C3′—O2—C7′	117.09 (14)	C4″—N1—C1″	108.00 (14)
C4′—O3—C8′	117.71 (14)		
C1″—N1—C1—O1	−1.9 (3)	C2—C3—C1′—C6′	−93.5 (2)
O1—C1—C2—C3	33.5 (3)	C7′—O2—C3′—C4′	−175.98 (15)
N1—C1—C2—C3	−146.33 (17)	C8′—O3—C4′—C3′	174.70 (15)
C1—C2—C3—C1′	−178.59 (17)		

The temperature of the crystal was controlled using an Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). Data were collected over a hemisphere of reciprocal space, by a combination of three sets of exposures. Each set had a different φ angle for the crystal and each exposure of 10 s covered 0.3° in ω. The crystal to detector distance was 5.01 cm. Coverage of the unique set was over 99% complete to at least 25° in θ. The absence of crystal decay was monitored by repeating the initial frames at the end of the data collection and analysing the duplicate reflections. H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; each H atom was given an isotropic displacement parameter equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which it is attached.

Data collection: *SMART* (Siemens, 1994*a*). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL/PC* (Siemens, 1994*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury Laboratory (Fletcher *et al.*, 1996) for access to the Cambridge Structural Database (Allen & Kennard, 1993). We also thank the Danish International Development Agency (DANIDA) and the Council for Scientific and Industrial Research (CSIR, New Delhi, India) for financial assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1181). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 365–367

1,4-Bis[3-(*N*-cyclohexyliminomethyl)-2-hydroxy-5-methylbenzyl]piperazine

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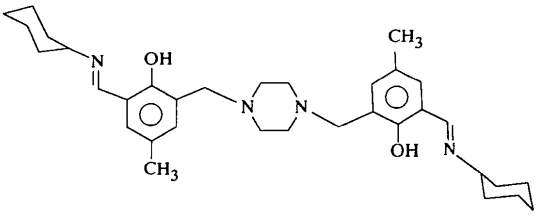
(*Received 20 October 1997; accepted 17 November 1997*)

Abstract

Molecules of the title molecule, $C_{34}H_{48}N_4O_2$, lie across crystallographic inversion centres. The piperazine and cyclohexyl rings adopt chair conformations and the hydroxyl group participates in an O—H···N intramolecular hydrogen bond.

Comment

The impetus for the study of binucleating ligands and their copper complexes has come mainly from three areas, *i.e.* homogeneous catalysis, as model systems for the study of mechanisms of magnetic exchange, and as speculative models for the copper active site in oxyhaemocyanin (Fenton *et al.*, 1982) and several metalloproteins (Kurtz, 1990). Many compounds of this type have more than one metal present. X-ray crystal structure analysis is useful for investigating the coordination-site change and transmetallation reactions (Casellato *et al.*, 1986).



(I)

Molecules of the title compound, (I), lie across crystallographic inversion centres and the asymmetric unit therefore contains one-half of a molecule. The N2 atom is in a pyramidal configuration. The bond lengths and

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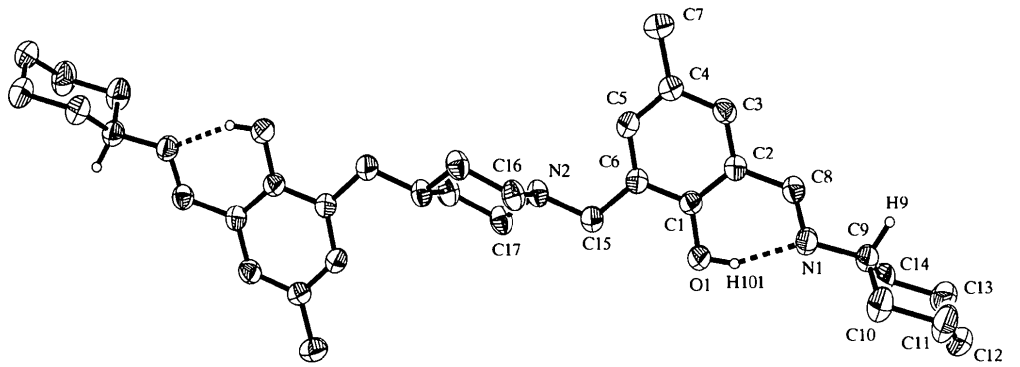

Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme for one asymmetric unit. The other half of the molecule is generated by inversion through the origin. The majority of the H atoms have been omitted for clarity; those shown are drawn as small spheres of arbitrary radii.

angles observed in the structure are normal (Allen *et al.*, 1987). The piperazine ring adopts a chair conformation, with the N2 atom deviating from the least-squares plane through the C atoms of that ring by 0.682 (1) Å. The cyclohexyl ring also adopts a chair conformation, with atoms C9 and C12 deviating from the least-squares plane through atoms C10, C11, C13 and C14 by 0.658 (2) and −0.629 (3) Å, respectively. The planes through the cyclohexyl and piperazine rings form dihedral angles of 83.88 (7) and 51.82 (6)°, respectively, with the phenyl-ring plane. Both the piperazine and cyclohexyl rings have their bulkier substituents equatorial, as expected. An intramolecular O—H···N hydrogen bond is observed between atoms O1 and N1 [O1—H1O1 0.86 (2), O1···N1 2.631 (2), H1O1···N1 1.83 (2) Å and O1—H1O1···N1 153 (2)°]. There are no similarly short intermolecular hydrogen bonds and the crystal structure is stabilized by van der Waals interactions.

Experimental

The title compound was synthesized according to the procedure of Hodgkin (1984) and was crystallized by slow evaporation from an ether–methanol (1:1) mixture (yield 60%, m.p. 481 K).

Crystal data

$C_{34}H_{48}N_4O_2$
M_r = 544.76
Monoclinic
$P2_1/c$
a = 11.4598 (10) Å
b = 12.5892 (11) Å
c = 11.1347 (12) Å
β = 97.996 (7)°
V = 1590.8 (3) Å^3
Z = 2
D_x = 1.137 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 39 reflections
θ = 5.42–12.48°
μ = 0.071 mm^{-1}
T = 293 (2) K
Rectangular
0.60 × 0.56 × 0.32 mm
Light yellow

Data collection

Siemens $P4$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4545 measured reflections
3635 independent reflections
1787 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 27.50°
$h = -14 \rightarrow 14$
$k = -16 \rightarrow 1$
$l = -1 \rightarrow 14$
3 standard reflections
every 97 reflections
intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.124
S = 0.866
3635 reflections
278 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.11 e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0147 (18)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.358 (2)	N2—C17	1.455 (2)
N1—C8	1.265 (2)	N2—C15	1.455 (2)
N1—C9	1.467 (2)	C2—C8	1.457 (2)
N2—C16	1.454 (2)	C6—C15	1.507 (2)
C16—N2—C17	108.45 (13)	C17—N2—C15	112.19 (13)
C16—N2—C15	111.61 (14)		

The title structure was solved by direct methods and refined by full-matrix least-squares techniques. All H atoms were located from a difference Fourier map and refined isotropically.

Programs used for data collection, cell refinement and data reduction: *XSCANS* (Siemens, 1994); for structure solution and molecular graphics: *SHELXTL/PC* (Sheldrick, 1990); for structure refinement: *SHELXL*93 (Sheldrick, 1993); for geometrical calculations: *PARST* (Nardelli, 1995).

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R&D No. 190-9609-2801. KC thanks the Universiti Sains Malaysia for a Visiting Post Doctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1205). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 367–368

8-Acetyl-4-methyl-9-phenylthio-7,8,9,10-tetrahydro-7,8-benzocoumarin†

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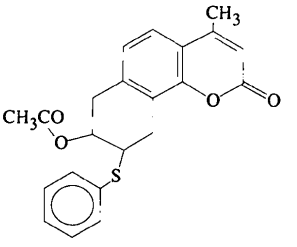
(*Received 27 May 1997; accepted 23 October 1997*)

Abstract

The coumarin and phenyl rings of the title molecule, $C_{22}H_{20}O_4S$, are individually planar. The tetrahydrobenzene ring adopts a half-chair conformation. The crystal structure is stabilized by C—H···O hydrogen bonds involving the carbonyl O atoms.

Comment

The coumarin sub-unit is of interest because it is found in many natural products displaying diverse biological activities. The range of compounds includes antifungal compounds, anticoagulants, and compounds active against psoraris and carcinogens (Parrish *et al.*, 1974; Barry & Toste, 1996). The amino- and hydroxycoumarin derivatives are widely used in dye lasers (Maeda, 1984). The crystal structure determination of the title compound, (I), was undertaken as part of our structural studies on coumarin derivatives.



(I)

Bond lengths and valence angles in the benzocoumarin ring system are comparable with those observed in related derivatives (Chinnakali *et al.*, 1998; Kumar *et al.*, 1997). The coumarin moiety is planar with a maximum deviation of 0.030 (2) Å for C6. The tetrahydrobenzene ring adopts a half-chair conformation with asymmetry parameter ΔC_2(C7–C8) = 0.013 (1) (Nardelli, 1983*a*). The thiophenyl and acetyl groups are planar and make dihedral angles of 62.08 (5) and 95.84 (7)°, respectively, with the best plane through atoms C7, C8, C12 and C15 of the tetrahydrobenzene ring. The carbonyl oxygen is involved in C—H···O hydrogen bonds, the geometries of which are given in Table 2.

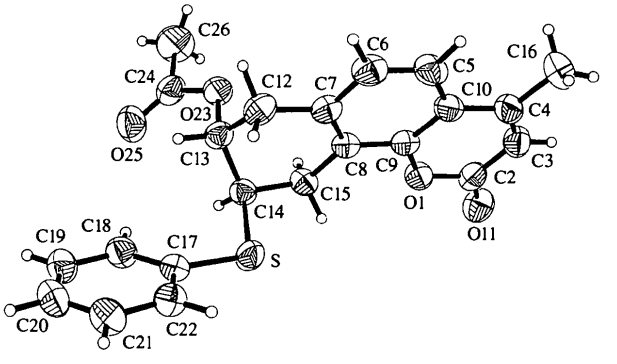


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.

Experimental

Ring opening of the compound 4-methyl-7,10-dihydro-7,8-benzocoumarin-8,9-oxide with thiophenyl furnished two regioisomeric hydroxycoumarins, which on acetylation gave the corresponding acetylated compounds (Sriraghavan, 1998). Single crystals were grown by slow evaporation of the compound from a chloroform–methanol solution.

† Alternative name: 4-methyl-9-phenylthio-7,8,9,10-tetrahydrobenzo-[*h*]coumarin-8-yl acetate.

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