

The oxygen atoms of the nitro groups of adjacent columns fit in with each other to give a contact in the same manner as the hydrogen atoms in n-hexatriacontane.

The rather low melting point of the present compound may be attributable to the lack of an intermolecular hydrogen bond.

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Molecular and Crystal Structure of the Alkaloid Vindolinine

BY CLAUDE RICHE AND CLAUDINE PASCARD-BILLY

Institut de Chimie des Substances Naturelles du CNRS, 91190 Gif/Yvette, France

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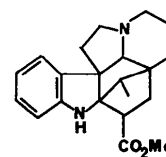
The dihydroindole alkaloid vindolinine forms a hemihydrochloride hemiperchlorate $C_{21}H_{25}N_2O_2 \cdot (ClO_4)_{0.5} \cdot Cl_{0.5}$ which crystallizes in the monoclinic space group *C2* with: $a=18.181$ (5), $b=8.959$ (4), $c=14.765$ (3) Å, $\beta=124.7$ (2)°, $Z=4$ and $V=1976$ Å³. Intensities for 2138 independent reflexions (1975 above the background) were measured on Weissenberg photographs. The structure was solved by direct methods and full-matrix least-squares refinement led to a final *R* value of 0.072. Two anions of different type appear on two separate twofold axes. One of these is the expected ClO_4^- ion, the second being an unexpected Cl^- ion. The latter is trapped between two molecules of vindolinine by strong hydrogen bonds: $N(4)-H \cdots Cl^-$ (3.07 Å). The perchlorate ion participates in two symmetrical hydrogen bonds $N(1)-H \cdots O$ of 3.05 Å. The X-ray results confirm the revised structure of vindolinine and establish the stereochemistry.

Introduction

Vindolinine is an alkaloid extracted from a variety of *Catharanthus* species (Janot, Le Men & Fan, 1959; Gorman, Neuss, Svoboda & Barnes, 1959) to which structure (I) had been assigned some time ago, mostly on the basis of mass-spectra analyses (Djerassi *et al.*, 1962; Djerassi, Cereghetti, Budzikiewicz, Janot, Plat & Le Men, 1964). Recently a ¹³C NMR analysis of vindolinine led to the allocation of the revised planar formula (II) to this alkaloid (Ahond *et al.*, 1974). The present X-ray determination was undertaken to confirm this formula and to establish the stereochemistry of vindolinine.*



(I)



(II)

The absolute configuration was deduced from a chemical correlation with (–)-vincadifformine (Rasoanaivo, Langlois & Potier, 1974) and confirmed by the more recent X-ray analysis of (–)-pseudocopsinine (14,15-dihydrovindolinine) (Nasyrov, Andrianov & Struchkov, 1974).

Experimental

Weissenberg films indicated space group *C2*. *Catharanthus* alkaloids are optically active and hence the

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mirror image (space group $C2/m$) cannot exist. Cell dimensions were obtained from a least-squares treatment of the θ values of 33 reflexions measured on Weissenberg films calibrated by Al lines. The crystal data are reported in Table 1.

Table 1. *Crystal data*

Molecular formula	$C_{21}H_{25}N_2O_2 \cdot 0.5Cl \cdot 0.5ClO_4$
F.W. 404.9	Monoclinic
Space group $C2$	$\beta = 124.7 (2)^\circ$
$a = 18.181 (5) \text{ \AA}$	$V = 1976 \text{ \AA}^3$
$b = 8.959 (4)$	$d_c = 1.36 \text{ g cm}^{-3}$
$c = 14.765 (3)$	$\lambda = 1.5418 \text{ \AA} (\text{Cu } K\alpha)$

Intensities were collected with multiple-film equi-inclination Weissenberg photographs. Layers 0 through 8 were recorded along the [010] axis, and 0 and 1 with a second crystal mounted parallel to the [110] axis. Intensities were measured with a microdensitometer and corrected for Lorentz, polarization and spot distortion on upper-level Weissenberg. No absorption corrections were made.

For each reflexion an estimate of the standard deviation $\sigma(F)$ was derived empirically taking into account densitometry errors and scaling indeterminations of the multiple films method. The data from the two different axes (respectively 2072 and 596 reflexions) were cross correlated by means of a least-squares procedure. Of the 'total' 2138 independent reflexions, 1975 were judged to have intensities above the background. The normalized structure factors $|E_h|$ were calculated by means of a Wilson plot.

Phase determination and refinement

The structure was solved by application of the symbolic addition procedure (Karle & Karle, 1966). The numerical values of the symbols were determined with the help of the phase function (Riche, 1973). The computer program *DEVIN* was used to perform the symbolic addition and the calculation of the phase function.

The starting set of phases listed in Table 2 was built up in two successive runs in which the phase function was computed after two cycles of weighted symbolic addition.

At the end of a first run the largest relationship between symbolic phases was accepted and two new

Table 2. *Starting set of phases*

k	$ E $	ϕ	
-3 1 9	2.11	0	} origin
-10 0 5	2.12	0	
-12 0 6	1.91	a	
-4 0 8	2.00	b	0 or π
-7 7 6	2.11	c	
-14 2 7	2.24	d	
3 7 2	2.01	s	$= b + c$
-10 4 10	2.16	e	
-8 0 8	1.97	f	0 or π
6 8 6	1.98	g	

symbols (f and g) were added. In Table 3 a section of the phase function corresponding to the last starting set of phases is given. Symbol c appeared to be enantiomorph sensitive and its possible values were restricted to: $\pi/4$, $\pi/2$ and $3\pi/4$, which effectively specified the reference frame. 20 maxima were found; three of them are shown in Table 3. The 20 corresponding solutions were subjected to refinements of phases with the tangent formula. The R of Karle clearly indicated two solutions which corresponded to the highest maxima of the phase function.

Table 3. *Section of the phase function*
 $F(a, b, c, d, e, f, g)$

The maxima of F were collected for each value of c and d with $a=0$, $b=0$ and $f=0$. The maximum, $F=100$, corresponds to the trivial solution where all phases are equal to zero.

c	d	0	1	2	3	4	5	6	$7\pi/4$
0		100	46	57	72	26	72	57	46
1		88	67	29	73	31	57	76	16
2		70	88	24	64	47	36	86	37
3		44	93	42	45	61	25	83	65
$\frac{4\pi}{4}$		21	80	61	25	64	25	61	80

The two E maps were practically identical and their features were unexpected. The higher peaks were concentrated on the twofold axes at $x=0$, $z=0$ and at $x=0$, $z=\frac{1}{2}$. Many other peaks in the map were doubled by a mirror plane perpendicular to b . A careful examination of the packing suggested that the four Cl atoms in the unit cell could be located in special positions on the twofold axes.

Accordingly, the recycling procedure of Karle (1968) was applied, starting from 11 atoms: two Cl in special positions and nine peaks indicating a 6 and a 5-membered ring joined together and weighted as C atoms. All the atoms of the alkaloid appeared in two cycles.

The coordinates of the 27 C, N, O and Cl atoms were subjected to a full-matrix least-squares refinement with a modified *ORFLS* program (Busing, Martin & Levy, 1962). A difference map revealed the two O atoms of the asymmetric unit linked with the Cl atom at $x=0$, $z=\frac{1}{2}$. None of the O atoms associated with the second Cl atom could be located. It became evident from a critical analysis of the intermolecular distances $Cl \cdots N(4)$ and $Cl \cdots C$ that this Cl could not be linked to any O atom. Therefore, a Cl^- ion was assumed from chemical and structural considerations.

All H atoms were located on three successive difference maps and their contributions were introduced in idealized positions ($C-H = 1.0 \text{ \AA}$, $C-C-H = 109$ or 120° , CH_3 : rigid group, B of $H = B$ of C atoms). The refinement ended with an R of 0.072 (weighted $R_w = 0.093$, with unobserved reflexions $R = 0.08$). The function

minimized was $\sum w(F_o - F_c)^2$ where $w = 1/\sigma(F)^2$. The scattering factors were those of Doyle & Turner (1968) for C, N, O, Cl and Cl⁻, and those of Stewart, Davidson & Simpson (1965) for H.

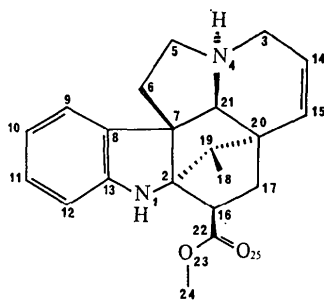


Fig. 1. Structural formula of vindolinine and atom numbering scheme.

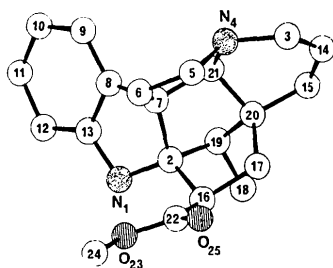


Fig. 2. Perspective view of the molecule.

Fractional coordinates and thermal parameters* for the heavy atoms are listed in Table 4 and the coordinates for the H atoms as derived from the calculation are listed in Table 5. Bond lengths and bond angles are given in Tables 6 and 7.

Molecular geometry

The stereochemistry and the atom numbering scheme are shown in Fig. 1. The overall shape of the molecule, depicting the correct absolute configuration (Rasochanova *et al.*, 1974), is illustrated in Fig. 2.

Benzene ring *A* is planar and the deviation of atoms in ring *B* from the least-squares plane of ring *A* are shown in Table 8. The H atom bonded to N(1) was unambiguously found on the difference map in the plane of the three atoms C(2), N(1) and C(13). Thus the hybridization of N(1) is *sp*² and not *sp*³ as could be expected for a dihydroindole alkaloid. This H atom is probably stabilized in this configuration by the hydrogen bond N(1)–H···O(27).

Torsional angles are shown in Fig. 3. Ring *B* has a pseudo-rotation phase angle (Altona, Geise & Romers, 1968) $\Delta = 28^\circ$ [if ϕ_0 is assigned to the rotation

* A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31605 (15 pp., 1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. Fractional coordinates and thermal parameters

The thermal parameters are of the form: $T = \exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Coordinates and temperature factors have been multiplied by 10^4 .

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	3444 (2)	5104 (5)	2803 (3)	39 (2)	83 (6)	44 (2)	-13 (2)	28 (2)	-16 (2)
C(2)	2660 (3)	5038 (5)	2825 (3)	43 (2)	42 (5)	39 (2)	-2 (4)	30 (2)	3 (2)
C(3)	9 (4)	3241 (8)	2025 (5)	46 (2)	160 (10)	79 (4)	-18 (4)	42 (3)	-16 (5)
N(4)	785 (3)	2692 (5)	1984 (3)	40 (2)	79 (6)	55 (2)	-2 (2)	31 (2)	-6 (3)
C(5)	1538 (3)	1872 (6)	2980 (4)	47 (2)	78 (7)	57 (3)	-5 (3)	35 (2)	2 (3)
C(6)	2340 (3)	2039 (5)	2907 (4)	46 (2)	45 (6)	57 (3)	-5 (3)	31 (2)	0 (3)
C(7)	2193 (3)	3514 (5)	2249 (3)	35 (2)	55 (6)	35 (2)	-1 (2)	20 (2)	-5 (3)
C(8)	2522 (3)	3370 (6)	1514 (3)	32 (2)	79 (6)	43 (2)	2 (2)	24 (2)	-8 (3)
C(9)	2232 (3)	2411 (6)	637 (4)	34 (2)	94 (7)	51 (3)	-6 (3)	23 (2)	-21 (3)
C(10)	2663 (4)	2461 (7)	94 (4)	51 (3)	132 (8)	57 (3)	-2 (3)	37 (3)	-34 (4)
C(11)	3386 (3)	3400 (7)	468 (4)	46 (2)	120 (8)	60 (3)	16 (3)	39 (2)	3 (4)
C(12)	3716 (3)	4324 (6)	1386 (3)	37 (2)	88 (6)	56 (3)	4 (3)	32 (2)	7 (3)
C(13)	3264 (3)	4287 (5)	1900 (3)	40 (2)	58 (6)	42 (2)	1 (2)	27 (2)	3 (3)
C(14)	-286 (4)	4803 (9)	1628 (5)	44 (2)	162 (10)	90 (4)	22 (4)	42 (3)	1 (5)
C(15)	273 (4)	5856 (7)	1715 (4)	49 (3)	120 (9)	76 (4)	23 (4)	39 (3)	11 (4)
C(16)	2760 (3)	5301 (5)	3921 (3)	51 (2)	56 (6)	39 (2)	-9 (3)	31 (2)	-15 (3)
C(17)	1758 (3)	5418 (6)	3504 (3)	60 (2)	64 (6)	49 (3)	7 (3)	41 (2)	-1 (3)
C(18)	2080 (4)	7817 (7)	2341 (4)	66 (3)	69 (7)	66 (3)	2 (3)	45 (3)	1 (4)
C(19)	1883 (3)	6174 (6)	2052 (3)	47 (2)	57 (6)	39 (2)	8 (3)	28 (2)	2 (3)
C(20)	1209 (3)	5393 (6)	2217 (3)	48 (2)	70 (7)	48 (3)	10 (3)	32 (2)	5 (3)
C(21)	1208 (3)	3894 (6)	1736 (3)	37 (2)	77 (6)	41 (2)	-2 (2)	25 (2)	-9 (3)
C(22)	3300 (3)	4215 (6)	4849 (3)	49 (2)	66 (6)	44 (2)	-12 (3)	29 (2)	-8 (3)
O(23)	4081 (2)	3911 (5)	5025 (3)	36 (1)	146 (6)	51 (2)	-5 (2)	20 (1)	25 (3)
C(24)	4649 (4)	2853 (10)	5913 (4)	39 (2)	202 (12)	59 (3)	-1 (4)	15 (2)	40 (5)
O(25)	3052 (3)	3693 (6)	5390 (3)	80 (3)	178 (8)	79 (3)	31 (4)	65 (2)	51 (4)
Cl(1)	0 (0)	576 (0)	0 (0)	37 (1)	91 (3)	52 (1)	0 (0)	21 (1)	0 (0)
Cl(2)	0 (0)	3368 (3)	5000 (0)	65 (1)	118 (4)	88 (2)	0 (0)	29 (1)	0 (0)
O(27)	155 (14)	2504 (20)	5828 (13)	416 (23)	700 (48)	321 (20)	371 (30)	306 (20)	339 (28)
O(28)	698 (11)	4228 (26)	5382 (19)	164 (12)	753 (57)	500 (34)	-224 (23)	73 (17)	66 (36)

about C(2)–C(7)], corresponding to an envelope form $C_s(2)$ with C(2) out of the plane formed by the other four atoms.

For ring *F* we calculate a phase angle Δ of 20° and a φ_m of 29° . Its conformation is intermediate between a $C_s(5)$ envelope and $N_2(4)$ half chair. Ring *G* has a 1,3 diplanar conformation (Bucourt & Hainaut, 1965) with approximate C_2 symmetry, its diad axis passing

through the midpoints of bonds C(14)–C(3) and C(20)–C(21). The four C atoms (3), (14), (15), (20) are in a quite planar configuration while the C atoms (14), (3), (21), and N(4) are slightly displaced from their mean plane (Table 8).

Table 5. *Hydrogen atomic parameters*

Positional parameters have been multiplied by 10^3 . Hydrogen atoms are numbered according to the carbon to which they are attached. α and β refer to the corresponding position in Fig. 1. Temperature factors are given according to the expression: $T = \exp(-B \sin^2 \theta/\lambda^2)$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	402	563	333	2.8
H(3 α)	-52	257	155	4.3
H(3 β)	19	319	280	4.3
H(4)	52	197	136	2.9
H(5 α)	138	80	295	3.1
H(5 β)	167	233	367	3.1
H(6 α)	237	116	251	2.9
H(6 β)	290	210	367	2.9
H(9)	173	170	40	3.0
H(10)	245	182	-57	3.8
H(11)	368	341	6	3.4
H(12)	425	498	166	2.9
H(14)	-91	517	127	4.6
H(15)	2	688	144	4.1
H(16)	303	631	419	2.7
H(17 α)	165	637	376	3.1
H(17 β)	159	455	378	3.1
H(18 <i>A</i>)	269	806	253	3.7
H(18 <i>B</i>)	162	842	169	3.7
H(18 <i>C</i>)	206	804	299	3.7
H(19)	169	602	128	2.7
H(21)	89	400	92	2.6
H(24 <i>A</i>)	444	181	564	5.0
H(24 <i>B</i>)	528	297	615	5.0
H(24 <i>C</i>)	461	306	655	5.0

Table 6. *Bond distances (Å) involving the non-hydrogen atoms with estimated standard deviations in parentheses*

N(1)–C(2)	1.445 (8)	C(10)–C(11)	1.383 (9)
N(1)–C(13)	1.387 (6)	C(11)–C(12)	1.399 (7)
C(2)–C(7)	1.576 (7)	C(12)–C(13)	1.402 (8)
C(2)–C(16)	1.541 (6)	C(14)–C(15)	1.338 (11)
C(2)–C(19)	1.580 (7)	C(15)–C(20)	1.476 (10)
C(3)–N(4)	1.528 (10)	C(16)–C(17)	1.559 (9)
C(3)–C(14)	1.493 (10)	C(16)–C(22)	1.501 (6)
N(4)–C(5)	1.511 (7)	C(17)–C(20)	1.563 (6)
N(4)–C(21)	1.485 (7)	C(18)–C(19)	1.517 (8)
C(5)–C(6)	1.530 (9)	C(19)–C(20)	1.546 (9)
C(6)–C(7)	1.570 (7)	C(20)–C(21)	1.519 (7)
C(7)–C(8)	1.515 (7)	C(22)–O(23)	1.318 (8)
C(7)–C(21)	1.532 (8)	C(22)–O(25)	1.213 (8)
C(8)–C(9)	1.383 (7)	O(23)–C(24)	1.463 (8)
C(8)–C(13)	1.393 (7)	Cl(2)–O(27)	1.334 (18)
C(9)–C(10)	1.406 (9)	Cl(2)–O(28)	1.306 (24)

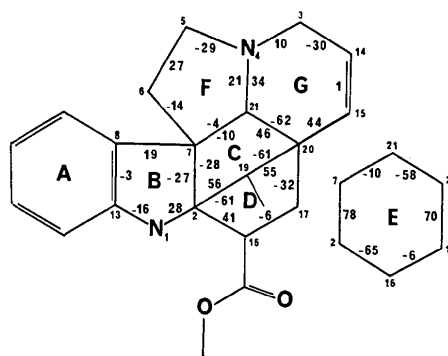


Fig. 3. Torsional angles ($^\circ$).

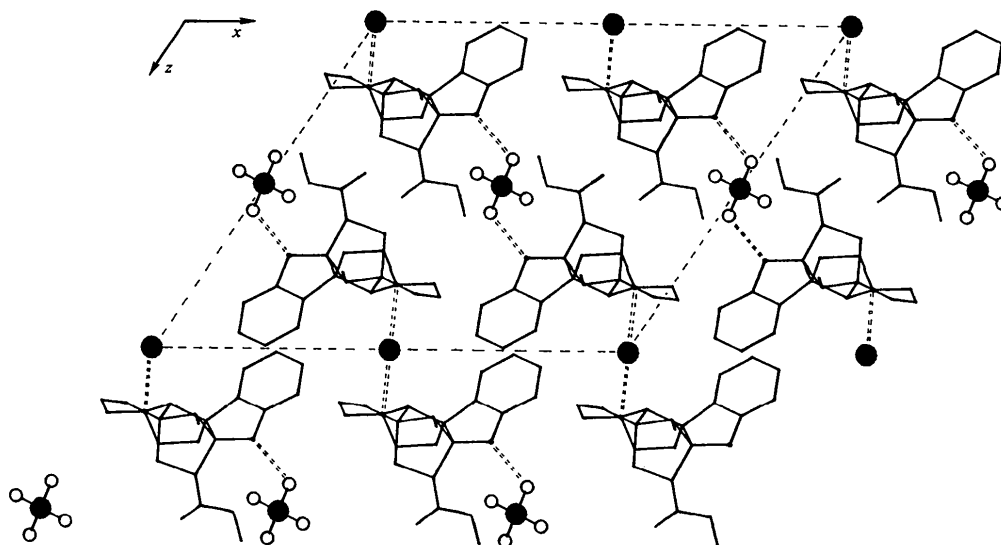


Fig. 4. Projection of the structure along *b*. The hydrogen bonds are identified by double broken lines.

Table 7. Bond angles ($^{\circ}$)

The standard deviations are near to a value of 0.5° (1.5° for O-Cl-O).

C(2)—N(1)—C(13)	107.7	C(3)—C(14)—C(15)	122.7
N(1)—C(2)—C(7)	105.0	C(14)—C(15)—C(20)	116.4
N(1)—C(2)—C(16)	119.3	C(2)—C(16)—C(17)	100.5
N(1)—C(2)—C(19)	116.4	C(2)—C(16)—C(22)	118.9
C(7)—C(2)—C(16)	113.8	C(17)—C(16)—C(22)	114.4
C(7)—C(2)—C(19)	100.6	C(16)—C(17)—C(20)	105.8
C(16)—C(2)—C(19)	100.5	C(2)—C(19)—C(18)	116.8
N(4)—C(3)—C(14)	114.8	C(2)—C(19)—C(20)	93.3
C(3)—N(4)—C(5)	117.6	C(18)—C(19)—C(20)	118.4
C(3)—N(4)—C(21)	113.3	C(15)—C(20)—C(17)	111.1
C(5)—N(4)—C(21)	106.5	C(15)—C(20)—C(19)	125.7
N(4)—C(5)—C(6)	104.7	C(15)—C(20)—C(21)	108.6
C(5)—C(6)—C(7)	107.0	C(17)—C(20)—C(19)	99.9
C(2)—C(7)—C(6)	123.1	C(17)—C(20)—C(21)	114.3
C(2)—C(7)—C(8)	98.5	C(19)—C(20)—C(21)	96.7
C(2)—C(7)—C(21)	101.1	N(4)—C(21)—C(7)	109.8
C(6)—C(7)—C(8)	111.9	N(4)—C(21)—C(20)	112.9
C(6)—C(7)—C(21)	103.5	C(7)—C(21)—C(20)	106.0
C(8)—C(7)—C(21)	119.5	C(16)—C(22)—O(23)	112.6
C(7)—C(8)—C(9)	128.9	C(16)—C(22)—O(25)	123.8
C(7)—C(8)—C(13)	110.0	O(23)—C(22)—O(25)	123.6
C(9)—C(8)—C(13)	120.9	C(22)—O(23)—C(24)	116.2
C(8)—C(9)—C(10)	118.4	O(27)—Cl(2)—O(28)	107.5
C(9)—C(10)—C(11)	120.2	O(27)—Cl(2)—O(27)	109.1
C(10)—C(11)—C(12)	122.1	O(27)—Cl(2)—O(28)	112.6
C(11)—C(12)—C(13)	116.9	O(28)—Cl(2)—O(27)	112.6
N(1)—C(13)—C(8)	110.4	O(28)—Cl(2)—O(28)	107.6
N(1)—C(13)—C(12)	128.2	O(27)—Cl(2)—O(28)	107.5
C(8)—C(13)—C(12)	121.4		

 Table 8. Deviations (\AA) of the atoms from least-squares mean planes through selected atomic groupings

N(1)	-0.003*	N(1)	0.008
C(2)	0.408*	C(2)	0.441*
C(7)	-0.035*	C(7)	-0.010
C(8)	0.019	C(8)	0.016
C(9)	-0.023	C(13)	-0.017
C(10)	0.007		
C(11)	0.014	C(16)	-0.002
C(12)	-0.010	C(22)	0.007
C(13)	-0.006	O(23)	-0.001
		O(25)	-0.003
		C(24)	0.013*
C(3)	-0.002		-0.067
N(4)	0.673*		0.029
C(21)	1.011*		-0.018
C(20)	0.001		-0.912*
C(15)	-0.003		-0.363*
C(14)	0.004		0.040

* Atoms not included in the least-squares calculations.

 Table 9. Short intramolecular distances (\AA)

C(22) \cdots H(6 β)	2.39	H(5 β) \cdots H(17 β)	2.01
O(23) \cdots H(6 β)	2.52	H(3 β) \cdots H(5 β)	2.34
O(25) \cdots H(5 β)	2.64	H(3 α) \cdots H(4)	2.14
O(25) \cdots H(17 β)	2.47	H(4) \cdots H(5 α)	2.21
C(22) \cdots H(17 β)	2.58	H(4) \cdots H(21)	2.16
H(3 α) \cdots H(4)	2.14	H(16) \cdots H(17 α)	2.21
H(3 β) \cdots H(5 β)	2.34	H(16) \cdots H(18c)	2.26
H(4) \cdots H(5 α)	2.21	H(17 α) \cdots H(18c)	2.25
H(4) \cdots H(21)	2.16	H(18b) \cdots H(19)	2.27
H(5 α) \cdots H(6 α)	2.26	H(19) \cdots H(21)	2.19
H(5 β) \cdots H(6 β)	2.26		

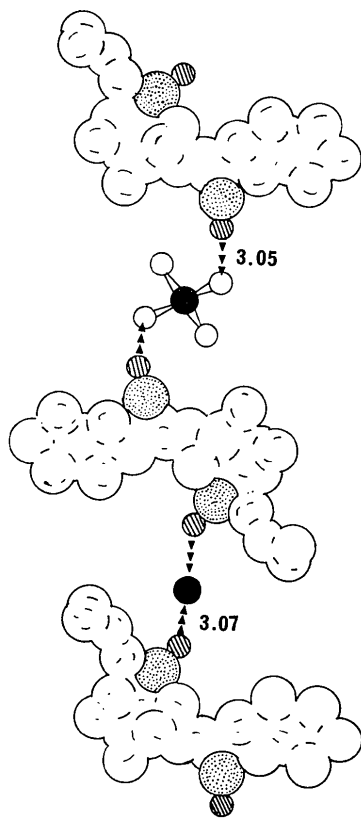


Fig. 5. Details of the hydrogen-bond scheme. View down the b axis. Distances are in \AA .

The 'cage-like' structure consisting of rings F , C and D and the *cis* junction between the rings F and G give rise to short intramolecular contacts $C \cdots H$ and $H \cdots H$.^{*} They are listed in Table 9. The lengthening of the three bond lengths $C(2)-C(7)=1.576$, $C(7)-C(6)=1.570$ and $C(2)-C(19)=1.580$ \AA (which are respectively 5σ , 4σ and 8σ greater than the comparable bond in diamond of 1.544 \AA), may result in part from these short intramolecular interactions. Short distances such as:

H(6 β) \cdots C(22)	2.39 \AA	H(17 β) \cdots O(25)	2.47 \AA
H(6 β) \cdots O(23)	2.52	H(16) \cdots C(19)	2.62
H(5 β) \cdots O(25)	2.64	H(16) \cdots C(18)	2.62

cannot be increased by changes in torsion angles because of the rigidity of this molecule. One may speculate that the free rotation in solution, of the methoxycarbonyl group, is probably hindered by the short intramolecular contacts involving O(23) and O(25).

* The hydrogen positions, fixed on geometric considerations were not refined so that some deformation of the H-C-C angles may have taken place to relieve these very close approaches. Even allowing for such adjustments the contact distances will remain below the sum of the normal van der Waals radii.

Packing

The packing of molecules is shown in Fig. 4 in a projection along [010]. The main features of the structure are the hydrogen bonds, running in the direction [101]. This hydrogen-bond network is illustrated in Fig. 5. The chloride ion is trapped between two molecules of vindolinine and linked by two symmetrical hydrogen bonds involving the protonated nitrogen N(4). The geometry of these bonds: $N^+ \cdots Cl^- = 3.07$, $H \cdots Cl^- = 2.07$ Å and $N-H \cdots Cl = 176^\circ$ indicates a fairly strong hydrogen bond. The perchlorate ion, on the other hand, accepts two symmetrical H bonds: $N(1)-H \cdots O(27) = 3.05$ Å, $N-H \cdots O = 156^\circ$.

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Magnesium Formate Dihydrate: a Crystal Structure Redetermination at 130 and 293 K

BY G. DE WITH, S. HARKEMA AND G. J. VAN HUMMEL

Chemical Physics Laboratory, Twente University of Technology, P.O. Box 217, Enschede, The Netherlands

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The structure of magnesium formate dihydrate has been redetermined at approximately 130 and 293 K by X-ray methods. The structure as proposed by Osaki, Nakai & Watanabé [*J. Phys. Soc. Japan* (1964), **19**, 717–723] proved to be essentially correct. H atoms are located and accurate values of parameters are presented.

Introduction

Some structural research has been carried out on metal formates in our laboratory. Structures investigated so far include lithium formate monohydrate (Enders-Beumer & Harkema, 1973) and sodium formate (Enders-Beumer & Harkema, 1976). In this paper we present the redetermination of the crystal structure of magnesium formate dihydrate at approximately 130 and 293 K.

Experimental

Small, single crystals of the title compound with linear dimensions of about 0.4 mm were grown by slow evaporation of a solution obtained by neutralizing aqueous formic acid with magnesium carbonate.

Data were obtained on a Philips PW1100 computer-controlled automatic four-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. The $\omega/2\theta$ scanning technique in the θ range 3 – 27° was used throughout. A detector aperture of 2° horizontally and 1° vertically was chosen.

At 130 K, 1304 reflexions were measured at a rate of 0.1° s^{-1} and a scan angle of 2° . 1158 reflexions had an intensity greater than twice the standard deviation as estimated from counting statistics.

At 293 K, 1310 reflexions were measured at a rate of $0.08^\circ \text{ s}^{-1}$ and a scan angle of 1.5° . Here 1184 reflexions had intensities greater than twice the standard deviation. In both cases no significant systematic change in standard reflexions was observed during the measurement.