Hydrogen Bond Studies

56.* Neutron and X-Ray Diffraction Studies of the 1:1 Addition Compound of Acetic Acid with Phosphoric Acid**

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The addition compound $CH_3COOH.H_3PO_4$ has been studied by X-ray and neutron diffraction. The crystals are triclinic, space group $P\bar{1}$, with four formula units in a cell of dimensions: $a = 9.627(1)$, $b = 11.505(1)$, $c = 6.456(1)$ Å, $\alpha = 97.98(1)$, $\beta = 90.11(1)$, $\gamma = 68.89(1)°$. The structure contains cyclic acetic acid dimers formed from two crystallographically independent molecules joined by $O-H\cdots O$ bonds. Two of the hydrogen atoms in each phosphoric acid molecule are engaged in $O-H\cdots O$ bonds with their phosphoric acid neighbors, thus giving rise to infinite layers of hydrogen-bonded phosphoric acid molecules. The remaining hydrogen atom in each phosphoric acid molecule is joined by a hydrogen bond to the carbonyl oxygen atom of an acetic acid dimer. Each dimer is in this way connected to two separate phosphoric acid layers. The internal hydrogen bonds of the acetic acid dimer have $H\cdots O$ distances of 1.697(6) and 1.699(6) Å, the $O\cdots O$ distances are 2.681(4) and 2.688(4) Å. The hydrogen bonds between the phosphoric acid molecules have $H\cdots O$ distances in the range 1.558 to 1.609 Å and $O\cdots O$ distances in the range 2.558 to 2.594 Å. All the hydrogen bonds in the structure are close to linear with $O-H\cdots O$ angles ranging from 171 to 177°.

A cetic acid forms addition compounds with several strong acids. The crystal structures of two such compounds, $CH_3COOH.H_2SO_4$ and $CH_3COOH.HSO_3F$, have been reported earlier.[1,2] Although the hydrogen positions could not be determined accurately by the X-ray diffraction methods used in these studies, it could nevertheless be shown that in both structures a proton is transferred from the strong acid to the acetic acid. The compounds should therefore be formulated as $CH_3C(OH)_2{}^+HSO_4{}^-$ and $CH_3C(OH)_2{}^+SO_3F^-$.

Sulfuric and fluorosulfuric acid are very strong acids. It is therefore of interest to study the structure of an addition compound formed with a

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moderately strong acid to investigate whether the same kind of proton transfer occurs in such a case. The 1 : 1 addition compound of acetic acid with phosphoric acid has been described by King and Walton [3] in connection with a study of the freezing point curve of the acetic acid − phosphoric acid system. The melting point was determined as 33.8°C.

This paper reports the structure of $CH_3COOH.H_3PO_4$ as studied by X-ray and neutron diffraction methods at room temperature.

CRYSTAL DATA

$CH_3COOH.H_3PO_4$. F.W. 158.05, m.p. 34.5°C. Triclinic,
$a = 9.627(1)$,* $b = 11.505(1)$, $c = 6.456(1)$ Å,
$\alpha = 97.98(1)$, $\beta = 90.11(1)$, $\gamma = 68.89(1)°$,
$V = 659.7$ Å³ at 22°C. $D_m = 1.59$ g cm⁻³ (by flotation),
$Z = 4$, $D_x = 1.591$ g cm⁻³. Space group $P\bar{1}$. Calculated linear absorption coefficients: 35.4 cm⁻¹ for $CuK\alpha$, 1.44 cm⁻¹ for 1.042 Å neutrons.

EXPERIMENTAL

Preparation. Crystalline water-free phosphoric acid was prepared by removing the water from analytical grade 85 % orthophosphoric acid according·to Weber and King.[4] The method was modified by using nitrogen gas dried by passing through a copper coil immersed in liquid nitrogen, instead of dry air. The resulting phosphoric acid was recrystallized three times by melting and allowing only part of the melt to crystallize before the crystals were drained off. The recrystallized acid was melted and mixed with an equimolar amount of water-free acetic acid. The mixture crystallized on cooling, the melting point was recorded as 34.5°C (lit.[3] 33.8°). The compound is very hygroscopic; the preparation and all handling of the compound were therefore performed in a dry box.

X-Ray study. Single crystals were grown in sealed glass capillaries (diameter about 0.2 mm and wall thickness 0.01 − 0.02 mm) by a zone-melting technique.

The unit-cell dimensions were determined from zero layer oscillation photographs taken with crystals rotating around the a, b, and c axes. Reflections from a quartz single crystal were superimposed on the photographs for calibration ($a = 4.9130$ Å for α quartz at 22°C). The cell dimensions and their estimated standard deviations as given above were obtained from 111 measured θ values by the method of least squares. The following wavelengths were used: $CuK\alpha_1 = 1.54051$ Å, $CuK\alpha_2 = 1.54433$ Å, $CuK\beta = 1.39217$ Å.

A cylindrically shaped crystal of length 2 mm and diameter 0.25 mm was used for collecting the intensity data on a paper tape controlled Stoe Weissenberg diffractometer. Ni-filtered $CuK\alpha$ radiation was used. The diffractometer was programmed to perform a rapid pre-scan of each reflection before the intensity was measured. Depending on the number of counts accumulated during this pre-scan, different strategies for the intensity measurement were employed. The intensity scan for strong reflections was carried out with the counter moving at 4°/min. For very weak reflections the scan rate was decreased to 0.25°/min, whereas intermediate rates were used for moderately weak reflections. In order to minimize coincidence losses when measuring very strong reflections, up to four filters could be inserted to attenuate the primary beam.

The intensity, I, of a reflection with Weissenberg coordinates ϕ_0 and Γ_0 was recorded in the following manner: (1) The counter was set to $\Gamma_1 = \Gamma_0 - \omega$. (2) The crystal was set to an angle $\phi_1 = \phi_0 - \omega/2$ and the first background, B_1, was counted for t_1 sec. (3) The crystal was rotated by ω degrees at a constant rate while the detector was simultaneously

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* Numbers in parenthesis here and throughout this paper are the estimated standard deviations in the least significant digits.

rotated at twice this rate until the crystal reached the angle $\phi_2 = \phi_0 + \omega/2$ and the detector reached the angle $\Gamma_2 = \Gamma_0 + \omega$. The number of counts accumulated during this scan is C, measured for t_c sec. (4) The second background, B_2, was measured for t_2 sec with the crystal at ϕ_2 and the detector at Γ_2.

With equi-inclination geometry, 1981 independent reflections for the layers $0 < l < 5$ in the range $5° \leq \Gamma \leq 128°$ were measured. The angle scanned, ω, was $2.0°$ for all reflections. A few reference reflections measured at irregular intervals showed no significant changes in intensity throughout the period of the data collection.

The data were corrected for background according to the formula $I = [C - t_c(B_1 + B_2)/ (t_1 + t_2)] \times A \times \omega/t_c$ where A is a filter factor.

Standard deviations were calculated from the expression:

$$\sigma(I) = \{C + [t_c/(t_1 + t_2)]^2 (B_1 + B_2)\}^{1/2} \times A \times \omega/t_c$$

Values of F^2 and $\sigma_c(F^2)$ were then calculated by applying Lorentz and polarization corrections to the values of I and $\sigma(I)$. The few negative values of F^2 were replaced by values of zero. No absorption corrections were applied.

Neutron study. A large single crystal was grown in a sealed glass tube by a zone-melting technique. The crystal used for the data collection was cut from the grown crystal and sealed into a thin-walled quartz tube. This cylindrical crystal had a radius of 1.34 mm and a volume of 13.9 mm³. It was mounted on a four-circle diffractometer at the Brookhaven National Laboratory High Flux Beam Reactor. The crystal was aligned about an axis normal to the (201) planes and the data collected automatically with the computer-controlled Multiple Spectrometer Control System.[5] A portion of reciprocal space extending out to $\sin \theta/\lambda = 0.60$ Å^{-1} was examined at a neutron wavelength of 1.042 Å. The $\theta - 2\theta$ step scan technique was used with $\Delta(2\theta) = 0.1°$. Two standard reflections were measured at regular intervals to provide a check on crystal and electronic stability. No significant changes were observed in these standards. A total of 2375 independent reflections were measured.

The data were corrected for background and assigned standard deviations based on Poisson counting statistics. Values of F^2 and $\sigma_c(F^2)$ were then calculated by applying the Lorentz factor and absorption corrections to the values of I and $\sigma(I)$. Negative values of F^2 were replaced by values of zero. The cylindrical shape of the crystal was represented approximately by 32 boundary planes in the calculation of the absorption correction. The resulting transmission factors fell in the range $0.73 - 0.76$. The linear absorption coefficient of 1.44 cm^{-1} was calculated; the value of 34 barns was used for the incoherent scattering cross-section for hydrogen.

STRUCTURE SOLUTION AND REFINEMENT OF THE X-RAY STRUCTURE

A scale factor and an overall temperature factor were obtained by the method of Wilson.[6] Normalized structure factor amplitudes were then calculated from the expression (valid for triclinic crystals) $E_{hkl}^2 = F_{hkl}^2 / \sum_{j=1}^{N} f_j^2$ *(hkl)*

Table 1. Statistical averages and distribution of normalized structure factors.

	Observed	Theoretical Centric	Acentric
$\langle E^2 \rangle$	1.000	1.000	1.000
$\langle |E| \rangle$	0.767	0.798	0.886
$\langle |E^2 - 1| \rangle$	1.043	0.968	0.736
$|E| > 3$	0.7 %	0.3 %	0.01 %
$|E| > 2$	5.8 %	5.0 %	1.8 %
$|E| > 1$	29.1 %	32.0 %	37.0 %

Table 2. Final fractional coordinates and thermal parameters for $CH_3COOH.H_3PO_4$. For each of the non-hydrogen atoms the neutron result is given on the first line and the X-ray result on the second. The value given on the third line is Δ/σ (see text). The parameter values for the half-hydrogen atoms denoted by Me are multiplied by 10^4 and the parameter values for all other atoms by 10^5. The anisotropic thermal parameters are defined as $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P(1)	25395(22)	35763(20)	19305(31)	456(24)	634(21)	1536(53)	−212(18)	21(27)	25(25)
	25374 (7)	35801 (7)	19276(12)	434(10)	622 (8)	2052(26)	−196 (7)	−7(10)	108 (9)
	−0.9	1.8	−0.9	−0.9	−0.5	8.8	0.9	−1.0	3.1
O(1)	20905(25)	37303(23)	−3430(32)	1143(31)	781(24)	1661(53)	−368(22)	−360(31)	275(28)
	20809(24)	37269(20)	−3442(32)	1181(32)	808(22)	2600(68)	−398(22)	−297(35)	219(28)
	−2.7	−1.1	−0.3	0.9	0.8	10.8	−1.0	1.4	−1.4
O(2)	32215(27)	21321(21)	19100(37)	921(31)	625(21)	2644(65)	−160(21)	67(37)	365(29)
	32160(24)	21341(20)	19129(35)	986(31)	690(22)	3477(72)	−220(21)	37(36)	374(30)
	−1.5	0.7	0.6	1.5	2.2	8.6	−2.0	−0.6	0.2
O(3)	11441(24)	40467(23)	34253(34)	506(27)	1093(26)	2097(58)	−286(20)	132(30)	−22(29)
	11486(22)	40459(22)	34205(33)	541(25)	1196(27)	2801(66)	−321(21)	115(30)	−16(31)
	1.4	−0.2	−1.0	1.0	2.8	8.0	−1.2	−0.4	0.1
O(4)	35713(22)	42193(21)	27010(33)	575(23)	942(23)	2140(56)	−438(19)	39(27)	−92(27)
	35662(22)	42217(21)	26970(32)	658(26)	1050(25)	2895(67)	−470(21)	115(31)	−116(30)
	−1.7	0.8	−0.9	2.4	3.2	8.6	−1.1	1.9	−0.6
H(1)	18539(40)	45727(37)	−8349(57)	1063(48)	786(39)	2339(97)	−334(34)	−110(52)	241(49)
H(2)	41412(47)	17007(35)	10133(65)	1077(55)	698(35)	3020(117)	−61(36)	14(65)	219(51)
H(3)	1736(41)	40782(35)	28507(58)	733(49)	952(39)	2817(109)	−359(34)	−3(56)	324(49)
P(11)	75367(22)	36097(20)	23927(32)	431(23)	601(20)	1777(54)	−200(17)	−18(27)	108(25)
	75398 (7)	36077 (7)	23956(12)	411(10)	652 (8)	2337(28)	−215 (7)	−11(10)	160 (9)
	1.3	−1.0	0.8	−0.8	2.3	9.2	0.2	1.9	1.9
O(11)	71820(28)	37198(24)	47458(35)	1494(36)	796(25)	1787(57)	−551(24)	−11(35)	257(31)
	71865(27)	37146(21)	47299(33)	1583(38)	888(24)	2398(72)	−539(25)	73(38)	214(29)
	1.1	−1.6	−3.3	1.7	2.7	6.7	0.3	1.6	−1.0
O(12)	81372(33)	21645(25)	17090(50)	1317(40)	782(25)	4777(104)	−580(26)	1040(54)	−548(41)
	81242(29)	21707(23)	17047(45)	1359(39)	872(27)	5684(107)	−598(26)	1135(52)	−672(41)
	−2.9	1.8	−0.6	0.7	2.4	6.1	−0.5	1.3	−2.1
O(13)	61039(27)	41928(31)	12830(42)	573(29)	2082(43)	3030(76)	−566(27)	−456(36)	1421(46)
	61076(25)	41955(29)	12962(39)	648(28)	2231(43)	3618(79)	−679(29)	−472(36)	1406(47)
	1.0	0.6	2.3	1.8	2.4	5.4	−2.9	−0.3	−0.2
O(14)	86255(21)	41830(20)	18418(33)	575(23)	803(21)	2343(57)	−355(18)	−157(28)	379(26)
	86234(21)	41850(19)	18375(32)	632(25)	908(23)	2930(64)	−388(20)	−193(30)	488(28)
	−0.7	0.7	−0.9	1.7	3.4	6.9	−1.2	−0.9	2.8

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
H(11)	69055(40)	45597(41)	56616(60)	966(46)	1011(44)	2288(99)	−418(36)	−15(53)	212(55)
H(12)	90673(50)	17940(37)	8918(67)	1229(59)	821(39)	3059(118)	−300(39)	267(67)	−150(52)
H(13)	51516(37)	41613(40)	17840(61)	626(42)	1271(46)	2987(111)	−364(35)	−136(52)	350(55)
O(5)	26976(28)	5408(27)	75311(41)	1005(33)	1154(30)	2181(67)	−147(25)	172(37)	280(37)
	26901(26)	5424(25)	75239(37)	1043(34)	1219(29)	2998(74)	−178(26)	101(37)	373(35)
	−2.0	0.4	−1.3	0.8	1.6	8.2	−0.9	−1.4	1.8
O(6)	7621(25)	10143(22)	97686(37)	811(28)	847(24)	2550(67)	−81(21)	123(33)	211(30)
	7654(25)	10150(22)	97784(36)	926(31)	911(26)	3367(81)	−162(23)	70(38)	239(33)
	1.0	0.2	1.9	2.7	1.8	7.7	−2.6	−1.1	0.6
C(1)	12940(21)	11445(18)	81219(30)	895(25)	731(19)	2153(52)	−217(18)	−219(28)	135(24)
	12926(38)	11461(30)	81196(56)	995(45)	756(32)	2962(112)	−315(32)	−101(51)	0(43)
	−0.3	0.5	−0.4	1.9	0.7	6.5	−2.7	2.0	−2.8
C(2)	4074(39)	19988(43)	66884(54)	1294(48)	1252(40)	2764(108)	−255(38)	−516(57)	606(55)
	4019(49)	19988(41)	67124(61)	1522(60)	1293(48)	3365(125)	−357(44)	−687(67)	646(59)
	−0.9	−0.0	3.0	3.0	0.7	3.6	−1.8	−1.9	0.5
H(5)	32002(47)	50(46)	85794(73)	1045(55)	1172(49)	2880(128)	−61(41)	233(66)	277(65)
Me(1)	1090(21)	2208(42)	5610(57)	214(24)	290(45)	330(67)	−83(30)	−20(39)	219(45)
Me(2)	680(70)	1583(39)	5096(53)	482(102)	265(42)	261(53)	93(48)	−186(57)	−53(36)
Me(3)	−296(40)	1579(37)	5921(61)	200(36)	194(32)	566(89)	−64(32)	−200(45)	102(40)
Me(4)	−749(21)	2277(46)	6978(78)	128(26)	203(37)	843(129)	0(24)	−63(41)	204(51)
Me(5)	−265(53)	2907(21)	7654(35)	368(57)	90(16)	392(57)	10(25)	−11(43)	50(24)
Me(6)	578(56)	2735(35)	6794(75)	396(73)	183(33)	462(110)	−115(42)	−112(56)	120(49)
O(15)	77235(28)	4742(28)	74888(43)	932(33)	1193(31)	2432(71)	−181(26)	252(38)	271(38)
	77271(26)	4761(25)	74873(37)	1036(34)	1239(29)	3064(75)	−244(26)	289(37)	347(35)
	0.9	0.5	−0.3	2.2	1.1	6.1	−1.7	0.7	1.5
O(16)	58025(24)	9240(21)	97028(36)	794(28)	712(22)	2664(66)	−185(19)	131(32)	338(29)
	57981(23)	9256(20)	97083(35)	858(29)	805(23)	3302(75)	−224(21)	196(35)	338(30)
	−1.3	0.5	1.1	1.6	2.9	6.4	−1.4	1.4	0.0
C(11)	63300(20)	10744(17)	80730(29)	834(24)	703(18)	2113(50)	−275(17)	45(27)	190(23)
	63247(36)	10780(30)	80772(56)	887(43)	692(31)	3416(114)	−337(30)	89(50)	64(43)
	−1.3	1.0	0.7	1.1	−0.3	10.4	−1.8	0.8	−2.6
C(12)	54504(41)	19246(34)	66376(58)	1331(53)	1168(41)	3256(106)	−184(34)	−14(60)	992(54)
	54494(48)	19377(41)	66868(63)	1398(57)	1262(48)	3787(131)	−272(43)	106(67)	858(61)
	−0.2	2.5	5.7	0.9	1.5	3.2	−1.6	1.3	−1.6
H(15)	82231(51)	−822(49)	85192(75)	1209(61)	1323(55)	2971(135)	−162(46)	222(71)	402(70)
Me(11)	5977(40)	1661(36)	5148(39)	314(54)	169(31)	303(47)	55(32)	−9(35)	44(29)
Me(12)	4991(72)	1374(36)	5531(67)	404(69)	323(52)	527(84)	−184(60)	−295(67)	203(58)
Me(13)	4380(22)	2013(35)	6713(66)	94(21)	188(30)	524(94)	−17(18)	−29(29)	149(37)
Me(14)	4511(55)	2665(41)	7447(46)	368(65)	166(31)	443(67)	131(35)	186(51)	98(36)
Me(15)	5484(50)	2851(23)	7211(64)	292(40)	107(19)	732(97)	−49(24)	29(47)	105(32)
Me(16)	6038(25)	2252(48)	5772(90)	170(24)	203(40)	762(133)	4(31)	126(54)	283(58)

where $F_{hkl}{}^2$ has been corrected for vibrational motion, $f_j(hkl)$ is the atomic scattering factor for the j:th atom in the unit cell, and N is the number of atoms in the unit cell. The statistical averages and distribution of the E values compared to the theoretical values for centric and acentric structures [7] are given in Table 1. These values indicate a centrosymmetric structure and accordingly the space group $P\bar{1}$ was assumed.

The 259 reflections with $|E| > 1.5$ were used as input data for Long's sign-determining program.[8] The program uses Sayre's equation [9] iteratively to predict the signs; seven signs were used in the starting set. Three linearly independent reflections were given plus signs to fix the origin of the unit cell, and all combinations of the other four were considered, giving sixteen solutions. Four of these solutions were found to have very good consistency and rapid convergence. One such solution which had all signs positive was rejected. Three-dimensional Fourier syntheses based on the 259 phased E values were calculated for each of the remaining three solutions, one of which revealed the structure. Among the twenty highest peaks in this E map four peaks could be rejected as being spurious. The remaining sixteen peaks represented all the non-hydrogen atoms in the structure except the two methyl carbon atoms which could subsequently be traced further down on the peak list. It was later found that for this solution all signs except one agreed with those of the calculated structure factors after final refinement.

The trial structure was refined by a few cycles of full-matrix least-squares refinements. The function minimized was $\sum w(|F_o| - |F_c|)^2$. All reflections with F^2 values larger than $2\sigma_c(F^2)$ were included; the total number of reflections was 1730. In these preliminary refinements positional parameters and first an overall and later individual isotropic thermal parameters were refined for the eighteen non-hydrogen atoms (referred to as "heavy atoms" below). All reflections were given unit weight. The refinement converged with agreement factors

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.146$$
$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2} = 0.170$$

The parameters obtained from this refinement were used as initial parameters to determine the hydrogen positions from the neutron data as described below. The refinement of the X-ray data was continued when the final results from the neutron study became available; the positional and thermal parameters of the hydrogen atoms as determined by neutron diffraction were now included. Each reflection was assigned a weight w inversely proportional to the estimated variance of the observation

$$w^{-1} = \sigma^2(F) = \sigma^2(F^2)/4F^2$$

and

$$\sigma^2(F^2) = \sigma^2{}_c(F^2) + (kF^2)^2$$

with k equal to 0.05 and $\sigma^2{}_c$ based on counting statistics alone. The parameters refined were 54 positional parameters, 108 anisotropic thermal parameters and an overall scale factor. No attempt was made to refine the hydrogen atom parameters. In the last cycle of least-squares refinement no parameters shifted

by more than 0.1 σ; the final agreement factors for the 1730 reflections used in the refinement were $R = 0.042$ and $R_w = 0.064$. The standard deviation of an observation of unit weight $S = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ was 2.14. In this expression w is the weight of an observation, m is the total number of observations, and n is the number of parameters varied. The final positional and thermal parameters are presented in Table 2 and the root-mean-square displacements along principal axes of the thermal ellipsoids are given in Table 3. The observed and calculated structure factors are listed in Table 4. Scattering factors for P, O, and C were those given by Hanson et al.[10] The spherical scattering factor proposed by Stewart et al.[11] was used for the hydrogen atoms.

REFINEMENT OF THE NEUTRON STRUCTURE

A three-dimensional difference map was produced for which the calculated structure factors were based on the heavy atom positions from the preliminary X-ray refinement. The positions of all hydrogen atoms except those of the methyl groups were clearly defined.

A least-squares refinement of an overall scale factor and positional parameters together with anisotropic thermal parameters for all atoms except the methyl hydrogen atoms converged with $R = 0.123$, $R_w = 0.191$. Only reflections with F^2 values larger than $2\sigma_c(F^2)$ were included; the total number of such reflections was 1579. The weights were assigned in the same way as for the final X-ray refinements except that a k value of 0.10 was used.

Difference Fourier syntheses with $(F_o - F_c)$ as coefficients were now calculated for the two planes, perpendicular to the $C - C$ bonds, through the expected methyl hydrogen atoms. These two difference maps looked very similar, having a continuous ring of negative scattering density centered at the projection of the $C - C$ bond. It was therefore assumed that the methyl hydrogen atoms were disordered. Approximate hydrogen positions corresponding to ordered methyl groups for each of the two independent acetic acid molecules were deduced by assuming that the regions of the most negative scattering density corresponded to the hydrogen positions.

In the subsequent least-squares refinements all 1845 reflections with F^2 values larger than $\sigma_c(F^2)$ were included. Their weights were calculated as described earlier with a k-value equal to 0.05. The parameters refined in each cycle were 96 positional parameters and 192 anisotropic thermal parameters together with an overall scale factor. Several cycles of least-squares refinement lowered the R values to $R = 0.071$ and $R_w = 0.066$. The shifts in the last cycle were less than 0.1 σ for all parameters except those of the methyl groups. The largest shift for a thermal parameter of a methyl hydrogen atom was 0.9 σ. The mean shift for the methyl hydrogen atom positional parameters was 0.18 σ and for the thermal parameters 0.34 σ. The corresponding values for the methyl carbon atoms were 0.27 σ and 0.12 σ, respectively. The values of the methyl carbon atom positional parameters were oscillating, and this was also true for the methyl hydrogen atom parameters. The refinement was therefore halted at this point. The parameters obtained will be referred to below as the final parameters for the ordered structure model.

Table 3. Root-mean-square amplitudes of vibration. For non-hydrogen atoms the neutron result is given on the first line and the X-ray result on the second. The units are 10^{-3} Å.

Atom	Axis 1	Axis 2	Axis 3
P(1)	133(4)	174(3)	199(3)
	131(2)	190(1)	208(1)
O(1)	172(3)	209(3)	225(3)
	205(3)	216(3)	240(3)
O(2)	178(3)	200(3)	243(3)
	191(3)	208(3)	271(3)
O(3)	137(4)	207(3)	262(3)
	143(4)	234(3)	277(3)
O(4)	132(4)	197(3)	250(3)
	145(3)	221(3)	274(3)
H(1)	208(5)	210(5)	221(5)
H(2)	181(5)	244(5)	253(5)
H(3)	166(6)	229(5)	245(5)
P(11)	130(4)	185(3)	194(3)
	125(2)	194(1)	220(1)
O(11)	180(3)	204(3)	249(3)
	209(3)	223(3)	258(3)
O(12)	180(4)	194(4)	357(4)
	192(3)	201(3)	385(4)
O(13)	137(4)	200(3)	366(4)
	142(4)	231(3)	375(4)
O(14)	140(3)	200(3)	229(3)
	148(3)	213(3)	254(3)
H(11)	192(5)	218(5)	241(5)
H(12)	198(5)	232(5)	272(5)
H(13)	154(6)	247(5)	273(5)
O(5)	189(3)	218(4)	280(3)
	201(3)	246(3)	287(3)
O(6)	172(3)	229(3)	247(3)
	189(3)	245(3)	266(3)
C(1)	185(3)	204(3)	225(3)
	200(4)	203(5)	257(5)
C(2)	194(2)	258(5)	287(4)
	211(5)	286(5)	286(5)
H(5)	192(5)	246(6)	293(5)
Me(1)	170(24)	294(16)	439(33)
Me(2)	191(22)	304(23)	610(53)
Me(3)	201(19)	338(22)	391(29)
Me(4)	199(22)	334(20)	449(33)
Me(5)	210(18)	285(21)	435(35)
Me(6)	262(28)	331(28)	411(38)
O(15)	182(3)	232(3)	280(3)
	195(3)	253(3)	285(3)
O(16)	176(3)	199(3)	244(3)
	183(3)	215(3)	268(3)
C(11)	181(3)	200(3)	212(2)
	182(4)	199(5)	270(4)
C(12)	195(4)	234(5)	315(5)
	230(5)	237(5)	318(5)
H(15)	210(6)	247(6)	304(6)
Me(11)	239(20)	255(21)	469(44)
Me(12)	219(18)	380(29)	479(42)
Me(13)	189(21)	274(19)	384(27)
Me(14)	195(21)	269(17)	557(43)
Me(15)	228(19)	339(24)	407(20)
Me(16)	192(23)	245(26)	502(37)

Table 4. Observed and calculated X-ray structure factors for $CH_3COOH.H_3PO_4$. The four columns are, in order, the indices h and k, $10|F_o|$ and $10|F_c|$ (in electrons). A negative value for F_o indicates a reflection with $F^2 < 2\sigma_c(F^2)$ (not included in the least-squares refinement).
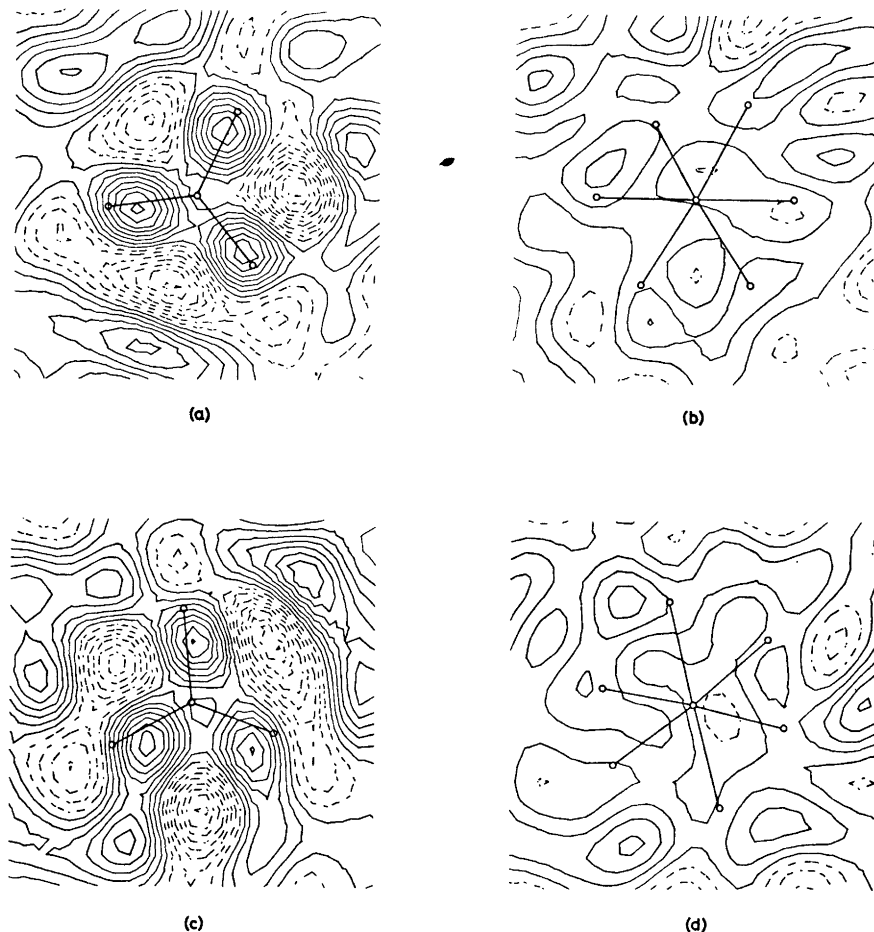
(a)

(b)

(c)

(d)

Fig. 1. Difference maps through the planes of the methyl hydrogen atoms. The circles indicate the positions of the atoms as determined by the preceding least-squares refinement. The contour interval in all four maps is 0.01×10^{-12} cm Å^{-3}. Contours: positive and zero, solid lines; negative, broken lines. (a) The C(2) methyl group with calculated structure factors based on the final parameters for the ordered structure model. The atom at the far left is Me(1) followed by Me(3) and Me(5) reading in an anticlockwise direction. (b) The C(2) methyl group with calculated structure factors based on the final parameters for the disordered structure model. Again, the atom at the far left is Me(1) followed by Me(2), Me(3), *etc.*, reading in an anticlockwise direction. (c) The C(12) methyl group. Calculated structure factors as for (a). The atom at the uppermost position is Me(15) followed by Me(11) and Me(13) reading in an anticlockwise direction. (d) The C(12) methyl group. Calculated structure factors as for (b). Again, the atom at the uppermost position is Me(15) followed by Me(16), Me(11), *etc.*, reading in an anticlockwise direction.

Difference maps were calculated through the planes of the methyl hydrogen . atoms (see Fig. 1a and c). These maps were interpreted as indicating two discrete equilibrium positions for the hydrogen atoms in each methyl group. The least-squares refinement was now continued for a model with 6 hydrogen atoms with occupancy factors of 0.5 for each methyl group. With anisotropic thermal parameters for all 38 atoms the total number of parameters to be refined was 343. Since the available core memory of the computer did not permit simultaneous refinement of all parameters, this disordered structure model had to be refined in blocks: the scale factor and all parameters for 31 atoms were refined at one time while the parameters for the remaining 7 atoms were kept fixed. In the next cycle another set of 7 atoms was held fixed. The parameters of the methyl group atoms were varied in all cycles. This procedure was repeated until in the last cycle no non-methyl parameter shifted by more than 0.2 σ. The largest shift for any of the methyl carbon atom parameters was 0.15 σ. The mean shift in the positional parameters of the methyl half-hydrogen atoms was 0.29 σ and the largest 0.7 σ. The corresponding values for the thermal parameters of these atoms were 0.21 σ and 0.6 σ, respectively. Since many of the methyl half-hydrogen atom parameters are highly intercorrelated, further refinement did not seem justified. The final residuals for the 1845 reflections used in the refinement were $R = 0.056$ and $R_w = 0.051$. Use of Hamilton's R ratio test [12] indicated that the improvement in R_w compared to that of the ordered model was significant. Difference maps calculated through the planes of the methyl hydrogen atoms of the disordered model showed much reduced scattering density compared to
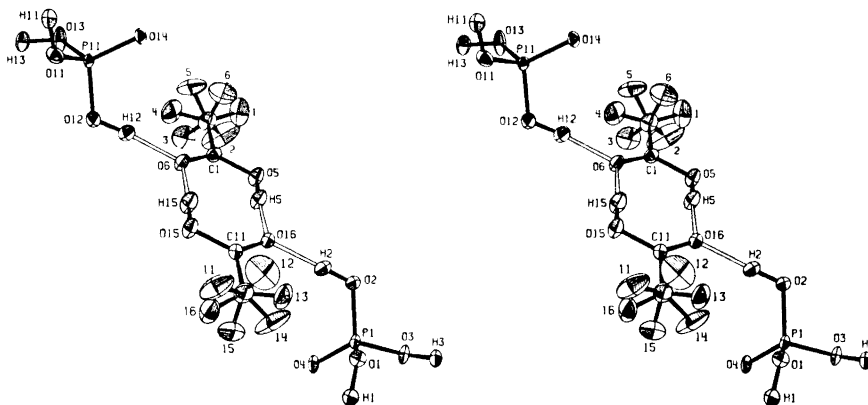

Fig. 2. Stereopair of an asymmetric unit of $CH_3COOH.H_3PO_4$. Thermal ellipsoids are scaled to include 20 % probability. Covalent bonds are filled and hydrogen bonds open. For clarity, the methyl half-hydrogen atoms only carry their respective numbers. The following symmetry operations have been applied to the coordinates of Table 2:

$$\begin{array}{llll}
\text{Atoms P(1)} & \text{to H(3):} & 1-x, & -y, & 1-z \\
\text{Atoms P(11)} & \text{to H(13):} & x-1, & y, & 1+z \\
\text{Atoms O(5)} & \text{to Me(6):} & x, & y, & z \\
\text{Atoms O(15)} & \text{to Me(16):} & 1-x, & -y, & 2-z
\end{array}$$

the difference density of the ordered model and no interpretable detail (see Fig. 1). The standard deviation for an observation of unit weight was 1.29. The final positional and thermal parameters for the disordered model are presented in Table 2 and the root-mean-square displacements along principal axes of the thermal ellipsoids are given in Table 3. The numbering of the atoms is shown in Figs. 2 − 4. The observed and calculated structure factors are listed in Table 5. The neutron scattering lengths used were, in units of 10^{-12} cm: 0.51, 0.58, 0.665, and -0.372 for P, O, C, and H, respectively.

COMPUTATION

The least-squares refinements of the neutron structure were carried out on the CDC 6600 computer at Brookhaven National Laboratory (BNL). The final refinements of the X-ray structure were done on the CDC 6600 computer at the CDC Data Center in Stockholm. Other calculations were performed
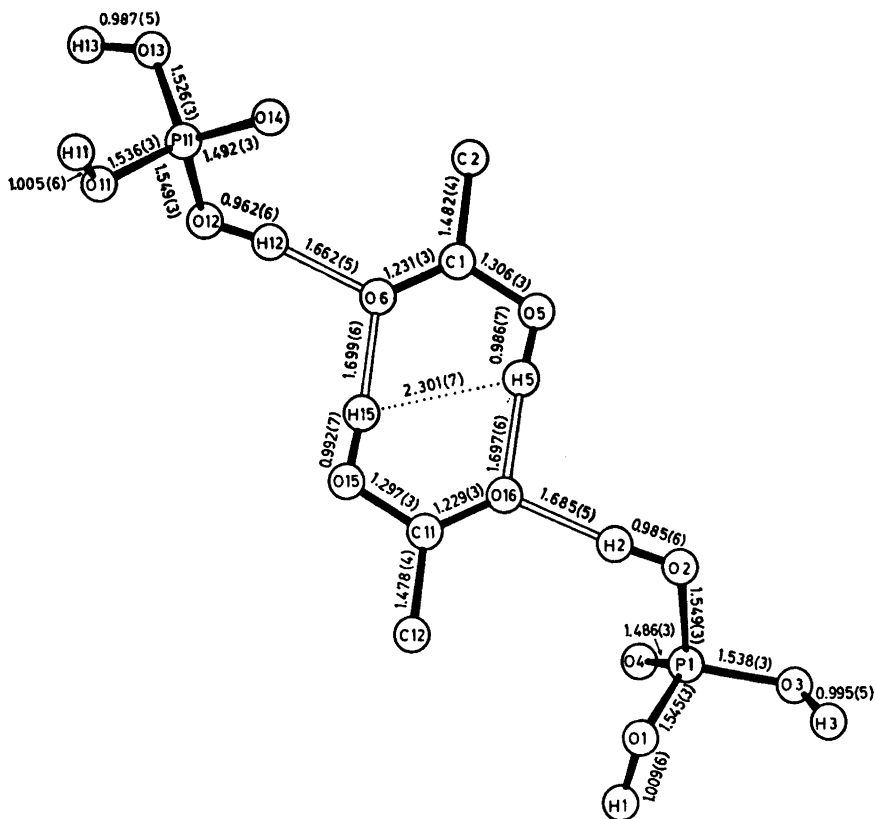

Fig. 3. Bond distances.

Table 5. Observed and calculated neutron structure factors for $CH_3COOH.H_3PO_4$. The four columns are, in order, the indices k and l, $100|F_o|$ and $100|F_c|$ (in units of 10^{-12} cm). A negative value for F_o indicates a reflection with $F^2 < \sigma_c(F^2)$ (not included in the least-squares refinement).

Table 5. Continued.

ANGLE	NEUTRON	X-RAY
O11–P11–O12	101.9(2)	102.0 (1)
O11–P11–O13	110.0(2)	109.8 (1)
O11–P11–O14	115.4(2)	115.7 (1)
O12–P11–O13	108.6(2)	108.4 (2)
O12–P11–O14	112.0(2)	112.4(1)
O13–P11–O14	108.5(2)	108.2(1)

ANGLE	NEUTRON	X-RAY
O1–P1–O2	104.4(2)	104.2(1)
O1–P1–O3	110.4(2)	110.2(1)
O1–P1–O4	114.1(2)	114.6(1)
O2–P1–O3	105.6(2)	105.2(1)
O2–P1–O4	112.7(2)	112.8(1)
O3–P1–O4	109.3(2)	109.3(1)

Fig. 4. Bond angles.

partly at BNL and partly on the CDC 3600 computer in Uppsala. In addition to the programs presented briefly by Jönsson and Liminga[13] the following programs from the BNL crystallographic program library were used: EFACT for calculation of normalized structure amplitudes, FORDAP for calculation and plotting of Fourier syntheses, and XDATA to perform the Wilson plot. These programs together with Long's sign-determining program [8] were also adapted for use on the CDC 3600 computer.

COMPARISON OF NEUTRON AND X-RAY RESULTS

The X-ray investigation was carried out chiefly with the intention of solving the structure and was not aimed at obtaining highly accurate X-ray data. For this reason no attempt was made to locate the hydrogen atoms using the X-ray data. Nevertheless, a comparison of the heavy atom parameters from the two final refinements is of some interest (see Table 2). In addition to the parameter values with standard deviations this table also gives the value of Δ/σ where Δ is defined as the X-ray obtained parameter value minus the neutron obtained parameter value and σ is the combined standard deviation defined as

$$\sigma = (\sigma^2_{\text{X-ray}} + \sigma^2_{\text{neutron}})^{1/2}$$

The agreement between the positional parameters is relatively satisfactory, only six of the positional parameters differ by more than twice the combined standard deviations.

A comparison of the X-ray and neutron obtained thermal parameters reveals large discrepancies for all β_{33} values. This must be due to the fact that the crystal used for collecting the X-ray data was longer than the cross-section of the primary beam so that, for the higher layers, a larger volume of the crystal was bathed in the X-ray beam. The crystal was rotated around the c axis so the systematic error introduced will mainly affect the β_{33} values.

Bond distances for the heavy atoms are compared in Table 6 and bond angles in Fig. 4. Table 6 also gives the bond lengths calculated from the final cycle of refinement for the ordered neutron structure model. With the exception of the two C − C distances, the results of the two neutron refinements have no differences larger than about 1.5 times the combined standard deviations. No significant differences therefore occur between distances not involving the methyl atoms. This is expected since the parameters of the non-methyl atoms are essentially uncorrelated with those of the methyl atoms.

Most of the neutron and X-ray obtained bond distances are in good agreement; there are, however, a few significant differences. Since the X-ray data are undoubtedly affected by systematic errors, only the neutron results will be considered in the following discussion.

DISCUSSION OF THE STRUCTURE

The structure is composed of uncharged acetic acid and phosphoric acid molecules. The asymmetric unit of the structure contains two acetic acid molecules and two phosphoric acid molecules. The two independent acetic

Table 6. Bond lengths. Neutron 1 is from the final refinement with an ordered model for the methyl hydrogen atoms. Neutron 2 is based on the parameters given in Table 2 for the results from the final refinement using a disordered model for the methyl hydrogen atoms. Distances given within brackets are corrected for thermal riding motion.[14]

	Neutron 1		Neutron 2		X-Ray	
P(1) —O(1)	1.546(4)	[1.559]	1.545(3)	[1.558]	1.545(2)	[1.558]
P(1) —O(2)	1.548(4)	[1.564]	1.549(3)	[1.564]	1.552(2)	[1.569]
P(1) —O(3)	1.540(4)	[1.553]	1.538(3)	[1.551]	1.533(2)	[1.549]
P(1) —O(4)	1.484(4)	[1.494]	1.486(3)	[1.496]	1.482(2)	[1.497]
O(1) —H(1)	1.008(7)		1.009(6)			
O(2) —H(2)	0.976(8)		0.985(6)			
O(3) —H(3)	0.986(7)		0.995(5)			
P(11)—O(11)	1.535(4)	[1.550]	1.536(3)	[1.551]	1.524(2)	[1.543]
P(11)—O(12)	1.552(4)	[1.586]	1.549(3)	[1.582]	1.541(2)	[1.579]
P(11)—O(13)	1.526(4)	[1.560]	1.526(3)	[1.560]	1.523(2)	[1.559]
P(11)—O(14)	1.491(4)	[1.499]	1.492(3)	[1.499]	1.492(2)	[1.501]
O(11)—H(11)	1.002(8)		1.005(6)			
O(12)—H(12)	0.946(9)		0.962(6)			
O(13)—H(13)	0.982(7)		0.987(5)			
C(1) —O(5)	1.308(4)	[1.322]	1.306(3)	[1.320]	1.302(4)	[1.316]
C(1) —O(6)	1.228(4)	[1.235]	1.231(3)	[1.239]	1.237(4)	[1.244]
C(1) —C(2)	1.492(4)	[1.512]	1.482(4)	[1.502]	1.470(5)	[1.494]
O(5) —H(5)	0.976(10)	[0.979]	0.986(7)	[0.992]		
C(2) —Me(1)	0.974(16)	[1.154]	1.07 (2)	[1.13]		
C(2) —Me(2)			1.06(3)	[1.22]		
C(2) —Me(3)	0.951(16)	[1.162]	1.05(3)	[1.11]		
C(2) —Me(4)			1.05(2)	[1.13]		
C(2) —Me(5)	0.969(17)	[1.155]	1.11(2)	[1.17]		
C(2) —Me(6)			0.91(4)	[0.99]		
Mean C(2) —Me	0.965(10)		1.04(1)			
C(11)—O(15)	1.296(4)	[1.314]	1.297(3)	[1.315]	1.305(4)	[1.318]
C(11)—O(16)	1.230(4)	[1.234]	1.229(3)	[1.232]	1.231(4)	[1.236]
C(11)—C(12)	1.492(4)	[1.516]	1.478(4)	[1.504]	1.462(5)	[1.486]
O(15)—H(15)	0.985(10)	[0.998]	0.992(7)	[1.006]		
C(12)—Me(11)	0.963(14)	[1.132]	1.04(3)	[1.11]		
C(12)—Me(12)			1.09(3)	[1.19]		
C(12)—Me(13)	0.942(15)	[1.146]	1.00(2)	[1.04]		
C(12)—Me(14)			1.07(2)	[1.18]		
C(12)—Me(15)	0.968(20)	[1.168]	1.09(3)	[1.16]		
C(12)—Me(16)			0.99(2)	[1.08]		
Mean C(12)—Me	0.958(10)		1.05(1)			

acid molecules are connected by O—H···O hydrogen bonds to form acetic acid dimers. Each acetic acid molecule is joined by an O—H···O bond to a phosphoric acid molecule as shown in Fig. 2. The remaining two hydrogen atoms in each phosphoric acid molecule are engaged in O—H···O bonds with phosphoric acid neighbors (see Fig. 5). A two-dimensional system of hydrogen-bonded phosphoric acid molecules is thus formed giving infinite puckered layers of phosphoric acid molecules in the structure. The acetic acid dimers are situated between the phosphoric acid layers (a packing diagram is given in Fig. 6).
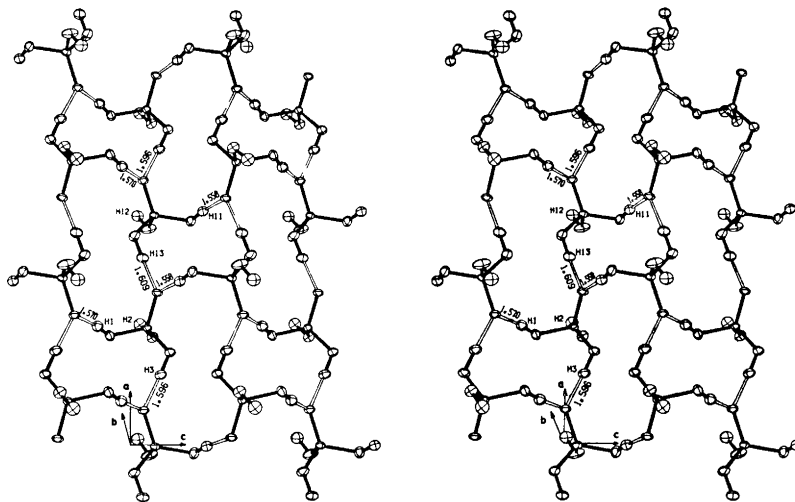
Fig. 5. Stereoscopic illustration showing part of a hydrogen-bonded layer of phosphoric acid molecules. Thermal ellipsoids are scaled to include 20 % probability.
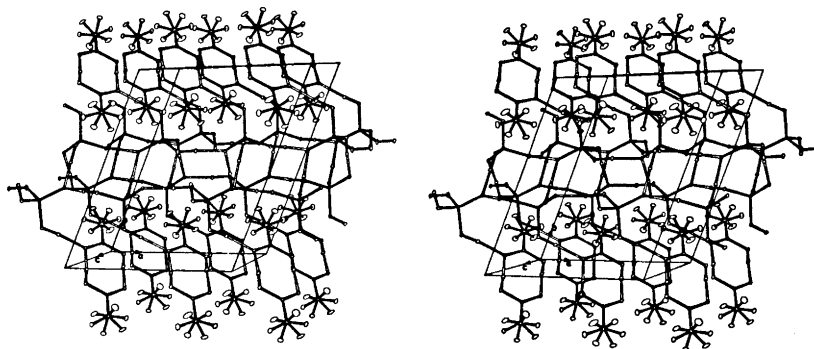

Fig. 6. Stereoscopic illustration of the packing in $CH_3COOH.H_3PO_4$. Thermal ellipsoids are scaled to include 2 % probability.

The acetic acid dimer

The structure contains acetic acid dimers composed of two crystallographically independent acetic acid molecules (Figs. 2−4). The methyl groups are disordered, the final cycles of least-squares refinement being performed using a model with six half-hydrogen atoms in each methyl group. The positional and thermal parameters of the half-hydrogen atoms are not very accurately determined since they are highly intercorrelated. The mean value for the C−H distances in the two disordered methyl groups are 1.04(1) and 1.05(1) Å. These values are significantly shorter than the commonly accepted value

of 1.09 Å. The mean C − H distances from the final ordered model refinement are appreciably shorter, 0.965(10) and 0.958(10) Å. It is clear that a relatively large correction for thermal motion has to be applied to these values. The corrected bond lengths assuming thermal riding motion,[14] are given in Table 6. As has been observed earlier for methyl groups [15,16] this correction leads to bond lengths which are too long; the riding motion model is thus not appropriate in these cases.

The heavy atoms and the hydroxyl hydrogen atom of each acetic acid molecule are coplanar. The equations for the least-squares planes of the acetic acid molecules calculated according to Hamilton[17] are listed in Table 7.

Table 7. Least-squares planes for acetic acid and distances of the atoms from these planes. Equations for the planes are of the form $Ax + By + Cz - D = 0$, where x, y, z are fractional coordinates of the unit cell axes a, b, and c, and D is the distance of the plane from the origin in Å. A prime indicates that the symmetry operation: $1 - x$, $- y$, $2 - z$ has been applied to the atom.

	Atoms defining plane	Equation
I	O(5), O(6), C(1), C(2), H(5)	$5.183\,x + 9.603\,y + 2.454\,z - 3.765 = 0$
II	O(15)′, O(16)′, C(11)′, C(12)′, H(15)′	$5.155\,x + 9.527\,y + 2.533\,z - 3.891 = 0$
III	O(5), O(6), C(1), C(2), H(5), O(15)′, O(16)′, C(11)′, C(12)′, H(15)′	$5.136\,x + 9.642\,y + 2.433\,z - 3.751 = 0$

Displacements from plane (Å)

	Plane I	Plane II	Plane III
O(5)	0.001(3)		− 0.012(3)
O(6)	0.001(3)		− 0.005(3)
C(1)	− 0.002(2)		− 0.007(2)
C(2)	0.007(5)		0.013(5)
H(5)	0.004(5)		− 0.015(5)
O(15)′		0.000(3)	0.005(3)
O(16)′		0.001(2)	0.019(2)
C(11)′		− 0.002(2)	0.000(2)
C(12)′		0.005(4)	− 0.019(4)
H(15)′		0.006(5)	0.029(5)

The weight for each atom was obtained from the inverse matrix of the final least-squares refinement cycle. Also listed is the equation of the plane for the dimer based on ten atoms. None of these atoms deviate from the plane by more than 0.03 Å, but some of the deviations from the plane are nevertheless highly significant.

The largest difference between corresponding bond lengths and angles in the two independent acetic acid molecules are, except for values involving the inaccurately determined half-hydrogen atoms, within twice their combined standard deviations. This good agreement holds not only for covalent bond lengths and angles but also for the corresponding parameters involving the two internal hydrogen bonds (Figs. 3 − 4). The bond distances and angles quoted in the following discussion of the acetic acid dimer will be the mean values rather than the individual values. This is justified since no significant differences exist between these values.

The normal crystalline modification of acetic acid has a structure comprising infinite hydrogen-bonded chains of acetic acid molecules.[16,18,19] A comparison of the hydrogen bond lengths and angles in the present acetic acid dimer with those of the acetic acid chain structure (neutron results) [16] reveals certain differences. The two internal hydrogen bonds of the dimer have a mean $H \cdots O$ distance of 1.698(4) Å, the mean $O \cdots O$ distance is 2.685(3) Å. In the chain structure the corresponding values are 1.642(13) and 2.631(8) Å. The hydrogen bonds in the dimer have a mean $O - H \cdots O$ angle of 175.3(3)° whereas the chain structure has a more bent hydrogen bond with an $O - H \cdots O$ angle of 164.8(10)°. The acceptor oxygen atoms in the dimer, O(6) and O(16), also act as acceptor atoms for hydrogen bonds donated by the phosphoric acid molecules (Fig. 2). It therefore seems reasonable that their $H \cdots O$ distances are slightly longer than in the chain structure.

The phosphoric acid layers

The two crystallographically independent phosphoric acid molecules show some significant differences between corresponding bond lengths and angles. This effect appears to be real. It must therefore be assumed that the geometry of the phosphoric acid molecule is easily affected by differences in the surrounding force fields.

A neutron diffraction study of crystalline phosphoric acid has been carried out by Cole.[20] The structure consists of phosphoric acid molecules connected in a sheet-like network by hydrogen bonds. It thus closely resembles the phosphoric acid layers in the present structure. The bond lengths and angles in the phosphoric acid molecules of the two structures agree reasonably well. The mean values for the $P - O(H)$ bond lengths are 1.546(2) Å in the phosphoric acid structure and 1.540(1) Å in the present structure. The $P - O$ distances involving the oxygen atoms with no hydrogen atom directly attached have a mean value of 1.489(2) Å in the present structure, compared with the value of 1.496(3) Å for phosphoric acid itself.

The $O - P - O$ angles in structures containing phosphoric acid are expected to fall into two classes: the $O(H) - P - O(H)$ angles should be smaller than the tetrahedral angle, whereas the $O - P - O(H)$ angles should be larger. This has also been confirmed by Baur and Khan [21] for a number of structures containing different phosphate groups. It is true for all the individual bond angles of these categories in the phosphoric acid structure.[20,21] The mean value for the $O(H) - P - O(H)$ bond angles was 105.9° and the mean value for the $O - P - O(H)$ bond angles was 112.7°. The corresponding values in the present structure are 106.8 and 112.0°, respectively. Several of the individual bond angles, however, do not agree with this general trend.

The $P - O - H$ bond angles are, in both structures, appreciably larger than the tetrahedral value. In crystalline phosphoric acid, the mean value for the $P - O - H$ angles is 117.0°, the corresponding value in the present structure is 118.6°. Values larger than the tetrahedral angle have also been found for the $P - O - H$ bond angles in the $H_2PO_4^-$ ion. The mean $P - O - H$ bond angle in $N_2H_5H_2PO_4$ and $N_2H_6(H_2PO_4)_2$ as determined by neutron diffraction were 114.7 and 115.7°, respectively.[13,22]

The bond lengths and angles of interest in connection with the hydrogen bonds in the structure are summarized in Table 8. The hydrogen bonds connecting the phosphoric acid molecules to one another are illustrated in Fig. 5. These hydrogen bonds are similar in length to the corresponding bonds in crystalline phosphoric acid for which the H···O distances were found to be 1.552(4) and 1.584(4) Å.[20]

Table 8. Hydrogen-bond distances and angles.

X	H	Y	Z	X····Y (Å)	X−H (Å)	H···Y (Å)	∠X−H···Y (°)	∠H···Y−Z (°)
O(1)	H(1)	O(14)	P(11)	2.574(3)	1.009(6)	1.570(5)	172.3(4)	122.4(2)
O(2)	H(2)	O(16)	C(11)	2.667(4)	0.985(6)	1.685(5)	174.2(4)	131.7(2)
O(3)	H(3)	O(14)	P(11)	2.590(3)	0.995(5)	1.596(5)	176.7(4)	128.8(2)
O(11)	H(11)	O(4)	P(1)	2.558(4)	1.005(6)	1.558(5)	172.9(4)	123.6(2)
O(12)	H(12)	O(6)	C(1)	2.617(4)	0.962(6)	1.662(5)	171.1(5)	128.8(2)
O(13)	H(13)	O(4)	P(1)	2.594(3)	0.987(5)	1.609(5)	175.5(5)	132.5(2)
O(5)	H(5)	O(16)	C(11)	2.681(4)	0.986(7)	1.697(6)	175.4(4)	124.5(2)
O(15)	H(15)	O(6)	C(1)	2.688(4)	0.992(8)	1.699(6)	175.2(5)	123.9(2)

Short intermolecular contacts

All interatomic distances shorter than 3.4 Å were calculated. Excluding the hydrogen bonds, seven intermolecular contacts were shorter than the sum of the van der Waals radii. The methyl half-hydrogen atoms were involved in two short contacts, O(1)···Me(14) = 2.54 Å and O(11)···Me(16) = 2.48 Å. An even shorter methyl hydrogen − oxygen contact of length 2.41 Å was observed in the neutron diffraction study of crystalline acetic acid.[16] The distance between the two hydroxyl hydrogen atoms in the acetic acid dimer, H(5)··· H(15), was 2.301 Å. The remaining short contacts involved the carbonyl carbon atoms: C(1)···H(15) = 2.595 Å, C(11)···H(5) = 2.599 Å (both these contacts are within one acetic acid dimer), C(1)···H(12) = 2.616 Å, and C(11)···H(2) = 2.665 Å. The carbonyl carbon atom has earlier been found to be involved in close approaches with oxygen atoms in a number of cyclic di- and triketones.[23,24]

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