involving C6 of uracil and O5′ of the uridine ribose. It seems likely that the short C—H···O distances in these different crystal environments arise as a result of electrostatic attractions very similar to those which we presently describe for 1-methyluracil.

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Structure of the Bromohydrin of an Octahydronaphthalene Derivative

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Abstract

(±)-3β-Bromo-2β-methyl-4aβ*H*,8aα*H*-decahydronaphthalen-2α-ol, $C_{11}H_{19}BrO$, $M_r = 247.2$, tetragonal, $I\bar{4}$, $a = 14.146$ (6), $c = 11.910$ (8) Å, $V = 2383$ (2) Å^3, $Z = 8$, $D_m = 1.37$ (2), $D_x = 1.38$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 3.38$ mm^{-1}, $F(000) = 1024$, $T = 213$ K, final $R = 0.043$ for 705 counter reflections. The *trans*-fused six-membered rings are chair-shaped but somewhat flattened. The torsion angle O—C(2)—C(3)—Br is −169.1 (6)°, the departure from 180° being almost entirely due to lateral displacement of the bromine atom.

Introduction

A mixture of the stereoisomeric octahydronaphthalenes (1) and (2) was obtained by use of a simple three-step reaction sequence (LaLonde & Tobias, 1963). Treatment of the liquid mixture of hydrocarbons with *N*-bromosuccinimide in aqueous

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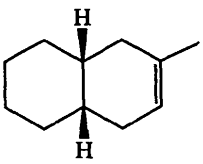
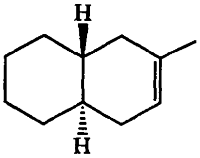
tetrahydrofuran afforded a crystalline bromohydrin (*A*) which was subsequently reduced with a zinc–copper couple. The resulting 'homogeneous olefin' was identified as the major component of the original mixture of hydrocarbons and was assigned the *trans*-fused structure (2). However, no definitive evidence in support of this structural assignment was provided.



(1)



(2)

Since it was proposed to use the alkene (2) as starting material for a multi-step synthesis, it seemed prudent to establish the structure unambiguously and to this end the crystal structure of the bromohydrin (*A*) has been determined.

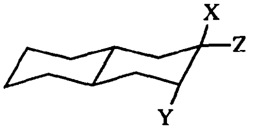
Experimental

Details of the preparation are outlined above. The compound was crystallized from acetonitrile over several weeks at 293 K. D_m by flotation in carbon tetrachloride/hexane.

Space group $I\bar{4}$, $I4$ or $I4/m$ ($h + k + l = 2n$); $I\bar{4}$ by successful refinement; cell parameters determined with a Nicolet *R*3*m*/V (Siemens Industries) four-circle diffractometer equipped with a graphite monochromator and are the means of 21 reflections with $4.2 < 2\theta < 14.7°$. Three standards measured every 197 reflections. No decomposition occurred. Temperature 213 K using Nicolet LT2 device. Data collected using the ω-scan technique with a scan width of $\pm 0.70°$ in θ from the calculated Bragg angle using a variable scan speed 3.00 to $15.00°\ s^{-1}$ in ω. Maximum 2θ 55°. No reflection was sufficiently intense to warrant the insertion of an attenuation filter. Data were processed using the Nicolet *SHELXTL-Plus* (MicroVAX II) (Version 4.IIV, Siemens Analytical X-ray Instruments Ltd, Karlsruhe, Germany) software. Values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects. Refinement on F. Goodness of fit 1.003, $w = [\sigma^2(F_o)]^{-1}$. No absorption correction was applied as face-indexing was not attempted at low temperature. 1545 reflections were collected, 1520 independent ($R_{\rm int} = 3.32\%$), from a clear tetragonal prism ($0.3 \times 0.2 \times 0.2$ mm), 705 reflections [$I > 3\sigma(I)$] used in analysis; index range $-16 < h < 18$, $0 < k < 18$, $0 < l < 15$. Br-atom parameters found from Patterson synthesis and all non-H atoms located in subsequent difference Fourier synthesis. All non-H atoms refined anisotropically using full-matrix least-squares methods with H atoms in calculated positions and refined using a riding model with a single isotropic thermal parameter (119 variables), final $R = 0.043$ and $wR = 0.040$ (for observed reflections); max. Δ/σ in final cycle 0.001. The absolute structure of the individual crystal chosen was identified by comparison with refinement of the inverted structure. Final difference Fourier synthesis peak 0.54 e $Å^{-3}$, trough -0.49 e $Å^{-3}$, both in the vicinity of the Br atom. Figure drawn using the Nicolet *SHELXTL-Plus* software.* Scattering factors and amomalous-dispersion corrections from *SHELXTL-Plus* software.

Discussion

Final fractional coordinates and thermal parameters for the bromohydrin (*A*) are given in Table 1, interatomic distances and bond angles in Table 2, and selected torsion angles in Table 3. A perspective view of the structure is shown in Fig. 1, together with the atom-numbering scheme used. The structure clearly indicates that the two six-membered rings are essentially chair-shaped and *trans*-fused. It also indicates that the hydroxyl group and the bromine atom are diaxially disposed, as expected on mechanistic grounds. The structure is therefore correctly represented by formula (3).



	X	Y	Z
(3)	OH	Br	Me
(4)	OH	NMe_2	H
(5)	OAc	$+NMe_3$	H
(6)	OTos	H	H

Closer examination of the structural data for (3) reveals a number of similarities with structures previously reported for three other *trans*-decalin deriva-

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54733 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0506]

Table 1. *Atomic coordinates* (× 10^4, Br × 10^5) *and equivalent isotropic displacement coefficients* ($Å^2$ × 10^3)

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
Br	37913 (9)	−43134 (9)	−39902 (12)	44.3 (5)
O	1323 (5)	−5327 (5)	−2526 (6)	32 (3)
C(1)	2385 (8)	−6289 (7)	−3574 (10)	35 (4)
C(2)	2045 (7)	−5293 (8)	−3412 (10)	32 (4)
C(3)	2842 (7)	−4673 (7)	−2870 (10)	26 (4)
C(4)	3322 (8)	−5145 (7)	−1885 (10)	34 (4)
C(4a)	3658 (8)	−6148 (7)	−2139 (10)	29 (4)
C(5)	4129 (10)	−6600 (9)	−1128 (13)	61 (5)
C(6)	4457 (10)	−7612 (10)	−1390 (12)	64 (6)
C(7)	3668 (10)	−8206 (9)	−1831 (12)	59 (6)
C(8)	3182 (9)	−7752 (8)	−2839 (11)	42 (5)
C(8a)	2839 (8)	−6753 (7)	−2573 (10)	29 (4)
C(9)	1619 (9)	−4878 (8)	−4434 (9)	41 (4)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

Br—C(3)	1.961 (11)	O—C(2)	1.469 (13)
C(1)—C(2)	1.501 (15)	C(1)—C(8a)	1.505 (16)
C(2)—C(3)	1.568 (15)	C(2)—C(9)	1.479 (16)
C(3)—C(4)	1.510 (16)	C(4)—C(4a)	1.526 (15)
C(4a)—C(5)	1.518 (18)	C(4a)—C(8a)	1.531 (15)
C(5)—C(6)	1.537 (19)	C(6)—C(7)	1.493 (20)
C(7)—C(8)	1.526 (19)	C(8)—C(8a)	1.526 (16)
C(2)—C(1)—C(8a)	116.4 (10)	O—C(2)—C(1)	106.5 (9)
O—C(2)—C(3)	102.8 (9)	C(1)—C(2)—C(3)	110.3 (8)
O—C(2)—C(9)	108.7 (8)	C(1)—C(2)—C(9)	113.5 (10)
C(3)—C(2)—C(9)	114.2 (9)	Br—C(3)—C(2)	110.9 (8)
Br—C(3)—C(4)	109.6 (7)	C(2)—C(3)—C(4)	113.3 (9)
C(3)—C(4)—C(4a)	113.4 (9)	C(4)—C(4a)—C(5)	111.8 (10)
C(4)—C(4a)—C(8a)	110.6 (9)	C(5)—C(4a)—C(8a)	111.3 (9)
C(4a)—C(5)—C(6)	111.3 (11)	C(5)—C(6)—C(7)	111.7 (11)
C(6)—C(7)—C(8)	112.1 (11)	C(7)—C(8)—C(8a)	111.7 (10)
C(1)—C(8a)—C(4a)	110.2 (9)	C(1)—C(8a)—C(8)	112.1 (10)
C(4a)—C(8a)—C(8)	110.3 (9)		

Table 3. *Selected torsion angles* (°) *and their e.s.d.'s*

Substituted ring	
C(8a)—C(1)—C(2)—C(3)	49.7 (13)
C(1)—C(2)—C(3)—C(4)	−46.1 (13)
C(2)—C(3)—C(4)—C(4a)	50.6 (12)
C(3)—C(4)—C(4a)—C(8a)	−54.9 (12)
C(4)—C(4a)—C(8a)—C(1)	55.0 (12)
C(4a)—C(8a)—C(1)—C(2)	−55.2 (13)
O—C(2)—C(3)—Br	−169.1 (6)
Unsubstituted ring	
C(7)—C(8)—C(8a)—C(4a)	55.1 (13)
C(8)—C(8a)—C(4a)—C(5)	−55.8 (13)
C(8a)—C(4a)—C(5)—C(6)	55.3 (13)
C(4a)—C(5)—C(6)—C(7)	−54.4 (15)
C(5)—C(6)—C(7)—C(8)	53.9 (16)
C(6)—C(7)—C(8)—C(8a)	−54.9 (15)

tives – the aminoalcohol (4) (Cabastaing & Watkin, 1973), the quaternary ammonium salt (5) (Lee & Henry, 1976), and the tosylate (6) (James, 1973). Specifically, all the endocyclic bond angles of both rings are greater than 109.5°, and all the endocyclic torsion angles are less than 60°, thereby indicating that, as in a compounds (4), (5) and (6), both rings are somewhat flattened compared with the perfect chair conformation of cyclohexane.

Table 4. *Comparison of endocyclic bond and torsion angles* (°) *for trans-decalin derivatives: mean values* (*with standard deviations in the means in parentheses*)

	Average for substituted ring	Average for unsubstituted ring
Endocyclic bond angles		
(3)	112.4 (25)	111.4 (6)
(4)[a]	111.3 (20)	111.1 (6)
(5)[b]	113.0 (31)	111.5 (6)
(6)[c]	112.3 (6)	111.7 (13)
Endocyclic torsion angles		
(3)	51.9 (37)	54.9 (7)
(4)[a]	55.2 (31)	55.8 (23)
(5)[b]	49.0 (85)	54.8 (19)
(6)[c]	52.5 (16)	54.0 (14)

References: (*a*) Cabastaing & Watkin (1973), (*b*) Lee & Henry (1976), (*c*) James (1973).

Table 5. *Comparison of angles* (°) *involving axial substituents*

	Torsion angle X—C(2)—C(3)—Y	Angle X[a]	Angle Y[b]
(3)	169.1 (6)	1.4	11.8
(4)[c]	167.9 (9)	5.6[d]	7.5[d]
(5)[e]	148.3 (3)	9.6	26.8

Notes: (*a*) angle between X—C(2) bond and normal of the mean plane of the substituted ring, (*b*) angle between C(3)—Y bond and normal of the mean plane of the substituted ring, (*c*) Cabastaing & Watkin (1973), (*d*) calculated from data lodged by Cabastaing & Watkin (1973) with the Cambridge Structural Database, (*e*) Lee & Henry (1976).

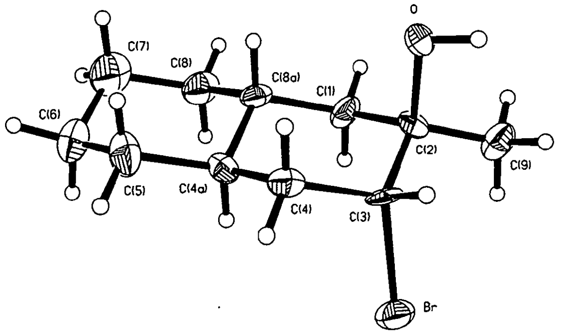

Fig. 1. Structure of $C_{11}H_{19}BrO$ showing the numbering scheme used. H atoms are drawn as circles of arbitrary small radius for clarity.

In the case of the ammonium salt (5), consideration of the average endocyclic bond and torsion angles for the substituted and unsubstituted rings led the original investigators (Lee & Henry, 1976) to conclude that ring flattening was more pronounced in the substituted ring. The values given for these average angles were as follows: average endocyclic bond angle for substituted ring 113.0 (4)°, for unsubstituted ring 111.5 (4)°, average endocyclic torsion angle for substituted ring 49.1 (5)°, for unsubstituted ring 54.8 (5)°; however, the errors given were actually the means of the e.s.d.'s of the relevant individual bond and torsion angles rather than the e.s.d.'s of the various means. The effects of such a difference in the type of statistical treatment used may be seen from the results presented for compounds (3)–(5) in Table 4. The magnitudes of the estimated errors of the mean angles now clearly preclude any comment concerning the relative degrees of flattening of the two rings in any of the four compounds.

The ring flattening under consideration arises, of course, from non-bonded interactions involving the axial substituents (X and Y) and appropriate axial hydrogens, and is necessarily accompanied by a reduction in the torsion angles X—C(2)—C(3)—Y. The observed angles for compounds (3)–(5) are listed in Table 5, together with information which shows that the departure from the 'ideal' angle of 180° arises from widely varying degrees of lateral displacement of the groups X and Y.

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A Quantitative Analysis of the Relative Importance of Symmetry Operators in Organic Molecular Crystals

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Abstract

The contribution of each symmetry operator to the lattice energy is calculated for a sample of 1068 non-hydrogen-bonded crystal structures in the most frequent space groups for organic molecules. The molecular coordination sphere is defined as the ensemble of neighbouring molecules each of which contributes more than 2% of the packing energy, and some geometrical aspects of this ensemble are studied. The frequency with which each operator is the most relevant one is estimated for each space group. It appears that some operators dominate, while others are silent by-products of the combinations of dominant ones. Pure translation gives the top contribution to the packing energy in a significant number of cases.

Introduction

The uneven distribution of organic crystal structures among space groups was recognized a long time ago by Kitaigorodski (1961), who classified the interactions among molecular objects in terms of favourable symmetry relationships. Even though a limited number of examples was then available, Kitaigorodski found that most crystal structures result from the action of one or two among a restricted set of symmetry operators, namely, the inversion centre (I), the twofold screw (S) and the glide (G). In this respect, the conclusion that only a few space groups are relevant to organic crystal chemistry follows naturally. This was confirmed later by analyses of space-group frequencies (Mighell, Himes & Rodgers, 1983; Donohue, 1985; Padmaja, Ramakumar & Viswamitra, 1990). Wilson (1988, 1990) has proposed quantitative rules to estimate the number of structures in each symmetry class from the type and number of symmetry operators; Scaringe (1990) has studied the distribution of structures throughout space groups, taking into account molecular symmetry, and has shown – in a beautiful confirmation of Kitaigorodski's principles – that groups containing twofold axes or mirror operators appear almost exclusively when the operator acts within the molecule, and not between molecules.

Since Kitaigorodski's time, there has been an exponential increase in the number of structure determinations which are available. This is due to the setting up of databases such as the Cambridge Structural Database (CSD; Allen, Kennard & Taylor, 1983), and the increasing speed and availability of electronic computers. Empirical formulations are available for a reasonably accurate estimation of

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