Department of Physics, Jawaharlal Institute of PG Medical Education & Research, Pondicherry 605 006,
B. KRISHNAN.
A. SRINIVASA RAO.
June 29, 1979.

1. Myers, H. M., *Exptl. Cell. Res.*, 1965, **38**, 686.
2. Myers, H. M., *Nature*, 1965, **206**, 713.
3. Little, M. F. and Casciani, F. S., *Arch. Oral Biol.*, 1966, **11**, 565.
4. Bender, G. T., *Chemical Instrumentation: A Laboratory Manual Based on Clinical Chemistry*, W. B. Saunders Co., Philadelphia, 1972, p. 49.
5. Pake, G. E. and Purcell, E. M., *Phys. Rev.*, 1948, **74**, 1184.
6. Van Vleck, J. H., *Phys. Rev.*, 1948, **74**, 1168.
7. Wheatley, P. J., *The Determination of Molecular Strcuture*, Oxford University Press, London, 1969, p. 248.
8. Lippincott, E. R. and Srinivaa Rao, A., *J. Chem. Phys.*, 1964, **41**, 3006.
9. Sirnivasa Rao, A. and Srinivasa Manja, K., *Ind. J. Pure and Appl. Phys.*, 1977, **15**, 567.

MOLECULAR CONFORMATION OF ADENOSINE-5′-DIPHOSPHORIC ACID ($C_{10}N_5O_{10}H_{14}P_2.3H_2O$)

ADENOSINE-5′-diphosphate, as the phosphate acceptor in the biosynthesis of ATP, through the pyruvate kinase enzyme plays a key role in the energy transfer reactions of the cell. Metal ions Mg^{2+} and K^+ are required as cofactors for this enzymatic reaction[1]. It is therefore of interest to know the detailed geometry of the molecule in the free and metal-bound states. We have earlier reported the structure of ADP as monopotassium and monorubidium salts[2–4]. We describe here its molecular structure as a free acid, as obtained from a single crystal X-ray analysis.

Experimental

Crystals of ADP–free acid were obtained during our attempts to crystallise ADP as a K^+ salt. One of the crystallisation tubes, containing acetone layered over 1 ml of ADP-free acid + KCl (1 : 1) solution at pH 3·5 was found to have needle shaped crystals showing good optical extinction. These crystals were thought to be of ADP–K. However their mass spectrometric analysis showed that K^+ ions were not present in the crystal lattice. The crystals were of ADP–free acid as confirmed by a detailed X-ray analysis. These were then mounted inside Lindemann capillaries along with traces of mother liquor, and were examined for their mosaic spread. The crystal measuring $1{\cdot}2 \times 0{\cdot}4 \times 0{\cdot}1$ mm^3 and showing minimum spread of X-ray spots were used in getting the crystal data. The crystal data is summarised below :

$a = 6{\cdot}714\,(3)$, $b = 10{\cdot}989\,(4)$, $c = 26{\cdot}320\,(8)$ Å

Space group $P22_12_1$; $d_m = 1{\cdot}64$, $d_c = 1{\cdot}64$, $z = 4$ $\langle \mu r \rangle \simeq 0{\cdot}14$. Three-dimensional intensity data to a 2θ limit of 120° were collected at room temperature on the CAD-4 diffractometer using filtered CuKα radiation and $\omega/2\theta$ scan. Two control reflections were measured at intervals of fifty, to monitor intensity changes. These fluctuations were less than 5%, indicating that crystals were stable to X-rays. The structure was solved by a combination of direct and Fourier methods and refined in a block diagonal least squares program to a final R-factor of 7·8%.

Results and Discussion

The bond lengths and bond angles between non-hydrogen atoms can be had from the authors. The average estimated standard deviations in C–C (O, N) and P–O bond lengths are about 0·02 and 0·01 Å respectively. Estimated standard deviations in bond angles are 1·5° for C–C–C, C–C–N, C–O–C and C–N–C and about 0·9° for O–P–O and P–O–P angles.

Molecular Geometry and Conformation

A view of ADP-free acid perpendicular to the base is shown in Fig. 1. The conformational features of

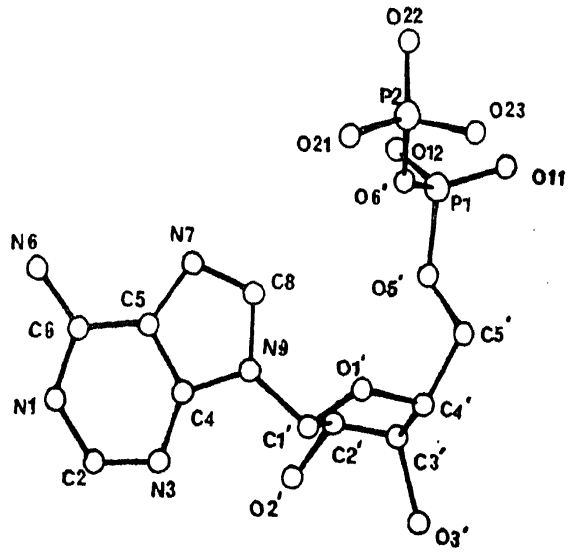

FIG. 1. ADP-free acid. Viewed down the perpendicular to the base.

the molecule are : (i) *anti* orientation of the base with respect to sugar ($\chi_{CN} \simeq 25°$), (ii) *trans* orientation of pyrophosphate about C5′–O5′ bond ($\phi = 152°$), (iii) *gauche-gauche* conformation about C4′–C5′ bond and (iv) disorder of the ribose sugar between C2′-*endo*-C1′-*exo* and C3′-*endo* geometries. The resulting molecular shape is very similar to that found in the K^+ and Rb^+ salts of ADP.

Figure 2 shows the two pairs of hydrogen bonds that link adenine base to pyrophosphate oxygens.

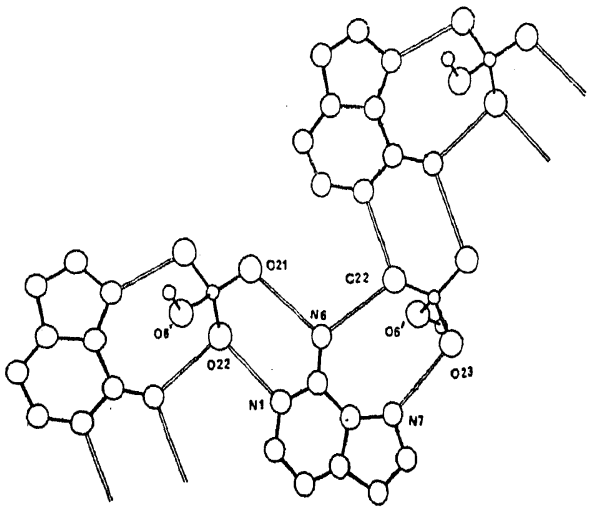

FIG. 2. The two pairs of hydrogen bonds between adenine base and phosphate oxygen.

Interestingly these pairs of hydrogen bonds are observed also in ADP-K and ADP-Rb structures. These interactions could be relevant to the recognition of the base and phosphate parts of ADP by polar side groups of specific amino acid residues in proteins[5]. The absence of the metal ion has apparently influenced the pyrophosphate bond lengths in ADP-free acid. While the two P–O (P) bonds are unequal in ADP–Rb, they are equal in ADP–free acid (P1–06′ = 1·60 Å = P2–06′). Such metal induced changes in P–O (P) lengths may influence chemical reactivity of the ADP molecule in a specific way.

We thank the DAE and DST for their financial support. One of us (MVH), thanks the Indian Council for Medical Research for the award of a Junior Research Fellowship.

Department of Physics and ICMR Centre on Genetics and Cell Biology,
Indian Institute of Science,
Bangalore 560 012,
August 17, 1979.

M. V. HOSUR.
M. A. VISWAMITRA.

1. Mahler, H. R. and Cordes, E. H., ' *Basic Physiological Chemistry*, Harper and Row, New York.
2. Viswamitra, M. A., Hosur, M. V., Shakked, Z. and Kennard, O., *Cryst. Struct. Comm.*, 1976, **5**, 819.
3. —, —, — and —, *Nature*, 1976, **262**, 234.
4. Katti, S. K. and Viswamitra, M. A., *Curr. Sci.*, (Communicated).
5. Hosur, M. V., *Ph.D. Thesis*, I.I.Sc. 1979.

THE CRYSTAL AND MOLECULAR STRUCTURE OF THE RADIOPROTECTANT CYSTAMINE DIHYDROCHLORIDE

CYSTAMINE dihydrochloride is known to be an effective radioprotectant[1]. Here we report the results of the x-ray analysis of this compound carried out as part of a programme of x-ray investigations on radioprotectants[2–4].

Crystal data : Space group $P2_1/c$

$a = 18{\cdot}15\ (1)$, $b = 4{\cdot}98\ \ (1)$, $c = 20{\cdot}88\ (1)$ Å, $\beta = 143{\cdot}9\ \ (1{\cdot}0)°$, $D_c = 1{\cdot}35$ gm. cm^{-3}. As the compound reacted with most of the commonly available solvents, the density could not be measured.

Intensity data from three reciprocal levels *hkl*, $k = 0$ to 2, were recorded by the multiple film equi-inclination Weissenberg method using CuKα radiation. As the only available crystal disintegrated at this stage, further data could not be collected and repeated attempts to recrystallize the sample were not successful. The intensities were estimated visually and this data set contained 476 observable reflections. The incomplete nature of the data set leads to high standard deviations associated with bond lengths and angles. The analysis, however, provides an adequate and reliable description of molecular conformation, especially that about the disulphide bridge, which indeed is its major objective. The crystal structure was solved by a combination of direct methods and Fourier techniques and refined anisotropically to $R = 0{\cdot}122$. The final positional coordinates are given in Table I.

TABLE I

Final positional coordinates in fractional units ($\times 10^3$) *and thermal parameters; e.s.d's in parentheses*

	x	y	z	B (Å^2)
S (1)	587 (1)	231 (4)	157 (1)	5·0
S (2)	538 (1)	61 (5)	209 (1)	4·4
Cl (1)	858 (1)	350 (4)	105 (1)	4·7
Cl (2)	122 (2)	777 (5)	15 (1)	7·3
C (1)	650 (5)	− 48 (15)	154 (5)	6·1
C (2)	773 (6)	−171 (15)	267 (5)	6·6
C (3)	374 (5)	− 57 (15)	83 (4)	3·8
C (4)	302 (5)	226 (13)	23 (4)	3·8
N (1)	874 (4)	55 (12)	338 (3)	4·5
N (2)	158 (3)	132 (13)	−84 (3)	4·5

Figure 1 gives the atomic numbering scheme and a view of the structure along the *b*-axis. The molecular dimensions are listed in Table II. The dimensions