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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)
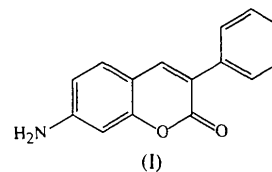
There are two crystallographically independent molecules (*A* and *B*) in the asymmetric unit. The geometric parameters of the two molecules are essentially the same. An *ORTEPII* (Johnson, 1976) drawing of one of them, molecule *A*, together with the atomic numbering scheme is shown in Fig. 1. The coumarin 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.

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7-Amino-3-phenylcoumarin

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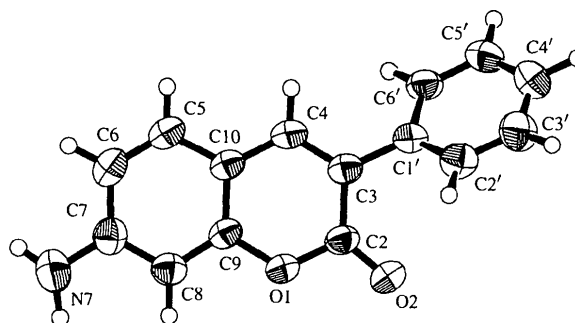
Abstract

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 phenyl and coumarin rings are 48.9 (4) and 54.4 (4)° in molecules *A* and *B*, respectively. There is a weak

Fig. 1. An *ORTEPII* (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

$C_{15}H_{11}NO_2$

and C4—C3—C1′ angles being markedly larger than the other angles. The O1—C9—C8 angle is smaller than the C4—C10—C5 angle and the C2′—C1′—C6′ angle of 118.3 (2)° is significantly smaller than the other endocyclic bond angles in the ring.

There is a very weak intermolecular hydrogen bond between the B molecules; O2$\cdots$H(N7) 2.34 (2), O2$\cdots$N7^i 3.244 (2) Å and O2$\cdots$H(N7)—N7^i 172 (2)° [symmetry code: (i) $1-x$, $-y$, $-z$]. The N7—C7 bond length in molecule B of 1.360 (3) Å is significantly shorter than the corresponding bond length of 1.375 (3) Å found in molecule A. Although the O2$\cdots$N7 distance is unusually long for an O$\cdots$H—N hydrogen bond, the shortening of the N7—C7 bond in molecule B suggests that there is a weak hydrogen bond.

Experimental

Crystals of the title compound were grown from a chloroform solution at 293 (5) K in a darkroom.

Crystal data

$C_{15}H_{11}NO_2$	Cu $K\alpha$ radiation
$M_r = 237.26$	$\lambda = 1.54184$ Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
$a = 9.648$ (2) Å	$\theta = 30$–$35°$
$b = 21.24$ (1) Å	$\mu = 0.740$ mm^{-1}
$c = 5.925$ (3) Å	$T = 293$ (2) K
$\alpha = 94.23$ (4)°	Plate
$\beta = 106.93$ (3)°	$0.36 \times 0.14 \times 0.05$ mm
$\gamma = 86.66$ (3)°	Yellow
$V = 1157.3$ (8) Å^3	
$Z = 4$	
$D_x = 1.36$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.017$
diffractometer	$\theta_{max} = 74.9°$
$\omega/2\theta$ scans	$h = -12 \rightarrow 12$
Absorption correction:	$k = -26 \rightarrow 26$
none	$l = -7 \rightarrow 0$
5241 measured reflections	3 standard reflections
4758 independent reflections	frequency: 60 min
3851 observed reflections	intensity decay: 0.56%
[$F > 3\sigma(F)$]	

Refinement

Refinement on F	Extinction correction:
$R = 0.058$	$F^* = |F_{calc}|/(1 + gI_{calc})$
$wR = 0.075$	Extinction coefficient:
$S = 3.45$	$g = 4.76689 \times 10^{-6}$
3851 reflections	Atomic scattering factors
414 parameters	from *International Tables*
$w = 1/\sigma^2(F)$	*for X-ray Crystallography*
$(\Delta/\sigma)_{max} = 0.01$	(1974, Vol. IV)
$\Delta\rho_{max} = 0.27$ e Å^{-3}	
$\Delta\rho_{min} = -0.27$ e Å^{-3}	

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

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O1A	0.8254 (2)	0.47515 (7)	0.0799 (2)	4.13 (3)
O2A	0.7446 (2)	0.38497 (8)	−0.0979 (3)	5.05 (4)
N7A	1.0463 (3)	0.6642 (1)	0.4451 (5)	6.07 (6)
C2A	0.7378 (2)	0.4254 (1)	0.0561 (3)	3.78 (4)
C3A	0.6490 (2)	0.4246 (1)	0.2174 (3)	3.68 (4)
C4A	0.6667 (2)	0.4701 (1)	0.3955 (3)	3.87 (4)
C5A	0.7856 (2)	0.5695 (1)	0.6022 (4)	4.31 (5)
C6A	0.8792 (3)	0.6161 (1)	0.6113 (4)	4.58 (5)
C7A	0.9556 (2)	0.6164 (1)	0.4424 (4)	4.34 (5)
C8A	0.9356 (2)	0.5681 (1)	0.2647 (4)	4.16 (5)
C9A	0.8413 (2)	0.5221 (1)	0.2595 (3)	3.60 (4)
C10A	0.7625 (2)	0.5203 (1)	0.4238 (3)	3.61 (4)
C1′A	0.5492 (2)	0.3719 (1)	0.1840 (3)	3.74 (4)
C2′A	0.4536 (2)	0.3556 (1)	−0.0375 (4)	4.49 (5)
C3′A	0.3610 (3)	0.3072 (1)	−0.0654 (5)	5.23 (6)
C4′A	0.3626 (3)	0.2726 (1)	0.1242 (5)	5.30 (6)
C5′A	0.4560 (3)	0.2880 (1)	0.3443 (4)	5.02 (6)
C6′A	0.5480 (2)	0.3375 (1)	0.3748 (4)	4.27 (5)
O1B	0.3436 (1)	0.06380 (7)	0.0930 (2)	3.99 (3)
O2B	0.1220 (2)	0.07321 (8)	−0.1385 (2)	5.15 (4)
N7B	0.8237 (2)	0.0209 (1)	0.5640 (4)	4.85 (4)
C2B	0.2063 (2)	0.0888 (1)	0.0522 (3)	3.74 (4)
C3B	0.1723 (2)	0.13109 (9)	0.2358 (3)	3.50 (4)
C4B	0.2763 (2)	0.1395 (1)	0.4470 (3)	3.68 (4)
C5B	0.5301 (2)	0.1177 (1)	0.7031 (3)	4.12 (4)
C6B	0.6620 (2)	0.0889 (1)	0.7271 (4)	4.20 (4)
C7B	0.6926 (2)	0.0512 (1)	0.5385 (3)	3.73 (4)
C8B	0.5821 (2)	0.0441 (1)	0.3246 (3)	3.77 (4)
C9B	0.4500 (2)	0.0734 (1)	0.3074 (3)	3.45 (4)
C10B	0.4167 (2)	0.11096 (9)	0.4896 (3)	3.54 (4)
C1′B	0.0261 (2)	0.16221 (9)	0.1884 (3)	3.46 (4)
C2′B	−0.0286 (2)	0.1993 (1)	−0.0059 (4)	4.04 (4)
C3′B	−0.1615 (3)	0.2303 (1)	−0.0415 (4)	4.47 (5)
C4′B	−0.2439 (2)	0.2251 (1)	0.1118 (4)	4.43 (5)
C5′B	−0.1921 (3)	0.1878 (1)	0.3020 (4)	4.50 (5)
C6′B	−0.0579 (2)	0.1571 (1)	0.3408 (4)	4.10 (4)

Table 2. *Selected bond distances (Å), angles (°) and torsion angles (°)*

	Molecule A	Molecule B
O1—C2	1.365 (2)	1.359 (2)
O1—C9	1.384 (2)	1.391 (2)
O2—C2	1.219 (2)	1.220 (2)
N7—C7	1.375 (3)	1.360 (3)
C2—C3	1.460 (3)	1.458 (3)
C3—C4	1.356 (3)	1.364 (3)
C3—C1′	1.484 (3)	1.481 (3)
C4—C10	1.420 (3)	1.412 (3)
C5—C6	1.365 (3)	1.353 (3)
C5—C10	1.410 (3)	1.415 (3)
C6—C7	1.406 (3)	1.417 (3)
C7—C8	1.394 (3)	1.403 (3)
C8—C9	1.367 (3)	1.366 (3)
C9—C10	1.402 (3)	1.396 (3)
C2—O1—C9	123.0 (1)	122.9 (1)
O1—C2—O2	115.5 (2)	115.7 (2)
O1—C2—C3	118.0 (2)	118.3 (2)
O2—C2—C3	126.5 (2)	126.0 (2)
C2—C3—C4	118.6 (2)	118.4 (2)
C2—C3—C1′	117.8 (2)	119.1 (2)
C4—C3—C1′	123.6 (2)	122.5 (2)
C3—C4—C10	122.7 (2)	122.3 (2)
C6—C5—C10	121.2 (2)	121.4 (2)
C5—C6—C7	120.9 (2)	121.3 (2)
N7—C7—C6	121.4 (2)	121.4 (2)
N7—C7—C8	119.4 (2)	120.1 (2)
C6—C7—C8	119.2 (2)	118.4 (2)
C7—C8—C9	118.8 (2)	118.7 (2)
O1—C9—C8	116.5 (2)	116.3 (2)
O1—C9—C10	119.7 (2)	119.4 (2)

C8—C9—C10	123.8 (2)	124.2 (2)
C4—C10—C5	126.0 (2)	125.5 (2)
C4—C10—C9	117.8 (2)	118.5 (2)
C5—C10—C9	116.2 (2)	116.0 (2)
C2—C3—C1'—C2'	−50.5 (3)	−56.2 (2)
O2—C2—C3—C4	172.7 (2)	174.6 (2)
O2—C2—C3—C1'	−4.2 (3)	−4.2 (3)

All non-H atoms were located by direct methods using *SIR*88 (Burla *et al.*, 1989) and refined anisotropically. All H atoms were found from difference Fourier maps and refined isotropically.

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

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Absolute Configuration of D-Bromphen-iramine Maleate

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Abstract

The crystal structure and absolute configuration of the title compound, 3-(4-bromophenyl)-*N*,*N*-dimethyl-3-(2-pyridyl)propylammonium hydrogen maleate, $C_{16}H_{20}BrN_2^+ \cdot C_4H_3O_4^-$, a potent anti-allergic agent, has been determined. The crystals are composed of two independent brompheniraminium cations, which differ

significantly in their conformations, hydrogen bonded to maleate anions, with N⋯O distances of 2.673 (9) and 2.664 (9) Å. The anions form seven-membered rings through strong intramolecular O—H⋯O hydrogen bonds, with O⋯O distances of 2.418 (10) and 2.430 (8) Å.

Comment

As a continuation of our studies (Parvez, 1990) on the anti-allergic drugs effective on H1 receptors, we have determined the crystal structure and absolute configuration of D-brompheniramine hydrogen maleate, (1).
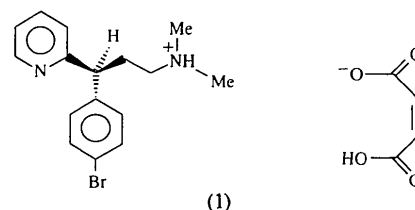
(1)

*ORTEP*II drawings (Johnson, 1976) of the two independent molecules, *A* and *B*, found in the crystal of (1), with the atomic numbering schemes, are shown in Fig. 1. The molecular dimensions in both molecules are unexceptional, with mean bond distances Br—C_{sp^2} 1.92 (1), N—C_{sp^3} 1.48 (2), N—C_{sp^2} 1.34 (1), C_{sp^3}—C_{sp^3} 1.52 (1), C_{sp^3}—C_{sp^2} 1.52 (3) and C—$C_{aromatic}$ 1.37 (3) Å in the cations, and C_{sp^2}—C_{sp^2} 1.49 (1), C=C 1.34 (1), C—O 1.29 (1), C—O^- 1.27 (1) and C=O 1.22 (1) Å in the anions. The angles at the C13*A* and C13*B* atoms [111.8 (9) and 118.3 (8)°, respectively] are significantly different in the two molecules, showing more strain in molecule *B*. The six-membered rings in the two molecules are essentially planar, with the maximum deviation from the least-squares planes being 0.03 (2) Å for atom C2*A*.

The maleate anions are hydrogen bonded to the dimethylamino groups of the brompheniraminium cations *via* normal N—H⋯O interactions (Table 3) and show typically strong intramolecular hydrogen bonding.

The two molecules show significant differences in their conformations. For instance, the mean-planes angles between the pyridyl and phenyl rings (*A*1), the pyridyl ring and C6—C13—C14 chain (*A*2), and the phenyl ring and C6—C13—C14 chain (*A*3) in molecule *A* are 72.5 (5), 82.9 (6) and 70.5 (7)°, respectively, compared with values of 79.6 (5), 79.3 (5) and 14.4 (9)°, respectively, in molecule *B*. The corresponding angles in the crystal structure of DL-pheniramine hydrogen maleate, (2) (Parvez & Rusiewicz, 1996), with values of 87.1 (3), 86.6 (3) and 6.9 (6)°, respectively, show it to have a conformation similar to that of molecule *B*. The conformation of neither of the