BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (1), 233—234 (1979)

A Refinement of the Crystal Structure of Creatine Monohydrate

Yoshihiro KATO,* Yoshitaka HAIMOTO, and Kiichi SAKURAI
Department of Physics, Osaka Kyoiku University, Tennoji-ku, Osaka 543

(Received July 10, 1978)

Synopsis. The crystal structure of creatine monohydrate has been refined from three-dimensional X-ray data. This refinement introduces minor modifications to the positional and thermal parameters and confirmed the zwitter ion structure.

Mendel and Hodgkin[1] have determined the crystal structure of creatine monohydrate from three-dimensional X-ray data and inferred that the structure of the molecule corresponds to that of a zwitter ion. They calculated the $h0l$ structure factors including hydrogen atoms placed at the probable positions, but the intensity data were not accurate enough to warrant the hydrogen atom positions. The present paper describes a refinement of the structure, which has determined the positions of the hydrogen atoms and confirmed that the molecule adopts a zwitter ion form.

Experimental

The intensities of 1411 independent reflections were measured visually from Cu $K\alpha$ Weissenberg photographs taken about b ($k=0$—4) and c ($l=0$). The cross-section of the crystal used was 0.35×0.35 mm. Corrections for Lorentz and polarization factors were applied in the usual way, but no correction for absorption was made. The lattice constants were determined from photographs taken with a Buerger's back-reflection Weissenberg camera calibrating the camera radius by using a silver wire. The crystal data are as follows: $a=12.510(6)$, $b=5.048(1)$, $c=12.191(1)$ Å, $\beta=108.9(3)°$, $P2_1/c$, $Z=4$.

Refinement of the Structure

Using the positional and thermal parameters taken from the previous determination,[1] the three-dimen-

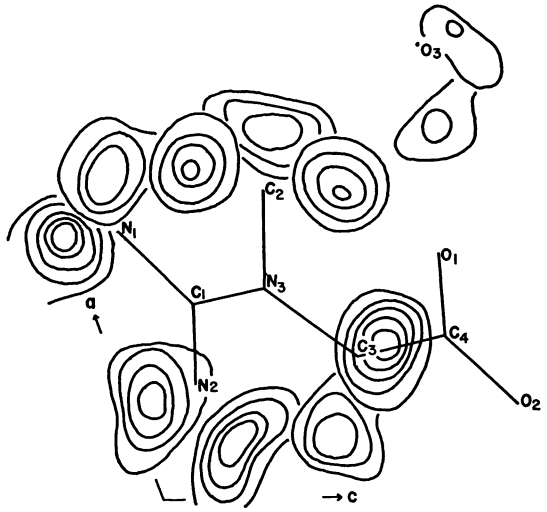

Fig. 1. A composite representation of the three-dimensional difference map on (010). Contours are at intervals of 0.1 e Å^{-3} begining with 0.1 e Å^{-3}.

TABLE 1. ATOMIC COORDINATES AND THEIR STANDARD DEVIATIONS

	x	M & H[a]	y	M & H[a]	z	M & H[a]
N_1	0.2894(2)	0.289	0.4702(8)	0.472	0.3083(2)	0.306
N_2	0.1184(2)	0.119	0.3678(8)	0.370	0.3277(2)	0.329
N_3	0.2255(2)	0.224	0.7147(8)	0.715	0.4351(2)	0.434
C_1	0.2113(2)	0.211	0.5217(9)	0.520	0.3582(2)	0.358
C_2	0.3308(3)	0.331	0.8674(11)	0.874	0.4719(3)	0.472
C_3	0.1507(3)	0.148	0.7429(9)	0.744	0.5049(3)	0.502
C_4	0.1705(2)	0.170	0.5408(9)	0.542	0.6012(2)	0.600
O_1	0.2568(2)	0.256	0.3950(7)	0.397	0.6250(2)	0.625
O_2	0.0981(2)	0.098	0.5289(7)	0.529	0.6520(2)	0.651
O_3	0.4848(2)	0.484	0.3577(8)	0.356	0.6891(3)	0.689
$H(N_1)$	0.362		0.550		0.322	
$H(N_1)$	0.278		0.340		0.243	
$H(N_2)$	0.111		0.226		0.270	
$H(N_2)$	0.051		0.422		0.345	
$H(C_2)$	0.354		0.935		0.404	
$H(C_2)$	0.395		0.723		0.511	
$H(C_2)$	0.325		1.010		0.526	
$H(C_3)$	0.069		0.717		0.450	
$H(C_3)$	0.156		0.920		0.535	
$H(O_3)$	0.402		0.395		0.674	
$H(O_3)$	0.496		0.555		0.729	

a) The coordinates given by Mendel and Hodgkin.

Table 2. Anisotropic temperature factors and their standard deviations ($\times 10^4$) expressed in the form $\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\}$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N_1	35 (2)	664 (21)	57 (2)	−25 (9)	52 (3)	−34 (10)
N_2	30 (2)	671 (21)	60 (2)	−36 (9)	43 (3)	−74 (10)
N_3	40 (2)	555 (18)	44 (2)	−17 (9)	39 (3)	−7 (9)
C_1	32 (2)	525 (20)	38 (2)	12 (9)	23 (3)	7 (10)
C_2	52 (2)	688 (28)	78 (3)	−108 (13)	62 (4)	−53 (14)
C_3	42 (2)	602 (23)	47 (2)	35 (10)	43 (3)	−12 (11)
C_4	30 (2)	540 (21)	38 (2)	7 (9)	26 (3)	−30 (9)
O_1	36 (1)	719 (19)	75 (2)	125 (8)	52 (3)	144 (10)
O_2	33 (1)	802 (19)	56 (2)	33 (8)	51 (2)	65 (9)
O_3	35 (2)	783 (21)	107 (3)	−65 (9)	42 (3)	−20 (12)

Table 3. Interatomic distances (Å) and bond angles (°)

		M & H[a]			M & H[a]
N_1-C_1	1.334 (6)	1.35	$N_1C_1N_2$	117.1 (4)	118
N_2-C_1	1.346 (6)	1.32	$N_1C_1N_3$	121.1 (4)	121
N_3-C_1	1.324 (6)	1.32	$N_2C_1N_3$	121.8 (4)	121
N_3-C_2	1.466 (7)	1.49	$N_3C_3C_4$	114.3 (4)	113
N_3-C_3	1.462 (6)	1.46	$C_1N_3C_2$	120.3 (4)	121
C_3-C_4	1.514 (6)	1.51	$C_1N_3C_3$	121.3 (4)	119
C_4-O_1	1.260 (6)	1.25	$C_2N_3C_3$	116.9 (4)	117
C_4-O_2	1.253 (6)	1.25	$C_3C_4O_1$	118.9 (4)	121
O_1-O_3	2.709 (6) [b]	2.71[b]	$C_3C_4O_2$	116.9 (4)	118
			$O_1C_4O_2$	124.1 (4)	123

a) The values given by Mendel and Hodgkin. The standard deviations in all bond lengths are 0.01 Å and those in bond angles are 4°. b) Hydrogen-bond distances.

sional refinements were carried out by the block-diagonal least-squares method for non-hydrogen atoms. The weighting scheme of the type $1-\exp(-15\,s^2)$ with $s=\sin\theta/\lambda$ was used. At a later stage of the refinement, hydrogen atoms were included in the calculations with a fixed thermal parameter ($B=3.5$ Å^2) and fixed positional parameters deduced from an F_o-F_c Fourier synthesis (Fig. 1). The final R value was 0.096. The final positional parameters are given in Table 1 together with those reported by Mendel and Hodgkin.[1] The thermal parameters are given in Table 2. A list of the observed and calculated structure factors are kept in the office of the Chemical Society of Japan (Document No. 7906).

The calculations were carried out on a NEAC SYSTEM 800 computer of the Computation Center of Osaka University using the program *HBLS V* written by Y. Okaya and T. Ashida for the least-squares refinement.

Description and Discussion of the Structure

The atoms N_1, N_2, C_1, and N_3 of the guanidine group are on the plane $0.2226X-0.6380Y+0.7371Z-1.6408=0$, and C_3, C_4, O_1, and O_2 are on the plane $0.3177X+0.6774Y+0.6634Z-6.3695=0$, where X, Y, and Z are referred to the orthogonal axes a, b, and c^* (Å). These planes intersect at an angle of 82.7° with each other. The interatomic distances and bond angles are listed in Table 3, which shows that these values are in good agreement with those reported by Mendel and Hodgkin.[1]

The F_o-F_c Fourier synthesis indicated clearly all the hydrogen atoms (Fig. 1). The four hydrogen atoms attached to the guanidine group are about 1 Å away from N_1 and N_2 atoms, while there appears no hydrogen peak around the carboxyl group, which shows that the hydrogen atom of the carboxyl group is transferred to the guanidine group. The molecule of creatine, therefore, corresponds conclusively to that of a zwitter ion in the crystal.

Reference

1) H. Mendel and D. C. Hodgkin, *Acta Crystallogr.*, **7**, 443 (1954).