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Two Diastereomers of Benzylidene-D-erythronolactone†

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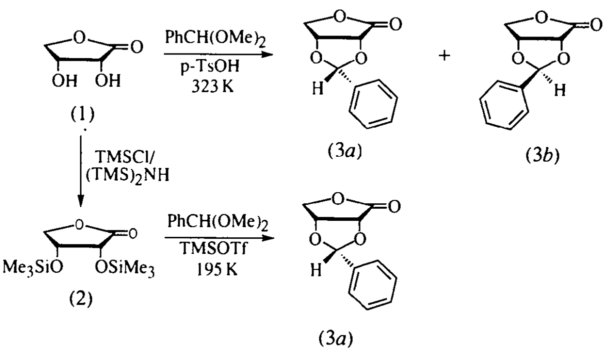
Abstract

The title compounds 2,3-*O*-(*R*)-benzylidene-D-erythronolactone (*endo* isomer) and 2,3-*O*-(*S*)-benzylidene-D-erythronolactone (*exo* isomer), $C_{11}H_{10}O_4$, which crystallize in the same space group with quite similar cell constants, are model compounds for the key intermediate in the synthesis of *endo*-brevicomine. The X-ray structure determination was performed in order to discover whether inherent molecular properties of these species might account for the observed *endo* selectivity, but no such features could be found. To substantiate this conclusion from the energetic point of view, we performed non-empirical as well as semi-empirical quantum chemical calculations, which revealed that both isomers are almost isoenergetic with a slight preference for the *exo* isomer. From our combined results we believe that the observed reactivity is most likely to be kinetically controlled.

Comment

We reported recently an efficient synthesis of *endo*-brevicomine (Gypser, Flasche & Scharf, 1994) involving an *endo*-selective acetalization of diol (1) as a key step. There are several possible reasons for the preferred formation of the *endo* isomer, for example secondary interactions between the aromatic system and parts of the lactone ring may kinetically facilitate the *endo* approach of the reactands (Meister, Shen & Scharf, 1984). Alternatively, both isomers might be formed under these experimental conditions. However, if there is an equilibrium relationship, the greater tendency of the *endo* isomer to crystallize might constantly precipitate this species from the reaction mixture and thus account for the selective formation of this isomer. Moreover, inherent molecular parameters might be responsible for this selectivity. To determine whether this is the case, we synthesized the model compounds 2,3-*O*-(*R*)-benzylidene-D-erythronolactone (3*a*, *endo* isomer) and 2,3-*O*-(*S*)-benzylidene-D-erythronolactone (3*b*, *exo* isomer) (Flasche, 1994) and determined their structures by means of X-ray crystallography.



The structure of a molecule in the solid state might differ significantly from that under the experimental conditions. However, except for chemically insignificant rotations about the C(2)—C(10) bonds (Fig. 1), the

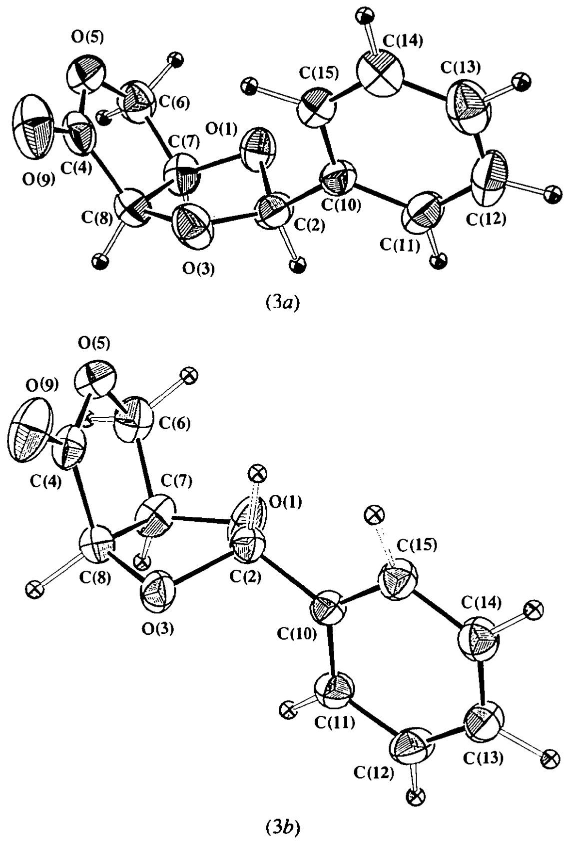


Fig. 1. Structures of (3*a*) and (3*b*) in the solid state. Displacement ellipsoids are plotted at the 30% probability level.

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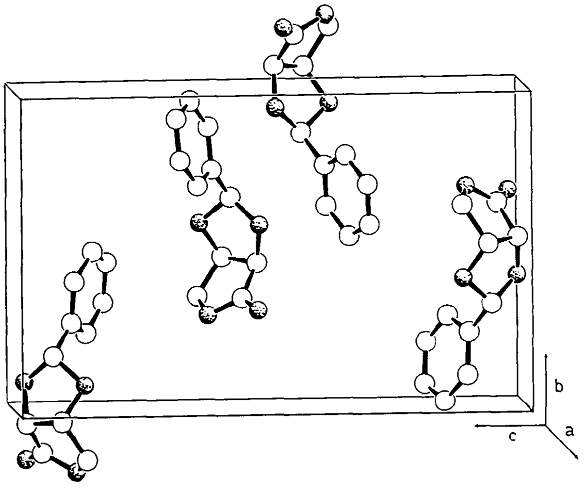
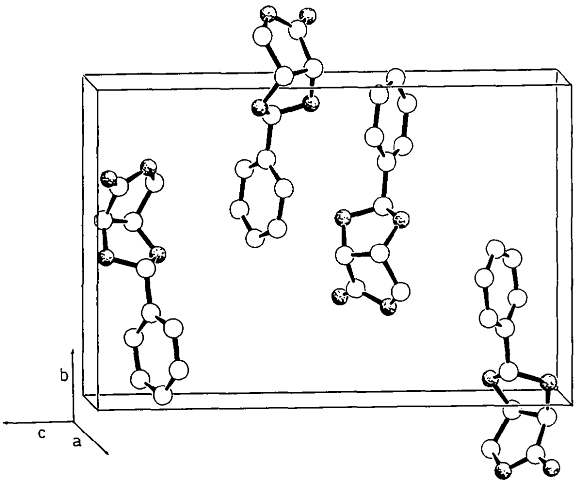
† Dedicated to Professor Dr H.-D. Scharf on the occasion of his 65th birthday.

molecular frameworks of both diastereomers are relatively rigid. The solid-state structures of (3*a*) and (3*b*) are, therefore, likely to be reliable approximations of their structures in the reaction mixture. To determine the relative energy of the isomers, we performed quantum chemical calculations for the free unperturbed molecules. *ORTEP* (Johnson, 1965) plots of the isomers are presented in Fig. 1, while Fig. 2 shows the arrangements of the molecules in their crystal lattices.



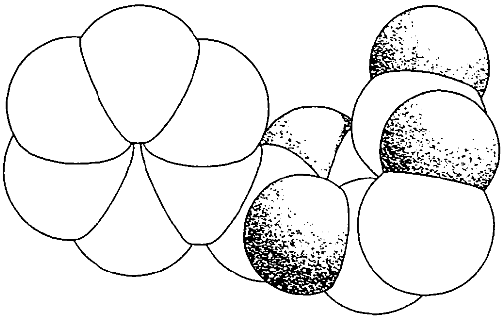
(3*a*)



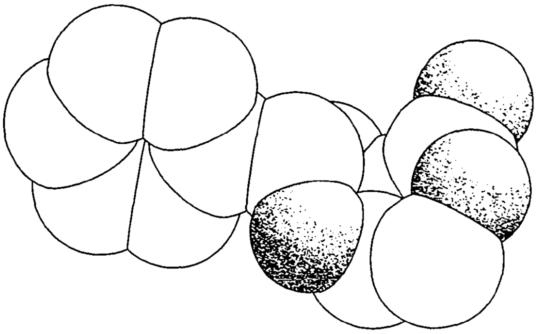
(3*b*)

Fig. 2. Packing of (3*a*) and (3*b*) in the unit cells.

Not only do both diastereomers crystallize in the same space group, but they do so with surprisingly similar cell constants. The longest intramolecular contacts between non-H atoms are 7.041 Å in (3*a*) [O(5)···C(12)] and 7.648 Å in (3*b*) [O(5)···C(13)]. Moreover, the molecular dimensions perpendicular to these axes are comparable for both isomers, yielding similar 'shapes' and thus having similar spatial demands (Fig. 3). These structural properties result in similar polarities as well as almost identical crystal lattices. The shortest intermolecular contacts in the lattice which involve at least one non-H atom are those between O(9) and H(7) [2.518 (3) Å] in (3*a*) and O(9) and H(6A) [2.563 (2) Å] in (3*b*). The corresponding intermolecular contacts between non-H atoms [O(9)···C(4) 3.040 (5) in (3*a*) and O(9)···C(8) 3.108 (3) Å in (3*b*)] are close to the sum of the van der Waals radii for C (1.70 Å) and O (1.52 Å) atoms (Bondi, 1964).



(3*a*)



(3*b*)

Fig. 3. Space-filling models of (3*a*) and (3*b*).

The lactone parts of both molecules deviate only slightly from planarity, with maximum deviations from the least-squares planes of 0.132 (4) Å in (3*a*) and 0.161 (3) Å in (3*b*). The puckering of the dioxole rings is stronger and the corresponding distances are 0.292 (4) Å in (3*a*) and 0.247 (3) Å in (3*b*). Repulsive interactions between the lactone segment and the phenyl substituent result in a larger deviation from planarity for the acetal system in (3*a*) as well as a significantly different conformation of this molecular segment in the two isomers. The O(1)—C(2)—O(3) moiety is bent slightly towards the lactone ring in (3*b*) but is turned away in (3*a*) with the phenyl ring occupying an equatorial position in both (3*b*) and (3*a*) as a result. Furthermore, the dihedral angle between the least-squares planes through the dioxole and lactone rings is 116.2 (1)° in (3*a*) and 105.2 (1)° in (3*b*). The planes through the aromatic and the dioxole rings intersect at an angle of 83.2 (1)° in (3*b*), while in (3*a*) they subtend an angle of 78.4 (1)°. As a result, H(15) is closer to O(9) in the latter compound than if both planes were orthogonal to each other. Energy-lowering interactions between carbon-based H atoms and carbonyl O atoms are well known (Taylor & Kennard, 1982; Bernstein, Etter & Leiserowitz, 1994). However, with an H(15)···O(9) distance of 3.484 (3) Å, the possible stabilizing interaction between these two centres is negligible for (3*a*). A thorough examination of all other available structural parameters for (3*a*) does not provide any explanation as to the preferred formation of this isomer. Moreover, the stronger steric crowding in this molecule might lead one to conclude that the *endo* diastereomer is energetically less favoured. This assumption is supported by the results of our quantum chemical calculations. Complete geometry optimizations were carried out for both isomers starting from the experimentally determined structures and employing semiempirical [*MINDO*/3 (Bingham, Dewar & Lo, 1975), *MNDO* (Dewar & Thiel, 1977), *AM*1 (Dewar, Zoebisch, Healy & Stewart, 1985) and *PM*3 (Stewart, 1989*a*,*b*)] methods as well as density functional theory in its local approximation (LDF). The computational results are summarized in Table 5, which lists the energies of (3*a*) relative to those of the more stable isomer (3*b*) together with the calculated dipole moments. All computational results agree that the dipole moments are quite similar for both species and the diastereomers are almost isoenergetic with a slight preference for the *exo* isomer (3*b*).

Experimental

Both diastereomers were synthesized by standard methods. The *endo* isomer (3*a*) was prepared selectively from D-erythronolactone (1) in a two-step process (Tsunoda, Suzuki & Noyori, 1981) while the *exo* isomer (3*b*) was obtained under standard acetalization conditions (Evans, 1972). Recrystallization was from *n*-hexane/diethyl ether (1:1).

Compound (3*a*)

Crystal data

$C_{11}H_{10}O_4$
$M_r = 206.2$
Orthorhombic
$P2_12_12_1$
$a = 5.938\ (1)$ Å
$b = 10.206\ (2)$ Å
$c = 16.447\ (4)$ Å
$V = 996.7$ Å^3
$Z = 4$
$D_x = 1.374$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 19.36$–$47.76°$
$\mu = 0.845$ mm^{-1}
$T = 293$ K
Irregular
0.5 × 0.5 × 0.5 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
6171 measured reflections
848 independent reflections
788 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.02\ (1)$
$\theta_{\max} = 73.2°$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 12$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 60 min
intensity decay: 6%

Refinement

Refinement on F
$R = 0.036$
$wR = 0.036$
$S = 5.150$
788 reflections
137 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.0002$
$\Delta\rho_{\max} = 0.1$ e Å^{-3}
$\Delta\rho_{\min} = -0.1$ e Å^{-3}

Extinction correction: Zachariasen (1967), Larson (1970)
Extinction coefficient: $r^* = 4108$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (3a)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O(1)	0.4717 (3)	0.5770 (2)	0.6361 (2)	0.0658 (9)
O(3)	0.6900 (4)	0.5792 (2)	0.5245 (2)	0.077 (1)
O(5)	0.6439 (4)	0.2966 (2)	0.6254 (2)	0.076 (1)
O(9)	0.9182 (4)	0.3237 (2)	0.5348 (2)	0.106 (1)
C(2)	0.5684 (6)	0.6621 (3)	0.5783 (2)	0.063 (1)
C(4)	0.7342 (6)	0.3529 (3)	0.5608 (3)	0.065 (2)
C(6)	0.4171 (6)	0.3442 (3)	0.6389 (2)	0.074 (1)
C(7)	0.3979 (5)	0.4662 (3)	0.5898 (2)	0.065 (1)
C(8)	0.5790 (5)	0.4548 (3)	0.5264 (2)	0.063 (1)
C(10)	0.7204 (5)	0.7580 (3)	0.6186 (2)	0.055 (1)
C(11)	0.6639 (6)	0.8893 (3)	0.6233 (2)	0.071 (1)
C(12)	0.8095 (8)	0.9770 (3)	0.6630 (3)	0.087 (2)
C(13)	1.0049 (7)	0.9325 (4)	0.6966 (3)	0.086 (2)
C(14)	1.0598 (6)	0.8037 (3)	0.6913 (2)	0.078 (1)
C(15)	0.9234 (6)	0.7161 (3)	0.6534 (2)	0.063 (1)

Table 2. *Selected geometric parameters (Å, °) for (3a)*

O(1)—C(2)	1.409 (4)	C(6)—C(7)	1.488 (5)
O(1)—C(7)	1.432 (4)	C(7)—C(8)	1.503 (5)
O(3)—C(2)	1.421 (4)	C(10)—C(11)	1.383 (4)
O(3)—C(8)	1.431 (4)	C(10)—C(15)	1.402 (5)
O(5)—C(4)	1.322 (5)	C(11)—C(12)	1.405 (5)
O(5)—C(6)	1.449 (4)	C(12)—C(13)	1.364 (6)
O(9)—C(4)	1.210 (4)	C(13)—C(14)	1.357 (5)
C(2)—C(10)	1.487 (4)	C(14)—C(15)	1.357 (5)
C(4)—C(8)	1.500 (5)		
C(2)—O(1)—C(7)	104.7 (2)	C(6)—C(7)—C(8)	104.9 (3)
C(2)—O(3)—C(8)	106.3 (2)	O(3)—C(8)—C(4)	109.9 (3)
C(4)—O(5)—C(6)	110.8 (3)	O(3)—C(8)—C(7)	106.0 (2)
O(1)—C(2)—O(3)	105.1 (2)	C(4)—C(8)—C(7)	103.4 (3)
O(1)—C(2)—C(10)	110.7 (3)	C(11)—C(10)—C(15)	118.8 (3)
O(3)—C(2)—C(10)	111.1 (3)	C(11)—C(10)—C(2)	121.0 (3)
O(9)—C(4)—O(5)	122.9 (3)	C(15)—C(10)—C(2)	120.2 (2)
O(9)—C(4)—C(8)	126.3 (4)	C(10)—C(11)—C(12)	119.6 (3)
O(5)—C(4)—C(8)	110.8 (3)	C(13)—C(12)—C(11)	120.0 (3)
O(5)—C(6)—C(7)	105.6 (3)	C(14)—C(13)—C(12)	120.1 (4)
O(1)—C(7)—C(6)	110.5 (3)	C(13)—C(14)—C(15)	121.6 (3)
O(1)—C(7)—C(8)	102.2 (2)	C(14)—C(15)—C(10)	120.0 (3)

Compound (3*b*)

Crystal data

$C_{11}H_{10}O_4$
$M_r = 206.2$

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å

Orthorhombic
$P2_12_12_1$
$a = 5.7000\ (7)$ Å
$b = 10.7002\ (9)$ Å
$c = 16.142\ (1)$ Å
$V = 984.5$ Å^3
$Z = 4$
$D_x = 1.391$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 18.04–41.12°$
$\mu = 0.855$ mm^{-1}
$T = 293$ K
Irregular
$0.4 \times 0.4 \times 0.4$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5773 measured reflections
1177 independent reflections
1092 observed reflections $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.02\ (1)$
$\theta_{\max} = 72.9°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity decay: <1%

Refinement

Refinement on F
$R = 0.035$
$wR = 0.030$
$S = 3.877$
1092 reflections
137 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.0003$
$\Delta\rho_{\max} = 0.1$ e Å^{-3}
$\Delta\rho_{\min} = -0.1$ e Å^{-3}

Extinction correction: Zachariasen (1967), Larson (1970)
Extinction coefficient: $r^* = 1731$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (3b)*

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O(1)	−0.5298 (3)	−0.4387 (2)	−0.6572 (1)	0.0700 (7)
O(3)	−0.7516 (3)	−0.4414 (1)	−0.5417 (1)	0.0548 (6)
O(5)	−0.6637 (3)	−0.7198 (2)	−0.6339 (1)	0.0589 (6)
O(9)	−0.9477 (3)	−0.6994 (2)	−0.5410 (1)	0.0777 (8)
C(2)	−0.7522 (5)	−0.4055 (2)	−0.6252 (1)	0.0444 (7)
C(4)	−0.7635 (4)	−0.6654 (2)	−0.5687 (2)	0.0489 (8)
C(6)	−0.4402 (5)	−0.6624 (2)	−0.6533 (2)	0.0620 (9)
C(7)	−0.4383 (4)	−0.5392 (2)	−0.6087 (2)	0.0542 (8)
C(8)	−0.6174 (4)	−0.5536 (2)	−0.5407 (1)	0.0492 (8)
C(10)	−0.7975 (4)	−0.2674 (2)	−0.6348 (1)	0.0422 (7)
C(11)	−0.6381 (4)	−0.1821 (2)	−0.6033 (2)	0.0507 (8)
C(12)	−0.6798 (5)	−0.0547 (2)	−0.6154 (2)	0.0578 (9)
C(13)	−0.8763 (5)	−0.0150 (2)	−0.6566 (2)	0.0550 (9)
C(14)	−1.0348 (5)	−0.0998 (2)	−0.6857 (2)	0.0563 (8)
C(15)	−0.9956 (4)	−0.2285 (2)	−0.6754 (1)	0.0494 (8)

Table 4. *Selected geometric parameters (Å, °) for (3b)*

O(1)—C(2)	1.413 (3)	C(6)—C(7)	1.502 (4)
O(1)—C(7)	1.428 (3)	C(7)—C(8)	1.507 (3)
O(3)—C(2)	1.402 (3)	C(10)—C(15)	1.371 (3)
O(3)—C(8)	1.423 (3)	C(10)—C(11)	1.385 (3)
O(5)—C(4)	1.330 (3)	C(11)—C(12)	1.398 (3)
O(5)—C(6)	1.449 (3)	C(12)—C(13)	1.371 (4)
O(9)—C(4)	1.198 (3)	C(13)—C(14)	1.363 (4)
C(2)—C(10)	1.508 (3)	C(14)—C(15)	1.405 (3)
C(4)—C(8)	1.526 (3)		
C(2)—O(1)—C(7)	108.5 (2)	C(6)—C(7)—C(8)	104.7 (2)
C(2)—O(3)—C(8)	104.1 (2)	O(3)—C(8)—C(7)	105.7 (2)
C(4)—O(5)—C(6)	111.2 (2)	O(3)—C(8)—C(4)	111.4 (2)
O(3)—C(2)—O(1)	106.2 (2)	C(7)—C(8)—C(4)	103.6 (2)
O(3)—C(2)—C(10)	111.5 (2)	C(15)—C(10)—C(11)	121.0 (2)
O(1)—C(2)—C(10)	111.2 (2)	C(15)—C(10)—C(2)	119.2 (2)
O(9)—C(4)—O(5)	122.5 (2)	C(11)—C(10)—C(2)	119.8 (2)
O(9)—C(4)—C(8)	127.3 (2)	C(10)—C(11)—C(12)	118.7 (2)
O(5)—C(4)—C(8)	110.1 (2)	C(13)—C(12)—C(11)	120.6 (2)
O(5)—C(6)—C(7)	106.0 (2)	C(14)—C(13)—C(12)	120.2 (2)
O(1)—C(7)—C(6)	113.4 (2)	C(13)—C(14)—C(15)	120.4 (2)
O(1)—C(7)—C(8)	103.2 (2)	C(10)—C(15)—C(14)	119.0 (2)

Table 5. *Energies ΔE_{rel} of (3a) relative to those of the more stable isomer (3b) (kcal mol^{-1}) and calculated dipole moments μ (D)**

Method	ΔE_{rel}	$\mu(3a)$	$\mu(3b)$
MINDO/3	0.05	3.6	4.3
MNDO	0.47	3.8	4.1
AM1	0.63	4.3	4.0
PM3	0.04	3.5	3.7
LDF†	0.17	4.4	3.9

* 1 kcal = 4.184 kJ; 1 debye $\simeq 3.33564 \times 10^{-30}$ Cm. † The total energies of (3*a*) and (3*b*) are −720.514488 and −720.514764 Hartrees (1 Hartree = 2643.6 kJ mol^{-1}), respectively.

Semi-empirical calculations were carried out using the *MOPAC5* package of quantum chemical routines (Stewart, 1989*c*), while *DMol*2.3 (Biosym, 1993) was used for the LDF calculations. These non-empirical calculations were performed with a numerical basis set of approximately 6-31G** quality and the Hedin–Lundqvist/Janak–Moruzzi–Williams local correlation functional (Hedin & Lundqvist, 1971; Moruzzi, Janak & Williams, 1978). All crystallographic and semi-empirical calculations were carried out on a local VAX 3100 work station, while the LDF calculations were performed on a Silicon Graphics Indigo.

The positions of all H atoms were located in a difference Fourier map for both compounds. Coordinates and displacement parameters were subjected to ten cycles of isotropic refinement. All H-atom parameters were kept fixed in the final full-matrix refinement.

For both compounds, data collection: *CAD*-4 *Diffractometer Control Software* (Enraf–Nonius, 1989); cell refinement: *CELDIM* (Enraf–Nonius, 1989); data reduction: *Xtal DIFDAT* (Hall, Flack & Stewart, 1992) ; program(s) used to solve structures: *Xtal GENSIN* and *GENTAN*; program(s) used to refine structures: *Xtal CRYLSQ*; molecular graphics: *ORTEP* (Johnson, 1965); *SCHAKAL* (Keller, 1986); software used to prepare material for publication: *Xtal ATABLE* and *BONDLA*.

The authors gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft. We thank Mr A. Neumann for the preparation of the *exo* isomer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1134). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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7-Amino-3-phenylcoumarin

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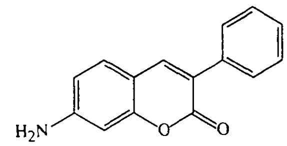
Abstract

There are two crystallographically independent molecules (*A* and *B*) having almost the same structure in the title crystal, $C_{15}H_{11}NO_2$. The phenyl ring attached at the 3-position is twisted markedly out of the plane of the coumarin moiety. The dihedral angles between the phenyl and coumarin rings are 48.9 (4) and 54.4 (4)° in molecules *A* and *B*, respectively. There is a weak O···H—N intermolecular hydrogen bond between the *B* molecules involving the carbonyl O atom.

Comment

Coumarin derivatives, of which the title compound, (I), is an example, have been found to be very useful as laser dyes. In order to understand the effects of the functional groups attached at the C3 and C7 atoms on both the molecular structure and characteristics of functional dyes having a coumarin skeleton, the present analysis was undertaken.



(I)

There are two crystallographically independent molecules (*A* and *B*) in the asymmetric unit. The geometric parameters of the two molecules are essentially the same. An *ORTEP*II (Johnson, 1976) drawing of one of them, molecule *A*, together with the atomic numbering scheme is shown in Fig. 1. The coumarin moiety, consisting of atoms O1, O2 and C2–C10, is planar with an average deviation of the atoms from the least-squares plane of 0.030 (3) and 0.027 (2) Å in molecules *A* and *B*, respectively. The phenyl ring attached at the C3 atom is twisted out of the coumarin plane, with dihedral angles of 48.9 (4) and 54.4 (4)° in the *A* and *B* molecules, respectively.

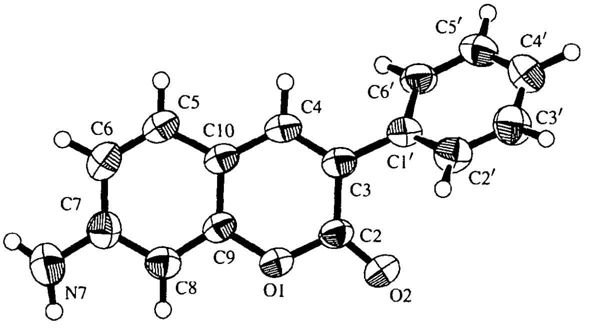


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of molecule *A* of the title compound, with heavy atoms represented by 50% probability ellipsoids and H atoms shown as circles of arbitrary radii.

The O1—C9 bond length is significantly longer than the O1—C2 bond and the C5—C6 and C8—C9 bonds are significantly shorter than the other C—C bonds in the phenyl ring. The C1′—C2′ and C1′—C6′ bonds are significantly longer and the C2′—C3′ bond is significantly shorter than the other ring C—C bonds. The exocyclic bond angles around the C2 and C3 atoms are highly asymmetric, with the O2—C2—C3