BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

CHEVALIER, R. & GASPERIN, M. (1970). *Bull. Soc. Fr. Minér. Crist.* **93**, 18–22.

COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *DATAP*1. Institute of Chemistry, Uppsala; Oak Ridge National Laboratories, Oak Ridge, Tennessee.

CROMER, T. (1965). *Acta Cryst.* **18**, 17–27.

CROMER, T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

GAINES, R. V. (1969). *Amer. Min.* **54**, 697–701.

GAINES, R. V. (1971). *Amer. Min.* **56**, 411–415.

GALY, J. & MEUNIER, G. (1971). *Acta Cryst.* **B27**, 608–616.

HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210–214.

JAHNBERG, L. (1971). *Chem. Commun.* p. 13.

KHODADAD, P. (1962). *C.R. Acad. Sci. Paris,* **255**, 1617–1618.

LECIEJEWICZ, J. (1961). *Z. Kristallogr.* **116**, 345–353.

LINDQVIST, O. (1968). *Acta Chem. Scand.* **22**, 977–982.

MEUNIER, G. & GALY, J. (1971). *Acta Cryst.* **B27**, 602–608.

PERTLIK, F. (1969). *Tschermaks Min. Petrogr. Mitt.* **13**, 219–232.

PERTLIK, F. (1971). *Tschermaks Min. Petrogr. Mitt.* **15**, 279–290.

SIEGEL, S., VISTE, A., HOEKSTRA, H. R. & TANI, B. (1972). *Acta Cryst.* **B28**, 117–121.

SRINIVASAN, R. (1960). *Acta Cryst.* **13**, 388–394.

WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318–321.

ZACHARIASEN, W. H. (1954). *Acta Cryst.* **7**, 783–787.

Bonding and Valence Electron Distributions in Molecules. The Crystal and Molecular Structure of 1,1,2,2-Tetracyanocyclopropane

BY YU WANG AND G. D. STUCKY

School of Chemical Sciences, Department of Chemistry and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801, U.S.A.

The crystal and molecular structure of 1,1,2,2-tetracyanocyclopropane, $H_2C[C(CN)_2]_2$, has been determined using three-dimensional X-ray data collected by counter methods. The structure was solved using acentric direct methods techniques and subsequently refined by a full-matrix least-squares procedure on 715 reflections to a final R index of 0·038 based on F. The space group is $P2_12_12_1$ with $a = 16·158(18)$, $b = 6·901(3)$, $c = 6·227(4)$ Å and $Z = 4$. The endocyclic C–C bond lengths are 1·503(4) Å for $H_2C–C(CN)_2$ and 1·561(4) Å for $(NC)_2C–C(CN)_2$. The average exocyclic C–C and C N distances are 1·450(4), 1·127(3) Å respectively. There are two different C–C N bond angles in the molecule, linear 179·5(5) and bent 177·3(3)°.

Introduction

Recent X-ray photoelectron studies have shown a significant difference (0·4 eV) in the 1*s* binding energies of the cyanide nitrogen atoms in tetracyanoethylene oxide (TCEO) and 1,1,2,2-tetracyanocyclopropane (TCCP) (Stucky, Matthews, Hedman, Klasson & Nordling, 1972). This was somewhat surprising and, in order to analyze the above results in terms of atomic charge distributions, it was necessary to know the detailed geometry of TCCP. The presence of the electron-withdrawing groups apparently results in a lengthening of the ring carbon–carbon bond lengths. For example, in cyclobutane (Rathjens, Freeman, Gwinn & Pitzer, 1953), tetracyanocyclobutane (Greenberg & Post, 1968), and octachlorocyclobutane (Owen & Hoard, 1951). the reported carbon–carbon bond lengths are 1·56(2), 1·561(3) and 1·59(3) Å. Similarly, the ring C–C bond lengths in ethylene oxide (Cunningham, Boyd, Myers, Gwinn & LeVan, 1951) and TCEO (Matthews Swanson, Mueller & Stucky, 1971) are 1·470(1) and 1·493(3) Å. A counter example may be provided by cyclopropane (Bastiansen & Hassel, 1952) and *cis*-1,2,3-tricyanocyclopropane (Hartman & Hirshfeld, 1966) which have C–C distances of 1·524(14) and 1·518(3); however, the experimental error in the bond distances in the cyclopropane structure prohibits a definitive comparison. In order to obtain a model for the ESCA studies and to further investigate the effect of electronegative substituents on the cyclopropane ring geometry, an investigation of the structure of TCCP was initiated.

Experimental

A sample of 1,1,2,2-tetracyanocyclopropane (TCCP), synthesized by the method of Scribner, Sansen & Prichard (1960), was kindly provided by Professor D. Hart of Michigan State University. A brick-shaped transparent crystal was obtained by slowly evaporating a dry-ethanol solution of the compound under an N_2 atmosphere. The data collection, structural determination and refinement procedures are detailed below.

Crystal data

Space group $P2_12_12_1$, No. 19 (*International Tables for X-ray Crystallography*).

$a = 16 \cdot 158(18)$, $b = 6 \cdot 901(3)$, $c = 6 \cdot 227(4)$ Å.

$\lambda(\text{Mo } K\alpha) = 0 \cdot 7107$ Å, $Z = 4$.

$\varrho_{cal} = 1 \cdot 316$ g cm^{-3}, $\varrho_{meas} = 1 \cdot 325(5)$ g cm^{-3}, by flotation in a carbon tetrachloride and n-heptane mixture.

Systematic absences: $h00$ $h \neq 2n$
$0k0$ $k \neq 2n$
$00l$ $l \neq 2n$.

Intensity measurement

A brick-shaped crystal with dimensions $0 \cdot 4 \times 0 \cdot 2 \times 0 \cdot 5$ mm was sealed in a glass capillary with the [401] direction along the diffractometer axis. A complete octant form of intensity data was taken to $50°$ in 2θ by the θ–2θ scan technique at a rate of $1°$ min^{-1} with a take-off angle of $1 \cdot 2°$, a factor of $0 \cdot 692$ for Mo $K\alpha$, using Mo $K\alpha$ radiation with a highly oriented graphite monochromator. Each reflection was scanned $1 \cdot 5°$ (wavelength dispersion corrected) on 2θ and background counts of 10 sec were taken both at the beginning and at the end of the scan. 715 reflections were measured and the raw intensities then corrected for Lorentz and polarization effects. The estimated standard deviations $\sigma(F)$ of the structure factors are based on the counting statistics:

$$\sigma(F) = \frac{F}{2I} \left[\text{CN} + 0 \cdot 25(\text{TC}/\text{TB})^2(B_1 + B_2) + p^2 I^2 \right]^{1/2}$$

where CN is the total integrated peak counts in a scan time of TC seconds; B_1, B_2 are the background counts in a time TB (in this case, 10 sec), I is the net peak counts and the p factor is chosen to be $0 \cdot 02$. Absorption corrections were neglected ($\mu = 0 \cdot 706$ cm^{-1}). This was estimated to introduce an error of no more than $2 \cdot 7\%$ in the intensity data.

Structure solution and refinement

The structure was solved by the application of 'direct methods' (Karle & Karle, 1966; Karle & Hauptman, 1956, 1961; Ahmed, Hall & Huber, 1970). Three two-dimensional reflections (501, 320, 053) were first as-

signed as the origin, using the program *MULTAN* (Germain, Main & Woolfson). This was then followed by a three-dimensional E map calculation with 229
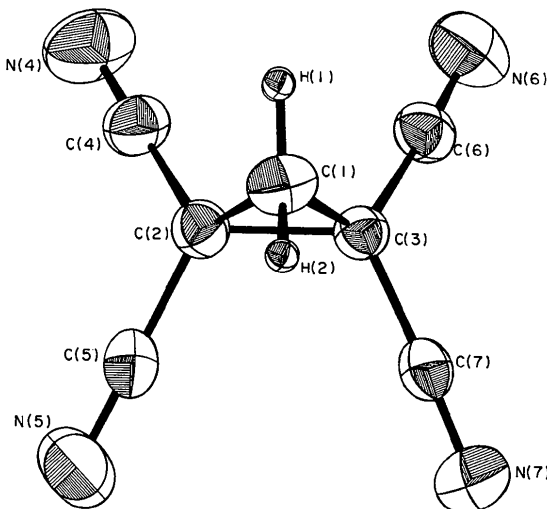

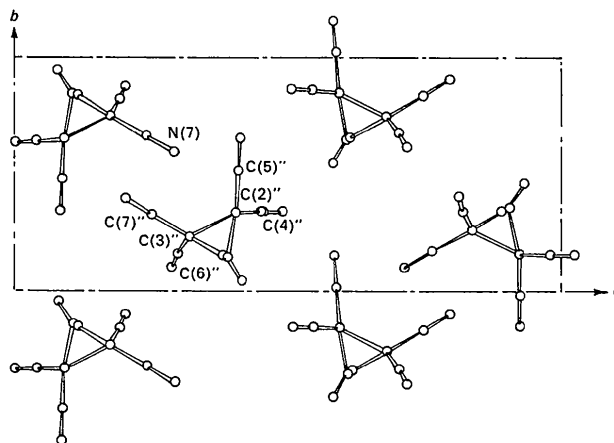Fig. 1. The molecular structure and thermal ellipsoids of TCCP.

Fig. 2. Molecular packing of TCCP in the solid.

Table 1. *Positional and thermal parameters of* H_2C–$[C(CN)_2]_2$

All parameters are $\times 10^4$ (excepting the hydrogen isotropic thermal parameters).

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	-3910 (2)	-3517 (5)	3596 (5)	33 (1)	168 (7)	194 (8)	-10 (3)	8 (3)	-11 (9)
C(2)	-4079 (1)	-1594 (4)	4652 (4)	25 (1)	140 (6)	196 (8)	1 (2)	2 (3)	-7 (7)
C(3)	-3220 (1)	-2613 (4)	4863 (4)	26 (1)	107 (5)	175 (8)	3 (2)	7 (3)	-5 (6)
C(4)	-4586 (2)	-1547 (5)	6571 (5)	34 (1)	153 (7)	253 (10)	-0 (2)	22 (3)	-16 (9)
N(4)	-4982 (2)	-1517 (4)	8080 (5)	59 (1)	243 (8)	384 (1)	-7 (3)	67 (3)	-34 (9)
C(5)	-4109 (2)	159 (5)	3367 (5)	26 (1)	182 (8)	221 (9)	-10 (3)	-4 (3)	8 (8)
N(5)	-4142 (2)	1529 (4)	2366 (5)	53 (1)	240 (7)	327 (9)	20 (3)	-8 (3)	57 (9)
C(6)	-3029 (2)	-3360 (4)	6973 (5)	34 (1)	121 (6)	182 (8)	8 (3)	11 (3)	-4 (7)
N(6)	-2909 (2)	-3966 (4)	8650 (5)	59 (1)	207 (7)	252 (9)	18 (3)	5 (3)	22 (7)
N(7)	-2030 (1)	-1003 (4)	2730 (4)	38 (1)	218 (7)	311 (9)	-8 (2)	14 (3)	29 (7)
C(7)	-2542 (2)	-1710 (4)	3713 (4)	26 (1)	124 (6)	191 (8)	4 (2)	2 (3)	-6 (7)
H(1)	-3839 (18)	-3466 (48)	2116 (52)	2·5					
H(2)	-4179 (17)	-4540 (42)	4245 (52)	2·5					

data and resulted in a satisfactory trial structure. Two hydrogen atoms were located in a difference Fourier synthesis after several cycles of least-square refinement (Busing, Martin & Levy, 1962). The R_2 $\{=[\sum\omega(F_o-F_c)^2/\sum\omega F_o^2]^{1/2}\}$ index was 0·075 after isotropic temperature factor refinement without hydrogen atoms, and 0·063 with hydrogen atoms. The inclusion of anisotropic thermal parameters for all the atoms except hydrogen atoms and several subsequent least-squares refinements on one scale factor and the positional and thermal parameters (106 parameters) gave final discrepancy indices of $R_2=0·038$ and R_1 $\{=\sum(F_o-F_c)/\sum F_o\}=0·057$. A final difference Fourier map showed no peaks higher than 0·14 e Å^{-3}. The estimated standard deviation of an observation of unit weight $S=(\sum\omega|F_o-F_c|^2/N_o-N_v)^{1/2}=1·74$, with N_o=number of observations$=715$. N_v=number of parameters$=106$. The values of $\omega(F_o-F_c)$ show no significant variation with the magnitude of F_o or $\sin\theta/\lambda$. The positional and thermal parameters from the last cycle of least-squares refinement are presented in Table 1, along with the standard deviations in these parameters. (The atomic numbering is given in Fig. 1). Bond distances and bond angles and their errors (Busing, Martin & Levy, 1964) are shown in Table 2. The scaled observed (scale factor was 5·734) and calculated structure factors for 715 reflections are listed in Table 3 The scattering factors for

all atoms were taken from the compilation of Hanson, Herman, Lee & Skillman (1964).

Discussion

The three-membered ring has the shape of an isosceles triangle with C(1)–C(2) = 1·506(4), C(1)–C(3) = 1·501(4) and C(2)–C(3) = 1·561(4) Å. Both C(1)–C(2) and C(1)–C(3) bond lengths are shorter than the C–C bond length in cyclopropane, 1·524(14) Å (Pauling & Brockway, 1937; Bastiansen & Hassel, 1946), and a little shorter than that in 1,2,3-*cis*-tricyanocyclopropane, 1·518(3) Å (Hartman & Hirshfeld, 1966). The bond between C(2) and C(3) is apparently lengthened by the strong electron-withdrawing cyano substituents. This can also be shown by the fact that the C(2)–C(1)–C(3) angle of 62·5(2)° is larger than both the C(1)–C(2)–C(3) and C(1)–C(3)–C(2) angles of 58·6(2) and 58·9(2)°. A comparison of this structure with the structure of an iso-electronic molecule, tetracyanoethyleneoxide (TCEO) (Matthews, Swanson, Mueller & Stucky, 1971), shows that the bond angles inside the ring are almost the same in the two structures, but that the structure of

Table 4. *Observed and calculated structure factors*

All the reflections for which the peak intensity is less than the background counts are set to zero.

Table 2. *Intramolecular bond distances and angles*

C(1)–C(2)	1·506 (4) Å	C(2)–C(1)–C(3)	62·5 (2)°
C(1)–C(3)	1·501 (4)	C(1)–C(2)–C(3)	58·6 (2)
C(2)–C(3)	1·561 (4)	C(1)–C(3)–C(2)	58·9 (2)
C(2)–C(4)	1·449 (4)	H(1)–C(1)–H(2)	121·4 (30)
C(2)–C(5)	1·451 (4)	C(4)–C(2)–C(5)	114·7 (3)
C(3)–C(6)	1·445 (4)	C(4)–C(2)–C(1)	118·8 (3)
C(3)–C(7)	1·449 (4)	C(4)–C(2)–C(3)	116·3 (2)
C(4)–N(4)	1·137 (3)	C(5)–C(2)–C(1)	120·0 (2)
C(5)–N(5)	1·134 (3)	C(5)–C(2)–C(3)	116·9 (2)
C(6)–N(6)	1·141 (3)	C(6)–C(3)–C(7)	116·2 (2)
C(7)–N(7)	1·139 (3)	C(6)–C(3)–C(2)	119·2 (3)
C(1)–H(1)	0·923 (30)	C(6)–C(3)–C(2)	115·3 (2)
C(1)–H(2)	0·929 (31)	C(7)–C(3)–C(1)	118·7 (2)
		C(7)–C(3)–C(2)	115·9 (2)
		N(4)–C(4)–C(2)	179·7 (4)
		N(5)–C(5)–C(2)	179·2 (6)
		N(6)–C(6)–C(3)	177·4 (3)
		N(7)–C(7)–C(3)	177·0 (4)

Table 3. *Selected intermolecular bond distances (Å)*

The symmetry element (1) is given by: $\frac{1}{2}-x$, $-y$, z.

	Translation along			Symmetry along	
	a	b	c		
N(6)···C(7)′	−1	−1	0	1	3·073 (4)
N(6)···C(3)′	−1	−1	0	1	3·078 (4)
N(6)···C(6)′	−1	−1	0	1	3·159 (4)
N(7)···C(6)″	−1	0	−1	1	3·050 (4)
N(7)···C(3)″	−1	0	−1	1	3·095 (4)
N(7)···C(2)″	−1	0	−1	1	3·177 (4)
N(7)···C(7)″	−1	0	−1	1	3·200 (4)
N(7)···C(4)″	−1	0	−1	1	3·230 (4)
N(7)···C(5)″	−1	0	−1	1	3·332 (4)

TCCP has a much longer C(2)–C(3) bond distance 1·561(4) Å than does TCEO, 1·496(2) Å. Exocyclic C–C, C≡N bonds have average distances of 1·450(4), 1·140(3) Å respectively, which are common for this type of compound (Hartman & Hirshfeld, 1966; Greenberg & Post, 1968; Bekoe & Trueblood, 1960; Matthews, Swanson, Mueller & Stucky, 1971).

An interesting part of this study is that the C–C≡N angles for the C≡N groups attached to C(2) are linear within the experimental error, whereas the corresponding angles for the groups attached to C(3) are non-linear. The non-linearity of the C–C≡N group has been noted elsewhere and possible causes for this effect have been discussed (Hartman & Hirshfeld, 1966; Ibers, 1967; Matthews, Swanson, Mueller & Stucky, 1971). The close intermolecular approaches from N(6) and N(7) to carbon atoms of adjacent molecules are listed in Table 4 and partly illustrated in Fig. 2. In contrast, there are no atoms closer than the sum of van der Waals radii around N(4) and N(5). Since C(2)–C(4)–N(4) and C(2)–C(5)–N(5) bond angles are linear (179·6 ± 0·4°), but C(3)–C(6)–N(6) and C(3)–C(7)–N(7) deviate 2 to 3° from linearity (177·4 ± 3°), it is concluded that the non-linearity of this structure is mainly caused by the intermolecular packing in the solid state.

Using a potential model, the above geometry for TCCP, and the 1s carbon and nitrogen binding energies; we obtain a net charge of −0·03 e for each cyano group in TCCP (Stucky, Matthews, Hedman, Klasson & Nordling, 1972). The INDO calculated value is −0·04 e. Both ESCA and INDO results suggest that the cyanide nitrogen atom is less negatively charged in TCEO by +0·02 and +0·03 e respectively. However, there is a corresponding decrease in the cyanide carbon atom charge so that the net cyano group charge remains the same.

References

AHMED, F. R., HALL, S. R. & HUBER, C. P. (1970). *Crystallographic Computing.* Chap. *A.* Copenhagen: Munksgaard.

BASTIANSEN, O. & HASSEL, O. (1946). *Tidsskr. Kjemi Bergvesen Met.* **6,** 71–72.

BEKOE, D. A. & TRUEBLOOD, K. N. (1960). *Z. Kristallogr.* **113,** 1–22.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE.* Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

CUNNINGHAM, G. L., BOYD, A. W., MYERS, R. J., GWINN, W. D. & LeVAN, W. J. (1951). *J. Chem. Phys.* **19,** 676–685.

GREENBERG, B. & POST, B. (1968). *Acta Cryst.* B**24,** 918–924.

HANSON, H. P., HERMAN, F., LEE, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17,** 1040.

HARTMAN, A. & HIRSHFELD, F. L. (1966). *Acta Cryst.* **20,** 80–82.

IBERS, J. A. (1967). *Perspectives in Structural Chemistry.* New York: John Wiley.

KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21,** 849–859.

KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9,** 635–651.

KARLE, J. & HAUPTMAN, H. (1961). *Acta Cryst.* **14,** 217–223.

MATTHEWS, D., SWANSON, J., MUELLER, M. H. & STUCKY, G. D. (1971). *J. Amer. Chem. Soc.* **93,** 5945–5953.

OWEN, T. B. & HOARD, J. L. (1951). *Acta Cryst.* **4,** 172–176.

PAULING, L. & BROCKWAY, L. O. (1937). *J. Amer. Chem. Soc.* **59,** 1223–1236.

RATHJENS, G. W., FREEMAN, N. K., GWINN, W. D. & PITZER, K. S. (1953). *J. Amer. Chem. Soc.* **75,** 5634–5642.

SCRIBNER, K. M., SANSEN, G. N. & PRICHARD, W. W. (1960). *J. Org. Chem.* **25,** 1440–1442.

STUCKY, G. D., MATTHEWS, D., HEDMAN, J., KLASSON, M. & NORDLING, C. (1972). *J. Amer. Chem. Soc.* **94,** 8009–8015.

The Crystal and Molecular Structure of 5-Chloro-2'-deoxyuridine

By D. W. Young and E. M. Morris

Carnegie Laboratory of Physics, University of Dundee, Dundee, Scotland

5-Chloro-2'-deoxyuridine ($C_9H_{11}ClN_2O_5$) crystallizes in the space group $P2_1$ with one molecule per asymmetric unit and with unit-cell dimensions $a=9\cdot118$ (8), $b=5\cdot090$ (5), $c=11\cdot992$ (8) Å and $\beta=107°40'$ (3). The structure was solved by Patterson interpretation methods and the positional and thermal parameters were refined by the method of least squares, using anisotropic temperature factors for the non-hydrogen atoms. The final R index for the 1228 reflexions used in the refinement process is 0·038 and the standard deviations in the bond lengths and angles are about 0·005 Å and 0·3° respectively. The glycosidic torsion angle χ_{CN} is 41·1° in the *anti* configuration and the atom C(2') of the sugar is displaced 0·62 Å *endo*. The conformation of the C(5')–O(5') bond is *gauche–trans* to C(4')–O(1') and C(4')–C(3') respectively.

Introduction

The investigation of the structure of 5-chloro-2'-deoxyuridine was undertaken as part of a series of structure determinations of nucleic acid components in progress in this laboratory. The structural formula of 5-chloro-2'-deoxyuridine and the atomic numbering scheme adopted for this paper are shown in Fig. 1.

The crystal structure reported here is isomorphous with that of 5-bromo-2'-deoxyuridine determined by Iball, Morgan & Wilson (1966).

Experimental

Crystals grown by slow evaporation from aqueous solution were colourless monoclinic prisms. Preliminary Weissenberg and precession X-ray photography showed the crystals to be monoclinic with systematic absences consistent with the space groups $P2_1$ and $P2/m$. Since the molecule is optically active the space group was taken as $P2_1$. Preliminary unit-cell dimensions were calculated from these exploratory X-ray diffraction photographs and then more accurate values

obtained from measurements on a Hilger and Watts linear diffractometer using Mo $K\alpha$ radiation ($\lambda=0\cdot71069$ Å). The unit-cell dimensions thus obtained were,

$$a=9\cdot118\pm0\cdot008 \text{ Å}$$
$$b=5\cdot090\pm0\cdot005$$
$$c=11\cdot992\pm0\cdot008$$
$$\beta=107°40'\pm3'$$

The calculated density with two molecules in the unit cell is 1·494 g cm^{-3}.

In all, 1232 significantly non-zero reflexions were measured on a Hilger and Watts linear diffractometer using Mo $K\alpha$ radiation and balanced filters. The data collected were equivalent to 92% of those available within the Cu $K\alpha$ limiting sphere. The diffraction intensities were measured from two different crystals about the *a* and *b* axes. The data on layer planes 0 to 3 about the *a* axis and on layer planes 0 to 6 about the *b* axis were collected. The crystals were small enough for absorption corrections to be ignored. The data so collected were scaled together to produce a value of the structure amplitude for each reflexion. The R value between the two independent sets of data for those reflexions in common was 0·06 where $R=\sum|(F_b-F_a)|/\sum|F_b|$.

Structure determination

The chlorine atom, the pyrimidine residue and C(1') were expected to be planar. The $I(\theta,\varphi)$ function of Tollin & Cochran (1964) was computed with the sharpened Patterson coefficients $|F_s(h)|^2$, calculated using the modification function proposed by Wunderlich (1965) with constants $a=2\cdot0$ and $p=7\cdot25$. The results, obtained by integrating the Patterson function over a disc of radius 3·5 Å, were plotted on a Sanson–Flamsteed projection (Fig. 2). The largest peak in this map, representing the direction of the normal to the pyrimidine residue, has spherical polar angles $\theta=49\cdot2°$, $\varphi=114\cdot6°$ with respect to the axial set 0 ($a^*,b,a^*\times b$).
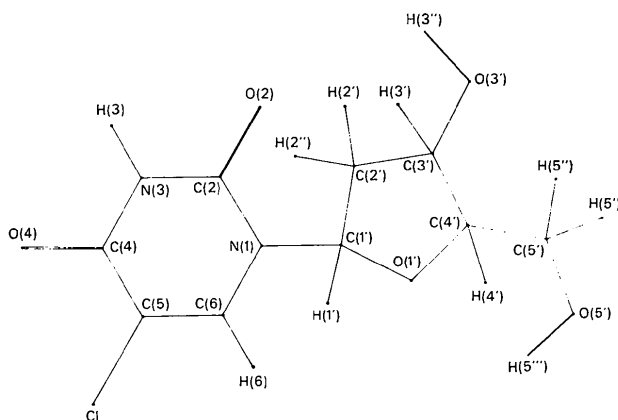

Fig. 1. 5-Chloro-2'-deoxyuridine and the atom numbering.