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Structure of Sinomenine* Hydrochloride Dihydrate, $C_{19}H_{24}NO_4^+.Cl^-.2H_2O$

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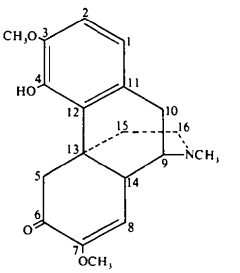
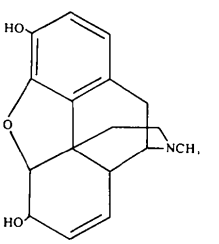
Abstract. $M_r = 401{\cdot}89$, m.p. 503–505 K, orthorhombic, $P2_12_12_1$, $a = 19{\cdot}256\ (8)$, $b = 14{\cdot}326\ (5)$, $c = 7{\cdot}224\ (3)$ Å, $Z = 4$, $V = 1992{\cdot}8\ (1{\cdot}4)$ Å^3, $D_x = 1{\cdot}339$ Mg m^{-3}. Diffractometer data were collected at 293·0 (5) K with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71073$ Å) to a limit in $(\sin\theta)/\lambda = 0{\cdot}65$ Å^{-1} and corrected for coincidence loss but not for absorption ($\mu = 0{\cdot}222$ mm^{-1}). The structure solution was initiated by the heavy-atom method with Cl positions determined from Harker sections. Least-squares refinement including H atoms converged at $R = 0{\cdot}031$ for 2512 F_o. Refinement of both enantiomers suggests that the absolute configuration of sinomenine is opposite to that of natural (−)-morphine. The sinomenine molecule has the usual T shape common to morphine alkaloids. Strain in the *A* ring of these alkaloids gives rise to aplanar distortions; the directions of the principal atomic shifts apparently depend on whether a 4,5 ether bridge is present or not. Ring *C* in sinomenine adopts a half-chair conformation with five C atoms roughly coplanar. The torsion angles in the phenylethylamine chain are 9·0 and 81·4° compared to 0·2 and −93·2°, respectively, in morphine.

Introduction. Sinomenine (I) belongs to the morphine group of alkaloids, which are derivatives of hydrophenanthrene containing a $-CH_2CH_2N(-CH_3)-$ bridge between positions 9 and 13. Morphine (II) possesses chiral centres at C atoms 5, 6, 9, 13 and 14; in sinomenine, with a carbonyl O at C(6) and no cyclic ether system, C(5) and C(6) are not chiral. The absolute configuration of natural morphine is the (−) form (Kartha, Ahmed & Barnes, 1962). For sinomenine the opposite absolute configuration was inferred from syntheses and measurements of optical rotation (Bentley & Cardwell, 1955). Sinomenine is used as starting material in a number of synthetic routes leading to (+)-morphine, (+)-codeine, and other derivatives of these bases. Unlike some of its stereochemically equivalent derivatives, sinomenine itself has only very weak analgesic properties. In large doses it is an abortifacient, and has found some therapeutic use in the treatment of rheumatism (Holmes, 1952).



(I)



(II)

We report here on the crystal structure of sinomenine hydrochloride dihydrate.

Experimental. Single crystals of sinomenine hydrochloride dihydrate were obtained from an ethanolic solution.

Cell dimensions were determined from the observed diffractometer setting angles of 18 reflections with 2θ in the range 45–55°. Repeated measurements during and after the data collection showed changes in the cell parameters less than $1{\cdot}5\sigma$. The parameters given are mean values and their errors correspond to the observed changes.

Intensity-data collection: Nb-filtered Mo $K\alpha$ radiation, four-circle diffractometer controlled by the Vanderbilt disk-oriented program system (Lenhert, 1975). Intensities measured without attenuators, maximum $(\sin\theta)/\lambda = 0{\cdot}65$ Å^{-1}, total of 2640 reflections; $\omega/2\theta$ scan mode, 1° min^{-1} in 2θ, low-angle scan width 1·2°. Backgrounds measured for 20 s at each limit of the scan. Three standard reflections measured every 60 reflections. Intensities scaled with a third-degree polynomial fitted to the normalized mean of the standards and corrected for coincidence loss. The experimental recovery constant with this crystal was $9{\cdot}6 \times 10^{-8}$ counts^{-1}. Net intensities were not corrected for absorption owing to the low absorbance of the crystal; mass absorption coefficients taken from *International Tables for X-ray Crystallography* (1974).

Of the 2640 reflections, 83 with $I < \sigma(I)$ were zero weighted; $I = C - TB$ = net intensity and $\sigma(I) = [(C' + T^2B') + S^2\ (C-TB)^2]^{1/2}$ where C is the number of counts in the peak, B is the total number of counts in the backgrounds and T is the ratio between scan time over peak and total background counting time. Primed symbols indicate measurements uncorrected for coincidence loss. The instability factor, S, was taken as 0·028

* 7,8-Didehydro-4-hydroxy-3,7-dimethoxy-17-methyl-9α,13α,-14α-morphinan-6-one.

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from an analysis of the scale-factor variance. 16 reflections were deleted due to interference of the Nb K absorption edge with the peak itself, another 29 were deleted because counting rates were beyond the range for coincidence-loss correction.

Structure determination: Initial phasing was based on the Cl atom alone with coordinates derived from Harker sections. A 13-atom fragment including seven non-H atoms in a largely correct arrangement eventually was identified. The conventional R for this model was 0·51. Identification of the remaining non-H atoms by alternating cycles of refinement and difference electron density (ΔF) maps was then straightforward and R for the isotropic model was 0·115. Following anisotropic refinement of the C, O, N and Cl atoms, all H atoms were located in a ΔF map and refined with isotropic temperature factors. The complete structure, model (p), was refined by the full-matrix least-squares method minimizing the quantity $\sum w(|F_o| - k|F_c|)^2$ with $w = \sigma^{-2}(F_o)$. The final R was 0·031. Some refinement characteristics are given in Table 1. Table 2 shows the final positional and thermal parameters for this enantiomer, and its molecular conformation is shown in Fig. 1.*

Refinement of the mirror image, model (m), which has the same absolute configuration as natural (−)-morphine, gave an $R = 0{\cdot}033$. These calculations did not converge properly inasmuch as a number of the H atoms showed oscillating behaviour. Temperature factors of all H atoms in the water molecules also increased rapidly and had to be constrained. The results (Table 1), although not definite, indicate that the correct absolute configuration of sinomenine is opposite to that of (−)-morphine, in agreement with previous assignments referred to above.

A set of local programs (Svinning & Mo, 1978) was used for analyses and reduction of the data. Other crystallographic programs were from the XRAY76 system (Stewart, 1976). Molecular drawings were made with *ORTEP* (Johnson, 1976). Atomic scattering factors were those of Doyle & Turner (1968) except for H (Stewart, Davidson & Simpson, 1965). Anomalous-dispersion values for Cl were taken from Cromer & Liberman (1970).

Discussion. *The molecular structure.* The atomic numbering and labelling of the rings (Fig. 1) is according to the scheme commonly used for morphine and related 4(axial)-phenylpiperidine derivatives (Tollenaere, Moereels & Raymaekers, 1979). The T-shaped ring system of sinomenine is similar to that of morphine, but lacks the ether bridge between C(4) and C(5). The dihedral angle between the mean planes

* Tables of structure factors, positional and thermal parameters for H, anisotropic thermal parameters for the non-H atoms and conformational details of the structure have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38068 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Refinement characteristics*

Model	(p)	(m)
(sin θ)/λ range (Å^{-1})	0–0·65	0–0·65
Number of reflections with $w \neq 0$, NO	2512	2512
Number of reflections with $w = 0$	83	83
Number of variables, NV	357	353
Scale factor, k	8·86 (2)	8·86 (2)
$R(F) = \sum\|\|F_o\| - k\|F_c\|\|/\sum\|F_o\|$	0·031	0·033
$R_w(F) = [\sum w(\|F_o\| - k\|F_c\|)^2/\sum wF_o^2]^{1/2}$	0·039	0·041
$R(F^2) = \sum\|F_o^2 - (kF_c)^2\|/\sum F_o^2$	0·046	0·050
GOF $= [\sum w(\|F_o\| - k\|F_c\|)^2/(\text{NO–NV})]^{1/2}$	2·21	2·34
Maximum shift/error, last cycle	0·14	0·70

Table 2. *Final atomic parameters for non-*H *atoms*

Coordinates are $\times 10^5$ and thermal parameters, U_{eq} (Å^2 $\times 10^4$), are calculated from $U_{eq} = \frac{1}{3}\sum U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$, where U_{ij} are defined by $T(\theta) = \exp\,[-2\pi^2(U_{11}\ a^{*2}\ h^2 + \ldots + 2U_{12}\ a^*b^*hk + \ldots)]$. E.s.d.'s are given in parentheses.

	x	y	z	U_{eq}
C(1)	41046 (8)	53881 (11)	14045 (23)	335 (7)
C(2)	34883 (8)	56993 (12)	21702 (25)	364 (8)
C(3)	34839 (8)	59829 (11)	39883 (24)	340 (8)
C(4)	40944 (8)	59865 (11)	50292 (22)	300 (7)
C(5)	55263 (8)	65190 (11)	66106 (21)	318 (7)
C(6)	55784 (8)	74041 (10)	55093 (23)	331 (8)
C(7)	59247 (7)	73326 (10)	36719 (24)	306 (7)
C(8)	61668 (7)	65189 (10)	30639 (24)	311 (7)
C(9)	59725 (7)	48180 (9)	27316 (22)	268 (7)
C(10)	53542 (8)	49769 (10)	14800 (21)	290 (7)
C(11)	47153 (7)	53742 (9)	24152 (21)	257 (6)
C(12)	47275 (7)	57008 (9)	42487 (20)	246 (6)
C(13)	54043 (7)	56632 (9)	53766 (19)	252 (6)
C(14)	60445 (7)	56215 (10)	40911 (21)	264 (7)
C(15)	54096 (8)	47572 (11)	65206 (22)	322 (7)
C(16)	53840 (8)	38989 (10)	52927 (22)	330 (7)
C(17)	22706 (10)	63116 (20)	39491 (41)	735 (15)
C(18)	63821 (10)	82028 (13)	11724 (34)	522 (11)
C(19)	59012 (9)	30705 (11)	26496 (29)	406 (9)
N	59436 (6)	39194 (8)	38378 (19)	298 (6)
O(1)	29056 (6)	62723 (11)	49335 (22)	555 (8)
O(2)	40701 (6)	62398 (10)	68545 (17)	481 (7)
O(3)	53788 (8)	81491 (9)	60958 (21)	581 (8)
O(4)	59807 (6)	81756 (7)	28210 (19)	389 (6)
O(51)	67736 (8)	27320 (12)	66980 (25)	691 (10)
O(61)	78622 (9)	60269 (12)	44473 (25)	689 (10)
Cl	76602 (3)	38446 (4)	36694 (8)	570 (3)

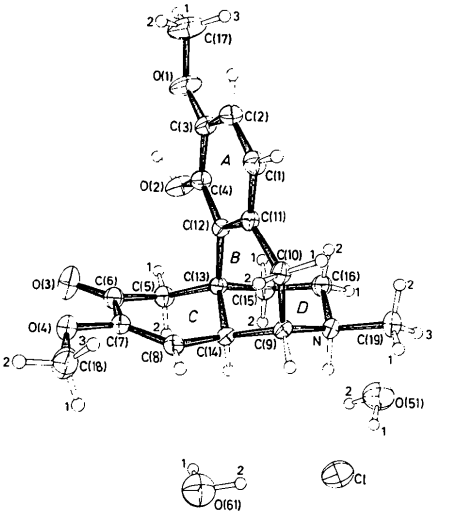

Fig. 1. Molecular conformation and atomic labelling. Sequential numbering of H atoms is given only where necessary. Thermal ellipsoids of the non-H atoms correspond to 40% probability.

through rings *A*/*B* and *C*/*D* is 87·1°, *i.e.* close to 90·9° in morphine hydrochloride trihydrate (Gylbert, 1973), 86·6° in morphine hydrate (Bye, 1976) and 88·4° in codeine hydrobromide dihydrate (Kartha *et al.*, 1962).

The phenyl ring *A* of sinomenine is not strictly planar, atomic distances from the mean ring plane ranging from −0·016 [C(11)] to +0·020 Å [C(12)]. Significantly nonplanar phenyl rings were also found in morphine (Gylbert, 1973; Bye, 1976) and closely related compounds like codeine (Kartha *et al.*, 1962), azidomorphine (Sasvári, Simon, Bognár & Makleit, 1974), oxymorphone (Sime, Dobler & Sime, 1976*a*), naloxone (Karle, 1974) and nalbuphine (Sime, Dobler & Sime, 1976*b*), all possessing a 4,5 ether bridge. On the other hand, dextromethorphan with the same chirality as sinomenine and also devoid of the ether bridge has a strictly planar ring *A* (Gylbert & Carlström, 1977). Gylbert & Carlström therefore suggested that removal of this bridge allows ring *A* to attain planarity. Sinomenine differs from dextromethorphan in the region of interest by having an OH group attached to C(4) instead of H. The O atom makes very short contacts with C(5), 2·838 (2) Å, and H(C51), 2·22 (2) Å. Thus, because of the close proximity of ring *C* it seems that any atom other than H at C(4) will involve strain in ring *A*, but the character of the resulting aplanarity will depend on whether a bridge to C(5) is formed or not. In the structures above where this bridge is present, atoms C(4) and C(11) are displaced out of the ring plane towards the C(5) side, C(12) being displaced in the opposite direction; in sinomenine these distortions are reversed.

Ring *C* in sinomenine is a half-chair with C atoms 5, 6, 7, 8 and 14 coplanar within 0·045 Å. This is an unusual conformation induced by the presence of both a carbonyl group at C(6) and the double bond C(7)–C(8). From a recent compilation of structure data on morphine and morphine-related drugs (Tollenaere *et al.*, 1979) it appears that ring *C*, as a rule, has the boat conformation when C(7)–C(8) is a double bond, but is a chair when this bond is single. Nalbuphine (Sime *et al.*, 1976*b*) with a saturated boat-shaped *C* ring is an exception to this rule. The piperidine ring *D* in sinomenine has the expected chair conformation.

Except for a change of sign, torsion angles of two characteristic atomic sequences connecting N with the phenyl ring compare well with the values of morphine (Bye, 1976) [in square brackets] below: C(11)C(12)C(13)C(15)C(16)N: −94·6 [85·8]; 61·0 [−63·1]; 52·7 [−51·5] and C(12)C(11)C(10)C(9)N: 9·0 [0·2]; 81·4° [−93·2°]. The distance from the N atom to the centre of the phenyl ring is 4·38 Å; Tollenaere *et al.* (1979) give a mean value of 4·5 (1) Å for these molecules.

Bond lengths and angles of sinomenine appear in Tables 3 and 4. Strain in the molecule is reflected in several bond angles. The angular asymmetry at C(12) and C(11) of the phenyl ring is more pronounced in sinomenine than in dextromethorphan, *cf.* C(4)C(12)C(13), C(4)C(12)C(11) and C(1)C(11)C(10) which differ by 1·7 to 0·7° in the two structures. There is also substantial deviation from tetrahedral symmetry at C(13). Except for C(12)C(13)C(5) which is the same in sinomenine and dextromethorphan, ~114·2°, the remaining bond angles at this atom show a stronger variation in the former structure, 105·0 (1)–111·2 (1)°, compared to 107·5 (5)–109·4 (5)° in the latter. The largest differences are in C(5)C(13)C(14), 3·8 (5)°, and C(5)C(13)C(15), 2·0 (5)°. The direction of these distortions is to relieve the increased repulsive strain in sinomenine due to the OH group at C(4). A quite different situation is encountered in the structures where O(2) and C(5) have pulled *together* in the formation of a bridge. Thus, there are several bond angles in the *A*/*C* region of morphine differing by 6–14° from parent angles in the sinomenine molecule, *cf.* C(1)C(11)C(10), C(4)C(12)C(13), C(11)C(12)C(13), C(12)C(13)C(5) and C(14)C(13)C(5) in Table 4. These angles and the aplanar distortions of ring *A* in morphine attest to the strain involved in closing the ether bridge.

Endocyclic angles of ring *A* in sinomenine and dextromethorphan differ over a range of 0·3–1·1° with a root-mean-square (r.m.s.) difference of 0·68°. Corresponding values for ring *B* and *D* are respectively 0·1–1·1 and 0·63°, 0·1–1·9 and 1·22°. The largest discrepancies in the *D* rings are in the angles at C(15), C(16) and N. There is an exocyclic angular asymmetry at N in sinomenine presumably caused by two contacts

Table 3. *Bond lengths* (Å) *with e.s.d.'s*

Ring *A*		Ring *C*	
C(1)–C(2)	1·383 (2)	C(13)–C(5)	1·534 (2)
C(2)–C(3)	1·375 (3)	C(5)–C(6)	1·500 (2)
C(3)–C(4)	1·396 (2)	C(6)–C(7)	1·489 (2)
C(4)–C(12)	1·404 (2)	C(7)–C(8)	1·330 (2)
C(12)–C(11)	1·405 (2)	C(8)–C(14)	1·503 (2)
C(11)–C(1)	1·384 (2)	C(6)–O(3)	1·211 (2)
C(3)–O(1)	1·371 (2)	C(7)–O(4)	1·359 (2)
O(1)–C(17)	1·416 (3)	O(4)–C(18)	1·420 (3)
C(4)–O(2)	1·368 (2)		
Ring *B*		**Ring *D***	
C(12)–C(13)	1·538 (2)	C(13)–C(15)	1·539 (2)
C(13)–C(14)	1·545 (2)	C(15)–C(16)	1·517 (2)
C(14)–C(9)	1·520 (2)	C(16)–N	1·505 (2)
C(9)–C(10)	1·512 (2)	N–C(9)	1·516 (2)
C(10)–C(11)	1·515 (2)	N–C(19)	1·491 (2)

Bonds involving H

Type	Number	Range	Mean	σ_{ave}
C–H (phenyl)	2	0·95–0·97	0·96	0·02
C–H (methyl)	9	0·86–1·02	0·95	0·03
C–H (other)	11	0·94–1·01	0·97	0·02
O–H (water)	4	0·80–1·03	0·89	0·04
O–H	1	–	0·83	0·03
N–H	1	–	0·90	0·02

Table 4. *Valency angles* (°) *with e.s.d.'s*

Endocyclic			
Ring *A*		Ring *C*	
C(11)C(1)C(2)	121·5 (2)	C(14)C(13)C(5)	105·0 (1)
C(1)C(2)C(3)	118·9 (1)		[115·7 (3)]
C(2)C(3)C(4)	120·7 (1)	C(13)C(5)C(6)	112·2 (1)
C(3)C(4)C(12)	120·9 (1)	C(5)C(6)C(7)	116·4 (1)
C(4)C(12)C(11)	117·5 (1)	C(6)C(7)C(8)	120·8 (1)
	[122·4 (4)]*	C(7)C(8)C(14)	122·1 (1)
C(12)C(11)C(1)	120·4 (1)	C(8)C(14)C(13)	112·9 (1)
	[116·9 (4)]		
Ring *B*		Ring *D*	
C(12)C(13)C(14)	111·0 (1)	C(15)C(13)C(14)	106·6 (1)
	[106·0 (3)]	C(13)C(14)C(9)	110·2 (1)
C(13)C(14)C(9)	110·2 (1)	C(14)C(9)N	107·8 (1)
C(14)C(9)C(10)	110·1 (1)	C(9)NC(16)	114·3 (1)
C(9)C(10)C(11)	115·4 (1)	NC(16)C(15)	111·7 (1)
C(10)C(11)C(12)	122·1 (1)	C(16)C(15)C(13)	111·7 (1)
C(11)C(12)C(13)	120·1 (1)		
	[127·1 (4)]		
Exocyclic			
C(1)C(11)C(10)	117·4 (1)	C(12)C(13)C(5)	114·2 (1)
	[124·4 (4)]		[100·3 (3)]
C(2)C(3)O(1)	124·8 (1)	C(12)C(13)C(15)	108·6 (1)
C(3)O(1)C(17)	117·6 (2)		[112·5 (4)]
O(1)C(3)C(4)	114·5 (2)	C(10)C(9)N	114·5 (1)
C(3)C(4)O(2)	119·4 (1)	C(5)C(6)O(3)	122·6 (2)
	[124·3 (4)]	O(3)C(6)C(7)	121·0 (1)
O(2)C(4)C(12)	119·6 (1)	C(6)C(7)O(4)	112·2 (1)
	[113·0 (3)]	C(7)O(4)C(18)	116·5 (1)
C(4)C(12)C(13)	122·2 (1)	O(4)C(7)C(8)	127·0 (2)
	[109·5 (3)]	C(8)C(14)C(9)	110·1 (1)
C(5)C(13)C(15)	111·2 (1)	C(9)NC(19)	113·0 (1)
		C(19)NC(16)	110·3 (1)

Angles involving H

Type	Number	Range	Mean	σ_{ave}
CCH (phenyl)	4	118·9–122·2	119·9	1·2
CC(8)H	2	116·6–121·3	119·0	1·2
*X*CH† (other)	25	104·3–112·6	108·8	1·2
OCH (methyl)	6	101·4–113·4	108·5	1·8
CNH	3	104·1–108·6	106·2	1·1
COH	1	–	111	2
HCH	13	99–118	109	2
HOH (water)	2	98–102	100	3

* Where two values are given, the lower (in square brackets) is from morphine hydrate (Bye, 1976).

† X = C, N.

C(3^{ix})···C(19), 3·427 (3), and C(4^{ix})···C(19), 3·558 (3) Å.*

Pairs of bonds of rings *A*, *B* and *D* in sinomenine and dextromethorphan have an r.m.s. difference of 0·012 Å, which is nearly the same for each ring. The maximum deviation is 0·027 (9) Å in C(2)–C(3).

Molecular packing

A major feature of the molecular packing (Fig. 2) is the ribbons of H-bonded water molecules and Cl atoms running along **c** roughly parallel to the (100) plane. The ribbons consist of consecutive pentagonal loops made up of three water molecules and two Cl. Each Cl is involved in H bonding with three water molecules at Cl···O distances 3·200 (2)–3·217 (2) Å; see Table 5 for details on geometry. Weaker N–H···Cl bonds with N···Cl = 3·310 (2) Å connect sinomenine molecules to the ribbons from both below and above. A second link is provided by the O(2)–H(2)···O(51) bonds in which the aromatic hydroxyl group is donor.

* The symmetry code is explained in Table 5.

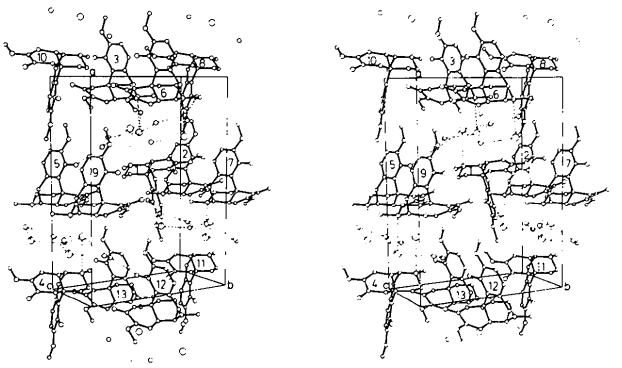

Fig. 2. Stereodrawing of the molecular packing with H bonds shown as broken lines. The molecular numbering corresponds to the symmetry code given in Table 5. (Arabic numerals are used in this figure to improve clarity.)

Table 5. *The geometry of the hydrogen-bonding system*

Symmetry code

(i) x, y, z	(viii) $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$
(ii) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$	(ix) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$
(iii) $\frac{3}{2}-x, 1-y, \frac{1}{2}+z$	(x) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$
(iv) $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$	(xi) $-\frac{1}{2}+x, \frac{3}{2}-y, 1-z$
(v) $1-x, -\frac{1}{2}+y, \frac{3}{2}-z$	(xii) $\frac{1}{2}-x, 1-y, -\frac{1}{2}+z$
(vi) $\frac{3}{2}-x, 1-y, -\frac{1}{2}+z$	(xiii) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$
(vii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$	

D–H···*A*	*D*···*A* (Å)	H···*A* (Å)	$(H\cdots A)^*_{corr}$ (Å)	$\angle(DHA)^*_{corr}$ (°)
N–H···Cl^{i}	3·310 (2)	2·56 (2)	2·45	139
O(2)–H(O2)···O(51^{ii})	2·882 (2)	2·11 (3)	1·98	153
O(51)–H(O512)···O(61^{iii})	2·756 (3)	1·74 (4)	1·79	169
O(51)–H(O511)···Cl^{i}	3·200 (2)	2·40 (4)	2·26	161
O(61)–H(O612)···Cl^{i}	3·200 (2)	2·41 (3)	2·22	176
O(61)–H(O611)···Cl^{iii}	3·217 (2)	2·31 (4)	2·25	171

* Distances and angles involving H have been recalculated assuming lengths 0·98 Å for the O–H (Brown & Levy, 1973) and 1·045 Å for the N(sp^3)–H bonds (Jönsson & Kvick, 1972; Kvick, Al-Karaghouli & Koetzle, 1977).

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Structure of σ(+)-5-Bromo-6,9-bis(dimethylsulphido)-*nido*-decaborane(12), $C_4H_{23}B_{10}BrS_2$, Determined with a Twinned Crystal

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Abstract. $M_r = 323{\cdot}5$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}181\ (3)$, $b = 9{\cdot}181\ (3)$, $c = 19{\cdot}447\ (5)$ Å, $V = 1639{\cdot}2\ (8)$ Å^3, $Z = 4$, $D_m = 1{\cdot}31$, $D_x = 1{\cdot}31$ Mg m^{-3}, Mo $K\alpha$ ($\lambda = 0{\cdot}71073$ Å), $\mu = 2{\cdot}70$ mm^{-1}, $F(000) = 656$, room temperature, final $R = 0{\cdot}069$ for 1232 observed reflections. The crystal used for structure determination was a twin [twin fraction $\alpha = 0{\cdot}377\ (4)$] with coinciding tetragonal lattices. The crystal structure of this twin was solved by a modified heavy-atom method. Determination of the absolute configuration was based upon the anomalous scattering of the Br atom.

Introduction. The present study reports on the X-ray investigation of $BrB_{10}H_{11}[S(CH_3)_2]_2$ previously prepared (Plešek, Heřmánek & Štíbr, 1969). This compound is the first example of optical isomerism in the decaborane series.

Experimental. Colourless crystals, stable in air and to X-rays, flotation method for D_m, crystal $0{\cdot}4 \times 0{\cdot}4 \times 0{\cdot}3$ mm, preliminary lattice constants and space group from photographs (Cu $K\alpha$ radiation), all parameters refined from 29 reflections centred on the diffractometer; lattice exhibits tetragonal symmetry because a and b are equal within the limits of the error of measurement; differences in intensities of a few pseudotetragonal equivalent reflections (see Fig. 1) exceeded the measuring error, so crystallographic system and space group are as in *Abstract*; Hilger & Watts four-circle diffractometer, Mo $K\alpha$ radiation, ω–2θ scan, $2\theta \leq 54°$, scan speed 1 to 4° min^{-1}, rapid prescan, scanning interval 2°, one standard reflection, no significant variation, 2058 measured independent reflections, 826 unobserved reflections [$I < 1{\cdot}96\sigma(I)$]; for unobserved reflections $F_{unobs} = \frac{2}{3}F_{min}$ and $\sigma(F_{unobs}) = (1/\sqrt{18})F_{min}$ (F_{min} is the minimum observable value of F); Lp correction, no absorption or extinction correction.

Heavy-atom method was used, but all the main peaks and their heights in a three-dimensional Patterson synthesis could not be explained satisfactorily.

The consequence of the equality of the a and b parameters as mentioned above is that the point symmetry of the lattice is $4/m\ 2/m\ 2/m$ (D_{4h}) and therefore higher than the point symmetry of the structure, which is 222 (D_2). This means that the necessary condition for twinning with superimposed reciprocal lattices is fulfilled. No sample showed disorder effects, such as splitting of the diffraction spots or diffuse reflections either on Weissenberg photographs or in the diffractometer measurements. Therefore we assumed the existence of two individuals related by a fourfold axis in the **c** direction (this rotation as twinning operation). These two individuals contribute independently to each measured intensity I_{hkl} (Catti & Ferraris, 1976). Thus we have

$$I_{hkl} = (1 - \alpha)\, J_{hkl} + \alpha J_{\bar{k}hl}, \qquad (1)$$

where J_{hkl} are the intensities which an untwinned crystal of the same total volume would give, α is the fraction of the smaller individual.

The relation (1) leads to the conclusion that our Patterson map is a weighted sum of Patterson maps of

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