(CYTCYP20) which has two molecules in the asymmetric unit. One has a conformation on the pseudorotational pathway at $P = 91°$; the other has the planar ribose ring already discussed. These conformations may differ in energy by up to 5 kcal mol^{-1} which can only be provided by differences in the local packing forces of the two fragments. Only by relation of the crystal environment of each fragment to P and ψ will complete prediction of molecular geometry become possible.

Conclusion

The approach outlined in these three papers is applicable to any molecular fragment provided that enough examples are available on file. [Fragments in totally inorganic structures will have to be retrieved manually; see, for example, Murray-Rust, Bürgi & Dunitz (1978).] When a fragment can show symmetry [for example a phosphate group may show T_d symmetry (or any subgroup of T_d)] the factor analysis involves group-theoretical considerations (to be published later). It is important that the total data file of retrieved fragments is made clear (see Table 8) so that the analysis can be independently verified. Equally important is the publication of the algorithms for screening (particularly on derived data) so that results are seen not to be due to biased rejection of cases.

The present study was accomplished over a few weeks and future analyses will be considerably quicker. Compared with manual methods, which would require several months, the computer retrieval and analysis can be seen as a new tool in crystallography and structural chemistry. As experience is gained and more software is written (particularly for examining crystal environments) major increases in understanding crystal structures and the geometry of molecules will be possible.

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The Camphoroxime System. I. An X-ray Study of (–)-Camphoroxime (m.p. 118°C)

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(–)-Camphoroxime (m.p. 118°C) is monoclinic, $P2_1$, with $a = 12{\cdot}06$ (2), $b = 11{\cdot}81$ (2), $c = 7{\cdot}16$ (2) Å, $\beta = 99{\cdot}81°$, $Z = 4$. The structure was determined from 1491 independent intensities and refined to $R = 0{\cdot}052$. Except for one intramolecular distance, C(6)—C(5), there are no significant differences between the conformations of the two molecules of the asymmetric unit, which are linked by hydrogen bonds.

Introduction

This work is part of a program concerned with the study of enantiomorphic compounds, the phase diagrams of which seem to predict the existence of solid solutions. Such solid solutions are characterized by equilibrium diagrams of three types, named Roozeboom I, II and III. Examples (Baert & Fouret,

1975; Foulon, Baert & Fouret, 1975; Kroon, van Gurp, Oonk, Baert & Fouret, 1976) belonging to types II and III have been reported. The phase diagram [Fig. 1(*a*)] of the camphoroxime system (Adriani, 1900) shows that the inactive and active substances have the same melting point (118°C). Adriani noticed that some polymorphic modifications occur during cooling, and it was expected by the author that at ordinary temperatures the (±)-crystal ought to be a racemic compound and not a pseudoracemate. The solubility diagram [Fig. 1(*b*)] confirms this assumption. However, we have undertaken this investigation to elucidate the relations between the arrangement of the molecules in the pseudoracemate at high temperature and the structure of the more stable crystal at room temperature, and to check the validity of the information given by the phase and solubility diagrams. In this case mixed crystals may exist near the equimolecular mixture.

In the racemate model the 1:1 [the (±)] composition is an ordered structure in which (+)-molecules are related to (−)-molecules by space group symmetry, whilst in the pseudoracemate the (+)- and (−)-molecules are randomly distributed over all lattice sites, so the 1:1 composition has a statistical center of symmetry and is a disordered structure.

In this contribution we report the details of the crystal analysis of (−)-camphoroxime, while in the near future, we hope to communicate on the racemic or pseudoracemic form.

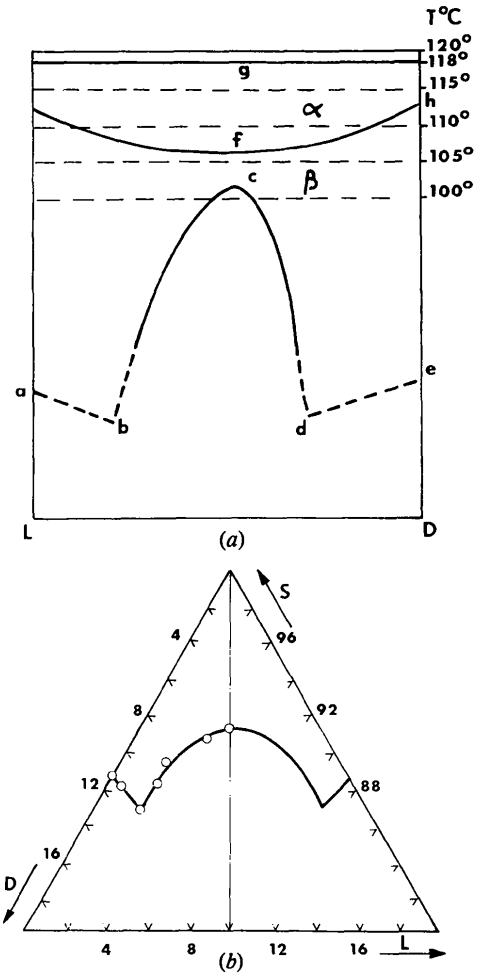

Fig. 1. (*a*) The solid–liquid equilibrium diagram of the system (+)-camphoroxime + (−)-camphoroxime (Adriani, 1900). α and β are crystal–crystal transitions. (*b*) The solubility diagram of the system (+)-camphoroxime + (−)-camphoroxime (Jacques & Gabard, 1972). S = Acetone, D and L = pure antipodes.

Experimental

A crystal 0·3 × 0·5 × 0·6 mm was mounted in a 0·5 mm diameter glass capillary. The crystallographic data are reported in Table 1. Intensities for 2033 reflections were measured by the ω–2θ scan on a four-circle diffractometer. The width of the scan was 1·0° + 0·5° tan θ. The data were corrected for Lorentz and polarization effects, but not for absorption or extinction. 1491 reflections with $I \geq 3\sigma(I)$ were used in the determination of the structure.

Table 1. *Crystal data*

$C_{10}H_{17}NO$, monoclinic $P2_1$	$Z = 4$
FW 167·25	$D_x = 1{\cdot}10$ g cm^{-3}
$a = 12{\cdot}064$ (23) Å	$D_m = 1{\cdot}03$
$b = 11{\cdot}805$ (21)	λ(Cu $K\alpha$) = 1·5418 Å
$c = 7{\cdot}162$ (16)	μ(Cu $K\alpha$) = 5·57 cm^{-1}
$\beta = 99{\cdot}81°$	$F(000) = 368$
$V = 1005{\cdot}1$ Å^3	Room temperature 21 (2)°C

Structure determination and refinement

The structure was solved by direct methods. 370 reflections with normalized structure factors $|E| \geq 1{\cdot}3$ were used in the *MULTAN* program (Germain, Main & Woolfson, 1971). A Fourier synthesis based on the solution with the highest $\sum_2$ consistency revealed the complete structure which was refined by full-matrix least squares. The H atoms were located from a difference synthesis and included in the refinement with the isotropic temperature factor of the carrier atom. Fig. 2 shows the atomic numbering.

The refinement converged to an R of 0·052 for all the reflections with $I \geq 3\sigma(I)$.

The final atomic parameters are listed in Table 2.* Scattering factors for the heavy atoms were those of

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33523 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

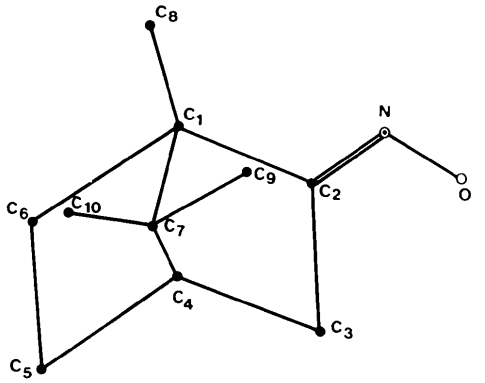

Fig. 2. Key to the numbering of the atoms in the camphoroxime molecule.

Table 2. *Fractional coordinates* ($\times 10^4$; *for* H $\times 10^3$) *and, for hydrogen atoms, isotropic temperature factors*

	x	*y*	*z*
O(1)	2601 (3)	944 (9)	4335 (6)
N(1)	3499 (4)	1189 (10)	3340 (7)
C(1)	5463 (4)	735 (10)	3239 (8)
C(2)	4373 (4)	617 (10)	3992 (7)
C(3)	4535 (5)	−237 (9)	5575 (8)
C(4)	5777 (5)	−588 (11)	5576 (8)
C(5)	6492 (6)	392 (11)	6434 (10)
C(6)	6272 (6)	1322 (10)	4881 (10)
C(7)	5898 (4)	−511 (10)	3467 (7)
C(8)	5386 (6)	1308 (11)	1365 (10)
C(9)	5141 (6)	−1341 (11)	2160 (10)
C(10)	7125 (5)	−667 (11)	3078 (10)
O(2)	2279 (3)	2790 (10)	854 (5)
N(2)	1432 (4)	2656 (10)	1962 (6)
C(11)	−384 (5)	3449 (10)	2481 (8)
C(12)	646 (4)	3371 (10)	1509 (7)
C(13)	567 (5)	4332 (10)	88 (9)
C(14)	−545 (5)	4893 (10)	384 (10)
C(15)	−320 (7)	5480 (10)	2296 (11)
C(16)	−195 (5)	4548 (10)	3718 (8)
C(17)	−1274 (5)	3880 (11)	781 (8)
C(18)	−639 (6)	2387 (11)	3533 (13)
C(19)	−1542 (7)	3049 (12)	−886 (12)
C(20)	−2394 (5)	4221 (11)	1375 (10)

Hanson, Herman, Lea & Skillman (1964), for H those of Stewart, Davidson & Simpson (1965). Unit weights were used throughout. Peaks and troughs in the final difference synthesis did not exceed $\pm 0{\cdot}2$ Å^{-3}. Fig. 3 is a perspective view of one of the two independent molecules, and shows the shapes and orientations of the thermal vibration ellipsoids.

Thermal vibration analysis

According to Adriani (1900), during cooling, the mixed crystals of phases α and β [Fig. 1(*a*)] must transform into a racemic compound, and we may suppose that reorientation and diffusion of the molecules occur during the decrease of temperature. It may be thought that at high temperature, *i.e.* after the transitions, the globular molecules of camphoroxime have important vibrational motions in an almost plastic crystal. For this reason a thermal motion analysis of the molecules might give information about the thermal agitation at high temperature and perhaps allow us to explain the formation of the mixed crystals.

When the thermal motions of the molecules in the asymmetric unit are analyzed separately in terms of a rigid-body motion, we find that these molecules do in fact behave very nearly as rigid bodies. The root mean square differences between the observed U_{ij} and those calculated from the derived **T**, **L** and **S** are respectively 0·0041 and 0·0053 Å^2. The rigid-body translations are almost isotropic with an average amplitude of 0·20 Å. For comparison we also calculated the rigid-body parameters for both molecules considered together. (The two molecules are linked by H bonds and form a dimer, Fig. 4.) The results of these calculations and of those for the separate molecules are given in Table 3, from which we can see that the eigenvalues of **T**

Table 2 (*cont.*)

	x	*y*	*z*	*B* (Å^2)		*x*	*y*	*z*	*B* (Å^2)
H(O1)	205	130	364	3·3	H(O2)	287	242	116	5·3
H(C3)	406	−75	521	2·9	H(C13)	41	391	−93	2·6
H′(C3)	441	22	675	2·9	H′(C13)	122	493	42	2·6
H(C4)	600	−127	632	2·6	H(C14)	−83	532	−54	3·2
H(C5)	719	5	698	4·6	H(C15)	−95	608	254	5·3
H′(C5)	622	71	753	4·6	H′(C15)	32	588	243	5·3
H(C6)	697	156	431	3·5	H(C16)	−78	447	475	3·4
H′(C6)	600	189	530	3·5	H′(C16)	48	454	455	3·4
H(C8)	510	226	136	4·6	H(C18)	−142	255	400	6·4
H′(C8)	487	90	40	4·6	H′(C18)	−8	243	437	6·4
H″(C8)	603	132	83	4·6	H″(C18)	−78	182	273	6·4
H(C9)	445	−131	215	5·1	H(C19)	−210	344	701	6·1
H′(C9)	539	−204	255	5·1	H′(C19)	−79	283	636	6·1
H″(C9)	547	−119	69	5·1	H″(C19)	−193	231	544	6·1
H(C10)	766	−6	379	4·4	H(C20)	−232	488	230	3·7
H′(C10)	708	−60	157	4·4	H′(C20)	−275	353	182	3·7
H″(C10)	732	−143	341	4·4	H″(C20)	−286	456	58	3·7

Table 3. *Rigid-body-vibration parameters for the heavy atoms of the two molecules with their e.s.d.'s analyzed separately and together*

	Molecule 1			Molecule 2			Both molecules		
T (Å²) ×10⁻⁴	277 (16)	9 (15)	−9 (15)	329 (21)	8 (20)	−43 (20)	327 (40)	−111 (42)	0 (42)
		367 (20)	−33 (16)		416 (24)	9 (21)		457 (54)	−73 (52)
			464 (19)			516 (26)			535 (62)
L (rad²) ×10⁻⁴	159 (8)	−38 (6)	−2 (6)	208 (10)	67 (8)	−13 (8)	70 (15)	−42 (9)	13 (5)
		76 (5)	−2 (4)		60 (7)	−8 (5)		39 (7)	−12 (4)
			58 (5)			46 (6)			14 (3)
S (Å rad) ×10⁻⁴	4 (11)	−18 (7)	3 (7)	7 (14)	−7 (9)	−39 (9)	−10 (18)	3 (14)	−6 (13)
	11 (6)	21 (9)	−31 (5)	13 (8)	−29 (12)	−45 (7)	−1 (11)	14 (12)	9 (9)
	3 (6)	48 (5)	25 (48)	−10 (7)	23 (6)	22 (62)	3 (7)	0 (5)	−4 (167)
r.m.s. $(U_o - U_c)$ (Å²)		0·0041			0·0053			0·0155	
e.s.d. U_{ij}^{obs} (Å²)		0·0048			0·0063			0·0167	

Table 4. **T** *and* **L** *referred to the inertial axes of the molecule*

	Principal axes (Å²) ×10⁻⁴		**T** (Å²) ×10⁻⁴		Principal axes (deg²)		**L** (rad²) ×10⁻⁴		Inertial moments	Direction cosines *x*	*y*	*z*
Molecule 1	357	352	12	22	20	61	3	0	491	−0·3570	−0·9131	−0·1968
(site *A*)	475		474	0	18		60	4	465	−0·0312	−0·1990	0·9795
	276			282	57			174	264	0·0933	−0·3558	−0·0425
Molecule 2	526	493	−53	−47	15	46	−1	−10	489	0·1199	−0·2518	0·9602
(site *B*)	420		420	−24	11		34	7	468	0·3583	−0·8910	0·2784
	349			349	77			234	265	0·9258	0·3775	−0·0165

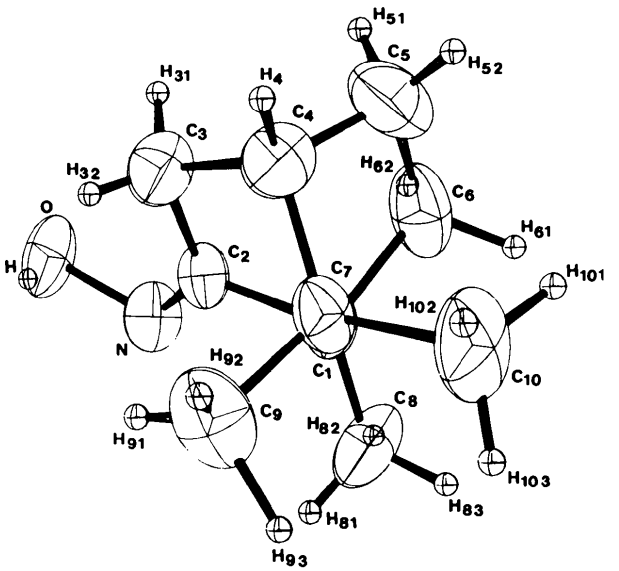

Fig. 3. A perspective view of the camphoroxime molecule.

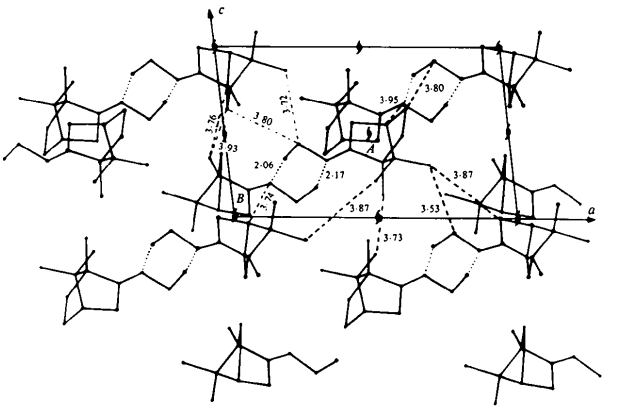

Fig. 4. Projection along *b* of the structure of camphoroxime. The two independent molecules are linked by hydrogen bonds.

represent the same anisotropic translation of the whole asymmetric unit as for the separate molecules; on the other hand the rotational motion is negligible (Schomaker & Trueblood, 1968).

In Table 4 the quantities **T** and **L** are referred to the inertial axes of the molecule. The off-diagonal elements of the libration tensor **L** are quite small, so it can be assumed that the molecules librate around their inertial axes.

The largest amplitude of vibration is around the axis with the smallest moment of inertia. It is worthwhile to emphasize that the thermal agitation is different for the two molecules.

Table 5. *Bond lengths* (Å) *before and after libration correction for the heavy atoms, and bond angles* (°), *with e.s.d.'s in parentheses*

	Uncorrected	Corrected
N(1)–O(1)	1·424 (7)	1·436
N(1)–C(2)	1·271 (11)	1·279
C(2)–C(1)	1·510 (8)	1·521
C(2)–C(3)	1·506 (12)	1·522
C(1)–C(8)	1·492 (11)	1·509
C(1)–C(6)	1·557 (11)	1·574
C(6)–C(5)	1·553 (15)	1·570
C(5)–C(4)	1·511 (16)	1·528
C(4)–C(3)	1·554 (9)	1·563
C(7)–C(4)	1·544 (8)	1·561
C(7)–C(1)	1·563 (17)	1·577
C(7)–C(9)	1·542 (13)	1·559
C(7)–C(10)	1·563 (8)	1·572
N(2)–O(2)	1·405 (6)	1·416
N(2)–C(12)	1·270 (12)	1·278
C(12)–C(11)	1·528 (8)	1·537
C(12)–C(13)	1·516 (14)	1·536
C(11)–C(18)	1·522 (16)	1·542
C(11)–C(16)	1·565 (15)	1·585
C(16)–C(15)	1·489 (15)	1·509
C(15)–C(14)	1·517 (12)	1·536
C(14)–C(13)	1·543 (11)	1·549
C(17)–C(14)	1·539 (15)	1·559
C(17)–C(11)	1·564 (10)	1·580
C(17)–C(19)	1·537 (14)	1·556
C(17)–C(20)	1·537 (10)	1·543

O(1)–H	0·86	C(6)–H(C6)	1·03
C(8)–H(C8)	1·18	C(6)–H′(C6)	0·82
C(8)–H′(C8)	0·97	C(5)–H(C5)	0·95
C(8)–H″(C8)	0·93	C(5)–H′(C5)	0·97
C(4)–H(C4)	0·99	C(9)–H(C9)	0·83
C(3)–H(C3)	0·84	C(9)–H′(C9)	0·91
C(3)–H′(C3)	1·03	C(9)–H″(C9)	1·19
C(10)–H(C10)	1·03	C(10)–H′(C10)	1·07
C(10)–H″(C10)	0·96		
O(2)–H	0·84	C(18)–H″(C18)	0·88
C(18)–H(C18)	1·07	C(14)–H(C14)	0·86
C(18)–H′(C18)	0·82	C(13)–H(C13)	0·88
C(13)–H′(C13)	1·06	C(19)–H(C19)	0·99
C(16)–H(C16)	1·11	C(19)–H′(C19)	0·90
C(16)–H′(C16)	0·93	C(19)–H″(C19)	1·07
C(15)–H(C15)	1·08	C(20)–H(C20)	1·02
C(15)–H′(C15)	0·91	C(20)–H′(C20)	1·0
C(20)–H″(C20)	0·84		

O(1)–N(1)–C(2)	111·1 (7)	O(2)–N(2)–C(12)	111·3 (7)
C(1)–C(2)–C(3)	108·7 (6)	C(11)–C(12)–C(13)	107·3 (7)
C(1)–C(2)–N(1)	122·5 (7)	C(11)–C(12)–N(2)	123·6 (8)
C(3)–C(2)–N(1)	128·7 (8)	C(13)–C(12)–N(2)	128·9 (8)
C(6)–C(1)–C(8)	114·3 (7)	C(16)–C(11)–C(18)	115·2 (7)
C(6)–C(1)–C(7)	100·6 (7)	C(16)–C(11)–C(17)	100·7 (7)
C(7)–C(1)–C(2)	99·9 (6)	C(17)–C(11)–C(12)	99·7 (7)
C(2)–C(1)–C(8)	115·9 (7)	C(12)–C(11)–C(18)	115·0 (7)
C(8)–C(1)–C(7)	119·3 (7)	C(18)–C(11)–C(17)	118·9 (7)
C(6)–C(1)–C(2)	104·1 (7)	C(16)–C(11)–C(12)	104·8 (7)
C(1)–C(6)–C(5)	103·5 (7)	C(11)–C(16)–C(15)	103·7 (7)
C(6)–C(5)–C(4)	103·6 (7)	C(16)–C(15)–C(14)	105·1 (8)
C(5)–C(4)–C(3)	106·2 (7)	C(15)–C(14)–C(13)	107·1 (7)
C(5)–C(4)–C(7)	102·1 (7)	C(15)–C(14)–C(17)	102·0 (7)
C(3)–C(4)–C(7)	103·6 (7)	C(13)–C(14)–C(17)	103·3 (7)
C(4)–C(3)–C(2)	100·4 (7)	C(14)–C(13)–C(12)	100·7 (7)
C(10)–C(7)–C(1)	113·8 (7)	C(20)–C(17)–C(11)	112·8 (7)
C(10)–C(7)–C(4)	114·6 (7)	C(20)–C(17)–C(14)	113·8 (7)
C(10)–C(7)–C(9)	107·3 (7)	C(20)–C(17)–C(19)	107·7 (7)
C(9)–C(7)–C(1)	112·4 (7)	C(19)–C(17)–C(11)	115·0 (7)
C(9)–C(7)–C(4)	114·2 (7)	C(19)–C(17)–C(14)	113·8 (7)
C(1)–C(7)–C(4)	94·1 (6)	C(11)–C(17)–C(14)	93·7 (6)

Table 6. *Angles* (°) *between principal planes of the molecules*

*P*1[C(1),C(8),C(7),C(4)] ∧ *P*2[C(9),C(7),C(10)]	89·56
*P*1[C(1),C(8),C(7),C(4)] ∧ *P*3[H(O1),O(1),N(1),C(2)]	54·75
*P*2[C(9),C(7),C(10)] ∧ *P*3[H(O1),O(1),N(1),C(2)]	84·85
*P*4[C(11),C(18),C(17),C(14)] ∧ *P*5[C(19),C(17),C(20)]	89·27
*P*4[C(11),C(18),C(17),C(14)] ∧ *P*6[H(O2),O(2),N(2),C(12)]	52·69
*P*5[C(19),C(17),C(20)] ∧ *P*6[H(O2),O(2),N(2),C(12)]	84·44

Results and discussion

Molecular geometry

The bond lengths, both uncorrected and corrected for the effects of molecular librations (Busing & Levy, 1964), and bond angles for the two molecules are reported in Table 5.

In general the bond lengths and angles in the two molecules agree well, except for C(6)–C(5) and C(16)–C(15). We have observed the same anomaly in (−)-carvoxime (Kroon, van Gurp, Oonk, Baert & Fouret, 1976). It could be that the antipode is not 100% optically pure and there may be a small number of (+)-molecules randomly distributed on *B* sites. (Site *B* corresponds to the more agitated molecule.) Such a disorder could explain the erroneous C(16)–C(15) distance. The values of the angles between some principal planes of the molecules (Table 6) show that the conformations of the two independent molecules are identical.

As in carvoxime the *anti* conformation of the oxime group is retained in the crystal.

The angles of the sp^2 bond involving C(2) and C(12) are different from the normal values, and are a consequence of the torsion of the cyclohexane ring in such a bridged molecule.

Molecular packing

Fig. 4 illustrates the packing of the molecules in the plane (101). As shown in Table 7 no intermolecular distances are less than the sum of the van der Waals

Table 7. *Intermolecular distances <4·0 Å between non-hydrogen atoms*

	Molecule *A*–molecules *A* and *B*			Molecule *B*–molecule *B*	
O(1)–C(16)	2|001*	3·80			
O(1)–C(15)	2|001	3·99			
O(1)–C(20)	2|001	3·72			
N(1)–C(4)	2|101	3·95	N(2)–C(14)	2|000	3·74
C(4)–O(2)	2|11$\bar{1}$1	3·69			
C(5)–O(2)	2|11$\bar{1}$	3·79			
C(8)–C(9)	2|11$\bar{1}$0	3·73	C(18)–C(19)	2|0$\bar{1}$1	>4·0
C(10)–O(2)	2|11$\bar{1}$0	3·52			
C(10)–C(13)	2|11$\bar{1}$0	3·87			
C(8)–C(5)	2|11$\bar{1}$0	>4·0	C(18)–C(15)	2|0$\bar{1}$1	3·76
C(8)–C(6)	2|11$\bar{1}$0	>4·0	C(18)–C(16)	2|0$\bar{1}$1	3·93

* Equivalent-position nomenclature: O(1)–C(16) 2|001 is taken to mean O(1) at equivalent position 1 to C(16) at equivalent position 2, translated 0, 0, 1 unit cells in the *a*, *b c* directions respectively. (1) x,y,z; (2) $-x, \frac{1}{2}+y, -z$.

radii of the atoms involved. The two independent molecules are situated on sites *A* and *B* respectively. They are held together by two strong hydrogen bonds between N(1)···H(O2) = 2·17 and N(2)···H(O1) = 2·06 Å. Fig. 4 shows some contacts between one molecule (on site *A*) and its nearest neighbors.

Table 7 shows that sites *A* and *B* are almost identical from the point of view of intermolecular distances, and this is in agreement with considerations of energy in an ideal solid solution. These results cannot explain, however, the differences between the thermal motions of molecules on sites *A* and *B*. Perhaps only a small disorder at site *B* is necessary for an understanding of these anomalies.

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A Neutron Diffraction Refinement of the Crystal Structure of α-L-Rhamnose Monohydrate*

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A three-dimensional neutron diffraction refinement at room temperature of α-L-rhamnose monohydrate has been completed. The heavy-atom coordinates are in good agreement with those from previous X-ray studies. The hydrogen bonding consists of two infinite chains which intersect at a four-coordinated water molecule. The H···O distances in the chains range from 1·740 to 1·981 Å. The anomeric hydroxyl is involved as a donor in the shortest bond and as an acceptor in the longest bond. There is also an isolated asymmetric bifurcated interaction with H···O distances of 1·949 and 2·715 Å, the weak component of which is an intramolecular interaction.

Introduction

Previous X-ray studies of the crystal structure of α-L-rhamnose monohydrate had been carried out by McGeachin & Beevers (1957), by Killean, Lawrence & Sharma (1971), and by Shiono (1971).

This refinement forms part of a neutron diffraction study of carbohydrates aimed at providing the accurate data relating to the hydrogen-atom positions which are necessary to understand the rules which govern the stereochemistry of the hydrogen-bonding in the crystal

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