

## Monoclinic

 $P2_1/n$  $a = 5.2789$  (12) Å $b = 25.266$  (11) Å $c = 7.139$  (3) Å $\beta = 103.49$  (3)° $V = 925.9$  (6) Å<sup>3</sup> $Z = 4$  $D_x = 1.121$  Mg m<sup>-3</sup> $D_m$  not measured

## Cell parameters from 26 reflections

 $\theta = 8$ –20° $\mu = 0.069$  mm<sup>-1</sup> $T = 293$  (2) K

Thin rod

 $0.50 \times 0.10 \times 0.10$  mm

Colorless

## Data collection

Siemens P3 diffractometer,  
scintillation counter pulse-  
height analysis $\omega$  scans

Absorption correction: none

2333 measured reflections

2123 independent reflections

505 reflections with

 $I > 2\sigma(I)$  $R_{\text{int}} = 0.120$  $\theta_{\text{max}} = 27.50^\circ$  $h = 0 \rightarrow 6$  $k = 0 \rightarrow 32$  $l = -9 \rightarrow 9$ 

3 standard reflections

every 97 reflections

intensity decay: none

## Refinement

Refinement on  $F^2$  $R[F^2 > 2\sigma(F^2)] = 0.056$  $wR(F^2) = 0.138$  $S = 0.60$ 

2123 reflections

102 parameters

H atoms riding

 $w = 1/[\sigma^2(F_o^2) + (0.0501P)^2]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\text{max}} = 0.000$  $\Delta\rho_{\text{max}} = 0.17$  e Å<sup>-3</sup> $\Delta\rho_{\text{min}} = -0.17$  e Å<sup>-3</sup>

Extinction correction:

SHELXL97

Extinction coefficient:

0.023 (4)

Scattering factors from

International Tables for  
Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O1—C1	1.443 (4)		
O1—C1—C2—C3	−70.5 (4)	C5—C6—C7—C8	−55.7 (5)
C10—C1—C2—C3	53.0 (4)	C6—C7—C8—C9	151.4 (3)
C1—C2—C3—C4	−151.2 (3)	C7—C8—C9—C10	−56.8 (5)
C2—C3—C4—C5	55.1 (5)	O1—C1—C10—C9	−167.8 (3)
C3—C4—C5—C6	65.7 (5)	C2—C1—C10—C9	67.3 (4)
C4—C5—C6—C7	−65.2 (5)	C8—C9—C10—C1	−64.4 (5)

H atoms on C atoms were refined as riding, while those on O atoms were refined as riding with the C—C—O—H torsion angle refined.

Data collection: P3 (Siemens, 1989a). Cell refinement: P3. Data reduction: XDISK (Siemens, 1989b). Program(s) used to solve structure: SHELXS93 (Sheldrick, 1993). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: XP (Siemens, 1989c). Software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1118). Services for accessing these data are described at the back of the journal.

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## 2-(4-Bromo-2-nitrophenyl)-1-(4-dimethylaminophenyl)-1-ethanone†

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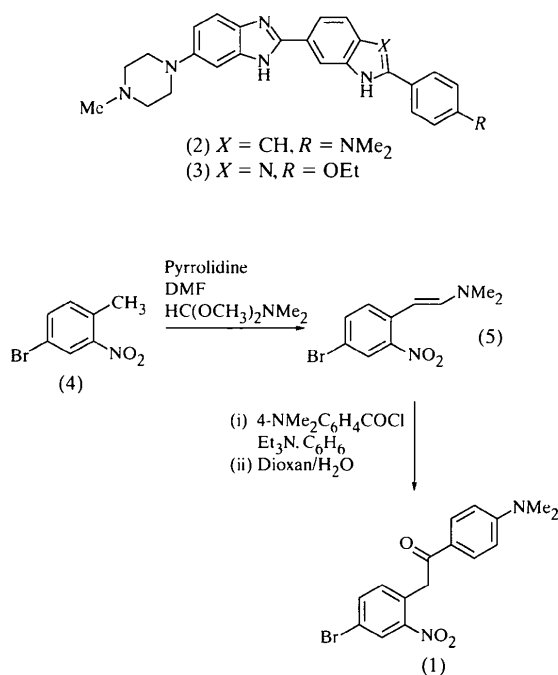
### Abstract

The title compound, C<sub>16</sub>H<sub>15</sub>BrN<sub>2</sub>O<sub>3</sub>, is a key intermediate in the synthesis of indole-substituted Hoechst 33258 analogues. Interaction between the dimethylamino substituent and the ketone through the aromatic ring is evident from the short N2—C4 distance, and the slightly lengthened C7—O3 bond.

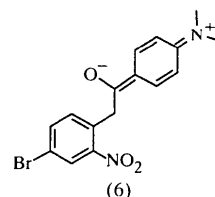
†Alternative name: 4-bromo-2-nitrobenzyl 4-dimethylaminophenyl ketone.

### Comment

The title compound, (1), is a key intermediate in the preparation of the indole-substituted benzimidazole (2). Compound (2) is related to the DNA minor groove binder Hoechst 33342, (3), which displays radioprotection of cells exposed to ionizing radiation (Denison *et al.*, 1992). This has implications in cancer radiotherapy, and compound (2) was required in order to attempt to improve on the radioprotector features of (3). The title compound, (1), was synthesized in three steps according to the scheme below. The bromonitrotoluene (4) was converted to the enamine (5) which was condensed with 4-dimethylaminobenzoyl chloride followed by hydrolysis. This procedure followed a general methodology reported previously (Garcia & Fryer, 1974).



The structure of (1) consists of two aromatic rings linked by a two-carbon fragment in an antiperiplanar orientation [ $\text{C1—C7—C8—C9} - 177.0(7)^\circ$ ] with respect to each other; in this conformation, the carbonyl O atom eclipses the phenyl substituent [ $\text{O3—C7—C8—C9} 4.4(11)^\circ$ ]. The planes of the two phenyl rings are nearly orthogonal to each other ( $110.4^\circ$ ). The dimethylamino substituent at C4 interacts strongly with the ketone carbonyl at C7; evidence for this is the very short N2—C4 distance of 1.349 (8), the short C1—C7 distance of 1.470 (9) Å and the C7—O3 distance of 1.230 (8) Å, which presents a slight lengthening compared with usual ketone C=O double-bond distances (*ca* 1.20 Å). These bond distances and the pattern of bond distances in the aromatic ring defined by atoms C1—C6 suggest signifi-



cant contributions of the resonance form (6) to the structure of (1).

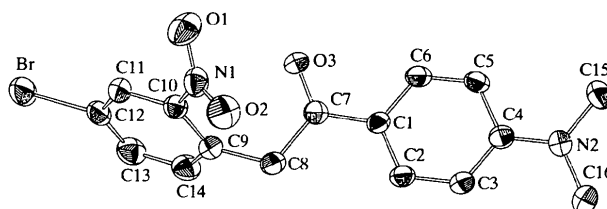


Fig. 1. ORTEP (Zsolnai, 1994) diagram of (1). Displacement ellipsoids are at the 30% probability level.

### Experimental

Colourless plates of (1) (m.p. 419–421 K) were grown from dichloromethane/pentane solution.

#### Crystal data

$\text{C}_{16}\text{H}_{15}\text{BrN}_2\text{O}_3$   
 $M_r = 363.21$   
 Orthorhombic  
 $P2_12_12_1$   
 $a = 7.9808(7)$  Å  
 $b = 11.720(1)$  Å  
 $c = 16.468(1)$  Å  
 $V = 1540.3(2)$  Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.566$  Mg m<sup>-3</sup>  
 $D_m$  not measured

Cu  $K\alpha$  radiation  
 $\lambda = 1.5418$  Å  
 Cell parameters from 25 reflections  
 $\theta = 20\text{--}30^\circ$   
 $\mu = 3.767$  mm<sup>-1</sup>  
 $T = 293(2)$  K  
 Plate  
 $0.22 \times 0.14 \times 0.03$  mm  
 Tan

#### Data collection

Enraf–Nonius CAD-4-Machs diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: Gaussian (Sheldrick, 1976)  
 $T_{\min} = 0.59$ ,  $T_{\max} = 0.89$   
 1796 measured reflections  
 1796 independent reflections

1252 reflections with  $I > 2\sigma(I)$   
 $\theta_{\max} = 74.83^\circ$   
 $h = 0 \rightarrow 9$   
 $k = 0 \rightarrow 14$   
 $l = 0 \rightarrow 20$   
 3 standard reflections frequency: 160 min intensity decay: 2%

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.048$   
 $wR(F^2) = 0.130$   
 $S = 1.037$   
 1796 reflections

Extinction correction: SHELXL97 (Sheldrick, 1997)  
 Extinction coefficient: 0.0002 (2)

200 parameters

H atoms riding

$$w = 1/[\sigma^2(F_o^2) + (0.0671P)^2 + 0.3777P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.285 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.397 \text{ e } \text{\AA}^{-3}$$

Scattering factors from

International Tables for

Crystallography (Vol. C)

Absolute structure: Flack

(1983)

Flack parameter = -0.05 (5)

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## Enantiopure $\delta$ -Hydroxy- $\beta$ -enamino Ketones

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### Abstract

The absolute configurations of 2-( $\alpha$ -methylbenzylamino)-3-(1-hydroxy-1-methylethyl)cyclopent-1-en-1-yl phenyl ketone, C<sub>23</sub>H<sub>27</sub>NO<sub>2</sub>, and 5-hydroxy-4,6,6-trimethyl-3-( $\alpha$ -methylbenzylamino)-1-phenyl-2-hepten-1-one monohydrate, C<sub>24</sub>H<sub>31</sub>NO<sub>2</sub>·H<sub>2</sub>O, obtained by a directed enantioselective aldol condensation, have been ascertained to be ( $\alpha$ R,3*S*) and ( $\alpha$ R,4*S*,5*S*), respectively. While in the first cyclic  $\delta$ -hydroxy- $\beta$ -enamino ketone the enaminoic N atom is hydrogen bonded to the carbonyl O atom, in the second acyclic compound, the N atom is hydrogen bonded to the hydroxyl group.

### Comment

$\delta$ -Hydroxy- $\beta$ -enamino ketones and related compounds are important structural subunits which are present in many synthetic targets of natural origin and in key intermediates in the construction of a wide variety of heterocyclic compounds. The introduction of an alkyl side chain containing a hydroxyl function of fixed configuration at the  $\gamma$ -position of  $\beta$ -enamino ketones and derivatives represents an important synthetic goal, since the added functionality would increase the synthetic scope of these intermediates. The aldol reaction is one of the more powerful tools for the stereoselective construction of acyclic molecules (Heathcock, 1991; Franklin & Paterson, 1994). Among the most important advantages of using an imine is the ability to introduce a 'stereogenic center' via an enantiomerically pure amine, thus enabling diastereoselective control of the C—C bond-forming process (Meyers *et al.*, 1981; Enders *et al.*, 1992; Denmark & Ares, 1988).

We have prepared two  $\delta$ -hydroxy- $\beta$ -enamino ketones with good stereoselectivity: 2-( $\alpha$ -methylbenzylamino)-3-(1-hydroxy-1-methylethyl)cyclopent-1-en-1-yl phenyl ketone, (1), and 5-hydroxy-4,6,6-trimethyl-3-( $\alpha$ -methylbenzylamino)-1-phenyl-2-hepten-1-one monohydrate, (2). As they have not been reported previously, it was necessary to determine their absolute configuration un-

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O3—C7	1.230 (8)	C1—C7	1.470 (9)
N2—C4	1.349 (8)	C2—C3	1.371 (8)
N2—C15	1.425 (9)	C3—C4	1.385 (9)
N2—C16	1.468 (9)	C4—C5	1.412 (9)
C1—C2	1.388 (8)	C5—C6	1.343 (8)
C1—C6	1.390 (8)		
C4—N2—C15	122.0 (6)	N2—C4—C3	123.2 (6)
C4—N2—C16	120.1 (6)	N2—C4—C5	120.5 (6)
C15—N2—C16	117.6 (6)	C3—C4—C5	116.2 (6)
C2—C1—C6	116.0 (6)	C6—C5—C4	120.6 (6)
C2—C1—C7	124.3 (6)	C5—C6—C1	123.6 (7)
C6—C1—C7	119.7 (5)	O3—C7—C1	121.6 (6)
C3—C2—C1	121.2 (7)	O3—C7—C8	118.4 (6)
C2—C3—C4	122.4 (6)	C1—C7—C8	120.0 (6)
C15—N2—C4—C3	-178.7 (7)	O3—C7—C8—C9	4.4 (11)
C16—N2—C4—C3	-5.1 (10)	C1—C7—C8—C9	-177.0 (7)
C15—N2—C4—C5	3.1 (11)	C7—C8—C9—C10	-63.2 (9)
C16—N2—C4—C5	176.7 (6)	O2—N1—C10—C11	139.7 (7)
C2—C1—C7—O3	176.2 (7)	O1—N1—C10—C11	-40.7 (10)
C6—C1—C7—O3	-5.4 (12)	O2—N1—C10—C9	-38.0 (10)
C2—C1—C7—C8	-2.4 (11)	O1—N1—C10—C9	141.6 (8)
C6—C1—C7—C8	176.0 (7)		

The title structure was solved by direct methods using *SHELXS86* (Sheldrick, 1990). Refinement was performed using *SHELXL97* (Sheldrick, 1997) using anisotropic displacement parameters for all non-H atoms and isotropic displacement parameters for the H atoms. Figures were drawn using *ZORTEP* (Zsolnai, 1994) and material for publication was prepared using *SHELXL97*. All calculations were carried out on a VAXstation 4000VLC computer system.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1201). Services for accessing these data are described at the back of the journal.

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