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The Structure of Multiflorine Perchlorate Hemihydrate

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Abstract

Multiflorine perchlorate hemihydrate, $C_{15}H_{23}N_2O^+.ClO_4^-.\frac{1}{2}H_2O$, M_r = 355·9, is orthorhombic, $P2_12_12_1$, with a = 12·648 (2), b = 23·744 (4), c = 11·304 (2) Å, Z = 8, D_m = 1·36, D_c = 1·39 Mg m^{-3}, V = 3394·5 Å^3 and μ(Cu $K\alpha$) = 2·28 mm^{-1}. The structure was solved by direct methods and refined by least-squares calculations to an R of 0·074 for 1987 unique diffractometer data. Ring C in the multiflorine cation has a chair conformation. The molecules are linked by a system of hydrogen bonds, N(16′)$^+$(Ib)···O(Ia) and N(16)$^+$(Ia)···O(water)···O′(Ib), to form infinite chains.

Introduction

A study of the structure and stereochemistry of various sparteine derivatives has revealed that these compounds contain two quinolizidine systems fused together: the rigid A/B system, and the C/D system which is susceptible to configurational–conformational changes. However, unequivocal determination of the conformations of the individual rings and of factors which may influence the conformation of the C/D system is difficult if only the chemical and spectroscopic data are taken into account.

Therefore, an X-ray analysis of multiflorine (Δ^2-dehydro-4-oxosparteine) monoperchlorate hemihydrate (Fig. 1) has been undertaken to obtain an accurate description of the geometry of the sparteine skeleton in crystals of this compound and to survey the molecular distortion resulting from the introduction of the conjugated bond system into ring A. Also, it should be possible to determine whether these changes in ring A influence the conformation of the C/D fragment.

The crystals were obtained by recrystallization from n-hexane solution. Systematic absences indicated space group $P2_12_12_1$. The unit-cell parameters were refined by a least-squares fit of 2θ, ω and χ settings for 15 diffractometer reflexions. 2642 independent reflexions were collected with a crystal of dimensions 0·08 × 0·15 × 0·25 mm on a Syntex $P2_1$ diffractometer to $2\theta_{\max}$ = 115°, using graphite-monochromated Cu $K\alpha$ radiation (λ = 1·54178 Å) and the θ–2θ scan technique with a variable scan rate (2–29·30° min^{-1}). Two standard reflexions monitored every 30 reflexions showed no significant change in intensity during the data collection. Intensities, of which 1987 had $I \geq 1{\cdot}96\sigma(I)$ and were considered observed, were corrected for Lorentz and polarization factors, but no correction for absorption effects was made.

The structure was solved using *MULTAN* (Germain, Main & Woolfson, 1971) with 228 E's ≥ 1·55. In the E map based on the set of phases with the best figures of merit all the non-hydrogen atoms were located. Full-matrix least-squares refinement of their positional and thermal parameters converged for the anisotropic model to an R value of 0·096. At this stage two successive ΔF maps revealed the positions of 40 of the 48 H atoms. The positions of the remaining eight H atoms were generated from the positions of the atoms to which they were bonded. H atoms were assigned B values of 5 Å^2 and their parameters were included in the structure factor calculations, but were not refined. Full-matrix least-squares refinement converged at R = 0·074 and R_w = 0·096, where $R = \sum(|F_o| - |F_c|)/\sum|F_o|$, $R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$. The function minimized in the least-squares calculations was: $\sum w(F_o - F_c)^2$. The weighting scheme used was: $w = (F_o/F_{\rm low})^2$ if $|F_o| < F_{\rm low}$; $w = 1$ if $F_{\rm low} \leq |F_o| \leq F_{\rm high}$; $w = (F_{\rm high}/F_o)^2$ if $|F_o| > F_{\rm high}$, with $F_{\rm low} = 11$ and $F_{\rm high} = 22$. Final positional parameters are given in Table 1.*

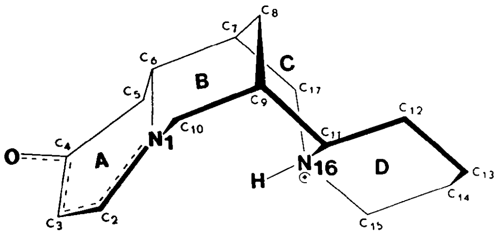

Fig. 1. The multiflorine cation (I).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35176 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final fractional atomic coordinates* ($\times 10^4$, $\times 10^3$ *for* H *atoms*) *and* B_{eq} (Å^2) *for non-hydrogen atoms*

B_{iso} for all H atoms is 5·0 Å^2.

	x	y	z	B_{eq}		x	y	z	B_{eq}
N(1)	870 (7)	4044 (3)	−825 (7)	3·5 (2)	N(1′)	2847 (7)	539 (3)	4115 (7)	3·6 (2)
C(2)	603 (9)	4286 (5)	−1863 (10)	4·0 (3)	C(2′)	2949 (8)	−23 (4)	4346 (9)	3·6 (3)
C(3)	62 (9)	4785 (5)	−1970 (9)	3·7 (3)	C(3′)	3572 (8)	−251 (4)	5187 (11)	3·9 (3)
C(4)	−250 (8)	5097 (4)	−950 (10)	3·7 (3)	C(4′)	4134 (8)	104 (4)	5999 (10)	3·4 (3)
C(5)	320 (9)	492 (4)	169 (10)	3·9 (3)	C(5′)	3860 (8)	709 (5)	5909 (9)	3·7 (3)
C(6)	396 (8)	4274 (4)	261 (9)	3·5 (3)	C(6′)	3660 (7)	889 (4)	4650 (9)	3·4 (3)
C(7)	989 (9)	4078 (4)	1349 (9)	3·9 (3)	C(7′)	3358 (8)	1520 (4)	4504 (10)	3·5 (3)
C(8)	938 (9)	3425 (5)	1403 (11)	4·5 (3)	C(8′)	3181 (9)	1639 (5)	3205 (11)	4·5 (3)
C(9)	1513 (8)	3214 (4)	291 (11)	4·2 (3)	C(9′)	2241 (9)	1325 (5)	2816 (9)	4·1 (3)
C(10)	986 (9)	3413 (4)	−825 (11)	4·5 (3)	C(10′)	2433 (9)	687 (5)	2906 (8)	4·4 (3)
C(11)	2682 (8)	3336 (4)	349 (9)	3·1 (3)	C(11′)	1244 (9)	1504 (5)	3488 (11)	4·5 (3)
C(12)	3240 (8)	3033 (4)	1358 (9)	3·6 (3)	C(12′)	844 (13)	2107 (6)	3109 (12)	6·7 (4)
C(13)	4416 (9)	3192 (6)	1407 (10)	5·1 (3)	C(13′)	−124 (11)	2271 (5)	3813 (16)	6·6 (4)
C(14)	4518 (9)	3828 (5)	1638 (11)	13·8 (3)	C(14′)	116 (12)	2238 (5)	5125 (16)	7·3 (5)
C(15)	3989 (9)	4115 (5)	620 (10)	4·2 (3)	C(15′)	458 (11)	1670 (5)	5461 (12)	5·9 (4)
N(16)	2840 (6)	3988 (3)	476 (7)	3·3 (2)	N(16′)	1399 (7)	1457 (3)	4791 (8)	3·8 (3)
C(17)	2145 (10)	4250 (4)	1417 (9)	4·1 (3)	C(17′)	2402 (10)	1722 (4)	5216 (9)	4·4 (3)
O	−871 (6)	5490 (3)	−986 (7)	4·7 (2)	O′	4725 (6)	−80 (4)	6754 (7)	5·0 (3)
Cl	7642 (3)	3213 (1)	1073 (3)	5·3 (1)	Cl′	7151 (3)	1231 (2)	4935 (3)	6·7 (1)
O(1)	7923 (13)	3698 (4)	1679 (9)	9·8 (4)	O(1′)	7619 (14)	1583 (14)	5706 (14)	21·5 (13)
O(2)	6915 (12)	3269 (5)	126 (11)	10·0 (4)	O(2′)	7653 (23)	1178 (18)	4034 (20)	27·3 (18)
O(3)	7050 (14)	2838 (6)	1816 (13)	12·7 (6)	O(3′)	6258 (18)	1377 (14)	4743 (43)	28·6 (21)
O(4)	8480 (12)	2889 (10)	862 (26)	21·1 (11)	O(4′)	6823 (42)	688 (15)	5269 (43)	34·5 (26)
O(*W*)	8173 (8)	599 (6)	1899 (9)	9·5 (4)					
H(21)	80	405	−273		H(21′)	249	−30	382	
H(31)	−9	490	−277		H(31′)	360	−70	522	
H(51)	113	497	−17		H(51′)	300	75	63	
H(52)	0	511	90		H(52′)	447	93	633	
H(61)	44	412	43		H(61′)	433	81	421	
H(71)	66	414	213		H(71′)	400	181	488	
H(81)	23	328	133		H(81′)	328	207	320	
H(82)	125	331	225		H(82′)	382	153	285	
H(91)	149	275	38		H(91′)	211	138	191	
H(101)	144	322	−156		H(101′)	292	52	227	
H(102)	25	325	−100		H(102′)	166	47	295	
H(111)	302	306	−39		H(111′)	65	121	328	
H(121)	291	317	226		H(121′)	69	207	214	
H(122)	314	260	121		H(122′)	142	244	329	
H(131)	486	309	204		H(131′)	−26	263	356	
H(132)	465	300	61		H(132′)	−79	200	366	
H(141)	406	391	241		H(141′)	56	255	512	
H(142)	530	397	172		H(142′)	−43	238	551	
H(151)	390	449	64		H(151′)	94	172	629	
H(152)	425	413	−25		H(152′)	−30	142	567	
H(161)	281	416	−44		H(161′)	149	104	490	
H(171)	226	461	145		H(171′)	275	170	605	
H(172)	258	415	219		H(172′)	236	217	528	
H(*W*1)	886	90	197						
H(*W*2)	872	27	174						

Discussion

The bond lengths and valency angles for the two crystallographically independent molecules are given in Tables 2 and 3. A detailed discussion of these lengths and angles is not warranted because their standard deviations are rather high. On the whole, these dimensions are comparable, within experimental error, with those found in other sparteine derivatives with the exception of the values for ring *A*.

In ring *A* the values for bonds C(4)—C(3) are 1·427 (15) Å for (I*a*) and 1·435 (15) Å for (I*b*); these are significantly smaller than the commonly accepted C_{sp^2}—C_{sp^2} single-bond value of 1·49 (1) Å (Kennard *et al.*, 1972). Both C(3)—C(2) bonds [1·373 (16) Å for (I*a*), 1·348 (15) Å for (I*b*)] are longer than the accepted average C_{sp^2}=C_{sp^2} distance of 1·337 (16) Å (Kennard *et al.*, 1972). The C(2)—N(1) distances [1·349 (14) Å for (I*a*) and 1·367 (12) Å for (I*b*)] are in good agreement with the value of 1·352 (5) Å (Kennard *et al.*,

Table 2. *Intramolecular distances* (Å) *with their e.s.d.'s*

	(I*a*)	(I*b*)		(I*a*)	(I*b*)		(I*a*)	(I*b*)
N(1)–C(2)	1·349 (14)	1·367 (12)	C(8)–C(9)	1·536 (17)	1·472 (16)	C(15)–C(14)	1·495 (16)	1·465 (18)
C(2)–C(3)	1·373 (16)	1·348 (15)	C(9)–C(10)	1·503 (17)	1·537 (15)	C(14)–C(13)	1·538 (18)	1·516 (25)
C(3)–C(4)	1·427 (15)	1·435 (15)	C(10)–N(1)	1·507 (13)	1·505 (13)	C(13)–C(12)	1·535 (15)	1·511 (22)
C(4)–O	1·220 (13)	1·216 (13)	C(7)–C(17)	1·520 (17)	1·530 (16)	C(12)–C(11)	1·522 (14)	1·578 (18)
C(4)–C(5)	1·518 (15)	1·480 (15)	C(17)–N(16)	1·515 (13)	1·495 (15)	Cl–O(1)	1·386 (11)	1·346 (25)
C(5)–C(6)	1·529 (13)	1·507 (14)	N(16)–C(11)	1·567 (12)	1·489 (15)	Cl–O(2)	1·417 (13)	1·207 (25)
C(6)–C(7)	1·515 (15)	1·555 (14)	C(11)–C(9)	1·507 (14)	1·533 (16)	Cl–O(3)	1·435 (16)	1·202 (25)
C(6)–N(1)	1·471 (13)	1·454 (13)	N(16)–C(15)	1·494 (14)	1·498 (16)	Cl–O(4)	1·332 (19)	1·404 (39)
C(7)–C(8)	1·551 (16)	1·513 (17)						

Table 3. *Bond angles* (°) *with their e.s.d's*

	(I*a*)	(I*b*)		(I*a*)	(I*b*)		(I*a*)	(I*b*)
N(1)–C(2)–C(3)	124·6 (10)	125·5 (9)	C(8)–C(7)–C(17)	107·9 (9)	109·5 (9)	C(13)–C(14)–C(15)	106·2 (9)	111·1 (12)
C(2)–C(3)–C(4)	121·0 (10)	120·4 (10)	C(6)–C(7)–C(17)	115·7 (9)	116·2 (9)	C(14)–C(15)–N(16)	115·3 (9)	114·5 (11)
C(3)–C(4)–C(5)	113·2 (9)	114·2 (9)	C(7)–C(8)–C(9)	106·0 (9)	108·4 (9)	C(15)–N(16)–C(17)	113·9 (8)	111·6 (9)
C(5)–C(4)–O	123·4 (10)	122·8 (10)	C(8)–C(9)–C(10)	112·0 (9)	110·6 (9)	C(15)–N(16)–C(11)	109·5 (7)	111·7 (9)
C(3)–C(4)–O	123·3 (10)	122·8 (10)	C(8)–C(9)–C(11)	111·5 (9)	112·1 (9)	C(11)–N(16)–C(17)	113·4 (7)	113·5 (8)
C(4)–C(5)–C(6)	111·7 (9)	112·3 (9)	C(10)–C(9)–C(11)	114·3 (9)	111·8 (9)	C(7)–C(17)–N(16)	114·4 (8)	111·7 (9)
C(5)–C(6)–N(1)	109·8 (8)	110·5 (8)	N(1)–C(10)–C(9)	110·8 (9)	110·2 (8)	O(1)–Cl–O(2)	117·5 (8)	112·3 (19)
C(5)–C(6)–C(7)	113·2 (8)	114·5 (8)	C(9)–C(11)–N(16)	108·6 (8)	111·2 (9)	O(1)–Cl–O(3)	111·1 (8)	110·5 (20)
C(7)–C(6)–N(1)	111·2 (8)	109·4 (8)	C(9)–C(11)–C(12)	113·3 (8)	112·4 (10)	O(2)–Cl–O(3)	99·4 (8)	111·9 (23)
C(6)–N(1)–C(2)	117·8 (8)	114·3 (8)	C(12)–C(11)–N(16)	109·8 (8)	112·2 (10)	O(1)–Cl–O(4)	111·4 (12)	121·8 (22)
C(6)–N(1)–C(10)	114·2 (8)	119·4 (8)	C(11)–C(12)–C(13)	111·1 (9)	110·5 (11)	O(2)–Cl–O(4)	115·8 (12)	106·7 (25)
C(2)–N(1)–C(10)	116·6 (9)	115·7 (8)	C(12)–C(13)–C(14)	109·2 (10)	109·9 (12)	O(3)–Cl–O(4)	99·2 (12)	92·1 (26)
C(6)–C(7)–C(8)	108·6 (9)	108·7 (9)						

1972) which is characteristic for a partial double bond in heterocyclic systems showing *p*–*π* overlap between the N atom free electron pair and the double bonds. All the above facts indicate noticeable conjugation in the $\mathrm{N(1)}\overset{\cdots}{-}\mathrm{C(2)}\overset{\cdots}{-}\mathrm{C(3)}\overset{\cdots}{-}\mathrm{C(4)}\overset{\cdots}{-}\mathrm{O}$ bond system. This is confirmed by the least-squares-plane calculations reported in Table 4, which indicate that the N(1), C(2), C(3), C(4), O systems in both cations are nearly planar.

The sparteine skeleton has the expected *trans*/*cis* configuration (Wiewiórowski & Wolińska-Mocydlarz, 1961). The conformations of the individual rings are described in terms of the torsion angles listed in Table 5 and the asymmetry parameters (Duax & Norton, 1975; Duax, Weeks & Rohrer, 1976) given in Table 6. In the two independent cations, ring *A* is observed in a slightly distorted half-chair conformation. The displacements of C(5) and C(6) from the least-squares planes through N(1), C(2), C(3) and C(4) are: 0·40 (1) and −0·27 (1) Å for (I*a*) and 0·43 (1) and −0·25 (1) Å for (I*b*) respectively. The rotation symmetry about a line joining the midpoints of the C(2)–C(3) and C(5)–C(6) bonds is reflected in the small values of the $\Delta C_2^{2,3}$ asymmetry parameter: 4·7° (I*a*) and 7·3° (I*b*).

Table 4. *Selected least-squares planes*

Atoms defining the planes, their equations and χ^2

Plane (1*a*): N(1), C(2), C(3), C(4)

$$0{\cdot}8698x + 0{\cdot}4931y - 0{\cdot}0146z - 5{\cdot}7067 = 0$$
$$\chi^2 = 0{\cdot}48$$

Plane (2*a*): N(1), C(2), C(3), C(4), O

$$-0{\cdot}8452x - 0{\cdot}5337y - 0{\cdot}0290z + 6{\cdot}0414 = 0$$
$$\chi^2 = 185{\cdot}62$$

Plane (1*b*): N(1′), C(2′), C(3′), C(4′)

$$0{\cdot}7847x - 0{\cdot}0251y - 0{\cdot}6194z + 0{\cdot}0947 = 0$$
$$\chi^2 = 10{\cdot}33$$

Plane (2*b*): N(1′), C(2′), C(3′), C(4′), O′

$$0{\cdot}7753x - 0{\cdot}0308y - 0{\cdot}6309z + 0{\cdot}1928 = 0$$
$$\chi^2 = 23{\cdot}63$$

Displacements from planes (Å)

	Plane (1*a*)	Plane (2*a*)		Plane (1*b*)	Plane (2*b*)
N(1)	−0·001 (8)	0·015 (8)	N(1′)	−0·007 (8)	0·010 (8)
C(2)	0·005 (11)	0·027 (11)	C(2′)	−0·020 (10)	−0·013 (10)
C(3)	−0·005 (11)	−0·022 (11)	C(3′)	0·023 (11)	0·015 (11)
C(4)	0·002 (10)	−0·119 (10)	C(4′)	−0·010 (10)	−0·040 (10)
O	−0·221 (8)	0·048 (8)	O′	0·059 (8)	0·015 (8)

The conformations of ring *B* in the two crystallographically independent cations are found to differ significantly; in both cases ring *B* adopts the distorted chair conformation but the modes of distortion are different. In the (I*a*) cation distortion involves the loss of the mirror plane, $\Delta C_s^6 = 9{\cdot}2°$, with retention of the orthogonal nearly perfect rotation symmetry, $\Delta C_2^{1,10} = 0{\cdot}7°$ (the ring is twisted); in the (I*b*) cation the mirror plane, $\Delta C_s^1 = 3{\cdot}8°$, is retained at the expense of rotation symmetry, $\Delta C_2^{6,7} = 17{\cdot}9°$ [the ring is flattened at N(1)].

The differences between the two cations in the conformation of ring *C* are much less pronounced.

Both *C* rings are observed as distorted chairs and in both cases distortion involves the loss of the rotation symmetry, $\Delta C_2^{7,17} = 18{\cdot}1°$ (I*a*) and 11·6° (I*b*), indicating flattening at N(16).

All the asymmetry parameters of the *D* rings have low values, showing nearly ideal chair conformations.

The unit-cell packing, with hydrogen bonds indicated, is shown in Fig. 2. Cations form infinite, twisted, hydrogen-bonded chains. The adjacent structural fragments (consisting of two independent cations and one water molecule) are translationally related (translation along **a**). Parameters of the intermolecular hydrogen bonds are listed in Table 7. A schematic drawing of the hydrogen-bond system viewed along the *c* axis is given in Fig. 3.

Analysis of the intramolecular distances N(1)···N(16) [2·896 (11) Å (I*a*), 2·947 (12) Å (I*b*)], H(161)···N(1) [2·51 Å (I*a*), 2·27 Å (I*b*)] and angles N(16)—H(161)—N(1) [99·1° (I*a*), 123·3° (I*b*)] might suggest the existence of an intramolecular hydrogen bond also. In such a case the molecules would be linked by bifurcated hydrogen bonds. However, the observed participation of N(1) in the conjugated bond system [N(1), C(2), C(3), C(4), O – see above] as well as a comparison of the N(1)···N(16) distances with those found in similar twin-chair systems having two *cis*-orientated lone pairs at the N atoms (Table 8) suggest that such a possibility is very unlikely.

A comparative analysis of the conformational data for the present structure and for the structure of sparteine monoperchlorate (Borowiak, Bokii &

Table 5. *Torsion angles* (°)

	Molecule (I*a*)	Molecule (I*b*)
Ring *A*		
N(1)—C(2)—C(3)—C(4)	1·2 (12)	5·3 (13)
C(2)—C(3)—C(4)—O	−167·8 (14)	−178·2 (13)
C(2)—C(3)—C(4)—C(5)	15·7 (12)	6·9 (13)
C(3)—C(4)—C(5)—C(6)	−42·8 (12)	−36·7 (11)
C(4)—C(5)—C(6)—N(1)	53·4 (11)	55·4 (11)
C(5)—C(6)—N(1)—C(2)	−38·0 (11)	−43·7 (11)
C(6)—N(1)—C(2)—C(3)	11·1 (13)	14·5 (12)
Ring *B*		
N(1)—C(6)—C(7)—C(8)	−60·4 (11)	−55·3 (10)
C(6)—C(7)—C(8)—C(9)	62·8 (12)	66·4 (12)
C(7)—C(8)—C(9)—C(10)	−61·2 (11)	−64·4 (11)
C(8)—C(9)—C(10)—N(1)	54·4 (12)	50·8 (10)
C(9)—C(10)—N(1)—C(6)	−49·9 (12)	−43·6 (11)
C(10)—N(1)—C(6)—C(7)	53·7 (10)	46·1 (10)
Ring *C*		
C(9)—C(11)—N(16)—C(17)	47·7 (9)	48·6 (13)
C(11)—N(16)—C(17)—C(7)	−48·3 (10)	−50·7 (11)
N(16)—C(17)—C(7)—C(8)	56·0 (13)	56·6 (12)
C(17)—C(7)—C(8)—C(9)	−63·4 (10)	−61·4 (13)
C(7)—C(8)—C(9)—C(11)	68·3 (10)	61·1 (12)
C(8)—C(9)—C(11)—N(16)	−59·0 (12)	−54·7 (13)
Ring *D*		
N(16)—C(11)—C(12)—C(13)	−55·9 (10)	−52·6 (13)
C(11)—C(12)—C(13)—C(14)	61·8 (13)	55·7 (15)
C(12)—C(13)—C(14)—C(15)	−60·9 (11)	−58·2 (16)
C(13)—C(14)—C(15)—N(16)	61·2 (11)	56·6 (15)
C(14)—C(15)—N(16)—C(11)	−57·0 (13)	−52·4 (14)
C(15)—N(16)—C(11)—C(12)	51·6 (9)	49·1 (13)

Table 6. *Asymmetry parameters* (°)

	Molecule (I*a*)	Molecule (I*b*)
Ring *A*	$\Delta C_2^{2,3} = 4{\cdot}7$	$\Delta C_2^{2,3} = 7{\cdot}3$
	$\Delta C_s^{2} = 15{\cdot}3$	$\Delta C_s^{3} = 14{\cdot}5$
	$\Delta C_s^{1} = 37{\cdot}3$	$\Delta C_s^{1} = 37{\cdot}6$
Ring *B*	$\Delta C_2^{1,10} = 0{\cdot}7$	$\Delta C_s^{1} = 3{\cdot}8$
	$\Delta C_s^{1} = 4{\cdot}2$	$\Delta C_2^{1,10} = 7{\cdot}2$
	$\Delta C_s^{6} = 9{\cdot}2$	$\Delta C_2^{6,7} = 17{\cdot}9$
Ring *C*	$\Delta C_s^{8} = 3{\cdot}4$	$\Delta C_s^{8} = 1{\cdot}7$
	$\Delta C_2^{8,9} = 6{\cdot}6$	$\Delta C_s^{7,8} = 4{\cdot}2$
	$\Delta C_2^{7,17} = 18{\cdot}1$	$\Delta C_2^{7,17} = 11{\cdot}6$
Ring *D*	$\Delta C_2^{11,16} = 0{\cdot}9$	$\Delta C_2^{11,16} = 0{\cdot}6$
	$\Delta C_s^{11} = 3{\cdot}8$	$\Delta C_s^{11} = 2{\cdot}9$
	$\Delta C_s^{12} = 6{\cdot}8$	$\Delta C_s^{12} = 6{\cdot}1$

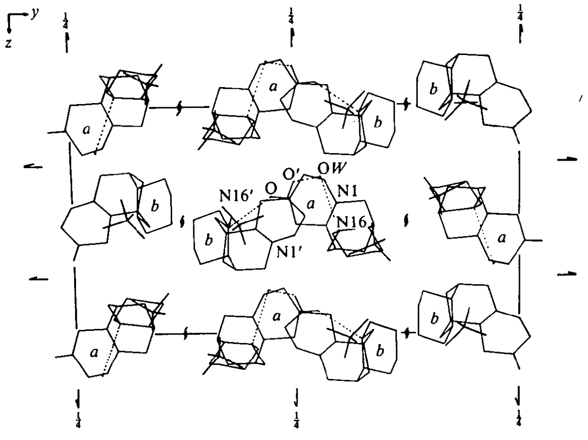

Fig. 2. Projection of the structure along **a**.

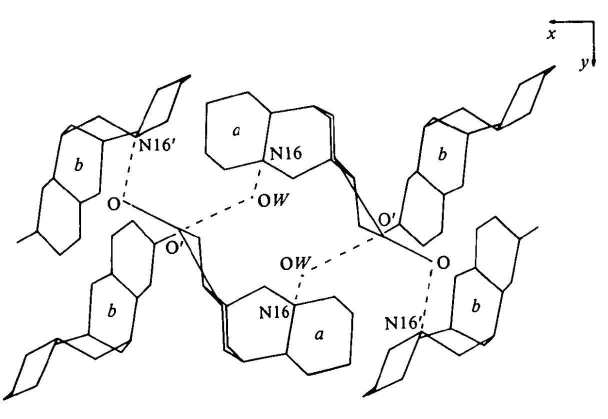

Fig. 3. A schematic drawing of the hydrogen-bond system viewed along **c**.

Table 7. *Hydrogen-bonding parameters*

D–H$\cdots A$	$D\cdots A$ (Å)	D–H (Å)	H$\cdots A$ (Å)	$\angle D$–H$\cdots A$ (°)
N(16)–H(161)$\cdots$O(W)$^{\rm i}$	2·889 (14)	1·11	1·81	163·3
O(W)–H(OW)$\cdots$O′$^{\rm ii}$	2·936 (14)	1·06	2·02	142·6
N(16′)–H(161′)$\cdots$O$^{\rm iii}$	2·748 (11)	1·01	1·95	133·9

Symmetry code

(i) $-\frac{1}{2}+x, \frac{1}{2}-y, -z$
(ii) $\frac{3}{2}-x, -y, -\frac{1}{2}+z$
(iii) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$

Table 8. *Comparison of* N(1)$\cdots$N(16) *distances in various sparteine derivatives*

Compound	N(1)$\cdots$N(16) (Å)	Reference
11-Cyano-α-isolupanine	2·883 (4)	(1)
13-β-Hydroxy-α-isolupanine	2·870 (5)	(2)
13-α-Hydroxy-α-isolupanine	2·895 (6)	(3)
Multiflorine perchlorate	2·896 (11) [molecule (I*a*)]	(4)
hemihydrate	2·947 (12) [molecule (I*b*)]	(4)

References: (1) Rychlewska & Wiewiórowski (1980); (2) Pyżalska & Borowiak (1980); (3) Pyżalska, Gawron & Borowiak (1980); (4) this work.

Struchkov, 1973) indicates that the structural modifications introduced into ring *A* in the case of multiflorine perchlorate hemihydrate do not cause any long-range conformational effects in the sparteine skeleton for the *C*/*D* fragment. The conformation is the same in all these cases.

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The Structure of an Optically Active Form of *O*-Tetramethylhaematoxylin

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Abstract

Crystals of (+)-*O*-tetramethylhaematoxylin, $C_{20}H_{22}O_6$, are orthorhombic, space group $P2_12_12_1$, with $a = 8{\cdot}545\ (2)$, $b = 8{\cdot}838\ (1)$, $c = 24{\cdot}022\ (11)$ Å, $Z = 4$. Refinement with 1430 diffractometer data converged to $R = 0{\cdot}053$. The tetracyclic molecule has an approximate propeller shape with the aromatic rings mutually inclined at 61·7 (4)°. The dihydropyran ring has a skewed conformation with four adjacent atoms coplanar within ±0·004 Å and the other two 0·418 (5) and 0·307 (5) Å above and below the plane respectively. The cyclopentene ring is an envelope with the out-of-plane atom 0·503 (5) Å from the mean plane of the other four. The cyclopentene and dihydropyran rings are *cis* fused.

Introduction

(+)-*O*-Tetramethylhaematoxylin (I), $C_{20}H_{22}O_6$, is a derivative of the naturally occurring (+)-haematoxylin, $C_{16}H_{14}O_6$, isolated by Chevreul (1810) from Logwood which occurs in *Haematoxylon campechianum* (family

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