation was undertaken as part of our study on the conformation and the hydrogen-bond system of this new aminophosphonic acid.

Experimental. Synthesis described by Zoń & Mastalerz (1976). Clear, colourless crystals from water at room temperature, dimensions 0·2 × 0·2 × 0·3 mm; density by flotation in bromoform/benzene; monoclinic Cc or $C2/c$ from Weissenberg photographs, $C2/c$ confirmed by refinement; Syntex $P2_1$ computer-controlled four-circle diffractometer, scintillation counter, graphite monochromator; cell parameters by least squares from setting angles of 15 reflexions with $16 \le 2\theta(\mathrm{Mo}) \le 25°$ measured on diffractometer; 3183 independent reflexions; $2\theta_{max} = 60°$; variable θ–2θ scans, scan rate 2·0–29·3° min^{-1}, depending on intensity; two standards ($42\bar{2}$, $51\bar{2}$) every 50 reflexions with average intensities and e.s.d.'s of 193 300 (2500) and 92 800 (1900); corrected for Lorentz and polarization, not for absorption; 1736 with $I > 1{\cdot}96\sigma(I)$ used for structure determination; index range h 0 to 31, k 0 to 8, l −25 to 24; calculations performed with Syntex (1976) *XTL* system; neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); direct methods, Syntex (1976) version of *MULTAN* (Germain, Main & Woolfson, 1971); full-matrix least squares, minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F)$;

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difference synthesis revealed H atoms; non-H atoms refined with anisotropic and H atoms with isotropic temperature factors; max. Δ in final LS cycle 0·01σ; max. electron density in final difference map 0·15 e Å^{-3}; max. negative electron density in final difference map −0·12 e Å^{-3}; $R = 0{\cdot}041$, $R_w = 0{\cdot}034$, $S = 1{\cdot}919$. Final positional parameters are given in Table 1.*

Discussion. The molecular structure and atom numbering are shown in Fig. 1. Bond distances and angles and torsion angles are in Table 2.

The C—H lengths vary from 1·02 (4) to 0·95 (3) Å, N—H lengths are 0·88 (3) and 0·89 (3) Å, and O—H lengths vary from 0·76 (3) to 0·85 (4) Å. The angles involving the H atoms in the amino group range from 105 (2) to 140 (2)° and in the CH_3 groups from 91 (2) to 136 (2)°.

The coordination around the P atom departs significantly from regular tetrahedral, the angles varying from 118·0 (1) [O(2)—P—O(3)] to 102·8 (1)° [O(2)—P—C(1)]. The smallest angle involves C(1) and an unprotonated O atom, although as a general rule the smallest O—P—C angle involves the C atom and the protonated O in organic phosphates (Corbridge, 1974).

Two O atoms of the phosphono group are in resonance with each other as indicated by the lengths of the bonds P—O(2) and P—O(3), which are 1·508 (2) and 1·495 (2) Å, respectively. The P—O(1) bond length of 1·559 (2) Å indicates a single bond. All P—O lengths agree within the limits of error with similar bonds in aminomethylphosphonic acid, β-AMPh (Darriet, Darriet, Cassaigne & Neuzil, 1975) and in 2-aminoethylphosphonic acid, β-ciliatine (Okaya, 1966). The P—C(1) distance, 1·858 (3) Å, is slightly longer (by 3σ) than the P—CH_2 distances in β-AMPh [1·817 (3) Å] and aminomethyl(methyl)phosphinic acid, AMMPh [1·807 (6) Å] (Głowiak & Sawka-Dobrowolska, 1977), and similar to those found in aminobenzylphosphonic acid [1·865 (7) Å] (Sawka-Dobrowolska, 1980) and in aminomethylethylphosphonic acid [1·841 (4) Å] (Głowiak & Sawka-Dobrowolska, 1984). The P—C(1)—N angle in the title compound [113·9 (2)°] is greater than the corresponding angle in β-AMPh [110·9 (1)°] and in aminobenzylphosphonic acid [107·1 (5)°]; this may be a result of the N substitution by the more bulky isopropyl group.

The phenyl moiety is nearly planar. Deviations from the best plane through the ring atoms are C(11) −0·025 (3), C(12) 0·019 (3), C(13) 0·002 (4), C(14) −0·019 (4), C(15) −0·008 (3) and C(16)

Table 1. *Positional parameters and B_{eq}(Å^2) values for the non-*H *atoms with e.s.d.'s in parentheses*

	x	y	z	B_{eq}*
P	−0·00049 (3)	0·45164 (11)	0·11303 (3)	2·10 (3)
O(1)	0·0295 (1)	0·6566 (3)	0·1009 (1)	2·8 (1)
O(2)	−0·0113 (1)	0·2802 (3)	0·0495 (1)	2·5 (1)
O(3)	0·0372 (1)	0·3941 (3)	0·2065 (1)	2·7 (1)
O(12)	−0·0804 (1)	0·9579 (3)	0·0469 (1)	3·5 (2)
O(*W*)	0·0	0·0039 (4)	0·25	3·8 (2)
N	−0·0878 (1)	0·6450 (3)	0·1463 (1)	2·3 (2)
C(1)	−0·0845 (1)	0·5189 (4)	0·0802 (1)	2·2 (2)
C(2)	−0·1559 (1)	0·6997 (5)	0·1210 (2)	3·3 (2)
C(3)	−0·1510 (2)	0·8469 (6)	0·1892 (2)	5·2 (3)
C(4)	−0·1936 (1)	0·4985 (6)	0·1097 (2)	5·0 (3)
C(11)	−0·1219 (1)	0·6164 (4)	−0·0095 (1)	2·2 (2)
C(12)	−0·1123 (1)	0·8280 (4)	−0·0231 (2)	2·4 (2)
C(13)	−0·1356 (1)	0·8999 (4)	−0·1061 (2)	3·1 (2)
C(14)	−0·1695 (1)	0·7627 (5)	−0·1746 (2)	3·4 (2)
C(15)	−0·1825 (1)	0·5562 (5)	−0·1631 (2)	3·1 (2)
C(16)	−0·1590 (1)	0·4840 (4)	−0·0803 (2)	2·7 (2)

* $B_{eq} = \frac{1}{3}\sum_i B_{ii}$.

Table 2. *Bond distances* (Å) *and angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

P—O(1)	1·559 (2)	C(2)—C(4)	1·510 (5)
P—O(2)	1·508 (2)	C(11)—C(12)	1·393 (4)
P—O(3)	1·495 (2)	C(12)—C(13)	1·394 (4)
P—C(1)	1·858 (3)	C(12)—O(12)	1·358 (3)
C(1)—N	1·501 (3)	C(13)—C(14)	1·373 (4)
N—C(2)	1·515 (4)	C(14)—C(15)	1·376 (4)
C(1)—C(11)	1·519 (3)	C(15)—C(16)	1·388 (4)
C(2)—C(3)	1·518 (5)	C(16)—C(11)	1·389 (3)
O(1)—P—O(2)	111·3 (1)	C(3)—C(2)—C(4)	112·4 (3)
O(1)—P—O(3)	109·2 (1)	C(1)—C(11)—C(12)	121·4 (2)
O(1)—P—C(1)	107·4 (1)	C(1)—C(11)—C(16)	119·0 (2)
O(2)—P—O(3)	118·0 (1)	C(12)—C(11)—C(16)	118·9 (3)
O(2)—P—C(1)	102·8 (1)	O(12)—C(12)—C(11)	117·4 (2)
O(3)—P—C(1)	107·5 (1)	O(12)—C(12)—C(13)	122·5 (3)
P—C(1)—N	113·9 (2)	C(11)—C(12)—C(13)	120·1 (3)
C(11)—C(1)—P	110·0 (2)	C(12)—C(13)—C(14)	119·6 (3)
N—C(1)—C(11)	114·5 (2)	C(13)—C(14)—C(15)	121·1 (3)
C(1)—N—C(2)	114·7 (2)	C(14)—C(15)—C(16)	119·3 (3)
N—C(2)—C(3)	108·4 (3)	C(15)—C(16)—C(11)	120·8 (3)
N—C(2)—C(4)	110·3 (3)		

τ|O(1)—P—C(1)—N|	−77·5 (2)
O(2)—P—C(1)—N	165·0 (2)
O(3)—P—C(1)—N	39·8 (2)
χ^1|P—C(1)—N—C(2)|	−179·5 (2)
χ^2|C(1)—N—C(2)—C(3)|	−173·8 (3)
$\chi^{2\prime}$|C(1)—N—C(2)—C(4)|	62·8 (3)
χ^3|P—C(1)—C(11)—C(12)|	−77·5 (3)
$\chi^{3\prime}$|P—C(1)—C(11)—C(16)|	92·8 (3)

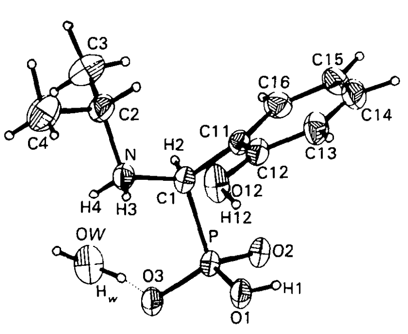

Fig. 1. An *ORTEP* (Johnson, 1976) drawing of the title compound with the atom-numbering scheme.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39720 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

−0·015 (3) Å. O(12) and H(12) are slightly displaced [0·089 (3), −0·27 (4) Å] from the plane. The mean C—C bond length is 1·386 Å as in benzene and C—C—C angles are close to 120°, mean 119·96° (e.s.d. *ca* 1·5°).

The C(12)—O(12) bond of length 1·358 (3) Å is significantly shorter than the usual C(sp^2)—O single bond, but agrees well with similar bonds in various tyrosine derivatives (Mostad & Rømming, 1973; Byrkjedal, Mostad & Rømming, 1974; Gaudestad, Mostad & Rømming, 1976). The distortions of the external angles from 120° [117·4 (2), 122·5 (3)°] at C(12) are analogous to the structure that has often been found in phenols and in various tyrosine derivatives and may be connected with hydrogen-bond formation by the oxygen atom bonded to this carbon atom.

The conformation of the molecule is described by the torsion angles χ^1, χ^2, χ^{21}, χ^3, χ^{31} and τ (IUPAC–IUB Commission on Biochemical Nomenclature, 1970) listed in Table 2. The molecule assumes an extended conformation with χ_1, the torsion angle about C(1)—N, −179·5 (2)°. τ[−77·5 (2)°] is within about 18° of that observed in β-AMPh (Darriet *et al.*, 1975).

Table 3. *Hydrogen-bond lengths* (Å) *and angles* (°)

D—H···A	D···A	D—H	H···A	∠D—H···A
O(1)—H(1)···O(2^{i})	2·610 (2)	0·76 (3)	1·85 (3)	174 (4)
O(12)—H(12)···O(2^{ii})	2·625 (2)	0·88 (3)	1·76 (4)	170 (4)
O(W)—H(OW)···O(3^{iii})	2·878 (3)	0·85 (3)	2·16 (4)	142 (4)
N—H(3)···O(W^{ii})	2·973 (3)	0·88 (3)	2·18 (3)	151 (3)
N—H(3)···O(12^{iii})	2·768 (3)		2·25 (3)	118 (3)
N—H(4)···O(3^{iv})	2·785 (2)	0·89 (3)	1·90 (3)	175 (3)

Symmetry code:
(i) $-x, 1-y, -z$;
(ii) $x, 1+y, z$;
(iii) x, y, z;
(iv) $-x, y, \frac{1}{2}-z$

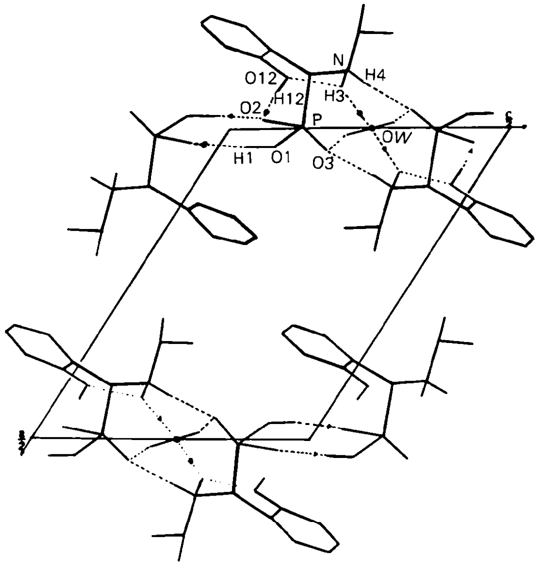

Fig. 2. The crystal packing projected along the *b* axis. Hydrogen bonds are shown by broken lines.

The crystal structure contains a network of hydrogen bonds (Table 3), which plays a role in the stabilization. It is interesting to note that there is a possible intramolecular hydrogen bond in this structure, N—H(3)···O(12), see Table 3. In addition, H(3) participates in a second hydrogen bond involving O(W) at x, $1+y$, z. The O(12) (hydroxy) atoms (as donors) form infinite hydrogen-bonded chains with O(2) parallel to **b** [O(12)—H(12)···O(2) (x, $1+y$, z)].

As depicted in Fig. 2, the molecules around the twofold axis are linked by N—H(4)···O(3) ($-x$, y, $\frac{1}{2}-z$) hydrogen bonds, to form a dimer. The water molecules lying on the twofold axes link these dimers *via* the N···O(W) and an O(W)···O(3) hydrogen bond to form a column along **b**.

There is also another type of hydrogen bond (O—H···O) between phosphonic acid groups related by a centre of symmetry. All relevant distances and angles are listed in Table 3.

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