

The conformational differences between the tripeptides in (III), (IV) and (V) are thus considerable. In the dihydroergotamine derivative ring *A* has a half-chair form with N(4) at  $-0.10$  and C(12) at  $0.16$  Å from the plane of the other three atoms, *B* is an envelope at C(12) and *C* is half-chair with C(10) above ( $+0.22$  Å) and C(11) below ( $-0.25$  Å) the plane of N(7), C(8) and C(9). In the *aci* isomer (V) ring *B* is a distorted half-boat, and rings *A* and *C* are both envelopes at C(2) and C(10).

The hydrogen bond between N(18) and O(15') of a neighbouring molecule gives rise to spirals of H-bonded molecules parallel to *a*. The pertinent data are: N(18)⋯O(15') =  $2.851(3)$ , N(18)–H(18,1) =  $0.85(3)$ , H(18,1)⋯O(15') =  $2.03(3)$  Å and N(18)–H⋯O(15') =  $165(3)^\circ$ . All other intermolecular contacts are longer than the sums of the corresponding van der Waals radii.

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## Structure of the Unstable Monoclinic 1,2,3,5-Tetra-*O*-acetyl- $\beta$ -D-ribofuranose\*

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#### Abstract

The unstable *A* form of 1,2,3,5-tetra-*O*-acetyl- $\beta$ -D-ribofuranose, C<sub>13</sub>H<sub>18</sub>O<sub>9</sub> (m.p. = 330–331 K), crystallizes in the monoclinic system,  $a = 12.649(2)$ ,  $b = 5.582(2)$ ,  $c = 11.078(2)$  Å,  $\beta = 97.92(1)^\circ$ , space group  $P2_1$ ,  $Z = 2$ ,  $D_c = 1.364$  Mg m<sup>-3</sup>. Final  $R = 0.045$  for 1142 reflexions. To shed light on the spontaneous and irreversible transition of form *A* into

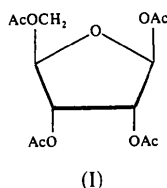
the stable orthorhombic form *B* (m.p. 358 K) the present structure determination of *A* is compared with that of *B* reported by James & Stevens [*Cryst. Struct. Commun.* (1973), **2**, 609–612] and Poppleton [*Acta Cryst.* (1976), **B32**, 2702–2705]. Neither the bonding of the molecules nor the puckering of the furanose rings reveals significant differences. However, two of the four acetyl moieties exhibit torsional parameters [C(4)–C(5)–O(5)–C(6) and C(1)–C(2)–O(2)–C(10)] which differ significantly ( $\Delta = 92.5$  and  $70.0^\circ$ ), indicating conformational dimorphism of *A* and *B*. There are three H⋯H intermolecular contacts in *A* which

\* Dedicated to Professor Géza Schay (first director of CRIC) on his 80th birthday.

are markedly shorter (1.96, 1.98 and 2.12 Å) than the sum of their van der Waals radii (2.4 Å). No such short contacts are present in *B*.

### Introduction

The structural dimorphism of 1,2,3,5-tetra-*O*-acetyl- $\beta$ -D-ribofuranose (**I**) was discovered when Zinner (1950) found that the title compound, obtained by direct acetylation of D-ribose, showed a considerably higher melting point (355 K) than had been found by Howard, Lythgoe & Todd (1947) and Brederick & Hoepfner (1948) (331 and 329 K, respectively). Davoll, Brown & Visser (1952) also prepared crystals which melted in the range 329–331 K, but repetition of the procedure described by Brederick & Hoepfner (1948) yielded a sample melting at 358 K. The identical molecular structure of the higher-melting crystals (hereafter *B*) with that of the lower-melting product (hereafter *A*) was proved by preparative methods. When crystals of *A* were exposed to the air in a laboratory inoculated with *B* their melting points rose to 358 K while the crystals rapidly became opaque and *A* could not be prepared thereafter. Their structural dimorphism was suggested by Farrar (1952) who pointed out that both forms exhibit the same specific rotation in chloroform. Patterson & Groshens (1954), who determined the lattice parameters and space group of both crystals (*A*: monoclinic  $P2_1$ ,  $Z = 2$ , *B*: orthorhombic  $P2_12_12_1$ ,  $Z = 4$ ), corroborated Farrar's conclusions. They also observed rapid and irreversible phase transformations of *A* into *B* catalysed by the presence of *B* crystals. Since then, no comparative structural studies of *A* and *B* have been reported, presumably because of fruitless attempts to prepare the unstable *A* (Poppleton, 1976). Accordingly, the crystal structure of *B* could only be determined to date (James & Stevens, 1973; Poppleton, 1976).



Recently, whilst preparing ribofuranosyl derivatives, we have synthesized the title compound and obtained crystals which melt at 331 K. Its optical rotation in chloroform was identical to that of the higher melting *B*. Since we have invariably grown *A* in several experiments it seemed worthwhile to determine its crystal structure by X-ray diffraction and compare it with that of *B*.

### Experimental

The title compound was prepared according to Guthrie & Smith (1968). Both base- and acid-catalysed acetylation gave the same product; colourless, 8–9 mm long, 2–3 mm thick columns were crystallized from ethanol (m.p. 330–331 K);  $[\alpha]_D = -12.7^\circ$  (chloroform,  $c = 1.1 \text{ g dm}^{-3}$ ),  $[\alpha]_D = -14.3^\circ$  (methanol,  $c = 1.2 \text{ g dm}^{-3}$ ).

Crystal data are given in Table 1. Intensities of 1173 independent reflexions were collected in the range  $2\theta \leq 50^\circ$  by an  $\omega$ - $2\theta$  scan on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo  $K\alpha$  radiation. Cell constants were determined by least squares from the setting angles of 25 reflexions. After data reduction 1142 reflexions with  $I - 2\sigma(I) > 0$  were taken as observed. No absorption correction was applied.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) by the use of 187 normalized

Table 1. *Crystal data*

$C_{13}H_{18}O_9$ ,  $M_r = 318$ , monoclinic, space group  $P2_1$ ,  $D_c = 1.364 \text{ Mg m}^{-3}$ ,  $Z = 2$ ,  $\mu(\text{Mo } K\alpha, \lambda = 0.71073 \text{ \AA}) = 0.126 \text{ mm}^{-1}$ .

	Present work	Patterson & Groshens (1954)
<i>a</i>	12.649 (2) Å	12.49 Å
<i>b</i>	5.582 (2)	5.58
<i>c</i>	11.078 (2)	11.12
$\beta$	97.92 (1)°	97.75°
<i>V</i>	774.7 (6) Å <sup>3</sup>	767.9 Å <sup>3</sup>

Table 2. *Fractional coordinates ( $\times 10^4$ ) and mean temperature factors ( $\text{\AA}^2$ ) for non-hydrogen atoms*

E.s.d.'s are given in parentheses.  $B_{\text{eq}} = 4|B_{11}B_{22}B_{33}/(a^*b^*c^*)|^{1/3}$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}$
O(1)	7996 (2)	816 (6)	5970 (2)	3.8 (1)
O(2)	5597 (2)	2688 (7)	7074 (3)	3.9 (1)
O(3)	6865 (2)	3410 (6)	9250 (3)	3.3 (1)
O(4)	7620 (2)	4777 (0)	6392 (3)	4.3 (1)
O(5)	9582 (2)	4095 (7)	7992 (3)	4.5 (1)
O(6)	10776 (3)	5810 (10)	9367 (4)	7.7 (2)
O(8)	6584 (3)	-457 (7)	9610 (3)	5.8 (2)
O(10)	4964 (3)	-455 (8)	5950 (3)	5.8 (2)
O(12)	8159 (3)	2169 (9)	4127 (3)	5.7 (2)
C(1)	7169 (3)	2548 (9)	6068 (4)	3.6 (2)
C(2)	6640 (3)	1708 (8)	7150 (4)	3.3 (2)
C(3)	7351 (3)	2801 (9)	8228 (4)	3.5 (2)
C(4)	7709 (3)	5142 (9)	7712 (4)	3.5 (2)
C(5)	8830 (4)	5950 (10)	8193 (4)	4.4 (2)
C(6)	10543 (4)	4224 (12)	8646 (4)	4.8 (2)
C(7)	11221 (4)	2216 (16)	8419 (5)	6.3 (3)
C(8)	6527 (4)	1575 (11)	9919 (4)	4.6 (2)
C(9)	6099 (5)	2524 (16)	11041 (5)	7.4 (3)
C(10)	4817 (3)	1391 (11)	6408 (4)	4.2 (2)
C(11)	3740 (4)	2592 (14)	6372 (5)	5.7 (3)
C(12)	8426 (3)	782 (11)	4925 (4)	3.8 (2)
C(13)	9201 (4)	-1167 (11)	4966 (5)	5.1 (2)

Table 3. Fractional coordinates ( $\times 10^4$ ) for H atoms

The e.s.d.'s are identical to those of the C atoms to which they are linked.  $B_{\text{iso}} = 4.0 \text{ \AA}^2$ .

	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	6635	2699	5222
H(2)	6561	-214	7202
H(3)	7951	1496	8560
H(4)	7210	6554	7986
H(51)	8884	6308	9158
H(52)	9014	7561	7724
H(71)	11990	2405	8970
H(72)	10853	563	8649
H(73)	11324	2190	7467
H(91)	5914	1041	11602
H(92)	6694	3649	11555
H(93)	5385	3558	10765
H(111)	3407	2927	5436
H(112)	3210	1437	6791
H(113)	3835	4268	6861
H(131)	9418	-1447	4068
H(132)	9904	-709	5591
H(133)	8853	-2788	5271

Table 4. Bond lengths ( $\text{\AA}$ )

O(1)—C(1)	1.440 (6)	O(12)—C(12)	1.188 (6)
O(1)—C(12)	1.346 (4)	O(10)—C(10)	1.175 (7)
O(2)—C(2)	1.420 (5)	O(8)—C(8)	1.190 (7)
O(2)—C(10)	1.358 (6)	C(1)—C(2)	1.524 (6)
O(3)—C(3)	1.402 (5)	C(2)—C(3)	1.520 (6)
O(3)—C(8)	1.367 (6)	C(3)—C(4)	1.520 (7)
O(4)—C(1)	1.395 (5)	C(4)—C(5)	1.512 (6)
O(4)—C(4)	1.465 (4)	C(6)—C(7)	1.454 (9)
O(5)—C(5)	1.444 (6)	C(12)—C(13)	1.460 (8)
O(5)—C(6)	1.329 (5)	C(10)—C(11)	1.513 (7)
O(6)—C(6)	1.202 (7)	C(8)—C(9)	1.519 (7)

structure factors with  $E \geq 1.5$ . An  $E$  map computed from a phase set with the best consistency (ABSFOM = 0.89, RESID = 16.6) gave the positions of all non-hydrogen atoms ( $R = 0.26$ ). Full-matrix least-squares refinement of positional and vibrational parameters reduced  $R$  to 0.076 for 1034 reflexions. At this stage H positions were generated from assumed geometries ( $C-H = 1.08 \text{ \AA}$ ) and checked in a subsequent difference map. Further anisotropic refinement of heavy-atom positions with fixed H atom coordinates gave  $R = 0.047$ . To follow Poppleton (1976) the generated H atom positions were also refined isotropically ( $R = 0.041$  for 837 reflexions with  $\sin \theta/\lambda \leq 0.5 \text{ \AA}^{-1}$ ). Further refinement of the non-hydrogen parameters based on 1142 observed reflexions led to a final  $R = 0.045$  ( $R_w = 0.057$ ). The greatest shift in positional parameters of the heavy atoms was  $0.13\sigma$ . Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). All calculations were performed on a PDP 11/34 mini-computer with the Enraf-Nonius *SDP-34* system. The

Table 5. Bond angles ( $^\circ$ )

C(1)—O(1)—C(12)	117.3 (6)	O(4)—C(4)—C(5)	109.5 (6)
C(2)—O(2)—C(10)	115.2 (6)	C(3)—C(4)—C(5)	115.9 (6)
C(3)—O(3)—C(8)	117.4 (6)	O(5)—C(5)—C(4)	109.7 (6)
C(1)—O(4)—C(4)	110.7 (5)	O(5)—C(6)—O(6)	121.7 (8)
C(5)—O(5)—C(6)	116.7 (6)	O(5)—C(6)—C(7)	112.4 (8)
O(1)—C(1)—O(4)	110.0 (6)	O(6)—C(6)—C(7)	125.9 (9)
O(1)—C(1)—C(2)	104.8 (6)	O(1)—C(12)—O(12)	121.5 (7)
O(4)—C(1)—C(2)	106.3 (6)	O(1)—C(12)—C(13)	109.4 (7)
O(2)—C(2)—C(1)	109.9 (6)	O(12)—C(12)—C(13)	129.1 (8)
O(2)—C(2)—C(3)	109.6 (6)	O(2)—C(10)—O(10)	123.8 (8)
C(1)—C(2)—C(3)	102.6 (6)	O(2)—C(10)—C(11)	111.3 (7)
O(3)—C(3)—C(2)	117.0 (6)	O(10)—C(10)—C(11)	125.0 (8)
O(3)—C(3)—C(4)	106.4 (6)	O(3)—C(8)—O(8)	121.5 (8)
C(2)—C(3)—C(4)	103.0 (6)	O(3)—C(8)—C(9)	110.8 (7)
O(4)—C(4)—C(3)	105.7 (5)	O(8)—C(8)—C(9)	127.6 (9)

final coordinates for non-hydrogen atoms are given in Table 2.\* The final parameters for the H atoms given in Table 3 correspond to ideal C—H geometry generated from the final C atom positions. Bond distances, angles and torsion angles are listed in Tables 4, 5 and 6.

## Discussion

Besides the identical melting points and space-group symmetries, the agreement between our cell constants and those given by Patterson & Groshens (1954) made us sure that the crystal structure of the unstable  $A$  modification had been determined. Taking into account the half-normal probability plot computed by Poppleton (1976) for his own structure analysis of  $B$  and that of James & Stevens (1973), only the molecular geometry revealed by Poppleton for  $B$  is discussed.

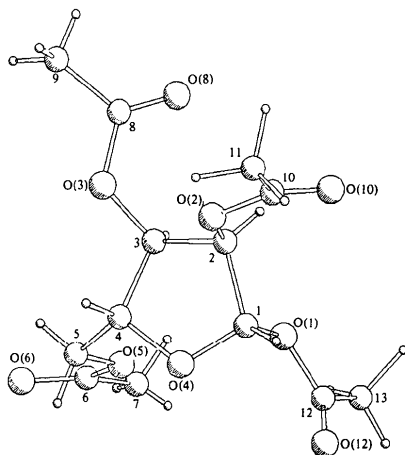
Beyond the identical connectivity of atoms (Figs. 1 and 3) the majority of the corresponding distances and angles on  $A$  and  $B$  agree within experimental error ( $3\sigma$  criterion). There is a pronounced difference between the endocyclic C—O distances in  $A$  ( $\Delta = 0.070 \text{ \AA}$ ) and those in  $B$  ( $\Delta = 0.044 \text{ \AA}$ ). The differences between the bond angles at C(2) can be attributed to the slightly different puckering of the ribofuranose ring in  $A$  and  $B$ . As shown by a manifold puckering analysis, performed with the program *RING* (Párkányi, 1979), the almost perfect  ${}^3T_2$  twist [or C(3)-endo, C(2)-exo] conformation of the furanose ring (Schwarz, 1973) found in  $B$  is slightly less puckered in  $A$  and assumes an intermediate  $E_2/{}^3T_2$  form (Table 7). The relevant torsion angles (Table 8) reveal the following similarities and differences. The four C—O—C—C<sub>Me</sub> torsion angles in both structures are characteristically antiperiplanar,

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35636 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 6. Torsion angles ( $^{\circ}$ )

O(2)–C(2)–C(1)–O(1)	–158.6 (6)	C(3)–C(2)–C(1)–O(4)	–31.6 (5)	C(6)–O(5)–C(5)–C(4)	–161.9 (7)
O(3)–C(3)–C(2)–O(2)	32.8 (6)	C(3)–C(4)–O(4)–C(1)	4.7 (5)	C(7)–C(6)–O(5)–C(5)	177.2 (10)
O(4)–C(1)–C(2)–O(2)	84.9 (6)	C(3)–C(4)–C(5)–O(5)	56.4 (6)	C(12)–O(1)–C(1)–O(4)	–81.6 (6)
O(4)–C(4)–C(3)–O(3)	–147.8 (6)	C(4)–O(4)–C(1)–O(1)	–95.9 (5)	C(12)–O(1)–C(1)–C(2)	164.5 (7)
O(5)–C(5)–C(4)–O(4)	–62.9 (6)	C(4)–O(4)–C(1)–C(2)	17.0 (5)	C(13)–C(12)–O(1)–C(1)	–176.7 (8)
C(1)–O(1)–C(12)–O(12)	2.2 (7)	C(4)–C(3)–C(2)–O(2)	–83.4 (6)	C(10)–O(2)–C(2)–C(1)	87.1 (7)
C(1)–C(2)–C(3)–O(3)	149.6 (6)	C(4)–C(3)–C(2)–C(1)	33.3 (5)	C(10)–O(2)–C(2)–C(3)	–160.9 (7)
C(2)–O(2)–C(10)–O(10)	2.4 (7)	C(5)–O(5)–C(6)–O(6)	–0.3 (8)	C(11)–C(10)–O(2)–C(2)	–179.4 (9)
C(2)–C(3)–C(4)–O(4)	–24.1 (5)	C(5)–C(4)–O(4)–C(1)	130.2 (7)	C(8)–O(3)–C(3)–C(2)	69.3 (7)
C(3)–O(3)–C(8)–O(8)	–4.3 (7)	C(5)–C(4)–C(3)–O(3)	90.8 (7)	C(8)–O(3)–C(3)–C(4)	–176.3 (7)
C(3)–C(2)–C(1)–O(1)	84.9 (6)	C(5)–C(4)–C(3)–C(2)	–145.5 (7)	C(9)–C(8)–O(3)–C(3)	175.7 (9)

*i.e.*  $180 \pm 10^{\circ}$  (Foces-Foces, Cano & García-Blanco, 1980; Ružić-Toroš, Kojić-Prodić & Rogić, 1980). Around the  $\beta$ -axial C(1)–O(1) glycosidic links the conformations of the acetoxy groups are alike. However, the spontaneous  $A \rightarrow B$  transition alters the torsional parameters of the other three acetyl moieties. The C(2) acetoxy group as a flag turns  $70^{\circ}$  (anticlockwise) around the axial C(2)–O(2) toward the C(3) acetoxy moiety. To avoid a collision between these acetoxy groups the latter rotates  $19.1^{\circ}$  (also anticlockwise) around the equatorial C(3)–O(3). The biggest rotation ( $92.5^{\circ}$  clockwise) is around C(5)–O(5). These indicate conformational polymorphism of these crystal forms (Bernstein & Hagler, 1978). Accordingly, the widely spread form of the molecule in *A* (Fig. 2) becomes rather compact (Fig. 3) in *B*. In the  $A \rightarrow B$  transition the volume of the asymmetric unit increases by 1.5%. This means that the compact molecule in *B* occupies a somewhat greater space than the less compact form in *A*. To estimate the role of crystal forces on the molecular conformation, the intramolecular non-bonded potential energy of molecules freed from *A* and *B* crystals (with empirical atom-pair potential curves) was minimized.

Fig. 1. A perspective view of the molecule in *A*.

The constants in the generalized Buckingham–Lennard-Jones equation:

$$U(r) = -Ar^{-6} + Br^{-n} \exp(-\alpha r)$$

were those given by Giglio (1969).

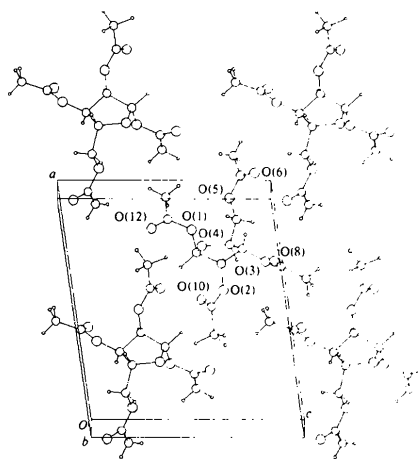
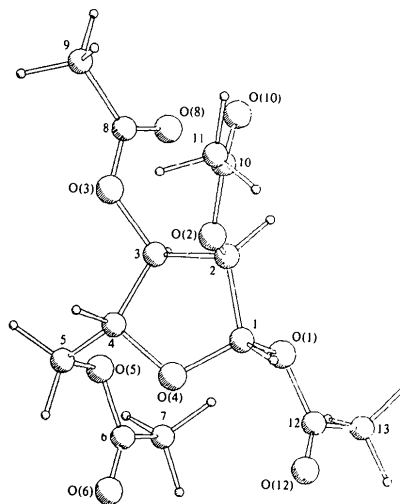
Fig. 2. A perspective view of the molecular packing in *A*.Fig. 3. A perspective view of the molecule in *B*. The drawing is computed from atomic coordinates published by Poppleton (1976).

Table 7. Analysis of the ribofuranose ring puckering in *A* and *B*

Torsion angles ( $\varphi_i$ ) around	<i>A</i>	<i>B</i>
C(1)–C(2)	–31.6°	–33.0°
C(2)–C(3)	33.3	37.3
C(3)–C(4)	–24.1	–29.6
C(4)–O(4)	4.7	9.1
O(4)–C(1)	17.0	15.6

Pseudorotation phase angle and $\varphi_{\max}$ (Altona, Geise & Romers, 1968)	<i>A</i>	<i>B</i>
$\Delta[\varphi_o \text{ at C(2)–C(3)}]$	–21.8°	–9.9°
$\varphi_{\max}$	34.6	38.4

Asymmetry parameters (Duax, Weeks & Rohrer, 1976)	<i>A</i>	<i>B</i>
$\Delta C_3$ [at C(2)]	5.2°	10.4°
$\Delta C_2$ [at O(4)]	10.2	5.2

Atomic displacements  $\varepsilon_i$  from the weighted best plane and puckering parameters  $Q$  and  $\varphi$  (Cremer & Pople, 1975)

	$\varepsilon_i$	
C(1)	$15 \times 10^{-2} \text{ \AA}$	$15 \times 10^{-2} \text{ \AA}$
C(2)	–21	–23
C(3)	19	22
C(4)	–10	–13
O(4)	–3	–2

Puckering parameters

$Q$	$34 \times 10^{-2} \text{ \AA}$	$38 \times 10^{-2} \text{ \AA}$
$\varphi$	260.8°	50.1°

Asymmetry factors (A. Kálmán, unpublished) calculated from  $\varepsilon_i$  displacements as follows:

$$fC_3 = \left[ \frac{\sum_{i=1}^m (\varepsilon_i - \varepsilon'_i)^2}{m} \right]^{1/2} \quad \text{and} \quad fC_2 = \left[ \frac{\sum_{i=1}^m (\varepsilon_i + \varepsilon'_i)^2}{m} \right]^{1/2}$$

where  $m$  is the number of the symmetry-related  $\varepsilon_i$  pairs

$fC_3$ [at C(2)]	$5.1 \times 10^{-2} \text{ \AA}$	$9.2 \times 10^{-2} \text{ \AA}$
$fC_2$ [at O(4)]	4.2	2.0

Table 8. Comparison between the relevant exocyclic torsion angles (°) of *A* and *B*

	<i>A</i>	<i>B</i>	$\Delta$
C(2)–C(1)–O(1)–C(12)	164.5	167.6	3.1
C(1)–O(1)–C(12)–C(13)	–176.7	–173.1	3.6
C(1)–C(2)–O(2)–C(10)	87.1	157.1	70.0
C(2)–O(2)–C(10)–C(11)	–179.4	–172.8	6.6
C(2)–C(3)–O(3)–C(8)	69.3	88.4	19.1
C(3)–O(3)–C(8)–C(9)	175.7	–173.4	10.9
C(3)–C(4)–C(5)–O(5)	56.4	48.4	8.0
C(4)–C(5)–O(5)–C(6)	–161.9	105.6	92.5
C(5)–O(5)–C(6)–C(7)	177.2	–178.0	4.8

As could be expected from the rough comparison of the two molecular geometries, the computed intramolecular potential energy of *B* was greater (by 15.7 kJ mol<sup>–1</sup>) than that for *A*. Employing the steepest-descent technique, all 13 relevant torsion angles were

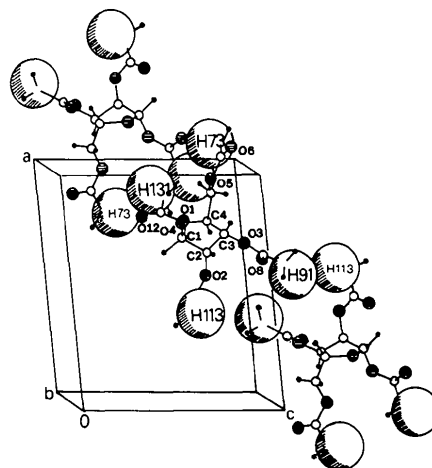


Fig. 4. A perspective view of the molecular packing in *A* indicating the intramolecular close contacts (1.98 and 1.96 Å) between H(73)···H(131) and H(91)···H(113). These H atoms are represented with their van der Waals radii.

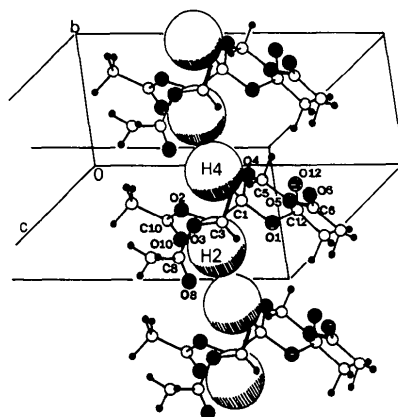


Fig. 5. A perspective view of the molecular packing in *A* indicating the intermolecular close contacts (2.12 Å) between H(2)···H(4) along *b*. These H atoms are represented with their van der Waals radii.

then refined for both molecular geometries. In both energy minimizations the rotations around C(2)–O(2), O(2)–C(10), C(5)–O(5) and O(5)–C(6) were the most affected. The types of torsion angles represented by O(2)–C(10) and O(5)–C(6), as shown by examples above, are kept fixed in the crystal. Consequently, potential-energy maps were computed for both conformers in terms of those two torsional parameters [ $\tau_1 = \text{C(1)–C(2)–O(2)–C(10)}$  and  $\tau_2 = \text{C(4)–C(5)–O(5)–C(6)}$ ] which also exhibited the greatest differences in the crystal structures. In both maps, plotted against  $\tau_1$  and  $\tau_2$  in the range 0–2 $\pi$ , there were minima at  $\tau_1 = 80$  and  $\tau_2 = 180^\circ$ , in the neighbourhood of those (87 and 162°) observed in *A*. These findings, even if the shortcomings of such an oversimplified energy calculation are taken into account, suggest

the following: the more stable molecular geometry could be developed in the low-melting *A*, while the less stable conformer is located in somewhat greater space per molecule in the high-melting stable *B*. Since the irreversible dimorphism could not be attributed to any hydrogen bonding, other types of close contacts were surveyed for both structures. *A* exhibits among the close contacts three H...H distances of 1.96, 1.98 and 2.12 Å (Figs. 4 and 5) which are considerably shorter than the sum of the van der Waals radii (2.4 Å). No such close contacts exist in *B*.

To summarize, we succeeded in determining the crystal structure of *A* and comparing it with that of *B*, but we found no marked difference which can account for the irreversible *A* → *B* phase transition. Nevertheless, our work may shed light on the strange realm of di- or polymorphism of crystals discussed by Woodard & McCrone (1975), e.g. D-mannitol (Kim, Jeffrey & Rosenstein, 1968).

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## 1,3-Diamino-4,7-methano-3a,4,5,6,7,7a-hexahydro-1λ<sup>4</sup>,3λ<sup>4</sup>,2-benzodithiazolium Chloride\* [C<sub>7</sub>H<sub>14</sub>N<sub>3</sub>S<sub>2</sub>]Cl, a Derivative of a New C<sub>2</sub>NS<sub>2</sub> Cationic Ring System

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#### Abstract

Trithiazyl trichloride [trichlorocyclotrithiazatriazene (NSCl)<sub>3</sub>] reacts with norbornene to give a mixture of products, aqueous hydrolysis of which provides the

novel dithiazolium compound C<sub>7</sub>H<sub>14</sub>N<sub>3</sub>S<sub>2</sub><sup>+</sup>.Cl<sup>-</sup>, *M<sub>r</sub>* = 239.78, tetragonal, *P*4<sub>2</sub>/*ncm*, *a* = 11.506 (1), *c* = 16.414 (2) Å, *V* = 2173 Å<sup>3</sup>, *Z* = 8, *D<sub>c</sub>* = 1.47 Mg m<sup>-3</sup>. The final *R* = 0.030 for 96 parameters and 653 reflexions [*I* > 3σ(*I*)]. The S–N distances are all 1.662 (3) Å, and SNS = 115.7 (4) and NSN = 115.9 (3)°, indicating the presence of a delocalized NSNSN cation chain. The structure and mechanism of formation are discussed.

\* Alternative name: 3,5-Diamino-3λ<sup>4</sup>,5λ<sup>4</sup>-dithia-4-azoniatricyclo[5.2.1.0<sup>2,6</sup>]deca-3,4-diene chloride.