

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

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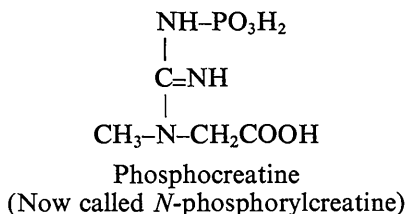
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*N*-Phosphorylcreatine, a biological 'high energy phosphate', serves as an energy reservoir in vertebrate muscles. Crystals of the disodium salt,  $\text{Na}_2\text{PN}_3\text{C}_4\text{O}_5\text{H}_8 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ , were prepared. The space group is  $P2_1/c$ , with unit-cell dimensions  $a=24.85$ ,  $b=6.64$ ,  $c=16.94 \text{ \AA}$  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  $K\alpha$  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):



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,  $\text{POCl}_3$ . 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 pH 9.0 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 six-sided 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 *N*-phosphorylcreatine–water–ethanol mixtures stored at  $20 \pm 0.5^\circ\text{C}$ . 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

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 moving-crystal ' $\omega$  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  $\text{Cu } K\alpha$  radiation. For this reason and because it is much less absorbed,  $\text{Mo } K\alpha$  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  $\theta-2\theta$  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  $\bar{9}$ . The

Table 1. *Crystal data for the disodium salt of N-phosphorylcreatine hydrate,  $\text{Na}_2\text{PC}_4\text{N}_3\text{O}_5\text{H}_8 \cdot 4\frac{1}{2}\text{H}_2\text{O}$*

Lattice parameters at room temperature using  $\text{Cu } K\alpha$  ( $\lambda=1.5418 \text{ \AA}$ ) radiation:

$$\begin{aligned} a &= 24.85 \pm 0.015 \text{ \AA} \\ b &= 6.64 \pm 0.005 \\ c &= 16.94 \pm 0.010 \\ \beta &= 109.54 \pm 0.05^\circ \\ \text{Cell volume} &= 2635 \pm 3 \text{ \AA}^3 \end{aligned}$$

Density:

$$\begin{aligned} \text{Measured,} & \quad 1.701 \pm 0.003 \text{ g.cm}^{-3} \\ \text{Calculated with eight formula units of } & \text{Na}_2\text{PC}_4\text{N}_3\text{O}_5\text{H}_8 \cdot 4\frac{1}{2}\text{H}_2\text{O} \text{ per unit cell, } 1.694 \text{ g.cm}^{-3} \end{aligned}$$

Other data

$$F(000) = 1400$$

Space group:

(1) True space group,  $P2_1/c$

$Z=4$ , two formula units per asymmetric unit

(2) Pseudo space group,  $C2/c$

$Z=8$ , one formula unit per asymmetric unit

Observed systematic absences

$hkl$ : none

$h0l$ :  $l$  odd

$0k0$ :  $k$  odd

$hkl$ :  $h+k$  odd\*

$h0l$ :  $l$  odd ( $h$  odd)

$0k0$ : ( $k$  odd)

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

Linear absorption coefficients

(1)  $\text{Cu } K\alpha$  ( $\lambda=1.5418 \text{ \AA}$ )  $\mu=30.85 \text{ cm}^{-1}$

(2)  $\text{Mo } K\alpha$  ( $\lambda=0.7107 \text{ \AA}$ )  $\mu=3.4 \text{ cm}^{-1}$

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  $h\bar{4}l$  through  $h\bar{9}l$  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  $h\bar{9}l$  section was measured, the reflections which occurred at values of  $\sin \theta/\lambda \leq 0.25 \text{ \AA}^{-1}$  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  $h0l$  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  $1/(2\pi)^{1/2} \exp[-\frac{1}{2}E(hkl)^2]$  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  $E_h, E_{h'}$  and  $E_{h-h'}$ . The groups of three reflections could then be used in either Sayre's (1952) sign relation or in the  $\Sigma_2$  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  $\pi$ ) of the twenty-four three-dimensional ( $h, k, l \neq 0$ ) reflections that had values of  $E(hkl) \geq 2.65$ . 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  $\sin \theta/\lambda \leq 0.5 \text{ \AA}^{-1}$ .

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  $1.0 \text{ \AA}^{-1}$ . The *R* value at this stage was 36% but dropped to 23% after several cycles of Fourier refinement.

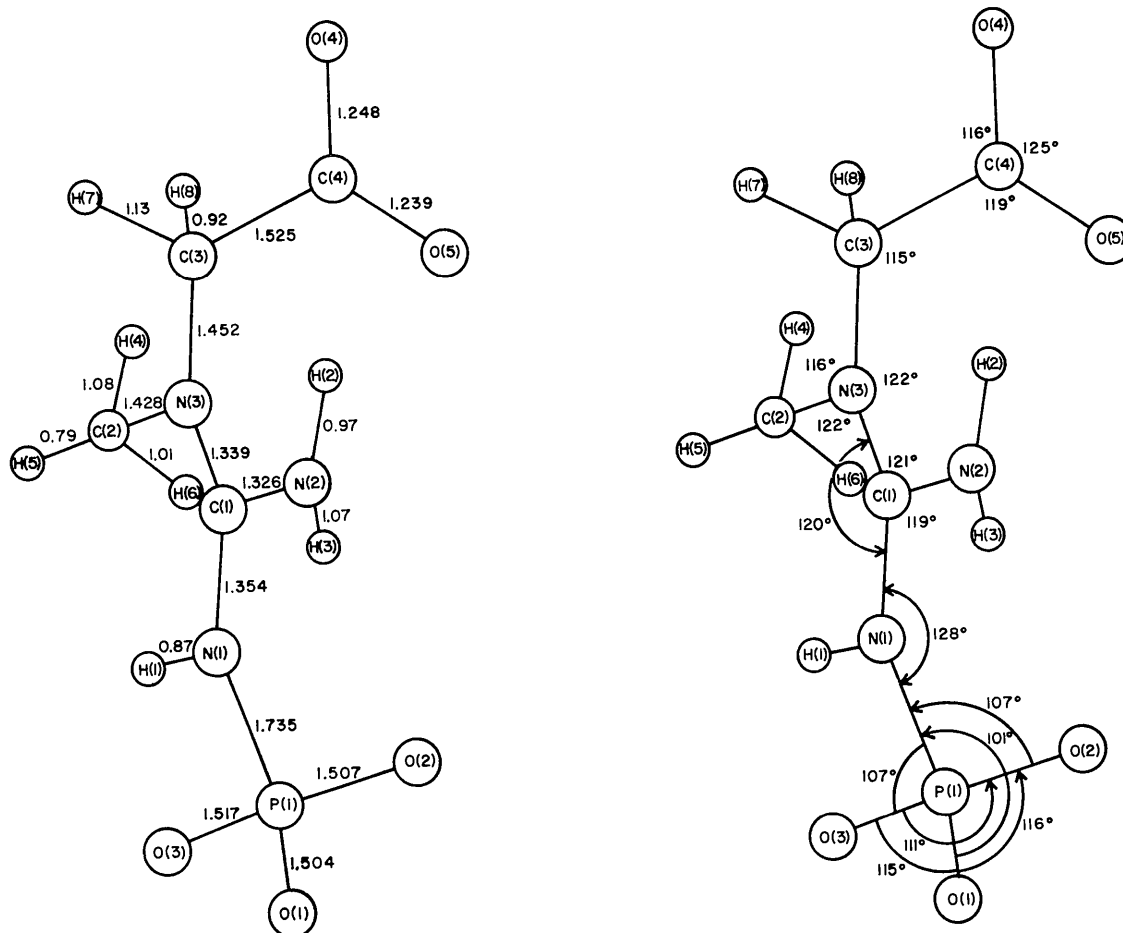


Fig. 1. Bond lengths and bond angles in the disodium salt of *N*-phosphorylcreatine hydrate. These values have not been corrected for thermal motion. Distances are in Å and angles are in degrees.

## Final refinement

Two cycles of full-matrix least-squares refinement were run minimizing  $\sum w(\Delta F)^2$  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 full-matrix least-squares refinement were run with individual anisotropic temperature factors for non-hydro-

gen atoms and the discrepancies were weighted using the expression

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

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

<i>R</i> , omitting unobserved reflections	0.083
<i>R</i> , with reflection multiplicity omitting unobserved reflections	0.083
Weighted <i>R</i> value, omitting unobserved reflections	0.102
<i>R</i> 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

$$\text{T.F.} = \exp \left[ -\frac{1}{4}(h^2a^2B_{11} + k^2b^2B_{22} + l^2c^2B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23}) \right].$$

	<i>x</i>	<i>y</i>	<i>z</i>
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(1)	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)	0.3565 (65)	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)	0.1407 (21)	0.7868 (77)	0.3551 (30)
H(12)	0.1581 (18)	0.8554 (62)	0.3199 (26)
H(13)	0.0561 (20)	0.9282 (76)	0.4099 (30)
H(14)	0.0649 (19)	0.7910 (69)	0.4779 (27)
H(15)	0.0244 (18)	0.6746 (69)	0.2829 (33)
H(16)	0.1181 (19)	0.8791 (69)	0.1267 (27)
H(17)	0.0750 (*)	0.9491 (*)	0.0547 (*)

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

to extinction) and so all eight of the reflections which occur at  $\sin \theta/\lambda \leq 0.1 \text{ \AA}^{-1}$  were given zero weight. They are: 200, 400, 002,  $\bar{2}02$ , 202,  $\bar{4}02$ ,  $1\bar{1}1$  and  $\bar{1}\bar{1}1$ .

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 full-matrix 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 least-squares refinement in which two atoms were allowed to vibrate anisotropically, and one cycle of block-diagonal 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)	6.00†					
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)	3.87†					
H(15)	4.18†					
H(16)	6.00†					
H(17)	4.00‡					

† Isotropic temperature factors for hydrogen atoms were constrained to lie between 2.00 and 6.00  $\text{\AA}^2$ .

‡ 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  $\sin \theta/\lambda = 0.5 \text{ \AA}^{-1}$ . These hydrogen atoms were included in the refinement but their isotropic temperature factors were arbitrarily confined to lie between 2.0 and 6.0  $\text{\AA}^2$ . 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  $\text{\AA}$ . 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  $\text{\AA}$  apart (Fig. 2) and therefore presumably hydrogen bonded. The difference map had a peak between these two water molecules about 1  $\text{\AA}$  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 non-hydrogen bond distances, indicated by the inverse matrix from the final least-squares refinement, average

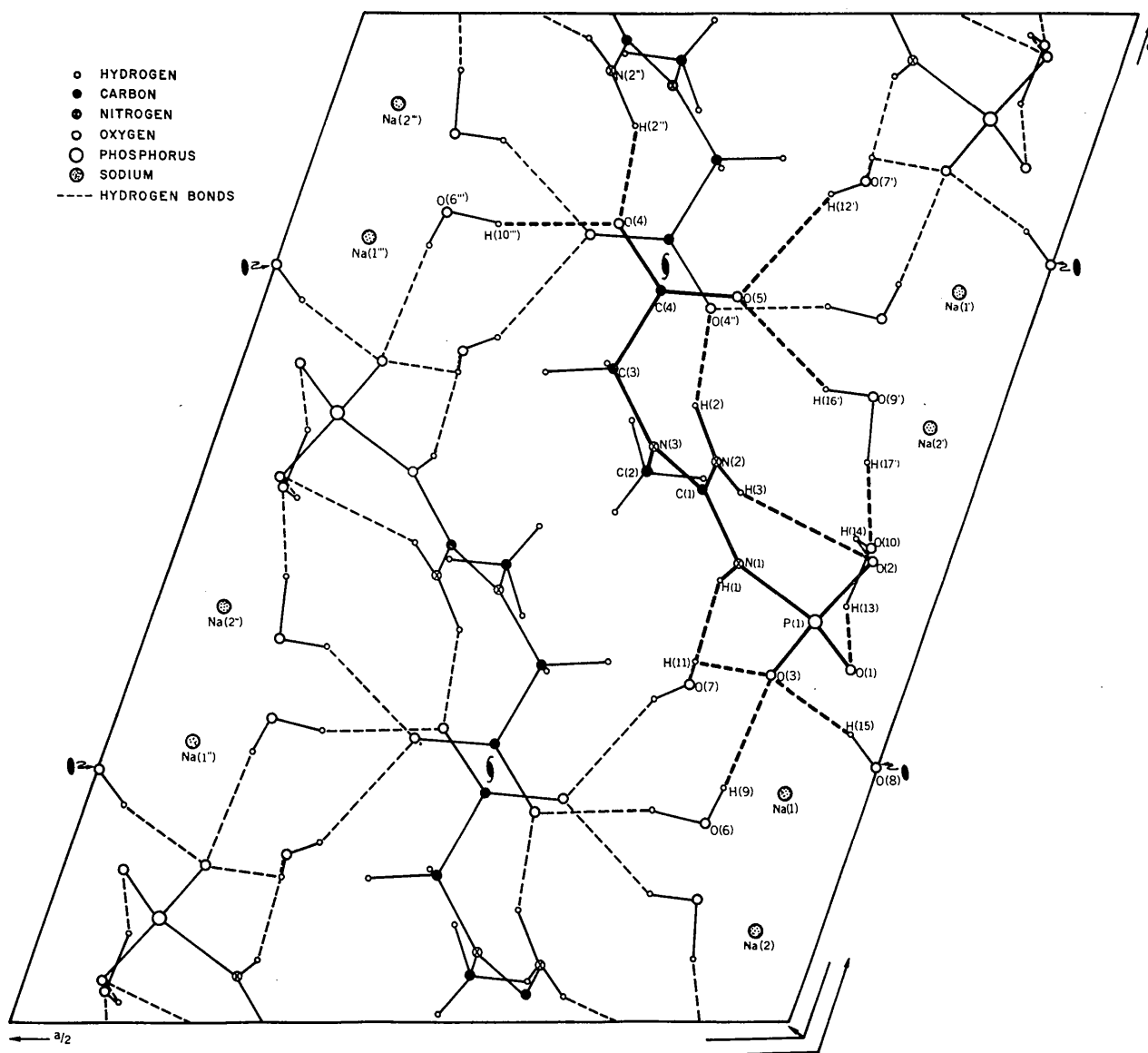


Fig. 2. Hydrogen bonding in the disodium salt of *N*-phosphorylcreatine hydrate. The structure is projected onto (010) with the plus *b* axis pointing up, out of the paper.

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.

$h$	$10F_o$	$10F_c$	$h$	$10F_o$	$10F_c$	$h$	$10F_o$	$10F_c$	$h$	$10F_o$	$10F_c$
000	0	0	100	100	100	200	200	200	300	300	300
100	100	100	101	101	101	201	201	201	301	301	301
101	101	101	102	102	102	202	202	202	302	302	302
102	102	102	103	103	103	203	203	203	303	303	303
103	103	103	104	104	104	204	204	204	304	304	304
104	104	104	105	105	105	205	205	205	305	305	305
105	105	105	106	106	106	206	206	206	306	306	306
106	106	106	107	107	107	207	207	207	307	307	307
107	107	107	108	108	108	208	208	208	308	308	308
108	108	108	109	109	109	209	209	209	309	309	309
109	109	109	110	110	110	210	210	210	310	310	310
110	110	110	111	111	111	211	211	211	311	311	311
111	111	111	112	112	112	212	212	212	312	312	312
112	112	112	113	113	113	213	213	213	313	313	313
113	113	113	114	114	114	214	214	214	314	314	314
114	114	114	115	115	115	215	215	215	315	315	315
115	115	115	116	116	116	216	216	216	316	316	316
116	116	116	117	117	117	217	217	217	317	317	317
117	117	117	118	118	118	218	218	218	318	318	318
118	118	118	119	119	119	219	219	219	319	319	319
119	119	119	120	120	120	220	220	220	320	320	320
120	120	120	121	121	121	221	221	221	321	321	321
121	121	121	122	122	122	222	222	222	322	322	322
122	122	122	123	123	123	223	223	223	323	323	323
123	123	123	124	124	124	224	224	224	324	324	324
124	124	124	125	125	125	225	225	225	325	325	325
125	125	125	126	126	126	226	226	226	326	326	326
126	126	126	127	127	127	227	227	227	327	327	327
127	127	127	128	128	128	228	228	228	328	328	328
128	128	128	129	129	129	229	229	229	329	329	329
129	129	129	130	130	130	230	230	230	330	330	330
130	130	130	131	131	131	231	231	231	331	331	331
131	131	131	132	132	132	232	232	232	332	332	332
132	132	132	133	133	133	233	233	233	333	333	333
133	133	133	134	134	134	234	234	234	334	334	334
134	134	134	135	135	135	235	235	235	335	335	335
135	135	135	136	136	136	236	236	236	336	336	336
136	136	136	137	137	137	237	237	237	337	337	337
137	137	137	138	138	138	238	238	238	338	338	338
138	138	138	139	139	139	239	239	239	339	339	339
139	139	139	140	140	140	240	240	240	340	340	340
140	140	140	141	141	141	241	241	241	341	341	341
141	141	141	142	142	142	242	242	242	342	342	342
142	142	142	143	143	143	243	243	243	343	343	343
143	143	143	144	144	144	244	244	244	344	344	344
144	144	144	145	145	145	245	245	245	345	345	345
145	145	145	146	146	146	246	246	246	346	346	346
146	146	146	147	147	147	247	247	247	347	347	347
147	147	147	148	148	148	248	248	248	348	348	348
148	148	148	149	149	149	249	249	249	349	349	349
149	149	149	150	150	150	250	250	250	350	350	350
150	150	150	151	151	151	251	251	251	351	351	351
151	151	151	152	152	152	252	252	252	352	352	352
152	152	152	153	153	153	253	253	253	353	353	353
153	153	153	154	154	154	254	254	254	354	354	354
154	154	154	155	155	155	255	255	255	355	355	355
155	155	155	156	156	156	256	256	256	356	356	356
156	156	156	157	157	157	257	257	257	357	357	357
157	157	157	158	158	158	258	258	258	358	358	358
158	158	158	159	159	159	259	259	259	359	359	359
159	159	159	160	160	160	260	260	260	360	360	360
160	160	160	161	161	161	261	261	261	361	361	361
161	161	161	162	162	162	262	262	262	362	362	362
162	162	162	163	163	163	263	263	263	363	363	363
163	163	163	164	164	164	264	264	264	364	364	364
164	164	164	165	165	165	265	265	265	365	365	365
165	165	165	166	166	166	266	266	266	366	366	366
166	166	166	167	167	167	267	267	267	367	367	367
167	167	167	168	168	168	268	268	268	368	368	368
168	168	168	169	169	169	269	269	269	369	369	369
169	169	169	170	170	170	270	270	270	370	370	370
170	170	170	171	171	171	271	271	271	371	371	371
171	171	171	172	172	172	272	272	272	372	372	372
172	172	172	173	173	173	273	273	273	373	373	373
173	173	173	174	174	174	274	274	274	374	374	374
174	174	174	175	175	175	275	275	275	375	375	375
175	175	175	176	176	176	276	276	276	376	376	376
176	176	176	177	177	177	277	277	277	377	377	377
177	177	177	178	178	178	278	278	278	378	378	378
178	178	178	179	179	179	279	279	279	379	379	379
179	179	179	180	180	180	280	280	280	380	380	380
180	180	180	181	181	181	281	281	281	381	381	381
181	181	181	182	182	182	282	282	282	382	382	382
182	182	182	183	183	183	283	283	283	383	383	383
183	183	183	184	184	184	284	284	284	384	384	384
184	184	184	185	185	185	285	285	285	385	385	385
185	185	185	186	186	186	286	286	286	386	386	386
186	186	186	187	187	187	287	287	287	387	387	387
187	187	187	188	188	188	288	288	288	388	388	388
188	188	188	189	189	189	289	289	289	389	389	389
189	189	189	190	190	190	290	290	290	390	390	390
190	190	190	191	191	191	291	291	291	391	391	391
191	191	191	192	192	192	292	292	292	392	392	392
192	192	192	193	193	193	293	293	293	393	393	393
193	193	193	194	194	194	294	294	294	394	394	394
194	194	194	195	195	195	295	295	295	395	395	395
195	195	195	196	196	196	296	296	296	396	396	396
196	196	196	197	197	197	297	297	297	397	397	397
197	197	197	198	198	198	298	298	298	398	398	398
198	198	198	199	199	199	299	299	299	399	399	399
199	199	199	200	200	200	300	300	300	400	400	400
200	200	200	201	201	201	301	301	301	401	401	401
201	201	201	202	202	202	302	302	302	402	402	402
202	202	202	203	203	203	303	303	303	403	403	







Table 5. Distances of atoms from the plane of the guanidino group

*N(1)	-0.0005 Å
*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...O distances range from 2.73 Å to 3.05 Å and O-H...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<sup>v</sup>) is octahedrally

coordinated while Na(2<sup>v</sup>) appears to be surrounded by four oxygen atoms in a distorted tetrahedron. The observed arrangement of oxygen atoms about Na(2<sup>v</sup>) could be described as octahedral but the two extra oxygen atoms, O(10<sup>'''</sup>) and O(8<sup>v</sup>) 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<sup>v</sup>) and Na(1<sup>'''</sup>), related by a twofold rotation axis share a face defined by O(1<sup>'''</sup>)-O(8<sup>v</sup>)-O(1<sup>v</sup>), and the tetrahedron about Na(2<sup>v</sup>) shares an edge defined by O(6<sup>v</sup>) and O(9<sup>v</sup>) with the octahedron about Na(1<sup>v</sup>). The oxygen-sodium distance O(10<sup>'''</sup>)-Na(2<sup>v</sup>) 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 *C*2/*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 *P*2<sub>1</sub>/*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 <sup>(a)</sup>	1.35	1.32	1.32	
Creatine monohydrate <sup>(b)</sup>	1.344	1.339	1.304	
Guanidinium chloride <sup>(c)</sup>	1.318	1.325	1.325	
<i>N</i> -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 <sup>(d)</sup> , * <sup>(e)</sup>	1.785	1.511	1.517	1.517
* later refinement	1.769*	1.522*	1.522*	1.522*
Calcium diphosphoimidazole <sup>(f)</sup>	1.77	1.47	1.50	1.51
Average distance for P-O <sup>-</sup> or P=O for six other compounds <sup>(g)</sup>	1.79	1.49	1.49	1.49
<i>N</i> -Phosphorylcreatine	1.735	1.505	1.505	1.505
		1.504	1.507	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 <sup>(a)</sup>	118	121	121	
Creatine monohydrate <sup>(b)</sup>	115.5	120.7	123.9	
Guanidinium chloride <sup>(c)</sup>	120.8	119.3	119.7	
<i>N</i> -Phosphorylcreatine	119.2	119.6	121.2	
(4) Average bond angles in the phosphoryl group	Average N-P-O angle	Average O-P-O angle		
Monosodium phosphoramidate <sup>(d)</sup>	102.9	115.2		
Monosodium phosphoramidate <sup>(e)</sup>	104	114		
Calcium diphosphoimidazole <sup>(f)</sup>	103.1	115.0		
<i>N</i> -Phosphorylcreatine	102.7	115.3		
	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 & Lenhart (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  $\sigma$ 's from least-squares refinement should be multiplied by a factor of 2 to get realistic standard deviations. Taking, therefore,  $\pm 0.01$  Å as the  $\sigma$  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  $\sim 10$  kcal.mole $^{-1}$ . The observed differences between the C-N bond distances

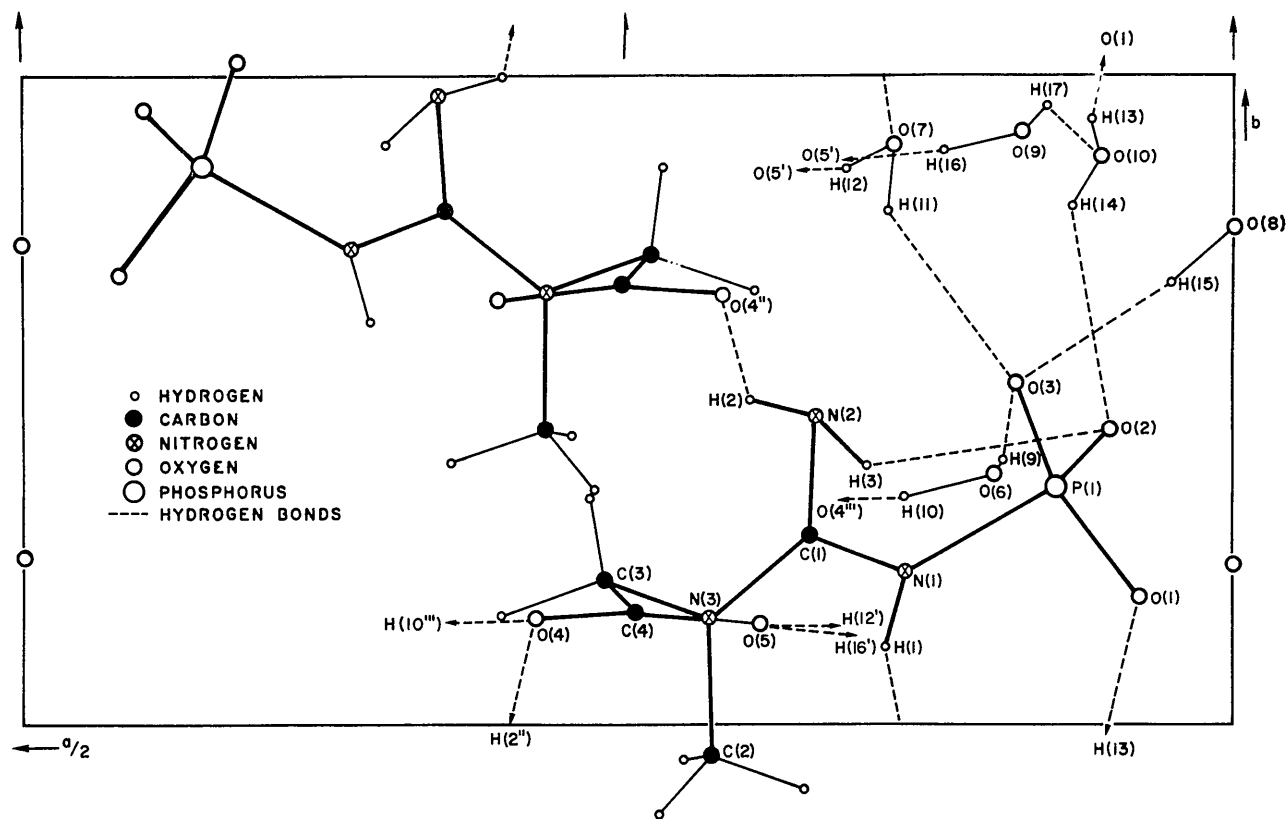


Fig. 3. Hydrogen bonds in the disodium salt of *N*-phosphorylcreatine hydrate which run approximately parallel to the *b* axis. Portions of the structure are projected along the *c* axis. The plus *c* axis points down, below the paper. This is an oblique parallel projection onto (001).

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<sup>-1</sup>. 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<sup>-1</sup> (Pauling, 1940), the strain energies are 1.2 and 1.4 kcal.mole<sup>-1</sup>. 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.

The authors are indebted to Professor James M. Stewart of the University of Maryland, who introduced us to the *X-RAY* 63 package of crystallographic computing programs and who generously gave his time to assist us in its use. Support of this work by the National Institutes of Health in the form of predoctoral fellowships (4F1 GM-15, 503) and a grant (2 RO1 AMO2528) is gratefully acknowledged.

#### References

BEARD, L. N. & LENHART, P. G. (1967). ACA meeting, Atlanta, Georgia, January 25-28, paper K9.

CARLSON, F. D. (1963). *Progr. Biophys. Biophys. Chem.* **13**, 262.

COCHRAN, W. & WOOLFSON, M. M. (1955). *Acta Cryst.* **8**, 1.

COREY, A. B. & PAULING, L. (1953). *Proc. Roy. Soc. B* **141**, 10.

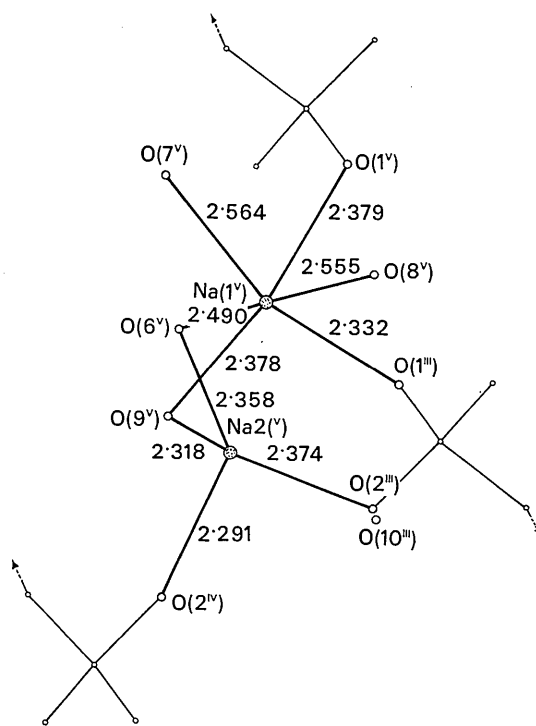


Fig. 4. The distribution of oxygen atoms about the two sodium ions. Distances are in Å.

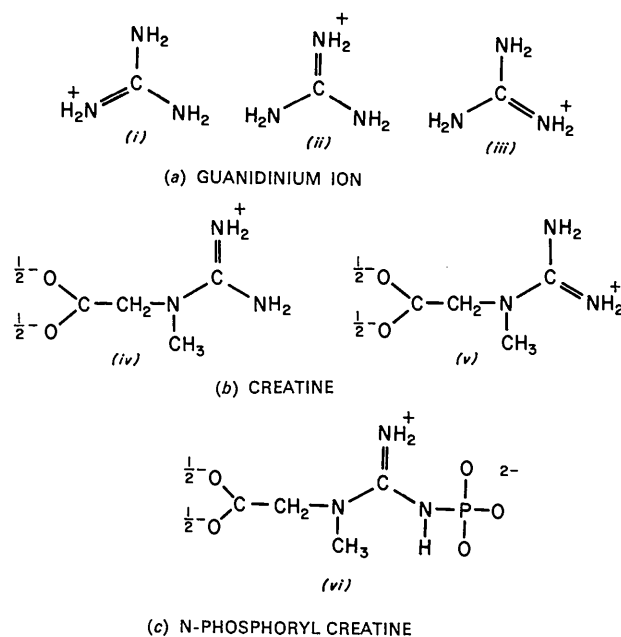


Fig. 5. Valence-bond structures for the guanidinium ion after substitution on (a) none, (b) one, and (c) two of the nitrogen atoms.

- CRUICKSHANK, D. W. J. (1961). *J. Chem. Soc.* p. 5486.
- DICKINSON, C., STEWART, J. M. & HOLDEN, J. R. (1966). *Acta Cryst.* **21**, 663.
- DONOHUE, J. (1952). *J. Phys. Chem.* **56**, 502.
- EGGELTON, P. & EGGELTON, G. P. (1927). *Biochem. J.* **21**, 190.
- ENNOR, A. H. (1957). In *Methods in Enzymology*. Edited by S. P. COLOWICK & N. O. KAPLAN. Vol. III, p. 855. New York: Academic Press.
- ENNOR, A. H. & STOCKEN, L. A. (1957). *Biochemical Preparations*. Edited by D. SHEMIN. Vol. 5, p. 9. New York: John Wiley.
- FISKE, C. H. & SUBBAROW, Y. (1927). *J. Biol. Chem.* **74**, p. xxii.
- FISKE, C. H. & SUBBAROW, Y. (1929). *J. Biol. Chem.* **81**, 629.
- GUILHEM, J. (1967). *Acta Cryst.* **23**, 330.
- HAAS, D. J., HARRIS, D. R. & MILLS, H. H. (1965). *Acta Cryst.* **19**, 676.
- HAMILTON, W. (1955). *Acta Cryst.* **8**, 185.
- HAMILTON, W. (1965). *Trans. Amer. Cryst. Assoc.* **1**, 17.
- HAUPTMAN, H. & KARLE, J. (1953). *Solution of the Phase Problem. I. The Centrosymmetric Crystal*. A.C.A. Monograph No. 3. Pittsburgh: Polycrystal Book Service.
- HILL, T. & MORALES, M. F. (1951). *J. Amer. Chem. Soc.* **73**, 1656.
- HOBBS, E., CORBRIDGE, D. E. C. & RAISTRICK, B. (1953). *Acta Cryst.* **6**, 621.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JENSEN, L. H. (1955). *Acta Cryst.* **8**, 237.
- KALCKAR, H. M. (1941). *Chem. Rev.* **28**, 71.
- KARLE, I. L. & BRITTS, K. (1966). *Acta Cryst.* **20**, 118.
- KIRKPATRICK, P. (1944). *Rev. Sci. Instrum.* **15**, 223.
- LINGAFELTER, E. C. & DONOHUE, J. (1966). *Acta Cryst.* **20**, 321.
- MENDEL, H. & HODGKIN, D. C. (1954). *Acta Cryst.* **7**, 443.
- PATTERSON, A. L. & LOVE, W. E. (1960). *Amer. Min.* **45**, 325.
- PAULING, L. (1950). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.
- SAYRE, D. (1952). *Acta Cryst.* **5**, 60.
- SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.
- STEWART, J. M. (1964). Technical Report Tr 64-6, NsG-398. Computer Science Center of the University of Maryland, College Park.

*Acta Cryst.* (1968). **B24**, 1027

## Structure Cristalline de $\text{MoNb}_{15}\text{O}_{40}\text{F}$

PAR J. GALY\*

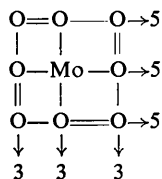
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(Reçu le 4 novembre 1967)

$\text{MoNb}_{15}\text{O}_{40}\text{F}$  crystallizes in the monoclinic system with lattice parameters  $a=22.29$ ,  $b=3.831$ ,  $c=20.27$  Å,  $\beta=114^\circ$ . The space group is  $C2$ . The original structure, refined by least-squares methods, contains  $\text{ReO}_3$ -type blocks of Nb-O octahedra,  $3 \times 5$  and infinite along  $b$ . The blocks are joined by sharing edges and with tetrahedrally coordinated Mo atoms at the junctions of every four blocks.  $\text{MoNb}_{15}\text{O}_{40}\text{F}$  can be represented by the structural formula:



Les systèmes binaires  $\text{MoO}_3$ - $\text{Nb}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ - $\text{Nb}_2\text{O}_5$  et  $\text{MoO}_3$ - $\text{Nb}_2\text{O}_5$  ont fait l'objet d'études approfondies. Si le système  $\text{MoO}_3$ - $\text{Nb}_2\text{O}_5$  ne révèle la présence d'aucune phase nouvelle, les deux autres systèmes sont par contre beaucoup plus riches.

Le système  $\text{Nb}_2\text{O}_5$ - $\text{Nb}_2\text{O}_5$  comporte quatre composés originaux  $\text{Nb}_3\text{O}_7\text{F}$ ,  $\text{Nb}_5\text{O}_{12}\text{F}$ ,  $\text{Nb}_{17}\text{O}_{42}\text{F}$  et

$\text{Nb}_{31}\text{O}_{77}\text{F}$ , dont la préparation et l'étude structurale sont dues à Andersson et Åström (Andersson, 1964, 1965a; Andersson & Åström, 1964; Åström, 1966).

Dans le système  $\text{MoO}_3$ - $\text{Nb}_2\text{O}_5$  deux phases ont été mises en évidence et leurs caractères cristallographiques précisés: l'une  $\text{Mo}_3\text{Nb}_{14}\text{O}_{44}$ , de symétrie quadratique, est isotype de  $\text{W}_3\text{Nb}_{14}\text{O}_{44}$ , l'autre  $\text{MoNb}_{12}\text{O}_{33}$ , monoclinique, est isotype de  $\text{WNb}_{12}\text{O}_{33}$ ; ces composés du tungstène ont été préparés et étudiés par Roth & Wadsley (1965).

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