

O4—S1—O2—C1	5.6 (3)	C6—C5—C10—C9	-20.4 (5)
C10—C5—C6—C7	49.4 (5)	C3—C2—C11—O1	36.5 (5)
C5—C6—C7—C8	-55.1 (5)	C1—C2—C11—C12	38.2 (5)
C6—C7—C8—C9	29.4 (5)	O3—S1—C19—C20	23.4 (3)
C7—C8—C9—C10	1.3 (5)	O4—S1—C19—C24	-22.9 (3)
C8—C9—C10—C5	-4.3 (5)		

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
C12—H12C...O2	0.96	2.28	2.987 (5)	130
C7—H7A...O3 ^a	0.97	2.47	3.238 (6)	136

Symmetry code: (i) 2 - x, 1 - y, -z.

Due to the low r/p ratio of 9.7 for observed reflections, all the H atoms were geometrically fixed and allowed to ride on the atoms to which they were attached. Rotating-group refinement was used for the methyl groups. The reflections 413, 400, 523 and 107 were suppressed during refinement as they showed very poor agreement between F_o^2 and F_c^2 . At the end of the refinement, a distinct peak of $0.74 \text{ e } \text{Å}^{-3}$ at 1.02 Å from C6 suggested the possibility of a conformational disorder for the cyclohexene ring. But the refinement based on a disorder model resulted in extreme displacement parameters for the minor component (0.2 occupancy) of C6 and unrealistic bond lengths and angles involving the same. Hence, the disorder model was abandoned.

Data collection: SMART (Siemens, 1996). Cell refinement: SAINT (Siemens, 1996). Data reduction: SAINT. Program(s) used to solve structure: SHELXTL (Sheldrick, 1997). Program(s) used to refine structure: SHELXTL. Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL, PARST (Nardelli, 1995) and PLATON (Spek, 1990).

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 Postdoctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1306). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Crouse, D. J., Hurlbut, S. L. & Wheeler, D. M. S. (1981). *J. Org. Chem.* **46**, 374–378.
- Hauck, F. P., Cimarusti, C. M. & Sundeen, J. E. (1977). *Chem. Abstr.* **86**, 43447u.
- Nardelli, M. (1983). *Acta Cryst.* **C39**, 1141–1142.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Sheldrick, G.M. (1996). *SADABS. Program for Absorption Correction*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXTL. Structure Determination Software Programs*. Version 5.10. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.
- Siemens (1996). *SMART and SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.

Acta Cryst. (1999). **C55**, 946–948

9-Hydroxy-8-iodo-4-methyl-7,8,9,10-tetrahydrobenzo[h]coumarin

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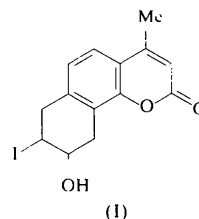
(Received 11 December 1998; accepted 1 February 1999)

Abstract

In the title molecule, C₁₄H₁₃O₃, the coumarin ring system is planar and the fused cyclohexane ring adopts a half-chair conformation. The planes of the coumarin and cyclohexane rings form a dihedral angle of $8.5 (1)^\circ$. In the crystal, the hydroxyl group and the carbonyl O atom are involved in an O—H...O intermolecular hydrogen bond. The molecules are stacked at a perpendicular distance of $3.588 (8) \text{ Å}$ along the *a* axis.

Comment

Coumarin derivatives are found in many natural products displaying diverse biological properties. They are found to exhibit antifungal and anticoagulant properties (Parrish *et al.*, 1974). The amino and hydroxy coumarin derivatives are widely used in dye lasers (Maeda, 1984). The structural study of the title compound, (I), one of the coumarin derivatives, was performed as part of our study on coumarin derivatives.



As observed in other coumarin derivatives, the C3—C4 and C5—C6 bonds in the coumarin moiety show double-bond character, and steric interactions cause the widening of angles C3—C2—O11 and C4—C10—C5, and the narrowing of angles O1—C2—O11 and O1—C9—C8 from 120° (Chinnakali *et al.*, 1997a,b; Kumar *et al.*, 1997). The coumarin ring system is planar, with the O11 atom deviating by a maximum

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of $-0.056(5)$ Å. The fused cyclohexane ring adopts a half-chair conformation, with C13 and C14 deviating from the mean plane by $-0.372(6)$ and $0.306(6)$ Å, respectively; the asymmetry parameter $\Delta C_2(\text{C14—C13})$ is $0.045(2)$ (Nardelli, 1983). The mean plane through the fused cyclohexane ring forms a dihedral angle of $8.5(1)^\circ$ with the coumarin ring plane. In the solid state, the glide-related molecules are linked by an O—H...O hydrogen bond involving the hydroxyl group and the carbonyl O atom (Table 2) to form an infinite one-dimensional chain. The molecules translated a unit along the *a* axis are stacked stepwise at a perpendicular distance of $3.588(8)$ Å, with no π — π interactions.

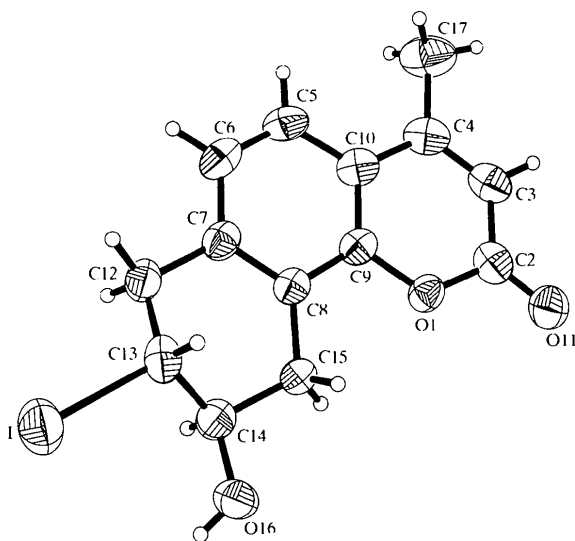


Fig. 1. The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

Experimental

Our ongoing synthetic project required the synthesis of 9-hydroxy-4,8-dimethyl-7,8,9,10-tetrahydro-7,8-benzocoumarin. To achieve our target compound, 4-methyl-7,10-dihydro-7,8-benzocoumarin 8,9-oxide (0.5 g, 2.19 mmol) in tetrahydrofuran (THF) was added to a solution of methyl magnesium iodide (1.2 equivalents, 0.437 g, 2.63 mmol) in THF under a nitrogen atmosphere. After completion of the reaction, the reaction mixture was quenched with saturated ammonium chloride. The resulting organic layer was separated and dried. The residue after chromatographic purification furnished the title compound, (I), instead of our target compound. Single crystals of (I) were grown by slow evaporation of a chloroform/methanol (1:1) solution of the compound.

Crystal data

$\text{C}_{14}\text{H}_{13}\text{O}_3$
 $M_r = 356.14$

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å

Monoclinic
 $P2_1/c$
 $a = 5.4931(1)$ Å
 $b = 22.2521(3)$ Å
 $c = 11.0350(2)$ Å
 $\beta = 104.230(1)^\circ$
 $V = 1307.45(4)$ Å³
 $Z = 4$
 $D_x = 1.809$ Mg m⁻³
 D_m not measured

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
Absorption correction: multi-scan empirical (SADABS; Sheldrick, 1997)
 $T_{\min} = 0.361$, $T_{\max} = 0.415$

Cell parameters from 2021 reflections
 $\theta = 2.64$ – 26.99°
 $\mu = 2.446$ mm⁻¹
 $T = 293(2)$ K
Parallelepiped
 $0.44 \times 0.38 \times 0.36$ mm
Light brown

8143 measured reflections
2824 independent reflections
2463 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$
 $\theta_{\max} = 26.99^\circ$
 $h = -6 \rightarrow 6$
 $k = 0 \rightarrow 28$
 $l = 0 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.151$
 $S = 1.208$
2824 reflections
165 parameters
H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0530P)^2 + 4.5488P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.03$ e Å⁻³
 $\Delta\rho_{\min} = -1.08$ e Å⁻³
Extinction correction: none
Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

C11—C13	2.175 (6)	C12—C13	1.505 (9)
C3—C4	1.357 (9)	C13—C14	1.527 (8)
C5—C6	1.356 (10)	C14—O16	1.395 (7)
C7—C12	1.528 (8)	C14—C15	1.526 (8)
C8—C15	1.509 (7)		
O11—C2—O1	115.8 (6)	O1—C9—C8	114.5 (5)
O11—C2—C3	127.1 (6)	C5—C10—C4	125.2 (5)
C12—C7—C8—C15	1.3 (8)	C12—C13—C14—C15	64.2 (6)
C8—C7—C12—C13	20.6 (7)	C7—C8—C15—C14	9.7 (7)
C7—C12—C13—C14	-53.9 (6)	C13—C14—C15—C8	-40.7 (6)

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O16—H16...O11'	0.82	1.95	2.761 (7)	168

Symmetry code: (i) $x - 1, \frac{1}{2} - y, \frac{1}{2} + z$.

After checking their presence in the difference map, the H atoms were fixed geometrically and allowed to ride on their attached atoms. The reflections 140 and 141 were suppressed during refinement as they showed very poor agreement between F_o^2 and F_c^2 . The highest difference peak, 1.03 e Å⁻³, was found near I1 at a distance of 0.94 Å.

Data collection: SMART (Siemens, 1996). Cell refinement: SAINT (Siemens, 1996). Data reduction: SAINT. Program(s) used to solve structure: SHELXTL (Sheldrick, 1997). Program(s) used to refine structure: SHELXTL. Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL and 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 Postdoctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1400). Services for accessing these data are described at the back of the journal.

References

- Chinnakali, K., Fun, H.-K., Sriraghavan, K. & Ramakrishnan, V. T. (1997a). *Acta Cryst.* **C54**, 367–368.
 Chinnakali, K., Fun, H.-K., Sriraghavan, K. & Ramakrishnan, V. T. (1997b). *Acta Cryst.* **C54**, 542–544.
 Kumar, S., Chinnakali, K., Sivakumar, K., Fun, H.-K. & Sriraghavan, K. (1997). *Acta Cryst.* **C53**, 1854–1855.
 Maeda, M. (1984). In *Laser Dyes: Properties of Organic Compounds for Dye Lasers*. New York: Academic Press.
 Nardelli, M. (1983). *Acta Cryst.* **C39**, 1141–1142.
 Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
 Parrish, J. A., Fitzpatrick, T. B., Tanenbaum, L. & Pathak, M. A. (1974). *New Engl. J. Med.* **291**, 206–209.
 Sheldrick, G. M. (1997). *SHELXTL. Structure Determination Software Programs*. Version 5.10. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.
 Siemens (1996). *SMART and SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1999). **C55**, 948–951

7-Methyl-3-(2-methylphenyl)-1,2,4-triazolo[3,4-*b*][1,3]benzothiazole, (I), and 7-methyl-3-(4-methylphenyl)-1,2,4-triazolo[3,4-*b*][1,3]benzothiazole, (II)

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(Received 23 September 1998; accepted 18 January 1999)

Abstract

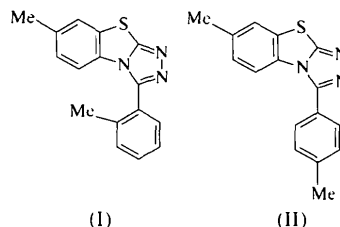
The two title compounds, both C₁₆H₁₃N₃S, were synthesized by photolysis of 4-(2-bromo-4-methylphenyl)-5-(2-methylphenyl)-1,2,4-triazole-3-thione and 4-(2-bromo-4-methylphenyl)-5-(4-methylphenyl)-1,2,4-triazole-3-thione, respectively. Both molecules consist of a 7-

methyl-1,2,4-triazolo[3,4-*b*][1,3]benzothiazole moiety linked to a methyl-substituted phenyl ring. The interplanar angle between the triazole–benzothiazole fused fragment and the phenyl ring is 66.8 (1)° in (I) and 35.4 (1)° in (II). The structures of both compounds are stabilized by weak C—H···N-type interactions.

Comment

The benzothiazole moiety possesses many useful pharmacological properties, such as acting as antitumour (Shi *et al.*, 1996), antifungal (Kü *et al.*, 1997), antimicrobial (Kü *et al.*, 1995), antineoplastic (Alarcón *et al.*, 1998) and anti-inflammatory (Dannhardt *et al.*, 1997) agents. Condensed [1,2,4]triazoles are also medically important compounds (Francis & Gelotte, 1988; Kottke *et al.*, 1983). Substituted 1,2,4-triazolo[3,4-*b*]benzothiazoles have been prepared from the respective triazole-3-thiones by a photochemical method. In order to confirm the identity of the compounds and to study the stereochemistry and the structure–activity relationships, a detailed crystallographic study has been carried out and the results are presented here.

In the following discussion, the values given without brackets are for (I), and those within square brackets are for (II). Figs. 1 and 2 show the *ORTEP* (Johnson, 1965) drawings of the two molecules in the same relative orientation. The structure consists of methylbenzothia-



zole–triazole fused fragments linked to a methylphenyl group. The N—N, C—N and S—C bond distances in the fused fragment system are comparable with those found in related structures (Ruiwu *et al.*, 1997; Palmer & Parsons, 1996). The S1—C7 distance of 1.728 (3) [1.736 (3) Å], and the C7—N1 and C7—N2 distances of 1.367 (3) [1.370 (3) Å] and 1.307 (4) [1.302 (3) Å], respectively, clearly show the resonance of the thiourea system (Valle *et al.*, 1970). The C7—S1—C1 angle of 89.3 (1) [89.4 (1)°] suggests that the S atom uses only *p*-orbitals to form bonds with C1 and C7. In order to maintain the planar conformation of the thiazole ring, the other bond angles, namely, C7—N1—C6, N1—C6—C1, C6—C1—S1 and S1—C7—N1, are in the range 110.1 (2)–114.4 (2)° [109.6 (2)–114.1 (2)°], which is less than the ideal 120° for *sp*² orbital hybridizations of C and N atoms and greater than the ideal 108° required for a regular planar pentagon. These results agree with a similar structure found in 2-amino-6-fluorobenzothiazole (Jai-Nhuknan *et al.*, 1997). The