Absorption correction:
empirical ψ scans (Sheldrick, 1991)
$T_{\min} = 0.632$, $T_{\max} = 0.947$
2845 measured reflections
2675 independent reflections
2413 observed reflections [$I > 2\sigma(I)$]

$h = 0 \rightarrow 11$
$k = 0 \rightarrow 12$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 97 reflections
intensity variation: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0401$
$wR(F^2) = 0.1064$
$S = 0.930$
2675 reflections
255 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.019$
$\Delta\rho_{\max} = 1.151$ e Å^{-3}
$\Delta\rho_{\min} = -1.052$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
C11	0.2636 (8)	0.5675 (10)	1.1483 (5)	0.028 (2)
O11	0.3907 (5)	0.6143 (5)	1.0959 (3)	0.0230 (10)
C12	0.4860 (7)	0.5105 (8)	1.0717 (5)	0.0191 (13)
O12	0.4658 (6)	0.3874 (5)	1.0828 (4)	0.0228 (11)
C13	0.6256 (6)	0.5761 (7)	1.0277 (4)	0.0171 (11)
Cl1	0.7709 (2)	0.6034 (2)	1.13400 (10)	0.0243 (3)
C14	0.6924 (6)	0.4767 (7)	0.9550 (4)	0.0176 (12)
Br1	0.52780 (6)	0.45769 (7)	0.84160 (4)	0.0202 (2)
C15	0.8407 (7)	0.5313 (7)	0.9178 (4)	0.0177 (12)
C16	0.9665 (7)	0.4403 (8)	0.9221 (4)	0.0222 (15)
C17	1.1032 (7)	0.4861 (9)	0.8874 (5)	0.029 (2)
C18	1.1149 (8)	0.6218 (9)	0.8488 (5)	0.029 (2)
C19	0.9817 (8)	0.7111 (9)	0.8419 (5)	0.029 (2)
C110	0.8485 (8)	0.6650 (8)	0.8765 (5)	0.0228 (13)
C21	0.7640 (8)	0.4117 (10)	0.6351 (5)	0.031 (2)
O21	0.8684 (6)	0.3859 (6)	0.5608 (4)	0.0295 (12)
C22	0.9510 (7)	0.4946 (7)	0.5373 (5)	0.0244 (14)
O22	0.9413 (6)	0.6133 (6)	0.5705 (4)	0.0370 (14)
C23	1.0632 (7)	0.4542 (9)	0.4619 (5)	0.0252 (13)
Cl2	1.01086 (14)	0.5443 (2)	0.34652 (9)	0.0177 (3)
C24	1.2262 (7)	0.5024 (8)	0.5005 (4)	0.0235 (13)
Br2	1.27458 (8)	0.40986 (8)	0.63417 (4)	0.0282 (2)
C25	1.3511 (7)	0.4646 (9)	0.4358 (4)	0.0209 (12)
C26	1.3568 (7)	0.3292 (8)	0.3927 (5)	0.0219 (14)
C27	1.4795 (8)	0.2950 (7)	0.3391 (5)	0.0202 (13)
C28	1.5968 (8)	0.3933 (9)	0.3290 (5)	0.025 (2)
C29	1.5911 (7)	0.5248 (9)	0.3705 (5)	0.026 (2)
C210	1.4672 (7)	0.5623 (8)	0.4247 (4)	0.0212 (13)

Table 2. *Selected geometric parameters* (Å, °)

C11—O11	1.444 (7)	C21—O21	1.446 (7)
O11—C12	1.346 (8)	O21—C22	1.311 (8)
C12—O12	1.187 (9)	C22—O22	1.213 (9)
C12—C13	1.538 (8)	C22—C23	1.535 (8)
C13—C14	1.520 (8)	C23—C24	1.520 (8)
C13—Cl1	1.819 (6)	C23—Cl2	1.788 (7)
C14—C15	1.523 (8)	C24—C25	1.509 (8)
C14—Br1	1.982 (5)	C24—Br2	2.007 (7)
C15—C16	1.385 (9)	C25—C26	1.407 (11)
C15—C110	1.385 (10)	C25—C210	1.386 (10)
C16—C17	1.391 (9)	C26—C27	1.390 (8)
C17—C18	1.391 (11)	C27—C28	1.396 (10)
C18—C19	1.425 (10)	C28—C29	1.364 (11)
C19—C110	1.365 (9)	C29—C210	1.412 (8)
C14—C13—Cl1	108.4 (4)	C24—C23—Cl2	107.0 (5)
C12—C13—Cl1	105.0 (4)	C22—C23—Cl2	110.0 (5)
C13—C14—Br1	105.1 (4)	C25—C24—Br2	109.1 (4)
C15—C14—Br1	109.8 (4)	C23—C24—Br2	105.7 (4)

Data collection, cell refinement and data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1994).

We thank Professor W. T. Robinson, University of Canterbury, for data collection, and Associate Professor J. Simpson and Dr L. R. Hanton for assistance with crystallography. This work is supported by a University of Otago Division of Sciences Research Grant.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: AB1198). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 135–139

(13-Methyl-1,4,7,8,13,13b-hexahydro[1′,2′]oxazepino[2′,3′:1,2]pyrido[3,4-*b*]indol-1-yl)methanol and its Unusual Packing Style

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(*Received* 5 *March* 1993; *accepted* 4 *August* 1994)

Abstract

The asymmetric unit of the crystal of (13-methyl-1,4,7,8,13,13b-hexahydro[1′,2′]oxazepino[2′,3′:1,2]-pyrido[3,4-*b*]indol-1-yl)methanol, $C_{17}H_{20}N_2O_2$, is

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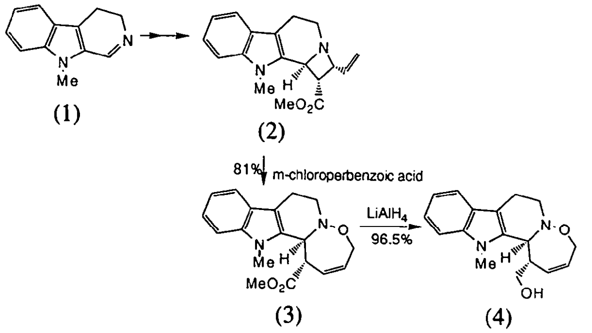
Acta Crystallographica Section C
ISSN 0108-2701 © 1995

composed of four molecules. These molecules adopt almost planar conformations except for the terminal seven-membered oxazepine ring. Each molecule is stabilized by both intermolecular hydrogen bonds between symmetry-related molecules and interplanar stacking interactions. It is worth noting that the molecules exist as a 3:1 mixture of enantiomers.

Comment

We recently reported the preparation of the unique ring system methyl 10-methyl-2-vinyl-1,2,4,5,10,10b-hexahydroazeto[1′,2′:1,2]pyrido[3,4-*b*]indole-1-carboxylate (2) from 3,4-dihydro-β-carboline (1) (Kurihara *et al.*, 1991). Treatment of (2) with *m*-chloroperbenzoic acid in methylene dichloride at 273 K gave product (3), $C_{18}H_{20}N_2O_3$, in 81% yield. ^1H and ^{13}C NMR spectra showed the presence of two olefinic protons at δ 5.61–5.79 as multiplets, as well as three CH_2 C atoms at δ 21.5, 53.0 and 72.0. Thus, the structure of (3) was tentatively confirmed as methyl 13-methyl-1,4,7,8,13,13b-hexahydro[1′,2′]oxazepino[2′,3′:1,2]pyrido[3,4-*b*]indole-1-carboxylate, whose framework corresponds to that of the (12*S*)-carba analog of eudistomin, a natural marine antiviral product. Thus, product (3) should prove to be an attractive compound for antiviral structure–activity studies. In order to obtain definitive evidence of the structure of (3) an X-ray crystallographic analysis of the corresponding alcohol (4), m.p. 414–415 K, obtained by reduction of (3) with $LiAlH_4$ in 96.5% yield, was carried out.



The molecular structure of the title compound (*ORTEP*II; Johnson, 1976) is presented in Fig. 1. Bond distances and angles are presented in Table 2, all of which show normal values within experimental error. Torsion angles including non-H atoms are also listed in Table 2. The wire-frame model of this compound viewed from the side of the tetrahydro-β-carboline moiety is shown in scheme below. A stereoscopic view of the molecular packing drawn by *PLUTO* (Motherwell & Clegg, 1978) is shown in Fig. 2 (*b* axis projection). Although this compound is almost planar the terminal oxazepine ring adopts a chair form. As shown in Fig. 1, four molecules (*A*, *B*, *C* and *D*) exist in the asymmetric unit of the crystal. Molecules *A*, *C* and *D* are conformational isomers with the same absolute configuration, whereas molecule *B* corresponds to the enantiomer with a different configuration. To our knowledge, it is unprecedented that four molecules exist as an enantiomeric mixture with a ratio of 3:1 in a single crystal. The molecules are stabilized by intermolecular hydrogen bonds between the N atom of the

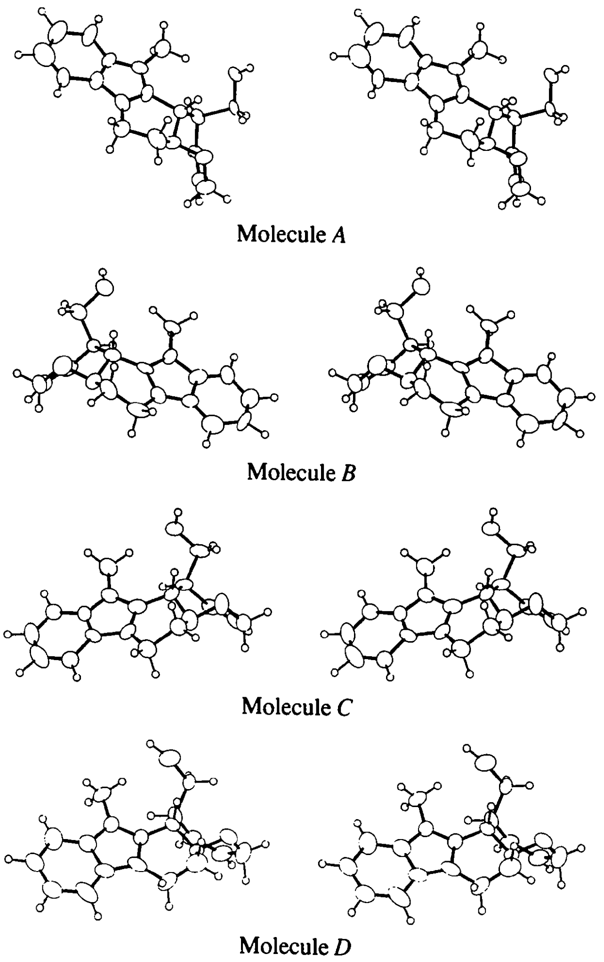


Fig. 1. The four molecules in the asymmetric unit drawn stereoscopically using *ORTEP*II (Johnson, 1976).

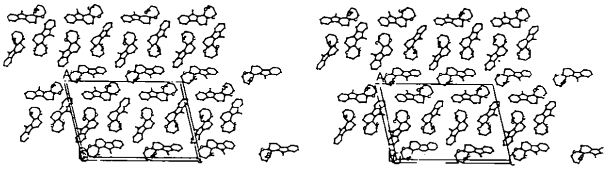
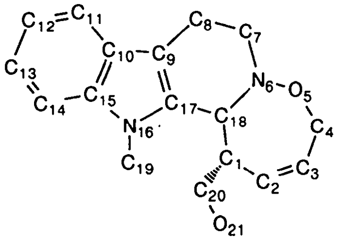
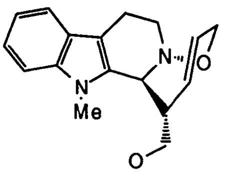


Fig. 2. Stereoscopic packing diagram of (13-methyl-1,4,7,8,13,13b-hexahydro[1′,2′]oxazepino[2′,3′:1,2]pyrido[3,4-*b*]indol-1-yl)-methanol viewed along the *b* axis.

indole moiety (N6) and the hydroxymethyl O atom of the oxazepine ring (O21) (N6···O21 = 2.9 Å) and also by stacking interactions between the indole moiety of the four molecules whose interplanar spacing is about 3.3 Å.

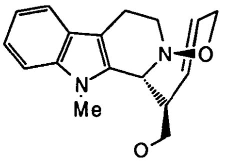




3

Molecules *A*, *C* and *D*

:



1

Molecule *B*

Three molecules (*A*, *C* and *D*) have almost the same conformations, but from the results of steric energy calculations variations in the energy values of three conformations are observed in the range −53963.6 to −54156.0 kJ mol^{-1}. These variations are caused by the conformational change of the terminal oxazepine ring and the surrounding substituents. On the other hand, molecule *B*, which is a mirror-image isomer of the other molecules (*A*, *C* and *D*), is energetically more stable by about 234 kJ mol^{-1} (−54295.3 kJ mol^{-1}). Conversion of ester (3) to (12*S*)-carbaeudistomin and its biological evaluation are in progress.

Experimental

Crystal data

$C_{17}H_{20}N_2O_2$
M_r = 284.359
Monoclinic
Pc
a = 18.499 (4) Å
b = 6.2149 (9) Å
c = 26.45 (1) Å
β = 103.16 (3)°
V = 2961 (1) Å^3
Z = 8
D_x = 1.2757 Mg m^{-3}

Cu *Kα* radiation
λ = 1.5418 Å
Cell parameters from 20 reflections
θ = 23.83–28.06°
μ = 0.638 mm^{-1}
T = 293 K
Needle
0.50 × 0.10 × 0.10 mm
Colourless

Data collection

Rigaku AFC diffractometer
ω–2θ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{\min}$ = 0.83, $T_{\max}$ = 0.93
5706 measured reflections
5168 independent reflections
4021 observed reflections [$F > 3.0\sigma(F)$]

$\theta_{\max}$ = 62.5°
$h = -21 \rightarrow 21$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 30$
4 standard reflections monitored every 100 reflections
intensity variation: 5%

Refinement

Refinement on F
R = 0.0615
wR = 0.0675
S = 1.232
4021 reflections
1078 parameters
Only coordinates of H atoms refined

$w = 1.0/[\sigma^2(F_o) - 0.09527F_o + 0.00606F_o^2]$
$(\Delta/\sigma)_{\max}$ = 0.11
$\Delta\rho_{\max}$ = 0.21 e Å^{-3}
$\Delta\rho_{\min}$ = −0.05 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
C1*A*	0.9428 (3)	0.2564 (8)	0.3598 (2)	3.5 (2)
C2*A*	0.9883 (3)	0.0971 (8)	0.4011 (2)	3.1 (2)
C3*A*	0.9693 (3)	−0.0007 (9)	0.4393 (2)	4.1 (2)
C4*A*	0.8930 (3)	0.002 (1)	0.4538 (2)	4.1 (2)
O5*A*	0.8397 (2)	0.1181 (6)	0.4155 (1)	4.3 (2)
N6*A*	0.8368 (2)	0.0175 (7)	0.3656 (1)	3.5 (2)
C7*A*	0.7570 (3)	−0.0460 (9)	0.3458 (2)	4.4 (3)
C8*A*	0.7562 (3)	−0.182 (1)	0.2968 (2)	4.4 (3)
C9*A*	0.8012 (2)	−0.0687 (8)	0.2650 (2)	3.4 (2)
C10*A*	0.8027 (3)	−0.1090 (9)	0.2115 (2)	3.7 (2)
C11*A*	0.7659 (3)	−0.2632 (9)	0.1738 (2)	3.8 (2)
C12*A*	0.7761 (4)	−0.267 (1)	0.1262 (3)	6.3 (3)
C13*A*	0.8293 (3)	−0.105 (1)	0.1121 (2)	6.1 (3)
C14*A*	0.8658 (3)	0.046 (1)	0.1482 (2)	5.3 (3)
C15*A*	0.8518 (3)	0.0404 (8)	0.1991 (2)	3.1 (2)
N16*A*	0.8787 (2)	0.1659 (6)	0.2394 (2)	3.0 (2)
C17*A*	0.8504 (2)	0.0960 (8)	0.2789 (2)	3.1 (2)
C18*A*	0.8645 (2)	0.1903 (7)	0.3354 (2)	2.9 (2)
C19*A*	0.9248 (4)	0.363 (1)	0.2396 (2)	4.5 (3)
C20*A*	0.9440 (3)	0.4801 (7)	0.3855 (2)	3.0 (2)
O21*A*	0.9246 (2)	0.6266 (5)	0.3458 (1)	3.6 (1)
C1*B*	0.0252 (2)	0.2531 (7)	0.6218 (2)	2.5 (2)
C2*B*	−0.0174 (3)	0.4002 (9)	0.5824 (2)	4.4 (2)
C3*B*	0.0028 (3)	0.4930 (9)	0.5417 (2)	4.1 (2)
C4*B*	0.0740 (4)	0.500 (1)	0.5321 (2)	5.7 (3)
O5*B*	0.1298 (2)	0.3813 (6)	0.5682 (2)	4.6 (2)
N6*B*	0.1336 (2)	0.4813 (7)	0.6183 (2)	3.3 (2)
C7*B*	0.2101 (3)	0.533 (1)	0.6401 (2)	4.5 (3)
C8*B*	0.2159 (3)	0.6687 (9)	0.6877 (2)	4.2 (2)
C9*B*	0.1684 (3)	0.5719 (9)	0.7218 (2)	3.6 (2)
C10*B*	0.1670 (3)	0.6110 (8)	0.7734 (2)	3.4 (2)
C11*B*	0.1996 (3)	0.764 (1)	0.8089 (3)	5.7 (3)
C12*B*	0.1847 (3)	0.7440 (9)	0.8605 (2)	4.0 (2)
C13*B*	0.1413 (3)	0.598 (1)	0.8720 (2)	4.8 (3)
C14*B*	0.1058 (3)	0.4443 (9)	0.8366 (2)	3.4 (2)
C15*B*	0.1189 (3)	0.4559 (9)	0.7883 (2)	4.0 (2)
N16*B*	0.0920 (2)	0.3246 (7)	0.7434 (1)	3.2 (2)
C17*B*	0.1236 (3)	0.3991 (7)	0.7019 (2)	2.9 (2)
C18*B*	0.1092 (3)	0.3150 (8)	0.6498 (2)	3.2 (2)
C19*B*	0.0499 (3)	0.1340 (8)	0.7490 (2)	3.6 (2)
C20*B*	0.0230 (3)	0.0320 (9)	0.5974 (2)	4.3 (3)
O21*B*	0.0517 (2)	−0.1269 (6)	0.6395 (1)	5.0 (2)

C1*C*	0.5396 (3)	0.4937 (8)	0.0947 (2)	4.1 (2)
C2*C*	0.6091 (3)	0.3420 (9)	0.1034 (2)	4.1 (2)
C3*C*	0.6475 (3)	0.2500 (9)	0.1425 (2)	4.9 (3)
C4*C*	0.6294 (3)	0.238 (1)	0.1926 (2)	4.7 (3)
O5*C*	0.5605 (2)	0.3619 (7)	0.1982 (1)	5.2 (2)
N6*C*	0.4988 (3)	0.2570 (9)	0.1612 (2)	4.8 (2)
C7*C*	0.4418 (3)	0.213 (1)	0.1893 (2)	4.4 (3)
C8*C*	0.3837 (3)	0.066 (1)	0.1510 (2)	4.4 (3)
C9*C*	0.3688 (3)	0.1793 (8)	0.1010 (2)	3.5 (2)
C10*C*	0.3049 (3)	0.1523 (8)	0.0575 (2)	3.3 (2)
C11*C*	0.2440 (3)	−0.004 (1)	0.0501 (2)	4.2 (2)
C12*C*	0.1940 (3)	0.015 (1)	0.0028 (2)	5.3 (3)
C13*C*	0.1988 (3)	0.164 (1)	−0.0308 (2)	5.0 (3)
C14*C*	0.2574 (3)	0.3101 (9)	−0.0240 (2)	3.2 (2)
C15*C*	0.3088 (3)	0.2993 (8)	0.0214 (2)	3.4 (2)
N16*C*	0.3683 (3)	0.4200 (7)	0.0392 (2)	3.9 (2)
C17*C*	0.4072 (3)	0.3453 (9)	0.0881 (2)	3.7 (2)
C18*C*	0.4777 (3)	0.4294 (8)	0.1235 (2)	3.9 (2)
C19*C*	0.3860 (4)	0.615 (1)	0.0130 (2)	5.4 (3)
C20*C*	0.5699 (3)	0.7214 (8)	0.1131 (3)	4.9 (3)
O21*C*	0.5136 (2)	0.8715 (5)	0.0919 (2)	4.5 (2)
C1*D*	0.4292 (2)	−0.0070 (9)	0.3884 (2)	3.2 (2)
C2*D*	0.3652 (3)	−0.1540 (8)	0.3823 (2)	4.6 (2)
C3*D*	0.3269 (3)	−0.2560 (9)	0.3359 (3)	5.2 (3)
C4*D*	0.3442 (4)	−0.250 (1)	0.2820 (3)	5.9 (3)
O5*D*	0.4061 (2)	−0.1436 (6)	0.2842 (1)	5.0 (2)
N6*D*	0.4658 (2)	−0.2381 (6)	0.3235 (2)	3.1 (2)
C7*D*	0.5237 (3)	−0.318 (1)	0.2955 (2)	4.9 (3)
C8*D*	0.5794 (3)	−0.4400 (9)	0.3310 (2)	4.2 (2)
C9*D*	0.6048 (3)	−0.3323 (9)	0.3834 (2)	3.8 (2)
C10*D*	0.6657 (3)	−0.3745 (8)	0.4234 (2)	3.6 (2)
C11*D*	0.7217 (3)	−0.519 (1)	0.4343 (2)	5.2 (3)
C12*D*	0.7775 (4)	−0.502 (1)	0.4804 (3)	6.0 (3)
C13*D*	0.7762 (3)	−0.328 (1)	0.5200 (2)	4.6 (3)
C14*D*	0.7168 (3)	−0.174 (1)	0.5096 (3)	5.8 (3)
C15*D*	0.6633 (3)	−0.2020 (9)	0.4623 (2)	4.0 (2)
N16*D*	0.5985 (2)	−0.0714 (7)	0.4438 (2)	3.4 (2)
C17*D*	0.5650 (3)	−0.1553 (8)	0.3962 (2)	3.1 (2)
C18*D*	0.4946 (3)	−0.0673 (8)	0.3624 (2)	3.0 (2)
C19*D*	0.5854 (3)	0.1216 (8)	0.4707 (2)	4.0 (2)
C20*D*	0.4006 (3)	0.2140 (9)	0.3728 (2)	4.3 (2)
O21*D*	0.4593 (2)	0.3691 (7)	0.3871 (2)	5.5 (2)

Table 2. *Geometric parameters* (Å, °)

	Molecule			
	A	*B*	*C*	*D*
C1—C2	1.569 (7)	1.473 (7)	1.568 (8)	1.475 (8)
C1—C18	1.503 (7)	1.608 (7)	1.565 (8)	1.567 (7)
C1—C20	1.545 (7)	1.515 (7)	1.559 (8)	1.496 (7)
C2—C3	1.294 (7)	1.347 (8)	1.252 (8)	1.419 (8)
C3—C4	1.545 (8)	1.398 (9)	1.441 (9)	1.531 (9)
C4—O5	1.437 (7)	1.440 (8)	1.525 (7)	1.312 (8)
O5—N6	1.450 (6)	1.451 (6)	1.475 (7)	1.457 (6)
N6—C7	1.502 (7)	1.438 (7)	1.448 (8)	1.518 (7)
N6—C18	1.497 (6)	1.462 (7)	1.455 (7)	1.490 (6)
C7—C8	1.545 (8)	1.499 (8)	1.588 (8)	1.441 (8)
C8—C9	1.488 (7)	1.519 (8)	1.468 (8)	1.514 (8)
C9—C10	1.444 (7)	1.392 (7)	1.459 (7)	1.384 (8)
C9—C17	1.363 (7)	1.385 (7)	1.340 (8)	1.407 (7)
C10—C11	1.438 (7)	1.375 (8)	1.467 (8)	1.352 (8)
C10—C15	1.389 (7)	1.427 (7)	1.335 (7)	1.494 (8)
C11—C12	1.315 (9)	1.458 (8)	1.381 (8)	1.42 (1)
C12—C13	1.51 (1)	1.293 (8)	1.300 (9)	1.50 (1)
C13—C14	1.398 (9)	1.393 (8)	1.394 (8)	1.436 (9)
C14—C15	1.428 (8)	1.355 (7)	1.353 (7)	1.418 (9)
C15—N16	1.323 (6)	1.433 (7)	1.327 (7)	1.438 (7)
N16—C17	1.343 (6)	1.433 (6)	1.408 (7)	1.373 (6)
N16—C19	1.492 (7)	1.444 (7)	1.470 (8)	1.443 (7)
C17—C18	1.571 (7)	1.441 (7)	1.515 (8)	1.505 (7)
C20—O21	1.374 (6)	1.493 (7)	1.415 (7)	1.437 (7)
C2—C1—C18	116.0 (3)	118.9 (3)	116.2 (3)	119.0 (3)
C2—C1—C20	108.0 (3)	107.7 (3)	106.0 (3)	108.3 (3)
C18—C1—C20	110.5 (3)	110.0 (3)	109.3 (3)	111.0 (3)
C1—C2—C3	129.9 (3)	129.1 (3)	133.5 (4)	127.0 (3)
C2—C3—C4	127.9 (3)	127.1 (4)	125.2 (4)	128.7 (4)
C3—C4—O5	110.5 (3)	115.3 (3)	116.0 (3)	109.7 (3)
C4—O5—N6	107.6 (3)	105.3 (3)	104.5 (3)	109.9 (3)
O5—N6—C7	105.1 (3)	107.5 (3)	106.7 (3)	106.8 (3)
O5—N6—C18	103.3 (3)	105.1 (3)	100.1 (3)	107.4 (3)
C7—N6—C18	115.5 (3)	109.4 (3)	112.2 (3)	112.9 (3)
N6—C7—C8	104.9 (3)	109.8 (3)	104.3 (3)	109.5 (3)
C7—C8—C9	108.4 (3)	109.6 (3)	105.1 (3)	113.0 (4)
C8—C9—C10	127.6 (3)	130.9 (3)	127.4 (3)	130.2 (3)
C8—C9—C17	128.9 (3)	117.3 (3)	126.7 (4)	119.7 (3)
C10—C9—C17	103.5 (3)	111.4 (3)	105.6 (3)	110.1 (3)
C9—C10—C11	133.1 (3)	133.4 (4)	129.9 (3)	137.7 (4)
C9—C10—C15	106.0 (3)	107.7 (3)	108.6 (3)	104.1 (3)
C11—C10—C15	120.9 (3)	118.9 (4)	121.5 (3)	118.1 (4)
C10—C11—C12	121.8 (4)	115.7 (3)	113.6 (3)	120.4 (4)
C11—C12—C13	117.9 (4)	122.7 (4)	123.0 (4)	122.0 (4)
C12—C13—C14	121.2 (4)	123.1 (3)	123.2 (4)	118.7 (4)
C13—C14—C15	117.7 (4)	116.0 (4)	116.8 (4)	115.9 (4)
C10—C15—C14	120.5 (4)	123.6 (3)	121.8 (3)	124.9 (4)
C10—C15—N16	110.5 (3)	106.0 (3)	108.0 (3)	108.9 (3)
C14—C15—N16	129.0 (3)	130.4 (3)	130.2 (3)	126.2 (3)
C15—N16—C17	107.1 (3)	109.0 (3)	110.4 (3)	105.4 (3)
C15—N16—C19	126.6 (3)	118.4 (3)	123.7 (4)	121.5 (3)
C17—N16—C19	125.9 (3)	131.9 (3)	125.7 (4)	132.6 (3)
C9—C17—N16	112.8 (3)	105.8 (3)	107.3 (3)	111.5 (3)
C9—C17—C18	119.5 (3)	127.5 (3)	122.7 (3)	124.8 (3)
N16—C17—C18	127.6 (3)	126.6 (3)	129.9 (3)	123.8 (3)
C1—C18—N6	112.4 (3)	107.3 (3)	114.2 (3)	106.4 (3)
C1—C18—C17	116.5 (3)	118.4 (3)	114.2 (3)	118.5 (3)
N6—C18—C17	103.7 (3)	105.9 (3)	103.2 (3)	106.0 (3)
C1—C20—O21	106.5 (3)	108.2 (3)	107.1 (3)	110.2 (3)
C18—C1—C2—C3	−45.8 (6)	48.2 (6)	−42.3 (7)	−45.0 (6)
C20—C1—C2—C3	78.9 (6)	−77.7 (7)	79.4 (8)	83.0 (6)
C2—C1—C18—N6	16.6 (4)	−16.7 (4)	9.6 (4)	16.1 (4)
C2—C1—C18—C17	−102.8 (4)	103.1 (5)	−108.8 (5)	−103.0 (5)
C20—C1—C18—N6	−106.8 (4)	108.1 (4)	−110.2 (5)	−110.5 (4)
C20—C1—C18—C17	133.8 (4)	−132.2 (5)	131.3 (5)	130.3 (5)
C2—C1—C20—O21	162.0 (4)	−168.2 (5)	162.8 (5)	169.3 (5)
C18—C1—C20—O21	−70.1 (4)	60.9 (4)	−71.2 (4)	−58.3 (4)
C1—C2—C3—C4	3.7 (5)	−11.7 (6)	9.4 (5)	3.6 (6)
C2—C3—C4—O5	5.0 (4)	4.7 (5)	−4.4 (5)	4.5 (4)
C3—C4—O5—N6	56.7 (4)	−61.7 (4)	63.4 (4)	55.3 (4)
C4—O5—N6—C7	122.7 (4)	−127.8 (5)	130.7 (5)	117.9 (5)
C4—O5—N6—C18	−115.8 (4)	115.7 (4)	−112.3 (4)	−120.8 (5)
O5—N6—C7—C8	−172.0 (4)	170.8 (5)	−170.6 (5)	−172.1 (5)
C18—N6—C7—C8	74.9 (4)	−75.6 (5)	80.8 (4)	70.1 (5)
O5—N6—C18—C1	61.6 (4)	−61.4 (4)	63.3 (5)	63.8 (4)
O5—N6—C18—C17	−171.8 (4)	171.2 (4)	−172.2 (4)	−169.2 (4)
C7—N6—C18—C1	175.7 (5)	−176.6 (5)	176.1 (5)	178.8 (5)
C7—N6—C18—C17	−57.7 (4)	56.0 (4)	−59.4 (4)	−51.8 (4)
N6—C7—C8—C9	−45.7 (4)	46.2 (4)	−49.5 (4)	−44.9 (5)
C7—C8—C9—C10	−165.0 (6)	165.2 (6)	−159.9 (6)	−166.0 (7)
C7—C8—C9—C17	15.0 (6)	−6.8 (5)	12.3 (6)	11.5 (5)
C9—C17—C18—C1	142.8 (5)	−136.1 (6)	140.0 (5)	136.0 (5)
C9—C17—C18—N6	18.8 (3)	−15.6 (4)	15.5 (4)	16.6 (4)
N16—C17—C18—C1	−41.1 (4)	41.5 (4)	−42.4 (4)	−44.0 (4)
N16—C17—C18—N6	−165.1 (4)	162.0 (5)	−166.9 (5)	−163.4 (5)

Intensities were measured with a scan rate of 7° min^{-1} in 2θ and a scan width of $\delta(2\theta) = (1.1 + 0.15\tan\theta)$. Background intensities were measured for 3 s at each end of a scan. The structure was solved by direct methods using *MULTAN*87 (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987). The structure was refined by a block-diagonal least-squares procedure. Calculations were carried out with the *UNICS* system (*The Universal Crystallographic Computation Program System – Osaka*, 1979) using the program *LSBL* for the refinement. The steric energy calculations were carried out using *CNDO*/2 (Pople & Segal, 1966).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and distances involving H atoms have been deposited with the IUCr (Reference: OH1042). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 139–141

2-[5-(Diethylaminosulfonyl)-2-methoxyphenylhydrazono]-3-oxo-*N*-phenylbutyramide

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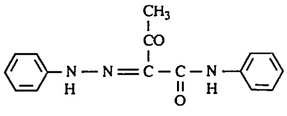
(*Received* 10 *January* 1994; *accepted* 10 *May* 1994)

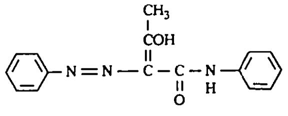
Abstract

The X-ray structure determination of the title compound, $C_{21}H_{26}N_4O_5S$, shows that it crystallizes as the hydrazone tautomer and that the H atom of the hydrazone group and that of the CONH group both take part in intramolecular hydrogen bonding typical of this type of azo pigment.

Comment

Crystal structure determinations of azo pigments derived from acetoacetanilide have highlighted the existence of several common features. Thus, in the solid, it has been found that molecules exist in the form of the hydrazone tautomer (1) rather than the azo form (2) and that the H atom in the hydrazone group and that in the CONH group both take part in hydrogen bonding (Whitaker, 1988). The availability of crystals of the title compound (3) prompted us to determine its structure to see what effects the presence of a diethylaminosulfonyl substituent and a methoxy group have on the overall structure.


(1)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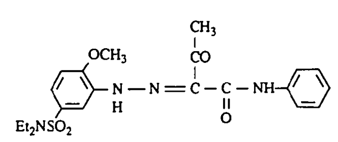
(3)

Examination of the observed bond lengths confirms that the hydrazone tautomer best describes the structure of (3). The interatomic distances O(1)···N(3) [2.569 (4) Å] and O(3)···N(3) [2.629 (4) Å] suggest that the N(3) atom has a bifurcated hydrogen-bond interaction with atoms O(1) and O(3). There is also a single hydrogen bond between the H atom on N(1) and O(2) [O(2)···N(1) 2.669 (3) Å]. Bifurcated hydrogen bonds with similar bond lengths have been found in previously

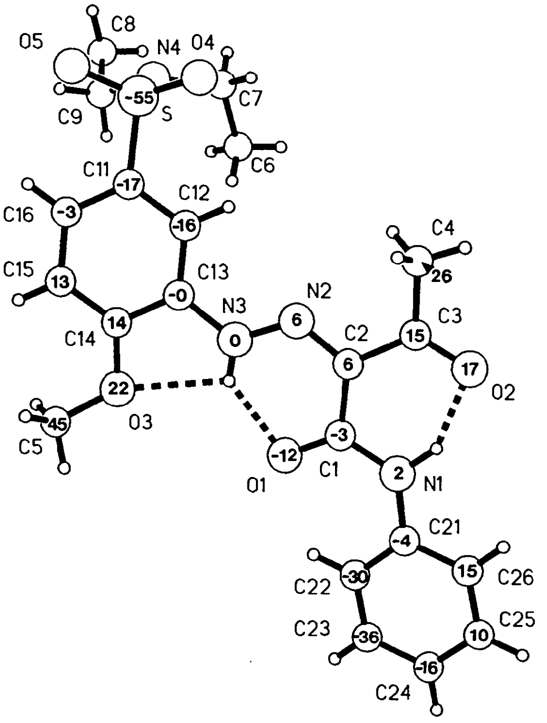

Fig. 1 Structure of the title molecule (*SHELXTL/PC*; Sheldrick, 1991) showing the deviations of the atoms (10^{-2} Å) from the plane of projection. The intramolecular bonds are indicated by broken lines.

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