Table 7. *Shorter intermolecular distances in VAAT*

$C-C < 3.6$, $C-O < 3.3$, $C-H < 3.0$, $O-H < 2.7$, $H-H < 2.6$ Å.

C(8)—H(13)	i	2·87 Å
C(9)—H(13)	i	2·89
C(16)–H(12)	ii	2·86
C(17)–H(20)	iii	2·85
H(3)—H(6)	iv	2·6
H(5)—H(5)	v	2·4
H(12)–H(14)	vi	2·4
H(15)–H(19)	vii	2·6
H(17)–H(20)	iii	2·5
H(18)–H(20)	iii	2·6
H(26)–H(27)	viii	2·4

	x	y	z
i	x	y	$1+z$
ii	$1+x$	y	$-2+z$
iii	$1+x$	y	z
iv	$-x$	$-y$	$1-z$
v	$-x$	$-y$	$2-z$
vi	$-1+x$	y	$2+z$
vii	$1+x$	y	$-1+z$
viii	$1-x$	$1-y$	$-z$

double-bond system of a double molecule. The molecules in adjacent strips within a slab, which are separated by a translation **c**, are practically on top of each other as illustrated in Fig. 9(*b*). Contacts are mainly between the carbon atoms (see Table 6). The distance between the mean planes of consecutive molecules is 3·60 Å, a normal value for the thickness of a planar conjugated system. The lateral contacts between the molecules in a strip is through the H atoms, with shortest distances of 2·5 Å.

The disorder in VAAT is understandable in terms of its packing. In VAAT the rings have more freedom of motion than in VAAM in which the ring double bond interacts with the double-bond system of an adjacent molecule (Fig. 8). The closer packing of the molecules in VAAM is also evident from the intermolecular contacts, of which there are more in VAAM than in VAAT (Tables 6 and 7).

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The Molecular Structure and Absolute Configuration of Chaetocin

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Chaetocin, $C_{30}H_{28}N_6O_6S_4$, a fungal metabolite dimer with an epidithiodiketopiperazine nucleus, crystallizes in $P2_12_12_1$, with $a = 23·30$, $b = 7·31$, and $c = 17·31$ Å, and four formula units in the cell. The structure was solved by direct methods with three-dimensional diffractometer data (graphite monochromated Mo $K\alpha$ radiation) and refined by block-diagonal least-squares methods to $R = 0·042$ for 1704 reflexions. The absolute configuration was determined by measuring the anomalous dispersion effect of sulphur with Cu $K\alpha$ radiation.

Introduction

Chaetocin, a fungal metabolite with antibacterial and cytostatic activity, has been isolated from the fermentation broth of *Chaetomium minutum* (Hauser, Weber & Sigg, 1970). This new natural product belongs to the class of 3,6-epidithio-diketopiperazines of which chetomin (Safe & Taylor, 1972), gliotoxin (Fridrichsons & Mathieson, 1967), sporidesmin (Fridrichsons & Mathieson, 1965), aranotin (Nagarajan, Huckstep,

Lively, Delong, Marsh & Neuss, 1968), oryzachloride (Kato, Saeki, Suzuki, Ando, Tamura & Arima, 1969) verticillin A (Minato, Matsumoto & Katayama, 1971) and the melinacidins (Argoudelis, 1972) are other known examples. Chaetocin is a molecular dimer, the two halves being related by an approximate (non-crystallographic) twofold axis. The two five-membered rings are *cis* fused.
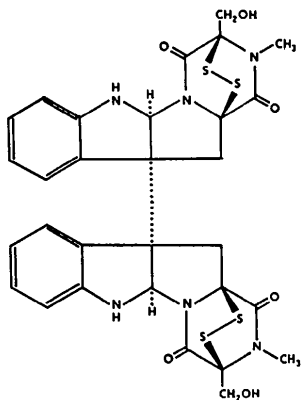
Chaetocin
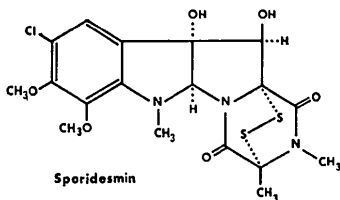
Sporidesmin
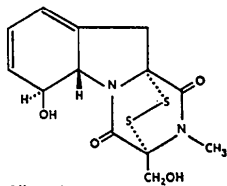
Gliotoxin

The chirality of the 3,6-epidithio-diketopiperazine moiety in chaetocin is opposite to the chirality in gliotoxin, sporidesmin, aranotin and oryzachloride, which may be of interest in connexion with the fact

that the latter compounds show antiviral activity (Brewer, Hannah & Taylor, 1966; Trown, 1968) whereas chaetocin does not.

Experimental

Chaetocin was obtained as yellow prismatic needles by crystallization from pyridine–methanol. Crystal symmetry and cell dimensions were determined from precession photographs.

Chaetocin	$C_{30}H_{28}N_6O_6S_4$
Molecular weight	696·85
Space group	$P2_12_12_1$
Cell dimensions	
a	23·30 (3) Å
b	7·31 (1)
c	17·31 (3)
Volume, V	3118 Å^3
Density, exp.	1·48 (1) g.cm^{-3}
Density, calc. ($Z=4$)	1·48
Linear absorption, μ(Mo $K\alpha$)	3·5 cm^{-1}.

Intensities were measured on a linear diffractometer using graphite-monochromated Mo $K\alpha$ radiation. Of 2527 measured reflexions with $\sin\theta/\lambda \leq 0.56$ Å^{-1} the intensities of 1704 reflexions were accepted as significant by the criterion $I \geq 3\sigma(I)$, where $\sigma(I) = \sqrt{I + B +}$ $0.02I$.

Absolute scaling of the data gave the following statistical values:

$\bar{B}$ (overall) $= 3\cdot1$ Å^2
$\langle|E|\rangle$ $= 0\cdot854$ (theor. 0·886)
$\langle|E^2-1|\rangle$ $= 0\cdot773$ (theor. 0·736)
$\langle|E^2|\rangle$ $= 0\cdot984$ (theor. 1·000) .

Phase determination and refinement

The six independent sulphur–sulphur vectors could not be located in the Patterson map. Direct phasing by application of the multi-solution method (Germain & Woolfson, 1968) was then used to solve the structure. Starting with four phases defining origin and enan-
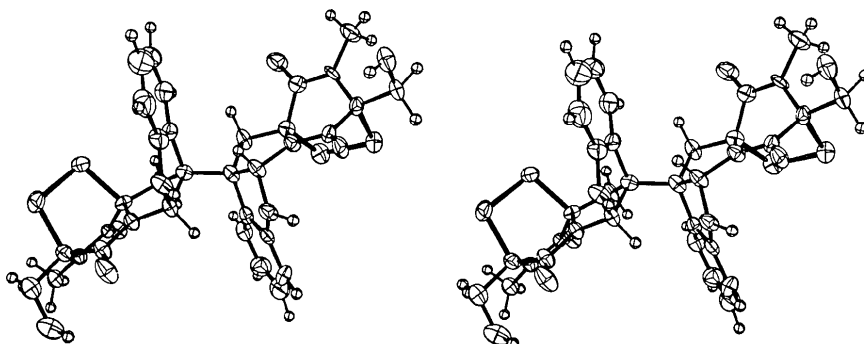

Fig. 1. A stereoscopic view of chaetocin in the absolute configuration. The 50% probability ellipsoid is drawn for the heavier atoms and a sphere for the hydrogen atoms corresponding to a uniform isotropic $B=1$ Å^2 [drawn with the computer program ORTEP (Johnson, 1965) adapted for a Univac 1108 computer].
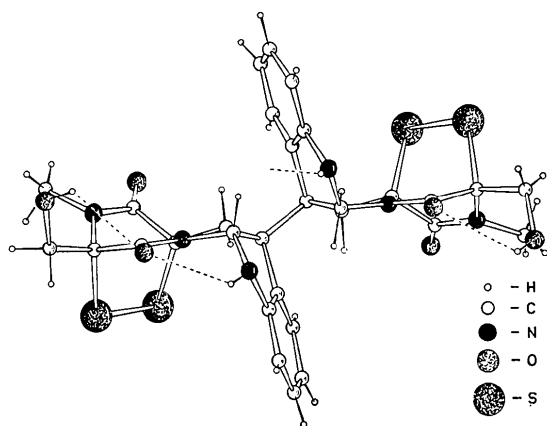
Fig. 2. Perspective view of the molecule in absolute configuration projected parallel to the approximate twofold axis. Hydrogen bonds are indicated by broken lines.

tiomer – the values 0 and π for the phase of an $h0l$ reflexion, and the values $\pm\pi/4$, $\pm3\pi/4$ for the phases of three general reflexions – the tangent formula was used with about 23000 phase relations derived from 516 reflexions with $|E| > 1\cdot1$. One of the E maps calculated with the most consistent phase sets showed the complete structure.

Refinement of the structure was carried out by block-diagonal least-squares analysis, using first isotropic, then anisotropic thermal parameters. In a difference Fourier map the positions of the 28 hydrogen atoms were located and included in the least-squares refinements with isotropic temperature factors. The weight-

ing scheme applied for significant reflexions was: $w(\mathbf{h}) = 1/\sigma(F_\mathbf{h})$, with $\sigma(F_\mathbf{h}) = F_\mathbf{h}[\sigma(I_\mathbf{h})/2I_\mathbf{h}]$, $\sigma(I_\mathbf{h})$ as defined above. An R value of $0\cdot042$ for 1704 significant structure amplitudes was reached at convergence of 525 atomic parameters and of the scale factor. A list of structure factors has been deposited with the National Lending Library, England.*

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* Supplementary Publication No. SUP 30013. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Measured (ΔI) and calculated (ΔF^2) differences of Friedel pairs $\Delta I = I(hkl) - I(h\bar{k}l)$*

$I(hkl)$ is the mean of $I(hkl)$ and $I(h\bar{k}l)$, $I(h\bar{k}l)$ the mean of $I(hkl)$ and $I(hkl)$. Measurements were made on a linear diffractometer with b = rotation axis, limiting observations to reflexions with $k \geq 0$.

| h	k	l	$I(hkl)$	$I(h\bar{k}l)$	ΔI_{hkl}	F^2_{hkl}	ΔF^2_{hkl}
4	1	1	1300	1143	157	1226	268
5	1	1	1287	1646	−359	1457	−311
7	1	6	824	1024	−260	1888	−342
8	1	1	3784	3506	278	6108	622
3	1	3	2025	1787	238	1816	268
2	1	3	2270	2026	244	2398	251
1	1	4	5786	5300	486	4425	559
8	1	5	529	668	−139	1546	−255
5	1	5	2300	2061	239	2415	403
9	2	1	1213	1137	76	1878	305
6	2	2	2748	3335	−587	3808	−534
10	2	3	1106	992	114	2506	425
2	2	4	2436	2177	259	2293	294
7	2	4	1109	1036	73	1700	259
9	2	6	390	317	73	1080	169
2	2	7	814	679	135	1964	250
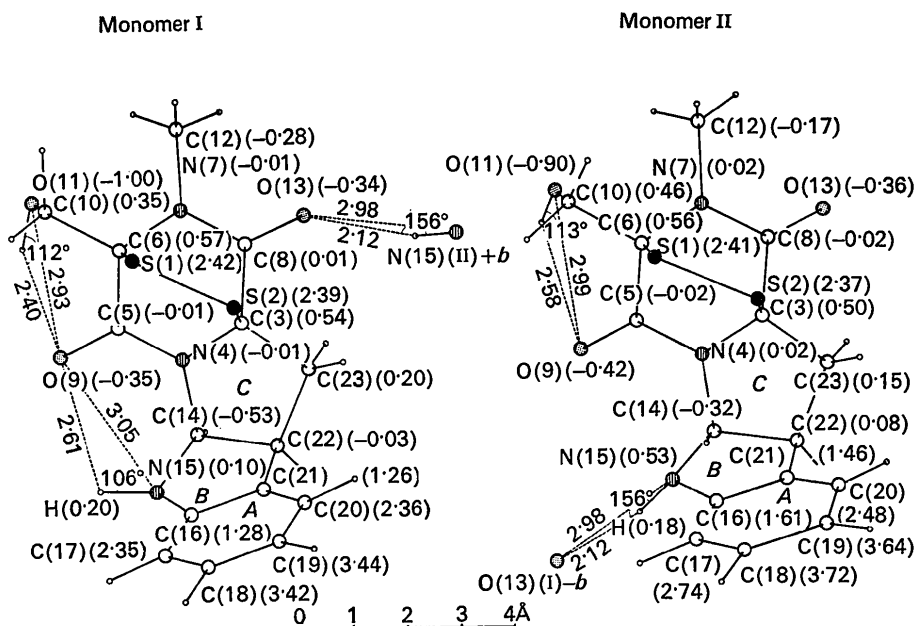
Fig. 3. Projection of the two monomer parts of chaetocin onto the mean plane through N(4), C(5), N(7) and C(8) (unnatural configuration). The numbers in brackets indicate the height above the plane of projection in ångströms. Dashed lines indicate the hydrogen bonds.

Determination of the absolute configuration

The anomalous dispersion effect of sulphur was used to determine the absolute configuration of chaetocin. The intensity differences for Friedel pairs were first estimated from the relation

$$\Delta F_h^2 = F_h^2 - F_{\bar{h}}^{2\parallel} = 4 \, (\Delta f_S'' / f_S) \, [B \cdot A_S - A \cdot B_S] \, ,$$

($\Delta f_S'' = 0.6$ for Cu $K\alpha$ radiation) and sixteen pairs for which $|\Delta F_h^2|$ was more than about 10% of F_h^2 were selected. The corresponding intensities $I(hkl)$, $I(\bar{h}k\bar{l})$, $I(\bar{h}k\bar{l})$ and $I(hk\bar{l})$ were carefully remeasured with graphite monochromated Cu $K\alpha$ radiation.

Comparison of observed differences, ΔI_h, and calculated ones, ΔF_h^2, (Table 1) led unequivocally to the enantiomer shown in Figs. 1 and 2. The asymmetric centres C(3), C(6), C(14) and C(22) are specified as S, S, R and R respectively in both parts of the dimer (for numbering of atoms see Fig. 3).

Results

The mean e.s.d.'s of the refined atomic positions (Table 2) are 0.002 for sulphur, 0.006 for oxygen, 0.007 for nitrogen, 0.008 for carbon, and 0.09 Å for hydrogen. The r.m.s.d.'s of the thermal vibration tensor components vary between 0.09 and 0.29 Å for the heavier atoms with a mean of 0.20 Å. The shapes and relative orientations of the thermal vibration ellipsoids can be seen from the stereoscopic drawing of the molecule

Table 2(a). *Coordinates* ($\times 10^4$) *and anisotropic* β_{ij} *values* ($\times 10^5$) *for the heavier atoms of chaetocin*

The expression used for the thermal anisotropic vibration is

$$T = \exp \, [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}) \times 10^{-5}].$$

Standard deviations determined by the block-diagonal least-squares procedure are given in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	6227 (0)	3544 (2)	−3810 (1)	129 (3)	1490 (33)	290 (7)	25 (10)	−12 (5)	−56 (15)
S(2)	6971 (0)	3931 (2)	−4449 (1)	161 (4)	1445 (34)	270 (7)	19 (10)	−25 (5)	−97 (14)
C(3)	7494 (2)	2945 (8)	−3756 (3)	114 (14)	1059 (98)	200 (26)	−27 (36)	−22 (17)	−34 (51)
N(4)	7328 (2)	1229 (6)	−3524 (3)	116 (12)	851 (93)	227 (22)	−40 (29)	−40 (13)	66 (41)
C(5)	6850 (2)	1045 (8)	−3106 (3)	78 (13)	1280 (95)	221 (26)	−26 (35)	−18 (16)	−3 (51)
C(6)	6570 (2)	2773 (8)	−2895 (3)	78 (13)	994 (99)	260 (29)	−21 (34)	−18 (16)	42 (52)
N(7)	7005 (2)	3980 (7)	−2631 (3)	126 (12)	1505 (94)	210 (22)	−21 (32)	−82 (14)	287 (44)
C(8)	7476 (3)	4185 (8)	−3071 (4)	136 (15)	1122 (97)	254 (30)	−80 (38)	−12 (18)	13 (52)
O(9)	6647 (1)	−360 (5)	−2916 (2)	108 (9)	1007 (76)	280 (19)	−61 (23)	−77 (12)	18 (34)
C(10)	6086 (2)	2453 (9)	−2315 (4)	85 (14)	1675 (98)	300 (31)	44 (40)	−46 (17)	166 (61)
O(11)	6305 (1)	1843 (5)	−1621 (2)	132 (10)	1618 (99)	304 (21)	68 (28)	−50 (12)	−77 (37)
C(12)	6877 (3)	5273 (9)	−2029 (4)	170 (18)	1784 (99)	385 (36)	−128 (47)	−99 (22)	390 (66)
O(13)	7862 (2)	5262 (6)	−2957 (2)	182 (12)	1394 (95)	354 (23)	−186 (28)	−70 (14)	250 (40)
C(14)	7706 (2)	−188 (7)	−3794 (4)	142 (15)	696 (97)	241 (28)	−25 (35)	−76 (18)	−59 (48)
N(15)	7413 (2)	−1465 (6)	−4256 (3)	133 (12)	925 (91)	244 (24)	−80 (29)	−54 (14)	82 (41)
C(16)	7405 (2)	−899 (7)	−5031 (3)	128 (15)	932 (91)	231 (28)	28 (34)	−46 (17)	224 (50)
C(17)	7062 (2)	−1506 (9)	−5638 (4)	100 (15)	1814 (98)	342 (33)	−107 (40)	−5 (20)	106 (64)
C(18)	7107(3)	−680 (10)	−6332 (4)	187 (18)	1921 (94)	290 (33)	163 (46)	24 (20)	25 (64)
C(19)	7487 (3)	679 (10)	−6442 (4)	213 (19)	1853 (95)	273 (33)	6 (50)	−5 (22)	−51 (65)
C(20)	7836 (2)	1239 (8)	−5848 (4)	142 (16)	1118 (99)	266 (30)	−13 (38)	−61 (18)	−82 (53)
C(21)	7794 (2)	418 (8)	−5131 (3)	103 (14)	1251 (98)	220 (28)	7 (35)	−42 (16)	−27 (53)
C(22)	8105 (2)	800 (7)	−4369 (3)	120 (14)	613 (97)	229 (26)	−84 (32)	−111 (17)	−2 (45)
C(23)	8085 (2)	2713 (8)	−4128 (3)	120 (14)	873 (96)	280 (29)	−61 (37)	−61 (17)	−47 (49)
S(1*)	10560 (0)	−2784 (2)	−4756 (1)	144 (3)	1921 (39)	239 (7)	175 (11)	50 (4)	12 (15)
S(2*)	10235 (0)	−327 (2)	−4557 (1)	128 (3)	1550 (34)	222 (7)	−22 (10)	11 (4)	155 (14)
C(3*)	9552 (2)	−592 (7)	−5144 (3)	91 (14)	1128 (91)	136 (25)	−93 (34)	−20 (15)	−25 (48)
N(4*)	9255 (2)	−2135 (6)	−4955 (3)	101 (11)	796 (85)	209 (21)	18 (27)	−45 (12)	−73 (40)
C(5*)	9484 (2)	−3695 (8)	−5167 (3)	126 (14)	1203 (97)	221 (28)	92 (39)	−51 (17)	−16 (54)
C(6*)	10066 (2)	−3459 (8)	−5564 (3)	126 (14)	1006 (98)	199 (26)	29 (35)	−31 (17)	28 (52)
N(7*)	10036 (2)	−2105 (6)	−6145 (2)	110 (11)	1070 (93)	134 (20)	31 (29)	−17 (13)	13 (38)
C(8*)	9787 (2)	−589 (7)	−5958 (3)	81 (13)	938 (92)	135 (24)	0 (33)	−24 (15)	−8 (44)
O(9*)	9261 (2)	−5071 (5)	−5040 (2)	184 (11)	938 (77)	386 (22)	−13 (25)	−124 (14)	−38 (38)
C(10*)	10316 (2)	−5186 (9)	−5850 (4)	145 (16)	1197 (91)	316 (31)	42 (39)	−45 (18)	−83 (55)
O(11*)	9963(2)	−5781 (5)	−6451 (2)	252 (13)	1258 (88)	289 (22)	−58 (30)	−52 (14)	13 (38)
C(12*)	10398 (2)	−2222 (9)	−6848 (3)	116 (15)	1680 (93)	212 (28)	72 (40)	−46 (16)	10 (59)
O(13*)	9772 (1)	678 (5)	−6376 (2)	155 (10)	981 (78)	246 (19)	33 (25)	−52 (12)	−112 (34)
C(14*)	8740 (2)	−1927 (7)	−4488 (3)	98 (13)	681 (97)	237 (27)	39 (32)	−24 (17)	1 (45)
N(15*)	8794 (2)	−2760 (6)	−3734 (3)	164 (12)	919 (89)	170 (21)	−5 (31)	−60 (14)	−77 (39)
C(16*)	8987 (3)	−1516 (9)	−3207 (3)	145 (16)	1786 (95)	153 (26)	43 (42)	−36 (17)	3 (57)
C(17*)	9170 (3)	−1818 (10)	−2455 (4)	203 (19)	2346 (96)	238 (31)	137 (50)	−40 (21)	−69 (66)
C(18)*	9376 (3)	−432 (12)	−2052 (4)	226 (21)	3354 (91)	264 (34)	169 (62)	−23 (23)	159 (79)
C(19*)	9422 (3)	1225 (11)	−2368 (4)	173 (18)	2765 (97)	295 (34)	24 (56)	−6 (21)	283 (76)
C(20*)	9225 (3)	1521 (9)	−3117 (4)	134 (16)	1836 (98)	338 (34)	−37 (44)	−26 (20)	68 (67)
C(21*)	8993 (2)	130 (8)	−3518 (3)	82 (13)	1461 (92)	228 (28)	−22 (38)	12 (16)	83 (54)
C(22*)	8737 (2)	86 (7)	−4339 (3)	128 (14)	844 (95)	143 (25)	−22 (35)	−25 (16)	27 (44)
C(23*)	9127 (2)	865 (7)	−4957 (3)	106 (14)	533 (96)	240 (27)	−3 (30)	−84 (17)	−57 (47)

Table 2(b). *Coordinates* ($\times 10^4$) *of the hydrogen atoms of chaetocin*

	x	y	z
H(1·C10)	5764 (22)	1853 (67)	−2656 (31)
H(2·C10)	5878 (30)	3691 (98)	−2104 (42)
H(·O11)	6477 (23)	648 (73)	−1625 (31)
H(1·C12)	7216 (31)	5943 (93)	−1891 (43)
H(2·C12)	6720 (35)	4780 (99)	−1544 (46)
H(3·C12)	6575 (27)	6218 (84)	−2311 (36)
H(·C14)	7969 (22)	−546 (70)	−3390 (30)
H(·N15)	7047 (22)	−2073 (74)	−4099 (31)
H(·C17)	6817 (31)	−2633 (94)	−5542 (43)
H(·C18)	6888 (27)	−1314 (86)	−6718 (35)
H(·C19)	7538 (29)	1303 (92)	−6972 (39)
H(·C20)	8089 (21)	2272 (69)	−5906 (29)
H(1·C23)	8347 (22)	3016 (66)	−3660 (31)
H(2·C23)	8134 (25)	3580 (82)	−4507 (35)
H(1·C10*)	10259 (19)	−6103 (61)	−5397 (27)
H(2·C10*)	10680 (25)	−4598 (77)	−5983 (33)
H(·O11*)	9652 (25)	−6175 (80)	−6347 (35)
H(1·C12*)	10787 (19)	−2076 (57)	−6620 (26)
H(2·C12*)	10382 (19)	−1399 (61)	−7230 (27)
H(3·C12*)	10316 (20)	−3374 (63)	−7110 (28)
H(·C14*)	8340 (26)	−2378 (89)	−4795 (36)
H(·N15*)	8551 (25)	−3623 (81)	−3579 (35)
H(·C17*)	9113 (33)	−3117 (91)	−2180 (47)
H(·C18*)	9470 (27)	−854 (84)	−1477 (35)
H(·C19*)	9566 (23)	2571 (76)	−2101 (32)
H(·C20*)	9227 (22)	2622 (69)	−3425 (29)
H(1·C23*)	9333 (32)	1759 (98)	−4791 (44)
H(2·C23*)	8906 (20)	1094 (64)	−5506 (29)

Table 3. *Bond lengths and angles in chaetocin*

	Monomer part I	Monomer part II
(a) Bond lengths		
S(1)—S(2)	2·079 (4) Å	2·074 (4) Å
S(1)—C(6)	1·872	1·884 (9)
S(2)—C(3)	1·871 (9)	1·900 (8)
C(3)—N(4)	1·439 (10)	1·416 (10)
N(4)—C(5)	1·336 (10)	1·369 (11)
C(5)—C(6)	1·532 (11)	1·532 (12)
C(6)—N(7)	1·451 (10)	1·453 (10)
N(7)—C(8)	1·345 (11)	1·347 (10)
C(8)—C(3)	1·525 (12)	1·512 (11)
C(5)—O(9)	1·229 (10)	1·205 (10)
C(6)—C(10)	1·530 (12)	1·538 (12)
C(10)—O(11)	1·388 (11)	1·403 (11)
N(7)—C(12)	1·474 (12)	1·484 (11)
C(8)—O(13)	1·241 (10)	1·219 (9)
N(4)—C(14)	1·480 (10)	1·456 (10)
C(22)—C(14)	1·561 (11)	1·562 (11)
C(22)—C(23)	1·537 (11)	1·534 (11)
C(23)—C(3)	1·531 (12)	1·533 (11)
C(14)—N(15)	1·443 (11)	1·459 (10)
N(15)—C(16)	1·411 (11)	1·400 (11)
C(16)—C(21)	1·374 (12)	1·382 (12)
C(21)—C(22)	1·533 (11)	1·543 (12)
C(16)—C(17)	1·402 (12)	1·389 (14)
C(17)—C(18)	1·364 (14)	1·366 (16)
C(18)—C(19)	1·387 (14)	1·397 (16)
C(19)—C(20)	1·382 (13)	1·393 (15)
C(20)—C(21)	1·397 (12)	1·389 (13)
C(22)—C(22*)	1·580 (11)	
C(10)—H(1·C10)	1·06 (7)	1·06 (8)
C(10)—H(2·C10)	1·13 (10)	0·99 (8)
O(11)—H(O11)	1·01 (10)	0·81 (9)
C(12)—H(1·C12)	0·97 (10)	1·00 (8)
C(12)—H(2·C12)	0·99 (11)	0·92 (8)
C(12)—H(3·C12)	1·13 (9)	1·02 (8)

Table 3 (cont.)

	Monomer part I	Monomer part II
C(14)—H(C14)	0·97 (8)	1·13 (9)
N(15)—H(N15)	1·01 (9)	0·92 (9)
C(17)—H(C17)	1·05 (9)	1·12 (9)
C(18)—H(C18)	0·97 (9)	1·07 (9)
C(19)—H(C19)	1·04 (9)	1·19 (9)
C(20)—H(C20)	1·00 (9)	1·00 (8)
C(23)—H(1·C23)	1·04 (8)	0·89 (9)
C(23)—H(2·C23)	0·94 (8)	1·10 (8)
(b) Bond angles		
S(2)—S(1)—C(6)	98·0 (3)°	98·9 (3)°
S(1)—S(2)—C(3)	98·3 (3)	96·8 (2)
S(2)—C(3)—N(4)	112·3 (4)	112·1 (4)
S(2)—C(3)—C(8)	102·9 (4)	101·1 (3)
S(2)—C(3)—C(23)	111·3 (4)	110·4 (4)
N(4)—C(3)—C(8)	110·8 (6)	113·1 (6)
N(4)—C(3)—C(23)	104·5 (5)	104·9 (5)
C(8)—C(3)—C(23)	115·2 (6)	115·4 (6)
C(3)—N(4)—C(5)	118·2 (6)	119·4 (6)
C(3)—N(4)—C(14)	115·8 (6)	115·9 (6)
C(5)—N(4)—C(14)	126·0 (6)	124·6 (6)
N(4)—C(5)—C(6)	113·0 (6)	111·1 (6)
N(4)—C(5)—O(9)	124·1 (6)	124·1 (6)
C(6)—C(5)—O(9)	122·9 (5)	124·7 (6)
C(5)—C(6)—S(1)	105·0 (5)	104·0 (5)
C(5)—C(6)—N(7)	109·8 (5)	110·6 (5)
C(5)—C(6)—C(10)	109·2 (6)	112·0 (6)
S(1)—C(6)—N(7)	111·1 (4)	110·1 (4)
S(1)—C(6)—C(10)	106·9 (4)	104·4 (4)
N(7)—C(6)—C(10)	114·4 (6)	114·9 (6)
C(6)—N(7)—C(8)	117·8 (6)	118·8 (6)
C(6)—N(7)—C(12)	121·2 (6)	119·7 (6)
C(8)—N(7)—C(12)	119·0 (7)	119·7 (6)
N(7)—C(8)—C(3)	112·9 (6)	112·3 (7)
N(7)—C(8)—O(13)	125·4 (6)	124·7 (6)
C(3)—C(8)—O(13)	121·7 (6)	122·9 (5)
C(6)—C(10)—O(11)	110·5 (5)	107·6 (5)
N(4)—C(14)-N(15)	113·6 (5)	112·2 (5)
N(4)—C(14)—C(22)	101·1 (5)	101·8 (5)
N(15)-C(14)—C(22)	105·3 (5)	106·8 (5)
C(14)—N(15)-C(16)	108·7 (5)	107·9 (6)
N(15)-C(16)-C(17)	128·1 (7)	126·4 (8)
N(15)-C(16)-C(21)	109·9 (6)	112·5 (6)
C(17)-C(16)-C(21)	122·0 (7)	121·1 (8)
C(16)-C(17)-C(18)	117·3 (7)	117·0 (8)
C(17)-C(18)-C(19)	121·7 (8)	123·1 (10)
C(18)-C(19)-C(20)	120·7 (8)	119·3 (9)
C(19)-C(20)-C(21)	118·5 (7)	117·7 (8)
C(20)-C(21)-C(22)	130·0 (7)	129·5 (8)
C(20)-C(21)-C(16)	119·7 (7)	121·5 (7)
C(22)-C(21)-C(16)	110·2 (6)	109·0 (6)
C(21)-C(22)-C(23)	113·8 (6)	113·6 (6)
C(21)-C(22)-C(14)	100·0 (5)	100·4 (5)
C(21)-C(22)-C(22*)	113·5 (6)	112·3 (6)
C(23)-C(22)-C(14)	106·3 (5)	106·3 (5)
C(23)-C(22)-C(22*)	111·4 (6)	112·7 (6)
C(14)-C(22)-C(22*)	111·0 (6)	110·7 (6)
C(22)-C(23)-C(3)	104·7 (8)	103·5 (7)

(Fig. 1). Because the molecule is a dimer, an additional check on the accuracy of the structure determination is possible by comparing chemically equivalent bond lengths and bond angles. As can be seen from Table 3 the internal consistency is quite good; for bond lengths the mean value of $|d_I - d_{II}|/\sqrt{\sigma_I^2 + \sigma_{II}^2}$ is 0·7; for bond angles the corresponding quantity is 1·6.

The dimeric molecule has an approximate twofold

axis perpendicular to the bond C(22)–C(22*) (Fig. 2). Although corresponding bond lengths and bond angles in the dimer agree quite well, some differences between chemically equivalent torsion angles are significant (Table 4). In monomer I, the indolene five-ring (B) and the cis-fused pyrrolidine ring (C) have almost exact C_S and C_2 symmetry respectively, but in monomer II the corresponding rings have conformations that deviate significantly from these symmetries. A further difference between the two monomers concerns the relative positions of the hydrogen atoms bonded to the indolene nitrogens N(15) and N(15*) (Fig. 3). The hydrogen atom H(N15) in monomer I is 0·4 (1) Å above the least-squares plane through the benzene ring and an intramolecular hydrogen bond to the keto-oxygen O(9) is formed. In monomer II the pyramidal nitrogen N(15*) is inverted and the hydrogen atom is 0·4 (1) Å below the benzene-ring plane. This increases the distance H···O(9*) to 3·2 (1) Å so that the intramolecular hydrogen bond to O(9*) is absent. Instead, an intermolecular hydrogen bond, N(15*)–H···O(13), is formed to the molecule one b-translation up (Fig. 4). The two intramolecular hydrogen bonds, O(11)–H···O(9), are formed in both monomer parts (Figs. 2 and 3). Note that the hydroxyl oxygen O(11) is in an antiperiplanar position (Dunitz & Prelog, 1960) to S(1), $\tau[S(1)–C(6)–C(10)–O(11)] = 179·0$ (1)°, in both monomer parts, although a stronger hydrogen bond to O(9) could be formed if the hydroxyl group were in the plane O(9)–C(5)–C(6)–C(10), i.e. anticlinal to S(1).

Table 4. *Torsion angles in the indolene five-membered rings (B) and the pyrrolidine rings (C)*

Ring B	Monomer I	Monomer II
C(14)–N(15)–C(16)–C(21)	15·3 (1·0)°	8·3 (1·0)°
N(15)–C(16)–C(21)–C(22)	−0·5 (1·1)	4·2 (1·1)
C(16)–C(21)–C(22)–C(14)	−14·3 (0·9)	−13·7 (0·9)
C(21)–C(22)–C(14)–N(15)	22·5 (0·8)	18·2 (0·8)
C(22)–C(14)–N(15)–C(16)	−24·1 (0·9)	−17·0 (0·9)
Ring C		
C(3)—N(4)—C(14)–C(22)	−9·2 (0·9)°	−2·7 (0·9)°
N(4)—C(14)–C(22)–C(23)	22·7 (0·8)	19·0 (0·8)
C(14)–C(22)–C(23)–C(3)	−28·3 (0·9)	−27·5 (0·8)
C(22)–C(23)–C(3)—N(4)	22·1 (0·9)	25·5 (0·8)
C(23)–C(3)—N(4)—C(14)	−8·1 (1·0)	−14·6 (0·9)

The two epidithio-diketopiperazine systems in chaetocin are identical within limits of error and have almost exact C_2 symmetry. The averaged structural parameters defining this system are compared with the corresponding parameters found in the structure of gliotoxin and sporidesmin in Table 5. The agreement is good. The difference in the sign of the C–S–S–C torsion angle expresses the opposite chirality of the epidithio-diketopiperazine part in chaetocin.

The torsion angles around C(22)–C(22*) linking the two monomers correspond to a staggered conformation about this bond. The shortest interatomic distances between the monomer parts are between 3·01 and 3·16 Å.

The packing of the molecule is shown in Fig. 4. Apart from the intermolecular hydrogen bond described above there are no other close intermolecular
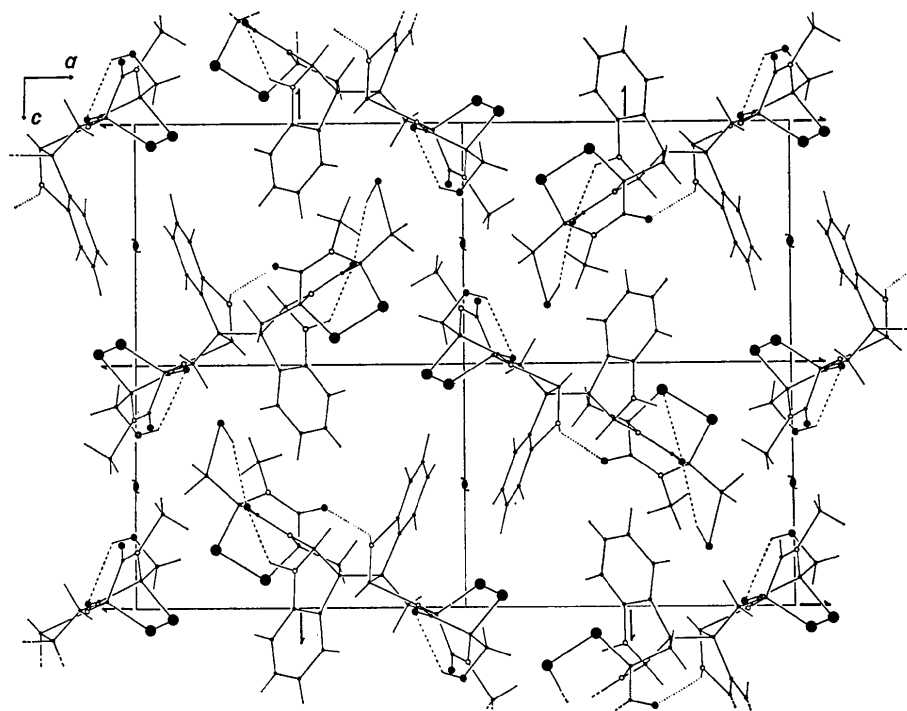

Fig. 4. Packing diagram of chaetocin. Dashed lines indicate intramolecular hydrogen bonds, the dotted line the only existing intermolecular hydrogen bond.

Table 5. *Comparison of structural parameters of the dithiodiketopiperazin moiety as found in sporidesmin, gliotoxin and chaetocin*

	Sporidesmin*	Gliotoxin†	Chaetocin
C–C(keto)	1·52 Å	1·51 Å	1·53 Å
C(keto)–N	1·37	1·35	1·35
N–C	1·43	1·45	1·45
C=O	1·23	1·23	1·23
C–S	1·90	1·89	1·88
S–S	2·08	2·08	2·077
C–C(keto)–N	113°	114°	113°
C=C(keto)–N	124	125	125
C–C(keto)=O	124	122	123
C(keto)–N–C	114	118	118
N–C–C(keto)	112	111	111
C(keto)–C–S	102	103	103
N–C–S	112	111	112
C(keto)–C–S	102	103	103
N–C–S	112	111	112
C–S–S	98	98	98
C–S–S–C	−10	−12	+11

* Fridrichsons & Mathieson (1965).
† Fridrichsons & Mathieson (1967).

contacts. The shortest distances found are $H \cdots H = 2 \cdot 2$ (2), $S \cdots H = 3 \cdot 0$ (1), $C \cdots N = 3 \cdot 30$ (1), $S \cdots C = 3 \cdot 41$ (1) Å.

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The Crystal Structure of Silver Diethyl Phosphate, AgPO2(OC2H5)2

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The crystal structure of silver diethyl phosphate, AgPO2(OC2H5)2, was determined with 853 diffractometer-collected intensities. The space group is orthorhombic, *Pccn*, and the unit cell contains two formula units. The unit-cell dimensions at 23°C are $a = 20 \cdot 19$ (1), $b = 14 \cdot 35$ (4) and $c = 5 \cdot 86$ (1) Å. The intensities were measured by the 2θ-scan method with Mo $K\alpha$ radiation and the structure was solved by Patterson methods and refined by block-diagonal least-squares calculations to an R value of 0·043. The silver ion is coordinated to four oxygen atoms in a distorted tetrahedral arrangement with a mean Ag–O distance of 2·36 Å. Thermal motion of the atoms in the diethyl phosphate anion is high and can be qualitatively explained as a rigid-body motion of the phosphate group coupled with a librational motion of the ester groups about the P–O bonds. The ester conformation with respect to the phosphate group is *syn*-clinal, *anti*-clinal.

Introduction

A study of the conformation of diester phosphates is of interest both for the light it might throw on bonding within the phosphate group (Collin, 1966, 1969) and for its implications to the structure of nucleic acids (Sundaralingam, 1969) and other molecules of biological interest.

Although the structures of a number of phosphate diesters have been determined, that of barium diethyl phosphate (Kyogoku & Iitaka, 1966) is the only acyclic ester in which the ester groups contain no ionic species, or species capable of hydrogen-bond formation.

Many silver salts exhibit short silver–oxygen distances in which partial covalent character may occur, and it is of interest to examine the effects of such interactions on the bonding scheme within the diester anion and on the resulting conformation. We suspect that conformational differences such as those between the