atom at a distance 2·64 Å. Four such oxygen atoms, a water molecule and a chromium atom thus form a distorted octahedron about each of the two chromium atoms in a molecule.

As in the case of cupric acetate, apart from van der Waals forces, hydrogen bonds again appear to be the main forces between the molecules. Each chromous acetate molecule is linked by eight such bonds (2·82 and 2·89 Å) to four neighbouring molecules at different levels. For further details about the atomic arrangement, reference should be made to the paper describing the structure of cupric acetate.

### Discussion of the bonds

When the paper on cupric acetate was sent for publication, no reliable magnetic data were available, so that only the interatomic distance suggested a direct Cu–Cu bond. Shortly afterwards Bleaney & Bowers (1952) published a paper containing detailed magnetic measurements, and suggested interaction between the copper atoms. These two independent determinations make it certain now that a bond does exist between the copper atoms. From the remarkable similarity between the chromous and cupric acetate structures, it seems reasonable to infer that a direct bond also exists between the two chromium atoms.

The configuration around the chromium atom described in this paper disagrees with the tetrahedral co-ordination proposed by King & Garner (1950) to explain the diamagnetism they observed for chromous acetate.

We wish to thank Mr J. H. Talbot for his help with the calculations and the Council for Scientific and Industrial Research for permission to publish this paper.

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# The Crystal Structure of a *cyclo*Nucleoside

By J. Zussman*

*Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England*

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X-ray analysis has been used to discover the nature of a chemical rearrangement undergone by certain nucleoside derivatives to form *cyclo*nucleosides. Crystals of the iodide of 2′:3′-*iso*propylidene, 3:5′-*cyclo*adenosine are orthorhombic with $a = 5{\cdot}4$, $b = 15{\cdot}4$, $c = 18{\cdot}1$ Å. The space group is $P2_12_12_1$ and there are four molecules in the unit cell. The $y$ and $z$ atomic coordinates were determined by use of the heavy-atom method applied to the (100) projection; $x$ coordinates by use of 'higher layer projection' techniques. The purine ring system is planar and makes an angle of 90° with the puckered furanose ring to which it is joined by a $\beta$ glycosidic linkage.

Crystals of 5′ iodo, 2′:3′ *iso*propylidene uridine are orthorhombic, $P2_12_12_1$, with $a = 5{\cdot}42$, $b = 15{\cdot}4$, $c = 16{\cdot}7$ Å, and the unit cell contains four molecules. This substance has been examined in the (100) projection only, and shows by contrast a normal covalent iodide structure.

## Introduction

In recent years, one of the projects undertaken in this laboratory has been the investigation of the crystal structures of nucleic acid constituents and their derivatives. It has consisted mainly in the detailed investigation of pyrimidines and purines, with particular interest in their tautomeric forms, but it was also intended that more complex units (i.e. nucleosides and nucleotides) should be examined.

The structures of 2-amino,4-methyl-6 chloropyrimidine and 2-amino,4-6 dichloropyrimidine (Clews & Cochran, 1948), 5-bromo,4-6 diaminopyrimidine and 4-amino, 2-6 dichloropyrimidine (Clews & Cochran, 1949), adenine hydrochloride hemihydrate (Broomhead, 1948; Cochran, 1951) and guanine hydrochloride monohydrate (Broomhead, 1951) have been reported.

The present study of certain nucleoside derivatives is part of this programme, and also provides the solution of a specific chemical problem. An account of part of this more recent work, mainly from a chemical standpoint, has already been published (Clark, Todd &

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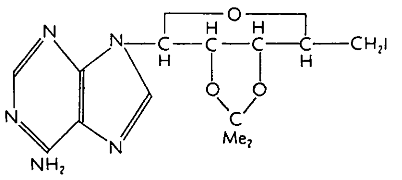
* Now at the Department of Geology, University of Manchester, Manchester 13, England.

Zussman, 1951). It is the purpose of this paper to give (*a*) a concise statement of the particular chemical problem involved, (*b*) a description of the completed crystallographic analysis and (*c*) discussion of the results obtained.

Symbols have their conventional meanings unless otherwise stated.

## The chemical problem

One of the most powerful methods applied to the study of nucleic acids is that of chemical synthesis. This has been used by Prof. A. R. Todd and his co-workers, who have attempted the synthesis of nucleosides, nucleotides and polynucleotides, demonstrating at each stage the constitution and configuration of their products. In the case of the particular synthesis described (Clark *et al.*, 1951), the compound 5′-iodo, 2′:3′-*iso*propylidene adenosine, formula



was required for the preparation of muscle adenylic acid (adenosine 5′phosphate). In the course of the synthesis, however, only an ionic iodide could be obtained, suggesting that a rearrangement had occurred involving either alkylation, which could be intra- or inter-molecular, or elimination of iodine to give the salt of a riboseen derivative. This latter possibility was ruled out through the evidence of infra-red absorption spectra. The possibility of intermolecular alkylation resulting in dimerization was disproved, and also the precise nature of the rearrangement was discovered, as a result of the X-ray crystal structure analysis described below.

## Determination of structure in projection

Crystals of the iodide, prepared by Dr J. Davoll, were in the form of needles approximately 0·03 mm. in diameter and 1–2 mm. in length. The cell dimensions were found to be

$$a = 5{\cdot}4,\ b = 15{\cdot}4,\ c = 18{\cdot}1\ \text{Å}\quad (\text{all } \pm 1\%)\,,$$

and the space group $P2_12_12_1$. The measured specific gravity was 1·81±1%. From these, the total weight of the cell content is given as 1640. The smallest number of asymmetric units per cell possible in this space group is 4. Thus the maximum weight of each unit is approximately 410. This corresponds to the molecular weight (417) of one unit of $C_{13}H_{16}O_3N_5I$. Thus the units in the crystal are monomers, and so the rearrangement must be intramolecular. Since the crystal possessed a short axis, it seemed likely that determination of the projection of the structure along it would be sufficient to show the nature of the rearrangement, and further X-ray work was undertaken to this end.

It was decided to use copper radiation for recording $0kl$ intensities in spite of the high linear absorption coefficient, since the crystal had a small and regular cross-section. The intensities were recorded in a Weissenberg camera, measured by visual comparison with an intensity scale, and corrected for Lorentz and polarization effects, yielding a set of values $G^2_{0kl}$. No correction was made for absorption since it was assumed that its effect would vary as a smooth function of $\sin\theta$. A Patterson map was derived using $G^2_{0kl}$'s as coefficients, and from this the coordinates of the iodine atoms were readily determined. These were used to estimate the phase angles (0 or $\pi$) of all but 60 of the 300 reflexions observed, and a Fourier synthesis using $G_{0kl}$ values gave the first approximate electron density map shown in Fig. 1. The six- and five-membered rings of the purine were easily recognisable and the remaining atoms of the sugar and its substituents were identified.

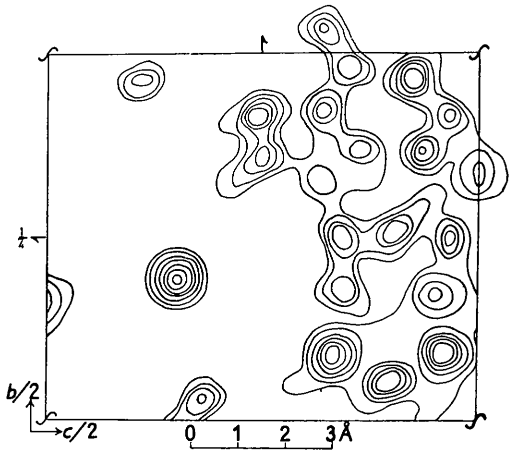


Fig. 1. *cyclo*Nucleoside: projection of electron density on (100), derived using phases angles determined by heavy atom alone. Contours at an arbitrary interval.

At this stage the nature of the rearrangement was apparent, but a more accurate representation of the electron density seemed desirable and so the process of Fourier refinement was undertaken. At first, structure factors were evaluated approximately for those terms omitted from the first synthesis, with the aid of a mechanical 'structure factor balance' (Bragg, 1952). Later, more accurate values of the structure amplitudes were calculated using the sampling method described by Sayre (1951), although the contributions of the iodine atoms were calculated separately and by other means. The model atoms used for the sampling were derived by transforming Hartree $f$ curves which had been modified by a temperature factor $\exp\,[-1{\cdot}0 \sin^2\theta]$. A similar factor was applied to the

Thomas–Fermi scattering curve for iodine, and the 'light atom' and iodine contributions were combined to give a set of calculated structure amplitudes ($F_c$'s). The $G$ values were placed on the scale of the $F_c$'s, and the agreement factor $R$ was found to be 0·185. An $(F_o-F_c)$ synthesis was performed, giving a $(\sigma_o-\sigma_c)$ map on the basis of which small changes were made in some atomic coordinates, after which $R = 0{\cdot}165$. The map also indicated that a ratio $f_I/f_L$ ($f_I$ and $f_L$ are atomic scattering factors for iodine and for the average light atom respectively) other than that assumed, would yield better structure-amplitude agreement. The 'light atom' scattering curves were assumed to be correct and values of $f_I$ were determined by a least-squares method which minimized $\Sigma(|F_o-F_c|)$. It seemed reasonable to assume that two modifications to the Thomas–Fermi curve could be expected: (1) a depression of the curve as a whole by a small amount (theoretically ~ 1 unit) due to the effect of dispersion; (2) modification by a temperature factor other than that assumed. Thus a curve $f'_I$ related to the Thomas–Fermi curve $f_{T.F.}$ by

$$f'_I = (f_{T.F.}-m)\exp(-K\sin^2\theta)\,,$$

where $K$ and $m$ are constants, was fitted as nearly as possible through the points determined by the least-squares solution, and this was used to give the iodine contributions in the next structure-amplitude calculation. $G$ values were rescaled to the new set of $F_c$'s, another difference synthesis was performed, followed by an $F_o$ synthesis the result of which is shown in Fig. 2. The value of $R$ attained was 0·14, and no further refinement of the projection was attempted.

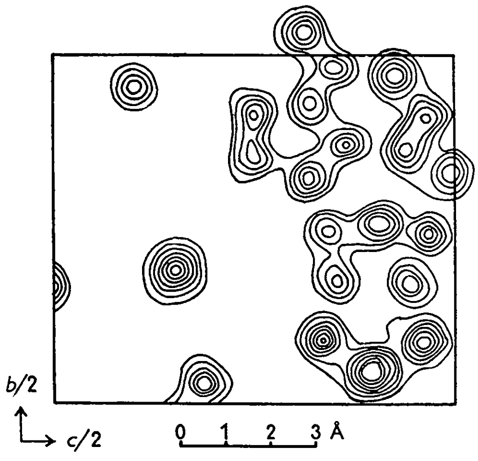


Fig. 2. *cyclo*Nucleoside: projection of electron density on (100) after refinement of parameters. Contour intervals: for iodine, 20 e.Å$^{-2}$, beginning at zero; for other atoms, 2 e.Å$^{-2}$, beginning at 2.

It was stated in the earlier paper (Clark *et al.*, 1951) that a model of the molecule used in conjunction with the electron-density projection gave the separation $C'_5$–$N_3$ as approximately 1·5 Å. Since then, the positions of the atoms have been determined explicitly in the manner described in the following section.

## Determination of '*x*' coordinates using 'higher layer projections'

The normal method of structure analysis by consideration of two projections did not promise to be useful in this case. The hair-like crystals could not be used for collecting reliable data for a projection along any but the needle axis, and even if such data were obtained, the projections would show excessive overlapping of molecules and iodine ions. It was decided, therefore, to use the method of higher layer syntheses, since reliable data could be collected for at least the first and second layers of the '*a*' axis projection, and these should furnish a moderately accurate determination of the '*x*' coordinates. The method has been mentioned and used in various applications by Clews & Cochran (1949), Dyer (1951) and Raeuchle & Rundle (1952), and a fuller description of it is given by Cochran & Dyer (1952). The scheme for using higher layer projections in the present case was as follows:

(*a*) Determination of very approximate '*x*' coordinates from first-layer Patterson map.

(*b*) Improvement on these using second-layer Patterson map.

(*c*) Further improvement and refinement using second-layer 'weighted density' maps.

Stages (*a*) and (*b*) involved a more detailed analysis of Patterson maps than had hitherto been required since it was necessary to obtain quantitative interpretations of the heights of iodine–'light atom' vector peaks. Sharpened Patterson maps were therefore prepared with each of the zero-, first-, and second-layer $|F|^2$ values. Two of these are shown in Figs. 3 and 4, and in Fig. 4 the calculated iodine–'light atom' vector set is marked by dots. (First- and second-layer intensity data were collected using equi-inclination Weissenberg photographs, and again no absorption correction was made.)

The coordinate, $x_1$, of the iodine atom was deter-

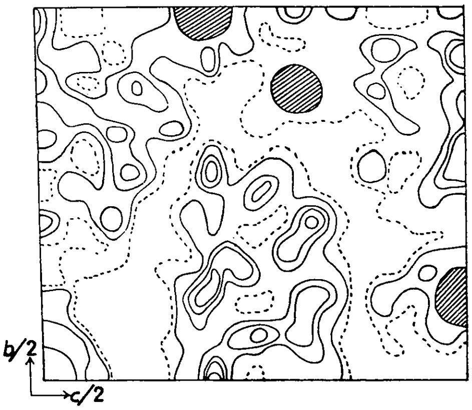


Fig. 3. *cyclo*Nucleoside: zero-layer Patterson projection on (100). Zero level broken.

mined unambiguously and directly from the first-layer Patterson map, since it showed three peaks due to iodine–iodine interaction, of heights proportional to $(-1)$, $(-\cos 2\pi 2x_1)$ and $(\cos 2\pi 2x_1)$ respectively. The coordinates of the other atoms were estimated by considering iodine–'light atom' peaks, expressing their heights as fractions of the origin peak height, and comparing these fractions with the fractional heights of corresponding peaks on the zero-layer map (see Dyer, 1951). In this way a first approximate set of $x$ parameters was obtained, using only those peaks which were seen to conform to two conditions: (i) good resolution from neighbouring (I–light atom) peaks, as shown by the calculated Patterson diagram; (ii) absence of a chance accumulation of (light atom–light atom) peaks, as shown by the zero-layer diagram.

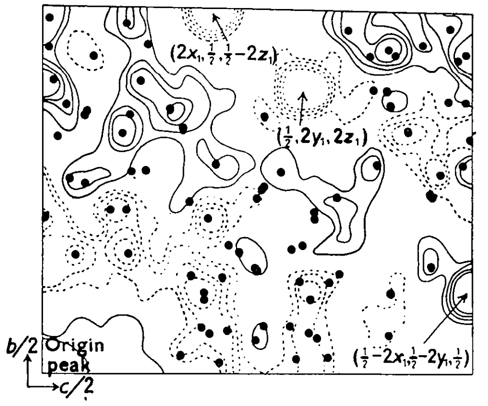


Fig. 4. *cyclo*Nucleoside: first-layer Patterson projection on (100), with calculated I–light-atom vectors superimposed. Broken lines indicate negative contours.

Each light atom was involved in four interactions with an iodine atom and so there was a reasonable chance of a resolved peak corresponding to one or more of them. Each peak gave a value for $\cos 2\pi(x-x_1)$ or $\cos 2\pi(x+x_1)$, where $x$ is the coordinate of the atom concerned. For an atom where both of these values was known, $x$ was given unambiguously, and this was the case for ten of the twenty-one atoms. In most of the remaining cases, use of a model enabled a correct choice to be made between the two solutions given by the value of only one of the above functions.

Table 1. 2′:3′-iso*Propylidene* 3:5′-cyclo*adenosine iodide*: *x coordinates derived from first- and second-layer Patterson diagrams*

| Atom | First layer | Second layer |
|---|---|---|
| $C_2$ | — | 0·95 |
| $C_4$ | — | 0·15 |
| $C_5$ | 0·00 | 0·00 |
| $C_6$ | 0·93 | 0·85 |
| $C_8$ | 0·27 | 0·30 |
| $C'_1$ | — | — |
| $C'_2$ | — | 0·32 |
| $C'_3$ | 0·36 | 0·35 |
| $C'_4$ | 0·40 | 0·44 |
| $C'_5$ | 0·34 | 0·32 |
| $C'_6$ | — | — |
| $C'_7$ | — | — |
| $C'_8$ | 0·65 | 0·65 |
| $N_1$ | 0·85 | 0·80 |
| $N_3$ | 0·07 | 0·14 |
| $N_6$ | 0·34 | 0·35 |
| $N_7$ | 0·01 | 0·09 |
| $N_9$ | 0·39 | 0·35 |
| $O'_1$ | 0·51 | 0·58 |
| $O'_2$ | — | 0·39 |
| $O'_3$ | 0·36 | 0·34 |
| I | 0·775 | 0·770 |

The heights of peaks in the second-layer Patterson map gave values of $\cos 2\pi 2(x-x_1)$ or $\cos 2\pi 2(x+x_1)$, so that from any one peak four values of $x$ were obtained, and the one nearest to that determined from the first layer map was taken as correct. The heights of second layer peaks are more sensitive to changes of '$x$' and so give a more accurate solution.

'$x$' coordinates derived from first and second layer Patterson maps are given in Table 1.

### Use of 'weighted density' projections

Let us define ${}_H\sigma_c$ and ${}_H\sigma_s$ by

$$\left.\begin{aligned} A\,{}_H\sigma_c &= V\int_{-\frac{1}{2}}^{\frac{1}{2}} \varrho_{(x,y,z)} \cos 2\pi Hx\,dx \\ \text{and}\qquad A\,{}_H\sigma_s &= V\int_{-\frac{1}{2}}^{\frac{1}{2}} \varrho_{(x,y,z)} \sin 2\pi Hx\,dx\,, \end{aligned}\right\} \qquad (1)$$

where $A$ is the area of projection, and $H$ is an even integer denoting a layer of the reciprocal lattice. Then it may be shown that for the $a$-axis projection of the space group $P2_12_12_1$

$$\left.\begin{aligned} A\,{}_H\sigma_c &= \sum_{k}\sum_{l}{}_{-\infty}^{\infty} A'_{Hkl} \cos 2\pi(ky+lz) \\ \text{and}\qquad A\,{}_H\sigma_s &= \sum_{k}\sum_{l}{}_{-\infty}^{\infty} B'_{Hkl} \cos 2\pi(ky+lz)\,, \end{aligned}\right\} \qquad (2)$$

where $A'_{Hkl}$ and $B'_{Hkl}$ are respectively the real and imaginary parts of the structure amplitudes of the $H$th layer (see Cochran & Dyer, 1952). That is, if $A'_{2kl}$ and $B'_{2kl}$ are used instead of $F_{0kl}$ in a Fourier synthesis, the map obtained will show not $\sigma$ $(= {}_0\sigma_c)$, but ${}_2\sigma_c$ and ${}_2\sigma_s$ respectively, which are projections of a weighted electron density, the density at a height $x$ being weighted by the factor $\cos 2\pi 2x$ or $\sin 2\pi 2x$.

It may also be shown that for a single atom at $(x, y, z)$

$$\left.\begin{aligned} {}_H\sigma_c &= {}_H\sigma'_{(yz)} \cos 2\pi Hx \\ \text{and}\qquad {}_H\sigma'_{yz} &= \frac{1}{A}\sum_{k}\sum_{l}{}_{-\infty}^{\infty} f_{Hkl} \exp\left[-2\pi i(ky+lz)\right]. \end{aligned}\right\} \qquad (3)$$

That is, whereas the normal projected electron density of an atom may be derived from the values of the atomic scattering factor for points on the zero

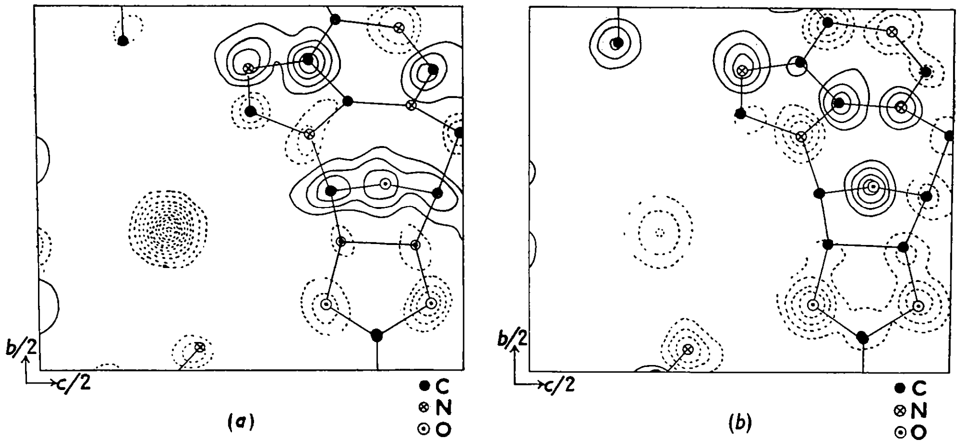


Fig. 5. *cyclo*Nucleoside: map of (*a*) $_{2}\sigma_{c}$, (*b*) $_{2}\sigma_{s}$. Contour interval for iodine is five times that for other atoms. Broken lines indicate negative contours.

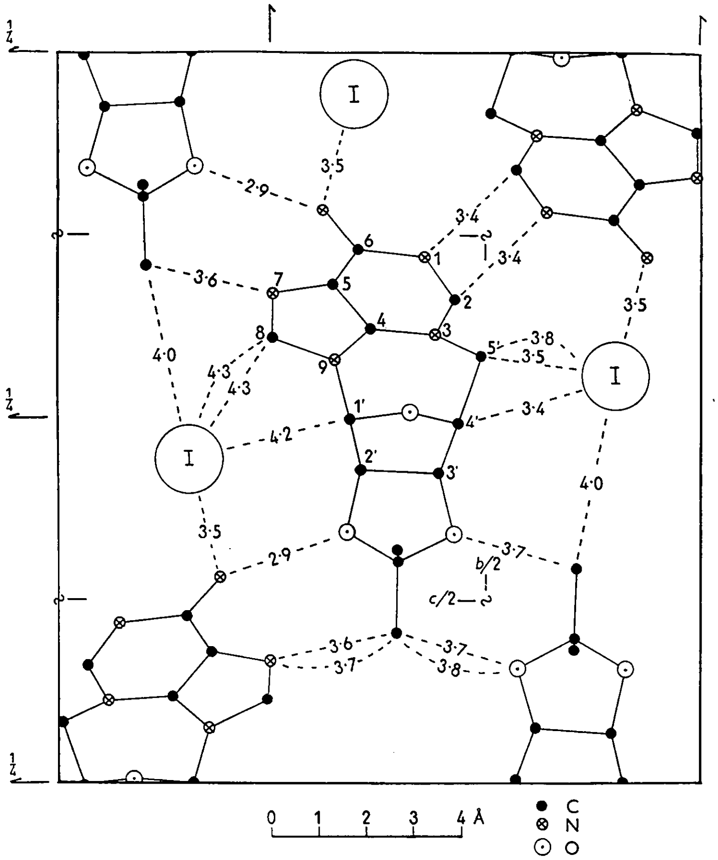


Fig. 6. *cyclo*Nucleoside: structure as viewed along *a* axis showing one molecule and its environment.

layer of the reciprocal lattice, $_{H}\sigma'_{(yz)}$ is derived from those for points on the *H*th layer.

If maps of $_{2}\sigma_{c}$ and $_{2}\sigma_{s}$ are prepared in accordance with the definitions of (3), they may be sampled and the values of $A'_{2kl}$ and $B'_{2kl}$ found. This was done using the *x* coordinates previously determined.

The calculated values of $A'_{2kl}$ and $B'_{2kl}$ were used to find $\alpha_{2kl}$ for each reflexion, and this was used to give a set of values $|F_c|$ which were compared with $|F_o|$'s derived from the observed intensities. The *R* index was found to be 0·28.

Using the calculated values of $\sin\alpha$ and $\cos\alpha$, $A'_o$ and $B'_o$ were derived and used as coefficients in Fourier syntheses to give maps of $_{2}\sigma_{c}$ and $_{2}\sigma_{s}$ in accordance with (2). From each of these a new set of coordinates was derived in the following way:

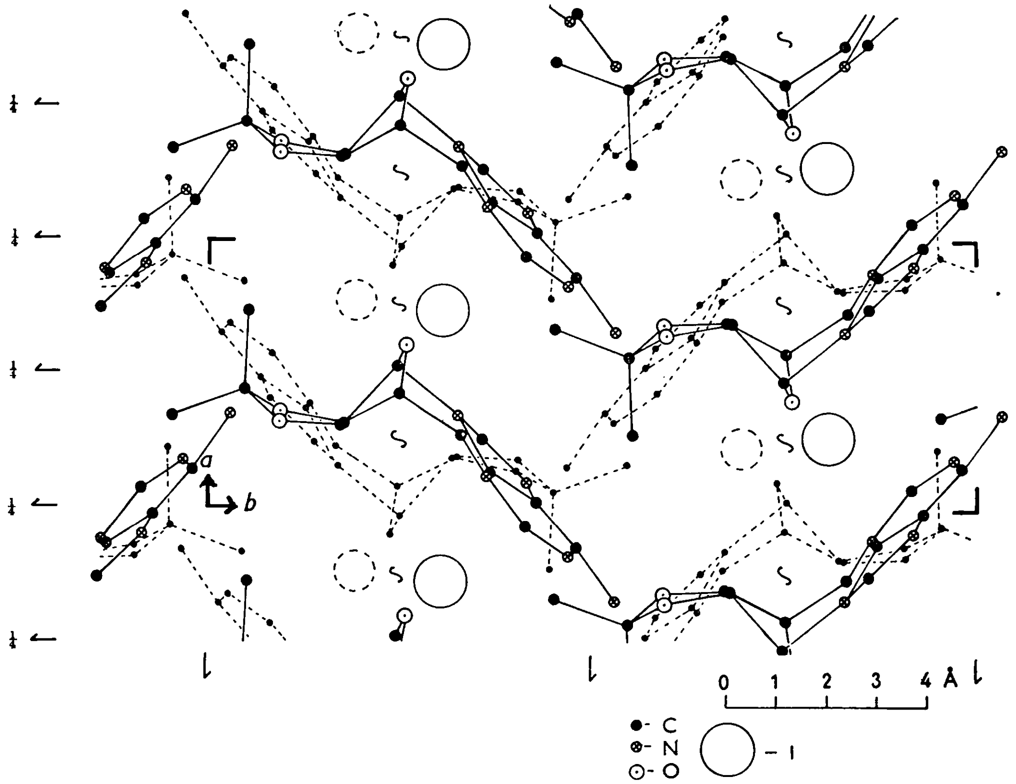


Fig. 7. *cyclo*Nucleoside: structure as viewed along *c* axis.

Table 2. 2′:3′-iso*Propylidene*, 3:5′-cyclo*adenosine iodide*: *atomic coordinates*

| Atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| $C_2$ | 0·932 | 0·416 | 0·466 |
| $C_4$ | 0·134 | 0·371 | 0·366 |
| $C_5$ | 0·022 | 0·430 | 0·320 |
| $C_6$ | 0·856 | 0·481 | 0·350 |
| $C_8$ | 0·260 | 0·358 | 0·250 |
| $C_1'$ | 0·530 | 0·248 | 0·343 |
| $C_2'$ | 0·315 | 0·180 | 0·355 |
| $C_3'$ | 0·310 | 0·175 | 0·445 |
| $C_4'$ | 0·427 | 0·250 | 0·469 |
| $C_5'$ | 0·277 | 0·331 | 0·495 |
| $C_6'$ | 0·440 | 0·051 | 0·397 |
| $C_7'$ | 0·730 | 0·053 | 0·399 |
| $C_8'$ | 0·659 | 0·454 | 0·103 |
| $N_1$ | 0·822 | 0·471 | 0·426 |
| $N_3$ | 0·120 | 0·365 | 0·439 |
| $N_6$ | 0·348 | 0·031 | 0·189 |
| $N_7$ | 0·098 | 0·417 | 0·248 |
| $N_9$ | 0·346 | 0·328 | 0·322 |
| $O_1'$ | 0·600 | 0·259 | 0·406 |
| $O_2'$ | 0·360 | 0·096 | 0·338 |
| $O_3'$ | 0·324 | 0·094 | 0·461 |
| I | 0·770 | 0·1942 | 0·1515 |

If there are $n$ atoms of one type with postulated coordinates $x_j$, and corresponding peak heights ${}_2\sigma_{cj}$, then the theoretical maximum peak height is given approximately by

$$ {}_2\sigma_{c_{\max.}} = \frac{1}{n} \cdot \sum_{j=1}^{j=n} \frac{{}_2\sigma_{cj}}{\cos 2\pi 2x_j} , \tag{4}$$

provided that $n$ is large and the postulated coordinates are nearly correct.

Using values of $\sigma_{\max.}$ estimated by (4), the $x$ coordinate of each atom was given by

$$ {}_2\sigma_{cj}/{}_2\sigma_{c_{\max.}} = \cos 2\pi 2x_j . $$

Similarly, a set of $x_j$ values was obtained from the ${}_2\sigma_s$ map, and averages of the two sets were used to recalculate $A'_{2kl}$ and $B'_{2kl}$. After rescaling by comparing averages of $|F_o|$ and $|F_c|$, $R$ was found to be 0·23.

$A'_o$ and $B'_o$ were recalculated using new values of $\alpha$, and new maps of ${}_2\sigma_c$ and ${}_2\sigma_s$ (Fig. 5) were derived from which were obtained the final list of $x$ coordinates shown in Table 2.

$|F_o|$ and $|F_c|$, for zero and second layers, are compared in Table 3.

## Description of structure

Figs. 6 and 7 show the structure as viewed along the '$a$' and '$c$' axes respectively. Fig. 8 shows bond lengths and bond angles, and also displays details of analogous parts of the adenine molecule (Cochran, 1951) and of cytidine (Furberg, 1950). The environment of the iodine ion and intermolecular contacts are shown in Fig. 6.

Table 3. *Comparison of* $|F_o|$ *and* $F_c$ *for the* cyclo*nucleoside*

(All $F$ values are for one molecule, but have been multiplied by 10)

$0kl$ reflexions

| | $l$ | $F_o$ | $F_c$ |
|---|---|---|---|
| $k = 0$ | 0 | — | 2060 |
| | 2 | 70 | −92 |
| | 4 | 428 | −459 |
| | 6 | 390 | 338 |
| | 8 | 23 | 24 |
| | 10 | 406 | −373 |
| | 12 | 169 | 187 |
| | 14 | 50 | 50 |
| | 16 | 128 | −144 |
| | 18 | — | −34 |
| | 20 | 101 | 133 |
| | 22 | 38 | −30 |
| $k = 1$ | 1 | 138 | 113 |
| | 2 | 72 | 83 |
| | 3 | 195 | −187 |
| | 4 | 356 | −331 |
| | 5 | 183 | 128 |
| | 6 | 248 | −257 |
| | 7 | 93 | 91 |
| | 8 | 168 | 174 |
| | 9 | 157 | −144 |
| | 10 | — | 2 |
| | 11 | 21 | −22 |
| | 12 | 198 | −196 |
| | 13 | 88 | 89 |
| | 14 | 98 | 94 |
| | 15 | 55 | 76 |
| | 16 | 61 | 73 |
| | 17 | — | −24 |
| | 18 | 88 | −90 |
| | 19 | — | −26 |
| | 20 | 22 | 22 |
| | 21 | — | 5 |
| | 22 | 51 | 53 |
| | 23 | — | −12 |
| $k = 2$ | 0 | 263 | −274 |
| | 1 | 172 | 165 |
| | 2 | 55 | 58 |
| | 3 | 199 | 158 |
| | 4 | 196 | 210 |
| | 5 | 331 | −341 |
| | 6 | 327 | −283 |
| | 7 | 170 | 156 |
| | 8 | 87 | −75 |
| | 9 | 129 | 131 |
| | 10 | 217 | 238 |
| | 11 | 108 | −100 |
| | 12 | 66 | −76 |
| | 13 | 35 | −51 |
| | 14 | 116 | −133 |
| | 15 | 122 | 134 |
| | 16 | 104 | 111 |
| | 17 | 103 | −104 |
| | 18 | 32 | 0 |
| | 19 | 46 | −51 |
| | 20 | 58 | −66 |
| | 21 | 43 | 51 |
| | 22 | 25 | 28 |
| | 23 | — | 7 |
| $k = 3$ | 1 | 271 | −248 |
| | 2 | 296 | −303 |
| | 3 | 293 | 316 |
| | 4 | 59 | 88 |
| | 5 | 20 | 21 |
| | 6 | 59 | 51 |
| | 7 | 302 | −289 |
| | 8 | 241 | −244 |
| | 9 | 96 | 62 |
| | 10 | 23 | 18 |
| | 11 | 48 | 42 |
| | 12 | 116 | 121 |
| | 13 | 131 | −151 |
| | 14 | 41 | −43 |
| | 15 | 43 | 35 |
| | 16 | — | −17 |
| | 17 | 61 | 72 |
| | 18 | 45 | 55 |
| | 19 | 79 | −75 |
| | 20 | — | −11 |
| | 21 | — | −30 |
| | 22 | — | −17 |
| | 23 | 33 | 34 |
| $k = 4$ | 0 | 34 | 38 |
| | 1 | 300 | −313 |
| | 2 | — | −3 |
| | 3 | 140 | −106 |
| | 4 | 183 | −181 |
| | 5 | 328 | 310 |
| | 6 | 20 | 22 |
| | 7 | 113 | −89 |
| | 8 | — | −13 |
| | 9 | 239 | −265 |
| | 10 | 73 | 71 |
| | 11 | 244 | 250 |
| | 12 | 28 | 35 |
| | 13 | 70 | 83 |
| | 14 | 35 | 32 |
| | 15 | 153 | −160 |
| | 16 | 68 | −80 |
| | 17 | 32 | 37 |
| | 18 | — | −13 |
| | 19 | 68 | 76 |
| | 20 | — | 17 |
| | 21 | 66 | −65 |
| | 22 | — | −3 |
| | 23 | — | 0 |
| $k = 5$ | 1 | 260 | 287 |
| | 2 | 128 | −135 |
| | 3 | 386 | −407 |
| | 4 | 24 | −37 |
| | 5 | 74 | 72 |
| | 6 | 45 | 68 |
| | 7 | 272 | 286 |
| | 8 | 35 | −29 |
| | 9 | 183 | −189 |
| | 10 | — | 5 |
| | 11 | 44 | −53 |
| | 12 | — | −9 |
| | 13 | 192 | 198 |
| | 14 | 96 | −98 |
| | 15 | 51 | −47 |
| | 16 | — | −3 |
| | 17 | 93 | −97 |
| | 18 | 66 | 63 |
| | 19 | 71 | 72 |
| | 20 | — | 6 |
| | 21 | 26 | 25 |
| | 22 | — | 4 |
| $k = 6$ | 0 | 85 | 81 |
| | 1 | 290 | 293 |
| | 2 | 93 | −86 |
| | 3 | 69 | 72 |
| | 4 | 127 | −133 |
| | 5 | 259 | −256 |
| | 6 | 137 | 157 |
| | 7 | 74 | 64 |
| | 8 | 16 | 18 |
| | 9 | 196 | 183 |
| | 10 | 95 | −111 |
| | 11 | 155 | −140 |
| | 12 | 51 | 43 |
| | 13 | 49 | −54 |
| | 14 | 140 | 152 |
| | 15 | 75 | 90 |
| | 16 | 23 | 19 |
| | 17 | — | −25 |
| | 18 | 31 | 5 |
| | 19 | 61 | −63 |
| | 20 | 36 | 43 |
| | 21 | 63 | 62 |
| | 22 | — | −7 |
| $k = 7$ | 1 | — | −5 |
| | 2 | 276 | 278 |
| | 3 | 136 | 158 |
| | 4 | 154 | −146 |
| | 5 | 32 | −47 |
| | 6 | 60 | −78 |
| | 7 | 125 | −138 |
| | 8 | 239 | 232 |
| | 9 | 74 | 90 |
| | 10 | — | 12 |
| | 11 | 39 | 42 |
| | 12 | 81 | −83 |
| | 13 | 78 | −81 |
| | 14 | 98 | 88 |
| | 15 | 23 | 17 |
| | 16 | — | 25 |
| | 17 | 55 | 60 |
| | 18 | 99 | −95 |
| | 19 | — | −20 |
| | 20 | — | −5 |
| | 21 | — | −11 |
| | 22 | — | 14 |
| $k = 8$ | 0 | 318 | −299 |
| | 1 | 96 | −110 |
| | 2 | 100 | 109 |
| | 3 | 73 | −79 |
| | 4 | 184 | 196 |
| | 5 | 83 | 98 |
| | 6 | 224 | −216 |
| | 7 | 73 | −79 |
| | 8 | 38 | −42 |
| | 9 | 83 | −86 |
| | 10 | 171 | 127 |
| | 11 | 73 | 93 |
| | 12 | 84 | −73 |
| | 13 | — | 13 |
| | 14 | 52 | −53 |
| | 15 | 62 | −62 |
| | 16 | 81 | 81 |
| | 17 | — | 22 |
| | 18 | 21 | −13 |
| | 19 | — | 2 |
| | 20 | 64 | −71 |
| | 21 | — | −20 |

Table 3 (*cont.*)

| | $l$ | $F_o$ | $F_c$ |
|---|---|---|---|
| $k = 9$ | 1 | 29 | 26 |
| | 2 | 293 | −279 |
| | 3 | — | −15 |
| | 4 | 84 | 79 |
| | 5 | 154 | −147 |
| | 6 | 171 | 184 |
| | 7 | 24 | −34 |
| | 8 | 144 | −153 |
| | 9 | 62 | 50 |
| | 10 | — | 18 |
| | 11 | 48 | −21 |
| | 12 | 200 | 183 |
| | 13 | — | −3 |
| | 14 | 105 | −110 |
| | 15 | 32 | −3 |
| | 16 | 71 | −76 |
| | 17 | 31 | −17 |
| | 18 | 81 | 82 |
| | 19 | — | −23 |
| | 20 | — | −22 |
| | 21 | — | 19 |
| $k = 10$ | 0 | 140 | 121 |
| | 1 | 84 | −85 |
| | 2 | 79 | −90 |
| | 3 | 125 | −146 |
| | 4 | 101 | −111 |
| | 5 | 63 | 76 |
| | 6 | 244 | 226 |
| | 7 | — | 23 |
| | 8 | — | 17 |
| | 9 | 70 | −66 |
| | 10 | 232 | −210 |
| | 11 | 133 | 94 |
| | 12 | 33 | 28 |
| | 13 | 61 | 69 |
| | 14 | 88 | 93 |
| | 15 | 59 | −69 |
| | 16 | 70 | −81 |
| | 17 | — | 27 |
| | 18 | 27 | −26 |
| | 19 | — | 26 |
| | 20 | 35 | 44 |
| $k = 11$ | 1 | 34 | 51 |
| | 2 | 173 | 198 |
| | 3 | 109 | −112 |
| | 4 | 102 | −109 |
| | 5 | 28 | 7 |
| | 6 | 46 | −39 |
| | 7 | 119 | 118 |
| | 8 | 124 | 129 |
| | 9 | — | 1 |
| | 10 | — | −21 |
| | 11 | 32 | 9 |
| | 12 | 33 | −28 |
| | 13 | 50 | 46 |
| | 14 | 57 | 64 |
| | 15 | 46 | −39 |
| | 16 | — | 8 |
| | 17 | 37 | −47 |
| | 18 | 57 | −56 |
| | 19 | 30 | 33 |
| $k = 12$ | 0 | — | −8 |
| | 1 | 153 | 175 |
| | 2 | 31 | 41 |
| | 3 | 37 | 33 |
| | 4 | 120 | 120 |
| | 5 | 121 | −130 |
| | 6 | — | 3 |
| | 7 | 78 | 72 |
| | 8 | 32 | −24 |
| | 9 | 87 | 102 |
| | 10 | — | 14 |
| | 11 | 105 | −107 |
| | 12 | 32 | −4 |
| | 13 | — | −16 |
| | 14 | 68 | −50 |
| | 15 | 39 | 49 |
| | 16 | 27 | 13 |
| | 17 | 30 | −22 |
| | 18 | 20 | 3 |
| $k = 13$ | 1 | 70 | −71 |
| | 2 | 81 | −78 |
| | 3 | 139 | 149 |
| | 4 | — | 10 |
| | 5 | 23 | −28 |
| | 6 | 23 | −14 |
| | 7 | 119 | −121 |
| | 8 | 95 | −84 |
| | 9 | 101 | 95 |
| | 10 | — | 5 |
| | 11 | 58 | 71 |
| | 12 | 31 | 27 |
| | 13 | 106 | −93 |
| | 14 | 36 | −40 |
| | 15 | — | −9 |
| | 16 | 24 | −3 |
| | 17 | 39 | 51 |
| $k = 14$ | 0 | 107 | −99 |
| | 1 | 105 | −122 |
| | 2 | 32 | −23 |
| | 3 | 23 | −38 |
| | 4 | 63 | 61 |
| | 5 | 113 | 119 |
| | 6 | 44 | −49 |
| | 7 | — | −5 |
| | 8 | 22 | 12 |
| | 9 | 60 | −65 |
| | 10 | — | 10 |
| | 11 | 71 | 76 |
| | 12 | 28 | −7 |
| | 13 | — | −12 |
| | 14 | — | −23 |
| | 15 | 63 | −75 |
| | 16 | 34 | 31 |
| $k = 15$ | 1 | 77 | 74 |
| | 2 | 32 | −36 |
| | 3 | 86 | −98 |
| | 4 | 36 | 36 |
| | 5 | — | 3 |
| | 6 | — | 15 |
| | 7 | 89 | 94 |
| | 8 | 58 | −62 |
| | 9 | 69 | −84 |
| | 10 | — | 3 |
| | 11 | 80 | −78 |
| | 12 | 36 | 39 |
| | 13 | 41 | 49 |
| | 14 | 29 | −17 |
| | 15 | — | −14 |
| $k = 16$ | 0 | 76 | 83 |
| | 1 | 23 | 20 |
| | 2 | 23 | −25 |
| | 3 | — | 6 |
| | 4 | 73 | −87 |
| | 5 | 69 | −83 |
| | 6 | 54 | 56 |
| | 7 | 30 | 20 |
| | 8 | — | 23 |
| | 9 | 20 | 4 |
| | 10 | 44 | −54 |
| | 11 | — | −15 |
| | 12 | 27 | 21 |
| | 13 | — | 1 |
| | 14 | 21 | 34 |
| $k = 17$ | 1 | 27 | −31 |
| | 2 | 42 | 55 |
| | 3 | 30 | 24 |
| | 4 | 50 | −51 |
| | 5 | 29 | 14 |
| | 6 | 37 | −35 |
| | 7 | — | −11 |
| | 8 | 46 | 56 |
| | 9 | — | 18 |
| | 10 | 23 | 5 |
| | 11 | 29 | 20 |
| | 12 | 19 | −39 |
| $k = 18$ | 0 | 105 | −112 |
| | 1 | — | −22 |
| | 2 | 25 | 35 |
| | 3 | — | −8 |
| | 4 | 38 | 45 |
| | 5 | — | 13 |
| | 6 | 54 | −54 |
| | 7 | — | −11 |
| | 8 | 32 | −5 |
| | 9 | — | 10 |
| | 10 | 56 | 94 |
| $k = 19$ | 1 | 58 | −45 |
| | 2 | 63 | −57 |
| | 3 | 38 | 39 |
| | 4 | 52 | 54 |
| | 5 | 39 | 21 |
| | 6 | 38 | 35 |
| | 7 | — | −4 |

2*kl* reflexions

| | $l$ | $\|F_o\|$ | $\|F_c\|$ | $\alpha°$ |
|---|---|---|---|---|
| $k = 0$ | 1 | — | 77 | 90 |
| | 2 | 156 | 149 | 0 |
| | 3 | 190 | 175 | 90 |
| | 4 | 420 | 377 | 0 |
| | 5 | 116 | 87 | 90 |
| | 6 | 375 | 322 | 180 |
| | 7 | — | 16 | 270 |
| | 8 | 61 | 88 | 180 |
| | 9 | 30 | 28 | 270 |
| | 10 | 271 | 262 | 0 |
| | 11 | — | 3 | 270 |
| | 12 | 119 | 96 | 180 |
| | 13 | — | 40 | 270 |
| | 14 | 124 | 127 | 180 |
| | 15 | 44 | 43 | 270 |

Table 3 (*cont.*)

| | $l$ | $\|F_o\|$ | $\|F_c\|$ | $\alpha°$ |
|---|---|---|---|---|
| | 16 | 91 | 78 | 0 |
| | 17 | — | 13 | 90 |
| | 18 | — | 6 | 0 |
| | 19 | — | 1 | 270 |
| | 20 | 41 | 70 | 180 |
| | 21 | — | 10 | 270 |
| | 22 | — | 19 | 0 |
| $k = 1$ | 0 | — | 233 | 270 |
| | 1 | 84 | 158 | 113 |
| | 2 | 426 | 500 | 6 |
| | 3 | 203 | 162 | 4 |
| | 4 | 288 | 281 | 169 |
| | 5 | 148 | 125 | 267 |
| | 6 | 236 | 210 | 184 |
| | 7 | 224 | 224 | 118 |
| | 8 | 229 | 286 | 360 |
| | 9 | 74 | 118 | 69 |
| | 10 | — | 48 | 122 |
| | 11 | 25 | 50 | 289 |
| | 12 | 144 | 147 | 177 |
| | 13 | 116 | 91 | 175 |
| | 14 | 112 | 112 | 13 |
| | 15 | 28 | 31 | 130 |
| | 16 | 28 | 43 | 358 |
| | 17 | 39 | 32 | 330 |
| | 18 | 96 | 83 | 186 |
| | 19 | — | 17 | 218 |
| | 20 | — | 17 | 292 |
| | 21 | — | 7 | 135 |
| | 22 | — | 30 | 2 |
| $k = 2$ | 0 | 246 | 314 | 0 |
| | 1 | 370 | 363 | 26 |
| | 2 | 210 | 170 | 188 |
| | 3 | 232 | 174 | 320 |
| | 4 | 207 | 233 | 209 |
| | 5 | 295 | 302 | 208 |
| | 6 | 297 | 272 | 354 |
| | 7 | 211 | 172 | 18 |
| | 8 | 111 | 84 | 347 |
| | 9 | 175 | 153 | 355 |
| | 10 | 200 | 198 | 183 |
| | 11 | 152 | 125 | 186 |
| | 12 | 67 | 68 | 31 |
| | 13 | 73 | 78 | 118 |
| | 14 | 89 | 85 | 23 |
| | 15 | 74 | 74 | 336 |
| | 16 | 28 | 46 | 170 |
| | 17 | 65 | 51 | 222 |
| | 18 | 37 | 6 | 201 |
| | 19 | 50 | 43 | 143 |
| | 20 | 22 | 44 | 353 |
| | 21 | — | 22 | 14 |
| | 22 | — | 10 | 152 |
| $k = 3$ | 0 | 128 | 181 | 90 |
| | 1 | 223 | 216 | 4 |
| | 2 | 355 | 278 | 168 |
| | 3 | 348 | 358 | 168 |
| | 4 | 138 | 168 | 302 |
| | 5 | 126 | 57 | 6 |
| | 6 | 149 | 106 | 12 |
| | 7 | 304 | 311 | 12 |
| | 8 | 176 | 174 | 177 |
| | 9 | 129 | 116 | 211 |
| | 10 | 118 | 161 | 270 |
| | 11 | 75 | 58 | 159 |
| | 12 | 120 | 114 | 357 |
| | 13 | 127 | 130 | 13 |
| | 14 | 87 | 109 | 131 |
| | 15 | 28 | 27 | 172 |
| | 16 | 51 | 41 | 231 |
| | 17 | 66 | 63 | 200 |
| | 18 | 45 | 54 | 354 |
| | 19 | 36 | 44 | 0 |
| | 20 | — | 18 | 120 |
| | 21 | — | 19 | 336 |
| | 22 | — | 15 | 217 |
| $k = 4$ | 0 | — | 3 | 180 |
| | 1 | 262 | 307 | 185 |
| | 2 | 93 | 71 | 297 |
| | 3 | 241 | 199 | 163 |
| | 4 | 131 | 148 | 61 |
| | 5 | 336 | 389 | 350 |
| | 6 | — | 47 | 106 |
| | 7 | 50 | 54 | 190 |
| | 8 | 107 | 107 | 280 |
| | 9 | 174 | 169 | 175 |
| | 10 | — | 16 | 65 |
| | 11 | 173 | 196 | 346 |
| | 12 | — | 17 | 87 |
| | 13 | 90 | 59 | 10 |
| | 14 | 57 | 47 | 230 |
| | 15 | 139 | 143 | 165 |
| | 16 | — | 4 | 79 |
| | 17 | 27 | 46 | 3 |
| | 18 | — | 15 | 82 |
| | 19 | 41 | 43 | 348 |
| | 20 | — | 9 | 258 |
| | 21 | 44 | 48 | 189 |
| | 22 | — | 2 | 63 |
| $k = 5$ | 0 | 57 | 40 | 90 |
| | 1 | 339 | 310 | 186 |
| | 2 | — | 18 | 20 |
| | 3 | 364 | 354 | 5 |
| | 4 | — | 65 | 91 |
| | 5 | 144 | 75 | 178 |
| | 6 | 65 | 58 | 325 |
| | 7 | 247 | 276 | 164 |
| | 8 | 30 | 11 | 265 |
| | 9 | 206 | 177 | 3 |
| | 10 | — | 3 | 318 |
| | 11 | 42 | 68 | 9 |
| | 12 | 72 | 61 | 16 |
| | 13 | 139 | 134 | 198 |
| | 14 | 37 | 20 | 257 |
| | 15 | — | 22 | 2 |
| | 16 | 55 | 31 | 123 |
| | 17 | 63 | 73 | 11 |
| | 18 | — | 10 | 40 |
| | 19 | 40 | 36 | 166 |
| | 20 | — | 16 | 247 |
| | 21 | 37 | 19 | 218 |
| $k = 6$ | 0 | 350 | 362 | 180 |
| | 1 | 256 | 271 | 354 |
| | 2 | 197 | 202 | 69 |
| | 3 | — | 26 | 323 |
| | 4 | 141 | 122 | 336 |
| | 5 | 264 | 280 | 192 |
| | 6 | 133 | 146 | 184 |
| | 7 | 87 | 83 | 338 |
| | 8 | 82 | 81 | 117 |
| | 9 | 165 | 150 | 13 |
| | 10 | 102 | 121 | 346 |
| | 11 | 128 | 138 | 159 |
| | 12 | 97 | 79 | 213 |
| | 13 | — | 22 | 128 |
| | 14 | 30 | 34 | 172 |
| | 15 | 88 | 74 | 18 |
| | 16 | — | 35 | 154 |
| | 17 | 54 | 26 | 153 |
| | 18 | — | 16 | 339 |
| | 19 | 42 | 40 | 179 |
| | 20 | — | 31 | 180 |
| | 21 | 42 | 34 | 15 |
| $k = 7$ | 0 | 63 | 119 | 90 |
| | 1 | 128 | 173 | 68 |
| | 2 | 169 | 172 | 339 |
| | 3 | 155 | 162 | 165 |
| | 4 | 183 | 170 | 191 |
| | 5 | 74 | 84 | 260 |
| | 6 | 94 | 109 | 165 |
| | 7 | 135 | 131 | 358 |
| | 8 | 151 | 136 | 17 |
| | 9 | 64 | 71 | 192 |
| | 10 | — | 37 | 302 |
| | 11 | 77 | 93 | 224 |
| | 12 | 87 | 92 | 148 |
| | 13 | 86 | 85 | 350 |
| | 14 | 70 | 45 | 345 |
| | 15 | — | 19 | 86 |
| | 16 | — | 16 | 351 |
| | 17 | 43 | 44 | 157 |
| | 18 | 55 | 45 | 183 |
| | 19 | 21 | 28 | 339 |
| | 20 | — | 18 | 78 |
| | 21 | — | 7 | 355 |
| $k = 8$ | 0 | 280 | 318 | 0 |
| | 1 | 166 | 143 | 207 |
| | 2 | 110 | 76 | 113 |
| | 3 | 87 | 37 | 204 |
| | 4 | 209 | 219 | 188 |
| | 5 | 86 | 60 | 51 |
| | 6 | 216 | 147 | 7 |
| | 7 | 64 | 63 | 113 |
| | 8 | 45 | 47 | 4 |
| | 9 | 82 | 64 | 199 |
| | 10 | 129 | 151 | 192 |
| | 11 | 56 | 58 | 337 |
| | 12 | 52 | 57 | 36 |
| | 13 | — | 29 | 131 |
| | 14 | 76 | 80 | 8 |
| | 15 | — | 26 | 196 |
| | 16 | 66 | 78 | 184 |
| | 17 | — | 23 | 285 |
| | 18 | — | 3 | 90 |
| | 19 | — | 15 | 5 |
| | 20 | 46 | 44 | 356 |
| $k = 9$ | 0 | — | 34 | 270 |
| | 1 | — | 66 | 275 |
| | 2 | 163 | 189 | 180 |
| | 3 | 65 | 111 | 280 |
| | 4 | 139 | 133 | 350 |
| | 5 | 42 | 74 | 74 |
| | 6 | 110 | 113 | 347 |
| | 7 | — | 47 | 284 |
| | 8 | 144 | 138 | 175 |
| | 9 | — | 35 | 283 |
| | 10 | — | 23 | 360 |
| | 11 | — | 29 | 71 |
| | 12 | 111 | 99 | 354 |
| | 13 | — | 19 | 63 |
| | 14 | 58 | 53 | 173 |
| | 15 | — | 24 | 278 |
| | 16 | 24 | 36 | 188 |
| | 17 | — | 30 | 90 |

Table 3 (*cont.*)

| | $l$ | $\|F_o\|$ | $\|F_c\|$ | $\alpha°$ |
|---|---|---|---|---|
| | 18 | 71 | 40 | 0 |
| | 19 | — | 3 | 101 |
| $k = 10$ | 0 | 200 | 209 | 180 |
| | 1 | 107 | 100 | 173 |
| | 2 | 74 | 44 | 349 |
| | 3 | 62 | 39 | 152 |
| | 4 | 160 | 159 | 358 |
| | 5 | 30 | 48 | 10 |
| | 6 | 144 | 173 | 179 |
| | 7 | — | 31 | 185 |
| | 8 | — | 14 | 205 |
| | 9 | 72 | 58 | 193 |
| | 10 | 121 | 126 | 353 |
| | 11 | 69 | 58 | 0 |
| | 12 | — | 32 | 195 |
| | 13 | — | 12 | 313 |
| | 14 | 56 | 57 | 184 |
| | 15 | — | 20 | 188 |
| | 16 | 73 | 68 | 2 |
| | 17 | — | 11 | 36 |
| | 18 | — | 6 | 53 |
| | 19 | — | 17 | 350 |
| $k = 11$ | 0 | — | 9 | 270 |
| | 1 | 45 | 75 | 131 |
| | 2 | 99 | 94 | 21 |
| | 3 | 94 | 106 | 8 |
| | 4 | 90 | 77 | 186 |
| | 5 | — | 40 | 279 |
| | 6 | 63 | 64 | 198 |
| | 7 | 71 | 85 | 185 |
| | 8 | 89 | 81 | 353 |
| | 9 | — | 18 | 358 |
| | 10 | — | 59 | 89 |
| | 11 | — | 31 | 290 |
| | 12 | 60 | 63 | 195 |
| | 13 | 54 | 57 | 174 |
| | 14 | — | 27 | 336 |
| | 15 | — | 20 | 82 |
| | 16 | — | 24 | 28 |
| | 17 | — | 20 | 340 |
| | 18 | — | 25 | 177 |
| $k = 12$ | 0 | 75 | 94 | 0 |
| | 1 | 106 | 125 | 25 |
| | 2 | 67 | 65 | 127 |
| | 3 | — | 33 | 321 |
| | 4 | 71 | 62 | 197 |
| | 5 | 108 | 111 | 154 |
| | 6 | 30 | 36 | 340 |
| | 7 | 57 | 44 | 42 |
| | 8 | — | 14 | 43 |
| | 9 | 86 | 99 | 333 |
| | 10 | 38 | 43 | 197 |
| | 11 | 73 | 71 | 205 |
| | 12 | 20 | 23 | 330 |
| | 13 | — | 12 | 167 |
| | 14 | — | 9 | 60 |
| | 15 | 30 | 41 | 9 |
| | 16 | — | 30 | 153 |
| | 17 | — | 19 | 173 |
| $k = 13$ | 0 | — | 40 | 90 |
| | 1 | 99 | 87 | 29 |
| | 2 | 59 | 36 | 199 |
| | 3 | 120 | 123 | 163 |
| | 4 | — | 35 | 279 |
| | 5 | 28 | 14 | 351 |
| | 6 | — | 40 | 89 |
| | 7 | 86 | 102 | 30 |
| | 8 | — | 21 | 160 |
| | 9 | 80 | 67 | 171 |
| | 10 | — | 16 | 314 |
| | 11 | 25 | 29 | 194 |
| | 12 | — | 14 | 343 |
| | 13 | 39 | 56 | 348 |
| | 14 | — | 8 | 110 |
| | 15 | — | 6 | 217 |
| $k = 14$ | 0 | 48 | 45 | 0 |
| | 1 | 68 | 80 | 200 |
| | 2 | — | 16 | 288 |
| | 3 | 25 | 29 | 202 |
| | 4 | — | 19 | 164 |
| | 5 | 88 | 99 | 0 |
| | 6 | 20 | 25 | 22 |
| | 7 | 30 | 32 | 180 |
| | 8 | — | 16 | 219 |
| | 9 | 36 | 52 | 165 |
| | 10 | — | 5 | 135 |
| | 11 | 44 | 55 | 10 |
| | 12 | — | 5 | 40 |
| | 13 | — | 12 | 6 |
| | 14 | — | 16 | 295 |
| | 15 | 41 | 43 | 183 |
| $k = 15$ | 0 | — | 10 | 270 |
| | 1 | 35 | 36 | 180 |
| | 2 | 35 | 48 | 176 |
| | 3 | 65 | 66 | 10 |
| | 4 | — | 29 | 34 |
| | 5 | — | 12 | 13 |
| | 6 | — | 30 | 28 |
| | 7 | 43 | 56 | 186 |
| | 8 | 30 | 34 | 188 |
| | 9 | 25 | 32 | 343 |
| | 10 | — | 14 | 77 |
| | 11 | 39 | 34 | 10 |
| | 12 | 20 | 25 | 343 |
| | 13 | 18 | 31 | 175 |
| $k = 16$ | 0 | 23 | 30 | 180 |
| | 1 | 25 | 46 | 320 |
| | 2 | — | 27 | 40 |
| | 3 | — | 22 | 54 |
| | 4 | 35 | 37 | 2 |
| | 5 | 35 | 44 | 168 |
| | 6 | 35 | 35 | 191 |
| | 7 | 22 | 30 | 333 |
| | 8 | — | 23 | 148 |
| | 9 | 20 | 25 | 29 |
| | 10 | 38 | 36 | 10 |
| | 11 | — | 17 | 151 |
| | 12 | — | 13 | 235 |
| $k = 17$ | 0 | — | 3 | 90 |
| | 1 | — | 10 | 8 |
| | 2 | 47 | 66 | 346 |
| | 3 | 25 | 28 | 183 |
| | 4 | 30 | 35 | 168 |
| | 5 | — | 19 | 244 |
| | 6 | — | 26 | 136 |
| | 7 | — | 6 | 13 |
| | 8 | 56 | 52 | 355 |
| | 9 | 21 | 9 | 172 |
| | 10 | — | 6 | 194 |
| $k = 18$ | 0 | 40 | 38 | 0 |
| | 1 | — | 16 | 69 |
| | 2 | — | 24 | 191 |
| | 3 | — | 25 | 270 |
| | 4 | 18 | 37 | 196 |
| | 5 | — | 2 | 161 |
| | 6 | 20 | 26 | 7 |
| | 7 | — | 8 | 126 |

## Estimation of accuracy

### (i) *By examination of results*

The standard deviation of individual bond lengths from their accepted values is 0·07 Å. The average value of those angles which might be expected to be tetrahedral is 109° and their standard deviation from the mean is 7°. These figures probably underestimate the accuracy attained.

### (ii) *Theoretical estimate*

From a $(\sigma_o - \sigma_c)$ map of the zero-layer projection, the standard deviation in $y$ or $z$ coordinate was found to be approximately 0·025 Å (for light atoms). The accuracy of an $x$ coordinate varies considerably according to the value of $x$. However, some estimate was made of the average error in $x$ coordinates by considering the average value of $|{}_2\sigma_c|$ and $|{}_2\sigma_s|$ in regions away from atoms. The standard deviation in $x$ coordinate was thus found to be approximately 0·05 Å. Thus the standard deviation in bond length would be $\sim$ 0·06 Å.

## Discussion of results

### (i) *General features of the molecule*

The separation $N_3$–$C_5'$ (1·41 Å) is approximately equal to that for a covalent single bond. The molecule resulting from this rearrangement to form a new seven-membered ring has been called 2′:3′-*iso*propylidene, 3:5′-*cyclo*adenosine. It is seen that the sugar is ribofuranose and is joined to the purine at $N_9$ by a $\beta$-glycosidic link. The atoms of the purine ring system

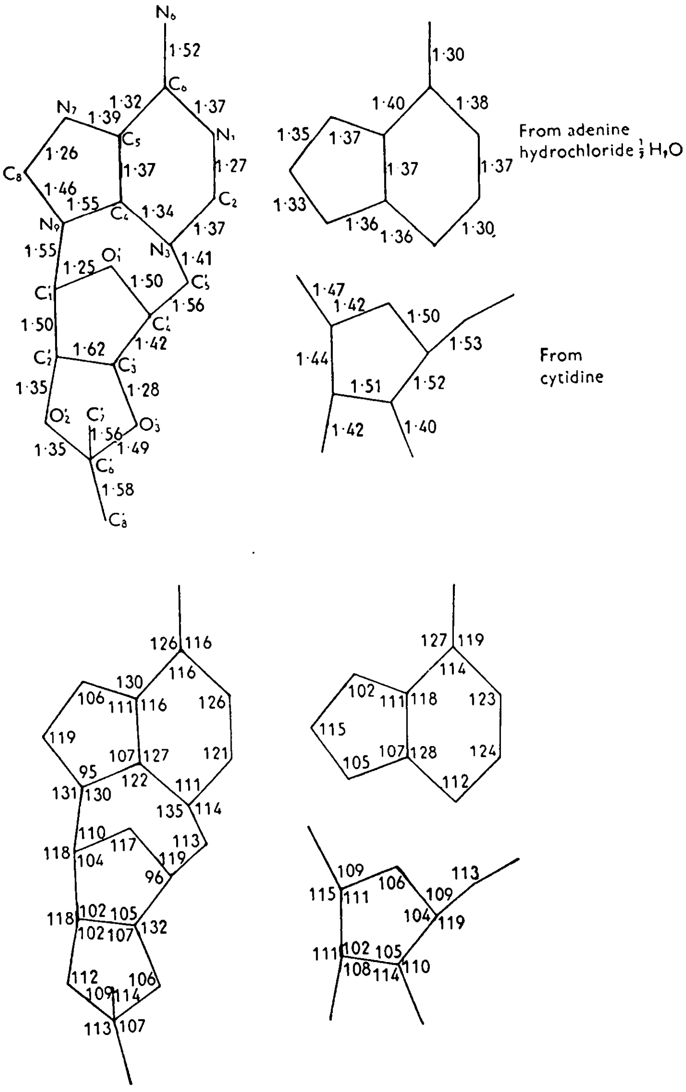


Fig. 8. Bond lengths and bond angles in the *cyclo*nucleoside, and those in analogous parts of adenine hydrochloride and of cytidine.

are, within the limits of experimental error, coplanar. $C_1'$ also lies in this plane, but $C_5'$ is 0·7 Å from it. The sugar ring is puckered so that $O_1'$ and $C_3'$ lie 0·3 Å away from, and on the same side of, the plane defined by $C_1'$, $C_2'$ and $C_4'$. This plane makes an angle of 90° with that of the purine.

### (ii) *Comparison with adenine hydrochloride and cytidine*

The standard deviation of bond lengths in the *cyclo*nucleoside is such that only differences greater than 0·15 Å from those in the above two compounds can be considered as significant. In the purine part of the molecule such differences occur at $C_6$–$N_6$, $C_4$–$N_9$ and $C_8$–$N_9$. In the latter two cases the fact that the sugar is attached at $N_9$ makes the occurrence of different bond lengths not unexpected, and it is seen that the angle $C_8N_9C_4$, also, is appreciably different in the two cases. It is probable that substitution at $N_3$ will alter the predominant tautomeric forms of the molecule, and it would seem that the percentage double-bond character of $C_6N_6$ is here less than in the adenine hydrochloride molecule. The average bond length (1·34 Å) in the purine ring system agrees with that (1·36 Å) in adenine hydrochloride.

When the bond angles are compared, the result is somewhat unexpected. The standard deviation for angles in the purine part of the molecule is only 2°, compared with the value 7° obtained for the rest of the molecule, and the marked divergences from symmetry in adenine hydrochloride are reproduced most faithfully in the *cyclo*nucleoside with the exception of $C_8N_9C_4$ (see above). Since no reason for greater accuracy in this part of the molecule has been discovered, the close resemblance must be taken as fortuitous, particularly as it is not reproduced with regard to bond lengths.

There appears to be little resemblance between the sugars of cytidine and of the *cyclo*nucleoside with regard to structural details. This is not surprising since the five membered ring of single bonds does allow some flexibility of configuration which could easily be influenced by the proximity of the iodine ion, and by the *iso*propylidene substituents.

### (iii) *Hydrogen bonds*

The only two hydrogen atoms associated with nitrogen or oxygen are those of the $NH_2$ group at $N_6$. One of these is certainly involved in formation of a hydrogen bond with $O_2'$ of a neighbouring molecule, as the separation 2·86 Å testifies. That the other hydrogen forms a bond between the nitrogen and the iodine ion is also suggested, since they are separated by only 3·5 Å in the direction in which the hydrogen would be expected to lie. It is also observed that $C_6$, $N_6$, $O_2'$ and I are approximately coplanar, which lends weight to the above interpretation.

### (iv) *The iodine environment*

Approaches of carbon or nitrogen to the iodine ion appear to be of two kinds. One, approximately 4·0 Å, is the expected van der Waals distance, and this type occurs on one side ($C_8$, $C_1'$) of the molecule. The other is approximately 3·5 Å, indicating some sort of weak bond formation, perhaps of an electrostatic nature, between the iodine ion and carbon atoms on the other side of the molecule. A gratifying check on the correctness of the $x$ coordinate of $C_5'$ is provided, since the iodine ion is approximately equidistant from $C_5'$ of the molecules above and below it, so that allocation of any coordinate other than that given would have resulted in an I–$C_5'$ separation even smaller than the 3·48 Å observed. None of the distances between carbon, oxygen and nitrogen of different molecules is significantly less than the normal van der Waals approach of 3·4–3·5 Å.

## X-ray investigation of a uridine derivative

It has been mentioned (Clark *et al.*, 1952) that synthesis of uridine 5′ phosphate was successfully achieved via the 5′iodo derivative of uridine, and consequently it may be assumed that this substance is a normal covalent iodide. In order to obtain direct evidence of this, and to emphasize the contrast between its structure and that of a *cyclo*nucleoside, X-ray analysis of its structure in one projection was undertaken. The material, 5′-iodo 2′:3′-*iso*propylidene uridine, was provided by V. M. Clark and was recrystallized from a mixture of water and alcohol. Its cell dimensions are:

$$a = 5{\cdot}42,\ b = 15{\cdot}4,\ c = 16{\cdot}7\ \text{Å}\ (\pm 1\%)\ .$$

Space group: $P2_12_12_1$. Number of molecules per unit cell: 4.

Intensity data were obtained on zero-layer (0*kl*) Weissenberg photographs using copper and molybdenum radiations, and the heavy-atom method was again used, followed by limited refinement, to provide the electron-density map shown in Fig. 9. Clearly there has been no rearrangement of the molecule in this case. (It is known that the similar cytidine derivative rearranges to form the ionic $O_2$:5′-*cyclo*cytidine iodide.) A ball-and-spoke model of the molecule 5′-iodo, 2′:3′-*iso*propylidene, $N_3$-β-ribofuranosido-uracil was seen to fit the projection almost exactly.

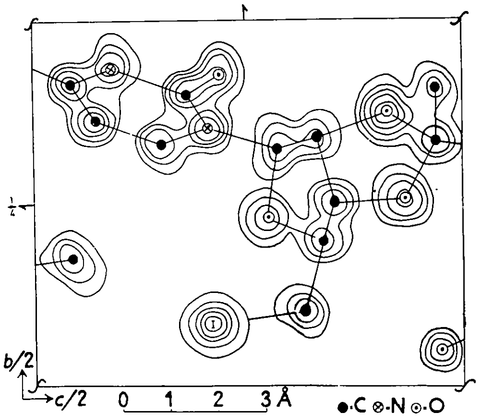


Fig. 9. 5′-Iodo, 2′ : 3′-*iso*propylidene uridine: electron density projected on (100). Contour interval for iodine is ten times that for other atoms.

As in cytidine (Furberg, 1950), and for similar reasons, the D-ribose ring lies in a position *trans* to $O_2$ (with reference to the bond $N_3$–$C'_1$), but in this case the I–$C_4$ distance is not short (cf. $O'_5$–$C_4$ in cytidine).

Various chemical and stereochemical aspects of the *cyclo*nucleoside structure not mentioned here are dealt with in the paper by Clark *et al.* (1952).

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