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Precision X-ray and Neutron Diffraction Studies of Methyl β-D-Ribopyranoside, $C_6H_{12}O_5$

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The structure of methyl β-D-ribopyranoside has been refined with three-dimensional X-ray and neutron diffractometer data. The crystals are orthorhombic, space group $P2_12_12_1$ with four molecules in a cell of dimensions: $a = 5{\cdot}753$ (5), $b = 19{\cdot}986$ (5), $c = 6{\cdot}413$ (5) Å. Full-matrix least-squares refinements have led to a conventional R factor of 0·040 for X-rays and 0·043 for neutrons. The X-ray and neutron results are in good agreement for the heavy atoms. The neutron study provides the precise determination of positional and thermal parameters for the H atoms which is especially important as the structure has both intermolecular and intramolecular hydrogen bonding.

Introduction

In 1972, a preliminary communication was published on the X-ray structure of methyl β-D-ribopyranoside (James & Stevens, 1972). Since this time, refinement of the X-ray data has been extended to include an isotropic extinction parameter (Larson, 1970), and the anomalous scattering factors for O from Cromer (1965). The locations of four H atoms were changed after the neutron refinement was completed and refined with the X-ray data. A short communication on this structure has also been reported by Hordvik (1974). The molecule exists in the $^1C_4(D)$ conformation, which is the conformation found for the anomeric thio analogue (Girling & Jeffrey, 1971), *viz* methyl 1-thio-α-D-ribopyranoside. In both structures there is intramolecular as well as intermolecular hydrogen bonding and the neutron study has been carried out in order to locate the H atoms and determine their thermal parameters accurately. This work is part of a series of neutron diffraction studies currently under way in this laboratory involving a comparison of X-ray and neutron diffraction studies on monosaccharides.

Crystal data

Methyl β-D-ribopyranoside, $C_6H_{12}O_5$, $M_r = 164$. Orthorhombic, $a = 5{\cdot}753$ (5), $b = 19{\cdot}986$ (5), $c = 6{\cdot}413$ (5) Å. $D_c = 1{\cdot}477$, $D_x = 1{\cdot}475$ (5) g cm^{-3}, space group $P2_12_12_1$, $\mu = 8{\cdot}6083$ (X-rays), $\mu = 2{\cdot}69 \pm 0{\cdot}09$ cm^{-1} (neutrons), wavelength (X-rays) Cu $K\alpha$ = 1·5418, neutrons 0·9810 Å.

X-ray study

Methyl β-D-ribopyranoside (Jackson & Hudson, 1941), prepared by debenzoylation of its tribenzoate (Jeanloz, Fletcher & Hudson, 1948), was crystallized from a mixture of methanol, ethyl acetate and petroleum spirit as thick plates, m.p. 81–82°C. A square bipyramid, base 0·4 mm, height 0·6 mm was mounted on a computer-controlled Siemens four-circle diffractometer. Cu $K\alpha$ radiation and Ni filters and attenuators were used. The unit-cell constants were calculated from the least-squares fit of selected high-angle reflections. The integrated intensities of 865 reflections ($\theta < 70°$) were recorded by using the five-value method (Hoppe, 1965). These were corrected for background and assigned standard deviations based on Poisson counting statistics. The values of F and $\sigma(F)$ were then corrected for Lorentz–polarization effects and for absorption. The absorption program also calculated vector components of the incident and diffracted beam and the mean path length through the crystal; these quantities were later used to apply a correction with an isotropic extinction parameter $R^* = (e^2/mc^2V)\lambda^3 r^*$ where the modified $F_c^* = k|F_c|(1 + 2r^*|F_c|^2\delta)^{-1/4}$,

$$\delta = \left(\frac{e^2}{mc^2V}\right)^2 \frac{\lambda^3}{\sin 2\theta} \frac{1 + \cos^4 2\theta}{1 + \cos^2 2\theta} \bar{T}$$

and $\bar{T}$ is the mean path length in the crystal (in cm) (Larson, 1970).

The non-hydrogen atoms were located with the direct-methods program *SYMTAN* (Grainger, 1973).

The structure was refined by a series of full-matrix least squares with isotropic and anisotropic temperature factors to a residual (R) of 0·107. The function minimized was $\Sigma\, \omega(F_o - F_c)^2$, where the weights were based on counting statistics alone. The coordinates of the H atoms were readily located from a Fourier difference synthesis and the structure was further refined, keeping the temperature factors of the H atoms fixed at the value of the atoms with which they were most closely associated. This led to a final R of 0·05.

The refinement of the X-ray data was continued when the neutron study was completed. This showed that the methyl H atoms and one hydroxyl H atom, H(4), were incorrectly chosen from X-rays. These H atoms were assigned the neutron values and the refinement was continued with the addition of anomalous scattering factors for O (Cromer, 1965) and the isotropic extinction parameter, R^*. A value of 0·0075 (5) for R^* was obtained, which is a factor of 10 larger than that normally obtained for such structures. The final R was 0·040 and R_ω = 0·047. The final positional parameters are listed in Table 1.†

Table 1. *Positional coordinates* ($\times 10^4$; *for* H $\times 10^3$) *with standard errors for X-rays* (*line* 1) *and neutrons* (*line* 2)

	x	y	z
O(1)	−643 (3)	8907·4 (8)	10278 (3)
	−637 (4)	8909 (1)	10277 (5)
O(2)	5072 (3)	8223·6 (7)	9761 (3)
	5074 (4)	8227 (1)	9753 (4)
O(3)	2674 (3)	7347·9 (7)	6923 (2)
	2662 (5)	7346 (1)	6932 (4)
O(4)	4944 (3)	8546·4 (8)	5565 (3)
	4934 (5)	8545 (1)	5565 (5)
O(5)	2353 (3)	9383·9 (6)	8303 (2)
	2348 (5)	9380·9 (9)	8300 (4)
C(1)	1749 (4)	8946·8 (9)	9949 (3)
	1747 (3)	8949·5 (8)	9950 (3)
C(2)	2618 (4)	8237·3 (9)	9567 (3)
	2631 (3)	8235·9 (8)	9562 (3)
C(3)	1780 (4)	7992·1 (9)	7434 (3)
	1784 (3)	7989·3 (8)	7443 (3)
C(4)	2490 (5)	8483 (1)	5743 (3)
	2482 (4)	8481·5 (9)	5739 (3)
C(5)	1522 (5)	9166 (1)	6309 (4)
	1511 (5)	9166 (1)	6316 (4)
C(6)	−1666 (5)	9505 (1)	11039 (5)
	−1653 (5)	9513 (1)	11040 (5)
H(1)	255 (4)	910 (1)	1125 (4)
	260·0 (9)	916·4 (2)	1132·1 (7)
H(2)	205 (4)	794 (1)	1070 (4)
	195·2 (9)	791·0 (2)	1079·6 (7)
H(3)	17 (5)	797 (1)	753 (4)
	−12·8 (8)	797·7 (2)	749·1 (9)
H(4)	190 (5)	835 (1)	442 (4)
	172 (1)	832·4 (2)	426·3 (8)
H(5)	−20 (5)	915 (1)	626 (5)
	−39 (1)	914·6 (3)	633 (1)
H(6)	213 (5)	951 (1)	543 (4)
	212 (1)	953·9 (2)	521·7 (8)
H(7)	554	841 (1)	885 (5)
	570·3 (9)	843·6 (3)	852 (1)
H(8)	236 (5)	709 (1)	787 (4)
	232 (1)	705·4 (2)	805·7 (7)
H(9)	550 (6)	822 (1)	502 (5)
	560 (1)	816·4 (2)	487·6 (8)
H(10)	−316 (5)	942 (1)	1129 (5)
	−327 (1)	943·0 (5)	1151 (3)
H(11)	−165 (5)	986 (2)	996 (6)
	−166 (3)	987·2 (5)	993 (2)
H(12)	−68 (5)	974 (1)	1204 (6)
	−72 (2)	971·9 (4)	1221 (2)

Neutron study

A crystal was prepared by addition of portions of light petroleum to a methanol–ethyl acetate solution over several days. The truncated square pyramid, base length 1·2 cm and height 0·6 cm, was ground to a cylinder 0·8 cm in diameter and 0·5 cm long, which for the purposes of absorption could be approximated by 18 rational crystal-boundary planes, the experimentally determined absorption coefficient being 2·69 ± 0·09 cm^{-1}. The cell constants were refined by least-squares techniques from the diffractometer settings of the first 100 reflections and they agree within 0·1% with those found by X-rays. The intensities of 1048 reflections were measured with the standard θ–2θ step-scan technique and standard reflections were measured after every 25 reflections. In order to determine systematic errors and to check the absorption corrections and crystal and instrumental drift, all reflections were measured for two equivalent positions and 200 reflections were measured more than twice.

The data were corrected for background and assigned standard deviations based on Poisson counting statistics. The values of I and $\sigma(I)$ were corrected for the Lorentz effect and for absorption with the experimentally determined linear absorption coefficient. Squared observed structure factors were averaged for symmetry-related reflections and scaled to an absolute level by means of a Wilson plot. The quantity minimized in the refinement was $\Sigma\, \omega(|F_o^2| - |F_c^2|)^2$. Each reflection was assigned a weight, ω, inversely proportional to the estimated variance of the observation, $\omega^{-1} = \sigma^2(F^2)$, and $\sigma^2(F^2) = \sigma^2_{\rm count}(F^2) + (\alpha + \beta F^2 + \gamma F^4)^{1/2}$ where $\sigma^2_{\rm count}$ is based on counting statistics alone and α, β and γ were determined by graphical methods (James & Moore, 1975). The values used for the coherent neutron scattering amplitudes were taken from the compilation of the Neutron Diffraction Commission (1969); *viz* 0·665, 0·577, −0·372 (in units of 10^{-12} cm) for C, O and H atoms

† Lists of X-ray and neutron structure factors, σ and $\bar{T}$ values and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32923 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

respectively. A difference map was now calculated where the calculated structure factors were based on the heavy-atom positions from the X-ray refinement. All the H atoms were clearly revealed. The structure was refined by full-matrix least-squares techniques with isotropic and then anisotropic thermal parameters for the H atoms. The heavy atoms were initially given the positional and thermal parameters from X-rays and an isotropic extinction parameter (Larson, 1970) was included in the refinement. The value of R^* was negligible in this case. The final R was 0·063 on all data, the conventional R was 0·043.

The final positional parameters are listed, together with those from X-rays, in Table 1.* Bond distances and angles are listed in Tables 2 and 3, torsion angles in Table 4 and H–H distances in Table 5.

Discussion

The weighted standard deviations (Hamilton, 1969) indicate no significant differences between the X-ray and neutron values for the positonal and thermal parameters of the heavy atoms. The final values $[\omega(F_o^2$

* See deposition footnote on p. 189.

Table 2. *Interatomic distances* (Å) *with standard deviations in parentheses*

Symmetry code: (′) $\frac{1}{2}+x, \frac{1}{2}-y, -z$; (″) $\frac{1}{2}+x, 1\frac{1}{2}-y, -z$.

	X-rays	Neutrons		X-rays	Neutrons
O(5)–C(1)	1·414 (2)	1·409 (3)	H(1)–C(1)	1·00 (3)	1·095 (5)
C(1)–C(2)	1·524 (2)	1·535 (3)	H(2)–C(2)	1·00 (3)	1·097 (5)
C(2)–C(3)	1·531 (3)	1·526 (3)	H(3)–C(3)	0·93 (3)	1·049 (7)
C(3)–C(4)	1·518 (3)	1·524 (3)	H(4)–C(4)	0·95 (3)	1·089 (6)
C(4)–C(5)	1·519 (3)	1·524 (3)	H(5)–C(5)	0·99 (3)	1·097 (8)
C(5)–O(5)	1·433 (3)	1·426 (4)	H(6)–C(6)	0·96 (3)	1·084 (6)
C(6)–O(1)	1·418 (3)	1·427 (4)	H(7)–O(2)	0·74 (3)	0·965 (8)
O(1)–C(1)	1·394 (2)	1·390 (4)	H(8)–O(3)	0·81 (3)	0·949 (7)
O(2)–C(2)	1·417 (2)	1·411 (4)	H(9)–O(4)	0·81 (3)	0·960 (7)
O(3)–C(3)	1·425 (2)	1·419 (3)	H(10)–C(6)	0·89 (3)	0·99 (1)
O(4)–C(4)	1·422 (3)	1·421 (5)	H(11)–C(6)	0·99 (4)	1·01 (1)
O(4)–O(2)	2·768 (3)	2·761 (5)	H(12)–C(6)	0·98 (3)	1·01 (1)
O(3)–O(2′)	2·841 (3)	2·837 (4)	H(7)–O(4)	2·15 (3)	1·959 (8)
O(4)–O(3″)	2·865 (3)	2·862 (4)	H(8)–O(2′)	2·11 (3)	1·989 (7)
C(2)–C(4)	2·502 (3)	2·502 (4)	H(9)–O(3″)	2·10 (3)	1·947 (7)

Table 3. *Bond angles* (°)

Neutron results only are given for angles involving hydrogen atoms.

	X-rays	Neutrons		
O(5)–C(1)–C(2)	112·0 (2)	111·4 (3)	H(3)–C(3)–O(3)	110·0 (4)
C(1)–C(2)–C(3)	109·8 (2)	109·8 (2)	H(4)–C(4)–C(3)	109·3 (4)
C(2)–C(3)–C(4)	110·3 (1)	110·2 (2)	H(4)–C(4)–C(5)	108·8 (4)
C(3)–C(4)–C(5)	108·2 (2)	108·0 (2)	H(4)–C(4)–O(4)	110·9 (5)
C(4)–C(5)–O(5)	111·3 (2)	111·3 (2)	H(5)–C(5)–C(4)	109·6 (4)
C(5)–O(5)–C(1)	113·2 (2)	113·8 (2)	H(5)–C(5)–O(5)	110·0 (4)
C(6)–O(1)–C(1)	114·4 (2)	114·0 (2)	H(5)–C(5)–H(6)	110·7 (5)
O(1)–C(1)–C(2)	107·2 (2)	107·3 (2)	H(6)–C(5)–C(4)	109·9 (4)
O(1)–C(1)–O(5)	113·0 (2)	113·0 (2)	H(6)–C(5)–O(5)	105·3 (4)
O(2)–C(2)–C(1)	109·3 (2)	109·2 (2)	H(7)–O(2)–C(2)	107·3 (4)
O(2)–C(2)–C(3)	112·9 (2)	113·0 (2)	H(8)–O(3)–C(3)	108·0 (4)
O(3)–C(3)–C(2)	112·4 (2)	112·6 (2)	H(9)–O(4)–C(4)	110·8 (4)
O(3)–C(3)–C(4)	108·8 (2)	109·0 (2)	H(10)–C(6)–O(1)	110·3 (6)
O(4)–C(4)–C(5)	107·6 (2)	107·6 (2)	H(11)–C(6)–O(1)	111·2 (6)
O(4)–C(4)–C(3)	112·5 (3)	112·1 (1)	H(12)–C(6)–O(1)	112·5 (5)
H(1)–C(1)–C(2)		110·2 (3)	H(10)–C(6)–H(11)	109 (1)
H(1)–C(1)–O(1)		110·1 (4)	H(10)–C(6)–H(12)	109 (1)
H(1)–C(1)–O(5)		104·7 (3)	H(11)–C(6)–H(12)	104 (1)
H(2)–C(2)–C(1)		108·5 (3)	H(2)–C(2)–O(2)	106·5 (4)
H(2)–C(2)–C(3)		109·7 (3)	O(3)–H(8)–O(2′)	147·1 (5)
H(3)–C(3)–C(2)		107·6 (4)	O(4)–H(7)–O(2)	139·0 (5)
H(3)–C(3)–C(4)		107·3 (4)	O(4)–H(9)–O(3″)	158·7 (5)

Table 4. *Torsion angles* (°)

	X-rays	Neutrons
O(5)–C(1)–C(2)–C(3)	−53·6 (2)	−53·8 (2)
C(1)–C(2)–C(3)–C(4)	54·3 (2)	54·4 (2)
C(2)–C(3)–C(4)–C(5)	−56·3 (2)	−56·2 (3)
C(3)–C(4)–C(5)–O(5)	58·3 (2)	58·1 (3)
C(4)–C(5)–O(5)–C(1)	−59·7 (2)	60·2 (3)
C(5)–O(5)–C(1)–C(2)	56·9 (2)	57·3 (3)
O(1)–C(1)–C(2)–O(2)	−165·5 (2)	−166·1 (3)
O(2)–C(2)–C(3)–O(3)	53·8 (2)	54·2 (4)
O(3)–C(3)–C(4)–O(4)	−61·4 (2)	−61·9 (3)
O(4)–C(4)–C(5)–O(5)	−63·4 (2)	−63·1 (3)
O(1)–C(1)–O(5)–C(5)	−64·3 (2)	−63·6 (3)
C(6)–O(1)–C(1)–C(2)	168·8 (2)	169·0 (3)
C(6)–O(1)–C(1)–O(5)	−67·3 (2)	−67·7 (4)
H(1)–C(1)–C(2)–H(2)		70·5 (5)
H(2)–C(2)–C(3)–H(3)		56·8 (6)
H(3)–C(3)–C(4)–H(4)		−57·7 (6)
H(4)–C(4)–C(5)–H(5)		54·9 (6)
H(4)–C(4)–C(5)–H(6)		−67·1 (7)
H(7)–O(2)–C(2)–C(3)		41·6 (7)
H(8)–O(3)–C(3)–C(4)		175·4 (7)
H(9)–O(4)–C(4)–C(5)		−163·9 (7)

Table 5. H–H *distances* (Å)

H(1)–H(2)	2·556 (7)	H(3)–H(5)	2·458 (8)
H(1)–H(3)	3·759 (8)	H(3)–H(6)	3·681 (7)
H(1)–H(4)	4·854 (8)	H(3)–H(10)	4·000 (10)
H(1)–H(5)	3·637 (9)	H(3)–H(11)	3·686 (11)
H(1)–H(6)	3·996 (7)	H(3)–H(12)	4·246 (11)
H(1)–H(10)	3·422 (11)	H(4)–H(5)	2·436 (8)
H(1)–H(11)	2·971 (14)	H(4)–H(6)	2·514 (7)
H(1)–H(12)	2·284 (10)	H(4)–H(10)	5·777 (10)
H(2)–H(3)	2·438 (8)	H(4)–H(11)	4·889 (10)
H(2)–H(4)	4·274 (8)	H(4)–H(12)	5·793 (10)
H(2)–H(5)	4·018 (8)	H(5)–H(6)	1·793 (10)
H(2)–H(6)	4·839 (8)	H(5)–H(11)	2·825 (13)
H(2)–H(10)	3·988 (1)	H(5)–H(10)	3·757 (19)
H(2)–H(11)	3·966 (10)	H(5)–H(12)	3·946 (13)
H(2)–H(12)	3·553 (11)	H(6)–H(10)	5·093 (10)
H(3)–H(4)	2·430 (7)	H(6)–H(11)	3·783 (14)
		H(6)–H(12)	4·783 (10)

$-F_c^2)^2/(N_{obs}-N_{var})]^{1/2}$, 8·0966 for X-rays and 1·3196 for neutrons, would indicate that $\sigma(F_o)$ for the X-ray refinement was underestimated. If this is considered, there is also reasonable agreement between the H atom positions (the greatest difference is approximately four standard deviations). The agreement with the parameters of Hordvik (1974) is similar to that of our two parameter sets, apart from the methyl H atoms where there is little agreement. These differences in positional parameters lead to the differences in the individual C–H bonds, the average value for X-rays being 0·12 Å smaller than that for neutrons, which are similar to those encountered for other structures studied by both X-ray and neutron techniques. This apparent contraction of C–H bond lengths has been justified by Stewart, Davidson & Simpson (1965) when a spherical scattering factor for H is used in the least-squares refinement of X-ray data. Likewise, the average O–H bond length for X-rays is 0·17 Å shorter than for neutrons, which agrees well with the values found for sucrose (Hanson, Sieker & Jensen, 1973).

The lengths of the C–O bonds involving hydroxyl O atoms are shorter for neutrons than for X-rays, but the difference is not significant. As this is usual for such systems, a further investigation with cumulant methods for refinement and a study of the orbital population is being undertaken elsewhere to show whether this is indeed a result of the bonding involved. These three hydroxyl O atoms each act as acceptors and donors in hydrogen bonds. The lengths and angles involved are listed in Tables 2 and 3, respectively, and illustrated in the vibrational-ellipsoid drawing, Fig. 1 (drawn by *ORTEP*, Johnson, 1965).

The six-membered ring in methyl β-D-ribopyranoside occurs in the chair conformation in which O(1) is axially oriented, the $^1C_4(D)$ conformation. The methoxyl group is oriented such that C(6) is antiperiplanar to C(2). This type of arrangement has been found for a large number of methyl glycosides in which O(1) is axially oriented on a six-membered ring: methyl α-D-glucopyranoside (Berman & Kim, 1968), methyl α-D-mannopyranoside (Gatehouse & Poppleton, 1970), methyl α-D-galactopyranoside monohydrate (Gatehouse & Poppleton, 1971*a*), methyl α-D-altropyranoside (Gatehouse & Poppleton, 1971*b*), methyl 5-thio-α-D-ribopyranoside (Girling & Jeffrey, 1973*a*), methyl α-D-xylopyranoside triacetate (James & Stevens, 1974), and methyl β-D-arabinopyranoside (McConnell, Schwartz & Stevens, 1977). Molecular-orbital calculations (Jeffrey, Pople & Radom, 1974) have shown that this arrangement corresponds to the minimum energy for the orientation of the methoxyl group. These calculations also predict that the bond lengths O(5)–C(1) and C(1)–O(1) should be smaller

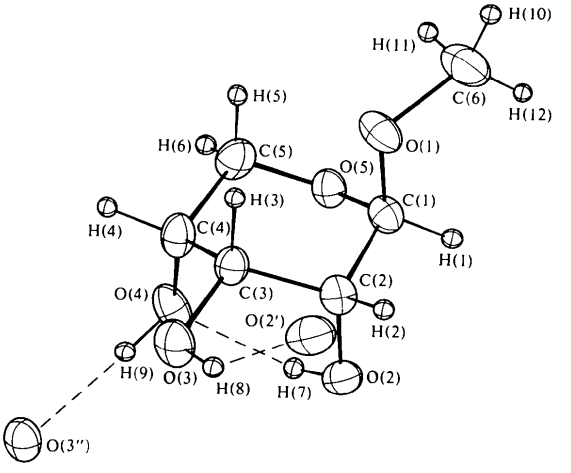

Fig. 1. Thermal-ellipsoid plot (*ORTEP*, Johnson, 1965) of the molecular structure.

Table 6. *Interatomic distances and bond angle in the hydrogen-bonded hydroxyl groups of potassium* D-*gluconate and the present compound*

	Atoms			Distances (Å)			Angle (°)
	i	j	k	d_{ij}	d_{jk}	d_{ik}	ijk
Potassium D-gluconate	O(2)	H(O4)	O(4)	1·737 (6)	0·975 (6)	2·610 (4)	147·1 (5)
Methyl β-D-ribopyranoside	O(4)	H(O2)	O(2)	1·959 (8)	0·965 (8)	2·768 (3)	139·0 (5)

than the experimental C—O bond length (1·428 Å) in methanol. The values given in Table 2 show that the experimental values agree with this prediction.

In common with other polyhydroxy compounds [see Jeffrey (1973*a*) for many references], the hydroxyl groups in methyl β-D-ribopyranoside are extensively involved in hydrogen bonding. Each hydroxyl group acts as both donor and receiver in the hydrogen-bonding scheme resulting in four intermolecular hydrogen bonds and one intramolecular hydrogen bond per molecule. Intramolecular hydrogen bonding in monosaccharides has been found in only three other structures. The first reported cases were in methyl 1-thio-α-D-ribopyranoside and methyl 1,5-dithio-α-D-ribopyranoside (Girling & Jeffrey, 1971), and later in potassium D-gluconate monohydrate (Jeffrey & Fasiska, 1972). In all three of these cases, the hydroxyl groups involved in intramolecular hydrogen bonding are arranged *syn*-axially as are the intramolecularly hydrogen-bonded groups in methyl β-D-ribopyranoside. The interatomic distances and bond angle involved in hydrogen bonding of the neutron-diffraction-determined structure of potassium D-gluconate monohydrate are compared with those determined for methyl β-D-ribopyranoside in Table 6. These values show that the intramolecular hydrogen bonds in the two compounds are very similar, that in the gluconate being marginally stronger.

Although the structures of methyl 1-thio-α-D-ribopyranoside (Girling & Jeffrey, 1973*b*) and methyl 1,5-dithio-α-D-ribopyranoside (Girling & Jeffrey, 1974) are from X-rays only, a comparison of the interatomic distances and bond angles involved in the intramolecular hydrogen bonds with the X-ray values reported for methyl β-D-ribopyranoside (James & Stevens, 1972) shows that the intramolecular hydrogen bonding is very similar for all three compounds. A pertinent review of intramolecular hydrogen bonding in carbohydrates in the solid state has been presented by Jeffrey (1973*b*).

We note that the H(5)—C(5)—H(6) bond angle of 110·6° is greater than the average value, 108·1°, for the H—C—H angles in C—CH_2—OH groups in sucrose (Brown & Levy, 1973), glucitol (Park, Jeffrey & Hamilton, 1971), α-D-glucose (Brown & Levy, 1965) and in the *A* and *B* forms of potassium D-gluconate monohydrate (Panagiotopoulos, Jeffrey, LaPlaca & Hamilton, 1974). The corresponding average for the C—C—O angle in these groups is 112·1°, which is slightly greater than the value of 111·3° in methyl β-D-ribopyranoside. It appears from these figures that the H—C—H angles in C—CH_2—O groups are generally larger than those in C—CH_2—C groups (Ermer, Dunitz & Bernal, 1973).

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Crystal and Molecular Structure of 3,3′-Diethylthiatricarbocyanine Iodide, an Infrared Photographic Sensitizing Dye

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The crystal structure of the title compound, a model infrared photographic sensitizing dye, has been determined by a single-crystal, three-dimensional X-ray diffraction study. The compound crystallizes in space group $P2_1/n$ with four $C_{25}H_{25}IN_2S_2$ units in each unit cell of dimensions $a = 17{\cdot}932$ (7), $b = 18{\cdot}244$ (9), $c = 7{\cdot}569$ (2) Å and $\beta = 102{\cdot}54$ (3)°. The structure was solved by the heavy-atom method and refined by least-squares techniques to a conventional R value of 0·084 for 2180 independent reflections with $F^2 > 2\sigma(F^2)$. The structure consists of sheets of $C_{25}H_{25}N_2S_2^+$ cations roughly parallel to $(10\bar{1})$ and separated by I ions. Between these sheets, the cations are centrosymmetrically related and stacked in columns along **c**. In contrast to many structures of thiacarbocyanine and imidocarbocyanine dyes, the cations in the present structure do not stack in the 'slipped deck of cards' arrangement with large intralayer areas of overlap between heterocyclic groups. The cations exist in the all-*trans* configuration and may roughly be described as S-shaped with the heterocyclic groups bent and twisted from the central chain in opposite directions. Bond distances within the seven-atom central chain are alternately long and short as indicated by a χ^2 test, suggesting incomplete electron delocalization between the cation halves.

Introduction

The response of modern photographic films to long-wavelength radiation is completely dependent on the action of sensitizing dyes (Mees & James, 1966). The limited blue and ultraviolet sensitivity resulting from direct absorption of light by silver halide microcrystals is augmented by adsorbed dyes which are thought to form close-packed aggregates on the crystal surface. In favorable cases, dye-adsorbed quanta are as effective as body-adsorbed quanta in generating the photographic latent image; this high quantum efficiency extends across the visible spectrum and into the near infrared (Bird, Zuckerman & Ames, 1968) where absorbed quanta have only approximately half the energy required for the direct production of an electron-hole pair in silver bromide.

Previous investigations of the dye sensitization process have shown that attachment of the organic dye to the substrate is a critical step (Bird, Norland, Rosenoff & Michaud, 1968). The total crystal surface available for occupancy is limited (Bird, 1974) and the formation of different aggregate structures may shift the region of absorption and sensitization. Since the nature of the aggregate formed must, to some extent, depend on the geometry of the dye itself, to understand the phenomena associated with dye adsorption, precise structural parameters for representative sensitizing dyes are required.

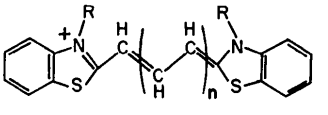

Fig. 1. Generic formula of a class of sensitizing dyes. When n = 0, 1, 2, or 3, the cations are thiacyanine, thiacarbocyanine, thiadicarbocyanine, and thiatricarbocyanine respectively.