Chiang, Karle & Seibert, 1983). Diaveridine, a molecule like trimethoprim with a similar conformation and similar packing but lacking one of the OCH_3 groups (Koetzle & Williams, 1978), has some antibacterial activity, but much less than trimethoprim. This remarkable difference in antibacterial properties appears to be associated with the number of methoxy groups and their disposition, not with the orientation of the two aryl groups with respect to each other. Increasing the number of methoxy groups, particularly since they protrude above and below the plane of the phenyl ring, obviously increases the thicknesss of this part of the molecule. Another factor that may be associated with the biological activity is the accessibility of the O atoms and the attractive forces they represent. In the tetra- and pentasubstituted molecules, the CH_3 groups tend to shield the O atoms from the exterior, while in trimethoprim the three O atoms present a concerted charge density to the exterior. Diaveridine, which exhibits partial activity, has only two O atoms to present to the exterior.

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The Structure and Thermal Motion of Phosphorylethanolamine at 122 K from Neutron Diffraction

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Abstract

At 122 K, the crystal structure of phosphorylethanolamine ($C_2H_8NO_4P$) is monoclinic, space group $P2_1/c$, $Z = 4$, with $a = 9.015$ (1), $b = 7.745$ (1), $c = 8.788$ (2) Å, $\beta = 102.51$ (1)°, $\lambda = 1.0470$ (1) Å, $\mu = 0.233$ mm^{-1}. Full-matrix least-squares refinement based on 2473 neutron reflections with $\sin \theta/\lambda \leq 0.79$ Å^{-1} gave convergence with $R_w(F^2) = 0.041$. Nuclear anisotropic thermal parameters have been analyzed to describe the molecular thermal motion including non-rigid vibrations. Librational corrections for the bond lengths [maximum 0.008 (1) Å] are highly significant in terms of the e.s.d.'s in uncorrected values [0.001 Å or less]. The C–H distances with both harmonic librational and anharmonic stretching-motion corrections range from 1.095 (4) to 1.099 (4) Å. These are estimated r_e bond lengths in satisfactory agreement with values determined for C–H theoretically and by other experimental methods. The conformation at the P–O bonds in the monoester H–O–P–O–C group is $(+)$-*ac*, $(-)$-*sc*. The terminal O–H and NH_3 groups are twisted 40° and 20° respectively from ideally staggered

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conformations, presumably because they form strong H bonds, having H$\cdots$O distances of 1·535 Å for O–H$\cdots$O and 1·713, 1·714, 1·747 Å for N–H$\cdots$O interactions. The ester O atom is not H bonded.

Introduction

The structure of 2-aminoethyl phosphate or phosphorylethanolamine (PEA, Fig. 1) is of interest because this is a simple molecule containing the phosphate monoester and ethanolamine groups, both of which occur widely in biological systems. The crystal structure of PEA, first determined by Kraut (1961) from X-ray photographic intensity data, shows the molecule to be zwitterionic with the molecular backbone (H–O–P–O–C–C–N) twisted both at the ester P–O bond and at the ethanolamine C–C bond. More detailed determinations of the crystal structure of PEA at low temperature (122 K) have now been carried out using both X-ray and neutron diffraction. The aim of the present neutron work is to provide more accurate values for the nuclear configuration, particularly for the H atoms. These results have been most useful in the subsequent X-ray determination of the charge density and electrostatic potential distributions (Swaminathan & Craven, 1984).

Experimental

Crystals of 2-aminoethyl phosphate grew readily as long prisms during evaporation of a saturated aqueous solution. The crystal used in the data collection was cleaved from a specimen several cm long; it had a volume of 4·26 mm^3 and was bounded by the forms {110} and {10$\bar{2}$}, the latter being the cleavage plane. The crystal was mounted with the c axis almost parallel to the φ axis of the four-circle diffractometer, following the experimental procedures previously described (Weber, Craven & McMullan, 1983). The crystal temperature was maintained at 122 ± 0·5 K.

The wavelength 1·0470 (1) Å of the incident neutron beam had been previously determined by a least-squares fit of sin^2 θ values for a standard KBr crystal, assuming the lattice parameter $a_0 = 6\cdot6000$ Å
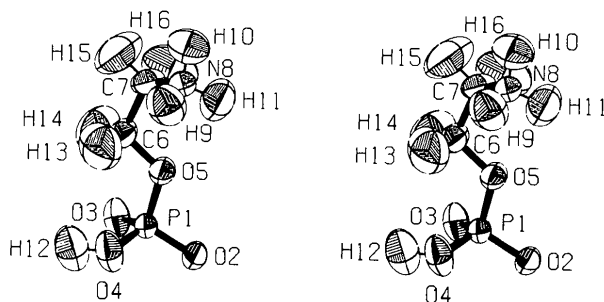

Fig. 1. Phosphorylethanolamine. Atomic nomenclature and thermal ellipsoids at 99% probability (Johnson, 1976).

Table 1. *Experimental conditions*

Monochromator	Be(002), reflection geometry
Scan mode	ω–2θ, stepwise
Scan range	2·8° for 2θ < 55°
	(1·9 + 2·53 tan θ)° for 2θ > 55°
Reference reflections	26$\bar{3}$, 5$\bar{2}$4
(sin θ/λ)$_{max}$	0·786 Å^{-1}
Wavelength	1·0470 (1) Å
Linear absorption coefficient	0·223 mm^{-1}
Transmission factors	0·72–0·82
Number of reflections measured	2670
Number of unique reflections used in refinement	2473
Number of reflections with $F_o^2 \leq 3\sigma(F_o^2)$	528

(at 295 K). Lattice parameters for PEA at 122 K were obtained by least-squares fit of sin^2 θ values measured for 54 reflections with 48° < 2θ < 53°.

Neutron intensities were measured for the quadrant in reciprocal space ($\pm h$, $\bar{k}$, l). Additional reflections were also measured in order to verify the diffraction symmetry (2/m). The intensities of two check reflections were constant within 2% throughout the data collection. Every third reflection profile was plotted to permit the visual determination of the peak width for use in estimating backgrounds. Constant values of the peak width were chosen for reflections within successive shells at intervals $\Delta 2\theta = 20°$. Integrated intensities were corrected for neutron absorption using an analytical procedure (de Meulenaer & Tompa, 1965; Templeton & Templeton, 1973). The linear absorption coefficient for PEA (Table 1) was calculated assuming the mass absorption coefficient of H to be 25·3 m^2 kg^{-1} (McMullan & Koetzle, 1979). The final agreement factor between symmetry-related reflections was $R = \sum |F_o^2 - \langle F_o^2 \rangle| / \sum \langle F_o^2 \rangle = 0\cdot043$. Further details of data collection and processing are given in Table 1.

The structure was refined with a locally modified version of the full-matrix least-squares program of Busing, Martin & Levy (1962). The function minimized was $\sum w(F_o^2 - F_c^2)^2$, where the weight, w, was assumed to have the form $[\sigma^2(F_o^2)_{counts} + (0\cdot01 F_o^2)^2 + (58\cdot53/F_o^2)^2]^{-2}$. The coherent neutron scattering lengths were taken from Koester (1977), and the initial values for the structure parameters were those of Kraut (1961). Final values are in Table 2.* In the last refinement cycle, the most significant parameter change was 0·02σ. Neutron extinction effects were not severe, but were found to be significantly anisotropic. The components of an anisotropic extinction tensor, assuming a crystal of type I with Lorentzian mosaicity (Becker & Coppens, 1974), had the

Table 2. *Nuclear parameters*

Fractional coordinates ($\times 10^5$) and anisotropic thermal parameters ($\text{Å}^2 \times 10^4$). Temperature factors have the form $\exp[-2\pi^2\sum_i\sum_j h_i h_j a_i^* a_j^* U_{ij}]$. E.s.d.'s given in parentheses refer to the least significant digit.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	23366 (6)	2421 (7)	11566 (7)	81 (2)	95 (2)	131 (2)	−4 (2)	2 (2)	8 (2)
O(2)	36975 (6)	−7696 (7)	19397 (8)	106 (2)	103 (2)	290 (3)	−2 (2)	−36 (2)	33 (2)
O(3)	16883 (6)	−1434 (8)	−5384 (7)	107 (2)	198 (2)	140 (2)	−9 (2)	22 (2)	−50 (2)
O(4)	10467 (6)	717 (9)	20889 (7)	120 (2)	320 (3)	120 (2)	−42 (2)	15 (2)	26 (2)
O(5)	28804 (6)	22109 (6)	13346 (7)	120 (2)	89 (2)	201 (3)	−2 (2)	−20 (2)	−3 (2)
C(6)	17964 (5)	35296 (6)	7341 (6)	136 (2)	107 (2)	181 (2)	7 (1)	−17 (2)	−4 (2)
C(7)	26311 (6)	52133 (6)	7048 (6)	190 (2)	106 (2)	139 (2)	1 (1)	5 (2)	18 (2)
N(8)	34736 (4)	57299 (4)	22864 (4)	114 (1)	100 (1)	153 (1)	3 (1)	22 (1)	7 (1)
H(9)	28305 (12)	55123 (14)	31218 (13)	235 (4)	283 (5)	241 (5)	−25 (4)	76 (4)	8 (4)
H(10)	37063 (12)	70517 (13)	22750 (14)	276 (5)	162 (4)	312 (5)	−35 (3)	41 (4)	−12 (4)
H(11)	45019 (11)	50699 (14)	26121 (13)	204 (4)	250 (5)	284 (5)	53 (3)	20 (4)	18 (4)
H(12)	−250 (11)	1016 (16)	14309 (13)	176 (4)	339 (5)	238 (5)	−37 (3)	41 (3)	1 (4)
H(13)	9690 (13)	36234 (16)	14800 (17)	250 (5)	281 (5)	453 (7)	9 (4)	122 (5)	−27 (5)
H(14)	11967 (14)	32133 (16)	−4551 (15)	355 (6)	274 (5)	300 (6)	−1 (4)	−122 (5)	−32 (5)
H(15)	18163 (15)	62297 (16)	2433 (16)	404 (6)	216 (4)	371 (7)	60 (4)	−94 (5)	45 (5)
H(16)	34367 (16)	51254 (18)	−608 (15)	458 (6)	371 (6)	279 (6)	−80 (5)	175 (5)	−23 (5)

least-squares values $g_{11} = 12\cdot4$ (8), $g_{22} = 4\cdot7$ (9), $g_{33} = 19$ (1), $g_{12} = 0\cdot8$ (8), $g_{13} = 0\cdot4$ (8), $g_{23} = -6\cdot9$ (8) rad$^{-1}\times10^{-4}$. The reflection most affected by extinction was $10\bar{2}$ with $0\cdot69F_c^2$. The final agreement index was $R_w(F^2) = [\sum w|F_o^2 - F_c^2|^2/\sum (w^2F_o^2)^2]^{1/2} = 0\cdot041$ (unweighted $R = 0\cdot038$), and the goodness of fit $S = [\sum w|\Delta F^2|^2/(n_{obs} - n_{param})]^{1/2} = 1\cdot201$.

Results and discussion

(a) Molecular packing and H bonding

In the crystal structure, molecules of PEA have their longest dimension approximately parallel to the *b* axis (Fig. 2). Short intermolecular H bonds (Table 3) give rise to a three-dimensional network. The O–H···O and two N–H···O interactions link the zwitterions in sheets parallel to the crystal cleavage plane ($10\bar{2}$). The fourth and longest H bond, N–H(9)···O(3), provides the cross-linking of sheets.* Although the sheets pack with partial overlap of methylene groups, there are no H···H intermolecular distances closer than 2·6 Å.

It is of interest that the ester oxygen atom O(5) is not H-bonded and is not involved in any intermolecular distances less than 2·8 Å. As was noted by Sundaralingam (1968), there is a short N(8)···O(5) intramolecular distance, presently determined as 2·867 (1) Å, which is well within the range observed for N–H···O interactions. However, the shortest H···O(5) distance, which involves H(11), has a value of 2·755 (1) Å and the N–H···O angle is only 85·4 (1)°. On the basis of such geometrical arguments, intramolecular H bonding is not important for determining the observed folded conformation of the molecule.

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* It is also useful to describe the crystal structure in terms of H-bonded sheets of zwitterions parallel to (001). As noted by Swaminathan & Craven (1984), the arrangement of PEA zwitterions in these sheets is very similar to the arrangement of the polar PEA head-groups in the bilayers of the crystal structure of 1,2-dilauroyl-DL-phosphatidylethanolamine (Hitchcock, Mason, Thomas & Shipley, 1974).

Table 3. *Hydrogen-bonding distances and angles*

These values are not corrected for thermal-motion effects.

D–H···A	D···A (Å)	H···A (Å)	D–H···A (°)
O(4)–H(12)···O(3^i)	2·546 (1)	1·535 (1)	176·1 (1)
N(8)–H(9)···O(3^{ii})	2·790 (1)	1·747 (1)	177·7 (1)
N(8)–H(10)···O(2^{iii})	2·740 (1)	1·713 (1)	166·6 (1)
N(8)–H(11)···O(2^{iv})	2·750 (1)	1·714 (1)	172·1 (1)

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

(b) The molecular conformation

The torsion angles in PEA (Table 4) are within the ranges of preferred values which have been compiled from X-ray studies of related crystal structures (Sundaralingam, 1968, 1969). Thus the N–C–C–O configuration has the ideal synclinal value within experimental error [−59·9 (1)°]. Indeed, in the view down
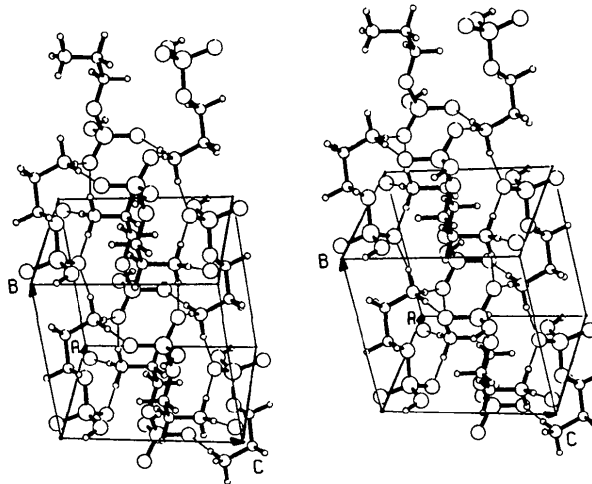

Fig. 2. Stereoscopic view of the crystal structure of phosphorylethanolamine. Circles in order of decreasing size represent P, O, N, C and H atoms. The thin lines connecting H atoms with O atoms represent H bonds. The O–H···O interactions (not shown) involve the phosphate groups of molecules which are related by the centers of symmetry at the origin and the center of the *bc* face of the unit cell.

Table 4. *Torsion angles* (°)

Values are calculated for the molecule shown in Fig. 1 using the positional parameters from Table 2. They are not corrected for thermal-motion effects. The e.s.d.'s in all torsion angles are 0·1°. The enantiomeric molecule in the structure has torsion angles with the opposite sign.

H(12)–O(4)–P(1)–O(5)	100·0	O(3)–P(1)–O(5)–C(6)	55·8
O(4)–P(1)–O(5)–C(6)	−61·6	H(13)–C(6)–C(7)–N(8)	59·9
P(1)–O(5)–C(6)–C(7)	−167·5	H(14)–C(6)–C(7)–N(8)	179·9
O(5)–C(6)–C(7)–N(8)	−59·9	H(15)–C(7)–C(6)–O(5)	179·7
C(6)–C(7)–N(8)–H(10)	−160·6	H(16)–C(7)–C(6)–O(5)	61·5
H(12)–O(4)–P(1)–O(3)	−17·6	H(9)–N(8)–C(7)–C(6)	−41·9
O(2)–P(1)–O(5)–C(6)	−178·0	H(11)–N(8)–C(7)–C(6)	80·1

the C–C bond, all six bonds including C–H are almost ideally staggered. The conformation about the C–O bond is close to antiperiplanar [−167·5 (1)°] and about the HO–P–O–C ester linkage it is synclinal [−61·6 (1)°]. The H–O–P–OC conformation is of interest since this is a feature which has not been well determined in the available X-ray studies of monoanionic monophosphate esters. In PEA, this torsion angle [100·0 (1)°] is almost anticlinal so that there is partial eclipsing of the O–H and phosphoryl P–O(3) bonds (Fig. 1). The ammonium group has approximate threefold rotation symmetry with C–N–H dihedral angles 118·7 (1), 119·3 (1), 122·0 (1)°. However, the NH_3.group is twisted (20°) about the C–N bond away from the ideally staggered conformation. The observed twists of both the OH and NH_3 groups enable the intermolecular O–H$\cdots$O and N–H$\cdots$O hydrogen bonds to become more nearly linear (Table 3), and hence stronger.

(c) The molecular thermal motion and bond-length corrections

The nuclear anisotropic thermal parameters in PEA have been analyzed in terms of assumed overall rigid-body motion (Schomaker & Trueblood, 1968) together with non-rigid librations of molecular fragments about selected bonds as axes (Dunitz & White, 1973). The residual $\sum_k w_k \Delta_k^2$, where $\Delta_k = (U_{ij})_o - (U_{ij})_c$ and $w_k = \sigma^{-2}(U_k)$, was minimized by full-matrix least-squares methods, using computer programs by Craven & He (1982). Subscripts o and c refer respectively to the anisotropic thermal parameters determined by neutron diffraction and those calculated from the assumed model for the molecular motion. The weights w_k come from the mean variances in $(U_{ij})_o$ for the kth atom.

A very poor fit ($R_w = 0.30$, $S = 17.7$)* was obtained by assuming simple rigid-body motion for the entire molecule. There was little improvement with the H atoms omitted ($R_w = 0.22$, $S = 18.1$). Strong indications of non-rigid motion came from the non-zero values for $\Delta(A, B) = \langle u_A^2 \rangle - \langle u_B^2 \rangle$. Here, $\langle u_A^2 \rangle$ and $\langle u_B^2 \rangle$ are mean-square (m.s.) amplitudes of thermal vibra-

tion for atoms A and B along the direction of the vector $A\cdots B$ within the molecule. Most notable were the large values for atoms at opposite ends of the molecule, such as $\Delta[N, O(4)] = 0.0202$ (3) $Å^2$.

Many models were tested in which up to five molecular fragments were considered to be librating about various bonds of the molecular backbone. A presumed internal libration was rejected as a parameter in the model if the resulting m.s. amplitude was less than 3σ. With the H atoms omitted, the best fit ($R_w = 0.125$, $S = 10.3$) was obtained with the molecule rigid except for atoms O(3) and O(4). This model involved the libration of O(3) and O(4) with m.s. amplitude 32 (4) deg^2 about the axis P–O(2).

The H atoms were then included in the analysis, with each methylene group assumed to be librating about the bonds to the two neighboring backbone atoms. These librations represent a combination of CH_2 scissor and wagging motion. Torsional motion was introduced for the NH_3 group about the C(7)–N bond. After the initial least-squares fitting, the residual values $(U_{ij})_o - (U_{ij})_c$ were transformed to local axes and checked for other plausible internal modes which might not be readily expressed as librations about bonds. There were residual features consistent with bond stretching and with an umbrella motion* of both the C(7)–NH_3 and O(5)–PO_3 terminal groups. These effects were included as fixed contributions to $(U_{ij})_c$. The average bond stretching estimated from $\Delta(A, H)$ values for the four C–H bonds in PEA was 0·0056 (4) $Å^2$, in good agreement with the corresponding average, 0·0061 (11) $Å^2$, for six C–H bonds in γ-aminobutyric acid (Weber, Craven & McMullan, 1983). Other values in PEA were 0·0057 (3) $Å^2$ for the N–H bonds and 0·0074 $Å^2$ for O–H. The m.s. amplitudes for the umbrella motion were 0·0150 and 0·0033 $Å^2$ for the $-NH_3$ and $-PO_3$ groups.

The parameters used in the final model consisted of the 20 rigid-body T, L and S components, the six internal librations about selected bonds, three bond-stretching and two umbrella-motion parameters. The least-squares fit, which involved 96 observations and 31 parameters, gave $R_w = 0.127$, $S = 8.10$. Although the model assumed for the PEA thermal motion is an improvement over the simple rigid body, it remains greatly oversimplified. The major limitation is the assumption that the molecules are vibrating independently, whereas they are actually strongly coupled by ionic and H-bonding interactions. The derived molecular thermal parameters are in Table 5.† Bond lengths and angles with harmonic librational corrections are in Table 6.

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* $R_w = [\sum_k w_k \Delta_k^2 / \sum_k w_k (U_{ij})_o^2]^{1/2}$; $S = [\sum_k w_k \Delta_k^2 / (m-n)]^{1/2}$, where $(m-n) = 76$ is the number of degrees of freedom for the simple rigid body including all atoms.

* In the C–NH_3 group, umbrella motion comes from each H atom vibrating with the same m.s. amplitude normal to the N–H bond and in the C–N–H plane.

† See deposition footnote.

Table 5. *Thermal-motion parameters*

The molecule is assumed to consist of five fragments with all of these contributing to the determination of the L, T and S components. The reference fragment consists of atoms O(3), O(4) and H(12). The second fragment consisting of the remaining framework atoms, O(2)–O(1)–O(5)–C(6)–C(7)–N(8), is considered to ride on the first fragment. The two methylene and the ammonium H atoms form three fragments which all ride on the second fragment.

(*a*) Overall rigid-body parameters

These components are referred to the molecular center of mass as origin and to the crystal Cartesian axes, *a*, *b*, *c**.

Translational tensor, T ($\text{Å}^2 \times 10^4$)

$$\begin{pmatrix} 126\,(9) & -16\,(5) & -86\,(10) \\ & 110\,(5) & 5\,(5) \\ & & 220\,(12) \end{pmatrix}$$

Librational tensor, L (deg^2)

$$\begin{pmatrix} 13\cdot5\,(14) & -4\cdot7\,(11) & 8\cdot0\,(9) \\ & 12\cdot1\,(16) & -0\cdot9\,(7) \\ & & 6\cdot7\,(7) \end{pmatrix}$$

Cross tensor, S (deg $\text{Å} \times 10^2$)

$$\begin{pmatrix} -17\,(5) & -1\,(1) & 28\,(4) \\ 13\,(3) & -3\,(3) & -34\,(3) \\ -15\,(2) & -8\,(1) & 20 \end{pmatrix}$$

Principal values: 0·0072, 0·0112, 0·0272 Å^2 for T
 1·1, 10·2, 21·0 deg^2 for L

(*b*) Non-rigid librations about bonds as axes

Axis	Librating atoms	m.s. amplitude (deg^2)
C(7)–N(8)	ammonium: H(9), H(10), H(11)	61 (9)
C(7)–N(8)	methylene: H(15), H(16)	69 (12)
C(6)–C(7)	methylene: H(15), H(16)	55 (13)
C(6)–C(7)	methylene: H(13), H(14)	67 (13)
O(5)–C(6)	methylene: H(13), H(14)	62 (13)
P(1)–O(2)	all except: O(3), O(4), H(12)	−25 (3)†

† A negative m.s. librational amplitude is interpreted as making a negative contribution to the m.s. amplitudes of motion of the atoms involved in the libration, or, conversely, a positive contribution to the atoms which are considered to be fixed, *i.e.* O(3), O(4), H(12). Thus negative m.s. librational amplitudes may have physical significance except when any atom takes on a total negative m.s. displacement in any direction.

Among bonds not involving H atoms, differences in the librational corrections from the simple rigid-body model and the more complex model are greatest for P–O(4): 0·0046 (7) and 0·0078 (6) Å respectively, the difference being 0·0032 (9) Å. It is concluded that in crystal structure determinations of organic molecules where the distances between thermally averaged atomic centers are determined with e.s.d.'s of 0·001 Å or less, as in PEA, the librational corrections to the bond lengths may be ~5–10 times greater than the e.s.d.

Taking the uncertainties in the thermal-motion corrections into account, there is satisfactory agreement with the PEA framework bond lengths and angles given by Kraut (1961). There is also agreement with values in the related molecule O-(L-α-glycerylphosphoryl)ethanolamine (DeTitta & Craven, 1973), and with other monoanionic monophosphate esters (Fig. 5 in Sundaralingam & Putkey, 1970).

Because H atoms have large m.s. amplitudes of vibration even at low temperature, bond lengths involving H atoms are particularly dependent on the model assumed for concerted atomic motion. In PEA, as in other structures, O–H and N–H bond lengths are most likely to be in systematic error due to neglect of the effect of H bonding on the molecular motion. However, in PEA the three N–H distances are similar both before and after correction (Table 6). For the C–H bonds the assumed model seems more appropriate. It should be noted (Table 6) that the C–H corrections for harmonic librations and anharmonic stretching are almost equal and opposite (~0·02 Å). The anharmonic stretching correction used for PEA was initially adopted from Kuchitsu & Bartell (1961) by Weber, Craven & McMullan (1983) without their realizing that the magnitude and significance of this correction in neutron crystallography had been accurately predicted by Ibers (1959). The resulting C–H bond lengths in PEA agree with the six values from γ-aminobutyric acid (Weber *et al.*, 1983) within experimental error ($\sigma = 0\cdot004$ Å), although there is possibly a significant difference between average values [1·097(2) Å in PEA; 1·101(1) Å in GABA].

Table 6. *Bond lengths (Å) and angles (°)*

Values are given for: (1) uncorrected distances and angles between thermally averaged atom centers, (2) distances and angles with harmonic librational corrections, and (3) corrections for harmonic libration and anharmonic bond stretching (Weber, Craven & McMullan, 1983).

	(1)	(2)	(3)		(1)	(2)		(1)	(2)
P(1)–O(2)	1·4923 (8)	1·496 (1)		O(2)–P(1)–O(3)	117·11 (5)	117·06 (5)	C(7)–C(6)–H(13)	111·05 (8)	111·10 (8)
P(1)–O(3)	1·5074 (9)	1·514 (1)		O(2)–P(1)–O(4)	110·11 (5)	110·04 (4)	C(7)–C(6)–H(14)	108·78 (8)	108·74 (8)
P(1)–O(4)	1·5663 (8)	1·574 (1)		O(2)–P(1)–O(5)	104·57 (4)	104·57 (4)	H(15)–C(7)–H(16)	107·39 (11)	107·33 (11)
P(1)–O(5)	1·5989 (9)	1·599 (1)		O(3)–P(1)–O(4)	109·11 (5)	109·22 (5)	C(6)–C(7)–H(15)	109·35 (8)	109·37 (8)
O(5)–C(6)	1·4328 (7)	1·435 (1)		O(3)–P(1)–O(5)	109·30 (5)	109·29 (5)	C(6)–C(7)–H(16)	110·91 (8)	110·95 (8)
C(6)–C(7)	1·5085 (7)	1·509 (1)		O(4)–P(1)–O(5)	106·01 (4)	106·05 (4)	N(8)–C(7)–H(15)	108·61 (8)	108·55 (8)
C(7)–N(8)	1·4871 (7)	1·488 (1)		P(1)–O(5)–C(6)	118·26 (5)	118·28 (5)	N(8)–C(7)–H(16)	108·60 (8)	108·70 (8)
N(8)–H(9)	1·043 (1)	1·059 (2)	1·041 (3)	O(5)–C(6)–C(7)	108·63 (4)	108·66 (4)	H(9)–N(8)–H(10)	107·95 (9)	107·99 (9)
N(8)–H(10)	1·046 (1)	1·061 (2)	1·043 (3)	C(6)–C(7)–N(8)	111·86 (4)	111·81 (4)	H(9)–N(8)–H(11)	108·92 (9)	108·92 (9)
N(8)–H(11)	1·043 (1)	1·060 (2)	1·042 (3)	P(1)–O(4)–H(12)	115·07 (8)	115·02 (8)	H(10)–N(8)–H(11)	108·32 (9)	108·28 (9)
O(4)–H(12)	1·013 (1)	1·019 (2)	0·997 (3)	H(13)–C(6)–H(14)	109·03 (10)	109·13 (10)	C(7)–N(8)–H(9)	111·42 (7)	111·49 (7)
C(6)–H(13)	1·097 (1)	1·117 (3)	1·099 (4)	O(5)–C(6)–H(13)	108·96 (8)	108·98 (8)	C(7)–N(8)–H(10)	108·51 (7)	108·52 (7)
C(6)–H(14)	1·095 (1)	1·115 (3)	1·097 (4)	O(5)–C(6)–H(14)	110·39 (8)	110·32 (8)	C(7)–N(8)–H(11)	111·61 (7)	111·53 (7)
C(7)–H(15)	1·093 (1)	1·113 (3)	1·095 (4)						
C(7)–H(16)	1·094 (1)	1·113 (3)	1·095 (4)						

(d) Estimated equilibrium (r_e) C–H bond lengths

The corrected C–H bond lengths from neutron diffraction as described above are of interest because they are estimated equilibrium (r_e) values, comparable with those determined theoretically and from other experimental methods (Kuchitsu & Oyanagi, 1977). Thus for C–H in ethane, theoretical calculations with an extended basis set, including electron correlation effects (MP2/6-31G*) give the value 1·094 Å (DeFrees, Levi, Pollock, Hehre, Binkley & Pople, 1979). Corresponding experimental values for ethane are 1·0877 Å from infrared spectra (Duncan, McKean & Bruce, 1979), 1·0940(2) Å from microwave spectra (Hirota, Endo, Saito & Duncan, 1981) and 1·089(5) Å from gas electron diffraction. The latter is an r_e value derived by Duncan et al. (1979) from the results of Bartell & Higginbotham (1965). These experimental C–H bond lengths, including the ten from neutron diffraction, lie within a range of 0·015 Å which is centered on the theoretical value.

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Electrostatic Properties of Phosphorylethanolamine at 123 K from Crystal Diffraction

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Abstract

Electrostatic properties for phosphorylethanolamine ($C_2H_8NO_4P$) at 123 K have been determined from X-ray (Mo $K\alpha$) intensity data (4150 reflections with $|F_o| \geq 3\sigma$ and $\sin\theta/\lambda < 1\cdot3$ Å^{-1}). Least-squares structure refinements were carried out using Stewart's rigid pseudoatom model (at convergence $R = 0\cdot029$, $R_w =$ 0·023). The promolecule consisted of neutral isolated Hartree–Fock atoms or contracted spherical H atoms with fixed neutron values for all atomic positional parameters and for H-atom thermal parameters. Electron population parameters were determined for charge deformations up to octapoles (quadrupoles for H atoms). The zwitterion is strongly polarized with a calculated dipole moment of 13 (2) debye