

C13—O7—C8—C9	-49.3 (5)	O7—C8—C9—C10	60.0 (5)
C8—C9—C10—C14	-40.5 (5)	C8—O7—C13—C14	22.6 (6)
O7—C13—C14—C10	-0.8 (6)	C9—C10—C14—C13	10.2 (5)

## Angelyloxy side chains

C10—O1'	1.442 (4)	C9—O1''	1.441 (5)
O1'—C2'	1.355 (5)	O1''—C2''	1.351 (6)
C2'—O3'	1.187 (5)	C2''—O3''	1.186 (6)
C2'—C4'	1.496 (6)	C2''—C4''	1.472 (7)
C4'—C6'	1.335 (10)	C4''—C6''	1.332 (10)
C4'—C5'	1.470 (10)	C4''—C5''	1.521 (12)
C6'—C7'	1.476 (13)	C6''—C7''	1.405 (15)
C10—O1'—C2'	116.7 (3)	C9—O1''—C2''	117.4 (3)
O1'—C2'—O3'	123.1 (3)	O1''—C2''—O3''	121.6 (4)
O1'—C2'—C4'	111.0 (3)	O1''—C2''—C4''	111.6 (4)
O3'—C2'—C4'	126.0 (4)	O3''—C2''—C4''	126.8 (5)
C2'—C4'—C6'	118.9 (6)	C2''—C4''—C6''	120.2 (7)
C5'—C4'—C6'	124.4 (6)	C5''—C4''—C6''	123.9 (7)
C4'—C6'—C7'	129.5 (7)	C4''—C6''—C7''	131.8 (9)
C10—O1'—C2'—O3'	-2.1 (6)	C9—O1''—C2''—O3''	6.6 (7)
C10—O1'—C2'—C4'	177.6 (4)	C9—O1''—C2''—C4''	-175.4 (4)
O3'—C2'—C4'—C6'	45.1 (7)	O3''—C2''—C4''—C6''	-26.3 (9)
O3'—C2'—C4'—C5'	-135.5 (6)	O3''—C2''—C4''—C5''	153.2 (8)
O1'—C2'—C4'—C6'	-135.7 (5)	O1''—C2''—C4''—C6''	155.8 (5)
C2'—C4'—C6'—C7'	1.3 (11)	C2''—C4''—C6''—C7''	-2.0 (13)
C5'—C4'—C6'—C7'	-178.0 (9)	C5''—C4''—C6''—C7''	178.5 (11)

Data collection: CAD-4 diffractometer software (Enraf-Nonius, 1977). Cell refinement: CAD-4 diffractometer software. Data reduction: CAD-4 diffractometer software. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DE1002). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Duax, W. L., Weeks, C. M. & Rohrer, D. C. (1974). In *A Specialist Periodical Report of Terpenoids and Steroids*. London: The Chemical Society.
- Enraf-Nonius (1977). *CAD-4 Operations Manual*. Enraf-Nonius, Delft, The Netherlands.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Gupta, B. D., Benerzee, S. K. & Handa, K. L. (1975). *Phytochemistry*, **14**, 598.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Murray, R. D. H., Stewart, J. M. & Brown, A. (1982). In *The Natural Coumarins*. New York: John Wiley.
- Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.

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7-Hydroxy-3-phenylcoumarin, C<sub>15</sub>H<sub>10</sub>O<sub>3</sub>

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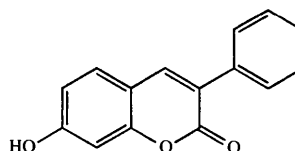
(Received 28 April 1995; accepted 28 June 1995)

## Abstract

In the title compound, the phenyl ring attached at the 3 position is twisted markedly out of the plane of the 2*H*-1-benzopyran-2-one (coumarin) moiety. The dihedral angle between the phenyl ring and the pyrone ring is 40.4 (3)°. These two rings are stacked in the crystal. The crystal structure is stabilized by intermolecular hydrogen bonds.

## Comment

Coumarin compounds have been found to be very useful as laser dyes. The title compound, (I), is one of the derivatives of coumarin. As part of studies to elucidate the relationships between the characteristics of the functional dyes containing coumarin skeletons and their molecular structures, the X-ray analysis of (I) was undertaken.



(I)

An *ORTEPII* (Johnson, 1976) drawing of the title compound together with the atomic numbering and ring-labelling scheme is shown in Fig. 1. The coumarin moiety is planar and the phenyl ring, A, attached at the C3 atom is twisted out of the coumarin plane. The dihedral angle between ring A and the pyrone ring, B, is 40.4 (3)°, and that between ring B and the benzene ring, C, in the coumarin skeleton is 1.43 (4)°.

The phenyl ring attached at the C3 atom significantly influences several bond lengths in the coumarin skeleton. The C2—C3 bond in particular is markedly longer than the corresponding bond of 1.433 (3) Å in 7-hydroxycoumarin (umbelliferone) (Ueno, 1985). In ad-

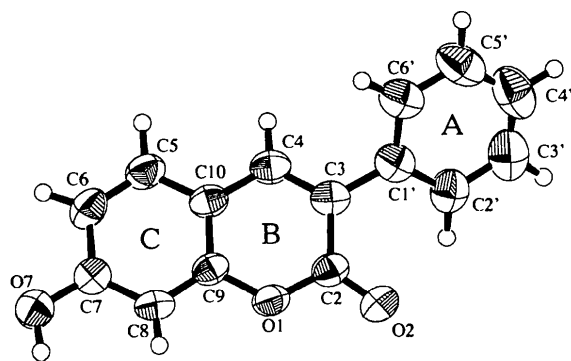


Fig. 1. ORTEPII (Johnson, 1976) drawing of the title compound showing the atomic numbering and ring-labelling schemes. Displacement ellipsoids of non-H atoms are shown at the 50% probability level; H atoms are shown as small spheres of arbitrary size.

dition, the C3—C4 bond is significantly longer and the C2—O2 and C8—C9 bonds are significantly shorter than the corresponding bonds in umbelliferone. The bond angles around the carbonyl group are highly asymmetric, as in umbelliferone.

The molecules are stacked in an antiparallel fashion. Ring A is sandwiched between two B rings of the neighbouring molecules in the crystal. The interplanar spacings between the A and B rings are 3.79 (7) and 3.71 (9) Å, which are longer than the van der Waals contact distance. The molecules are linked by an intermolecular hydrogen bond of the O—H...O type [O7...O2(−x,  $\frac{1}{2} + y, \frac{1}{2} - z$ ) 2.73 (4) Å, O7—H...O2 161.2 (1)°].

## Experimental

The crystals were grown from an ethanol solution at 293 (5) K in a darkroom.

### Crystal data

C<sub>15</sub>H<sub>10</sub>O<sub>3</sub>  
*M<sub>r</sub>* = 238.24  
 Orthorhombic  
*P*2<sub>1</sub>2<sub>1</sub>  
*a* = 12.0126 (8) Å  
*b* = 13.075 (2) Å  
*c* = 7.4562 (8) Å  
*V* = 1171.1 (2) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.35 Mg m<sup>−3</sup>

Cu *K*α radiation  
 $\lambda$  = 1.54184 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 30–35°  
 $\mu$  = 0.776 mm<sup>−1</sup>  
*T* = 293 (2) K  
 Rod  
 0.75 × 0.15 × 0.15 mm  
 Colourless

### Data collection

Enraf–Nonius CAD-4 Turbo diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: none  
 1425 measured reflections  
 1425 independent reflections  
 1175 observed reflections [*F* > 3σ(*F*)]

$\theta_{\max}$  = 74.9°  
*h* = 0 → 15  
*k* = −16 → 0  
*l* = −9 → 0  
 3 standard reflections  
 frequency: 60 min  
 intensity decay: 1.21%

### Refinement

Refinement on *F*

*R* = 0.038  
*wR* = 0.043  
*S* = 2.01  
 1175 reflections  
 204 parameters  
 $w = 1/\sigma^2(F)$   
 $(\Delta/\sigma)_{\max} = 0.02$   
 $\Delta\rho_{\max} = 0.15 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.14 \text{ e } \text{Å}^{-3}$

Extinction correction:

$$F^* = |F_c|/(1 + gI_c)$$

Extinction coefficient:

$$g = 1.501 \times 10^{-6}$$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$B_{\text{eq}} = (4/3)\sum_i \beta_i \mathbf{a}_i \cdot \mathbf{a}_i$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>eq</sub></i>
O1	0.0944 (9)	0.1658 (1)	0.1873 (2)	4.25 (3)
O2	0.0627 (1)	0.0038 (1)	0.2342 (2)	5.43 (3)
O7	0.1343 (2)	0.5219 (1)	0.0860 (3)	5.69 (4)
C2	0.1294 (2)	0.0669 (2)	0.1834 (3)	4.20 (4)
C3	0.2426 (2)	0.0454 (2)	0.1209 (3)	4.17 (4)
C4	0.3047 (2)	0.1258 (2)	0.0639 (3)	4.36 (4)
C5	0.3254 (2)	0.3139 (2)	0.0051 (3)	4.87 (5)
C6	0.2813 (2)	0.4100 (2)	0.0137 (3)	5.08 (5)
C7	0.1741 (2)	0.4250 (2)	0.0821 (3)	4.37 (4)
C8	0.1128 (2)	0.3417 (2)	0.1425 (3)	4.23 (4)
C9	0.1587 (2)	0.2467 (1)	0.1309 (3)	3.82 (4)
C10	0.2659 (2)	0.2285 (2)	0.0661 (3)	4.11 (4)
C1'	0.2840 (2)	−0.0610 (2)	0.1222 (3)	4.58 (5)
C2'	0.2177 (2)	−0.1435 (2)	0.0708 (4)	5.35 (6)
C3'	0.2612 (3)	−0.2423 (2)	0.0704 (4)	6.53 (7)
C4'	0.3684 (3)	−0.2602 (2)	0.1202 (4)	7.37 (8)
C5'	0.4350 (3)	−0.1801 (3)	0.1693 (4)	6.95 (7)
C6'	0.3934 (2)	−0.0807 (2)	0.1733 (3)	5.67 (6)

Table 2. Selected geometric parameters (Å, °)

O1—C2	1.360 (2)	C2—O2	1.212 (2)
C2—C3	1.464 (3)	C3—C1'	1.478 (3)
C3—C4	1.358 (3)	C4—C10	1.421 (3)
C10—C9	1.396 (3)	C10—C5	1.402 (3)
C5—C6	1.365 (3)	C6—C7	1.399 (3)
C7—O7	1.355 (3)	O7—H7	0.89 (3)
C7—C8	1.389 (3)	C8—C9	1.361 (3)
C9—O1	1.376 (2)		
C9—O1—C2	123.4 (1)	O1—C2—O2	115.8 (2)
O1—C2—C3	118.5 (2)	O2—C2—C3	125.7 (2)
C2—C3—C4	117.5 (2)	C1'—C3—C4	123.1 (2)
C2—C3—C1'	119.4 (2)	C3—C4—C10	123.2 (2)
C10—C5—C6	121.3 (2)	C5—C6—C7	120.0 (2)
C6—C7—O7	117.6 (2)	O7—C7—C8	122.6 (2)
C6—C7—C8	119.8 (2)	C7—C8—C9	118.7 (2)
C8—C9—O1	117.1 (2)	C8—C9—C10	123.4 (2)
O1—C9—C10	119.5 (2)	C4—C10—C5	125.6 (2)
C4—C10—C9	117.9 (2)	C9—C10—C5	116.5 (2)
C2'—C1'—C3	122.3 (2)	C3—C1'—C6'	119.6 (2)
C2—C3—C1'—C2'	40.9 (3)	C4—C3—C1'—C6'	39.8 (3)
O7—C7—C6—C5	179.4 (2)	O7—C7—C8—C9	178.9 (2)
O2—C2—O1—C9	178.6 (2)	O2—C2—C3—C4	178.1 (2)
O2—C2—C3—C1'	1.9 (3)	C10—C4—C3—C1'	178.6 (2)

All non-H atoms were located by direct methods; H atoms were found from difference Fourier maps. All non-H atoms were refined anisotropically; H-atoms were refined isotropically.

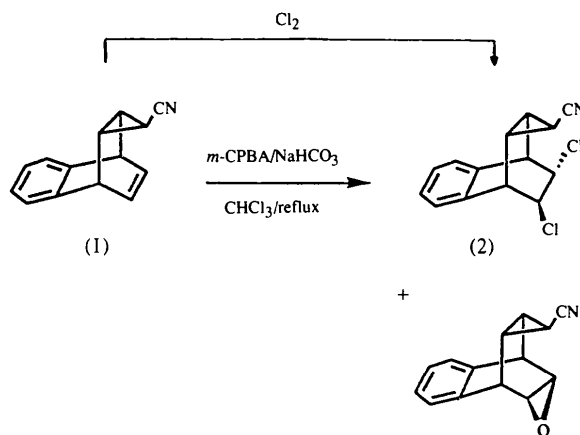
Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*. Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1992). Molecular graphics: *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1193). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Fan, H. F. (1991). *SAPI91. Structure Analysis Programs with Intelligent Control*. Rigaku Corporation, Tokyo, Japan.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1992). *TEXSAN. Crystal Structure Analysis Package*. MSC, 3200, Research Forest Drive, The Woodlands, TX 77381, USA.
- Ueno, K. (1985). *Acta Cryst.* **C41**, 1786–1789.

tetrahydro-2,7-etheno-1*H*-cyclopropa[*b*]naphthalene-1-carbonitrile, (1), in CHCl<sub>3</sub> was reacted with *m*-chloroperbenzoic acid (*m*-CPBA) in order to find out whether electrophiles can attack the double bond from the *endo* face or the *exo* face. Compound (2) was obtained as the major product.



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## Unusual Chlorination During an Epoxidation Reaction of an Etheno-cyclopropa[*b*]naphthalene Derivative

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## Abstract

The structure of (1 $\alpha$ ,1 $\alpha$ ,2 $\beta$ ,7 $\alpha$ ,8*R*,9*R*)-8,9-dichloro-1 $\alpha$ ,2,7,7 $\alpha$ -tetrahydro-2,7-ethano-1*H*-cyclopropa[*b*]naphthalene-1-carbonitrile, C<sub>14</sub>H<sub>11</sub>Cl<sub>2</sub>N, consists of two non-planar six-membered carbon rings (constituting a [2.2.2] bicyclic system), one of which shares two C atoms with a benzene ring and has two Cl substituents; the other is fused to a cyclopropane ring carrying a C $\equiv$ N substituent. The two Cl atoms of the —C—C(Cl)—C(Cl)—C— bridging system have an *anti* arrangement with respect to the plane of the four C atoms.

## Comment

In connection with our recently developed high-temperature bromination reactions (Dastan & Balcı, 1994; Dastan, Balcı, Hókelek, Ülkü & Büyükgüngör, 1994), a solution of the *exo*-cyano compound 1 $\alpha$ ,2,7,7 $\alpha$ -

During this reaction we expected only the formation of an epoxide. The formation of a chlorinated compound is unusual. We believe that *m*-chloroperbenzoic acid (as an oxidative reagent) forms chlorine upon oxidation of the chloroform used as solvent, which adds to the double bond. The mechanism of formation of this product is currently under investigation. The same compound was also synthesized by an independent route involving direct chlorination (yield 55%).

The least-squares plane through C1, C2, C3, C4, C5, C6, C11 and C12 indicates that C11 and C12 lie practically in the plane of the benzene ring (Fig. 1), being displaced by 0.032 (7) and –0.008 (8) Å, respectively, from the plane of the benzene ring. The C11—C13 [1.799 (9) Å] and C12—C14 [1.795 (8) Å] bond lengths are not significantly different. The C11—C13—

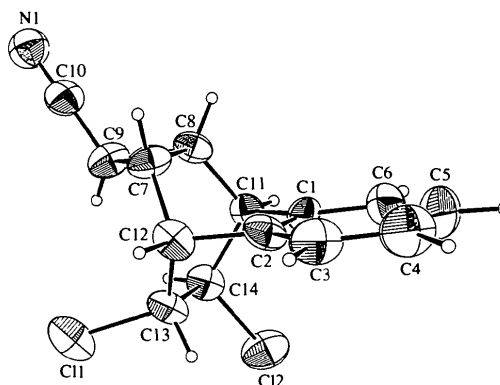


Fig. 1. ORTEPII (Johnson, 1976) drawing of C<sub>14</sub>H<sub>11</sub>Cl<sub>2</sub>N with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.