The Crystal Structure of the Disodium Salt of N-Phosphorylcreatine Hydrate*

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N-Phosphorylcreatine, a biological 'high energy phosphate', serves as an energy reservoir in vertebrate muscles. Crystals of the disodium salt, Na₂PN₃C₄O₅H₈.4¹₂H₂O, were prepared. The space group is $P2_1/c$, with unit-cell dimensions a=24.85, b=6.64, c=16.94 Å and $\beta=109.5^{\circ}$ and two formula units per asymmetric unit. If a few weak reflections are ignored, the symmetry is that of the space group C2/c with the same unit-cell dimensions and one formula unit per asymmetric unit. The symmetry of the centered cell was assumed and the intensities of 4953 independent reflections were measured with use of balanced filters, Mo Ka radiation and a Buerger-Supper-Pace automated diffractometer. Sayre's sign relation was used to determine the phases (signs) of 275 reflections and the resulting model was refined by Fourier and least-squares methods to a final R value for observed reflections of 0.083.

The guanidino group is planar. All hydrogen atoms available for hydrogen bonding are used and form both inter- and intramolecular bonds. Observed differences between bond distances found in *N*-phosphorylcreatine and those found in the hydrolysis product creatine are not statistically significant and thus the structural basis of the instability of *N*-phosphorylcreatine remains unresolved.

Introduction

Eggelton & Eggelton (1927) showed that frog muscle contains an organic phosphate compound which is rapidly hydrolyzed under acid conditions. They called this compound 'phosphagen', a name which is now used as a generic term for all of the naturally occurring guanidino phosphates. At about the same time, Fiske & Subbarow (1927) reported that they had isolated an unstable compound of phosphoric acid and creatine from voluntary muscle. This compound was hydrolyzed on stimulation and resynthesized when the muscle was permitted to recover. They named the compound 'phosphocreatine' and proposed the following structural formula (Fiske & Subbarow, 1929):



(Now called *N*-phosphorylcreatine)

Our present view of the energetics of muscle contraction is based largely on the work of Lundsgaard, done in the 1930's (Carlson, 1963). It is now generally believed that the primary source of energy for contraction is the hydrolysis of adenosine triphosphate, and that a guanidino phosphate acts as an energy reservoir, coupled to the adenine nucleotide by way of a kinase. In vertebrate muscle the reserve guanidino phosphate is *N*-phosphorylcreatine.

Living organisms make extensive use of the ability to store energy in the form of 'high energy phosphate' compounds, but it is not known why some molecular species are 'high energy' while others are not. We decided to attempt to determine the structure of N-phosphorylcreatine in the hope that we might find the structural basis for its thermodynamic instability, *i.e.* how this molecule stores energy. Furthermore, there were two independent determinations of the structure of creatine itself, thus enabling comparison before and after the exergonic hydrolysis of the N-P bond.

Crystal preparation

N-Phosphorylcreatine was synthesized by reacting creatine hydrate with phosphorus oxychloride, $POCl_3$. The procedure used is the one described by Ennor (1957) through the step where the ethanol concentration is raised to 75%. The remaining steps are those described by Ennor & Stocken (1957).

Most attempts to crystallize various salts of N-phosphorylcreatine resulted in very thin lath-shaped crystals or precipitates of fine oil droplets which resisted all efforts to make them crystallize. Crystals suitable for single-crystal work were obtained by dissolving the sodium salt in water which had been adjusted to pH9.0 with sodium hydroxide, adding four volumes of ethanol, and then seeding with fragments of a six-sided plate-like crystal. The crystal used for seeds grew owing to a fortuitous combination of circumstances in preparations made eighteen months earlier. The sodium salt of N-phosphorylcreatine had been dissolved in ethylene glycol, heavy-atom salts added, and acetone used to drive the salts of N-phosphorylcreatine out of

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solution. Corks were placed in the tubes, which were then stored at 4°C. Over a period of a year and a half, some of the acetone evaporated and a few large sixsided plates formed in some of the tubes. Analysis of these crystals indicated that they contained bound creatine (presumably as the phosphoryl derivative), and essentially no free creatine. One of these crystals was crushed and the fragments used as seeds in Nphosphorylcreatine-water-ethanol mixtures stored at 20 ± 0.5 °C. Crystals grew in these preparations in 24 hours and these crystals were used for structure determination. Elementary analysis performed by a commercial laboratory showed that the ratios phosphorus: nitrogen: carbon were within experimental error of the predicted ratios 1:3:4.

Crystal data

Crystals grown by the method described above are prismatic, elongated along b and belong to the monoclinic system. Precession photographs of three zero levels and five upper levels showed that the space group is $P2_1/c$ but if a few weak spots with (h+k) odd are ignored, the symmetry is that of the space group C2/c. The few reflections which are inconsistent with the symmetry of C2/c varied in intensity from crystal to crystal, and in the case of the specimen used for data collection are best described as 'very weak'. It was therefore decided to treat this crystal as having the symmetry of the space group C2/c, with one molecule per asymmetric unit. Lattice parameters and their standard deviations were obtained from precession

(2)

photographs (Patterson & Love, 1960) and the density was measured by flotation. These data are shown in Table 1.

Data collection

The Buerger diffractometer as manufactured by the Charles Supper Company and automated by the Pace Controls Corporation uses the general inclination Weissenberg geometry, and integrated intensities are measured by means of stationary-counter movingcrystal ' ω scans'. The input information and the resulting output data were punched on paper tapes that were prepared and processed by an LGP-30 computer in this laboratory. The crystals used in this work scatter strongly and the diffraction pattern extends farther into reciprocal space than the region accessible with Cu $K\alpha$ radiation. For this reason and because it is much less absorbed. Mo Ka radiation was used for data collection.

Balanced filters were prepared using zirconium, yttrium and aluminum foils as described by Kirkpatrick (1944), and balanced by means of θ -2 θ step scans through a reflection which contained no long wavelength contributions from reflections of the type h/n, k/n, l/n and no contamination by short wavelengths from reflections of the type *nh*, *nk*, *nl*.

Because the crystals are hygroscopic, the specimens used for data collection were mounted in thin-walled glass capillaries. The three-dimensional data were collected with a crystal (dimensions $0.17 \times 0.47 \times 0.22$ mm) mounted parallel to the b axis and the intensities measured in sections of constant k for k=0 through $\overline{9}$. The

Table 1. Crystal data for the disodium salt of N-phosphorylcreatine hydrate, Na₂PC₄N₃O₅H₈.4 $^{1}_{2}$ H₂O

Lattice parameters at room temperature using Cu Ka ($\lambda = 1.5418$ Å) radiation:

$a = 24.85 \pm 0.015 \text{ A}$ $b = 6.64 \pm 0.005$ $c = 16.94 \pm 0.010$ $\beta = 109.54 \pm 0.05^{\circ}$ Cell volume = 2635 \pm 3 Å ³	
Density:	
Measured, 1.701 ± 0.003 g.c Calculated with eight formula units of Na ₂ PC ₄ N ₃ O ₅ H ₈ .4 $\frac{1}{2}$ H ₂ C	m ⁻³ D per unit cell, 1·694 g.cm ⁻³
Other data	
F(000) = 1400	
Space group:	Observed systematic absences
(1) True space group, $P2_1/c$	hkl: none h0l: l odd
Z=4, two formula units per asymmetric unit	0k0:k odd

Pseudo space group, $C2/c$	<i>hkl</i> : $h+k$ odd*
	h0l: l odd (h odd)
Z=8, one formula unit per asymmetric unit	0k0:(k odd)

* A few general reflections were observed for which h+k was odd but they were ignored.

Linear absorption coefficients

Cu Ka ($\lambda = 1.5418$ Å) $\mu = 30.85$ cm⁻¹ (1)

Mo $K\alpha$ ($\lambda = 0.7107$ Å) $\mu = 3.4$ cm⁻¹ (2)

reflections within a given level were measured serially along rows in reciprocal space. In order to monitor the overall performance of the system, a 'reference' reflection was measured before and after the measurement of the intensities in each row. A second crystal (dimensions $0.11 \times 0.45 \times 0.25$ mm) was later mounted parallel to the c axis and the hk0 reflections were collected in order to scale the previous levels together and to collect the row 0k0. It was noted that the resulting interlevel scale factors for the levels $h\overline{4l}$ through $h\overline{9l}$ increased as the magnitude of the level index k increased. The effect of absorption was estimated and found to be inadequate to explain the observed phenomenon.

After the $h\overline{9}l$ section was measured, the reflections which occurred at values of $\sin \theta / \lambda \le 0.25 \text{ Å}^{-1}$ on h0l were remeasured because the beam stop had partially obscured the innermost reflections (especially 200). In order to put these observations on the same scale as the other hol reflections, it was necessary to multiply them by a scale factor of about 1.5. This indicated that at least one of the following effects was being observed. (1) The X-ray flux incident on the crystal had decreased, (2) the specimen crystal had been damaged as a result of exposure to the X-ray beam or (3) the detection system had become less sensitive to X-rays. The first possibility seemed unlikely after the mechanical alignment was checked and found to be adjusted for maximum intensity from the X-ray tube. Precession photographs of the specimen crystal failed to show any evidence of radiation damage. The possibility that the scintillation crystal had begun to deteriorate seems to be the most likely explanation. In any case, replacement of the scintillation counter has since eliminated the problem.

Because the 'reference' reflection for any given level did not show any noticeable tendency to decline in intensity during the collection of that level (although the scintillation crystal was probably deteriorating monotonically, the time spent collecting a given level was short compared with the total time elapsed between the collection of the first and the last levels) it was concluded that the data within a level were close to being on the same relative scale and thus the set of data was a meaningful one.

Of the 4953 independent reflections measured, 2142 had an observable intensity. The minimum observed intensity was estimated from a strip chart which displayed the profile of each peak scanned. If the peak was noticeably higher than the background on either side, then the reflection was called observed and if not, it was treated as unobserved. The intensity of the unobserved reflections was not set equal to zero or to $\frac{1}{3}$ of *I* (minimum), as suggested by Hamilton (1955), but was left as the measured value which ranged from zero to the minimum observed intensity. The small number of reflections whose measured intensity, after adjustment for background and balanced filters, was actually negative were given an intensity equal to zero.

It was found that the distribution of values for the intensity of the 'reference' reflection had a larger standard deviation than that calculated for any one determination on the basis of counting statistics. The fact that the integrated intensity is a function of six measurements (background was measured before and after the peak was scanned for each of the two filters) was included in the treatment of errors. The discrepancy between the observed and calculated standard deviations was attributed to variations in the detecting system and/or the X-ray source. After Lorentz and polarization corrections were applied to the data, the uncertainties in the intensities were estimated by calculating the standard deviations based on counting statistics and then correcting these values for the instability of the system by the addition of 1% to the relative error for each reflection.

The computing package of programs, X-RAY 63, was obtained from Dr James Stewart and used for nearly all of the remaining calculations (Stewart, 1964).

Structure determination

Estimates of an overall isotropic temperature factor and an intensity scale factor were obtained by fitting the data to the known distribution for normalized structure factors. According to Hauptman & Karle (1953), the probability distribution for the normalized structure factors, E(hkl), is approximately equal to $1/(2\pi)^{1/2} \exp \left[-\frac{1}{2}E(hkl)^2\right]$ regardless of crystal symmetry or complexity. Normalized structure factors were calculated and the values of K and B were chosen so that the data fit the theoretical distribution as closely as possible (Dickinson, Stewart & Holden, 1966). This is done by the conversion program developed for the X-ray 63 system. The atomic scattering factors were obtained from International Tables for X-ray Crystallography (1962).

A computer program, written by Dr Herman Ammon and obtained from Dr Stewart, was used to sort the reflections with large values of E(hkl) into groups of three reflections whose Miller indices were related as $E_{\rm h}$, $E_{\rm h'}$ and $E_{\rm h-h'}$. The groups of three reflections could then be used in either Sayre's (1952) sign relation or in the Σ_2 relation of Hauptman & Karle (1953). The program also evaluates the probability that the product of the three signs is positive using the formula of Cochran & Woolfson (1955).

Sayre's sign relation was used and the procedure was as follows: Letters were assigned to represent the phases (0 or π) of the twenty-four three-dimensional $(h,k,l\neq 0)$ reflections that had values of $E(hkl) \ge 2.65$. These reflections were then used as 'generators' (reflections whose phases were known in terms of letters) in the first cycle of the program. Several cycles were run in which the computer found relations among the reflections and their associated probabilities and between cycles the substitution of letters for phases and the reduction of the number of letters was done by hand. A fourth and final cycle was run in which the lower limit for the magnitude of E(hkl)'s used was reduced from 1.90 to 1.75. When this cycle was completed, the phases of 275 reflections had been determined in terms of three remaining letters, A, B, and H. Choosing the phases represented by the letters A and B fixed the origin and two E maps (Fourier syntheses with E(hkl) as coefficients) were calculated, one for H=0 and one for $H=\pi$, using the 275 reflections whose phases had been determined.

The structure was not completely revealed in either map nor was it obvious which one represented the correct set of phases. A three-dimensional Patterson function was calculated and all the vectors among the largest three peaks in each E map (assumed to represent the phosphorus atom and the two sodium ions) were computed. It was found that the Patterson map was consistent with the three peaks in the map made with $H=\pi$ but inconsistent with the arrangement of peaks in the map for H=0. It was decided to try to refine the model using the peaks in the E map made with $H=\pi$. The vectors between each peak in the E map and the presumed phosphorus position were calculated and the Patterson map searched to see if peaks existed in the predicted locations. Twelve additional peaks from the E map were found which were consistent with the Patterson function and these twelve peaks together with the three larger peaks formed the basis of a trial structure.

It was possible to fit a phosphoryl group and a guanidino group to the peaks in the *E* map but the carboxyl end of the molecule was not evident. A structure-factor calculation using these fifteen peaks from the *E* map gave an *R* value of 43% when the data were compared to the calculated structure factors out to $\sin \theta/\lambda \le 0.5 \text{ Å}^{-1}$.

Successive cycles of structure-factor calculations followed by $(F_o - F_c)$ syntheses revealed the location of the remaining five atoms and showed that one of the peaks in the *E* map which had been 'verified' in the Patterson function was, in fact, spurious. Structure factors were calculated out to the limit of the data, $\sin \theta/\lambda$ just under 1.0 Å⁻¹. The *R* value at this stage was 36% but dropped to 23% after several cycles of Fourier refinement.





Fig. 1. Bond lengths and bond angles in the disodium salt of *N*-phosphorylcreatine hydrate. These values have not been corrected for thermal motion. Distances are in Å and angles are in degrees.

Final refinement

Two cycles of full-matrix least-squares refinement were run minimizing $\Sigma w(\Delta F)^2$ using unit weighting of the discrepancies and including individual isotropic temperature factors and interlevel scale factors in the adjustment. These two cycles reduced the *R* value from 23% to 12%.

Several additional cycles of block-diagonal and fullmatrix least-squares refinement were run with individual anisotropic temperature factors for non-hydrogen atoms and the discrepancies were weighted using the expression

weight =
$$w^{1/2} = 1/\sigma(I \text{ relative})$$
.

This weighting scheme has the virtue that no trends are apparent when the averages of $w(\Delta F)^2$ are plotted versus $|F_o|$. Note, however, that only relative weights were used.

A number of structure factors which occurred at low values of $\sin \theta / \lambda$ were consistently calculated to be greater than the observed reflections (presumably due

Table 2. Values from final cycle of least-squares refinement

R, omitting unobserved reflections	0.083
R, with reflection multiplicity omitting unobserved reflections	0.083
Weighted R value, omitting unobserved reflections	0.102
R of unobserved reflections	0.132
Number of unobserved reflections calculating greater than intensity minimum	149 of 2811
Total number of observations	4953
Total number of variables	176

Table 3. Final atomic parameters

The errors (one standard deviation) are given in parentheses. The anisotropic temperature factors are defined by the equation T.F. = exp $\left[-\frac{1}{2}(h^2a^{*2}B_{11}+k^2b^{*2}B_{22}+l^2c^{*2}B_{33}+2hka^{*b}B_{12}+2hla^{*}c^{*}B_{13}+2klb^{*}c^{*}B_{23})\right]$.

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	x	у	Z
P(1)	0.0731 (1)	0.3575 (2)	0.3959 (1)
Na(1)	0.0538 (1)	0·0704 (2)	0.2230 (1)
Na(2)	0·0425 (1)	0.5999 (3)	0.0878 (1)
N(Ì)	0.1353 (1)	0.2336 (5)	0.4534 (2)
N(2)	0·1721 (1)	0.4754 (5)	0.5554 (2)
N(3)	0.2164 (1)	0.1636 (5)	0.5677 (2)
O(1)	0.0386 (1)	0.1849 (4)	0.3469 (2)
O(2)	0.0502 (1)	0.4553 (4)	0.4584 (2)
O(3)	0.0895 (1)	0.5153 (4)	0.3433 (2)
O(4)	0.2885 (1)	0.1542 (5)	0.7906 (2)
O(5)	0.1959 (1)	0.1478 (5)	0.7205 (2)
O(6)	0.0982 (1)	0.3874 (5)	0.1958 (2)
O(7)	0.1383 (1)	0.8967 (4)	0.3326 (2)
O(8)	0.0000 (0)	0.7647 (7)	0.2500 (0)
O(9)	0.0856 (1)	0.9127 (5)	0.1205 (2)
O(10)	0.0544 (2)	0.8746 (5)	0.4687 (2)
C(1)	0.1750 (1)	0.2917 (6)	0.5264 (2)
C(2)	0.2151 (2)	-0.0433 (7)	0.5442 (3)
C(3)	0.2601 (2)	0.2189 (6)	0.6460 (2)
C(4)	0.2464 (2)	0.1679 (6)	0.7250 (2)
H(1)	0.1439 (18)	0.1176 (65)	0.4365 (25)
H(2)	0.1994 (20)	0.5014 (76)	0.6105 (31)
H(3)	0.1501(21)	0.6061(70)	0.5242 (30)
H(4)	0.2363(21)	-0.1398(76)	0.5964 (31)
H(5)	0.2267 (18)	-0.0552(65)	0.5065 (28)
H(6)	0.1766(22)	-0.1005(73)	0.5396 (30)
H(7)	0.3032(18)	0.1664(65)	0.6451(28)
H(8)	0.2651(18)	0.3262(62)	0.6525 (28)
H(9)	0.0941(18)	0.4019(66)	0.2304 (29)
H(10)	0.1352(18)	0.3459 (64)	0.2088(29)
H(11)	0.140/(21)	0.7808(77)	0.3551(30)
H(12)	0.1581(18)	0.8334(62)	0.3199 (20)
H(13)	0.0201(20)	0.7010 (60)	0.4099(30)
H(14)	0.0049(19)	0.7910(09)	0.2920 (22
$\pi(12)$	0.0244 (18)	0.0740(09) 0.9701(60)	0.2027 (33)
H(10)	0.0750 (*)	0.0/91(9)	0.0547 (27)
$\mathbf{H}(1/)$	0.0730 (*)	0.9491 (*)	0.0347 (*)

* H(17) coordinates were assigned but not refined.

After the data were put on an absolute scale, the interlevel scale factors were allowed to vary as refinement proceeded through the second cycle of fullmatrix least-squares refinement, during which time only isotropic temperature factors were used for each atom. The resulting values for refined interlevel scale factors did not differ from the overall absolute scale factor by more than the experimental error in the individual scale factors.

The degeneracy between the interlevel scale factors and one of the anisotropic thermal parameters, in this case B_{22} (Lingafelter & Donohue, 1966), was not recognized until after one cycle of full-matrix leastsquares refinement in which two atoms were allowed to vibrate anisotropically, and one cycle of blockdiagonal least-squares refinement in which all atoms were given anisotropic temperature factors (excluding hydrogen atoms). Interlevel scale factors were allowed to vary during these two cycles and, as a result, a definite trend was observed among the scale factors;

they increased as the index k increased. It then became apparent that the degeneracy between the interlevel scale factors and the B_{22} values was leading to meaningless values for these parameters. To correct this situation, one cycle of full-matrix least-squares refinement was run, in which all atoms were constrained to vibrate isotropically and all parameters were allowed to vary, excluding hydrogens but including the interlevel scale factors. The resulting values for the scale factors were very similar to those obtained previously with isotropic temperature factors. The tendency of the scale factors to increase as the level index k increased was eliminated. Next, one cycle of full-matrix least-squares refinement was run in which the scale factors were held constant but the atoms were allowed to vibrate anisotropically. The resulting B_{22} values were higher, as expected, than before the corrective steps were taken and were now not noticeably different from the B_{11} or B_{33} values. The agreement factors from the last cycle of least-squares refinement are shown in Table 2. The final atomic parameters along with their estimated standard deviations are shown in Table 3.

Table 3 (cont.)

	B_{11}	B ₂₂	B ₃₃	B_{12}	B_{13}	B ₂₃
P(1)	1.20(3)	0.95 (3)	1.03 (3)	0.06 (3)	0.27(2)	-0.10(3)
Na(1)	1.67 (6)	2.11(7)	1.97 (6)	0·26 (̀5)́	0·54 (̀5)́	-0.43(6)
Na(2)	3·18 (8)	5.01 (11)	1.98 (7)	-1.89(8)	0.94 (6)	-0.55 (7)
N(1)	1.49 (10)	1.21 (12)	1.04 (10)	0.23 (9)	0.06 (8)	-0.33(10)
N(2)	2.72 (14)	1.11 (13)	1.85 (12)	-0.21(12)	-0.16(11)	-0.53(11)
N(3)	1.64 (11)	1.59 (13)	1.21 (10)	0.29 (10)	-0.07(9)	0.13 (10)
O (1)	1.47 (9)	1.47 (11)	1.60 (9)	-0.18(9)	-0.04(8)	-0.55 (9)
O(2)	2.24(11)	2.04 (12)	1.53 (9)	0.60 (10)	0.88 (8)	-0.42(10)
O(3)	2·45 (11)	1.51 (12)	2.08 (10)	0.21(10)	0.79 (9)	0.92 (10)
O(4)	2·30 (11)	3.63 (16)	1.79 (10)	0.13(12)	0.10 (9)	0.66 (11)
O(5)	1.86 (10)	4.57 (18)	2.54 (12)	-0.12(12)	0.90 (9)	0.69 (13)
O(6)	2.74 (12)	3.95 (17)	2.28 (12)	-0.59 (12)	1.08 (10)	-0.02(12)
O(7)	3.09 (13)	1.79 (13)	2.87 (12)	-0·24 (11)	1.42 (11)	-0.22(11)
O(8)	2.70 (20)	1.94 (20)	7.24 (34)	0.00 (0)	-1.98 (20)	0.00 (0)
O(9)	3.05 (13)	3.10 (16)	2.21 (12)	0.54 (12)	0.94 (10)	-0.46(12)
O(10)	9.38 (29)	2.20 (16)	4.47 (20)	-1·33 (18)	2.97 (20)	0.06 (15)
C(1)	1.45 (12)	1.34 (14)	0.93 (11)	-0·40 (11)	0.42 (10)	-0.04(11)
C(2)	4.05 (22)	1.71 (19)	2.51 (17)	0.70 (18)	0.51 (16)	-0.15 (16)
C(3)	1.38 (12)	2.25 (17)	1.49 (12)	-0·32 (13)	0.00 (10)	0.18 (13)
C(4)	2.06 (15)	1.60 (16)	1.37 (12)	0.07 (13)	0.30 (11)	0.04 (13)
H(1)	2.00†					
H(2)	4·70†					
H(3)	3.57†					
H(4)	3.11+					
H(5)	4.00†					
H(6)	6.004					
H(7)	2.00					
H(8)	2.00					
H(9)	2.00					
H(10)	3.72†					
H(11)	2.00					
H(12)	2.00					
H(13)	5.42†					
H(14)	3.8/7					
H(15)	4.187					
H(10)	0.001 4.00+					
H(1/)	4·00‡					

† Isotropic temperature factors for hydrogen atoms were constrained to lie between 2.00 and 6.00 Å².

 \ddagger The temperature factor for H(17) was never refined.

Hydrogen atoms

Sixteen of the seventeen hydrogen atoms were located from difference syntheses computed using data out to $\sin \theta/\lambda = 0.5 \text{ Å}^{-1}$. These hydrogen atoms were included in the refinement but their isotropic temperature factors were arbitrarily confined to lie between 2.0 and 6.0 Å^2 . The positional parameters refined to values close to those for the peaks in the difference maps. A glance at the interatomic distances (Fig. 1), however, reveals that the hydrogen positions are probably not exactly correct. For example, the three C-H distances in the methyl group are 1.08, 0.79, and 1.01 Å. Differences of this magnitude, unexpected for bonds that seem to be equivalent, are attributed to errors in the data. The seventeenth hydrogen atom could not be located uniquely on the basis of the difference maps alone. Calculations showed that oxygen atoms O(9) and O(10)were 2.8 Å apart (Fig.2) and therefore presumably hydrogen bonded. The difference map had a peak between these two water molecules about 1 Å from O(9). A hydrogen atom was placed at this position but its coordinates were not refined.

Discussion

The bond lengths and angles for N-phosphorylcreatine are shown in Fig.1. Standard deviations for nonhydrogen bond distances, indicated by the inverse matrix from the final least-squares refinement, average



Fig.2. Hydrogen bonding in the disodium salt of *N*-phosphorylcreatine hydrate. The structure is projected onto (010) with the plus *b* axis pointing up, out of the paper.

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Table 4. Observed and calculated structure factors

The table contains three columns, the index h, $10F_o$ and $10F_c$, respectively. Reflections tagged L are unobserved and reflections marked E were given zero weight.

	10 115 17 10 10 17 100 -11 100 -41 10 10 11 11 10 -41 100 -41 10 10 11 10 11 100 -41 10 10 11 10 100 -41 100 -41 10 10 -11 10 100 100 -41 100 -41 10 100 -11 100 <t< th=""><th>-18 71154 H1-10 1 565 -511 1 222 -511 1 213 -217 9 103 -207 9 103 -207 1 1072 -1035 1 5 645 -618 17 184 -51 17 184 -158 21 265 -257 23 1191 -115</th><th>-20 1881 155 31 1841 -48 -31 1841 78 -31 1841 48 -31 1841 48 -35 1281 -105 m1-5 1 406 410 -11551 -1352 3 887 907 -27186 -22420 4 211 -19 -2419 -2629 7 566 566 -71011 720 9 427 -422</th><th>-111599 -1566 -11578 -578 -15387 -578 -15387 -158 -15387 -158 -15387 -158 -17537 -158 -17537 -158 -17537 -158 -19184, -26 -211964, -37 -21356 -158 -21164, -158 -2327 -298 -2537 -168 -27164, -110 -27164, -110 -27164, -100 -27164, -100 -27164, -100 -27164, -100 -27164, -100 -27164, -100 -27164, -000 -27164, -000</th><th>7 200 -183 -7 700 -721 9 1741 -110 -7 910 -721 11 100 -99 -13 200 -140 -13 100 -140 -13 122 -120 -14 100 -141 -15 160, 174 -15 160, 174 -15 160, 174 -17 184, 184 -17 411 420 -191 -14 220 -191 -14 220 -191 -14 220 -103</th><th>$\begin{array}{c} F_{12}=11,19\\ -29,184,1-116\\ -31,1721,201\\ F_{12}=428\\ -1,416,-179\\ -1,416,-179\\ -1,416,-179\\ -1,416,-179\\ -1,194,-222\\ -2,230,251\\ -2,124,-143\\ -2,259,-331\\ -2,164,-143\\ -2,259,-331\\ -2,164,-143\\ -2,259,-331\\ -3,164,-143\\ -3,164,-144,-144\\ -3,164,-144,-144\\ -3,164,-144,-144,-144\\ -3,164,-144,-144,-144,-144,-144,-144,-144,$</th><th>10 189 184 -10 412 -388 32 164 143 -12 201 -110 -14 250 243 -12 201 -210 -14 250 243 -12 204 -14 200 243 -130 243 -1</th><th>$\begin{array}{cccccccccccccccccccccccccccccccccccc$</th><th>$\begin{array}{c} \mu_{3}-2,11\\ C & 944 & -526\\ 2 & 1631 & -261\\ -2 & 980 & -9498\\ 4 & 1671 & 193\\ -4 & 1804 & 0\\ e & 751 & 727\\ -8 & 653 & 651\\ 8 & 457 & 453\\ -8 & 880 & 854\\ 10 & 244 & -211\\ 12 & 257 & -218\\ -12 & 342 & -270\\ -14 & 971 & -273\\ -14 & -273 & -173\\ -14 & -273 & -273\\ -1$</th></t<>	-18 71154 H1-10 1 565 -511 1 222 -511 1 213 -217 9 103 -207 9 103 -207 1 1072 -1035 1 5 645 -618 17 184 -51 17 184 -158 21 265 -257 23 1191 -115	-20 1881 155 31 1841 -48 -31 1841 78 -31 1841 48 -31 1841 48 -35 1281 -105 m1-5 1 406 410 -11551 -1352 3 887 907 -27186 -22420 4 211 -19 -2419 -2629 7 566 566 -71011 720 9 427 -422	-111599 -1566 -11578 -578 -15387 -578 -15387 -158 -15387 -158 -15387 -158 -17537 -158 -17537 -158 -17537 -158 -19184, -26 -211964, -37 -21356 -158 -21164, -158 -2327 -298 -2537 -168 -27164, -110 -27164, -110 -27164, -100 -27164, -100 -27164, -100 -27164, -100 -27164, -100 -27164, -100 -27164, -000 -27164, -000	7 200 -183 -7 700 -721 9 1741 -110 -7 910 -721 11 100 -99 -13 200 -140 -13 100 -140 -13 122 -120 -14 100 -141 -15 160, 174 -15 160, 174 -15 160, 174 -17 184, 184 -17 411 420 -191 -14 220 -191 -14 220 -191 -14 220 -103	$\begin{array}{c} F_{12}=11,19\\ -29,184,1-116\\ -31,1721,201\\ F_{12}=428\\ -1,416,-179\\ -1,416,-179\\ -1,416,-179\\ -1,416,-179\\ -1,194,-222\\ -2,230,251\\ -2,124,-143\\ -2,259,-331\\ -2,164,-143\\ -2,259,-331\\ -2,164,-143\\ -2,259,-331\\ -3,164,-143\\ -3,164,-144,-144\\ -3,164,-144,-144\\ -3,164,-144,-144,-144\\ -3,164,-144,-144,-144,-144,-144,-144,-144,$	10 189 184 -10 412 -388 32 164 143 -12 201 -110 -14 250 243 -12 201 -210 -14 250 243 -12 204 -14 200 243 -130 243 -1	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} \mu_{3}-2,11\\ C & 944 & -526\\ 2 & 1631 & -261\\ -2 & 980 & -9498\\ 4 & 1671 & 193\\ -4 & 1804 & 0\\ e & 751 & 727\\ -8 & 653 & 651\\ 8 & 457 & 453\\ -8 & 880 & 854\\ 10 & 244 & -211\\ 12 & 257 & -218\\ -12 & 342 & -270\\ -14 & 971 & -273\\ -14 & 971 & -273\\ -14 & 971 & -273\\ -14 & 971 & -273\\ -14 & 971 & -273\\ -14 & 971 & -273\\ -14 & 971 & -273\\ -14 & 971 & -273\\ -14 & 971 & -273\\ -14 & 971 & -273\\ -14 & 971 & -273\\ -14 & 971 & -273\\ -14 & 971 & -273\\ -14 & 971 & -273\\ -14 & -273 & -173\\ -14 & -273 & -273\\ -1$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	-14 186L 27 -12 176L -114 -16 186L -72 -13 114L -127 -18 186L -54 -16 271 161 -06 82L -12 -18 167 127 -72 126L -2 -16 167 127 -74 126L -2 -16 167 127 -74 168L -11 -44 165 -13 -14 165 -14 -14 1	27 1161 -168 29 185 -229 31 625 58 31 1221 119 m.=1.1 1 8785-1025 -115681 1946 1 1414 -179 -1 769 802 31263 -1325 -1 1654 -356	-9 667 616 11 390 -418 11 344 13 13 442 -426 14 947 917 464 15 947 917 464 15 947 917 464 17 314 -294 -17 711 -102 19 221 194 -29 197 -29 197 -2	-20 1841 54 -11 190 205 -33 1841 101 -35 1261 -136 -37 1841 55 m1,10 1 863 -920 -1 1621 126 1 863 -920 -3 673 660 5 511 -508	-25 1461 95 -27 1864 7 -27 1864 7 -1844 -211 -11 1844 -211 -13 1844 -213 -13 1844 -261 -15 1371 -65 -1 170 -378 -1 170 -378 -1 1294 -124	11 1844 -4 11 1201-112 13 761 -84 15 1841 -1 17 1841 -1 19 1841 -1 19 1841 -1 21 191 -171 23 1231 -62 25 611 -62 27 195 163 29 286 52 31 1626 84 	10 1891 218 10 231 218 12 312 296 -12 333 -292 14 1891 -86 -14 363 -296 16 121 186 -16 270 -261 18 321 -42 -18 323 271 26 272 318 -27 13 22 1891 -105	28 135 1-55 30 1241 127 -30 1361 -138 -32 1771 167 -34 1600 -147 -16 1690 60 m2,7 0 691 -19 2 269 -273 -2 4C0 -385	16 497 -504 18 278 309 -18 1841 173 20 1894 -70 -20 492 469 22 1894 -56 -22 555 599 24 161 -346 -24 291 310 -24 204 -248 -30 423 -389 -32 92 -242
	-2 (23) 100 -2 (27) -5 (4) -5 (-7 646 -634 9 335 -295 9 335 -295 -9 164 -12# 11 217 -212 -11 917 -212 -13 120, 82 15 1621 -161 -15 1631 -176 -17 1631 -776 -19 322 -3 -19 216 -3	21 1661 - 1500 23 272 278 25 4C5 - 196 25 241 - 262 27 191 - 227 29 184 - 40 29 184 - 4 -29 384 - 4C4 31 081 135 -31 185 - 125 -31 241 - 2C4 -35 166 148 m1.6	-3 A48 D26 7 1844 -7 -7 798 792 9 247 -252 -9 331 0 11 387 569 -11 188 133 13 1251 87 -13 404 -418 15 184, 78 -15 178 -757 17 141 152 -17 279 280	- 5 193 -122 - 5 193 -122 - 7 134L 6 - 7 134L -103 - 9 155L -107 - 9 435 436 - 11 282 -268 - 11 6 L 113 - 13 18GL -109 - 15 134L -178 - 15 208 -195 - 17 242 -238 - 17 143L -217	1 237 224 -1 360 729 3 961 -95 -3 1861 262 5 881 -147 -5 1493 62 7 1844 -152 -7 324 -254 -9 144 164 -11 1131 -85 -13 1844 -187	24 253 322 -24 1854 132 26 135 134 -26 135 134 -26 276 236 -28 186 17 36 255 -177 37 255 -177 36 1851 185 17 1264 123 -34 1851 2 -34 1851 2	-41423 1652 6 726 -731 -6 1884 -24 81322 -1165 -8 742 718 -10 314 296 -121011 945 -14 566 351 -14 566 351 -16 425 -537	-32 223 124 -32 1771 204
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-33 184L 59 -35 240 -215 m1.2 11158 -1215 -1 444 -403 -3 141L 80 -5 405 -1509 -5 405 -1509 -7 70 805 -7 7143 -1415 -7 74 805 -7 7143 -1415	13 601 605 131247 -1225 15 714 714 -15 848 -762 17 272 317 -17 341 -357 -19 463 -427 21 450 -467 -21 251 216 23 222 -236 23 1841 394	-37 1ABL 57 H-1411 1 652 669 -1 150L -131 3 602 -571 -3 419 411 5 634 -600 -5 366 387 7 682 -691 -7 139L 91 9 366 577 -4 186 7	1 354 369 -1 931 -104 3 453 468 -3 380 -372 5 381 579 -5 861 -879 -7 415 -138 -7 414 -189 9 1412 -98 -9 380 388 11 315 328 13 1845 21 -13 456 465	3 1271 - 134 -3 1844 - 26 5 1811 - 162 5 1351 - 7 -7 1781 - 158 -0 1261 - 41 -11 1201 - 44 -13 861 2 -17 210 214 -19 105 257 -17 210 214 -19 1051 7 -21 198 - 161 -23 266 - 258	-121400 -1472 14 837 -810 14 1310 -1265 10 717 -650 -16 584 -31 18 617 -658 -18 325 -518 -20 534 623 22 674 156 -22 619 314 24 156 255 -24 169 76	-34 1364 -215 -36 129L -215 -36 129L -35 m,-2,8 0 361 -368 2 331 375 -2 467 -480 4 720 716 -41408 -1351 6 129L -25 -6 356 -270 8 179L 182	22 1294 -3 24 1891 38 -24 1891 38 -24 1891 38 -26 1811 -128 -28 205 192 -35 801 -0 -12 1571 74 -34 1701 33 -32 1891 -36 P2,13 C 42L -43
	0 170 18 171 18 171 18 171 18 171 18 171 18 <t< td=""><td>- 4 248 276 - 11124 1045 - 111174 7 - 11454 1045 - 111174 7 - 11454 1045 - 11654 456 - 11654 455 - 15862 - 716 - 15862 - 716 - 15862 - 1086 - 171622 - 1086 - 101824 152 - 101824 155 - 21 356 - 335 - 21 356 - 355 - 21 356 - 356 - 21 356 - 355 - 21 356 - 356 - 21 356 -</td><td>27 127L 111 -27 547 587 29 1602 212 -29 222 242 31 208 161 -31 261 -253 -33 405 -318 -35 205 -217 -4-1+7 1 242 145 -1 186L -60</td><td>11 1431, 107 -11 282 -271 13 573 604 -13 431, 100 15 248 244 -15 63C 613 17 551 26 -17 499 -493 19 213 -105 24 302 -281 21 302 -281 -21 318 -143 -21 318 -143</td><td>15 104 42 -15 184 -123 -17 184 -123 -17 156 -186 -19 53: -87 -19 107: -155 -21 173: -87 -21 173: -87 -23 116 317 -25 95, 110 -27 184, -146 -11 104 -125 -31 184, -10</td><td>-27 200 -148 +,-1,23 1 247 277 -1 1840 55 3 1331 -10 -3 1841 -41 -5 331 -290 -7 1154 -105 -9 189 40 -11 1201 104 -13 1611 215</td><td>-20 330 -273 28 6CL -35 -28 9CL -36 9C 631 36 -30 1541 164 37 244 58 -34 1611 26 m,-2,4 0 1381 -137 2 456 -498 6 812</td><td>-8 1671 98 10 571 -554 -101111 988 12 118 -345 -12 231 -234 14 451 79 462 16 240 -265 -16 1221 165 -18 1621 -166 -18 591 -51 20 1691 92 -20 511 -124</td><td>2 539 -336 -2 505 -677 -4 433 447 -4 330 346 c 18L -124 -c 684 663 8 277 301 -8 39L 65 1C 360 376 -1C 270 209 12 239 -173 -12 590 -533 14 298 -312 -14 635 -611</td></t<>	- 4 248 276 - 11124 1045 - 111174 7 - 11454 1045 - 111174 7 - 11454 1045 - 11654 456 - 11654 455 - 15862 - 716 - 15862 - 716 - 15862 - 1086 - 171622 - 1086 - 101824 152 - 101824 155 - 21 356 - 335 - 21 356 - 355 - 21 356 - 356 - 21 356 - 355 - 21 356 - 356 - 21 356 -	27 127L 111 -27 547 587 29 1602 212 -29 222 242 31 208 161 -31 261 -253 -33 405 -318 -35 205 -217 -4-1+7 1 242 145 -1 186L -60	11 1431, 107 -11 282 -271 13 573 604 -13 431, 100 15 248 244 -15 63C 613 17 551 26 -17 499 -493 19 213 -105 24 302 -281 21 302 -281 -21 318 -143 -21 318 -143	15 104 42 -15 184 -123 -17 184 -123 -17 156 -186 -19 53: -87 -19 107: -155 -21 173: -87 -21 173: -87 -23 116 317 -25 95, 110 -27 184, -146 -11 104 -125 -31 184, -10	-27 200 -148 +,-1,23 1 247 277 -1 1840 55 3 1331 -10 -3 1841 -41 -5 331 -290 -7 1154 -105 -9 189 40 -11 1201 104 -13 1611 215	-20 330 -273 28 6CL -35 -28 9CL -36 9C 631 36 -30 1541 164 37 244 58 -34 1611 26 m,-2,4 0 1381 -137 2 456 -498 6 812	-8 1671 98 10 571 -554 -101111 988 12 118 -345 -12 231 -234 14 451 79 462 16 240 -265 -16 1221 165 -18 1621 -166 -18 591 -51 20 1691 92 -20 511 -124	2 539 -336 -2 505 -677 -4 433 447 -4 330 346 c 18L -124 -c 684 663 8 277 301 -8 39L 65 1C 360 376 -1C 270 209 12 239 -173 -12 590 -533 14 298 -312 -14 635 -611
	14 211 227 -28 186 -24 16 215 87 -15 116 -17 16 215 87 -15 116 -17 16 245 87 -15 116 -17 16 245 87 -15 116 -17 18 245 87 -15 116 -17 18 191 -24 184 427 137 20 1984 -16 -18 901 -10 20 1984 -16 -18 901 -10 20 1984 -16 -28 1984 -11 -20 1984 -16 -29 1984 -11 -22 134 -15 -28 934 -15 20 23 -34 -55 26 934 -55	-31 1281 -135 -35 1894 -13 -25 1894 -10 -27 256 -10 -27 256 -10 -27 614 10 -29 1894 115 -31 1894 149 -33 1894 149 -33 1894 149 -35 1071 -174	-3 410 389 5 1411 -72 -5 929 636 7 493 461 -7 494 434 9 694 654 -9 769 736 11 244 -255 -11 336 -302 23 662 -612 -13 156 -338 15 1661 -75 -15 601 -543	25 1311 40 -25 1312 -117 -27 251 258 -20 240 247 -11 231 16 -33 1841 -187 -35 1841 -187 -1 1841 -36 -1 544 -540 -1 544 -540	He-1+17 1 482 -400 -1 427 -438 3 851 -45 -3 1681 -141 5 1711 155 -5 1461 493 -7 471 69 9 401 387 -9 671 -35	-17 1801 24 -10 414 -424 -21 1291 2 -23 1431 121 -25 1101 5 Fu-1u24 -1 871 16 -3 1044 -127 -5 411 -101 -7 1604 2 -9 1845 79	41147 1116 -4 1521 -114 6 268 295 -61678 -1046 6 1664 -19 -8 818 -865 -101681 -1024 12 577 -496 -12 513 -476 14 186 -295 -14 1801 134 16 464 -426	-22 1101 -80 24 1711 123 -24 419 -424 26 1801 -26 26 1711 -181 20 1781 -88 -28 271 -187 -10 1791 -88 -28 271 -187 -10 1791 -88 -32 248 208 -34 151 144 -34 1031 23 	16 41103 -16 225 -195 18 189L -72 -18 370 329 20 190 127 -2C 539 5C8 27 254 272 -72 222 -93 -74 144L -128 -76 129L -218 -76 189L -13 -30 161L 86 -32 778 249 -14 195 195
22 000 311 -44 128L -37 24 070 -311 -44 128L -37 24 070 -48 -48 128L -31 -24 071 -48 -48 128L -31 24 520 -51C +cC,12 -26 581 -61C +C,12 28 500 -51C +cC,12 -28 500 -51C +cL,13 10 226 -10 -51 0 480 -657 -38 542 -244 2 14 325 10 226 -41 -4 132 331 -31 284 -41 - 4 332 -31 -31 -31 -31 -31 -31 -31 -31 -31 -31	-24 1041 99 2 7 901 1 -24 1041 99 2 7 901 -10 271 -166 -4 1041 -5 -10 271 -166 -4 281 27 -10 151 167 6 169 -17 -12 120 -6 -6 501 -11 -13 1261 67 -4 1061 - -16 1261 67 -10 126 - -16 1261 67 -10 126 - -17 11 4 -1 126 - -16 1261 67 -17 128 - -40 111 4 -1 128 - -40 111 4 -1 128 - -40 111 4 -1 128 - -40 - -40 128 - -4	H-113 1205 -208 1202 210 31201 134 -3144 161 51424 1407 -51421 -2010 7764 679 -7465 457 -9461 103 -11793 801	17 853 612 17 854 612 19 205 214 19 205 205 21 400 481 -21 652 305 23 1131 150 -23 292 23 1131 150 -24 292 24 292 25 1841 12 -27 211 -244 29 1841 -218 -29 1841 -185	-3 348 -334 5 370 389 -5 1722 -190 7 297 292 -7 482 485 9 253 213 -9 1842 -18 11 203 173 -13 1845 -714 -13 248 234 15 216 -197 -15 513 501	TI 184, 78 TI 184, 78 TI 250 TI 177, -63 TI 377, -63 TI 384, -619 TI 184, -39 TI 184, -39 TI 184, -39 TI 184, -39 TI 284, -49 TI 284, -49 TI 294, -47 TI 24, 144, 16 -27 194, -48 TI 294,	-13 001 215 -15 1042 -11 -17 1084 -53 -19 258 -262 -21 1084 -57 -21 1084 -57 -21 1084 -10 -1 1084 1151 -7 941 151 -7	18 1854 101 -18 485 426 20 1864 70 -20 854 -90 -20 854 -90 -21 854 18 -22 372 -991 24 1754 -138 -24 1104 -92 26 244 112 -26 1854 86 28 1004 70 -28 1854 -01 30 1854 -13	0 196 186 2 405 -406 -2 406 -628 4 863 814 -4582 1597 6 281 288 -6 603 -583 8 1894 45 -8 1411 -80 10 811 124 -101348 1518 12 310 -309 -12 865 865	+2,14 C 112L -04 2 474 475 -7 60L -4 4 604 -646 -4 183L 70 6 235 -217 -6 535 597 8 217 -229 -8 71L 111 1C 150L -116
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Table 4 (cont.)

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-8 47L 10 109L -10 17LL	130	0 134L - 2 77L - -2 189L	17 -91 31 11 30 -11	029 9 154L -1 173L -1	62 62	н,-3,5 1 325 -		r,-3,19		+,-3,20 1 766	154	28 2COL - -24 1C8L 10 140L -	131 26 152	2/ 14AL -175 -27 122L 40 24 195L -255	-26 67L -28 200L -10 165L	-144	9 1911 9 200L	151	1 544 -59 -1 1811 -24 5 747 -4	2	4 127L -5 112 7 464	275
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16 201 -16 139L - 18 102L	111	12 101 -2 14 1301 1 16 211 1	89 17 01 -17 54 19	367 - 72L 521	91 91	5 681 -5 180 7 505	721 350 501	-3 294 5 181L -5 190L	103	-5 183L -	201	9 328 -	31.3	-28 2001 -149 -16 2001 -68 -12 1551 -80	0 264	-248	-6 200L 8 200L	-36	-7 929 81 9 755 7 -9 700 7		11 247	202
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12 97L -12 406 -14 162L	-89 382 -169	-1 687 5 90L	-632 2 640 -2 27 2	5 95L 5 236 7 190L 7 190	-111	-17 64L 19 19CL -19 19CL	-94	-31 272	340	4 2CCL 6 913 8 926	-21 68C 791	-10 82L 12 636 -12 38L	- 4 3 3	A 274 335 -2 456 433 3C 74L 76 -10 1371 -145	-26 169L -28 329 -30 223 -12 200L	-267	11 267 13 230 15 16#L 17 212L	-266 -258 -66 -229	-21 68L 23 425 3 -23 197L -2 25 72L 1	16 02	1 129L -1 218	-124 -188
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0.004 Å and range from 0.003 to 0.006 Å. The errors in the angles average 0.26° and range from 0.11 to 0.40° . The bond angles and distances are in good agreement with those found in other molecules which contain similar groups (Table 6).

The guanidino group is planar. The equation of the least-squares plane (Schomaker, Waser, Marsh & Bergman, 1959) through the four atoms of the guanidino group N(1), C(1), N(2), and N(3) is

$$19.65x + 2.30y - 12.54z = -2.49$$

where the coordinates x, y, and z are in fractions of a cell edge. The deviations of some of the atoms from this plane are shown in Table 5. The angle between the plane of the guanidino group and the plane through the three atoms of the carboxyl group, C(4), O(4) and O(5), is 81.35° , to be compared to the value 84.5° obtained by Mendel & Hodgkin (1954) for creatine monohydrate. This similarity, together with the agreement between the bond angles and distances, indicates that the creatine portion of the molecule adopts a similar configuration in the two structures.

 Table 5. Distances of atoms from

 the plane of the guanidino group

Å

*N(1)	-0.0005
*C(1)	0.0015
*N(2)	0.0005
*N(3)	-0.0005
P(1)	0.2168
H(1)	-0.1145
H(2)	0.0930
H(3)	-0.2598
C(2)	0.2054
C(3)	-0.0046

* Atoms included in the calculation of the plane.

The structure, projected down the *b* axis, is shown in Fig. 2. The hydrogen bonding is seen to be complete; all hydrogen atoms available for hydrogen bonding are used. Those hydrogen bonds which run approximately parallel to the *b* axis are shown in Fig. 3, a projection of part of the structure down the *c* axis. Hydrogen bond distances appear to be normal (Donohue, 1952); $N-H\cdots O$ distances range from 2.73 Å to 3.05 Å and $O-H\cdots O$ distances all lie between 2.72 Å and 2.85 Å. Because the hydrogen atoms are not accurately placed, detailed discussion of distances and angles involving these atoms would be unjustified.

The distribution of oxygen atoms around the two sodium ions is shown in Fig.4. Na (1^{v}) is octahedrally

coordinated while Na(2^v) appears to be surrounded by four oxygen atoms in a distorted tetrahedron. The observed arrangement of oxygen atoms about Na(2^v) could be described as octahedral but the two extra oxygen atoms, O(10''') and O(8^v) are 2.915 and 3.436 Å from the sodium ion, rather too far to be considered as taking part in the coordination.

The octahedra about the two sodium ions Na(1^v) and Na(1^{'''}), related by a twofold rotation axis share a face defined by $O(1''')-O(8^v)-O(1^v)$, and the tetrahedron about Na(2^v) shares an edge defined by $O(6^v)$ and $O(9^v)$ with the octahedron about Na(1^v). The oxygen-sodium distance $O(10''')-Na(2^v)$ of 2.915 Å is the shortest interatomic distance between unbonded atoms, excluding hydrogen.

The water molecule oxygen atoms O(8) and O(10) have large apparent anisotropies in their thermal motions. This is tentatively attributed to disorder. This hypothesis is particularly attractive in the case of O(8)which was treated as lying on the twofold rotation axes of the space group C2/c. If this position is disordered in a direction perpendicular to the rotation axis, perhaps linked to a disorder of the O(10) position, this symmetry element is destroyed and the symmetry reduces to that of the space group $P2_1/c$. The occurrence of a few weak reflections for which h+k is odd is consistent with this hypothesis but it is not suggested that this constitutes a proof of disorder.

 Table 6. Comparison of bond angles and distances found in N-phosphorylcreatine with those found in other structures

Distances are in Å and angles in degrees. For purposes of comparison, the error in a bond length may be taken as ± 0.01 Å and the error in the measurement of a bond angle to be ± 1 to 2 degrees.

(1) Bond distances in the guanidino group	N(1)-C(1)	N(2)-C(1)	N(3)-C(1)				
Creatine monohydrate ^(a) Creatine monohydrate ^(b) Guanidinium chloride ^(c)	1·35 1·344 1·318	1.32 1.339 1.325	1·32 1·304				
N-Phosphorylcreatine	1.354	1.326	1.339				
(2) Bond distances in the phosphoryl group	N(1)-P(1)	P(1)-O(1)	P(1)-O(2)	P(1)-O(3)			
Monosodium phosphoramidate ^(d) , * ^(e) * later refinement	1·785 1·769*	1·511 1·522*	1·517 1·522*	1·517 1·522*			
Calcium diphosphoimidazole ^(f)	1·77	1·47	1.49	1.51			
Average distance for P-O ⁻ or P=O for six other compounds $^{(g)}$ N-Phosphorylcreatine	1.735	1.505 1.504	1·505 1·507	1·505 1·517			
(3) Bond angles in the guanidino group	N(1)-C	(1)-N(2) N((1)-C(1)-N(3)	N(2)-C(1)-N(3)			
Creatine monohydrate ^(a) Creatine monohydrate ^(b) Guanidinium chloride ^(c) N-Phosphorylcreatine	11 11 12 11	8 5·5 0·8 9·2	121 120·7 119·3 119·6	121 123·9 119·7 121·2			
(4) Average bond angles in the phosphoryl group	Avera	ige N–P–O a	ingle Averag	e O-P-O angle			
Monosodium phosphoramidate ^(d) Monosodium phosphoramidate ^(e)		102·9 104	-	115·2 114			
Calcium diphosphoimidazole (f)		103·1 102·7		115·0 115·3			
N-Phosphorylcreatine		104.8		113.8			

References: (a) Mendel & Hodgkin (1954), (b) Jensen (1955), (c) Haas, Harris & Mills (1965), (d) Hobbs, Corbridge & Raistrick (1953), (e) Cruickshank (1961), (f) Beard & Lenhert (1967), (g) Karle & Britts (1966).

Biochemical implications

The relatively large decrease in free energy which occurs when an energy-rich compound undergoes hydrolysis implies that the products are thermodynamically more stable than the reactants. Ever since the concept of opposing resonance was introduced by Kalckar (1941), the instability of high energy phosphate compounds has been explained largely in terms of a number of resonance forms, some of which are blocked in the parent compound but available to the products of hydrolysis. Now that X-ray structure analyses of guanidinium chloride (Haas, Harris & Mills, 1965), creatine monohydrate (Mendel & Hodgkin, 1954; Jensen, 1955) and N-phosphorylcreatine are available, a comparison of the bond distances found in the guanidino group of N-phosphorylcreatine with those found in creatine and the guanidinium ion can be made.

The guanidinium ion is shown in Fig. 5(a). The three nitrogen atoms are chemically equivalent and thus the three valence bond structures (i), (ii), (iii) make equal contributions to the resonance stabilization. One of the nitrogen atoms in creatine, Fig. 5(b), is doubly substituted and one might suppose that the two forms, (iv) and (v), make the important contributions to the res-

onance energy. N-Phosphorylcreatine [Fig. 5(c)] is substituted on two of the three nitrogen atoms and as a result, the resonance in this molecule is thought to be less than in either of the above compounds.

The bond distances and angles for these compounds are included in Table 6. The average C-N bond distance in the guanidino group for guanidinium chloride, creatine and N-phosphorylcreatine are 1.32, 1.33 and 1.34 Å respectively; the bond distances increase as the predicted resonance energy decreases. But are these differences significant? There is increasing evidence that the estimated standard deviations which are produced by the least-squares procedure are too small. Hamilton (1965) and Guilhem (1967) suggest that the σ 's from least-squares refinement should be multiplied by a factor of 2 to get realistic standard deviations. Taking, therefore, ± 0.01 Å as the σ for bond lengths in these compounds, it is clear that these differences in average bond length cannot be considered significant.

When *N*-phosphorylcreatine is hydrolyzed to creatine plus phosphate, the change in free energy is approximately -10 kcal.mole⁻¹ (Carlson, 1963). The bond length-bond energy curve for C-N bonds indicates that in the region of 1.33 Å, a change of 0.04 Å results in an energy change of ~10 kcal.mole⁻¹. The observed differences between the C-N bond distances



Fig. 3. Hydrogen bonds in the disodium salt of N-phosphorylcreatine hydrate which run approximately parallel to the b axis. Portions of the structure are projected along the c axis. The plus c axis points down, below the paper. This is an oblique parallel projection onto (001).

in N-phosphorylcreatine and those in creatine add up to 0.03 Å, which could account for much of the energy released upon hydrolysis but, because these differences are not statistically significant, the question of the relative resonance stabilization of the guanidino group must remain unresolved.

The oxygen-phosphorus distances in N-phosphorylcreatine are also equal within the experimental error and are close to those expected for bonds between phosphorus and unprotonated oxygen atoms (Table 6). It appears that little resonance stabilization is to be gained as a result of hydrolysis.

Hill & Morales (1951) discussed the fact that the hydrolysis of guanidino phosphates involves the splitting of N–P and H–O bonds and the formation of N–H and O–P bonds. Using estimates of bond energies obtained from Pauling (1940), they concluded that the difference could account for only about 1.5 kcal.mole⁻¹. This effect, small to begin with, is counteracted by the electrostatic attraction between the negatively charged phosphoryl group and the positively charged guanidino moiety, which tends to stabilize the molecule.

In the crystalline state there is rotation about the C(1)-N(1) and the C(1)-N(3) bonds of 9.2 and 9.8° respectively, bringing the P(1) and C(2) atoms out of the plane of the guanidino group (Table 7). Corey & Pauling (1953) calculated the strain energy due to rotation about a C-N peptide bond using the expression: Strain energy = $A \sin^2 \delta$, where A represents the resonance energy of the amide group when in the planar configuration. Using this same relation and approximating the resonance energy by that of guanidine, 47 kcal.mole⁻¹ (Pauling, 1940), the strain energies are 1.2 and 1.4 kcal.mole⁻¹. Mendel & Hodgkin (1954) found that the methyl carbon C(2) of creatine was out of the plane of the guanidino group by 0.10 Å or about half the distance found in N-phosphorylcreatine. It appears that there is a difference in stability due to strain between the two molecules when crystallized. Whether this is true in solution is another matter.

In conclusion, the X-ray results are consistent with the theory that the stability of the guanidino group is greater in creatine than in N-phosphorylcreatine, but because the differences in bond lengths are of the same magnitude as the uncertainties in these distances, the results cannot be used to prove or disprove the theory.

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Fig.4. The distribution of oxygen atoms about the two sodium ions. Distances are in Å.



(c) N-PHOSPHORYL CREATINE



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Structure Cristalline de MoNb₁₅O₄₀F

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MoNb₁₅O₄₀F crystallizes in the monoclinic system with lattice parameters $a=22\cdot29$, $b=3\cdot831$, $c=20\cdot27$ Å, $\beta=114^{\circ}$. The space group is C2. The original structure, refined by least-squares methods, contains ReO₃-type blocks of Nb–O octahedra, 3×5 and infinite along b. The blocks are joined by sharing edges and with tetrahedrally coordinated Mo atoms at the junctions of every four blocks. MoNb₁₅O₄₀F can be represented by the structural formula:



Les systèmes binaires MoO_3-NbO_2F , $NbO_2F-Nb_2O_5$ et $MoO_3-Nb_2O_5$ ont fait l'objet d'études approfondies. Si le système MoO_3-NbO_2F ne révèle la présence d'aucune phase nouvelle, les deux autres systèmes sont par contre beaucoup plus riches.

Le système $NbO_2F-Nb_2O_5$ comporte quatre composés originaux Nb_3O_7F , $Nb_5O_{12}F$, $Nb_{17}O_{42}F$ et $Nb_{31}O_{77}F$, dont la préparation et l'étude structurale sont dues à Andersson et Åström (Andersson, 1964, 1965*a*; Andersson & Åström, 1964; Åström, 1966).

Dans le système $MoO_3-Nb_2O_5$ deux phases ont été mises en évidence et leurs caractères cristallographiques précisés: l'une $Mo_3Nb_{14}O_{44}$, de symétrie quadratique, est isotype de $W_3Nb_{14}O_{44}$, l'autre $MoNb_{12}O_{33}$, monoclinique, est isotype de $WNb_{12}O_{33}$; ces composés du tungstène ont été préparés et étudiés par Roth & Wadsley (1965).

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