Glusker, 1961) and 0·8 in H-Leu-Pro-Gly-OH (Leung & Marsh, 1958)]. The role of water molecules as hydrogen-bond donors seems to be less important than that as hydrogen-bond acceptors. This is because potential hydrogen-bond acceptors not accepting a bond are very common, but potential hydrogen-bond donors (OH or NH) not participating in hydrogen bonds are rarely found in crystals. In the latter case the role of water as an acceptor seems to be important.

References

Arnott, S., Dover, S. D. & Elliott, A. (1967). J. Mol. Biol. 30, 201–208.

Ashida, T. (1973). UNICS – Osaka, pp. 55–61. The Computation Center, Osaka Univ.

Ashida, T. & Kakudo, M. (1974). Bull. Chem. Soc. Jpn, 47, 1129–1133.

Ashida, T., Tanaka, I., Shimonishi, Y. & Kakudo, M. (1977). Acta Cryst. B33, 3054–3059.

Chou, P. Y. & Fasman, G. D. (1977). J. Mol. Biol. 115, 135–175.

Germain, G., Main, P. & Woolfson, M. M. (1971). Acta Cryst. A27, 368–376.

Hudson, J. M., Shaw, B., Schurr, J. M. & Jensen, L. H. (1972). Am. Crystallogr. Assoc. Winter Meeting. Abstracts, p. 67.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Itoh, H., Yamane, T., Ashida, T., Sugihara, T., Imanishi, Y. & Higashimura, T. (1976). Acta Cryst. B32, 3355–3357.

Leung, Y. C. & Marsh, R. E. (1958). Acta Cryst. 11, 17–31.

Marsh, R. E. & Donohue, J. (1967). Adv. Protein Chem. 22, 235–256.

Marsh, R. E. & Glusker, J. P. (1961). Acta Cryst. 14, 1110–1116.

Schellman, J. A. & Schellman, C. (1964). The Proteins, Vol. 2, edited by H. Neurath, p. 1. New York: Academic Press.

Sugino, H., Tanaka, I. & Ashida, T. (1978). Bull. Chem. Soc. Jpn, 51, 2855–2861.

Torii, K. & Iitaka, Y. (1971). Acta Cryst. B27, 2237–2246.

Trommel, J. & Bijvoet, J. M. (1954). Acta Cryst. 7, 703–709.

Weeks, C. M., Cooper, A. & Norton, D. A. (1969). Acta Cryst. B25, 443–450.

The Structure of 3-(2-Methoxyphenyl)-1,1,2,2-cyclopropanetetracarbonitrile

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Abstract

Crystals of $C_{14}H_8N_4O$ are monoclinic, space group $P2_1$. Unit-cell constants are $a = 13·241$ (4), $b = 7·446$ (2), $c = 6·436$ (2) Å, $\beta = 93·23$ (2)°. $V = 633·5$ Å^3, $Z = 2$, $D_{obs} = 1·30$ (flotation), $D_{calc} = 1·300$ Mg m^{-3} and $\mu(Cu\,K\alpha) = 0·72$ mm^{-1}. The structure, solved by direct methods, has been refined to an R value of 3·5% using 1245 intensity measurements. The combined effect of electron-withdrawing and -donating substituents on the geometry of the cyclopropane ring is discussed.

Introduction

The cyclopropane ring undergoes drastic geometrical changes under the influence of electron-withdrawing and -donating substituents. According to Walsh (1947, 1949), trigonal methylene groups are brought together

to form the ring by overlap of their σ orbitals at the center and of their p or π orbitals around the periphery (Fig. 1). The three σ orbitals combine to produce a strongly bonding A_1' level and an antibonding E' pair (degenerate). The three methylene p orbitals interact less strongly to yield a bonding E' pair and an antibonding A_2' level. The resulting orbitals, shown in Fig. 2, are reproduced from Jorgensen & Salem (1973). The
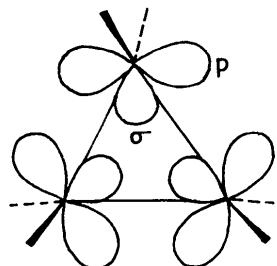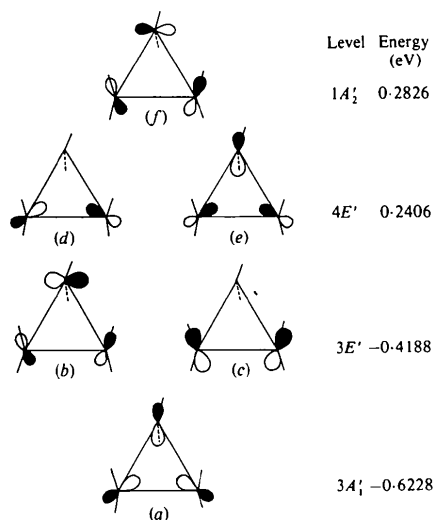

Fig. 1. The Walsh model.

Level	Energy (eV)
$1A_2'$	0·2826
$4E'$	0·2406
$3E'$	−0·4188
$3A_1'$	−0·6228

Fig. 2. Walsh orbitals.

Table 1. *Fractional coordinates* ($\times10^4$) *of the non-hydrogen atoms with e.s.d.'s in parentheses*

	x	y	z
C(1)	1562 (1)	9709 (3)	8040 (3)
C(2)	1360 (1)	8750 (3)	5917 (3)
C(3)	1926 (1)	7787 (3)	7727 (3)
C(4)	3017 (1)	7352 (3)	7534 (3)
C(5)	3266 (2)	6215 (3)	5912 (4)
C(6)	4261 (2)	5730 (3)	5701 (4)
C(7)	5000 (2)	6344 (4)	7157 (5)
C(8)	4765 (2)	7429 (4)	8792 (4)
C(9)	3767 (2)	7940 (3)	8981 (3)
C(10)	2662 (2)	4578 (4)	2921 (5)
C(11)	2269 (2)	11185 (3)	8108 (3)
C(12)	671 (2)	9995 (3)	9239 (3)
C(13)	1923 (1)	9393 (3)	4205 (3)
C(14)	343 (1)	8152 (3)	5332 (3)
N(1)	2824 (2)	12341 (3)	8186 (3)
N(2)	−35 (2)	10232 (4)	10108 (4)
N(3)	2357 (2)	9893 (3)	2849 (3)
N(4)	−445 (2)	7642 (4)	4875 (3)
O(1)	2466 (1)	5667 (0)	4650 (3)

Table 2. *Fractional coordinates* ($\times10^3$) *for* H *atoms*

	x	y	z
H(1)	151 (2)	694 (4)	832 (4)
H(2)	449 (2)	487 (5)	465 (5)
H(3)	566 (3)	613 (5)	686 (6)
H(4)	533 (2)	785 (5)	976 (4)
H(5)	355 (2)	880 (4)	1003 (4)
H(6)	307 (3)	328 (5)	342 (5)
H(7)	204 (3)	446 (7)	216 (7)
H(8)	318 (2)	512 (4)	213 (5)

present study was undertaken to study the geometry of the cyclopropane ring when it bears an electron-donating substituent in addition to four strong electron acceptors.

Experimental

The title compound was synthesized and single crystals were obtained from a solution in ethanol/chloroform by slow evaporation. The crystal used in the data collection had the approximate dimensions 0·4 × 0·3 × 0·2 mm. Preliminary Weissenberg photographs indicated the monoclinic space groups $P2_1$ or $P2_1/m$. Intensity data were collected on a CAD-4 diffractometer using monochromated Cu $K\alpha$ radiation by the $\omega/2\theta$ mode to a limit of $\theta = 60°$ using a scan speed of 1° min⁻¹. Two reflections were checked after every fifty reflections and they showed only statistical fluctuations. 1325 reflections were measured, of which 1245 were significant $[|F_o| > 2\sigma(|F_o|)]$. Corrections were then made for Lorentz and polarization factors but not for absorption.

Structure solution and refinement

The structure was solved using the direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971) in the space group $P2_1$. Since $Z = 2$ and there is no symmetry in the molecule and the distribution of normalized structure factors is noncentrosymmetric, the space group $P2_1$ was preferred to $P2_1/m$. An E map calculated with the best set of phases ($R_{Karle} = 16·47\%$, ABSFOM = 1·18 and combined figure-of-merit = 1·85) revealed all the non-hydrogen atoms. Block-diagonal least-squares refinement [program by

Table 3. *Bond distances* (Å) *with e.s.d.'s in parentheses*

C(1)–C(2)	1·552 (3)	C(6)–H(2)	0·99 (3)
C(1)–C(3)	1·527 (3)	C(7)–C(8)	1·376 (4)
C(1)–C(11)	1·443 (3)	C(7)–H(3)	0·92 (3)
C(1)–C(12)	1·461 (3)	C(8)–C(9)	1·387 (3)
C(2)–C(3)	1·528 (3)	C(8)–H(4)	0·99 (2)
C(2)–C(13)	1·446 (3)	C(9)–H(5)	0·98 (3)
C(2)–C(14)	1·448 (3)	C(10)–O(1)	1·413 (3)
C(3)–C(4)	1·492 (3)	C(10)–H(6)	1·15 (4)
C(3)–H(1)	0·93 (3)	C(10)–H(7)	0·94 (4)
C(4)–C(5)	1·398 (3)	C(10)–H(8)	0·96 (3)
C(4)–C(9)	1·393 (3)	C(11)–N(1)	1·131 (3)
C(5)–C(6)	1·380 (3)	C(12)–N(2)	1·130 (3)
C(5)–O(1)	1·361 (3)	C(13)–N(3)	1·135 (3)
C(6)–C(7)	1·394 (4)	C(14)–N(4)	1·133 (3)

Shiono (1968), modified by B. S. Reddy to suit an IBM 360/44 computer] of the non-hydrogen atoms, with the H atoms which appeared in a difference map, gave a final R index of 0·035. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(|F_o|)$. The coordinates and temperature factors of the non-hydrogen and H atoms are listed in Tables 1 and 2. Fig.

Table 4. *Bond angles* (°) *with e.s.d.'s in parentheses*

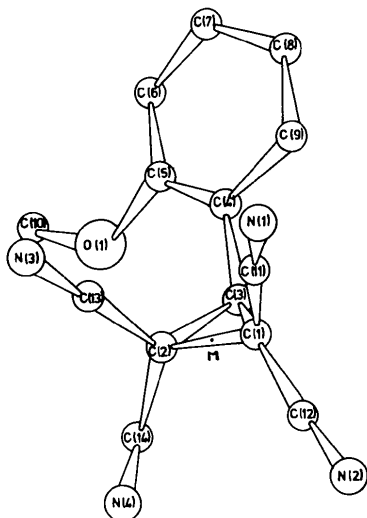|			
C(2)—C(1)—C(3)	59·5 (1)	C(2)—C(1)—C(11)	117·2 (2)
C(2)—C(1)—C(12)	115·3 (2)	C(3)—C(1)—C(11)	120·6 (2)
C(3)—C(1)—C(12)	118·5 (2)	C(11)—C(1)—C(12)	114·5 (2)
C(1)—C(2)—C(3)	59·5 (1)	C(1)—C(2)—C(13)	116·6 (2)
C(1)—C(2)—C(14)	118·8 (2)	C(3)—C(2)—C(13)	119·0 (2)
C(3)—C(2)—C(14)	117·6 (2)	C(13)—C(2)—C(14)	114·5 (2)
C(1)—C(3)—C(2)	61·0 (1)	C(1)—C(3)—C(4)	121·9 (2)
C(2)—C(3)—C(4)	118·2 (2)	C(1)—C(3)—H(1)	112·6 (1·7)
C(2)—C(3)—H(1)	110·8 (1·7)	C(4)—C(3)—H(1)	118·7 (1·7)
C(3)—C(4)—C(5)	117·6 (2)	C(3)—C(4)—C(9)	122·2 (2)
C(5)—C(4)—C(9)	120·0 (2)	O(1)—C(5)—C(4)	114·8 (2)
O(1)—C(5)—C(6)	125·3 (2)	C(4)—C(5)—C(6)	119·9 (2)
C(5)—C(6)—C(7)	119·1 (2)	C(5)—C(6)—H(2)	124·6 (1·9)
C(7)—C(6)—H(2)	116·1 (1·9)	C(6)—C(7)—C(8)	121·7 (3)
C(6)—C(7)—H(3)	116·4 (2·2)	C(8)—C(7)—H(3)	121·2 (2·2)
C(7)—C(8)—C(9)	119·1 (2)	C(7)—C(8)—H(4)	118·0 (1·7)
C(9)—C(8)—H(4)	122·9 (1·7)	C(4)—C(9)—C(8)	120·1 (2)
C(4)—C(9)—H(5)	116·1 (1·6)	C(8)—C(9)—H(5)	123·5 (1·6)
O(1)—C(10)—H(6)	111·6 (1·8)	O(1)—C(10)—H(7)	105·6 (2·7)
O(1)—C(10)—H(8)	110·3 (1·8)	H(6)—C(10)—H(7)	116·8 (3·3)
H(6)—C(10)—H(8)	99·5 (2·6)	H(7)—C(10)—H(8)	113·1 (3·3)
C(1)—C(11)—N(1)	179·1 (2)	C(1)—C(12)—N(2)	177·7 (2)
C(2)—C(13)—N(3)	179·4 (2)	C(2)—C(14)—N(4)	178·3 (2)

Fig. 3. Perspective view of the molecule.

3 shows a perspective view of the molecule. Tables 3 and 4 give the bond lengths and angles involving the non-hydrogen atoms.*

Discussion

The geometry of the cyclopropane ring

When two electron-withdrawing substituents (the CN groups in the present structure) are vicinally bound,

the 3E' orbital in Fig. 2(c) has the proper symmetry to accommodate interactions with both the groups. As a result of such an interaction, the bond flanked by the CN groups becomes longer than the other two bonds [1·552 (3) vs 1·528 (3) and 1·527 (3) Å]. The corresponding bond in 1,1,2,2-cyclopropanetetracarbonitrile (Lemley, Skarstad & Hughes, 1976) is similarly lengthened [1·559 (2) Å]. The phenyl ring has the ability to either accept electron density from or donate it to the cyclopropane ring. From energetic considerations (Jorgensen & Salem, 1973), donation is preferred over withdrawal. Such a donation can take place through either the $1A'_2$ orbital (Fig. 2f) or the $4E'$ orbitals (Fig. 2d,e). The former requires the bisected conformation (Fig. 4a) and the latter require the perpendicular conformation (Fig. 4b) for maximum overlap. The acute angle, θ, between the normals to the plane of the benzene ring and the plane defined by C(7), C(4), C(3) and M [the midpoint between C(1) and C(2)] (Fig. 3) is taken as a measure of the interorbital angle. For the bisected and perpendicular conformations, the values of θ are 0 and 90° respectively. For the present case, θ is 87·9°. The $4E'$ orbital (Fig. 2e) has bonding character for the opposite bond and antibonding character for the adjacent bonds. Influx of electron density into the cyclopropane ring from the phenyl ring through this orbital should weaken the adjacent bonds and strengthen the opposite bond. This is indeed what is observed in the present case. A comparison of the present structure with 1,1,2,2-cyclopropanetetracarbonitrile (Lemley et al., 1976) reveals that the opposite bond of the former is shorter than the corresponding bond in the latter [1·552 (3) vs 1·559 (2) Å] and the adjacent bonds of the former [1·528 (3) and 1·527 (3) Å] are longer than those of the latter [1·516 (2) and 1·512 (2) Å] where the phenyl substituent is absent. This result supports the conformational dependence of the substituent–cyclopropane interaction, although Jason & Ibers (1977) have concluded that there is no correlation between the angle θ and the geometry of the cyclopropane ring.

The CN groups

Although the bond lengths involving the CN groups in the present structure are much shorter than the accepted spectroscopic value of 1·158 Å (Britton, 1967), they are in good agreement with those in similar
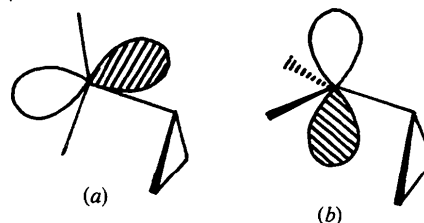
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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34798 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 4. (a) Bisected conformation. (b) Perpendicular conformation.

Table 5. *High-angle refinement and* C≡N *lengths*

With full data	With data above 0·4 (sin θ Cu Kα)	With data above 0·6 (sin θ Cu Kα)	Reference
1·131 (3) Å	1·130 (3) Å	1·133 (4) Å	Present study
1·130 (3)	1·131 (3)	1·132 (4)	
1·135 (3)	1·137 (3)	1·141 (4)	
1·133 (3)	1·133 (3)	1·137 (4)	
1·137 (2) Å	1·150 (2) Å	Not given	Lemley,
1·138 (2)	1·149 (2)		Skarstad &
1·140 (2)	1·150 (2)		Hughes
1·138 (2)	1·147 (2)		(1976)

structures determined by X-ray methods. Lemley *et al.* (1976), while studying the structure of 1,1,2,2-cyclopropanetetracarbonitrile, have carried out refinements using only high-angle data in order to avoid bond shortening of the CN groups by delocalization. High-angle refinements similar to this were carried out for the present structure and the results are given in Table 5, which shows that there is no significant improvement in the CN lengths upon the removal of the low-angle reflections in the present case. Harel & Hirshfeld (1975) state that the bond shortening of the CN groups arises from low-frequency C—C≡N bending vibrations. The neglect of such internal vibrations accounts for the shortness of most crystallographically determined C≡N bond lengths.

Two of the C—C≡N fragments in the present structure are significantly non-linear. It is interesting to note that the bond connecting the cyano carbon [C(12)] with the cyclopropane ring is much longer [1·461 (3) Å] than the other three corresponding bonds; it is this C atom which is involved in the most highly bent CN group [177·7 (2)°]. Matthews, Swanson, Mueller & Stucky (1971) have explained the bending of the C—C≡N fragments based on the electrostatic repulsion between any electrons occupying the π^* orbital and electrons in the C—C bond and N lone-pair orbital. As a result of such a repulsion, if the linear *sp* hybridization which determines the σ-bond framework of the CN group were to change from *sp* to sp^2, the bond angles of the C—C≡N fragment would decrease from 180 toward 120°. Such an argument was first used by Ingold & King (1953) to postulate a bent configuration for the excited state of acetylene.

Packing of the molecules

The packing of the molecules as viewed down the *c* axis is shown in Fig. 5. The molecules are packed in such a way that the phenyl rings are in one column and the cyclopropane rings, with the cyano groups jutting out, are in a parallel column. These columns are parallel to the *b* axis. Each molecule is surrounded by six other molecules. Some selected intermolecular contacts involving the cyano nitrogens are given in
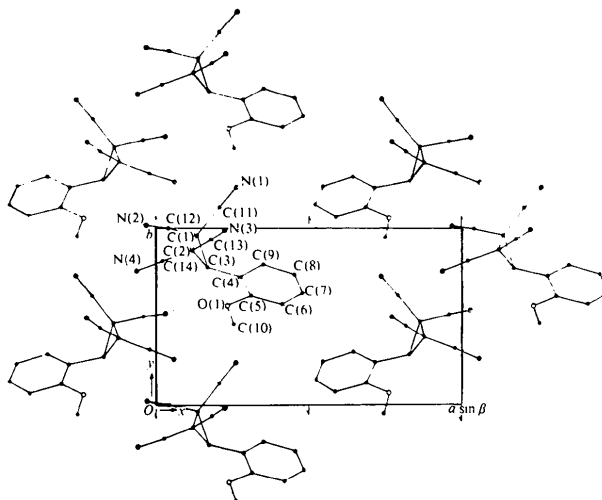

Fig. 5. Packing of the molecules viewed down the *c* axis.

Table 6. *Intermolecular contacts* (<3·5 Å) *involving the cyano nitrogens*

N(1)ⁱ⋯C(5)ⁱⁱ	3·304 (3) Å	N(1)ⁱ⋯O(1)ⁱⁱ	3·374 (3) Å
N(1)ⁱ⋯C(10)ᵛⁱⁱ	3·495 (3)	N(2)ᵛⁱⁱⁱ⋯C(3)ⁱ	3·489 (3)
N(3)ⁱⁱⁱ⋯C(1)ⁱ	3·217 (3)	N(3)ⁱⁱⁱ⋯C(11)ⁱ	3·195 (3)
N(3)ⁱⁱⁱ⋯C(12)ⁱ	3·135 (3)	N(4)ⁱᵛ⋯C(11)ᵛ	3·182 (3)
N(4)ᵛⁱ⋯C(1)ⁱ	3·182 (3)	N(4)ᵛⁱ⋯C(2)ᵛ	3·168 (3)
N(4)ᵛⁱ⋯C(12)ⁱ	3·295 (3)	N(4)ᵛⁱ⋯C(13)ⁱ	3·189 (3)
N(4)ᵛⁱ⋯C(14)ⁱ	3·351 (3)		

Symmetry code: (i) *x*,*y*,*z*; (ii) *x*, 1 + *y*, *z*; (iii) *x*, *y*, 1 + *z*; (iv) −*x*, *y* − ½, 1 − *z*; (v) *x*, *y* − 1, *z*; (vi) −*x*, ½ + *y*, 1 − *z*; (vii) *x*, 1 + *y*, 1 + *z*; (viii) −*x*, *y* − ½, 2 − *z*.

Table 6. Two of the four nitrogens [N(3) and N(4)] make close approaches to the electron-deficient cyano carbons. Such a packing arrangement is found in crystal structures which contain a C(CN)$_2$ group such as monoclinic ethylenetetracarbonitrile (Bekoe & Trueblood, 1960), tetracyanoquinodimethane (Long, Sparks & Trueblood, 1965) and in *meso-β,β'*-dibromoadiponitrile (Rabinovich & Shakked, 1978). If we accept 3·4 Å as the van der Waals distance for C⋯N with no acid–base character (Witt, Britton & Mahon, 1972), then the observed C⋯N contacts indicate a weak acid–base interaction.

References

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

BRITTON, D. (1967). *Perspectives in Structural Chemistry*, Vol. I, edited by J. DUNITZ & J. A. IBERS, pp. 109–171. New York: John Wiley.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.

HAREL, M. & HIRSHFELD, F. L. (1975). *Acta Cryst.* B31, 162–172.

INGOLD, C. K. & KING, G. W. (1953). *J. Chem. Soc.* pp. 2702–2704.

JASON, M. E. & IBERS, J. A. (1977). *J. Am. Chem. Soc.* 99, 6012–6021.

JORGENSEN, W. F. & SALEM, L. (1973). *The Organic Chemists' Book of Orbitals.* New York: Academic Press.

LEMLEY, J. T., SKARSTAD, P. M. & HUGHES, R. E. (1976). *Acta Cryst.* B32, 35–40.

LONG, R. E., SPARKS, R. A. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* 18, 932–939.

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

RABINOVICH, D. & SHAKKED, Z. (1978). *Acta Cryst.* B34, 1176–1182.

SHIONO, R. (1968). Private communications.

WALSH, A. D. (1947). *Nature (London),* 159, 712–713.

WALSH, A. D. (1949). *Trans. Faraday. Soc.* 45, 179–190.

WITT, J. R., BRITTON, D. & MAHON, C. (1972). *Acta Cryst.* B28, 950–955.

Structural Studies of Pyrimidine Cyclonucleoside Derivatives. IV.* Structure of 2,5'-Anhydro-1-(2',3'-O-isopropylidene-β-D-ribofuranosyl)-2-thiouracil

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Abstract

The title compound, $C_{12}H_{14}N_2O_4S$, crystallizes in the orthorhombic system with space group $P2_12_12_1$, $Z = 4$ and unit-cell dimensions $a = 7.694$ (1), $b = 9.470$ (3) and $c = 17.628$ (7) Å. The structure was solved by the heavy-atom method and refined to a final R value of 0.077 (weighted $R = 0.088$). The glycosyl torsion angle lies in the *syn* range ($\chi_{CN} = 244.2°$) and the ribose ring conformation is C(4')-*endo*,O(1')-*exo*.

Introduction

The fixed conformation of the cyclonucleosides is expected to be preserved both in the crystalline state and in solution, and this type of compound has been used to investigate the relationships between sign and magnitude of Cotton effects and glycosyl torsion angles (Rogers & Ulbricht, 1970; Ikehara, Kaneko, Nakahara, Yamada & Uesugi, 1971; Ueda & Shibuya, 1974) and to test the applicability of coupling constants to the Karplus relation (Manor, Saenger, Davies, Jankowski & Rabczenko, 1974). Structural con-

* Part III (Structural Studies of O-Cyclocytidine Derivatives): Yamagata, Suzuki, Fujii, Fujiwara & Tomita (1979).

siderations suggested that the title compound, 2,5'-anhydro-1-(2',3'-O-isopropylidene-β-D-ribofuranosyl)-2-thiouracil (2,5'-S-cyclo U), may adopt either of two conformations: the *exo* form ($\chi \simeq 180°$) with S positioned above O(1'), or the *endo* form ($\chi \simeq 240°$) with S over the center of the sugar ring. In order to clarify the situation, we have determined the molecular structure of 2,5'-S-cyclo U by X-ray diffraction. In this paper, the results of this study are described and compared with the molecular geometry of 2,5'-anhydro-1-(2',3'-O-isopropylidene-β-D-ribofuranosyl)uracil (2,5'-O-cyclo U).

Experimental

2,5'-S-cyclo U was synthesized from 2,5'-O-cyclo U (Ueda & Shibuya, 1974) and recrystallized as colorless needles from benzene containing a small amount of ethanol. X-ray photographs showed the crystals to be orthorhombic with space group $P2_12_12_1$. Unit-cell dimensions were determined from the 2θ values of 18 diffractometer-measured reflexions in the range $20° < 2\theta < 40°$ (Mo $K\alpha$) by a least-squares procedure. The density was measured by the flotation method in a benzene–carbon tetrachloride mixture. The crystallographic data are shown in Table 1.