

Final parameters are given in Table 1* for isomers (I) and (II).

Discussion. The two stereoisomers whose structures are described here show good similarities in bond distances and regular structures with no significant departures from expected bond lengths or angles. The disorder at C12 in isomer (I) makes comparisons in that region meaningless, but for the rest of the molecule these statements hold true (Table 2). The nine-membered ring has a certain amount of flexibility, but the two conformations, while differing at C1, are otherwise nearly equivalent. The carbonyl bond in both isomers exhibits normal van der Waals contacts across the ring: Si to the center of (C10, O3) is 3.56 Å in isomer (I) and 3.62 Å in isomer (II). We expected 3.55–3.65 Å based on data taken from Pauling (1960). The shortest (relatively speaking) contact we observed is Si—C10 = 3.39 Å in isomer (I); this is still approximately a van der Waals distance (radii for Si = 1.95, C = 1.50 Å).

In both structures the ketone O atom O3 has some contacts with H atoms on the benzene ring. In isomer (I) O3...H3 = 2.59 Å and in isomer (II) O3...H4 = 2.71 Å. These are not short enough to be considered as hydrogen bonds, but may indicate a

* Lists of structure factors, anisotropic thermal parameters, complete distances and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54215 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

small interaction between molecules in the crystal. Fig. 1 shows the numbering schemes for isomers (I) and (II). Figs. 2 and 3 show the packing of the isomers (I) and (II).

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References

- CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 149–151. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 99–101. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- DUCHAMP, D. J. (1964). Am. Crystallogr. Assoc. Meet., Bozeman, Montana, Paper B14, p. 29.
- JOHNSON, C. K. (1976). ORTEPII. Report ORNL-3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.
- LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MYERS, A. G. & WIDDOWSON, K. L. (1990). *J. Am. Chem. Soc.* **112**, 9672–9674.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca, NY: Cornell Univ. Press.

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Structure of a Chiral Cyclopentanone Precursor in Neocarzinostatin Synthetic Studies, C₂₀H₂₁NO₃S.H₂O

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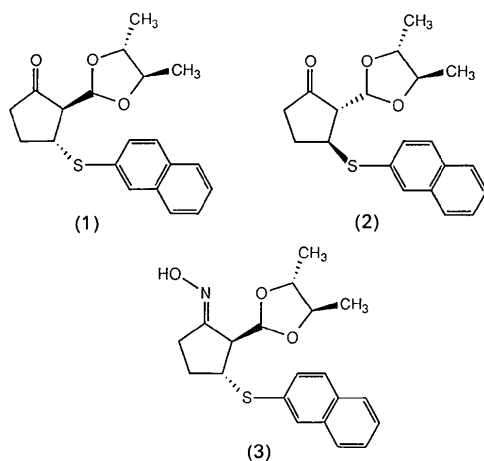
Abstract. (1*E*,2*S*,3*R*)-2-[(4*R*,5*R*)-4,5-Dimethyl-1,3-dioxolan-2-yl]-3-(2-naphthylthio)cyclopentanone oxime, *M_r* = 373.47, orthorhombic, *P*2₁2₁2₁, *a* = 5.374 (13), *b* = 18.135 (3), *c* = 20.487 (5) Å, *V* = 1997 (5) Å³, *Z* = 4, *D_x* = 1.24 g cm⁻³, Mo *K*α, λ = 0.71073 Å, μ = 1.87 cm⁻¹, *F*(000) = 792, room tem-

perature, crystal volume 2.7 × 10⁻⁴ mm³, final *R* = 0.127 for 971 reflections with *F_o*² > 0 out of 1131 data, *R* = 0.065 for 467 reflections with *F_o*² > 3σ(*F_o*²). Despite the small crystal size (all larger crystals were twinned), a structural solution of adequate precision was obtained. Bond distances and angles in the molecule are normal; the water molecules are hydrogen bonded in a chain along the *a* axis and each

* Contribution No. 8229.

accepts a hydrogen bond from the oxime group and donates a weak hydrogen bond to O3 in the dioxolane group.

Introduction. The enantiomerically pure cyclopentanone derivative (1), a key intermediate in studies directed towards the synthesis of the antitumor antibiotic neocarzinostatin chromophore, was obtained by selective crystallization from a hexane solution containing equal parts of (1) and its diastereomer (2) (Myers, Harrington & Kuo, 1991). It was necessary to determine unambiguously the relative stereochemistry of (1) for these studies. Although we were unable to obtain suitable crystals of (1), the *anti* oxime derivative (3) provided small crystals, one of which was usable for our purposes.



Experimental. Needle-like crystal with diamond cross-section 0.19 mm long, with perpendicular diamond diagonals of 0.04 and 0.07 mm (total weight ~0.3 μ g); many other larger crystals shown to be twins. CAD-4 diffractometer; 25 reflections used in the range $12 < 2\theta < 24^\circ$ for unit-cell dimensions; no absorption correction ($\mu r_{\max} = 0.04$); $(\sin\theta/\lambda)_{\max} = 0.48 \text{ \AA}^{-1}$; data collected for $h = 0$ to 5, $k = 0$ to 17, $l = 0$ to 19; two standard reflections (034, 004) showed no variations greater than those expected from counting statistics; 1164 reflections measured, 1131 unique (only the standards were duplicated); all reflections used in solution and refinement of structure; structure solved by *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), which gave positions of sulfur and five carbon atoms; remainder found by successive structure-factor Fourier cycles; refinement on F_o^2 ; hydrogen atoms placed by calculation ($C-H = 0.95 \text{ \AA}$) with staggered geometry (oxime-hydrogen atom left out); final cycles included coordinates and anisotropic displacement parameters for the sulfur, oxime-oxygen, methyl-carbon and water-oxygen atoms, coordinates

and isotropic thermal parameters for the remaining oxygen and carbon atoms and a scale factor; absolute configuration from the dioxolane moiety; a secondary-extinction parameter went negative so it was not used. For 971 reflections with $F_o^2 > 0$, $R = 0.127$, $wR = 0.021$; for 467 reflections with $F_o^2 > 3\sigma(F_o^2)$, $R = 0.065$, $wR = 0.010$; $S = 1.27$ for 1131 reflections and 131 parameters; variances of the reflections based on counting statistics plus an additional term $0.02I^2$; weights taken as $1/\sigma^2(F_o^2)$; maximum shift/e.s.d. in final cycle 0.01; maximum and minimum heights in final difference map + 0.52, - 0.49 $e \text{ \AA}^3$; atomic scattering factors taken from Cromer & Waber (1974), dispersion correction from Cromer (1974); programs used were those of the *CRYM* crystallographic computing system (Duchamp, 1964), *MULTAN* (Main *et al.*, 1980) and *ORTEP* (Johnson, 1976). Much effort was expended trying to grow larger crystals but no better material could be produced. As the data are weak the results, while unequivocal, are not highly precise and the R index is larger than is usual.

Discussion. Table 1 lists the final refined parameters and Table 2 gives selected distances and angles.* Figs. 1 and 2 show the molecule and how it packs in the cell.

The two sulfur-carbon distances are quite unequal [$S-CN_2$, 1.744 (15) \AA and $S-C_3$, 1.826 (15) \AA] but are in the same order as expected [1.819 \AA for $S-CHC_2$, 1.773 \AA for $S-C(\text{aromatic})$] (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The bonds in the naphthalene group average 1.39 (4) \AA (the precision is not high enough to distinguish the various types of naphthalene bonds) and the other C-C distances are acceptably close to expected values. The water molecule is hydrogen bonded to O(N), the oxime oxygen atom [$O\cdots O$, 2.68 (2) \AA] and to O3, in the dioxolane group [$O\cdots O$, 2.97 (2) \AA]. There are weak water-water interactions along the a axis, with $O4\cdots O4$ distances of 3.36 (2) \AA . If these are considered hydrogen bonds, then there is a chain of water molecules along a , with each water molecule donating a hydrogen bond to another water molecule and to O3, and accepting one from O(N) and another water molecule. The geometry about one water molecule is roughly tetrahedral, with O-O-O angles ranging from 68 to 144 $^\circ$; the average difference from 109.5 $^\circ$ of the six angles involved is 26 $^\circ$.

* Figures showing the numbering system and lists of anisotropic displacement parameters, complete distances and angles, structure factors and assigned H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54229 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

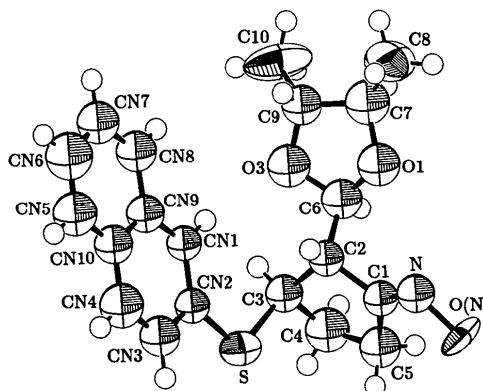
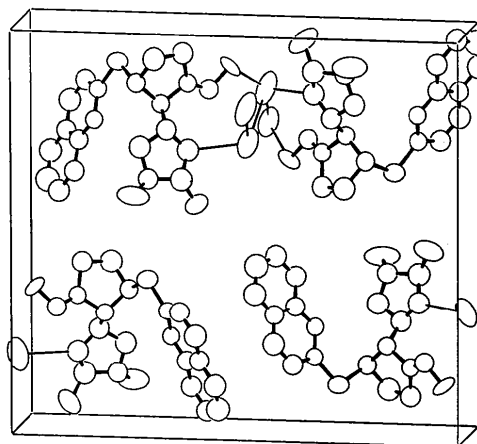
Table 1. Final atomic coordinates ($\times 10^4$) and U_{eq} values ($\text{\AA}^2 \times 10^4$) for C₂₀H₂₃NO₄S

	x	y	z	$B_{iso}/U_{eq}(\text{\AA}^2)$
S	1720 (10)	1109 (2)	2025 (2)	711 (13)†
CN1	1853 (32)	2533 (8)	1502 (6)	4.0 (4)
CN2	740 (31)	1841 (8)	1536 (0)	4.1 (4)
CN3	-1536 (35)	1748 (9)	1155 (7)	5.4 (4)
CN4	-2396 (37)	2294 (10)	763 (8)	6.6 (5)
CN5	-2224 (37)	3533 (10)	332 (8)	6.7 (5)
CN6	-1086 (45)	4177 (10)	318 (8)	7.6 (6)
CN7	1056 (38)	4335 (9)	664 (7)	6.0 (5)
CN8	2084 (33)	3787 (9)	1059 (7)	5.5 (4)
CN9	849 (35)	3090 (9)	1103 (7)	4.9 (4)
CN10	-1271 (35)	2969 (9)	728 (7)	5.0 (4)
C1	2063 (31)	1569 (8)	3611 (7)	4.2 (4)
N	407 (26)	1793 (7)	4002 (6)	4.8 (3)
O(N)	-260 (21)	1258 (5)	4460 (4)	714 (33)†
C2	2957 (30)	2045 (7)	3044 (6)	4.2 (4)
C3	4133 (31)	1493 (8)	2553 (7)	4.6 (4)
C4	5059 (35)	857 (8)	2993 (7)	6.5 (5)
C5	3241 (35)	794 (8)	3559 (7)	5.6 (4)
C6	5057 (36)	2563 (9)	3267 (7)	5.5 (4)
O1	4138 (23)	3096 (6)	3704 (5)	6.1 (3)
O3	5990 (23)	2956 (5)	2714 (5)	6.1 (3)
C7	5829 (37)	3726 (10)	3632 (8)	6.7 (5)
C8	4521 (53)	4393 (10)	3911 (9)	1483 (90)†
C9	6251 (33)	3710 (9)	2908 (8)	5.3 (4)
C10	8704 (36)	4006 (9)	2682 (9)	1100 (78)†
O4	1056 (29)	3046 (7)	4905 (5)	1268 (48)†

$$\dagger U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

Table 2. Distances (\AA) and angles ($^\circ$) not involving H atoms for C₂₀H₂₃NO₄S

S—CN2	1.744 (15)	C4—C5	1.52 (2)
S—C3	1.826 (15)	C6—O1	1.41 (2)
CN1—CN2	1.39 (2)	C6—O3	1.43 (2)
CN1—CN9	1.41 (2)	O1—C7	1.47 (2)
CN2—CN3	1.46 (2)	O3—C9	1.43 (2)
CN3—CN4	1.36 (2)	C7—C8	1.51 (3)
CN4—CN10	1.37 (2)	C7—C9	1.50 (3)
CN5—CN6	1.32 (3)	C9—C10	1.50 (2)
CN5—CN10	1.40 (2)	C1—C2	1.53 (2)
CN6—CN7	1.38 (3)	C1—C5	1.54 (2)
CN7—CN8	1.40 (2)	N—O(N)	1.396 (16)
CN8—CN9	1.43 (2)	C2—C3	1.55 (2)
CN9—CN10	1.39 (2)	C2—C6	1.54 (2)
C1—N	1.265 (19)	C3—C4	1.55 (2)
C3—S—CN2	105.4 (7)	O(N)—N—C1	112.5 (12)
CN9—CN1—CN2	120.8 (14)	C3—C2—C1	104.8 (11)
CN1—CN2—S	125.8 (11)	C6—C2—C1	110.5 (12)
CN3—CN2—S	118.2 (11)	C6—C2—C3	106.7 (12)
CN3—CN2—CN1	115.9 (13)	C2—C3—S	109.9 (10)
CN4—CN3—CN2	121.2 (15)	C4—C3—S	106.9 (10)
CN10—CN4—CN3	122.2 (16)	C4—C3—C2	103.5 (12)
CN10—CN5—CN6	119.3 (17)	C5—C4—C3	107.1 (13)
CN7—CN6—CN5	123.9 (18)	C4—C5—C1	104.3 (13)
CN8—CN7—CN6	118.7 (16)	O1—C6—C2	110.5 (13)
CN9—CN8—CN7	118.8 (15)	O3—C6—C2	109.0 (12)
CN8—CN9—CN1	119.6 (14)	O3—C6—O1	106.6 (12)
CN10—CN9—CN1	121.4 (15)	C7—O1—C6	104.7 (12)
CN10—CN9—CN8	118.9 (15)	C9—O3—C6	106.9 (12)
CN5—CN10—CN4	121.4 (16)	C8—C7—O1	107.3 (14)
CN9—CN10—CN4	118.3 (15)	C9—C7—O1	100.2 (13)
CN9—CN10—CN5	120.3 (15)	C9—C7—C8	117.3 (16)
C2—C1—N	121.4 (13)	C7—C9—O3	106.1 (13)
C5—C1—N	128.7 (14)	C10—C9—O3	110.1 (13)
C5—C1—C2	109.5 (12)	C10—C9—C7	115.6 (15)

Fig. 1. An ORTEP drawing of the molecule with 50% thermal ellipsoids. Hydrogen atoms were given small arbitrary B values.Fig. 2. An ORTEP projection of four molecules with a unit cell outlined. Atoms are shown as 60% thermal ellipsoids; hydrogen atoms are not shown. Two extra water-molecule oxygen atoms are shown (top center) to illustrate the chain of water molecules along a . Hydrogen bonding is indicated by thin bonds.

References

- ALLEN, F. H., KENNARD, O., WATSON, D. G., BRAMMER, L., ORPEN, A. G. & TAYLOR, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S13–S14.
- CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 149–151. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 99–101. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- DUCHAMP, D. J. (1964). *Am. Crystallogr. Assoc. Meet.*, Bozeman, Montana, Paper B14, p. 29.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- MYERS, A. G., HARRINGTON, P. M. & KUO, E. Y. (1991). *J. Am. Chem. Soc.* 113, 694–695.

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