O(14) donates its proton H(14) to the neighbouring host O(24) hydroxyl oxygen atom. This oxygen atom in turn donates its proton, H(24) to the acceptor oxygen O(99) of the water guest molecule. The water proton H(991) is then donated to the hydroxy oxygen atom of the adjacent host O(14) atom. Both structures show a remarkable similarity in the complexation of their guest molecules, the host-to-guest interactions being dominated by the triangular arrangement of O—H···O=C hydrogen bonds (detailed in Table 2). The O···O distances, and hence their strengths of interaction are similar in both structures. In both structures the O(guest)···O(24)(host) interaction is particularly strong.

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Structure of an Antipyrine–Monophosphoric Acid Complex

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Abstract. 1,2-Dihydro-1,5-dimethyl-2-phenyl-3*H*-pyrazol-3-one–phosphoric acid (2/1), $2C_{11}H_{12}N_2O.H_3PO_4$, $M_r = 474{\cdot}454$, monoclinic, $C2/c$, $a = 25{\cdot}14\ (2)$, $b = 11{\cdot}393\ (7)$, $c = 18{\cdot}55\ (2)$ Å, $\beta = 116{\cdot}07\ (7)°$, $V = 4773\ (15)$ Å^3, $Z = 8$, $D_x = 1{\cdot}321$ Mg m^{-3}, λ(Ag $K\alpha$) = 0·5608 Å, $\mu = 0{\cdot}095$ mm^{-1}, $F(000) = 2000$, room temperature, final $R = 0{\cdot}053$ for 2859 reflections. The main building unit of this arrangement is a centrosymmetrical complex $(antipyrine)_4(H_3PO_4)_2$ made up of a central cluster of two H_3PO_4 groups connected by hydrogen bonds to four neighbouring antipyrine molecules. The hydrogen-bond scheme is described.

Introduction. This work is part of an investigation of the interactions of phosphoric acids with various organic compounds: amines, amino alcohols and amino acids. The present work is the first study of such an interaction with an organic molecule containing a ketone function.

Experimental. The present compound is readily prepared by the action of monophosphoric acid on an aqueous solution of antipyrine at room temperature. By slow evaporation, at room temperature, of such a solution corresponding to the stoichiometry antipyrine/$H_3PO_4 = 2$, large stout monoclinic prisms (up to 25 mm) can be grown within 2–3 weeks.

Crystal size: 0·40 × 0·40 × 0·32 mm. Density not measured. Nonius CAD-4 diffractometer, graphite monochromator. 21 reflections ($10{\cdot}0 < \theta < 13{\cdot}5°$) for refining unit-cell dimensions. $\omega/2\theta$ scan, scan width 1·20°, scan speed 0·02° s^{-1}. Total background measuring time: 28 s. θ range: $2 < \theta < 35°$, $\pm h,k,l$, $h_{max} = 42$, $k_{max} = 16$, $l_{max} = 27$.

Two orientation and intensity control reflections, $\bar{1}6,\bar{6},7$ and $\bar{1}7\bar{4}$, were measured every 3 h without any significant variation. 3958 reflections were obtained after averaging Friedel pairs ($R_{int} = 0{\cdot}04$). Lorentz and polarization corrections, no absorption correction.

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Table 1. *Final atomic coordinates and B_{eq} values for non-H atoms*

Estimated standard deviations are given in parentheses.

$B_{eq} = \frac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{b}_j$.

	x	y	z	B_{eq}(Å^2)
P	0·82898 (3)	0·15503 (6)	0·05067 (4)	3·91 (1)
O(1)	0·79916 (6)	0·2101 (1)	0·09590 (8)	4·33 (4)
O(2)	0·80453 (7)	0·1994 (2)	−0·03597 (9)	5·74 (5)
O(3)	0·82224 (7)	0·0205 (1)	0·0511 (1)	6·17 (5)
O(4)	0·89631 (7)	0·1756 (2)	0·0884 (1)	5·32 (5)
N(11)	0·13350 (7)	0·2049 (2)	0·1305 (1)	3·29 (4)
N(12)	0·10422 (7)	0·1673 (2)	0·1753 (1)	4·01 (5)
C(11)	0·17754 (9)	0·2946 (2)	0·1592 (1)	3·05 (5)
C(12)	0·18233 (9)	0·3707 (2)	0·1045 (1)	3·58 (6)
C(13)	0·2260 (1)	0·4560 (2)	0·1312 (1)	4·52 (6)
C(14)	0·2638 (1)	0·4652 (2)	0·2108 (2)	5·40 (8)
C(15)	0·2583 (1)	0·3903 (3)	0·2655 (2)	5·69 (8)
C(16)	0·2154 (1)	0·3040 (2)	0·2396 (1)	4·29 (6)
C(17)	0·0798 (1)	0·2558 (3)	0·2089 (2)	5·49 (7)
C(18)	0·0771 (1)	0·0642 (2)	0·1423 (2)	4·92 (7)
C(19)	0·4628 (1)	0·5061 (3)	0·3272 (2)	8·7 (1)
C(110)	0·4075 (1)	0·5307 (2)	0·4161 (2)	4·82 (7)
C(111)	0·12882 (9)	0·1183 (2)	0·0755 (1)	3·75 (6)
O(11)	0·15478 (7)	0·1268 (1)	0·03153 (9)	5·10 (4)
N(21)	0·44087 (7)	0·0783 (2)	0·1288 (1)	3·73 (5)
N(22)	0·39880 (8)	0·1645 (2)	0·1197 (1)	4·13 (5)
C(21)	0·49219 (9)	0·1059 (2)	0·1172 (1)	3·44 (6)
C(22)	0·4537 (1)	0·0646 (2)	0·3288 (1)	4·21 (6)
C(23)	0·4041 (1)	0·0889 (3)	0·3401 (2)	5·41 (7)
C(24)	0·4083 (1)	0·1555 (3)	0·4040 (2)	5·64 (7)
C(25)	0·4623 (1)	0·1962 (3)	0·4571 (2)	6·31 (8)
C(26)	0·4879 (1)	0·1722 (3)	0·0532 (2)	5·54 (8)
C(27)	0·4194 (1)	0·2780 (2)	0·1579 (2)	5·69 (8)
C(28)	0·3497 (1)	0·1085 (2)	0·1142 (1)	4·33 (6)
C(29)	0·2982 (1)	0·1755 (3)	0·1119 (2)	7·04 (9)
C(210)	0·14277 (9)	0·4908 (2)	0·3881 (1)	4·42 (7)
C(211)	0·08526 (9)	0·4688 (2)	0·3798 (1)	3·82 (6)
O(21)	0·05791 (6)	0·3761 (1)	0·3796 (1)	4·90 (4)

Table 2. *Main interatomic distances* (Å), *bond angles* (°) *and hydrogen-bond geometry* (Å, °) *in the atomic arrangement of* $2C_{11}H_{12}N_2O.H_3PO_4$

Estimated standard deviations are given in parentheses.

PO_4 tetrahedron

P	O(1)	O(2)	O(3)	O(4)
O(1)	1·488 (2)	2·512 (3)	2·474 (2)	2·537 (3)
O(2)	112·5 (1)	1·533 (2)	2·516 (3)	2·459 (2)
O(3)	109·4 (1)	109·8 (1)	1·543 (2)	2·436 (2)
O(4)	113·9 (1)	106·4 (1)	104·5 (1)	1·539 (2)

P—O(2)—H(2)	115 (2)	P—O(4)—H(4)	117 (2)
P—O(3)—H(3)	117 (2)		
P—P	4·177 (3)		

$C_{11}H_{12}N_2O$ (molecule 1)

C(11)—C(12)	1·379 (3)	C(11)—C(12)—C(13)	119·3 (2)
C(12)—C(13)	1·385 (3)	C(12)—C(13)—C(14)	120·5 (3)
C(13)—C(14)	1·365 (3)	C(13)—C(14)—C(15)	120·1 (2)
C(14)—C(15)	1·379 (4)	C(14)—C(15)—C(16)	120·1 (2)
C(15)—C(16)	1·381 (4)	C(15)—C(16)—C(11)	119·6 (2)
C(16)—C(11)	1·377 (3)	C(16)—C(11)—C(12)	120·5 (2)
N(11)—C(11)	1·427 (3)	N(12)—N(11)—C(11)	121·5 (2)
N(11)—N(12)	1·398 (3)	N(12)—N(11)—C(111)	108·9 (2)
N(11)—C(111)	1·386 (3)	C(11)—N(11)—C(111)	125·8 (2)
N(12)—C(17)	1·456 (4)	N(11)—N(12)—C(17)	118·3 (2)
N(12)—C(18)	1·361 (3)	N(11)—N(12)—C(18)	106·7 (2)
		C(17)—N(12)—C(18)	124·6 (2)
C(18)—C(19)	1·505 (5)	N(12)—C(18)—C(19)	119·7 (3)
C(18)—C(110)	1·356 (5)	N(12)—C(18)—C(110)	109·9 (3)
		C(19)—C(18)—C(110)	130·5 (2)
C(110)—C(111)	1·407 (4)	C(18)—C(110)—C(111)	108·4 (2)
C(111)—O(11)	1·253 (4)	N(11)—C(111)—C(110)	105.8 (2)
		N(11)—C(111)—O(11)	121·7 (2)
		C(110)—C(111)—O(11)	132·5 (2)

$C_{11}H_{12}N_2O$ (molecule 2)

C(21)—C(22)	1·371 (3)	C(21)—C(22)—C(23)	119·5 (2)
C(22)—C(23)	1·380 (4)	C(22)—C(23)—C(24)	120·7 (2)
C(23)—C(24)	1·372 (4)	C(23)—C(24)—C(25)	119·1 (3)
C(24)—C(25)	1·361 (3)	C(24)—C(25)—C(26)	120·8 (3)
C(25)—C(26)	1·374 (5)	C(25)—C(26)—C(21)	120·0 (2)
C(26)—C(21)	1·371 (4)	C(26)—C(21)—C(22)	119·8 (2)
N(21)—C(21)	1·434 (3)	N(22)—N(21)—C(21)	120·7 (2)
N(21)—N(22)	1·398 (3)	N(22)—N(21)—C(211)	108·9 (2)
N(21)—C(211)	1·386 (3)	C(21)—N(21)—C(211)	126·3 (2)
N(22)—C(27)	1·456 (3)	N(21)—N(22)—C(27)	118·4 (2)
N(22)—C(28)	1·354 (3)	N(21)—N(22)—C(28)	107·1 (2)
		C(27)—N(22)—C(28)	125·0 (2)
C(28)—C(29)	1·490 (4)	N(22)—C(28)—C(29)	120·9 (2)
C(28)—C(210)	1·357 (4)	N(22)—C(28)—C(210)	109·4 (2)
		C(29)—C(28)—C(210)	129·7 (3)
C(210)—C(211)	1·408 (4)	C(28)—C(210)—C(211)	108·9 (2)
C(211)—O(21)	1·259 (3)	N(21)—C(211)—C(210)	105·3 (2)
		N(21)—C(211)—O(21)	121.6 (2)
		C(210)—C(211)—O(21)	133·1 (2)

Hydrogen bonds

O—H	O···H	H···O	O···O	O—H···O
O(2)—H(2)···O(1)	0·91 (3)	1·67 (3)	2·559 (2)	164 (2)
O(3)—H(3)···O(11)	0·83 (3)	1·69 (3)	2·506 (3)	164 (3)
O(4)—H(4)···O(21)	0·82 (3)	1·69 (3)	2·510 (2)	170 (2)

The structure was solved by direct methods (*MULTAN*77; Main, Lessinger, Woolfson, Germain & Declercq, 1977) and interpretation of the Patterson map followed by successive Fourier syntheses. H atoms were located by difference Fourier syntheses. Anisotropic full-matrix least-squares refinement (on F), isotropic for H atoms. Unit weights. Final refinements with 2859 reflections corresponding to $I > 3\sigma$. Final $R = 0{\cdot}053$ ($wR = 0{\cdot}041$), $S = 1{\cdot}98$, max. $\Delta/\sigma = 0{\cdot}07$. Max. peak height in the final difference Fourier synthesis = 0·30 e Å^{-3}. No secondary-extinction correction. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B). Enraf–Nonius (1977) *SDP* was used for all calculations. Computer used: MicroVAX II.

Discussion. Table 1 reports the final atomic coordinates while interatomic distances and bond angles are given in Table 2.*

This complex atomic arrangement whose main building unit is made up of two H_3PO_4 and four antipyrine molecules can be briefly described as follows. The $(H_3PO_4)_2$(antipyrine)$_4$ building unit is centrosymmetrical around the inversion centre at $\frac{1}{4},\frac{1}{4},0$. Around this inversion centre is located a cluster made up of two H_3PO_4 molecules interconnected by a set of hydrogen bonds: O(2)—H(2)···O(1). Inside this cluster the P—P distance (4·177 Å) is significantly shorter than those measured in normal organic or inorganic monophosphates, in which the P—P distances are mostly larger than 5 Å, but quite comparable to the P—P distance previously observed by Bagieu-Beucher, Durif & Guitel (1989) in a rather similar phosphoric cluster in $C_2H_{10}N_2.3H_3PO_4$.

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and main interatomic distances and bond angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53220 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

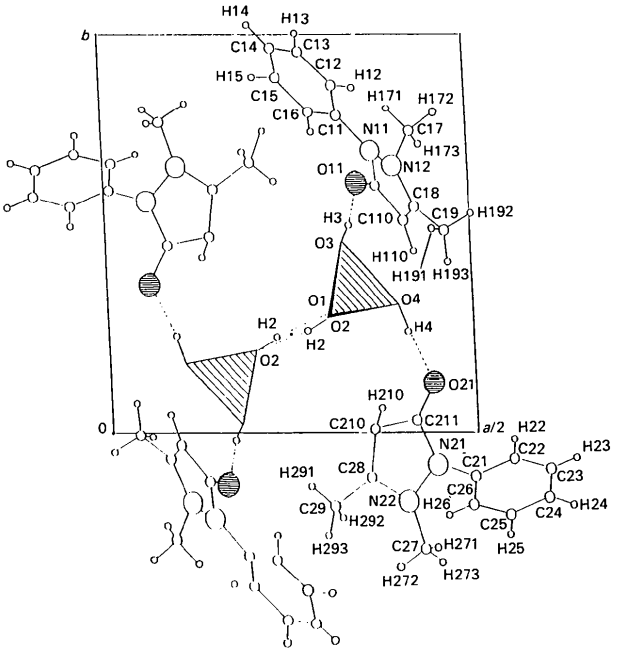

Fig. 1. Projection of the atomic arrangement of $2C_{11}H_{12}N_2O.H_3PO_4$ along the c axis.

The four remaining H atoms of this phosphoric group form hydrogen bonds with the O atoms of the ketonic groups of the four neighbouring antipyrine molecules. Fig. 1 shows a view of this building unit in projection along the c axis.

As expected, in the H_3PO_4 group the three P—OH distances, 1·533, 1·543 and 1·539 Å, are significantly longer than the P—O distance (1·488 Å) and the three P—O—H angles are close to 116° as is commonly observed in acidic phosphoric groups.

Two independent antipyrine molecules coexist in this atomic arrangement. As shown in Table 2 their conformations do not differ significantly.

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1-(Benzylideneamino)-3-hydroxyguanidinium Tosylate

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Abstract. $C_8H_{11}N_4O^+.C_7H_7O_3S^-$, $M_r = 318·3$, monoclinic, $P2_1/n$, $a = 14·539$ (3), $b = 20·551$ (4), $c = 6·062$ (3) Å, $\beta = 103·24$ (2)°, $U = 1763$ (1) Å^3, $Z = 4$, $D_x = 1·20$ Mg m^{-3}, $\lambda = 0·7107$ Å, $\mu = 1·67$ mm^{-1}, $F(000) = 736$, $T = 298$ K, final $R = 0·067$ for 2163 observed reflections with $F > 4\sigma(F_o)$ and 274 variable parameters. The structure consists of a disordered tosylate anion linked to a guanidine cation in the asymmetric unit, with two N···O and one O···O distance < 3 Å. The cationic part of the guanidine moiety is best described by a resonance structure where the equilibrium is shifted towards HO—NH—CR=N$^+$H$_2$, rather than the delocalized HO—NH—C^+R—NH$_2$ structure.

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Introduction. Hydroxyguanidine contains both the amino group of guanidine and the hydroxy group of hydroxyurea. These functional groups are known to be important for antiviral and anticancer activity (Adamson, 1972). It is also known that size and lipophilicity are important contributing factors towards enhanced activity (T'ang, Lien & Lai, 1985). Therefore a number of novel *N*-hydroxy-*N'*-aminoguanidine derivatives were designed, synthesized and evaluated for biological activity. The basic model compound 1-(benzylideneamino)-3-hydroxyguanidinium tosylate was used to study the effect of various electron-donating, electron-withdrawing, hydrophilic and lipophilic groups on activity of the molecule. The tosylate salt was synthesized to stabilize the molecule and to enhance solu-